Hydrogen gas sensing with magnetic nanomaterials

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There is currently a lot of interest in magnetic multilayer films with uniaxial, ‘perpendicular’ magnetic anisotropy (PMA) for next-generation spintronic applications. Previously, these materials have revolutionised the technology of magnetic hard drives and, more recently, have also shown promise for next-generation nano-scale data storage devices. PMA can be induced in certain ferromagnetic nano-layers by covering the ferromagnetic layer with a layer of Platinum or Palladium.

Hydrogen gas sensors (HGS) are currently garnering significant interests because of the development of hydrogen as a clean and renewable fuel. Palladium (Pd) is one of the key materials for HGS, since Palladium has a large hydrogen absorption capacity. A number of its physical properties change upon hydrogenation and it is highly selective to the gas. However, there are still a number of drawbacks in today’s proposed hydrogen gas sensors and sensing techniques. The development of fully safe, low-cost, remotely-measuring (ie. non-contact) sensors having compatibility with a wide range of gas concentrations and a high sensitivity is most desirable.

It was recently shown that the PMA strength in Palladium-Cobalt (Pd/Co) bilayer films can be reduced by exposing them to hydrogen gas. It was suggested that this effect could be used for hydrogen gas sensing. In this thesis, the physics underlying this magnetic hydrogen gas sensing is studied. The focus is on the ferromagnetic resonance (FMR) response of Pd-Co materials in the presence of the hydrogen gas. Multiple bi-layer Pd/Co and tri-layer Pd/Co/Pd film samples are designed and fabricated by using magnetron sputtering. Their FMR response is measured in the presence of hydrogen in a very broad range of gas concentrations. Also, the response to hydrogen gas of alloyed PdCo films is investigated and compared to layered continuous films and nanostructures.
The main results of this study are as follows are investigated:

Related to physics underlying functionality of magnetic hydrogen gas sensors

- Bi-layer and tri-layer thickness optimisation for magnetic hydrogen gas sensor (m-HGS)
- Effects of FMR measurement geometry (OOP or IP) on the performance of m-HGS
- Effects of sample orientation (face up or down) on the hydrogenation response time
- Effect of In-situ annealing on the performance of m-HGS
- Role of the elastic strain in the m-HGS response
- Nano-patterned vs continuous thin films as an active sensor medium of m-HGS

Related to demonstration of functional prototypes of hydrogen gas sensors

- Nano-patterned tri-layer film
- Adjustable sensing for selection of wide hydrogen concentrations
- Continuous thin film CoPd alloy
# TABLE OF CONTENTS

Chapter 1: Introduction, literature review and thesis outline

1.1: Introduction 1
   1.1.1 Background 1
   1.1.2 Concept and detection principle 3

1.2 Literature review 8
   1.2.1 Mechanism of hydrogen gas absorption by palladium 9
   1.2.2 Factors which affect hydrogenation response in palladium 10
   1.2.3 Effect of sample annealing on hydrogenation of Co/Pd interface 13
   1.2.4 Differences in hydrogenation effect for bulk materials and thin films – crystallinity and lattice expansion 14
   1.2.5 Hydrogenation of CoPd alloys 17

1.3 Thesis outline 18

Chapter 2: Experimental setups and techniques

2.1 Sample fabrication setup and techniques 20
   2.1.1 Thin films deposition 20
      2.1.1.1 Basic principle of thin film sputtering 21
      2.1.1.2 Features of the in-house sputter machine 22
      2.1.1.3 Details of sputtering conditions 26
# TABLE OF CONTENTS

2.1.1.4 Deposition rate calibration 26  
2.1.2 “In-situ” high-temperature annealing of the sputtered thin films 28  
2.1.3 Nano-patterned tri-layer and CoPd alloy single-layer film samples 31  

2.2 Ferromagnetic resonance (FMR) setups and measurement methods 33  
2.2.1 Basics of the FMR method and details of the employed FMR setups 33  
2.2.1.1 lock-in with field modulation technique 37  
2.2.1.2 Interferometric detection technique -- microwave receiver 41  
2.2.1.3 FMR field and linewidth extraction  
    from experiment results 45  
2.2.2 Details of measurement methods 46  
2.2.2.1 Gas chamber for the in-plane and  
    perpendicular-to-plane FMR measurements 46  
2.2.2.2 Time resolved FMR measurement method  
    for HGS demonstration 49  
2.2.2.3 In-situ FMR measurement with elastic strain  
    applied to the sample 52  

2.3 Other characterisation setups and techniques 56  
2.3.1 Gas blending system 56  
2.3.2 SQUID magnetometry 58  
2.3.3 X-ray Diffraction (XRD) 60  

2.4 Chapter Summary 64
<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chapter 3: Details of physics underlying functionality of magnetic</td>
<td></td>
</tr>
<tr>
<td>hydrogen gas sensors</td>
<td></td>
</tr>
<tr>
<td>3.1 Definitions of parameters for characterisation of m-HGS</td>
<td>65</td>
</tr>
<tr>
<td>3.1.1 Definition of sensitivity for the m-HGS</td>
<td>66</td>
</tr>
<tr>
<td>3.1.2 Definition of hydrogenation response times for the m-HGS</td>
<td>69</td>
</tr>
<tr>
<td>3.2 Cobalt thickness optimisation for both bi- and tri-layers m-HGS</td>
<td>71</td>
</tr>
<tr>
<td>3.2.1. Co thickness dependence in bi-layer films</td>
<td>71</td>
</tr>
<tr>
<td>3.2.2 Co thickness dependence in tri-layer structures</td>
<td>75</td>
</tr>
<tr>
<td>3.2.3 Hydrogen sensitivity of Co/Pd super-lattices</td>
<td>79</td>
</tr>
<tr>
<td>3.3 Effect of FMR measurement geometry on sample sensitivity to</td>
<td>82</td>
</tr>
<tr>
<td>hydrogen gas and response time.</td>
<td></td>
</tr>
<tr>
<td>3.3.1 Hydrogen sensitivity affected by FMR measurement geometry</td>
<td>83</td>
</tr>
<tr>
<td>3.3.2 Hydrogen response times affected by FMR measurement geometry</td>
<td>88</td>
</tr>
<tr>
<td>3.4 Effect of sample orientation on hydrogen response times</td>
<td>93</td>
</tr>
<tr>
<td>3.5 High temperature (in-situ) annealing effect on bi-layer Co/Pd of m-HGS</td>
<td>98</td>
</tr>
<tr>
<td>3.6 Role of the elastic strain in the sensor response</td>
<td>106</td>
</tr>
<tr>
<td>3.7 Nano-patterned samples vs. continuous thin film samples</td>
<td>120</td>
</tr>
<tr>
<td>3.8 Chapter Summary</td>
<td>126</td>
</tr>
<tr>
<td>TABLE OF CONTENTS</td>
<td></td>
</tr>
<tr>
<td>-------------------</td>
<td></td>
</tr>
<tr>
<td><strong>Chapter 4: Demonstration of functional prototypes of hydrogen gas sensors</strong></td>
<td></td>
</tr>
<tr>
<td>4.1: Demonstration by patterned tri-layers structure with IP FMR configuration</td>
<td>129</td>
</tr>
<tr>
<td>4.2: Demonstration of wide range hydrogen gas detection by adjustable m-HGS</td>
<td>143</td>
</tr>
<tr>
<td>4.3: Demonstration of wide range hydrogen gas detection by CoPd alloy as active sensor of m-HGS</td>
<td>157</td>
</tr>
<tr>
<td>4.4 Chapter Summary</td>
<td>172</td>
</tr>
<tr>
<td><strong>Chapter 5: Conclusions, outlook and further actions</strong></td>
<td></td>
</tr>
<tr>
<td>5.1: Conclusions and outlook</td>
<td>173</td>
</tr>
<tr>
<td>5.1.1: The m-HGS concept is realised and demonstrated</td>
<td>173</td>
</tr>
<tr>
<td>5.1.2: Conclusions from fundamental studies on m-HGS</td>
<td>174</td>
</tr>
<tr>
<td>5.1.3: Outlook from the three m-HGS demonstrations</td>
<td>179</td>
</tr>
<tr>
<td>5.2: Further actions</td>
<td>180</td>
</tr>
<tr>
<td>5.2.1: Improvement on the hydrogenation responses time</td>
<td>181</td>
</tr>
<tr>
<td>5.2.2: Increment on the FMR signal level</td>
<td>182</td>
</tr>
<tr>
<td>5.2.3: Improvement on bias scheme for the active sensor medium</td>
<td>182</td>
</tr>
</tbody>
</table>
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To my lovely kids, Isaac Lueng and Sharon Lueng, thank you for bringing happy moments to me all the time.
This thesis contains work that has been published.

<table>
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<th>Details of the work:</th>
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<tr>
<td>We study the dependence of the shift of the resonance peak on the cobalt layer thickness. We observe a decrease in the resonant field shift of the resonance linewidth with an increase in the cobalt layer thickness. We also observe a stronger change in the amplitude of absorption in the presence of hydrogen gas for thicker cobalt layers. Our results are important for optimization of Pd/Cobalt multi-layers as a novel platform for hydrogen gas sensing applications.</td>
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<tr>
<th>Location in thesis:</th>
</tr>
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<tbody>
<tr>
<td>Section 3.2.1</td>
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<th>Student contribution to work:</th>
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<tr>
<td>The student is the first author on the publication. His contribution includes fabrication of all the samples studied in the work and their characterisation with FMR under hydrogen and pure nitrogen atmospheres.</td>
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<th>Co-author signatures and dates:</th>
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<tr>
<td>Peter Metaxas</td>
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<tr>
<td>Mikhail Kostylev</td>
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**Details of the work:**

We demonstrate that the sensitivity to hydrogen gas is enhanced when the static magnetic field is applied perpendicular to the Pd/Co film plane. A factor of eight times improvement is observed with respect to the in-plane FMR configuration studied previously. An analysis based on the Kittel equation for FMR frequencies of a ferromagnetic film is carried out in order to understand the mechanism of sensitivity enhancement. The result is important for optimizing Pd/Co bi-layered thin films for use in novel platforms for hydrogen gas sensing.

**Location in thesis:**

Section 3.3.1

**Student contribution to work:**

The student is the first author on the publication. His contribution includes sputtering and in-situ annealing of all the studied samples. Furthermore, he performed all FMR measurements reported in the work.

**Co-author signatures and dates:**

- Peter Metaxas
- Mikhail Kostylev
AUTHORSHIP DECLARATION: CO-AUTHORED PUBLICATIONS

Details of the work:
We have demonstrated clear advantages of nanopatterned Pd/Co films over continuous Pd/Co films as candidates for future hydrogen gas sensing devices based upon Hydrogen-absorption-modified ferromagnetic resonance. Nanopatterning results in a higher sensitivity to hydrogen gas and a much faster hydrogen desorption rate. It also avoids the need for an external biasing magnetic field which may be important for practical sensor implementation. A wide range of hydrogen gas concentrations has been detected with the nanopatterned material: from 0.1% to 50%, across the threshold of hydrogen flammability in air (4 %).

Location in thesis:
Section 4.1

Student contribution to work:
The student is the first author on the publication. He delivered important contribution to the sample design and performed all the experimental measurements. Moreover, he designed and built a computer-controlled gas blending system used in this work for demonstration of functionality of the samples as hydrogen gas sensors able to measure a wide range of gas concentrations.

Co-author signatures and dates:

<table>
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<th>Name</th>
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<tr>
<td>Pierpaolo Lupo (formerly at NUS)</td>
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<td>Peter Metaxas (UWA)</td>
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<td>Mikhail Kostylev (UWA)</td>
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<tr>
<td>Adekunle O. Adeyeye (NUS)</td>
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<td>We demonstrate that magnetic ferromagnetic resonance based hydrogen gas sensors (mHGS) are able to operate in a very broad hydrogen gas concentration range. A m-HGS device-prototype is tested for hydrogen concentrations from 0.2% to 100% using nitrogen as a carrier gas. The sensitivity of the device to gas concentration is found to be significant for the entire tested range.</td>
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<th>Location in thesis:</th>
</tr>
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<tbody>
<tr>
<td>Section 4.2</td>
</tr>
</tbody>
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<tr>
<td>The student is the first author on the publication. His contribution to the paper the suggestion of a novel concept of the “adjustable detection range” of m-HGS and carrying out all the sample fabrications and experimental measurements.</td>
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<tr>
<td>Peter Metaxas (UWA)</td>
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<td>Manu Sushruth (UWA)</td>
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<td>Mikhail Kostylev (UWA)</td>
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This thesis contains work that has been prepared for publication.

Details of the work:

We study the physical origins of the hydrogen gas induced reduction of the strength of the perpendicular magnetic anisotropy (PMA) at the interface of cobalt and palladium layers. Qualitative analysis of these results demonstrates that the magneto-elastic contribution to the hydrogen-induced change in PMA is very small and is of opposite sign to the electronic contribution related to the influence of hydrogen ions on the hybridisation of Cobalt and Palladium orbitals at the interface.

Location in thesis:

Section 3.6

Student contribution to work:

The student is the first author on the publication. His works includes sputtering all the samples and FMR characterisation of them in hydrogen and nitrogen atmospheres. He also performed investigation of bending of the samples in the presence of hydrogen.

Co-author signatures and dates:

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D. Faurie (University Paris 13)

Mikhail Kostylev (UWA)
Details of the work:

In this study, performance as hydrogen gas sensors of CoPd alloyed films with different Pd concentrations was studied. It was demonstrated that the studied Co_{39}Pd_{61} alloy thin film can be used as an active medium for m-HGS. It is capable to cover a wide range of hydrogen gas concentrations (from <0.1% to 100%) with only one value of the magnetic bias field. Furthermore, the investigated Co_{24}Pd_{76} alloy thin film was found to be very sensitive to ultra-low hydrogen gas concentrations (0.00001% to 0.01%).

Location in thesis:

Section 4.3

Student contribution to work:

Suggestion of the new method of evaluation the hydrogen detection range for the m-HGS.

Carrying out all the experiments

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Pierpaolo Lupo (formerly at NUS) 

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Mikhail ostylev (UWA)

Student signature:

Date: 02 AUG 2017

I, Mikhail Kostylev certify that the student statements regarding their contribution to each of the works listed above are correct

Coordinating supervisor signature:

Date: 02 AUG 2017
Chapter 1: Introduction, literature review and thesis outline

1.1 Introduction

1.1.1 Background:

The use of hydrogen as a clean, renewable and long lasting energy fuel [1] is severely limited by significant safety issues related to storage and handling, due to its extreme flammability and explosiveness; the lower flammability level of hydrogen in air is just 4 vol% while its lower explosive limit is 18 vol% [2]. The extensive usage of this flammable/explosive gas thus requires specialised detection techniques and the development of sensors. As such, the detection of hydrogen leakages and the continuous monitoring of its concentration in industrial environments is the object of intensive research.

Palladium (Pd) has an extremely large hydrogen absorption capacity [1]. Furthermore, upon charging with hydrogen a number of its physical properties change. Palladium is also highly selective to Hydrogen gas ($H_2$), exhibiting extremely low sensitivity to other gases such as $CO$, $Cl_2$, $SO_2$, $H_2S$, $NO_x$ and hydrocarbons [3]. These properties make this material unique for applications in hydrogen sensing. The problem however, is how to exploit this extreme affinity of palladium to hydrogen gas in real sensor systems, in particular, how to detect in an economical and practical way, the changes in physical properties of palladium which originated from hydrogen absorption.

Palladium is also a prospective candidate material for future spintronic applications. Spintronics has been successfully employed in various sensing applications outside of hydrogen sensing. The most striking example is the reading of information stored in modern magnetic hard drives. There have also been suggestions to use spintronics
devices for detection of extremely small magnetic fields originating from the heart beat and brain activity [4], monitoring biological activity of cell membranes [5], in industrial sensors for magnetic flux leakage detection [6], in heat sensors [7], for position sensing [8] and for strain sensing [9].

Although there exist significant works on Hydrogen gas sensors (HGS), a number of drawbacks remain. In particular, HGS based on variation of resistance of semiconductors [10], or on catalytic oxidation of noble metals [11] have poor selectivity and require sensor heating. Optical [2, 12-16] and micro-mechanical sensors [17] require sophisticated optical detection systems that have limited feasibility in terms of creating an economical, simple to fabricate and practical HGS sensor.

Under exposure to $H_2$ at room temperature, palladium metal exhibits lattice expansion to reversibly form palladium hydride [18]. Most of the above mentioned sensors exploit this property. The hydride phase of palladium has increased electrical resistance and a variety of electrical HGS employing this property have been developed [19-21]. Nano-structuring of such sensors (eg. $Pd$ nano-wires) has led to higher efficiencies and reduced the occurrence of irreversible changes to the $Pd$. However, making reliable electrical contacts to individual nanowires can be cost prohibitive [20, 21]. Furthermore, the usage of electricity in the presence of hydrogen is dangerous due to the concern of possible arcing [3].

The ultimate goal of the study carried out in this thesis, is development of a working prototype of a hydrogen gas sensor (HGS), which will be able to sense the presence of hydrogen gas via a fully safe, low cost, remote approach, with wide range of concentrations and high sensitivity. This will be achieved by combining the unique physical and chemical properties of palladium with the extreme sensing capabilities of magneto-electronics-based devices. The concept of the magnetic HGS was suggested
CHAPTER ONE: Introduction, literature review and thesis outline

in an earlier work carried out at UWA [22]. It is based on modification of magnetic properties of interfaces between ferromagnetic (FM) and non-magnetic (NM) metallic layers in the presence of hydrogen gas ($H_2$). In the present thesis, the concept is further developed and physics behind the sensitivity of these materials to $H_2$ is investigated.

1.1.2 Concept and Detection Principle:

In thin magnetic films, the magnetisation vector naturally lies in the film plane due to the out-of-plane demagnetising field $H_d$ in thin films (>1.8 Tesla for Cobalt films). At the interface of a cobalt (Co) layer with a platinum (Pt) group NM layer, perpendicular magnetic anisotropy (PMA) is induced [23-28] and the effective magnetic field of anisotropy $H_u$ can be even larger than $H_d$. In the latter case ($H_u>H_d$) the static magnetisation vector for the FM layer spontaneously re-orientates perpendicular to the film plane, as shown in figure 1.1. For $H_u<H_d$ which usually happens for thicker Co layers, the magnetisation vector naturally lies in the film plane.

![Figure 1.1: A Pd/Co film exhibiting a perpendicular magnetisation.](image)

One way of probing the anisotropy experimentally is via measurements of ferromagnetic resonance (FMR) [29-31]. FMR refers to the resonant precession of the magnetic moment within a material. FMR has been used in microwave technology for
many decades [32]. FMR measurements generally require a strong static external magnetic field (a “saturating field”) and a weaker microwave-frequency field which is orthogonal to the saturating field to drive the precession. The frequency of this precession is given by the saturating field and the geometry and structural composition of the sample. The onset of FMR is registered as an increase in absorption of microwave power by the sample.

Thin continuous films are characterised by a mode of spatially uniform precession. However, if the film is nanostructured in its plane spatially non-uniform FMR modes in the form of standing spin waves are excited instead [29].

In this thesis I explore in detail the concept of a magnetic hydrogen gas sensor recently developed by our research team [22]. It is based on a change in the strength of perpendicular magnetic anisotropy (PMA) upon hydrogen absorption by a Pd/ferromagnetic-metal bilayer film. This change can be measured with FMR spectroscopy. In Ref [22] a custom-made air-tight chamber (Figure 1.2) was fabricated to enable controlled continuous flow of gas at atmospheric pressure through the chamber while performing FMR experiments. The cell contains a coplanar waveguide (CPW) on which the sample under study sits. Coaxial cables feed microwave power from a microwave generator into CPW from one end and carry the transmitted power out through the other end into a microwave receiver. The cell is fixed between the poles of an electromagnet such that the magnetic field is applied along the CPW. This orientation maximizes the FMR response. Figure 1.3 shows the FMR spectra measured for a Co(5nm)/Pd(10nm) film under nitrogen and hydrogen atmospheres.
Figure 1.2: Experimental air-tight cell for FMR measurements under $N_2/H_2/Air$ atmosphere. It also shows the coplanar waveguide (on which the sample sits), microwave feed ports and gas flow inlet/outlet (from [22]).

Figure 1.3: Experimental FMR spectra taken in nitrogen atmosphere (solid line) and hydrogen atmosphere (dash line). A shift of the resonance peak towards the lower fields upon absorption of hydrogen is visible in the data [22].
CHAPTER ONE: Introduction, literature review and thesis outline

This non-contact gas sensing method has a number of potential advantages over current HGS concepts. Firstly, the fabrication of magnetic / non-magnetic multi-layers is well established and is an inexpensive technique. As in some optical sensors, the method is non-contact but does not require optical readout. Additionally, it can sense the presence of $H_2$ through an optically opaque barrier. Furthermore, a very simple and convenient tool could be exploited to read the HGS state: FMR. Moreover, since no DC current passes through the sensor, it is a safer approach that prevents arcing which potentially may happen if the sensor’s electronics malfunctions.

In contrast to many palladium based optical [3] and electrical sensors [33], this approach does not require mechanical stretching/shrinking (strain) of the Pd layer. Strain based sensors can be disadvantageous since they have limited lifetimes due to irreversible deformation [34, 35] and hysteretic sensitivity [36]. Strain based sensing also normally requires larger palladium thickness to overcome the substrate clamping effect [36]. As the experiment in [22] suggests, for the magneto-electronic sensor, the substrate clamping effect may be of less importance, since the interface perpendicular anisotropy is formed in its presence and the effect in [22] was observed for a film which is thin compared used to those in traditional electrical sensors [35]. This is potentially a huge advantage, since in very thin Pd films, cyclical charging with hydrogen does not produce noticeable irreversible deformation of the palladium layer (see figure 1.4) [35]. Therefore, whereas the sensitivity of an electrical sensor decreases with decreases in palladium thickness [35], the magneto-electronic sensor operates with palladium layer thickness below 10nm, (thanks to the interface nature of the involved physical effects). Furthermore, no hysteretic sensitivity has been observed in [22]. In sensors measuring cyclical concentration changes, the presence of hysteretic behaviour is a major drawback [35].
Figure 1.4: SEM images of the surface of Pd films of different thickness, $t$, after exposure to atmosphere with 2% of $H_2$ [35].

FMR is not the only way to characterise variation of magnetic properties of a ferromagnetic/non-magnetic ($FM/NM$) bi-layer (e.g. $Co/Pd$) but it has some important advantages with respect to other approaches to $FM/NM$-based HGS from the literature [36-39]. Previous studies of the impact of hydrogen absorption on magnetic properties of $FM/NM$ multi-layers utilised x-ray diffraction, neutron diffraction, and vibrating sample magnetometry to read the magnetic state [37-39]. However, these methods cannot be integrated into a small, cheap sensor. Secondly, in the experiment in [22], the sensor state could be easily read out in a setting mimicking $H_2$ sensing through a non-transparent wall of a vessel containing hydrogen. Thirdly, due to the perfect microwave shielding effect in metallic films with sub-skin-depth thicknesses [40] the microwave field applied to the cobalt side of the bi-layer is negligible in the space behind the palladium layer [41], i.e. inside the vessel containing $H_2$. This eliminates possibility of arcing. Table 1.1 shows potential advantages of m-HGS over the other currently proposed HGS concepts.
CHAPTER ONE: Introduction, literature review and thesis outline

<table>
<thead>
<tr>
<th>Proposed m-HGS</th>
<th>Other methods</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Low cost</td>
<td>Optical/Micromechanical methods: detection sophisticated hardware is required</td>
</tr>
<tr>
<td>2. Safer approach</td>
<td>Semiconductor type sensor: heating is required.</td>
</tr>
<tr>
<td>3. Non-contact detection</td>
<td>Pd resistor type: application of electrical current is required</td>
</tr>
<tr>
<td>4. Thinner Pd (&lt;20nm) can be used which can reduce chance of permanent deformation</td>
<td>Pd resistor type: thick Pd layer is required to increase sensitivity</td>
</tr>
<tr>
<td>5. No hysteretic response</td>
<td>Stress / strain type Pd sensor</td>
</tr>
<tr>
<td>6. Wide detection range (&lt; 0.1% ~ 100% hydrogen)</td>
<td>Have to be achieved by combination of difference HGS concepts</td>
</tr>
</tbody>
</table>

Table 1.1: Advantages of the proposed m-HGS over currently proposed HGS concepts (compiled by the thesis author).

1.2 Literature Review:

There are a huge number of studies which have been done in hydrogen gas sensing. It is difficult to include all of them into the thesis. However, in order to make the literature review part more effective, some key literature concepts and results that relate to our m-HGS concept and design parameters will be discussed in this section. To be started with, mechanism of hydrogen gas absorption by palladium will be discussed. Secondly, some of the structural and environmental factors affecting hydrogen responses of palladium will be presented. They provide some hints for the performance improvement of m-HGS. Furthermore, since an investigation of physical origins of modification of the PMA in Pd/Co layered films in the presence of hydrogen gas is included in the thesis, it is important to discuss the differences in hydrogenation effect on the lattice expansion of bulk palladium and thin palladium films. Finally, experimental results obtained in the thesis show that alloying of Co with Pd improves
significantly performance of $m$-HGS. Therefore, a brief introduction into the hydrogenation effect on Co/Pd alloy thin films is included into the introduction section, as well as discussion of how the effect of thermal annealing of the interface between Co and Pd layers affects bilayer sample response to hydrogen absorption.

1.2.1 Mechanism of hydrogen gas absorption by palladium

A theoretical study by W.M. Bartczak [42] shows that when a hydrogen molecule approaches the surface of palladium metal, the distance between the two hydrogen atoms increases due to a strong interaction between $Pd$ and $H$ atoms. Through this process the strength of the $H-H$ bond is weakened [42] and finally the hydrogen molecule is dissociated into two unbonded hydrogen atoms. The atomic radius of a hydrogen atom is small (around 0.52 Å in the ground state) [43], therefore it can easily diffuse into materials.

Figure 1.5 shows a phase diagram of palladium hydride. Hydrogen atoms absorbed in palladium may form $\alpha$- and $\beta$- palladium hydride phases depending on the hydrogen concentration inside the metal. Hydrogen atoms mainly occupy the interstitial sites of the crystalline lattice for the both phases [44]. At low hydrogen concentrations, the solid solution, $\alpha$-phase, is formed. While the hydrogen concentration increases, the metal hydride, $\beta$- palladium hydride, is formed. The hydrogen molecules are dissociated into atoms and firstly adsorbed at the surface of palladium by the high-symmetry hollow chemisorption sites, and then filling the octahedral interstitial sites in the first subsurface layer and finally diffuse and penetrate the interstitial sites inside the bulk [44]. At room temperature, the pure $\alpha$-phase palladium hydride corresponds to a stoichiometry $x<0.017$ while pure $\beta$-phase is realised for $x > 0.58$ (where $x$ is the stoichiometry of $PdH_x$). The intermediate $x$ values correspond to mixtures of both phases. At lower hydrogen concentration ($< PdH_{0.017}$, i.e. $\alpha$-phase), the lattice of
palladium expands a little bit, from 3.889 Å to 3.895 Å. For higher concentrations the β-phase Pd-H will form and the palladium lattice size will increase to 4.025 Å. [45, 46].

Figure 1.5: Phase diagram of the Pd-H system. Source: [47]

1.2.2 Factors affecting hydrogenation response of palladium

A number of structural factors affect the hydrogenation response of palladium. They include the difference in phases of palladium hydride (i.e. α- and β- palladium hydride), defects, step edges, surface morphology and crystallinity (single or polycrystal) of the crystal structure.
Firstly, there is a significant difference in the $H_2$ desorption times between the $\alpha$- and $\beta$- phase palladium hydrides. Hydrogen atoms in the $\alpha$-phase are usually more stable, and it takes a longer time to desorb them than for the $\beta$-phase. Experimental results by W.C. Lin et al. show two different desorption time constants which confirms this [43]. The first step of the hydrogen atoms desorption sequence is desorption from the $\beta$-phase and/or of the atoms physically adsorbed on the palladium surface. Desorption from the $\alpha$-phase follows this step, as hydrogen atoms occupy the interstitial sites of the $Pd$ crystalline lattice for this phase. W.C. Lin et al. explain their result [48] based on the idea from Ref. [49]. The microscopic mechanism of desorption in the $\alpha$-phase can be considered as hydrogen atoms diffusing between the interstitial sites of the crystalline lattice from the underlayer towards the palladium top atomic layer. For a $Pd/Co$ bi-layer film, the dehydrogenation of $Pd/Co$ interface will take place first and then later on the dehydrogenation of the palladium cover layer will proceed [48].

Secondly, defects and imperfections in the alloy / structure help reduce the hydrogen atoms absorption time [50]. As found by E. Lee et al., the absorption time of $Ni_x-Pd_{1-x}$ alloy with ($x=0$~$7\%$) is significantly reduced when compared with pure palladium thin film. By introducing a small amount of $Ni$ into $Pd$, imperfections (dislocations and grain boundaries) are formed which compensate the lattice mismatch between $Ni$ and $Pd$. The imperfections quickly interact with hydrogen atoms and reduce the absorption time [50]. Moreover, a study by Gdowski et al. [51] also found that by roughening the surface of $Pd$ (111) by ion bombardment, one can increase the hydrogen absorption rate by four times when compared with a reference one. Furthermore, crystallinity and surface morphology may also catalyse the hydrogen desorption and absorption responses (Pages 68, 44, 52 in [18])

Furthermore, crystallinity (single-crystal or nano-crystal) can affect the hydrogen diffusivity and solubility inside palladium. Figure 1.6 compares values of the diffusion coefficient between single-crystal and nano-crystal $Pd-H$ samples [53]. From the figure,
one sees that the diffusivity of hydrogen in single-crystal Pd is independent of hydrogen concentration. On the contrary, it increases with hydrogen concentration in the nano-crystal Pd case. The solubility of H₂ in nano-crystal Pd also higher than in single-crystal Pd. However, the diffusivity for nano-crystal Pd at lower hydrogen concentrations is lower. (This is in contrast with grain boundary diffusivity measured for substitutional atoms. Grain boundary diffusivity is normally orders to magnitude higher than bulk diffusivities [54]). A. Pundt suggested that the lower grain-boundary diffusivity for interstitial diffusion of hydrogen can be explained by its trapping at low-energy sites at grain boundaries [53, 56]

Figure 1.6: Diffusion coefficient comparison between single-crystal and nano-crystal Pd-H. X-axis is solubility. Source: [53, 56]
Environmental factors are also important in determining hydrogenation response time beside the above-mentioned crystallinity factors. One important parameter pointed out by A.S. Darling [57] is the environmental conditions; they affect significantly the hydrogen permeability inside palladium. In his study, he compared the hydrogen diffusion coefficient for palladium between static atmosphere and circulating hydrogen [57]. A significant difference in diffusion coefficients was observed in the experiment. The measurement taken in the static hydrogen atmosphere showed a negligible diffusion coefficient, while in the circulating one a high level of diffusion was maintained. A.S. Darling suggests that the reason for this difference is that the apparent loss of permeability in the static atmosphere is due to a stagnant layer of impurities developed close to the surface of palladium. The stagnant layer of impurities can be easily removed by circulating hydrogen even with relatively low flow rate [57]. Several other groups also found consistent results while applying the circulating atmosphere [58-59]. An important aspect of this finding is that hydrogen circulation is naturally present in commercial hydrogen purifiers [Page 99 in 18].

1.2.3 Annealing effects (alloy formation) on hydrogenation of Co/Pd interface

Recent studies by W. C. Lin et al. of the effect of hydrogenation on the magnetism of Pd/Co and Pd/Fe multilayers are also important for the topic of this thesis. The authors found that because of interlayer diffusion, an alloy formed at the interface of Pd with another metal crucially affects the strength of the hydrogenation effect on magnetism [48, 52, 60-62]. According to their works [48], as-deposited, tri-layer structures Pd/Co/Pd/Al2O3(0001) exhibited only in-plane magnetization, and no hydrogenation effect on the magneto-optical Kerr Effect (MOKE, MOKE is an effect of rotation of the light polarisation plane upon its reflection from a magnetized surface) response of the tri-layers was observed. On the contrary, a post-annealed tri-layer thin film sample demonstrated an oblique magnetic easy axis. On exposure to hydrogen gas at 1 atm
both the magneto-optical Kerr signal and the magnetic coercivity, $H_c$, increased for that sample. That implies that post-annealing promoted alloy formation at the Co/Pd interface, which resulted in the interfacial perpendicular anisotropy. Cobalt atom diffusion into the top Pd layer was confirmed by X-ray Absorption Near Edge Structure (XANES) analysis [48]. The enhancement of $H_c$ for the post-annealed sample may relate to the hydrogenation of the Co/Pd alloy interface. It is because the interface anisotropy dominated the magnetic behaviour.

It has been reported that hydrogen absorption by Pd changes its electronic structure significantly; the hydrogen-induced $H_c$ change can be due to a change in the strength of spin-orbit coupling, especially at the Pd-Co alloy interface, in the presence of hydrogen atoms [48]. Similar finding of post-annealing promoting the alloy formation at the Pd/Co interface and resulting in enhanced surface magnetic anisotropy is also reported in [63]. This suggests that a study of the effect of annealing on hydrogenation of Co/Pd bi- or multi-layers as well as CoPd alloy single-layer films will be crucial for paving a way to performance enhancement of magnetic hydrogen gas sensors.

1.2.4 Differences in hydrogenation effects in bulk and thin film samples – crystallinity and lattice expansion

The effect of hydrogenation can differ a lot between bulk and thin-film samples. Application of thin films in hydrogen gas sensors is important because thin film devices can be integrated with control electronics within the same microchip fabricated within the same manufacturing platform, e.g. Complementary Metal-Oxide-Semiconductor (CMOS). This can produce low-cost, small size, integrated and effective sensors. Films can be single-crystal, poly-crystal or amorphous. The film quality strongly depends on the employed deposition method, deposition conditions, and substrate. For example, the choice of a deposition method and conditions can affect the crystallinity of the film.
as well as the grain size. Misfit of lattice parameters between films and substrates may also affect the films’ microstructure (defects, dislocations, grain boundaries, etc) and internal stress [64]. As discussed in the previous sections, those parameters crucially affect hydrogen solubility, absorption and desorption for the bulk material. For thin films those effects will be further enhanced; this is not only because the surface area to bulk volume ratios are large for them, but also because the density of dislocations is larger in the case of thin films [53]. Salomons et al. also proposed [65] that the hydrogen solubility for thin films has a strong contribution from surfaces and grain boundaries.

In the following text, the phenomenon of crystal lattice expansion upon metal charging with hydrogen will be discussed. We will focus on differences between bulk and thin films.

Niobium is a material in which this effect has been studied in detail. Charging bulk Nb with hydrogen usually leads to isotropic 3-dimensional expansion of its crystal lattice. H. Zabel et al. have experimentally demonstrated that the correlation between the relative expansion $\Delta d/d0$ of the Nb lattice and the hydrogen concentration $c$ is $\Delta d/d0 = 0.058 \cdot c (H/Nb)$, and the correlation can be linear up to $c (H/Nb) = 1$ [66]. In contrast to the bulk samples, no in-plane expansion is allowed for thin films due to the substrate clamping effect. The lattice expansion for thin films is then anisotropic – the film expands in the out-of-plane direction only. Based on a theoretical study by Q.M. Yang et al., the relative expansion is $\Delta d/d0 = 0.136 \cdot c (H/Nb)$, which is larger than for the bulk samples. [67]. Later on, this was experimentally verified by U. Laudahn et al [68]. Figure 1.7 illustrates the differences between the hydrogen gas induced lattice expansion effects for the bulk materials and thin films.
It has also been found that substantially larger mechanical stresses are induced when metal films clamped to substrates are loaded with interstitial atoms. As estimated by M. Hamm et al., the mechanical stress which hydrogen loaded films clamped to rigid substrates can withstand is huge - up to 10 GPa [70]. If the internal mechanical stress exceeds the yield stress (i.e. the stress level at which a material no longer behaves elastically) of the thin-film/substrate system, the stress is then released by the formation of dislocations [71-73] or by film delamination [75]. The yield stress of the thin-film/substrate system depends on the
CHAPTER ONE: Introduction, literature review and thesis outline

characteristic sample dimension with typically an inverse square root dependency on it [70]. M.D. Uchic et al. [76] showed that the critical film thickness for dislocation formation at the thin-film/substrate system interface is of the same order or below that of dislocations formed at a metal-hydride interface. For instance, Grier et al. determined that Nb films deposited on Al₂O₃ have a critical thickness of 7.2nm for the formation of dislocations between Nb and Al₂O₃ [77].

1.2.5 Hydrogenation of CoPd alloys

As discussed in the Section 1.2.3, annealing of tri-layer Pd/Co/Pd samples results in formation of a CoPd alloy at the interface that enhances the effectiveness of hydrogen gas detection. Since the interface anisotropy dominates the magnetic behaviour, formation of the Co-Pd alloy at the interface plays a very important role in the material’s response to the presence of H₂ [48]. From this point of view, it would be interesting to check whether CoPd alloy single-layer films have potential as active components for the HGS, as these materials possess bulk perpendicular anisotropy and can absorb hydrogen gas. This was shown in a recent work by W.C. Lin et al [43]. They studied the effect of hydrogenation on magnetic properties (MOKE and Hc) of CoPd alloy thin films. Several observations from this work are relevant to the topic of the present thesis.

Firstly, they found two distinct rates characterising the hydrogen gas desorption process for these materials, which is similar to the bi-layer Co/Pd thin films. It is speculated that the two rates are observed because the desorption rates for the α- and β- phase palladium hydrides are different, the α-phase palladium hydride having a smaller desorption rate because the bonding strength being higher for the α-phase than for the β one. [43].
Secondly, they studied a series of cobalt compositions $x$, $Co_xPd_{1-x}$, where $x=65$, 39, 24 and 14). The Co-rich $Co_{65}Pd_{35}$ alloy thin film shows in-plane magnetic anisotropy, while the magnetic easy axis of the other samples (which are Pd-rich films) turns to a canted direction. The Pd-rich films exhibited a larger perpendicular magnetic anisotropy [43]. Furthermore, magnetic hysteresis loops taken for them show enhancement of perpendicular $H_c$ upon hydrogenation. The thicker the Pd-rich films (10, 14.8 and 20nm), the stronger the $H_c$ enhancement [43]. However, the Co-rich $Co_{65}Pd_{35}$ alloy thin film shows no $H_2$ effect on the hysteresis loop. This was explained by a strong contraction of the crystal lattice of $CoPd$ alloys with respect to pure Pd [43, 78], strongly reducing solubility of hydrogen atoms. The higher the cobalt content in the alloy, the larger the reduction in the hydrogen atoms solubility is.

Lastly, MOKE studies suggested reduction of magnetic moment in $CoPd$ alloy systems in the presence of hydrogen. It could be theoretically explained by a hydrogen atom attracting around 17% of electron charge from the Pd-Co chemical bond. This reduces the overlap of orbitals of Co and Pd leading to reduction in the exchange coupling between Co and Pd and therefore to reduction of the magnetic moment induced on Pd atoms due to the proximity effect to Co [43, 79].

1.3 Thesis outline

Chapter 2 provides an overview of the experimental methods and techniques used to characterise samples studied in this thesis. This chapter will be divided into three main sections. The first section will discuss sample fabrication techniques. Details of experimental setups and methodology how to use ferromagnetic resonance (FMR) to sense hydrogen gas will be discussed in the second section. Finally, techniques used to characterise the thin film samples will be highlighted in Section 3.
Chapter 3 focuses on understanding the physical mechanisms underlying functionality of magnetic hydrogen gas sensors. A number of aspects are dealt with. The effects of layer thickness, applied field and sample orientations, as well of material nanopatterning are discussed. Optimisation of the films as efficient hydrogen gas sensors is carried out. Furthermore, the effect of sample annealing leading to alloying at the interface between Co and Pd layers is investigated. The importance of annealing for layered Co/Pd films is then discussed. It is concluded that CoPd alloys may be a very important system for further study. The other aspect is understanding of the roles of two main contributions to PMA in the formation of the hydrogen induced FMR peak shift – the electronic and the magnetostriction ones. The goal is to separate and quantify them. This is achieved by growing Co/Pd bi-layer films film on flexible (Kapton) substrates and comparing results of their FMR characterisation in the presence of hydrogen gas and under an externally applied elastic stress. The latter study was carried out in co-operation with Université Paris-13 (France).

Chapter 4 focuses on demonstration of basic functional prototypes of magneto-electronic hydrogen gas sensors (m-HGS). Based on the knowledge presented in the previous chapters, three types of functional m-HGSs have been designed and demonstrated. These are tri-layer nano-wire arrays, continuous bi-layer (Co/Pd) thin films in the presence of an adjustable magnetic bias field and CoPd alloy films. Details of those experiments will be discussed in this chapter.

Chapter 5 provides conclusions and suggestions for future work.
Chapter 2: Experimental Setups and Techniques

A number of experimental setups and techniques will be discussed in this chapter. It also includes basic principles and data interpretation for the individual methods. A wide variety of experimental setups and techniques were used to achieve the objective of the project. For easier understanding, the chapter is divided into three individual sections. Section 2.1 provides detailed information on the sample fabrication setup and technique. Section 2.2 describes the setup and the methods of demonstration of HGS through ferromagnetic resonance (FMR) and related studies. Other experimental setups and techniques for the characterisation of the thin film samples are highlighted in Section 2.3.

2.1 Sample fabrication

2.1.1 Thin film deposition

Most of the continuous thin films studied in the project were sputtered using an in-house magnetron sputtering machine. The sputtering machine originally was a thermal evaporation machine; however it was modified into a sputtering machine equipped with three sputter guns for sputtering of different materials without breaking the vacuum. The lowest achievable base pressure for the system is $5 \times 10^{-8}$ Torr. It is achieved by using a rotary and a diffusion pump. The diameter of the sputter targets used in the machine is 2 inches while the distance between a target and a sample is 9 cm. Some features of the in-house sputtering machine will be discussed in Section 2.1.1.2. Since the sputtering machine was upgraded from an evaporation machine, a lot of sputtering parameters need to be controlled manually. For example, the flow rate of argon during sputtering. The sputtering time is controlled by closing and
open a shutter separating sputtering guns from a film substrate during sputtering. Most of the results from Chapter 3 and 4 were obtained with the thin films sputtered by the machine. Figure 2.1 shows a photo of the in-house sputtering machine.

![Image of in-house sputtering machine](image)

Figure 2.1: The in-house sputtering machine.

### 2.1.1.1 Basic principles of thin film sputtering

Sputtering is a technique used to deposit thin films of a material onto a substrate. This is achieved by creating a plasma and accelerating the ions from this plasma onto the source material, called target. The source material is eroded by the ions impinging on it and is ejected in the form of neutral particles. Once ejected, the particles travel along a straight line. If a substrate is located in the path of these ejected particles, a thin film of the target material is deposited onto the surface of the substrate [64].
2.1.1.2 Features of the in-house sputter machine

There are several features on the in-house sputtering machine; they include magnetron sputtering, DC or RF sputtering and a feedback substrate temperature control system.

a) Magnetron sputtering

As mentioned above, there are three sputter guns in the system. All three guns are basically identical. They contain strong magnets inside them that enables the system to become magnetron sputtering [80].

The method of magnetron sputtering deposition make uses of a closed loop magnetic field to trap electrons, enhancing not only the efficiency of the initial ionization process, but also allowing plasma to be ignited at a relatively lower argon pressures. Figure 2.2 shows the working principle of magnetron sputtering. This technique was pioneered in 1952 and gained commercial success in the industry in the 1960's and 1970's. This technique is very efficient, but there is one important drawback, which is an erosion track which forms on the target surface. This decreases the target surface area which can be used for sputtering. Figure 2.3 shows a deep groove formed on the surface of one of the used cobalt targets.
CHAPTER TWO: Experimental Setups and Techniques

Figure 2.2: The working principle of magnetron sputtering. [80]

Figure 2.3 shows one of the sputter targets after several sessions of magnetron sputtering.
b) DC and RF sputtering options

The in-house sputtering machine can apply either DC (direct current) or RF (radio frequency) voltage to the sputtering guns for sputtering. During the DC sputtering process, a direct current voltage is applied between a target and a substrate. Our RF sputtering source produces an AC voltage with frequency of 13.56 MHz. The advantages of RF sputtering are that a non-conducting target can be sputtered and relatively faster sputtering rate. In this project, DC sputtering was used to sputter both cobalt and palladium targets. Figure 2.4 shows the power generators for both DC and RF voltage. Both generators were purchased from HUTINGER Electronics. The model number of DC power generator is TruPlasma DC 3002, while the RF power generator is PFG 600 RF.

Figure 2.4: the power supplies for both DC (top instrument) and RF (bottom instrument) voltage.
c) Substrate heating during sputter deposition

Our sputtering machine is equipped with a substrate heating system with a temperature feedback loop. The system consists of a thermocouple, heating globes, cooling line and a temperature controller circuit. The sensing part of the thermocouple is located close to the substrate; the heating globes are located above the substrate holder in order to provide direct heating of the substrate. Figure 2.5 shows the schematics of the sample column, including the thermocouple, cooling line and heating system [81]. The substrate heating capability enabled me to develop in-situ annealing for improving the quality of the active element of the m-HGS. Details of this process will be discussed in Section 2.1.2.
2.1.1.3 Details of sputtering conditions

The quality of sputtered films is highly dependent on sputtering conditions, such as vacuum chamber’s base pressure, sputtering power, argon pressure, etc. A large number of trial film sputter runs were carried out in order to determine optimal conditions which result in satisfactory quality of thin films for application in m-HGS. In summary, the active sensing part of the m-HGS proposed is a simple bi- or tri-layer structure consisting of cobalt and palladium layers. It was found that the optimal conditions for sputtering cobalt thin films are as follows:

- Initial base chamber pressure lower than $10^{-7}$ Torr,
- Sputter power 100 W
- Plasma ignited at argon pressure around 4-6 mTorr.

The optimal conditions for depositing palladium layers are different: sputtering power of 60 W and at argon pressure around 8-10 mTorr.

2.1.1.4 Deposition rate calibration

Since there is no deposition rate monitoring system available in the chamber, the deposition rates have to be pre-determined by calibration. The individual calibrations have to be done for particular target materials, sputter guns and sputtering power. The procedures for the pre-determined sputter deposition rate are as follow. Firstly, a silicon substrate partly covered by adhesive tape was put inside the chamber. The chamber is then pumped down following the usual procedure. A particular sputter material, sputter gun and sputtering conditions are chosen and the plasma is ignited. The sputter deposition time is recorded in order to calculate the sputter deposition rate for the set conditions. Upon completion of the
process, the freshly sputtered film is removed from the chamber. The tape is then removed which produces a sharp film edge. The thickness of the sputtered film is then measured as the height of so-formed step on the sample surface with a Veeco Dektak 150 profilometer (figure 2.6). The sputter deposition rate is calculated by dividing the measured thickness of the film by the time of sputtering. (As already mentioned above, this sputtering rate calibration is valid only for a set sputtering conditions). Table 2.1 shows the typical sputtering rates for different sputtering parameter combinations.

A film thickness uniformity study of the sputter machine was carried out. The typical film thickness uniformity is less than 4.4% over a rectangular substrate with the in-plane size 1.8 cm by 1.4 cm. Because the typical size of the samples fabricated in this work is 5mm by 5mm, the thickness uniformity is better than 3%.

<table>
<thead>
<tr>
<th>Target material</th>
<th>Gun number</th>
<th>Sputter power (RF/DC)</th>
<th>Sputter power (W)</th>
<th>Argon pressure (mTorr)</th>
<th>Deposition rate (nm/sec)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cobalt</td>
<td>1</td>
<td>DC</td>
<td>100</td>
<td>6</td>
<td>0.61</td>
</tr>
<tr>
<td>Permalloy</td>
<td>1</td>
<td>DC</td>
<td>60</td>
<td>6</td>
<td>0.39</td>
</tr>
<tr>
<td>Nickel</td>
<td>2</td>
<td>RF</td>
<td>60</td>
<td>6</td>
<td>0.05</td>
</tr>
<tr>
<td>Palladium</td>
<td>2</td>
<td>DC</td>
<td>60</td>
<td>8</td>
<td>1.04</td>
</tr>
<tr>
<td>Tantalum</td>
<td>3</td>
<td>DC</td>
<td>60</td>
<td>6</td>
<td>0.40</td>
</tr>
<tr>
<td>Copper</td>
<td>3</td>
<td>DC</td>
<td>60</td>
<td>6</td>
<td>0.54</td>
</tr>
</tbody>
</table>

Table 2.1: Some typical sputtering rates for different sputtering combinations
2.1.2 “In-situ” high-temperature annealing of the sputtered thin films

The in-house magnetron sputtering machine possesses a function of substrate heating during sputtering. Heating is controlled by a closed loop controller with temperature feedback enabled by a presence of a thermocouple in close vicinity of the sample. A technique of “in-situ” high-temperature annealing was developed based on this feature. “In-situ” annealing means performing high-temperature annealing of a sample within the sputter chamber, under a high level of vacuum and immediately after sample sputtering. This newly developed technique significantly improves the quality of sputtered thin films and improves their response to hydrogen gas. The reason for the improvement is formation of CoPd alloy at the interface between cobalt and
palladium during the annealing process. The interface alloy plays an important role in the magnetic response to hydrogenation which was already discussed in Section 1.2.3 [48]. Results of the detailed study and data analysis will be discussed in Section 3.5. The details of the procedure and conditions for the “in-situ” high-temperature annealing are shown in figure 2.7, while the temperature profile during the “in-situ” high temperature annealing is shown in figure 2.8.

Figure 2.7: Details of the procedure and conditions for the “in-situ” high-temperature annealing of the sputtered thin films.
I tried several different ex-situ techniques for high-temperature annealing of the sputtered films prior introducing this “in-situ” method. They included normal and rapid thermal annealing (at the school of Electrical, Electronic and Computer Engineering, UWA), under pure nitrogen or ambient air atmospheres at different temperatures and for various annealing times. However, benefits of high temperature annealing with these alternative techniques were not obvious. On the contrary, some annealing conditions even weakened the FMR signal. It is intuitive that the sputtered films form oxides on the cobalt layer once the films contact normal air [82], which prevents forming the Co-Pd alloy at the interface.

One of the proposed m-HGS demonstrations reported in Section 4.2 of this thesis is based on a sputtered continuous thin film which has undergone “in-situ” high-temperature annealing. (Sputtered continuous thin films which were not “in-situ” annealed show much poorer performance, in terms of lower sensitivity. Please refer to Section 3.5 for details). This is the reason why “in-situ” high-temperature annealing of
CHAPTER TWO: Experimental Setups and Techniques

thin films is one of the important methods developed in the framework of this PhD research in order to significantly improve the hydrogen gas sensor’s performance. Finally, this process can be applied to produce an operational m-HGS device-prototype.

2.1.3 Nano-patterned tri-layer and CoPd alloy single-layer film samples

One of the most important objectives for this project is to demonstrate an advanced concept of m-HGS sensor. Based on the results obtained in Chapter 3 of this thesis, several new ideas were put forward aimed on improving operational characteristics of the proposed m-HGS. Beside continuous bi-layer thin films with “in-situ” high temperature annealing (detailed in Section 4.2), there are at least two more “candidates” which can be used to demonstrate the m-HGS. One of them is tri-layer (Pd/Co/Pd) thin films nanopatterned into an array of very long parallel nanowires with rectangular cross-section while the other one is a continuous CoPd-alloy single-layer thin film. However, either of these systems cannot be fabricated with our group’s equipment. Therefore, we collaborated with Prof. A.O. Adeyeye’s group at the Department of Electrical and Computer Engineering, National University of Singapore (NUS) in order to fabricate those samples.

Firstly, a highly advanced Deep UV optical lithography techniques available at Prof. A.O. Adeyeye’s lab was employed to fabricate the nano-wire arrays [83]. The respective photo-resist pattern was formed on the surface of a Si substrate by using this method, followed by electron beam layer deposition of the three metallic layers and subsequently, a lift-off process [83]. Not only nano-wires, but also other nano-structures, such as dots, anti-dots etc., can be prepared with this technique by the group at NUS. Figure 2.9 shows SEM images of some other nanopatterns prepared by Prof. A.O. Adeyeye’s group. However, only nano-wires samples were investigated in the present thesis.
CHAPTER TWO: Experimental Setups and Techniques

In terms of FMR peak magnitude and linewidth, the quality of the reference continuous tri-layer films deposited at NUS with the e-beam deposition method is quite similar to the quality of the films fabricated and with the magnetron sputtering machine at UWA.

![SEM micrographs of nanostructures showing a) nano-wires, b) anti-dots and c) dots.](image)

Figure 2.9: SEM micrographs of nanostructures showing a) nano-wires, b) anti-dots and c) dots. [83]

One more candidate for m-HGS demonstration is CoPd alloy films with different cobalt and palladium contents. The sputtering machine at NUS can perform co-sputtering of two materials at the same time; in this way the composition of the sputtered film can be controlled with high precision. With their promising sample preparation and fabrication techniques, the proposed concept of m-HGS can be implemented as functional device prototypes (detailed in Section 4.1 and 4.3).
CHAPTER TWO: Experimental Setups and Techniques

2.2 Ferromagnetic resonance (FMR) setups and measurement methods

As a part of its design, our concept of m-HGS uses FMR to probe the hydrogen concentration levels. Therefore the methods of taking FMR measurements are a crucial part of the project. This section focuses on FMR setups and measurement methods. Firstly, features of the FMR setups used in the project will be discussed. Secondly, the gas chamber setup for FMR and the time scan measurement method for HGS demonstration will be introduced, followed by a brief discussion on the in-situ FMR measurements under an elastic strain.

2.2.1 Basics of the FMR method and details of the employed FMR setups

Ferromagnetic resonance (FMR) is also known as the fundamental mode of uniform precession of magnetization, which means a mode for which all spins in the material precess with the same phase and amplitude across the whole volume of the magnetic material [84]. The schematic diagram of spin dynamics for this mode is shown in figure 2.10. In terms of spin wave dynamics, FMR is a specific case of a spin wave with an infinite wavelength or zero wave number. The effect of FMR was discovered unintentionally by Arkad’yev in 1911, as a resonant absorption of ultra-high frequency radiation by ferromagnetic materials [85]. A qualitative explanation of FMR was provided by Dorfmann in 1923 [86].
CHAPTER TWO: Experimental Setups and Techniques

Figure 2.10: The schematic diagram of fundamental mode of uniform precession of magnetization, FMR.

Figure 2.11 shows an example of a ferromagnetic film on top of a microwave microstrip FMR transducer, with representation of FMR coordinates.

The frequency of a uniform FMR mode for a ferromagnetic ellipsoid is given by the Kittel equation [87]

\[ \omega^2 = \gamma^2 [H_{res} + (N_{yy} - N_{zz})\pi M_s] [H_{res} + (N_{xx} - N_{zz})\pi M_s] \]  

(Eq 2.1)

where the \( N_{ii} \) is the demagnetising factors along the axes of the ellipsoid and \( \sum_i N_{ii} = 1 \).

In the case when the vector of static magnetisation is parallel to the film surface (x direction), i.e. “the in-plane FMR”, \( N_{xx} = N_{yy} = 0 \), and \( N_{yy} = 1 \), and the equation (2.1) reduces to:

\[ \omega_{in-plane}^2 = \gamma^2 [H_{res} + \pi M_s] [H_{res}] \]  

(Eq 2.2)
When the static magnetisation vector is perpendicular to the film surface (i.e. aligned along the \(z\) direction), one deals with the “perpendicular-to-plane (PP) FMR”. In this case, \(N_{xx} = N_{yy} = 0\), and \(N_{zz} = 1\), and the equation (2.1) reduces to:

\[
\omega_{pp}^2 = \gamma^2 [H_{res} - 4\pi M_s]^2
\]

or

\[
\omega_{pp} = \gamma \left[ H_{res} - 4\pi M_s \right]
\]

(Eq 2.3)

where \(\omega\) is the resonant frequency and \(H_{res}\) is the resonance magnetic field. This resonant mode can be excited if the microwave magnetic field of the driving source is uniform across the thickness of the film [88]

![Diagram of Ferromagnetic film on top of a microwave microstrip FMR transducer.](image)

Figure 2.11: Ferromagnetic film on top of a microwave microstrip FMR transducer.

In this project, instead of using a high-sensitivity single-frequency microwave cavity for FMR measurements, the Stripline Broadband FMR method is employed [84]. Figure 2.12 shows the cavity FMR setup and the sample fixture / chamber. There are several limitations of the cavity method. Firstly, a cavity can be only operated at one particular frequency. This limits the amount of information extracted from FMR traces. Secondly, the cavity method is difficult to use for characterising samples with very small magnetic loss. It is because the intrinsic Q-factor of those samples is high, resulting in a strong coupling between the
CHAPTER TWO: Experimental Setups and Techniques

ferromagnetic resonance in the sample and the cavity that may lead to a shift of the resonance frequency of the cavity. Therefore, it makes the measurement of the FMR frequency impossible [89, 90]. Moreover, FMR cavities (including our group’s one) typically operate at about 9.5 GHz. This frequency is often too low for characterisation of nanopatterned films. For instance, the FMR frequency for zero applied field for the nanowire array studied in the present thesis is 10.2 GHz. Hence the cavity method cannot be used for this sample. (details will be discussed in Section 4.1). Furthermore, the cavity is quite big in size. This places a lower limit to the distance between pole pieces of the electromagnet in whose pole gap it is installed. A larger pole gap results in a smaller maximum field produced by the electromagnet. It can be an issue for perpendicular-to-plane FMR measurements which normally require high magnetic fields.

Figure 2.12: Photo of the cavity FMR setup (left photo) and the sample fixture/chamber part (right photo).
On the contrary, the stripline method can be used for broadband FMR measurements (several hundreds of MHz to 40 GHz [91, 92]). It provides room for extracting information from measurements taken at different FMR frequencies and fields. One then can use equations (2.2 and 2.3) to extract the $M_{\text{eff}}$ and $\gamma$ for a sample (some results will be shown in Section 3.3). Furthermore, as mentioned above, the broadband FMR enables us to tune the microwave frequency in order to enable zero applied field hydrogen gas sensing (i.e. the HGS sensor demonstration without applying external magnetic field).

Despite a number of advantages of FMR measurements using stripline over cavity, there is one important drawback of this method - it is less sensitive. This drawback becomes a problem when measuring an FMR response of a very thin and small active ferromagnetic layer (a sample having a 5nm-thick cobalt layer and an area 5 mm by 5 mm). There are two solutions for improving sensitivity of microstrip line FMR. They are lock-in amplification with applied field modulation and interferometric detection techniques, both are employed in our microstrip line FMR setup.

2.2.1.1 Lock-in with field modulation technique

In order to improve the signal to noise ratio of the FMR spectrometer, lock-in amplification technique is often employed with a reference signal in the form of small-amplitude sine wave modulation of the applied magnetic field [93-96]. In order to implement this technique, some hardware modifications are needed. They include installation of modulation coils at the pole pieces of the electromagnet and utilisation of a lock-in amplifier for signal processing. Figure 2.13 shows the block diagram of the required setup [84].
The microwave signal transmitted through the device under test (DUT) is incident on a microwave diode where it is rectified to produce a d.c. signal with a small a.c. signal at the modulation frequency on top of it. The amplitude of the a.c. signal is measured by the digital lock-in amplifier as a function of applied magnetic field for particular frequencies. Alternatively, instead of measuring transmitted signal, one can measure the reflected signal from the DUT with a circulator [97, 98]; the microwave circuitry remains in this case very similar to the circuitry shown in figure 2.13. The two small modulation coils produce an AC magnetic field at a frequency of 220 Hz and RMS amplitude of a couple of Oe. The output power of the microwave generator is adjusted in order to achieve optimal conditions for operation of the diode (maximum sensitivity and linearity). The signal from DUT (either transmitted or reflected) is rectified by the diode and fed into the lock-in amplifier together with a reference signal at the same frequency of 220 Hz as the signal driving the modulation coils. The digital output signal of the lock-in is then proportional to the field derivative of the imaginary part of the microwave susceptibility $\chi$ [98]. The mathematical expression can be described as follows.
CHAPTER TWO: Experimental Setups and Techniques

The microwave susceptibility of the DUT is a function of DC magnetic field, $H_{DC}$. i.e. $\chi (H_{DC})$. The modulation produces an AC field on the top of the DC magnetic field. Therefore, the susceptibility of the DUT becomes: $\chi (H_{DC} + H_M e^{jwt})$, where $H_M$ is the magnetic field provided by the modulation coils and $\omega$ is the modulation frequency. By Taylor expansion, the first two terms of the DUT susceptibility are:

$$\chi (H_{DC}) + i\omega H_M e^{jwt} \frac{d\chi}{dH_{DC}}$$

$$\chi(H_{DC} + H_M e^{jwt}) \approx \chi(H_{DC}) + \frac{d(\chi(H))}{dH} \bigg|_{H_{DC}} H_M e^{jwt}$$  \hspace{1cm} \text{(Eq 2.4)}

Since the rectified signal is fed into a lock-in amplifier, the first DC term will be filtered out. The second term is an AC oscillating signal having the same frequency as the frequency of modulation. Therefore, the second term is what the lock-in amplifier is sensitive to. It is proportional to the amplitude of the modulation field, $H_M$, and also to the first derivative of the susceptibility with respect to the applied field called “differential absorption”. The resonance magnetic field and the linewidth of FMR can be obtained by fitting the differential absorption curve with a model equation.

Figure 2.14 shows the comparison of an FMR differential absorption curve and its first anti-derivative [99]. One can notice that features are more expressed in the differential absorption curve than in the “anti-derivative one” (or simply absorption curve). This is because differentiation enhances the effect of slope changes in the FMR curve. Furthermore, all background signals from sample, microstrip line and other magnetic components located between the electromagnet poles are normally broadband, while signals from the magnetic resonances in the sample are sharp. Therefore, the derivative of the background signals will be much smaller than ones of the resonance signals. Vanishing of the background signal
implies that the sensitivity of the lock-in amplifier can be set to the level of the sample resonance signal. The sensitivity of the lock-in amplifier can be maximised in this way. For the same reason, there is no need to make a separate measurement of the background signal which is an essential procedure of VNA FMR measurements.

![Figure 2.14: The comparison of FMR differential absorption curve (Blue line) and its first anti-derivative (Red line) [99].](image)

It is possible to reduce 1/f noise from the collected data by increasing the modulation frequency [100]. However, the coil inductive impedance increases with frequency, especially when the modulation coils are attached to the poles of electromagnet (similar to shown in Figure 2.12). The increase in the inductance results in a drop of the current passing through the modulation coils which lowers the modulation field, $H_M$. Therefore, there is a trade-off between a lower 1/f noise and a higher amplitude of the modulation field. For a coil attached to a magnet pole, the modulation frequency is typically several hundreds of Hertz [101]. Accordingly, in this project, the modulation frequency is set to 220 Hz.

Beside the modulation field parameters optimization, one can further improve the signal-to-noise ratio of the lock-in method by optimizing lock-in’s settings. An effective
CHAPTER TWO: Experimental Setups and Techniques

way to further lower down the noise level is by increasing lock-in’s time constant and collecting the lock-in signal for a longer time correspondingly (around 6 times the time constant). In this project, the time constant of lock-in amplifier is normally set to 0.3 second and the time to collect the lock-in output signal is 2 seconds. For some samples with extremely low FMR responses, the time constant was set to 1 second and time to collecting signals was 6 seconds.

2.2.1.2 Interferometric detection technique -- Microwave receiver

Beside the lock-in and field modulation technique, the interferometric detection technique is the most efficient way to reduce the noise floor. This technique is enabled by replacing the diode connected to the output of DUT with a microwave interferometric instrument (usually called “microwave receiver”) [102]. Professor Eugene Ivanov (Frequency Standards and Metrology Research Group at UWA Physics) is credited for building the receiver for use in our group’s experiments. The schematic diagram of the receiver is shown in figure 2.15.

Figure 2.15: The schematic diagram of the microwave receiver [22].
CHAPTER TWO: Experimental Setups and Techniques

The microwave receiver is basically a “double” Mach-Zehnder type interferometer. Its concept is better known from Optics where it is used to measure variations of the relative phase shift between two collimated beams from the same light source (one of them is the reference beam, while the other having variations that caused by DUT). However, for the microwave receiver, instead of an optical light source, microwave signals are the input source, and relative phase variations between two microwave signals are compared (one is a reference microwave signal while the other signal is one perturbed by DUT). As mentioned before, the receiver represents a “double” interferometer; there are two interferometers in the circuitry. The major one consists of Paths A and path B (the latter one includes the minor interferometer). After passing those paths the respective signals recombine at a mixer which performs demodulation (rectification) of the microwave signal. The minor one consists of Path C and Path D; the respective signals recombine at Point E. A phase shifter and an attenuator in path C are used to tune to the carrier signal level minimum by arranging destructive interference of the recombining signals. There are two purposes for the minor “interferometer”, firstly, the destructive interference eliminates the background signal such that the signal at Point E is solely the FMR signal from DUT. This operation is often termed "carrier suppression". As a result, the lock-in sensitivity can be set to DUT signal level. Moreover, the presence of the minor “interferometer” also prevents overloading the signal port of the mixer.

The signals recombined at Point E are amplified and split into two more paths: Paths F and G. Path F is connected to the RF port of the mixer while Path G is connected to voltmeter and oscilloscope via a microwave diode for output level monitoring and receiver tuning purposes.

A frequency mixer is a device that performs frequency conversion by multiplying two signals. It has three ports, which are the radio frequency (RF) port, the local oscillator (LO) port and the intermediate frequency (IF) port. Figure 2.16 shows two mixer types,
one is up-conversion while the other is down-conversion mixer [103].

![Diagram of mixer types](image)

**Up-conversion Mixer**

**Down-conversion Mixer**

Figure 2.16: The two types of mixers differing by port connections [103]

The configuration used in the microwave receiver is down-conversion, i.e. the frequency of signal output from the mixer become lower. The input microwave signal splits into two paths: Path A (a major loop of the receiver, i.e. reference signal) is connected to the mixer’s LO port. While Path B passes through DUT (being part of the minor “interferometer”) and ends up at the RF port of the mixer. The mathematical model for the mixer is as follows [103]:

The reference signal (Path A) input to LO port is

$$V_{LO}(t) = A_{LO} \cos(\omega_{LO}t)$$

The modulated signal passing through the DUT then input to RF port is

$$V_{RF}(t) = A(t) \cos(\omega_{RF}t + \theta(t))$$

The mixer multiples the LO and RF signals; the output signal at the IF port is

$$V_{IF}(t) = V_{LO}(t) \times V_{RF}(t)$$

$$V_{IF}(t) = \frac{A(t)A_{LO}}{2} \left[ \cos \theta \left[ \cos(\omega_{LO} + \omega_{RF})t + \cos(\omega_{LO} - \omega_{RF})t \right] - \sin \theta \left[ \sin(\omega_{LO} + \omega_{RF})t + \sin(\omega_{LO} - \omega_{RF})t \right] \right]$$
Recall the trigonometry identity: \[ \cos(A + B) = \cos A \cos B - \sin A \sin B \]

\[ V_{IF}(\omega) = \frac{4|A|^2 f_0}{2} \left[ \cos \left[ \left( \omega_{LO} + \omega_{RF} \right) \tau + \phi(\tau) \right] + \cos \left[ \left( \omega_{LO} - \omega_{RF} \right) \tau + \phi(\tau) \right] \right] \]

(Eq 2.5)

The output (IF) signal of the mixer transforms the LO and RF signals into a low frequency \((\omega_{LO} - \omega_{RF})\) and a high frequency \((\omega_{LO} + \omega_{RF})\) components. The high frequency component is filtered out by the lock-in amplifier; the remaining lower frequency part will have frequency equal to difference between the frequencies of the signals incident on LO and RF port. In the microwave receiver case, both LO and RF have the same carrier frequency, therefore, the mixer output (IF) signals is a DC term with low-frequency modulation on top of it \(A(t)\), which is same output format as from a photo diode.

By using the custom-made receiver, one can demonstrate that there is no observable noise background for an FMR peak amplitude above 100 nV in a single measurement when the time constant of lock-in amplifier is set to 0.3 second [101]. There still plenty of room for further improvement of the noise level by increasing frequency of the modulation coil and / or longer the time constant at lock-in amplifier. The microwave receiver not only helps to reduce the noise level, but also allows one to measure complex-valued signals - either real or imaginary part of the complex microwave magnetic susceptibility can be measured by properly tuning of the receiver. For the measurement of the imaginary part of the magnetic susceptibility, the phase in path A is set to a maximum or a minimum of the IF voltage (at Point H in Fig. 2.15), \(V_{IF}\), dependence on phase \(\phi\), i.e. to the point where \(\frac{\Delta V_{IF}}{\Delta \phi}\) = 0. On the contrary, to measure the real part of the susceptibility, \(\frac{\Delta V_{IF}}{\Delta \phi}\) is set to a maximum. All the results
presented in the project are measurements of the imaginary part of the complex susceptibility. Figure 2.17 shows a photo of the actual setup of the microwave receiver.

2.2.1.3 FMR field and linewidth extraction from experimental results

The shape of the differential trace recorded by FMR is determined by the interference with the background and also by the phase of coupling of the magnetisation dynamics to the microwave current in the stripline. The phase and the interference are taken care by allowing the amplitude of the FMR peak to be a complex-valued quantity. Furthermore, the baseline is subtracted while fitting the data with the model.

Experimentally the response amplitude $r^{(\text{exp})}$ is obtained by fitting the recorded FMR traces with an equation below,

$$A_{\text{exp}}(H) = \frac{r^{(\text{exp})}}{H - (H_p + \text{tan})}$$  \hspace{1cm} (eq. 2.6)
which implies that the height of the experimental peak
\[ |A_{\text{exp}}(H_0)| = \frac{|r^{(\text{exp})}|}{\Delta H} \]
where \( H_0 \) is the resonance field, \( \Delta H \) is the resonance linewidth. As in our experiments we utilize the Field-Modulated FMR, the actual experimental traces have the shape given by

\[
\text{Re}\left(\frac{dA_{\text{exp}}(H)}{dH}\right) = \frac{d}{dH} \left(\frac{(H-H_0)\text{Re}(r^{(\text{exp})}) - \Delta H\text{Im}(r^{(\text{exp})})}{(H-H_0)^2 + \Delta H^2}\right) \quad (\text{eq. 2.7})
\]

where \( r^{(\text{exp})} \) is allowed to take complex values in order to account for potential asymmetries of the FMR absorption lines.

### 2.2.2 Details of the measurement methods

#### 2.2.2.1 Gas chamber for the in-plane and perpendicular-to-plane FMR measurements

Because the project is focused on hydrogen gas sensing, the sample and the stripline transducer should be housed in an air-tight chamber. The gas chamber has to be small enough to fit between the pole pieces of a dedicated electromagnet. The chamber size along the magnetic field direction should be as small as possible in order to reduce separation of the electromagnet pole pieces and hence to maximise the magnetic field produced by the electromagnet. This is especially important for the perpendicular-to-plane FMR measurements. Furthermore, a smaller chamber volume results in a faster change of atmosphere in the chamber, e.g. a faster change in hydrogen concentration in it while performing concentration resolved measurements.

In the initial stage of the project, an air-tight chamber for an in-plane FMR measurement configuration was utilised (Figure 2.18). A co-planar waveguide is
located at the bottom of the chamber. The sample with \textit{Pd} layer facing down sits on top of the waveguide. Two SMA connectors are connected to both ends of the co-planar waveguide to transmit the microwave power from one end of the waveguide to the other. The gas chamber is fixed between the pole pieces of an electromagnet such that the applied magnetic field is in plane and parallel to the co-planar waveguide. A modulation coil is located outside of the chamber providing the modulation field during FMR measurement. A number of important results were obtained with the chamber, such as verification of the m-HGS concept by a former PhD candidate [22], bi-layer thickness optimization [104] and tri-layer thickness optimization (Section 3.2).

Figure 2.18: Photo of the gas chamber used in the initial stage of the project.
CHAPTER TWO: Experimental Setups and Techniques

In order to broaden the understanding of the characteristics of m-HGS, especially for the perpendicular-to-plane (PP) FMR measurements, one more air-tight chamber was fabricated. It enables both in-plane and perpendicular-to-plane FMR measurements (Figure 2.19) with a single fixture. This is important because a significant difference between transmission characteristics of different fixtures was found. The size of this air-tight chamber is 3 cm x 4cm x 8 cm. A microstrip line having a 0.3mm-wide microstrip is used instead of a co-planar waveguide in this fixture. In order to further reduce the chamber size, the chamber has just one connector and just one coaxial cable connected to it, and therefore the FMR measurements are taken in reflection from the chamber’s microwave port. A clamp is added in the fixture to hold the sample in on top of the microstrip line. A modulation coil is mounted on one of the pole pieces of electromagnet to provide a modulation field. Figure 2.20 shows FMR measurements under IP and PP configurations.

Figure 2.19: Photo of the 2nd generation gas chamber for both IP and PP FMR measurements. Figure on the left shows the chamber located between the magnetic poles while figure on the right shows the fixture for mounting the sample on the top of stripline.
2.2.2.2 Time resolved FMR measurement method for HGS demonstration

It is important to demonstrate how the FMR response of m-HGS samples varies in time in the presence of $H_2$. This is also crucial because time-resolved FMR traces can be used for HGS demonstration which is one of the main results of this project.

Time resolved FMR traces are obtained as follows [22, 105-106]. A fixed dc magnetic field (bias magnetic field, whose magnitude depends on the individual sample which is usually close to the FMR field at a frequency of interest) is applied to the sample (IP or PP depending on the FMR configuration of interest). Application of the bias magnetic field is needed, because for a continuous film, the FMR frequency for a zero internal field is zero [84]. On the contrary, a bias magnetic field is not necessarily needed for nano-patterned samples as for them the FMR frequency may be non-vanishing at zero magnetic field [105].

Figure 2.20: Orientation of FMR measurements under IP (left) and PP (right) configurations.
As shown in our works [22, 104-107], FMR peaks are shifted during sample hydrogenation. If the applied field and the microwave frequency are kept constant, but the resonance peak shifts, the amplitude of the microwave signal from the microstrip line output should vary. To register this amplitude variation, the digital output of the lock-in amplifier is recorded as a function of time, in this way one can observe transient processes in the sensor and determine sensor “response” and “recovery” times – i.e. the time required to stabilize the FMR signal at a new level during the hydrogenation process, and the one required to recover the original signal level, once the $H_2/N_2$ mix in the chamber has been replaced with pure $N_2$ (“de-hydrogenation process”). The time constant of the lock-in amplifier is kept at 0.3 seconds, thus enabling reliable measurement of transient processes with characteristic rates larger than approximately 2 seconds. This is fully appropriate for $H_2$ characterization of continuous films since their fastest response times, as measured with FMR, are usually on the order of tens of seconds [105].

Figure 2.21 illustrates the above method. To obtain the traces shown in the figure, a c.w. (continuous wave) microwave signal at a frequency of 8.2 GHz was applied to the sample. First field-resolved FMR traces were obtained for two atmospheres - pure nitrogen gas and 50% hydrogen and 50% nitrogen gas (Panel (a)). Then the applied magnetic field was applied perpendicular to the film plane and set to a value corresponding to some specific point within the field-resolved FMR trace (shown by the red vertical line in Panel (a)). The chamber was then purged with 800 sccm of pure nitrogen for 5 minutes while keeping both microwave frequency and the applied field constant. The atmosphere was then changed to 50% hydrogen and 50% nitrogen gas for 5 minutes. This time has been found to be sufficient to complete the transient process associated with hydrogen intake by Pd. Finally, the chamber is flushed with pure nitrogen gas leading to FMR signal recovery to (almost) the same level.
CHAPTER TWO: Experimental Setups and Techniques

From this figure one sees that the device-prototype response time, as measured at 90% of the steady amplitude (relative to the original level), is 20 seconds. The recovery time (the time needed to recover 90% of the total change in signal, once \( H_2 \) has been removed from the atmosphere in the chamber) is noticeably larger – 120 seconds.

Figure 2.21: Diagram illustrating the physical principle underlying the time-resolved FMR measurements. (a) Conventional field-resolved FMR traces obtained in pure nitrogen gas (black line) and 50%/50% hydrogen/nitrogen gas mix (blue dashed line). The microwave frequency is kept constant at 8.2 GHz. (b) Black solid line: amplitude of the FMR response as a function of time, when the applied field has been set to a constant value of 12988 Oe [see red vertical line in (a)] with the frequency of 8.2 GHz. The atmosphere in the chamber is originally pure nitrogen gas, constantly flowing through the chamber. It is replaced with the constantly flowing gas mix at time = 300 seconds. The chamber is then flushed with pure nitrogen at time = 600 s. This pure gas remains constantly flowing afterwards. The red dashed line shows the hydrogen concentration in the chamber (right-hand axis) [106].

All the results in chapter 4 demonstrating functionality of m-HGSs (including nanopatterned samples and continuous film based ones) rely on the time-resolved method [105-107].
2.2.2.3 In-situ FMR measurement with elastic strain applied to the sample

One project direction was to study physical origins of the perpendicular magnetic anisotropy (PMA) induced at the interface of cobalt and palladium layers and the origins of PMA reduction in the presence of hydrogen gas (see Section 3.6 for a detailed discussion). To understand this, we combined ferromagnetic resonance (FMR) measurements under two different stimuli – hydrogen gas and external elastic strains. Therefore, a setup which is able to measure FMR under strain applied to the sample is needed. Such a setup is not available at UWA, therefore, this was a co-operative project study with Université Paris 13, France. They are experts in magneto-elasticity and have a unique custom-built setup which can take microstrip line FMR measurements in the presence of an elastic strain applied to the sample. In parallel, they can record the magnitude of the strain by using Digital Image Correlation technique [108].

A strain can be applied to a thin film either by gluing it to a piezoelectric actuator or bending the thin film. In this study, the piezoelectric actuator method is used. The thin film is attached to the actuator using special glue. Then a DC voltage is applied to the actuator which has the effect of straining the sample (figure 2.22). The deformations are perfectly transmitted through interfaces (actuator/Kapton substrate) and (Kapton substrate/thin film) as shown in Zighem et al for the piezoelectric actuator [108] and Gueye et al. for bending the sample [109].
CHAPTER TWO: Experimental Setups and Techniques

Figure 2.22: The deformation applied to the thin film samples by piezoelectric actuator.

[108]

The Digital Image Correlation (DIC) technique based on the optical observation of the film surface is utilised to estimate the in-plane strains applied to the samples [108]. DIC method enables accurate measurements of changes in digital images [110, 111]. This method employs tracking and image registration in order to make full-field non-contact measurements of movements (in terms of strains and displacements) in the area of engineering applications (mechanical properties of materials). Figure 2.23 shows the results of the piezoelectric actuator setup by DIC method [108].
Figure 2.23: (a) Top view sketch of the system showing the spray-painted speckle pattern in order to generate a contrast at the surface of the film. The blue and red areas correspond to the top surface of the film region and to an uncoated area of the actuator, respectively. (b) Extracted mean in-plane strains from the blue (film surface) to red (uncoated actuator surface) areas by performing DIC calculations. Continuous lines correspond to $\varepsilon_{xx}$ and $\varepsilon_{yy}$, while, and symbols correspond to $\varepsilon_{11}$ and $\varepsilon_{22}$. [108]

By using the above setup at Université Paris 13, France, one can convert the magnitude of a voltage applied to the actuator into the respective strain applied to the sample and measure an FMR field shift associated with the strain. In this project, this capability is utilised in order to study physical origins of the perpendicular magnetic anisotropy (PMA) induced at the interface of cobalt and palladium layers and the origins of its reduction in the presence of hydrogen gas (Section 3.6). Figure 2.24 is the photo of the in-situ FMR measurement setup with strain applied.
CHAPTER TWO: Experimental Setups and Techniques

Figure 2.24: Photo of the in-situ FMR measurement setup with strain applied. (a) Setup image of the combined MS-FMR/DIC experiment. The circled number correspond to: (1) Keithley Model 2400; (2) CCD camera (AVT-Pike-f421b); (3) Objective lens for the CCD camera; (4) White light source; (5) Electromagnet; (6) Schottky detector; and (7) Modulation coils. Pin and Pout are the injected and transmitted radio frequency current. (b) Zoom in showing the sample mounted onto the microstrip line. A typical calculated strain field map is present at the top of the sample. (c) Zoom in of the speckled pattern (spray-painted) at the top of the sample necessary for the strain fields calculations.
2.3 Other characterisation setups and techniques

2.3.1 Gas blending system

In order to demonstrate the gas sensing capability, one needs a wide range of hydrogen/carrier-gas mix concentrations. To this end, we employed home-made gas mixture preparation equipment, incorporating Alicat® mass flow controllers and software (Flow Vision® MX). This allows one to produce a gas mixture with precisely controlled concentration and flow rate. The gas mixture constantly flows through the chamber containing the sample and the microstrip line. The block diagram of the gear is shown in figure 2.25. The gas mixing system includes three Alicat® mass flow controllers: two of them are for hydrogen gas (path A) while the remaining one is either for nitrogen or air (path B). The two mass flow controllers for hydrogen (path A) with different maximum flow rates (one is 50sccm while another is 1000sccm) enable a wide range of hydrogen concentrations of the carrier gas (nitrogen or air). For the bottles connected to mass flow controllers are both highly pure gases (i.e. 100% $H_2$ and 100% $N_2$), the concentration of $H_2$ in the carrier gas (either $N_2$ or air) can range from 100% to 0.1%. Yet lower $H_2$ concentrations (say 0.001%) can be obtained if one uses diluted $H_2$ from a bottle instead of pure $H_2$ as the input gas.

All the results shown in this project have been obtained under a constant flow rate of 800 sccm at atmospheric pressure (unless specified otherwise). The gas flow rate will not affect the sensor sensitivity, however it will affect the sensor’s hydrogenation response times. A finite time is needed to achieve the gases’ concentration equilibrium in the gas chamber. The time is related to the chamber’s volume, the volume of transfer gas pipes and also the gas flow rate. The volume of the custom-made chamber is around 20 cm$^3$ while the volume of the transfer gas pipes is around 50 cm$^3$. 
CHAPTER TWO: Experimental Setups and Techniques

The flow rate we used for the study is 800 sccm; this implies that the concentration equilibrium in the chamber is achieved within less than 6 seconds.

As the measurements have been taken in a very broad range of concentrations across the threshold of hydrogen flammability in air (4%), nitrogen is utilized as a carrier gas for fire safety. This is also done for hydrogen gas concentrations below 4%, in order to compare that data with data taken at higher concentrations. For the specific purpose of the present work this arrangement is fully appropriate. Furthermore, in our recent work [105] we have demonstrated that the responses in air and nitrogen converge when approaching the 2% concentration point. Figure 2.26 shows the photo of the tailor-made gas mixing system.

Figure 2.25: Schematic of the gas blending system.

Figure 2.26: Photo of the gas blending system.
2.3.2 SQUID magnetometry

The superconducting quantum interference device (SQUID) is the most sensitive technique and enables the measurement of the absolute magnetic moment of the sample involved. Detailed information on the principle of operation of the SQUID detector can be found in the literature [112-114]. In general, a direct-current SQUID detector consists of a superconducting loop broken by two Josephson junctions as shown in figure 2.27 [115].

![Figure 2.27: A schematic diagram and working principle of SQUID.](image)

The great sensitivity of the SQUID devices is because of its measuring changes in magnetic field associated with one flux quantum which is also one of the discoveries associated with Josephson junctions that flux is quantized in units

\[
\Phi_0 = \frac{2\pi h}{2e} = 2.067\times 10^{-15}\text{esu}\cdot\text{cm}^2
\]
CHAPTER TWO: Experimental Setups and Techniques

A constant biasing current is provided in the SQUID device, the measured voltage oscillates with the changes in phase at the two junctions, which depends upon the change in the magnetic flux. By counting the oscillations, it allows us to evaluate the flux change which has occurred [115].

The device employed in this project is Quantum Design MPMS3. Figure 2.28 shows the photo of the SQUID setup.

As discussed above, SQUID is able to measure the absolute magnetic moment of the sample. One can use the data to estimate the PMA field, $H_{PMA}$, by using the below equation:

$$H_{PMA} = 4\pi M_s - 4\pi M_{Eff}$$

Where $4\pi M_s$ can be obtained by SQUID and $4\pi M_{Eff}$ can be obtained by taking FMR measurements in a range of frequencies and fitting the recorded FMR traces either with equation (Eq 2.2) for IP or (Eq 2.3) for PP cases. The detailed method of estimating $H_{PMA}$ will be introduced and discussed in Section 3.3.

Figure 2.28: The photo of the SQUID system.
2.3.3 X-ray Diffraction (XRD)

The X-ray diffraction (XRD) is a powerful technique for identifying crystalline phases existing in a material. It can be used to measure the structural properties of the materials such as strain, grain size, epitaxy, composition, preferred orientation and defect structure. XRD is a non-contact and non-destructive measurement and can be used for in-situ studies. Detailed information on the principle of operation of the XRD can be found in the literature [116]. Some basic principles of X-ray related to this project will be briefly discussed; one of the main measurement modes of XRD is $2\theta$ measurement. In the XRD $2\theta$ measurement, the diffracted intensity is measured as a function of $2\theta$ and the orientation of the sample, which then yields the diffraction pattern (figure 2.29).

Figure 2.29: The measurement orientation of $2\theta$ XRD measurement. [117]
CHAPTER TWO: Experimental Setups and Techniques

Figure 2.30 shows crystal planes of atoms that are spaced at a distance \( d \) apart. However, they can be resolved into many different atomic planes with different \( d \) spacings. In order to identify them, a coordinate system is introduced with unit vectors \( a, b, \) and \( c \). Let us consider a cubic crystal with \( a=b=c \), an orthogonal system can be formed by using these unit vectors. We can now identify any atomic plane uniquely defined by its Miller indices. There are three reciprocal intercepts of the plane with the \( a-, b- \) and \( c- \) axes. They are reduced to the smallest integers having the same ratio. Therefore, an \((hkl)\) plane intercepts the crystallographic axes at \( a/h, b/k \) and \( c/l \). For cubic crystals, the atomic plane spacing \( d \) between \((hkl)\) planes, denoted by \( d_{hkl} \), is equal to:

\[
d_{hkl} = \frac{a_o}{\sqrt{h^2 + k^2 + l^2}}
\]

where \( a_o \) is the lattice constant of the crystal. However, for a hexagonal structure, the atomic planes would have another representation, \((hkil)\), which are defined by two different lattice constants, \( a \) and \( c \) of the crystal. The atomic plane spacing \( d \) between \((hkil)\) planes, \( d_{hkil} \), in a hexagonal structure is equal to:

\[
d_{hkil} = \frac{1}{\sqrt{\frac{h^2 + k^2 + l^2}{a^2} + \frac{h^2}{c^2}}}
\]

(Eq 2.8)

When there is constructive interference between X rays scattered by the atomic planes in a crystal, a diffraction peak is observed. The condition for a constructive interference from planes with spacing \( d_{hkl} \) (for cubic structure) or \( d_{hkil} \) (for hexagonal structure) is given by the Bragg’s law:

\[
n\lambda = 2a_{hkl} \sin \theta_{hkl}
\]

\[
n\lambda = 2a_{hkil} \sin \theta_{hkil}
\]
Where \( \lambda \) is the wavelength of the X-rays, \( \Theta_{hkl} \) and \( \Theta_{h'k'l'} \) are the angle between the atomic planes and the incident X-rays beam. In order to observe the diffraction peaks, the detector must be placed at the diffraction angle equal to \( 2\Theta \), and the sample must be oriented with the angle between the diffracting plane and the incident X-rays equal to the Bragg angle, \( \Theta \).

Figure 2.30: Several atomic planes and their spacing in a cubic crystal. [117]
CHAPTER TWO: Experimental Setups and Techniques

Materials composed of different elements or layered structure can be analysed with XRD. However, XRD is more sensitive to elements with higher atomic numbers because the diffracted intensities from these elements are much stronger. Furthermore, if the sample is too thin (thinner than the X-ray can penetrate, around couple of micrometres), the diffracted intensity also drops. Therefore, the sensitivity of XRD depends on the material and also on its thickness. When the diffracted intensities are small, a longer time measurement is recommended for the better signal to noise ratio.

In this project, the active layers of the m-HGS are very thin cobalt (5 nm) and palladium (10nm) layers, therefore, in order to obtain a better result, a single run of XRD measurement lasts for more than 18 hours.

The XRD setup used in this project is located at Centre of Microscopic and Chemical Analysis, CMCA, University of Western Australia. The model of the XRD is “Empyrean” and the software for data analysis is “HighScore plus”. Figure 2.31 shows the photo of the X-ray system used in the project, while figure 2.32 shows some typical peak angles for cobalt and palladium from XRD.

![Figure 2.31: the photo of the XRD.](image)
As discussed above, one important parameter obtained from 2Θ XRD measurement is the lattice constant of the crystal. We will make use of the results to compare the sample with and without in-situ annealing (details will be discussed in Section 3.5).

2.4 Chapter Summary

This chapter provides an overview of the sample fabrication, experimental methods and techniques used in the entire thesis. Since this section includes wide variety of setups and techniques, it is difficult to mention all of them in detail here; however, ones can obtain more information by checking the references quoted in the sections devoted to description of individual methods.
Chapter Three: Details of physics underlying functionality of magnetic hydrogen gas sensors

3.1 Definitions of parameters for characterisation of m-HGS

This chapter focuses on results of a number of experiments aimed to gaining understanding of physics that affects films’ sensitivity to hydrogen gas and response. The effect of active sensor layers’ thickness, FMR applied field configuration, sample orientation, in-situ annealing during sputtering process, as well as the impacts of elastic strain and film nano-patterning on the films’ performance as hydrogen gas sensors are discussed. This is one of the most important chapters in this thesis, as it includes not only a large number of details of physics that underlie the functionality of the m-HGS, but also reports on attempts to optimise the materials as efficient hydrogen gas sensors.

First of all, the role of thickness of the magnetic layer of the layered film will be discussed in this chapter. The discussion then will turn to the effect of the FMR measurement configuration (In-Plane (IP) or Perpendicular-to-Plane (PP)) on both sensitivity and response times of the films. Section 3.4 deals with the effect of sample orientation with respect to the microwave probing stripline (the thin film facing it (“film down”) or film’s substrate facing the stripline (“film up”)) on the hydrogenation response time. Section 3.5 discusses an in-situ annealing technique for bi-layer films that enhances hydrogenation sensitivity. Furthermore, the role of elastic strain in the sensor response will be shown in Section 3.6. The last but not least, responses of nano-patterned and continuous film samples will be compared in Section 3.7.
CHAPTER THREE: Details of physics underlying functionality of m-HGS

We start with defining two parameters which are important for HGS performance; this will allow quantitative comparison between different samples. They are material’s sensitivity to hydrogen gas and its hydrogenation response time.

3.1.1 Definition of sensitivity for the m-HGS

As far as the sensitivity of samples to hydrogen gas is concerned, two methods can be usually used for samples’ comparison. The first one is the field swept FMR measurement (this is the static magnetic field applied either In-Plane or Perpendicular to the film plane) under pure nitrogen or hydrogen-nitrogen mix atmospheres. A shift of the resonance field due to hydrogenation can be observed in the presence of hydrogen gas (refer to Section 2.2.2). The larger the resonance field shift, the higher the sensitivity. Figure 3.1 compares sensitivity to hydrogen between two CoPd alloy samples. As seen from the figure, Sample 3 shows a much larger resonance field shift (y-axis) than Sample 2 for the whole range of displayed hydrogen gas concentrations in the gas mix (X-axis). Thus, the sensitivity of Sample 3 to hydrogen is higher than that of the other sample.
CHAPTER THREE: Details of physics underlying functionality of m-HGS

Figure 3.1: Resonance field shift vs hydrogen gas concentration for two samples. Sample 3 demonstrates significantly higher hydrogen sensitivity than Sample 2. The samples are CoPd alloy films with different contents of cobalt. The static field is applied perpendicular to the plane of the samples.

The second method is “$\Delta V$” output of time resolved measurements when the atmosphere in the chamber is cycled between pure nitrogen and a nitrogen-hydrogen gas mix. Details of the time resolved measurements have been already discussed in Section 2.2.2.2. From the time resolved traces, one can obtain the delta V (Figure 3.2) values for a particular change of atmosphere content - from the initial 100% nitrogen to a $X$ % of hydrogen + 100-$X$ % nitrogen mix. Figure 3.2 shows a typical time resolved profile for a m-HGS. From the profile, $\Delta V$ is around 3.5 $\mu$V for a 50% hydrogen + 50% nitrogen gas mix relative to 100% nitrogen atmosphere. $\Delta V$ is a convenient parameter to compare sensitivities of different samples. Figure 3.3 shows one example of hydrogen sensitivity comparison by using $\Delta V$ extracted from the time-resolved profiles obtained for the same film but for two different measurement conditions.
Figure 3.2: A typical time-resolved profile for an m-HGS. From the profile, the sensor output $\Delta V$ is around 3.5 $\mu$V when the atmosphere is changed from 100% nitrogen atmosphere to a gas mix of 50% hydrogen + 50% nitrogen.

Figure 3.3: Comparison of sensitivities to hydrogen by using the $\Delta V$ values extracted from the time resolved profiles. Both data sets are for the same sample, but taken in different measurement conditions (at different microwave frequencies).

Here it is important to note that, in order to have a fair comparison, all the conditions for FMR characterisation (for both field-resolved sweeps and time resolved profiles)
have to be the same during measurements in different atmospheres. For example, the power and frequency of the microwave generator inputs, time constant and sensitivity settings for the lock-in amplifier should be kept precisely the same during the whole process of hydrogenation and dehydrogenation of the sample.

At the same time, the FMR signal shape and amplitude are affected by the sample dimensions and how the sample is placed on the stripline. Therefore, the sample fixture is equipped with a clamp that fixes the sample rigidly on top of the stripline, in order to prevent the sample movement during gas purging. The samples size does affect the amplitude of FMR response. However, the FMR amplitude and the FMR peak position do not correlate, therefore if the measurements in different atmospheres are taken for the same sample it is fair to compare the FMR amplitudes. The absolute values of the amplitudes do not carry useful information (because they depend on the sample size and position), but the ratio of FMR amplitudes for different atmospheres does not depend on these parameters and represents a valid characteristic of a sample.

3.1.2 Definition of hydrogenation response times for the m-HGS

The time resolved trace is the sole method used to compare response times of different samples in this thesis. Figure 3.4 shows a typical time resolved profile for the m-HGS, and two characteristics of the profile are explained in the figure. The hydrogen absorption time, is defined as a time to reach 90% of the new steady amplitude relative to the original level once the atmosphere in the chamber has been swapped from hydrogen-free to hydrogen-containing one. The hydrogen desorption time is a time needed for the system to recover from its exposure to hydrogen by getting rid of 90% of the total change in signal induced by the exposure. By using the definitions discussed above, one finds that the hydrogen absorption time is 20 seconds while the hydrogen desorption time is 120 seconds from the example in figure 3.4.
Similar to the comparison of hydrogen sensitivities, in order to enable fair comparison of the response times, all the settings for an FMR measurement (for both field sweeps and time resolved profiles) have to be kept the same. This pertains to the microwave generator’s output power and frequency and lock-in amplifier’s time constant and sensitivity settings. However, the most important is to keep the gas flow rate the same during the whole course of the time resolved FMR measurements. In this thesis, a 800 sccm flow rate is utilised for all the time resolved FMR measurements, unless otherwise specified.

Figure 3.4: A typical time-resolved profile for the m-HGS.
CHAPTER THREE: Details of physics underlying functionality of m-HGS

3.2 Cobalt thickness optimisation for both bi- and tri-layer m-HGS

3.2.1 Objective:

In the initial stage of the project, we looked for an optimal layer composition for the film m-HGS. The effect of the Co layer thickness is also of fundamental importance for understanding physics behind films’ sensitivity to hydrogen gas. Three different types of structures are investigated. They are bi-layers (Section 3.2.1), tri-layers (Section 3.2.2) and super-lattices of cobalt and palladium layers (Section 3.2.3). All the measurements in the study have been carried out in the in-plane FMR configuration.

3.2.1. Co thickness dependence in bi-layer structures

The work presented in this section is based on a peer-reviewed first-authored work by the author of the present thesis [104]. This project deals with the simplest structure – a bi-layer, Si//Co/Pd film – as an active element of the m-HGS. Since the amplitude of the FMR response scales as the volume of the resonating material, it is important to keep the thickness of the cobalt layer at least a couple of nanometres thick for sensing applications. In this study, thickness of palladium is fixed at 10 nm while the thickness of cobalt varies from 5 to 25 nm (Co = 5, 6.6, 8, 10, 15, 20 and 25 nm). All the samples were sputtered by the in-house sputtering machine.

FMR field sweeps were taken at fixed frequency at 10 GHz and resonance field shifts were observed while changing atmosphere between pure nitrogen and pure hydrogen gas (refer to Section 3.1). The larger the FMR peak shift due to hydrogenation, the higher sample’s sensitivity to hydrogen. A single-layer 5 nm thick cobalt film was also prepared to act as a control sample.
CHAPTER THREE: Details of physics underlying functionality of m-HGS

The control sample (Si//Co 5nm) does not show any FMR peak shift under exposure to hydrogen. Moreover, FMR peak positions for all the samples are totally reversible while cycling between 100% N₂ and 100% H₂ atmospheres. The FMR characterization revealed a clear tendency: the FMR peak shift due to the presence of H₂ rapidly decreases with an increase in the thickness of the Co layer (figure 3.5). This is consistent with the resonance shift being due to an interface effect, related to a reduction in the perpendicular magnetic anisotropy at the interface of the Co and Pd layers, as previously suggested [22, 37, 48].

Figure 3.5a): Dependence of the hydrogen-gas induced ferromagnetic resonance field shift as a function of the cobalt thickness. The line is a guide for the eye. Driving frequency is 10 GHz. Palladium layer thickness is the same for all cobalt layer thicknesses: 10 nm. Figure 3.5b) The same, but as a function of 1/cobalt thickness. A clear linear dependence is observed. Points: experiment, solid line: fit with a straight line fit.

Figure 3.6 demonstrates typical examples of the respective raw FMR traces. These particular traces were taken at the microwave frequency of 10 GHz. These figures confirm our previous observation based on characterising a single film thickness [22]: in the presence of hydrogen gas the absorption amplitude is increased and the resonance linewidth is reduced, in addition to the shift of the resonance field.
Figure 3.6: Raw field-resolved FMR traces taken at 10GHz (a) Cobalt thickness is 5nm; (b) 10nm and (c) 25 nm. Red circles: $H_2$ atmosphere; black squares: $N_2$ atmosphere. Palladium layer thickness is the same for all cobalt layer thicknesses: 10 nm.

We suggest two contributions to these changes. One of them is the effect of spin pumping [118] through the interface. The absorption of $H_2$ is known to reduce
conductivity of $Pd$ [18]; consequently the efficiency of spin pumping is reduced and the total resonance linewidth becomes smaller. In parallel, this increases the absorption amplitude, since the amplitude of any resonance driven by an external force is inversely proportional to the losses in the system.

The second effect which may influence the resonance amplitude is the reduction in the strength of microwave shielding of the FMR dynamics in the $Co$ layer by microwave eddy currents in the overlaying $Pd$ layer. Recently it has been shown that this effect can be significant in substrate/ferromagnet/non-magnet metallic bilayer films [119]. The decrease in the $Pd$ conductivity upon absorption of $H_2$ should lead to a drop in the shielding effect and the amplitude of the FMR response should grow accordingly. On the contrary, the change in shielding effect is not expected to affect noticeably the resonance linewidth, because the impact of the eddy current losses on the total FMR linewidth of materials with sub-skin-depth thicknesses is usually negligible.

There are two crucial conclusions from the study: Firstly, a clear tendency of “hydrogen sensitivity” of the m-HGS to rapidly decrease with an increase in the thickness of the cobalt layer. This confirms that we are dealing with an interface effect - a reduction in the $PMA$ at the interface of the $Co$ and $Pd$ layers. Furthermore, the optimal thickness for the $Co$ layer of the bi-layer structures also follows from this study. It is 5 nm, as optimised based on capabilities of the in-house sputtering machine and the sensitivity of our FMR setup. This thickness was accepted as the “optimal configuration” for all subsequent studies involving bi-layer structures. Fine-tuning of the bi-layer structure properties has been done based on this configuration (e.g. by adding in-situ annealing to the fabrication tool set). Also, one of the device prototypes demonstrating m-HGS functionality is based on this configuration.
3.2.2 Co thickness dependence in tri-layer structures

A Si//Pd/Co/Pd tri-layer is one more simple structure for the active medium of the m-HGS. The initial idea for the tri-layers study was that adding one more interface of Co with Pd will yield increased hydrogen sensitivity when compared with bi-layer structures. In this study, the thickness of both palladium layers is fixed at 10 nm while the thickness of cobalt varies from 5 to 50 nm (Co = 5, 6, 8, 10, 15, 20, 30, 40 and 50 nm). All the samples were sputtered with the in-house sputtering machine. Similarly to the bi-layer studies, the method for the comparison of samples’ sensitivities is using FMR field sweeps at fixed frequency of 10 GHz and swapping between pure nitrogen and pure hydrogen atmospheres. The more the peak is shifted due to hydrogenation, the higher the sensitivity is.

FMR responses of all the tri-layers samples are totally reversible upon the atmosphere change except for the thickest tri-layers - having 40 and 50 nm thick cobalt layers. The two samples show signature of delamination after exposure to 100% H₂. Such delamination has been discussed previously in section 1.1.2 [35]. Therefore, the FMR peak shift data could only be obtained for samples with 30nm cobalt layer thicknesses. Figure 3.7 shows the dependency of hydrogen sensitivity as a function of cobalt thickness for the tri-layers. Surprisingly, this study revealed a totally different tendency with respect to the bi-layer structure case: When the tri-layer film has a thickness smaller than 10 nm, a behaviour similar to the one exhibited by the bi-layers can be observed - a small decrease in hydrogen sensitivity with the increase in the cobalt thickness. However, a pronounced peak of hydrogen sensitivity is found for a cobalt thickness of 20 nm (figure 3.7), followed by a rapid drop in the sensitivity for 30nm of cobalt. This suggests that there is an optimal cobalt thickness for the tri-layers structure of 20 nm. This experiment was repeated two more times employing samples fabricated with the in-house sputtering machine, and similar findings were obtained.
Also, similar tri-layers were sourced from the University of Lorraine, France; they demonstrated the same behaviour.

Figure 3.7: Hydrogen-gas induced ferromagnetic resonance field shift as a function of the cobalt thickness for tri-layer Pd/Co/pd//Si films. The line is a guide for the eye. Driving frequency is 10 GHz. Thickness of the palladium layers is the same for all samples: 10 nm.

Figure 3.8 demonstrates typical examples of the respective raw FMR traces. These particular traces were taken at the microwave frequency of 10 GHz. Similar to the bi-layer structures, in the presence of hydrogen gas the absorption amplitude is increased and the resonance linewidth is reduced, in addition to the shift of the resonance field.
CHAPTER THREE: Details of physics underlying functionality of m-HGS

Figure 3.8: Raw field-resolved FMR traces taken at 10GHz for tri-layer structures. (a) Cobalt thickness is 5nm; (b) 10nm; (c) 20 nm and (c) 30 nm. Red circles: pure $H_2$ atmosphere; black squares: pure $N_2$ atmosphere. Top and bottom palladium layer thicknesses are the same for all cobalt layer thicknesses: 10 nm.

The tri-layer films demonstrate behaviour similar to the one of bi-layers: In the presence of hydrogen gas the absorption amplitude is increased and the resonance linewidth is reduced, in addition to the shift of the resonance field. The explanation is the same as for the bi-layers (refer to Section 3.2.3).
CHAPTER THREE: Details of physics underlying functionality of m-HGS

At this stage we do not fully understand the physical origins of the maximum of the curve in figure 3.7. One possible idea is that there are two competing processes running in parallel in the system. One is the generic 1/thickness dependence of the impact of an interface effect on properties of a whole layer. The second is that growing a Co layer on top of a seed Pd layer potentially improves quality of the Co layer, and the quality increases with an increase in the Co layer thickness. The latter leads to a bigger hydrogen-induced FMR field shift for thicker films. For small Co layer thicknesses the second process dominates, but for thicknesses >20 nm the 1/thickness law takes over leading to formation of the maximum at 20 nm.

Although so far we cannot fully understand the dependence of hydrogen sensitivity on cobalt layer thickness for tri-layer structures, but the effect has been shown to be reproducible. The optimal thickness of Co for the tri-layers structure is 20nm with both top and bottom Pd layers being 10nm thick. One important consequence of this result is that it allows us using 4-times thicker layers with respect to the bi-layer films which theoretically [84] boosts the amplitude of the FMR response of the films by 4 times. The latter improvement in the signal quality will be particularly important for the investigation of nano-patterned tri-layer structures and demonstration of their strong potential as an active medium for m-HGS reported in Section 4.1 below. This is because nanopaterning has been found to significantly decrease the FMR absorption amplitude with respect to continuous films.
3.2.3 Hydrogen sensitivity of Co/Pd super-lattices

A number of research groups have been interested in super-lattices of cobalt and palladium because they exhibit perpendicular magnetic anisotropy (PMA) and therefore are promising candidates for perpendicular recording media [120, 121]. PMA occurs in Co/Pd super-lattices and is understood as Néel surface magnetic anisotropy with regard to reduced symmetry of Co atoms at the Pd/Co interface [122]. Multiple studies for optimisation magnetic properties of Co and Pd super-lattices have been carried out. In particular, optimisation of sputtering conditions for the Pd underlayer was performed [123, 124] and search for an appropriate underlayer [125, 126]. Researchers have also been interested in hydrogen sensing with Co/Pd multilayers. [38, 127]. Therefore it was crucial to check the hydrogen sensitivity of Co/Pd super-lattice in the framework of the present PhD study. Two different batches of Co/Pd super-lattice samples were under the study. The first lot of samples was sputtered by our in-house sputtered machine. It was designed based on the found optimal thicknesses for both bi-layer and tri-layer structures. The second sample(s) was fabricated by Prof. A.O. Adeyeye’s group at the Department of Electrical and Computer Engineering, National University of Singapore (NUS). The layers of this super-lattice were significantly thinner. Details of the configurations are shown in table 3.1. The same method of the FMR field sweeps at fixed frequency of 10 GHz taken in pure nitrogen and pure hydrogen atmospheres was employed to carry to this study.
CHAPTER THREE: Details of physics underlying functionality of m-HGS

Sample Si//Pd Co Pd Co Pd Deposition

Bi-layers reference 5 10 In house sputtering machine

double bi-layers 5 10 5 10

Bi-layers reference 5 10 In house sputtering machine

double bi-layers with thin Pd 5 5 5 5

bi- + Tri-layers 5 10 20 10

5 layers 7 15 7 5 7

double Tri-layers 10 20 10 20 10

Ten layers [Co3nm/Pd6nm]_5 by NUS

Table 3.1: The Co/Pd super-lattices deposited by in-house sputtering machine or NUS.

FMR responses of all the super-lattice samples were found to be totally reversible upon returning samples to original atmospheres except for the double-trilayers Si//Pd10nm/Co20nm/Pd10nm/Co20nm/Pd10nm. For the latter samples, delamination was observed in pure H₂ not allowing taking the FMR measurements. The results obtained for the other samples are shown in table 3.2. The reference bi-layers sample show FMR peak shifts consistent with our previous studies (see Sections 3.2). However, for all the other super-lattices noticeably poorer hydrogen sensitivity than for the reference sample was found.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Si//Pd</th>
<th>Co</th>
<th>Pd</th>
<th>Co</th>
<th>Pd</th>
<th>Deposition</th>
<th>Peak shift (Oe) upon hyrogenation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bi-layers reference</td>
<td>5</td>
<td>10</td>
<td></td>
<td></td>
<td></td>
<td>In house sputtering machine</td>
<td>66</td>
</tr>
<tr>
<td>double bi-layers</td>
<td>5</td>
<td>10</td>
<td>5</td>
<td>10</td>
<td></td>
<td></td>
<td>3</td>
</tr>
<tr>
<td>double bi-layers with thin Pd</td>
<td>5</td>
<td>5</td>
<td>5</td>
<td>5</td>
<td></td>
<td></td>
<td>18</td>
</tr>
<tr>
<td>bi- + Tri-layers</td>
<td>5</td>
<td>10</td>
<td>20</td>
<td>10</td>
<td></td>
<td></td>
<td>30</td>
</tr>
<tr>
<td>5 layers</td>
<td>7</td>
<td>15</td>
<td>7</td>
<td>5</td>
<td>7</td>
<td></td>
<td>24</td>
</tr>
<tr>
<td>double Tri-layers</td>
<td>10</td>
<td>20</td>
<td>10</td>
<td>20</td>
<td>10</td>
<td></td>
<td>Nil</td>
</tr>
<tr>
<td>Ten layers</td>
<td>[Co3nm/Pd6nm]_5</td>
<td>by NUS</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>1</td>
</tr>
</tbody>
</table>

Table 3.2: Hydrogen sensitivity for Co/Pd super-lattices
CHAPTER THREE: Details of physics underlying functionality of m-HGS

Figure 3.9 demonstrates typical examples of the respective raw FMR traces. These particular traces were taken at the microwave frequency of 10 GHz. Similar to the previous studies, in the presence of hydrogen gas the absorption amplitude is increased and the resonance linewidth is reduced, in addition to the shift of the resonance field.

Figure 3.9: Raw field-resolved FMR traces taken at 10GHz for structures, (a) is bi-layer Co 5nm/Pd10nm; (b) is double bi-layer; (c) is double bi-layer with thin Pd; (d) is bi- plus Tri-layers; (e) is 5 layers and (f) is 10 layers sample deposited by NUS.
CHAPTER THREE: Details of physics underlying functionality of m-HGS

The Co/Pd super-lattices structure shows behaviour similar to both bi- and tri-layers: in the presence of hydrogen gas the absorption amplitude is increased and the resonance linewidth is reduced, in addition to the shift of the resonance field and can be explained in a similar way (Section 3.2.3).

All the super-lattices show smaller hydrogen sensitivity than bi-layers with 5nm thick cobalt layers. This is surprising because Co is supposed to be non-transparent to hydrogen gas. Therefore Pd layers buried below Co ones should not absorb hydrogen. This experiment however shows a behaviour consistent with the 1/thickness dependence law we found on section 3.2.1 [104] if one considers the total thickness of Co in the stack. This may suggest that hydrogen may penetrate through thin Co layers and reach buried Pd ones.

Due to the above findings, Co/Pd super-lattices structures were not studied further and the optimisation and demonstration works will be focused on optimal bi- and tri-layers structures.

3.3 Effect of FMR measurement geometry on hydrogen sensitivity and response time.

In this work it was found that hydrogen sensitivity and response times are affected by the measurement geometry –IP or PP (Section 2.3) - in which FMR measurements are taken. In this section, we will discuss this effect. Importantly, the configuration influence on both sensitivity and response times is not subtle; therefore this result is crucial for m-HGS performance optimisation.

The sample used in both investigations is a bi-layer film (Si//Co5nm/Pd10nm), deposited with the in-house sputtering machine; the deposition was followed by in-
CHAPTER THREE: Details of physics underlying functionality of m-HGS

situ annealing at 200°C for 30mins (as per in Section 2.1.2). The gas chamber used for this study is a slim one (mentioned in Section 2.2.2). The small chamber thickness enables positioning the chamber in a narrow pole gap of an electromagnet needed to reach magnetic fields required for taking PP FMR measurements which are noticeably higher than for the IP configuration.

3.3.1 Hydrogen sensitivity affected by configurations of FMR measurement

The work presented in this section is based on a peer-reviewed published first-authored work [107]. As discussed above, the magnitude of the FMR peak shift upon hydrogenation is critical for determining the sensor’s sensitivity: the more the FMR peak shifts at a given hydrogen gas concentration, the higher the sensitivity to small concentrations. In this study we demonstrate that the hydrogen sensitivity is enhanced when the static magnetic field is applied perpendicular to the film plane (i.e. in the PP FMR configuration). A factor of eight times improvement is observed with respect to the IP FMR configuration studied previously. An analysis based on the Kittel equation for FMR frequencies of a ferromagnetic film is carried out in order to understand the mechanism of sensitivity enhancement.

The FMR field sweep measurements were taken at 12.6 GHz in both IP and PP FMR configurations, and in two atmospheres – in pure nitrogen and pure hydrogen. From figure 3.10, one sees that the field shifts for IP and PP configurations ($\delta H_{IP}$ and $\delta H_{PP}$ respectively) are in different directions – one observes a downward shift for the field applied IP (figure 3.10(a)) and an upward shift for the PP configuration (Fig. 3.10(b)). The resonant field shifts and the resonance linewidths extracted from the data in figure 3.10 are given in table 3.3.
CHAPTER THREE: Details of physics underlying functionality of m-HGS

Figure 3.10: Typical raw FMR traces taken in pure $N_2$ (black open dots) and pure $H_2$ (red filled dots) gas atmospheres. (a) The static magnetic field is applied in the film plane. (b) The field is applied perpendicular to the film plane. Frequency is 12.6 GHz.

<table>
<thead>
<tr>
<th>Measurement Config.</th>
<th>FMR peak (Oe)</th>
<th>Linewidth (Oe)</th>
<th>Peak shift upon $H_2$ (Oe)</th>
</tr>
</thead>
<tbody>
<tr>
<td>IP</td>
<td>1500</td>
<td>119</td>
<td>-60</td>
</tr>
<tr>
<td>PP</td>
<td>15620</td>
<td>104</td>
<td>510</td>
</tr>
</tbody>
</table>

Table 3.3: The resonant field shifts and the resonance linewidths extracted from the data in figure 3.10
CHAPTER THREE: Details of physics underlying functionality of m-HGS

From figure 3.10, one also sees that $|\Delta H_{PP}| \gg |\Delta H_{IP}|$. Whereas in the IP configuration the field shift amounts to 50% of the resonance linewidth, in the PP case the resonance is shifted by at least 490% of the resonance linewidth.

To understand this behaviour we carry out an analysis of Kittel Equation for the FMR frequency $f$,

$$f = \gamma \sqrt{(H - H_x + H_z)(H - H_y + H_z)}$$  (Eq 3.1)

where $\gamma$ is the gyromagnetic ratio for the material, $H$ is the applied field and $H_x$, $H_y$ and $H_z$ are, respectively, the anisotropy fields along the $x$, $y$ and $z$ axes. The axis $z$ is along the applied field and the static magnetization direction for the material, and $x$ and $y$ are the two directions transverse to the applied field. Equation (3.1) accounts for both shape and crystalline anisotropy of the sample (including PMA).

Let us first consider the effect of a small change in the transverse anisotropy field (say $H_x$). Solving equation (3.1) for $H$ for a fixed $f$ and differentiating the obtained expression with respect to $H_x$ one obtains

$$S \equiv \frac{dH}{dH_x} = \frac{1}{2} + \frac{H_x - H_y}{2\sqrt{(H_x - H_y)^2 + (2f / \gamma)^2}}$$  (Eq 3.2)

One sees that the sensitivity $S$ strongly depends on the interplay between $H_x$, $H_y$ and $H_z$. For instance, for a very long magnetic rod with circular cross-section magnetized along its length the shape anisotropy fields $H_x=H_y$ and one reaches the maximum sensitivity of $S = 1 / 2$. For a continuous IP magnetized film with PMA $H_{xx} = -4\pi M_{eff} = -4\pi M + H_{PMA}$, $H_y = 0$ (where $M$ is saturation magnetization and $H_{PMA}$ is the effective PMA field). As a result, equation (3.2) reduces to
The second term of Eq. (3.3) is close to $+\frac{1}{2}$ for $H_{\text{PMA}} \ll 4\pi M$ and reasonably small frequencies. Hence, the sensitivity $S$ is much smaller than $\frac{1}{2}$. The maximum sensitivity in this case is reached for $H_x = 0$ which corresponds to $H_{\text{PMA}} = 4\pi M$, i.e. to the threshold of magnetization vector naturally flipping perpendicular to the film plane in zero field. i.e. the reorientation transition thickness.

Let us now consider the PP case. In this case, $H_x = H_y = 0$ and the absorption of $H_z$ leads to variation in the anisotropy field $H_z$ which is along the applied field. The expression for the sensitivity of the FMR response to slight changes of the longitudinal anisotropy field is much simpler:

$$S_{pp} \equiv \frac{dH}{dH_z} = -1$$  \hspace{1cm} (Eq 3.4)

The result in equation (3.4) is consistent with the experimental data in Figure 3.10. The resonance field shift in the PP configuration is significantly larger than for the IP orientation and it is in the opposite direction.

We checked the validity of this conclusion numerically. The value of $\gamma = 2.88 \text{ MHz·Oe}^{-1}$ and $4\pi M_{\text{eff}} = 10490 \text{ Oe}$ were estimated from the frequency dependence of the PP FMR field for this sample (Figure 3.11). IP and PP magnetometry of the saturated film (figure 3.12(a) and (b) respectively) was used to extract a value of $4\pi M = 17500 \text{ Oe}$. The field at which the film is observed to be magnetized perpendicular to the plane via PP magnetometry compares well with the FMR-derived value of $4\pi M_{\text{eff}} = 10490 \text{ Oe}$ (compare the lateral position of vertical dashed line in figure 3.12(b) to the start of the magnetization plateau). This implies $H_{\text{PMA}} = 4\pi M - 4\pi M_{\text{eff}} = 7010 \text{ Oe}$. Most importantly though, on substitution of the $\gamma$ and $4\pi M_{\text{eff}}$ values into Eq.(3.3) we obtained $S_{IP} = 0.116$ giving $\frac{S_{IP}}{S_{PP}} = 0.116$. This value is in
excellent agreement with the ratio of the experimentally measured peak shifts (Table 3.3)

\[
\left| \frac{\Delta H_{IP}}{\Delta H_{FF}} \right| = \frac{60}{510} = 0.118
\]

Figure 3.11: Frequency dependence of PP FMR field.

Figure 3.12: (a) In-plane magnetization versus in-plane magnetic field and (b) perpendicular-to-plane magnetization versus perpendicular-to-plane magnetic field obtained with a Quantum Design MPMS3.
In this work we demonstrated that the response of the ferromagnetic resonance signal of a Pd/Co bilayer film to hydrogen absorption by its Pd layer is significantly larger for the magnetic static field applied perpendicular to the film plane. This is due to the fact that the sensitivity of the ferromagnetic resonance method to small changes of an effective anisotropy field is larger (or significantly larger, depending on the strength of the anisotropy) for the static magnetic field applied along the anisotropy axis, a result confirmed both via experiment and FMR theory.

The result is important for optimizing Pd/Co bi-layered thin films for use in novel platforms for hydrogen gas sensing. For example, due to sensitivity range difference between DC fields applied in plane and perpendicular to plane, one can use the two individual sensors for different ranges of hydrogen concentration detection. The PP sensor will be then used to measure low hydrogen concentrations while the IP sensor to measure higher hydrogen concentrations.

3.3.2 Hydrogen response times affected by configurations of FMR measurement

In the preceding section, we discussed the effect of FMR measurement geometry on sensitivity. The hydrogen induced resonance field shift can be up to eight times bigger for the PP configuration than for the IP one. Beside hydrogen sensitivity, response times are also of great importance. In this section, we will compare the hydrogenation response (absorption and desorption) times between IP and PP FMR measurements.

Time resolved FMR measurements are used for the hydrogenation responses time comparison (mentioned in section 2.2.2). Frequency is fixed at 8.2 GHz and time resolved FMR traces are taken in pure $N_2$ and in a mix of 50% $H_2$ and 50% $N_2$. 
CHAPTER THREE: Details of physics underlying functionality of m-HGS

Figure 3.13 shows the normalized time resolved profiles measured in both IP and PP FMR configurations. The applied field (refer to section 2.2.2.3) for the IP FMR measurement is 612 Oe, while the applied field for the PP one is 12988 Oe. A higher field is needed in the PP FMR measurement because of the need to compensate a strong demagnetising field in the direction of the film thickness which arises when a film is magnetised PP. Figure 3.13 shows that the PP configuration is characterised by a significantly faster hydrogen desorption time than the IP one.

![Time resolved FMR profiles for IP and PP configurations](image)

Figure 3.13: Time resolved FMR profiles for IP and PP configurations. The graph in the inset is for IP and for the full time interval of observation of hydrogen desorption. It demonstrates that the profile returns to the original signal level upon completion of hydrogen desorption process.

Table 3.4 show the response times for IP and PP configurations. A significantly shorter hydrogen desorption time is observed when the static magnetic field is applied PP (120 s vs 1800 seconds for the field applied IP). On the contrary, a slightly longer hydrogen absorption time is found for PP with respect to IP (25 vs 20 seconds). The results could be reproduced for other samples.
CHAPTER THREE: Details of physics underlying functionality of m-HGS

<table>
<thead>
<tr>
<th>FMR configurations</th>
<th>Hydrogenation response times</th>
<th>Bias magnetic field (Oe)</th>
</tr>
</thead>
<tbody>
<tr>
<td>In-plane (IP)</td>
<td>absorption time (sec)</td>
<td>desorption time (sec)</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>1800</td>
</tr>
<tr>
<td>Perpendicular to plane (PP)</td>
<td>25</td>
<td>120</td>
</tr>
</tbody>
</table>

Table 3.4: Summarised hydrogenation response (absorption / desorption) times for IP and PP FMR configurations.

One may suspect that the much shorter desorption time for the PP FMR configuration may be due to stronger magnetic biased field applied to the film (12988 vs 612 Oe). To verify this, two independent experiments are carried out. In the first experiment, which focuses on the PP FMR configuration, a strong bias field (12988 Oe) is intermittently switched on/off during the hydrogen desorption process. The whole time resolved profile is recorded and compared to the previously taken PP FMR trace for which the bias field was kept constant. The focus of the second experiment is the IP FMR configuration. A much stronger bias field (12988 Oe) is applied to the samples intermittently with the usual bias field (612 Oe). The whole time resolved profile is also recorded and compared with the original IP FMR trace.

Figure 3.14 shows the result of the first experiment. There is no significant difference between the two time-resolved profiles. The intermittent on/off switching of the bias field does not produce any difference in the desorption time. Hence, the magnetic field applied during the hydrogen desorption process is not a factor affecting the desorption rate.
CHAPTER THREE: Details of physics underlying functionality of m-HGS

Figure 3.14: PP FMR time-resolved profiles. black line: bias field “always on”; Blue line: bias field periodically switched off.

The results of the second experiment are shown in figure 3.15. Similar to the first experiment, both time resolved profiles are very close and there is no significant difference between the two cases of constantly applied bias field and the bias field periodically increased to a much higher level (12988 vs 612 Oe). Hence, increasing the applied field does not accelerate hydrogen desorption in the IP FMR case.
CHAPTER THREE: Details of physics underlying functionality of m-HGS

Figure 3.15: The IP FMR Configuration time resolved profiles comparison between the “bias field always on” case (reference one, black line) and the “intermittently much higher bias field case” (blue line). The sudden jumps in the signal shown by the blue line correspond to the moments when the higher field is applied to the sensor.

In conclusion, both experiments demonstrate that the magnitude of the magnetic bias field applied to the samples is not a significant factor defining the hydrogen desorption time. At the moment, we have no clear explanation of the differences in hydrogen desorption times between the in-plane and perpendicular-to-plane FMR configurations. This will be a good topic for a follow-up study.
CHAPTER THREE: Details of physics underlying functionality of m-HGS

3.3.3 Conclusion

A conclusion can be drawn from the performed study that if continuous films employed as an active medium for an m-HGS the PP FMR configuration provides much better performance in terms of both higher hydrogen sensitivity and much shorter response time. Without this section’s findings, basically, the continuous thin films could not be considered as suitable candidates for HGS sensor active medium, since the response time for them is unreasonably long. On the contrary, the result of this section opens an alternative way for the continuous thin films to be used as prototypes of HGS. Two demonstrations of HGS functionality, enabled by this finding, are carried out in these thesis employing continuous films. One employs “standard” bi-layers fabricated with our sputtering machine (Si/Co5nm/Pd10nm, see Section 4.2) while the other one exploits CoPd alloy continuous thin films fabricated by NUS (Section 4.3).

3.4 Effect of sample orientation on hydrogen response times

As discussed in Section 1.2.2, environment also affects significantly permeability of palladium by hydrogen [57], and the hydrogen response times. In this study, we looked at the influence of sample orientation with respect to the microstrip line on its hydrogen response times. Figure 3.16 shows the geometries under test. Usually we take FMR measurements with the film facing the microstrip line (“face down” configuration). This is because the active medium (the thin film) is then closer to the microstrip line that provides a stronger FMR signal [84]. One can also place the film with its substrate facing the stripline (“face up configuration”), in order to improve the film contact with the gas environment, the cost, however, is a drop in the signal amplitude. The drop of amplitude depends on the thickness of the substrate; in our case, the amplitude drops by about 40% when compared with the face down configuration.
CHAPTER THREE: Details of physics underlying functionality of m-HGS

In all our experiments, gas is continuously flowing through the gas chamber. However, when the film faces down, the influx of the gas to the film surface is obstructed by the film mechanical contact with the stripline. Here we test the influence of this modified flow on the response time.

![Diagram of Face up and Face down geometries](image)

**Figure 3.16:** “Face up” and “face down” geometries.

The sample tested in this experiment represents a continuous tri-layer Si//Pd10nm/Co20nm/Pd10nm film. It was fabricated at NUS. The In-plane field-sweep and time-resolved FMR measurements at a fixed frequency of 13 GHz are employed, the probed gas environments are pure nitrogen and pure hydrogen. Figure 3.17 shows the FMR field sweep results for the continuous thin film sample when it is exposed to pure $N_2$ and pure $H_2$ in both geometries (face up and face down), while table 3.5 provides a data summary for all the FMR field sweep measurements. From the summary table one sees that there is no significant data discrepancy between sample facing up and facing down: both show very similar FMR peak shifts and the linewidth changes, although the absolute FMR peak locations seem to shift a little bit due to unknown reason. One may notice that the signal for face up is around 40% smaller when compared with the film facing down (figure 3.17). This is because the longer distance between stripline and cobalt layer on face up case.
Chapter Three: Details of physics underlying functionality of m-HGS

Figure 3.17: The FMR field sweep results for the continuous film sample from NUS for pure $N_2$ and pure $H_2$. a) The film is facing down and b) the film is facing up.

<table>
<thead>
<tr>
<th></th>
<th>Facing down</th>
<th>facing up</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>FMR peak (Oe)</td>
<td>Line width (Oe)</td>
</tr>
<tr>
<td>100% $N_2$</td>
<td>1327</td>
<td>113.8</td>
</tr>
<tr>
<td>100% $H_2$</td>
<td>1291</td>
<td>93.6</td>
</tr>
<tr>
<td>Hydrogenation shift</td>
<td>-36</td>
<td>-20.2</td>
</tr>
</tbody>
</table>

Table 3.5: The data summary on the FMR field sweep results with difference sample geometries.

Because the peak shifts for the two geometries are very similar, it is possible to compare time resolved profiles for them. The bias field applied to the sample during the measurements is 1330 Oe. Figure 3.18 shows the obtained time resolved profiles and Table summarised absorption and desorption rates extracted from this graph.
CHAPTER THREE: Details of physics underlying functionality of m-HGS

From the figure and data summary, one can observe a noticeable difference in the duration of both processes. The difference between the two configurations is around 30~40%.

Figure 3.18: The FMR field sweep results obtained on the continuous film sample from NUS exposed to 100% \( N_2 \) and 100% \( H_2 \). Blue line: film is facing up; black line: film is facing down. The bias field applied to the film is 1330 Oe. The graph in the inset is for the face down and for the full time interval of observation of hydrogen desorption. It demonstrates that the profile returns to the original signal level upon completion of hydrogen desorption process.

<table>
<thead>
<tr>
<th>Facing down</th>
<th>Facing up</th>
</tr>
</thead>
<tbody>
<tr>
<td>hydrogen response times (sec)</td>
<td>hydrogen response times (sec)</td>
</tr>
<tr>
<td>absorption</td>
<td>desorption</td>
</tr>
<tr>
<td>33</td>
<td>2900</td>
</tr>
</tbody>
</table>

Table 3.6: Parameters extracted from the time resolved profiles in figure 3.18.
CHAPTER THREE: Details of physics underlying functionality of m-HGS

From the result, it is clearly observed that the sample orientation can lead to differences in hydrogen desorption response time of 30 to 40%. Unfortunately, no literature is available which compares diffusivity of hydrogen for static and circulating atmospheres at room temperature. A.S. Darling carried out this comparison at a temperature of \( \sim 660^\circ C \). As shown in figure 3.19 [57], he observed that the diffusion rate drops immediately, once the atmosphere was switched to static. There is around 30% drop after the first 12 minutes, and around 60% drop after 22 minutes. Our result seems to be lying within the ballpark.

![Figure 3.19: Comparison on the rate of diffusion on Pd between static pressure and with gas circulation [57].](image)

This investigation confirms that the sample geometries (face up or down) are one crucial aspect that can improve the desorption time. By employing the face up geometry, one can reduce the hydrogenation response times by 30 to 50%. However, in the face-up configuration, coupling of the film to the stripline is significantly weaker because of the significant distance between the film and the stripline (the film substrate acts a spacer between the two.) This results in a smaller FMR peak height [84]. One possible way to get around this issue is by using thinner silicon substrates or by integrating the micro strip line on the back side of the active sensor through multi-step lithography [128].
3.5 High temperature (in-situ) annealing effect on bi-layer Co/Pd of m-HGS

As discussed in section 1.2.3, stimulating alloying at the interface between Co and Pd with post-annealing promotes formation of a CoPd alloy [48]. Since the m-HGS concept employed in this thesis relies on the detection of a change in PMA in the presence of hydrogen gas, having a material with a strong PMA could be beneficial, as for a larger PMA one may expect a larger hydrogen-induced change in it. The study of the effect of high-temperature in-situ annealing on bi-layer Si//Co 5nm/Pd 10nm samples is performed in this section in order to confirm the effect of annealing on the hydrogenation sensitivity m-HGS. Some further studies beside FMR (TEM and XRD) are also performed in order to gain further understanding of the physical mechanisms behind the effect of annealing.

In the present study, the in-situ annealing temperature is fixed at 200°C (optimal temperature). This value is based on prior investigation of a series of samples annealed at various temperatures. This series includes a control un-annealed bi-layer Si//Co 5nm/Pd 10nm film, and similar bi-layer films in-situ annealed at 150, 200, 250 or 300°C. Their FMR characterisation in the presence of hydrogen gas revealed that only the film in-situ annealed at 200°C shows much bigger IP & PP FMR peak shifts due to hydrogenation than the reference film. On the contrary, the one annealed at 150°C shows a shift similar to the control one; it may be due to temperature being not high enough to form an alloyed layer at the Co/Pd interface. Furthermore, the thin films annealed at higher temperatures (250 and 300°C) show degraded FMR signals, and the FMR signal is completely lost after annealing a film at 300°C.
CHAPTER THREE: Details of physics underlying functionality of m-HGS

The samples for the investigation were fabricated with the in-house sputter machine using the standard deposition procedures (section 2.1.2). All of the 3 samples have the same composition of Si//Co 5nm/Pd 10nm. One of the samples acts as a control sample, while the other two samples undergo in-situ annealing in different conditions. Figure 3.20 shows the two recipes for the in-situ annealing. The main difference between them is the phase of the film fabrication process when the in-situ annealing is applied – either right after completion of sputtering of the cobalt layer (referred to as “in-situ anneal cobalt only” below) or after completion of sputtering of both (cobalt and palladium) layers (termed “in-situ anneal both” below).

In-situ Annealing recipes

• In-situ annealing after Co is sputtered

- Sputter 5nm of Co on silicon substrate
- Without breaking vacuum, anneal the sample at 200°C for 30 mins
- Cool down the sample to 50°C
- Sputter 10nm of Pd on top of Co
- Break vacuum and take out the sample

• In-situ annealing after Co & Pd are sputtered

- Sputter 5nm of Co on silicon substrate
- Sputter 10nm of Pd on top of Co
- Without breaking vacuum, anneal the sample at 200°C for 30 mins
- Cool down the sample to 50°C, break vacuum and take out the sample

Figure 3.20: The two in-situ annealing recipes used for the study.

The new IP and PP capable gas chamber (refer to Section 2.2.2) and the standard gas blending setup (section 2.3.1) with controlled 800 sccm flow rate are used in the study. Furthermore, both of the “lock-in and field modulation techniques” (section 2.2.1) are employed to record the FMR traces. The frequency of the microwave signal applied to the samples is 10 GHz.
Figure 3.21 shows the in-plane field sweep FMR profiles for the 3 samples (control, In-situ Anneal Cobalt Only and In-situ Anneal Both) for 100% $N_2$ and 100% $H_2$ atmospheres, while Figure 3.22 shows the out-of-plane field sweep FMR profiles for the same samples.

Figure 3.21: In-plane field sweep FMR profiles for the a) control sample, b) in-situ anneal cobalt only and c) in-situ anneal both.
CHAPTER THREE: Details of physics underlying functionality of m-HGS

Figure 3.22: Out-of-plane field sweep FMR profiles on the a) control sample, b) in-situ anneal cobalt only and c) in-situ anneal both.

Table 3.7 displays a summary of the obtained data. Based on the results, one can state that the in-situ annealing of both layers leads to a much larger hydrogenation FMR peak shift in both in-plane and out-of-plane FMR configurations. On the contrary, in-situ annealing of the cobalt layer only does not produce any significant difference with respect to the control sample.
CHAPTER THREE: Details of physics underlying functionality of m-HGS

Table 3.7: Summary of in-situ annealing results.

<table>
<thead>
<tr>
<th>Sample configurations</th>
<th>in-situ annealing recipes</th>
<th>FMR peak shifted due to hydrogenation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si/Co 5nm/Pd 10nm</td>
<td>Nil (control)</td>
<td>-61 190</td>
</tr>
<tr>
<td></td>
<td>after cobalt sputtered</td>
<td>-60 203</td>
</tr>
<tr>
<td></td>
<td>after both Co/Pd sputtered</td>
<td>-82 510</td>
</tr>
</tbody>
</table>

The results clearly indicated that the in-situ annealing is effective when performing it after sputtering of both cobalt and palladium layers (i.e. the “In-situ Anneal Both” recipe). The high temperature of in-situ annealing provides energy to enhance the interface Co/Pd alloy formation [48]. That we are dealing with the effect of alloy formation at the interface is confirmed with the “In-situ Anneal Cobalt Only” experiment. The latter procedure is not effective, as no palladium is present on the top of cobalt to form an alloy during the time of in-situ annealing. Also, one may expect that in-situ annealing of the Pd layer may improve hydrogen solubility in Pd thus also contributing to improvement of the hydrogenation sensitivity which will be discussed below.

Further analysis of the effect of annealing was carried out with TEM and XRD. Firstly, a cross-sectional TEM imaging of the “in-situ anneal both” sample is performed in order to confirm the existence of a Co/Pd alloy at the interface. The Scanning Transmission Electron Microscopy Energy-dispersive X-ray spectroscopy (STEM-EDS) results in figure 3.23 are suggestive of some interface alloying between Co and Pd (details please refer to Section 4.2).
CHAPTER THREE: Details of physics underlying functionality of m-HGS

Figure 3.23: a) cross-sectional TEM picture of the “in-situ anneal both” sample, b) The STEM-EDS results. [106]

XRD measurement of both the control and “in-situ anneal both” samples were performed (details and measurement conditions can be found in Section 2.3.3). Figure 3.24 shows “Two Theta” traces for the samples. One sees that XRD peaks are almost the same for both samples, except one peak. This peak occurs at two theta of 39.4° for the “In-situ Anneal Both” sample and at 40° degree for the control sample. Processing the data with specialised software (“HighScore plus”, section 2.3.3) shows that both of the peaks belong to Pd (111) crystal plane. The differences in the deflection angle suggest that the “in-situ anneal both” sample has a larger lattice constant for palladium in the (111) plane (2.28515 Å) than the control sample (2.25167 Å). Increasing the lattice constant of palladium promotes solubility of hydrogen atoms [78]. This is one possible reason why in-situ annealing can enhance the sensitivity of the layered samples to hydrogen gas.
Figure 3.24: a) The X-ray diffraction (XRD) traces for the “In-Situ Anneal Both” and control samples. Expected peak positions for diffraction from the shown cubic Co, Pd and Co$_3$O$_4$ planes as well as hcp Co are shown as labelled, vertical lines. b) The enlarged XRD traces between the 2 theta at 35-45°. One notices a peak at about 40° whose characteristics differ for the samples. For the “In-Situ Anneal Both” it is located at 39.4° and is narrow and sharp, but for the control one it is located at 40° and is significantly broader.
Our results suggest that the in-situ annealing promotes the hydrogenation sensitivity of the bi-layer film based m-HGS sensor. The annealing results in ~30% increase in the FMR peak shift for the IP FMR configuration and a factor of 2.5 for the PP one. The improvement can be explained as increased alloying of Co with Pd at the interface which strengthens PMA. Furthermore, it increases the lattice constant for Pd (in the (111) plane). That increases solubility of hydrogen in Pd. This method to improve material properties was used in one of the device-prototypes for demonstration of HGS functionality – see Section 4.2 [106].

An idea how to further improve the performance of m-HGS also follows from this study. As discussed above, stronger intrinsic PMA leads to better m-HGS performance. For the bi-layer samples exploiting the interfacial PMA, in the FMR response the effect of PMA takes the form of an effective bulk-like PMA field whose effective field scales as 1/thickness of ferromagnetic layer. Therefore, decreasing the thickness of the layer increases the peak shift and hence the m-HGS sensitivity. However, the height of the FMR peak scales as the ferromagnetic layer thickness. Therefore, if the films are too thin (<5nm), the FMR response of the samples is very weak and requires sensitive electronics for its detection which is not useful for real-world applications requiring that an m-HGS is inexpensive. Therefore, the experiment above suggests that if the sample is a Co/Pd alloy all across its thickness, one may expect a strong PMA, but now of a bulk type. Hence its strength will no longer depend on the ferromagnetic layer thickness. This will allow the film thickness to be increased in order to boost the FMR peak amplitude which may ultimately allow the use of a much simpler electronics to detect the FMR response thanks to a higher signal. A detailed study and demonstration of m-HGS based on CoPd alloys will be discussed in Section 4.3.
3.6 Role of the elastic strain in the sensor response

3.6.1 Introduction

The result from this section is based on a manuscript which recently has been prepared for publication with the author of the present thesis as the first author. The interface perpendicular magnetic anisotropy (PMA) is known to be induced at the interface between a ferromagnetic metal (FM) layer and a non-magnetic (NM) heavy-metal layer such as Platinum or Palladium (Pd) in a FM/NM bilayer or multilayer film [27, 129, 130]. This phenomenon has been a focus of an intense research for several decades. Several origins of/contributions to the interface anisotropy have been identified; the most important are (1) breaking the crystal symmetry at the interface; (2) interface alloying and (3) the effect of magnetostriction [131]. The first two mechanisms are underlain by a direct effect of a heavy metal on the spin system of the ferromagnetic layer, whereby spin orbit coupling plays an important role. Hence these effects are of electronic nature [132] and for this reason in the following we will term these two contributions “the electronic contribution”. The Contribution (3) is indirect – elastic strain at the interface mediates the effect of NM on the magnetism of the FM layer [133]. If the FM layer is thin enough, the elastic strain originating from the presence of the interface can propagate across the whole thickness of the FM layer and induce perpendicular anisotropy all across the layer’s bulk via the magnetostriction effect. We will term this contribution to PMA “magneto-elastic”.

For completeness, one has to also mention one more possible contribution to PMA - interface roughness [133]. It is of magnetostatic nature which suggests that the presence of the NM metal on the other side of the interface should not matter, and the effect of the roughness should be obviously the same as of roughness of the
CHAPTER THREE: Details of physics underlying functionality of m-HGS

surface of a single ferromagnetic layer (i.e. not interfaced with an NM metal). For this reason we will neglect this contribution in the discussion below.

Recently several authors have shown that $Pd/FM$ multilayer systems represent a very interesting model system for studying physics behind the interface $PMA$ [22, 36-39, 48, 62, 105]. This is because incorporation of Hydrogen atoms into $Pd$ leads to a reversible change in the $PMA$ strength. $Pd$ has very high affinity to hydrogen gas ($H_2$) – it absorbs large amounts of the gas reversibly at atmospheric pressure and room temperature. This makes control of $PMA$ in $Pd/MN$ system an easy task, as the change of the effective $PMA$ field has been found to scale with the partial pressure of the hydrogen gas in the layered film’s environment. Interestingly, it has been recently observed that breaking continuity of the films through lateral nanopatterning strongly decreases the characteristic time for the transient process of the change in $PMA$ due to sample exposure to $H_2$ [62, 105].

One important question in $PMA$ research is the interplay between the three contributions to it which we mentioned above. The experiment with the nanopatterned samples [105] may suggest that the magneto-elastic contribution may be important, even dominating, since breaking continuity of the films may allow easier lateral expansion of the film while exposed to $H_2$ atmosphere. However, bulk cobalt is known to possess a negative magnetostriction coefficient [134], therefore one may expect that the resonance field shift due to the magneto-elastic contribution is positive, which is in contradiction to a negative one observed in all previous in-plane FMR measurements in the presence of hydrogen gas [22, 104, 105].

In this work, to answer this question on the physics behind the change in the strength of $PMA$ in the presence of hydrogen gas for $Pd/FM$ layered films, we grow continuous $Pd$/Cobalt bi-layer and $Pd/Co/Pd$ tri-layer films on flexible Kapton® ($Kpt$) substrates ($Kpt//Film$) and expose the grown films to hydrogen gas or elastic stress. Ferromagnetic resonance (FMR) measurements are taken in the presence of those
CHAPTER THREE: Details of physics underlying functionality of m-HGS

stimuli. Exposing the samples to $H_2$ results in a downshift of the FMR field for both substrate types. On the contrary, FMR measurements carried out in the presence of an externally applied predominantly tensile elastic stress show an up-shift in the field consistent with negative values of the saturation magnetostriction coefficients for our samples. We carry out quantitative analysis of these data and find that the magnetostriction contribution to the $H_2$-induced FMR peak shift does not exceed 0.3 Oe for our films grown on $Kpt$ and is much smaller than and of the opposite sign to the electronic contribution (20 to 30 Oe).

In-plane continuous polycrystalline bi-layers $Co(5nm)/Pd(10nm)$ and tri-layers $Pd(20nm)/Co(10nm)/Pd(20nm)$ were deposited with d.c. magnetron sputtering under argon atmosphere. Previously these two systems showed quite different responses to the presence of hydrogen gas [104], potentially due to difference in textures of the cobalt and the capping Pd layers. Therefore it is worth investigating both systems.

The base pressure of the sputter system was below $5 \times 10^{-8}$ torr. The film sputtering was repeated twice in order to produce two batches of $Pd/Co$ and two of $Pd/Co/Pd$ films on $Kpt$ substrates. This was done in order to be able to collect enough statistics.

One sample from each batch was characterised with a FMR-under-stress setup [135, 136] by the French colleagues. To this end, the sample was glued to a piezoelectric actuator and a dc voltage was applied to the actuator to strain the sample. The second film of each batch (fabricated in the same sputtering run as the first one) was used to take measurements of the FMR response first in the presence of pure nitrogen gas ($N_2$) and then of pure hydrogen gas.

For both types of measurements, the broadband stripline field-modulated FMR method [84] was used. Microwave microstrip lines were utilised in order to couple
microwaves to magnetisation dynamics in the samples and to read samples’ FMR responses. A small-amplitude ac magnetic field was applied to a sample in parallel to a large static magnetic field. The fields were oriented in the sample plane and along the stripline. A lock-in amplifier locked to the ac field frequency was employed to detect the FMR absorption signal. During the measurements, the microwave frequency was kept constant while the static magnetic field was swept. The measurements under stress were carried out for several frequencies (6-12 GHz) while measurements under exposure to $H_2$ were performed at 10 GHz. Further details of the FMR-under-stress method can be found in Ref. [136] and of the FMR measurements in the presence of $H_2$ in Ref. [22].

3.6.2 Experimental results

Typical examples of the obtained raw FMR traces are shown in figure 3.25. One sees that application of elastic strain shifts the FMR field upwards (Fig. 3.25(a)), whereas exposure of the sample to $H_2$ leads to an FMR field downshift (Fig. 3.25(b)). Previously we interpreted this downshift as a decrease in PMA [22, 104].
CHAPTER THREE: Details of physics underlying functionality of m-HGS

Figure 3.25: Examples of raw FMR traces taken for a \(Kpt//Pd/Co/Pd\) sample. (a) FMR-under-stress, frequency is 8 GHz. Blue solid line: voltage applied to piezo-actuator \(V=0\). Red dashed line \(V=100\) V. (b) FMR in the presence of \(H_2\). Blue solid line: taken in the atmosphere of pure \(N_2\). Red dashed line: the atmosphere is pure \(H_2\). Frequency for (b) is 10 GHz.

The last experiment we carried out was observation of film bending in the presence of hydrogen gas. To this end two extra films were grown on 21mm-long and 2mm-wide Kapton® substrates. One of them was a \(Co(5nm)/Pd(10nm)\) bi-layer film and the second one a tri-layer \(Pd(20nm)/Co(10nm)/Pd(20nm)\) film. They were placed in a transparent pressure-tight container which could be filled either with pure hydrogen or air. The short (i.e. 2 mm-long) edge of the strip was oriented vertically in order to avoid the effect of gravity on the measurement result. One short edge was fixed with a clamp and the other one was free to move. The position of the free edge was monitored with a microscope. We found that in the presence of hydrogen gas the edge of the \(Pd/Co\) bi-layer sample moves by 59% of the substrate thickness and one of the \(Pd/Co/Pd\) tri-layer film by 157%. The shift is in the direction of the sample’s substrate which is consistent with elongation of the Pd layer in the presence of hydrogen and the known fact that palladium expands upon absorption of hydrogen gas [1].
CHAPTER THREE: Details of physics underlying functionality of m-HGS

A noticeable in-plane uniaxial anisotropy $H_u$ is present for the samples grown on $Kpt$ substrates (Fig. 3.26(a)). One explanation for this is a bending of the substrate during sputtering as observed [137]. Indeed, positioning of the sample on the stripline for taking the FMR measurements modifies the substrate’s curvature. This leads to the anisotropy through magnetostriction. The FMR field shift due to application of a voltage $V$ to the piezo-actuator is slightly non-linear due the in-plane strains ($\varepsilon_{xx}$ and $\varepsilon_{yy}$) variations with voltage (see Fig. 3.26(b)).

From the FMR measurements taken for the $Kpt//Film$ samples in their virgin states, sample’s magnetic parameters were determined (Table 3.8). The Co layers used in our study are thin enough such that the effective anisotropy field present at the interface does not need to be considered as leading to interface pinning of magnetisation [138]; instead one can use a simpler approach whereby the effective interface anisotropy field is replaced with an effective field of bulk PMA for the FM layer [139]. (In our previous work [104] we found that the effective bulk-like PMA field scales as $1/\text{thickness}$ for our bi-layer films (grown on Si substrates) which confirms the validity of the effective bulk anisotropy approach [139] for the Co layer thicknesses we deal with.)

Using the method from Ref. [135], values of the saturation magnetostriction coefficients for the 4 films were extracted from the results of samples’ FMR characterisation under stress. These parameters are also listed in Table 3.8.
CHAPTER THREE: Details of physics underlying functionality of m-HGS

Figure 3.26: (a) Results of the in-plane angle resolved FMR measurements for the same sample as in Fig. 3.25(a). (b) FMR field shift as a function of the voltage $V$ applied to the piezo-actuator.

Table 3.8: Parameters of the samples extracted from the FMR measurements. Parameters of cobalt which were fixed to produce the results in the table are as follows: saturation magnetisation: 17.5 kOe, gyromagnetic ratio: 3.4 MHz/Oe, Young modulus and Poisson ratio for it: 200 GPa and 0.3 respectively.

From the table one sees that the saturation magnetostriction coefficient for our film is negative, as typical for cobalt [134]. Furthermore, we used the observed magnitude of
CHAPTER THREE: Details of physics underlying functionality of m-HGS

bending of the long reference films in the presence of \( H_2 \) in order to extract the elastic strain \( \varepsilon_{H_2} \) in the cobalt layer induced by expansion of the Pd one. We employed formalism based on Ref. [140] to carry out this calculation. Its details are given below (see the sub-section “Employed formalism” below). We obtained \( \varepsilon_{H_2} = 2.8 \times 10^{-5} \) and \( 2.3 \times 10^{-4} \) for the bi-layer and tri-layer film respectively. By using the parameters from Table 3.8, the strain values were converted into the magnetostriction contribution \( \delta H_{PMA} \) to the PMA field. To this end we employed the following expression

\[
\delta H_{PMA} = 3\lambda E_{Co} \varepsilon_{H_2} / \left[ \mu_0 (\nu - 1) M_s \right],
\]

(Eq 3.5)

where \( \lambda \) is the saturation magnetostriction coefficient, \( Y_{Co} = 200 \) GPa and \( \nu = 0.3 \) are the Young modulus and Poisson ratio respectively for Cobalt, \( M_s \) is the saturation magnetisation for the cobalt layer and \( \mu_0 \) is the magnetic permeability of vacuum. The obtained change in the PMA field was further converted into the magnetostriction contribution to the \( H_2 \)-induced change in the FMR field by using Kittel Equation for the in-plane FMR. It follows from Kittel Equation that the ferromagnetic resonance field reads

\[
H_{res} = \left( \sqrt{M_s - H_{PMA} + H_u + (2f / \gamma)^2} - M_s + H_{PMA} + H_u \right) / 2, \text{ (Eq 3.6)}
\]

where \( H_{PMA} \) and \( H_u \) are effective fields of PMA and the in-plane uniaxial anisotropy respectively, \( f \) is microwave frequency and \( \gamma = 3.4 \) MHz/Oe is the gyromagnetic ratio.

We obtained +0.27 and +0.31 Oe for the bi-layer film of Batch 1 and the tri-layer of Batch 3 respectively. One sees that these values are positive, in agreement with the negative values of \( \lambda \) from Table 3.8 and also negligible with respect to the total \( H_2 \) induced field shifts (last column of Table 3.8).
3.6.3 Discussion

By combining FMR measurements under two different stimuli we acquired experimental evidence that absorption of hydrogen gas by the \( Pd \) layer of \( Pd/Co \) and \( Pd/Co/Pd \) layered films results in modification of electronic properties of the interface between the materials which leads to a change in the interface \( PMA \) strength. This contribution to the change in \( PMA \) is negative, resulting in a negative in-plane FMR field shift.

On top of this there may be a magneto-elastic contribution to the \( FMR \) peak shift. A free-standing piece of palladium expands uniformly in all three spatial directions when it absorbs hydrogen. If the palladium sample is a film clamped to a substrate, it cannot easily expand in its plane and a compressive bi-axial stress is induced in the sample. One may think of the stress as of a hydrostatic pressure built-up in the sample. For thick \( Pd \) layers, the stress relaxes through formation of folds [35]. Thin films, as in our case, can withstand huge stresses due to the clamping effect without deformation [70].

In contrast to single-layer \( Pd \) films used in Refs. [35, 70], the films studied here are multilayers. Only the overlaying \( Pd \) layer of the tri-layer structures is able to absorb hydrogen, as cobalt is non-transparent to the gas. Hence, the layer which is capable to expand under the influence of \( H_2 \) is separated from the substrate either by a Cobalt layer or by a combination of \( Co \) and \( Pd \) layers. However, these layers do not contribute to the mechanics, because of their negligible thickness with respect to the thickness of the substrate. Only the elastic properties of the capping \( Pd \) layer and the substrate matter and the role of the other two metallic layers is just to translate the stress built-up in the capping \( Pd \) layer to the substrate in full.
CHAPTER THREE: Details of physics underlying functionality of m-HGS

Our experiment demonstrates that the magneto-elastic contribution to the change in PMA exists for samples grown on Kapton, but it is very small and is of the opposite sign to the electronic contribution. It arises because the flexible Kapton substrates can bend noticeably under the influence of the stress induced in the palladium layer by incorporation of Hydrogen into Pd lattice.

In all our previous works [22, 104-106] we used samples grown on much more rigid silicon substrates. Because of the much larger rigidity of silicon (Young modulus >130 GPa), bending of those samples due to the H₂-induced stress in the capping Pd layer is negligible, as follows from the value of the free-standing H₂-induced stress for the Pd layer found in the present work (see below). Accordingly, the magnetostriction contribution to the FMR peak shift for Pd/Co and Pd/Co/Pd films grown on silicon substrates is completely vanishing.

3.6.3.1 Employed formalism (developed by M. Kostylev)

From the theory of bi-metal plates it is known that a difference in strains in thin layers which are in a mechanical contact to each other leads to either spherical or cylindrical bending of the layered structure, depending on the stiffness of the materials (see e.g. Ref. [140]). Ferromagnetic films on Kapton substrates are characterised by cylindrical bending (see figure 3 in Ref. [137]). Furthermore, in our bending experiment we are using a sample which is quasi-one-dimensional – a long and narrow (21x2 mm²) strip. Therefore, in the following we utilise the model of bending into a cylindrical roll to evaluate the strain.

The samples are fixed at one edge with the second edge free to move upwards or downwards. Assume that the sample is originally flat and its plane is parallel to the
CHAPTER THREE: Details of physics underlying functionality of m-HGS

horizontal axis. Also assume that the Kpt substrate is facing up. This implies that elastic expansion of the Pd layer will result in the free edge of the strip moving up. The uplift $h$ of the edge with respect to the horizontal axis relates to the radius of bending $R$ in the following way

$$R = \frac{l^2}{2h},$$

(Eq 3.7)

where $l$ is the strip length. The theory of tri-metals [141] tells us that the effect of the Co and Pd layers sandwiched between the capping Pd layer and the substrate on bending is negligible. This is because of smallness of the thicknesses of these buried layers with respect to the Kpt substrate thickness ($d_{Kpt} = 0.127$ mm), and is seen from the fact that (Eq.(6) in [141]) for the bending radius reduces to a very simple equation into which parameters of the buried layers do not enter:

$$R = \frac{Y_{Kpt}d_{Kpt}^2}{6\varepsilon Y_{Pd}d_{Pd}}.$$  (Eq 3.8)

Here $Y_{Kpt} = 4$ GPa and $Y_{Pd} = 120$ GPa are Young moduli for Kpt and Pd respectively, $d_{Pd} = 10$ nm is the thickness of the capping Pd layer, and $\varepsilon$ is the “free-standing” strain for Pd. The free-standing strain is the elastic strain which would be induced in the Pd layer if the layer was free-standing, i.e. not interfaced with the underlying Co layer and hence not mechanically coupled to the remainder of the layered structure. The actual strain in the Pd layer is smaller than $\varepsilon$ because the Kpt substrate does not allow the Pd layer to expand freely.

Equation (Eq 3.8) is actually the Stoney formula for bi-metals (see e.g. [140]). This implies that we may use the theory for bi-layered materials to evaluate the actual strain in the capping Pd layer. The strain in the buried Co layer will be the same as in the capping Pd layer, given the similarity of the Young modulus for Co (200 GPa) to the
CHAPTER THREE: Details of physics underlying functionality of m-HGS

one of Pd and its strong dissimilarity from the one for Kpt. It is appropriate to assume that there is no free-standing strain in Kpt (e=0 for Kpt). Let us also assume that the axis in the direction of the bending radius is z, and z=0 coincides with the free surface of the Kpt substrate. Then the free-standing strain in the stack has a profile as follows

\[ \begin{align*}
  e &= 0, \quad 0 < z < d_{Kpt} \\
  e &= \varepsilon, \quad d_{Kpt} < z < d_{Kpt} + d_{Pd}.
\end{align*} \]  

(Eq 3.9)

Given (Eq 3.9) and under the condition \( d_{Kpt} \gg d_{Pd} \), the formulas (Eq 3.8-3.10) from Ref. [140] reduce to a simple expression for the actual strain in the bending direction in the capping Pd layer (\( \varepsilon_{act}(z = d_{Kpt} + d_{Pd}) \equiv \varepsilon_{act} \)):

\[ \varepsilon_{act} = \frac{d_{Kpt}}{R} \frac{3\nu_{Pd}(\nu_{Kpt} - 2\nu_{Pd} - 1) + 2(\nu_{Kpt} + 2)}{6(\nu_{Kpt} + 1)(\nu_{Kpt} - 2\nu_{Pd} + 1)}, \]  

(Eq 3.10)

where \( \nu_{Pd}=0.39 \) and \( \nu_{Kpt}=0.34 \) are the Poisson ratios for Pd and Kpt respectively. As \( \varepsilon_{act} \) is the same for the Co layer, this formula can be used to evaluate \( \varepsilon_{act} \) in Co based on the experimentally measured value of \( R \).

The respective free-standing strain in the capping Pd layer is given by the expression as follows:

\[ \varepsilon = \frac{Y_{Kpt}d_{Kpt}^2}{6Rd_{Pd}(\nu_{Pd} + 1)(\nu_{Kpt} - 2\nu_{Pd} + 1)} \]  

(Eq 3.11)

(which reduces to equation (Eq 3.8) in the limit \( \nu_{Kpt} = \nu_{Pd} \)).

Importantly, the ferromagnetic films on Kpt develop a strain during their growth (see Fig. 3 in Ref. [137]). For our strips this natural cylindrical bending is visible with naked eye. The radius of natural bending \( R_0 \) is easily found by measuring the elevation \( h_0 \) of
the strip edge before \( H_2 \) has been let into the chamber and using equation (Eq 3.7) to convert the elevation into \( R_0 \). Then the actual strain due to \( H_2 \) absorption reads

\[
\varepsilon_{H_2} = \varepsilon_{\text{act}}(R_{H_2}) - \varepsilon_{\text{act}}(R_0) \tag{Eq 3.12}
\]

where \( R_{H_2} = l^2 / [2(h_0 + \delta h)] \) is the radius of strip bending in the \( H_2 \) atmosphere and \( \delta h \) is the change in the elevation of the edge when the atmosphere in the chamber is changed to hydrogen gas from the original one (air in our experiment).

### 3.6.3.2 Results of processing of the experimental data with this theory

The original elevation of the edge of the 21mm-long \( Kpt//Co/Pd \) strip was 0.9 mm. The uplift due to absorption of hydrogen \( \delta h = 0.59d_{Kpt} = 75 \mu m \). This yields a \( H_2 \) induced free-standing strain in \( Pd \) \( \varepsilon = 2.4 \cdot 10^{-3} \). This value translates into \( \varepsilon_{H_2} = 2.8 \cdot 10^{-5} \) which corresponds to expansion of the \( Co \) layer of the strip by 0.6 \( \mu m \). Similarly, for the \( Kpt//Pd/Co/Pd \) strip our measurements yielded \( h_0 = 0.58 \) mm, \( \delta h = 1.57d_{Kpt} = 199 \mu m \).

Interestingly, in its virgin state this strip was bent in the opposite direction with respect to the bending direction due to \( H_2 \) absorption. In other words, originally the metallic layers were compressed. Absorption of \( H_2 \) reduced the negative strain and increased the bending radius. This has to be taken into account by changing the sign in front of \( \delta h \) in the expression for \( R_{H_2} \) (now \( R_{H_2} = l^2 / [2(h_0 - \delta h)] \)). The whole procedure yields \( \varepsilon = 2 \cdot 10^{-2} \) and \( \varepsilon_{H_2} = 2.3 \cdot 10^{-4} \). The latter value corresponds to \( Co \) layer elongation of 4.8 micron.
3.6.4 Significance of the study:

In this work we studied the physical origins of the hydrogen gas induced reduction of the strength of the perpendicular magnetic anisotropy (PMA) at the interface of cobalt and palladium layers. Qualitative analysis of these results demonstrates that the magneto-elastic contribution to the hydrogen-induced change in PMA is very small and is of opposite sign to the electronic contribution related to the influence of hydrogen ions on the hybridisation of Cobalt and Palladium orbitals at the interface. This finding may suggest that nanopatterning-induced modification of magneto-elastic effects should be excluded as a potential reason for the recently observed drastic improvement in the time of response of nanopatterned Si//Pd/Co/Pd films to their exposure to hydrogen gas [105].
CHAPTER THREE: Details of physics underlying functionality of m-HGS

3.7 Nano-patterned samples vs continuous thin film samples

3.7.1 Introduction

A number of studies related to palladium-based nano-patterned structures for hydrogen gas sensing applications have been carried out [21, 142-151]. Most of them find that nano-patterning of the active medium can boost the hydrogen sensitivity and shorten the hydrogen response times. (In all of above-quoted works palladium was used as an active sensing material and the sensor’s output was a change in its resistivity.) Here we try to use nano-patterned structures in our m-HGS concept and see whether this leads to some improvement of m-HGS performance. Furthermore, as suggested in [22], there may be a predictable benefit from employing nano-patterned structures which is elimination of a need to apply an external magnetic field (“bias magnetic field” mentioned in Section 2.2.2.2) to the ferromagnetic layer in order to trigger its FMR response. The concept and the details of this study will be discussed on Section 4.1. In the present section, we will focus on the performance comparisons between nano-patterned and continuous film samples instead.

The samples for the present study were designed at UWA and fabricated by A.O. Adeyeye’s group at the Department of Electrical and Computer Engineering of National University of Singapore (NUS). They represent tri-layers $Pd(10 \text{ nm})/Co(20 \text{ nm})/Pd(10 \text{ nm})$, which was found to be an optimal configuration, in Section 3.2.2). The films are either continuous in the plane or represent strips with a sub-micrometer cross-section and a macroscopic length. For convenience, we will call the latter geometry “nanowires”. These nanowires, having a width of 300nm and a pitch of 600 nm, were fabricated using deep-ultraviolet lithography, followed by electron beam layer deposition and, subsequently, lift-off [83]. The above-mentioned continuous film was deposited together with the nanostructure and represented a reference sample. The SEM image of the fabricated nanowire array is shown in figure 3.27.
CHAPTER THREE: Details of physics underlying functionality of m-HGS

Figure 3.27: Scanning electron micrograph of the tri-layer nano-wire sample.

The new IP / PP FMR capable gas chamber (Section 2.2.2.1) and standard gas blending gear (Section 2.3.1) with controlled 800 sccm flow rate were utilised in the experiment. The “lock-in and field modulation technique” (Section 2.2.1.2) combined with the “interferometric detection technique” (Section 2.2.1.3) were employed to obtain the best signal to noise ratio in the FMR measurements. The frequency of the microwave signal probing the FMR response of the samples is 13 GHz.

3.7.2 Experimental results

Figure 3.28 shows the field sweep FMR profiles for a) continuous film and b) nano-wires. The measurements were taken in pure \( \text{N}_2 \) and pure \( \text{H}_2 \) atmospheres. Table 3.9 provides the data summary for all the FMR field sweep measurements for easier comparison. From the FMR profiles measured at the same frequency of 13 GHz, one sees that the FMR field for the nano-wires is much lower than for the continuous film. This is due to a strong contribution of shape anisotropy to the total dynamic effective field for the nanowires. We also observed a larger resonance linewidth for the nano-wires which is possibly due to the roughness of
nano-wires’ edges inducing width variation of nano-wires. From the same figure and Table 3.9 one also sees that a much larger FMR field shift is found for the nanowires (36 vs 113 Oe) and also a more pronounced change in the resonance linewidth (14 vs 34 Oe).

Figure 3.28: FMR profiles taken at 13 GHz and obtained in the gas chamber: pure nitrogen (black lines) and pure hydrogen (dotted red lines) gas.

<table>
<thead>
<tr>
<th></th>
<th>Continuous film</th>
<th>Nano-wires</th>
</tr>
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<tbody>
<tr>
<td></td>
<td>FMR peak (Oe)</td>
<td>Line width (Oe)</td>
</tr>
<tr>
<td>100% $N_2$</td>
<td>1327</td>
<td>111.8</td>
</tr>
<tr>
<td>100% $H_2$</td>
<td>1291</td>
<td>97.7</td>
</tr>
<tr>
<td>FMR peak shift</td>
<td>-36</td>
<td>-14.1</td>
</tr>
</tbody>
</table>

Table 3.9: data summary for the FMR measurements taken at 13 GHz in pure nitrogen and pure hydrogen atmospheres.
CHAPTER THREE: Details of physics underlying functionality of m-HGS

Time resolved FMR measurements are then performed for the two samples. The microwave frequency is fixed to 13 GHz. FMR fields for the samples are different for this frequency: the resonance field for the continuous sample is 1330 Oe while a field of 510 Oe has to be applied to the nano-wire sample in order to bring it to resonance. The experiment shows that nanostructuring the samples not only boosts hydrogen sensitivity, but also decreases the hydrogen response times. Figure 3.29 compares the time resolved profiles for the continuous film and the nano-wires. A significant improvement especially of hydrogen desorption times is observed for the nano-wires (120 vs 2900 seconds). Table 3.10 shows the data summary for the time resolved profile FMR measurement taken from figure 3.29.

Figure 3.29: Time resolved FMR profile comparison between nano-wires and continuous film.
### 3.7.3 Discussion

Our work shows that the nano-wires sample strongly improves both hydrogen sensitivity and response times. F. Yang et al. [149] found that the hydrogen response times should be directly proportional to surface area to volume ratio ($SA / V$ ratio). This result was obtained for single-layer $Pd$ films while measuring the change in resistivity upon hydrogenation. However, from the time resolved profile we obtained one sees that the decrease in the hydrogen response times (especially in the desorption time – by 24 times) is much more significant than the change in the surface area to volume ratio for the nano-patterned sample with respect to the continuous film (only 13%). Therefore, the surface area to volume ratio rule established based on the studies of $Pd$ resistivity does not apply to our m-HGS concept. Similar result was also obtained by W.C. Lin group on their MOKE measurements [62]; the patterned structures of $Co/Pd$ multilayers film shows significantly reduced of hydrogenation response time than a continuous film with the exactly same configuration.
3.7.4 Significance of the study

Our results demonstrate that nanopatterning significantly improves both hydrogen sensitivity and response times with respect to continuous films. The effect is much stronger than found for resistivity based sensors employing single-layer Pd films [144, 149]. It is definitely an important method to improve m-HGS performance. Recall that the hydrogen desorption time for continuous thin films (as measured with in-plane FMR) is more than 48 minutes. For our nanowire sample the response time is less than 2 minutes which represents a strong improvement. In Section 4.1 this is used to demonstrate a highly efficient magnetic hydrogen gas sensor.
3.8 Chapter Summary

In this chapter, a broad scope of studies related to improving the performance (hydrogen sensitivity and response times) of m-HGS was presented. The effects of sample composition, FMR measurement configuration, sample geometry, sample post-processing after fabrication (in-situ annealing) on the sample response to $H_2$ absorption were investigated. Also the influence of the elastic strain and nanopatterning on the active medium of the sensor were studied. A clearer picture of the physics behind $Pd/Co$ films functionality as hydrogen gas sensors emerged from these investigations. Although those studies look independent from each other, each of them tackling a particular problem, their results can be combined to design an efficient sensor. For example, on the one hand, a simple continuous film (either a bi- or a tri-layers structure) combined with “perpendicular-to-plane FMR configuration” can be used to demonstrate m-HGS functionality (this will be discussed in Section 4.2). On the other hand, it is advantageous to use a tri-layer structure instead of a bi-layer if the film is nano-patterned, because the maximum of FMR sensitivity for the tri-layers is reached for a larger thickness (20nm) of cobalt. Nanopatterning is known to significantly reduce the amplitude of FMR absorption with respect to continuous films. Using thicker cobalt layers, as possible with the tri-layers, allows one to compensate the decrease in the FMR amplitude associated with the nanopatterning. (this will be discussed in Section 4.1). Study on the in-situ annealing delivered some crucial requirements for the active medium of m-HGS. $CoPd$ alloy was then tried and found to be a very good candidate for the m-HGS’s active medium (this will be discussed in Section 4.3). All the investigations discussed in the chapter provide a lot of room for cross-over in order to enhance the performance of m-HGS.
Chapter Four: Demonstration of functional prototypes of hydrogen gas sensors

This chapter focuses on presenting several demonstrations of functional prototypes of magnetic hydrogen gas sensors. The prototypes are based on a number of results of the studies discussed in previous chapters. A variety of sample materials, compositions and structures, as well as FMR measurement configurations is used to demonstrate the m-HGS functionality. The first system to demonstrate will be a tri-layer film Si/Pd10nm/Co20nm/Pd10nm patterned into a plane array of parallel nano-wires. In-plane FMR configuration was utilised in this case. This is a very important result, because nano-patterning provides not only a higher sensitivity and a much faster hydrogen desorption time, as discussed on Section 3.7, but also removes the need for an external bias field for sensor operation.

With the nano-patterned film a very wide range of detected hydrogen gas concentrations - from 0.1% to 50%. has been achieved. According to [139, 152, 153], the concentration detection range of sensors employed for safety purposes should be 0.01 ~ 10%, while a HGS that monitors fuel cells should have a sensitivity from 1% to 100%. We would like our m-HGS to be able to cover the whole range from 0.01% to 100%. Since the gas blending setup we used cannot provide hydrogen concentration less than 0.1% it is difficult to verify the detectability of the m-HGS for the lower part of the concentration range – from 0.01% to 0.1%. The lowest concentration which we could detect with the nanopatterned material was 0.1%. However, from the latter data, it follows that there is still some room for lowering the lower limit for hydrogen concentration detection.
CHAPTER FOUR: Demonstration of functional prototypes of hydrogen gas sensors

Detection of higher concentrations of hydrogen detection is also important; however, most of the proposed HGS concepts target the 10% hydrogen concentration range, with only few concepts capable to operate with concentrations close to 100% [153, 154]. Therefore, our second demonstration targets achieving the largest concentration detection range. To this end, we use a simple continuous bi-layer film and measure it in the PP FMR configuration. We demonstrate a hydrogen concentration detection range spanning from 0.1% to 100%. To achieve this, we adjust the static magnetic field applied to the sample in order to maximise material sensitivity to particular sub-ranges of this broad range of concentrations. Details of this study will be discussed in Section 4.2.

The final demonstration makes use of the properties of CoPd alloys in order to achieve a wide-range detection of hydrogen gas concentrations - from 0.1% to 100%. Just a single 15nm-thick CoPd and a single value of the applied field are needed to cover this range. Furthermore, another advantage brought by the CoPd alloy magnetic properties is a much lower saturation magnetisation than the one for the bi-layer (Si//Co/Pd) structure, hence this sensor requires a much smaller perpendicular-to-plane bias field to operate. Details of this work are given in Section 4.3.

The results from Sections 4.1 and 4.2 are based on recently peer-reviewed published papers with the author of the present thesis as the first author [105, 106]. The results from Section 4.3 have been prepared for publication.
CHAPTER FOUR: Demonstration of functional prototypes of hydrogen gas sensors

4.1: Device-prototype utilising a patterned tri-layer structure probed in IP FMR configuration

4.1.1: Introduction

A number of advantages of the m-HGS concept over other existing concepts were discussed in Section 1.1.2 and listed in Table 1.1. The result presented in this Section is the first demonstration of a fully functional prototype of a magnetic hydrogen gas sensor. The text below closely follows the recent paper [105]. Also the introduction to that paper is included for completeness.

One important concern of the m-HGS from the previous work on continuous layers [22, 104] however is that the device requires application of a magnetic field for its operation. The field is required because the FMR frequency for a continuous ferromagnetic film at zero external magnetic field is zero. One needs to apply a field in order to obtain a non-vanishing FMR frequency and hence to enable a finite-frequency FMR response for the material. In [22] it was speculated that film nanopatterning might eliminate the need for the applied field. In this work we experimentally demonstrate an improved device-prototype which does not require a magnetic field for its operation. The capability to detect the change in the FMR at remanence (i.e. for a zero applied field) is obtained, as suggested in [22], via nanopatterning, the continuous film being replaced by a periodic array of macroscopically long Pd/Co/Pd stripes with nanometer-range cross-section. The nanopatterning results in a non-vanishing FMR frequency for $H=0$ and thus enables $H_2$ detection in zero external magnetic field, here using microstrip line-based FMR spectroscopy (Figure 4.1).
Figure 4.1: Schematic diagram of the experiment. A structure in the form of very long palladium (Pd)/cobalt (Co) tri-layer wires with a nanometer-range cross-section lithographically formed on a silicon substrate (shown in dark gray) sits on top of a microwave microstrip line consisting of the microstrip itself made of gold-plated copper (shown in yellow, labeled “Microstrip line”). The dielectric substrate of the microstrip line is shown in light grey. The outmost bottom layer in the figure (shown in yellow) is the ground plane of the line, also made of gold-plated copper. This assembly is placed inside a pressure tight chamber (not shown) which is filled with a hydrogen-nitrogen or hydrogen-air gas mix, the gas molecules being shown as pairs of red balls. Two microwave ports of the chamber (not shown) are connected to an external microwave circuit which is used to measure attenuation of microwave power in the microstrip line due to ferromagnetic resonance (FMR) in the cobalt layer. The chamber is placed between pole pieces of an electromagnet in order to allow magnetic-field resolved FMR measurements. The magnetic field of the electromagnet is applied along the length of the nanowires - the black arrow indicates the direction of the resulting magnetization vector for the Co layer.
CHAPTER FOUR: Demonstration of functional prototypes of hydrogen gas sensors

In the present work we carry out measurements for a range of \( H_2 \) concentrations - from 1000 ppm to 100% - in the measurement chamber and show that the presence of \( H_2 \) in nitrogen gas can be reliably detected all across this broad concentration range. In air, our device prototype can detect concentrations of \( H_2 \) starting from 0.3%.

4.1.2: Experimental Section

The samples under study are based on tri-layer \( Pd(10\, \text{nm})/Co(20\, \text{nm})/Pd(10\, \text{nm}) \) structures (Figure 4.1) in the form of continuous films and patterned strips, the latter with a sub-micrometer cross-section and a macroscopic length. For convenience, we will call the latter “nanowires”. These nanowires, having a width of 300nm and a pitch of 600 nm, were fabricated using deep-ultraviolet lithography, followed by electron beam layer deposition and, subsequently, lift-off [83] (Section 2.1.3). Moreover, a reference continuous tri-layer film was deposited together with the nanostructure. The SEM image of the fabricated nanowire array is shown in figure 4.2.

Figure 4.2: Scanning electron micrograph of the Pd/Co/Pd nanowires.
In this study, the standard In-plane FMR setup with field-modulated and microwave receiver techniques (Section 2.2) together with new generation gas-tight chamber (Section 2.2.2.1) were used. The standard gas blending setup (Section 2.3.1) was also employed to control the flow rate precisely.

4.1.3: Experimental Results

Figure 4.3 shows the FMR response of the virgin material, obtained using vector-network-analyzer FMR [84] over a broad range of applied fields and frequencies. Note that the range of the applied fields in the graph spans across the width of the major hysteresis loop for the sample. In this particular figure, the magnetic field was swept from negative saturation to positive, i.e. the measurements were taken for the lower half of the hysteresis loop. It is known [128] that the hysteresis loop for nanowires is close to square, the nano-wires switching sharply between single-domain states in which the magnetization vector points along the nano-wire axis. A sharp jump in the FMR frequency takes place when the magnetization vector for the nanowires switches from the negative direction to the positive one. The same behaviour is seen in figure 4.3. Importantly however, at remanence ($H=0$) the ground state of the static magnetization vector is along each nanowire’s long axis, leading to a finite FMR frequency which here is on the order of 10 GHz. This large frequency is due to a strong contribution of dynamic demagnetizing (dipolar) field to the FMR frequency in this confined nanowire geometry.
CHAPTER FOUR: Demonstration of functional prototypes of hydrogen gas sensors

Figure 4.3: 2-dimensional (amplitude vs. applied field and frequency) FMR map for the as deposited nanowire array taken after lift-off.

Typical field-modulated FMR responses of the continuous film (a) and the nanopatterned sample (b) are shown in figure 4.4. The measurements were taken at 13 GHz for pure nitrogen and hydrogen atmospheres. Similar to our previous measurements (Section 3.2.1 and 3.2.2), a significant FMR peak shift to lower fields as well as a resonance line narrowing is observed upon hydrogenation for both types of samples. By fitting the data with the first derivative of the Cauchy-Lorentz function, resonance fields and resonance linewidths can be extracted. The extracted parameters are shown in table 4.1. From the table 4.1 one sees that the nanowire array is characterized by significantly better performance than continuous film as a hydrogen gas sensor, both in terms of the absolute values of extracted parameter variations and percentage change with respect to the continuous film. Indeed, the shift in the resonance peak position is over three times higher in the nanowire sample, a shift equivalent to \( \frac{3}{4} \) of the resonance linewidth.
CHAPTER FOUR: Demonstration of functional prototypes of hydrogen gas sensors

Figure 4.4: FMR response at large applied fields for the continuous film (a) and for the nanowires (b). Field-modulated FMR has been utilized to take these measurements. The frequency is 13 GHz. Circular dots and triangles: experimental data for $H_2$ and $N_2$ atmospheres respectively. Solid and dashed lines: respective fits with a complex Lorentzian.

<table>
<thead>
<tr>
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<th>Continuous film</th>
<th>Nano-wires</th>
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<td>FMR peak (Oe)</td>
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<td>100% $N_2$</td>
<td>1327</td>
<td>111.8</td>
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<tr>
<td>100% $H_2$</td>
<td>1291</td>
<td>97.7</td>
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<tr>
<td>FMR peak shift</td>
<td>-36</td>
<td>-14.1</td>
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Table 4.1: FMR peak positions, FMR peak linewidths and associated changes ($\Delta H$ and $\Delta LW$ respectively) obtained at 13 GHz.
As one can see from the table, at this frequency the FMR response of the nanowires is obtained in a finite magnetic field. This is in full agreement with the data in figure 4.3. Also consistent with figure 4.3, setting the microwave frequency to 10.2 GHz enables the observation of a finite FMR signal at zero external magnetic field. Field resolved FMR traces taken at this frequency, scanned across zero field, are shown in figure 4.5. From this graph one sees that for $H=0$ the FMR amplitude is finite in the presence of $H_2$ but nearly zero for the $N_2$ atmosphere. Hence, by registering the amplitude of the FMR response for $H=0$ it will be possible to reliably detect the presence of hydrogen gas in the atmosphere, provided the microwave frequency is set appropriately.

![Graph showing FMR responses](image)

Figure 4.5: FMR responses taken at 10.2 GHz and obtained for two atmospheres in the chamber – pure nitrogen gas and pure hydrogen gas. To obtain the traces, the field-modulated FMR was employed. Note that the traces look very similar to typical vector-network-analyzer data. This is because there is a phase shift of nearly 90 degree related to the way the magnetization dynamics in the material couples to the stripline for this particular sample and for this particular field range.
We now present time-resolved FMR measurements for the nanowire sample under different concentrations of $H_2$. These measurements were carried out at 10.2GHz. Again, a FMR response is obtained at remanence (i.e. in a zero external magnetic field). Figure 4.6(a) displays the time-resolved response from our device-prototype while stepping the hydrogen gas concentration in a $N_2$ “carrier gas” from 1% to 10%. Figure 4.6(b) is for 10% to 60%. To obtain these traces, the concentration of $H_2$ was switched between zero concentration (minima of the black trace) and stepped finite concentrations (maxima of the black trace). The red traces correspond to the instantaneous $H_2$ concentration. From figure 4.6(c) one sees that registering the amplitude of the FMR response allows the measurement of the concentration of $H_2$ in the chamber atmosphere. Although the amplitude of the response does not scale perfectly linearly with the concentration (Figure 4.6(c)), no hysteretic response is observed [35]. Indeed, as seen from figure 4.6(a) and (b) the response amplitude always returns to the same level for zero $H_2$ concentration (the variation in the zero level does not exceed 10% and is random). From figure 4.6 one also sees that we are able to distinguish between 1% and 60% of hydrogen gas in the hydrogen-nitrogen gas mix.

Noteworthy is the $H_2$ absorption rate, as measured with this method. Firstly one sees that the transient times for both absorption and desorption decrease with an increase in the $H_2$ concentration. Also, as previously found for switching between 100% $H_2$ and 100% $N_2$ [22], the desorption time is noticeably larger than the absorption one. Furthermore, both rates for the nanopatterned material are much smaller than for the continuous film (refer to section 3, figure 3.29); for instance, for the nanowires at 60% $H_2$, the absorption time is 22 seconds while desorption occurs over 60 seconds. This is more than 30 times smaller than for the continuous film (Figure 3.29). This result is consistent with the observation in [62] of significant acceleration of magneto-optical detected absorption / desorption to $H_2$ of nanopatterned materials with similar composition.
CHAPTER FOUR: Demonstration of functional prototypes of hydrogen gas sensors

Figure 4.6: Sensor device-prototype response as a function of hydrogen gas concentration in nitrogen as a carrier gas. (a): the concentration is stepped from 1% to 10% hydrogen. (b): the same but for 10% to 100%. Minima of the peaks: pure nitrogen gas; maxima: hydrogen-nitrogen mix, after completion of the $H_2$ absorption process (“Equilibrium state”). (c) Amplitude of FMR response for the equilibrium state as a function of hydrogen gas concentration for the concentration range 1-10%. Red dashed lines in (a) and (b) shows the respective instant concentrations of hydrogen gas (right-hand vertical axis). Figure 4.6 (d) Repeatability of the hydrogenation/de-hydrogenation cycles. Sample used: the tri-layer nanowire array from NUS with the thickness of the Co layer of 20nm. The trace was recorded at 10.2 GHz and without providing external magnetic field under the cycling between pure nitrogen and 10% hydrogen gases. Figure 4.6(e) shows the hydrogenation response times with difference hydrogen concentrations range from 3% to 60% under NUS tri-layer cobalt nanowire samples. Ones can observe hydrogen absorption times remain constant among wide range of hydrogen concentrations. However, the de-hydrogenation time has a logarithmic dependence on hydrogen concentration.
In order to understand the performance of m-HGS under different carrier gases, concentration-resolved measurements were also taken using air as the carrier gas. Because the flammability threshold for hydrogen in air is 4% $H_2$ [2], for safety reasons these measurements were carried out only for $H_2$ concentrations below or equal to 3%. The results of those measurements are shown in figure 4.7. In the same figure, we show the response of our sample for hydrogen gas concentrations below 1%. One sees (Figure 4.7(a)) that for the hydrogen+nitrogen gas mix we are able to reliably detect the device response down to 0.1% of $H_2$. In air, the signal starts to deteriorate with an approach to 0.3% from above and is not visible any more on the noise background for 0.2%. For 0.8%, the response amplitude is about 2 times smaller in air than in $N_2$, but the difference diminishes quickly with an increase in the $H_2$ concentration, such that for 2% the two responses are practically the same (Figure 4.7(b)). One also notices that the sensor response time increases in air for small concentrations. Interestingly, the recovery time actually reduces in air with respect to $N_2$. 
Figure 4.7: (a) Comparison of time-resolved traces taken in air and nitrogen as carrier gases. (b) Difference in responses between a carrier gas (air or pure nitrogen gas) and the respective atmosphere with admixture of hydrogen gas. These points have been extracted from the raw data in Panel (a). Black line in (a) and black squares in (c) are for nitrogen. Blue lines in (a) and (b) and blue circles in (c) are for air. Red dashed lines in (a) and (b) show the respective instant concentrations of hydrogen gas (right-hand vertical axes).
4.1.4: Discussion

As for the difference between the device-prototype responses in air and nitrogen gas, a similar effect was observed for Pd nanowires in [149]. There, the reduction of the Pd nanowire response to hydrogen charging in air was explained by a chemical reaction of removal of Hydrogen atoms adsorbed on the sample surface as suggested in [155]: at the Pd surface atomic oxygen chemically binds with atomic hydrogen forming water which evaporates from the surface. Interestingly, similar to our sample, they also observed a decrease in the material recovery time in air. It was explained as hydrogen-removal oxygen assisted acceleration of the desorption process. While they observed a decrease in the response time, our sample displayed an increase.

Let us now discuss possibility of implementation of the suggested concept as a cheap fully integrated device compatible with the modern CMOS platform. We believe that creating such a device should not be difficult, given that fabrication of simple digitally controlled microwave oscillators and detectors of weak microwave signals, fully integrated with digital electronics, is well established, for instance, in the telecommunications industry. Deposition of Pd/Co nanostructures is fully compatible with CMOS technology [83]. Furthermore, the main reason why we needed to use a microwave receiver and a lock-in amplifier in the present experiment is because the amplitude of the FMR response of a 10nm-thick cobalt layer is small – on the order of 10 microvolts (see figure 4.5). However, the nanostructure may be formed directly on top of a microscopic microwave stripline [156] and have a length along the line of 1 to 2 cm, instead of 4 mm, as for the present sample. A thin electrically insulating and $H_2$-impermeable spacer may separate the deposited Pd/Co structure from the surface of the stripline, thus making the sensor contactless and fire safe. Notably, the sensitivity of FMR stripline transducers scales as $1/w$, where $w$ is the characteristic width of the stripline [84]; hence one may expect a 10-fold increase in sensitivity if a 10-fold narrower stripline is used instead of the one used here (0.4 mm wide). Combined with
a potential 5-fold boost in the response due to a larger length of the sample, one may expect an FMR response on the order of 0.5 mV. This level of signal should be large enough, in order to detect it in a simple, on-chip approach without the use of a modulation coil, lock-in amplifier and microwave receiver. Indeed, even at the present level of the signal, the FMR response is strong enough in order to be detected in a modulation-coil and lock-in-amplifier-free approach using a VNA (Figure 4.3).

The simple on-chip design combined with a possibility of contactless sensing makes the FMR based approach appealing. Currently, the leading technology for contactless H\textsubscript{2} sensing is optical. Significant progress has been achieved in optical fibre sensors recently [153], however, unfortunately, they do not meet many of recommended performance specifications [153]. Magneto-optical methods have also been suggested [7, 37-39, 48]. Nanopatterning of utilized film media has recently been shown to decrease the response time of the magneto-optical film sensors [62] However, similar to all other optical sensors, they will potentially need calibration to compensate for drift and aging of the optical surface [153]. Furthermore, fibre-optic elements are required to build the device. Our concept is all-electrical, can be implemented as a planar lithographically formed structure on a silicon substrate using materials compatible with the CMOS platform. Electronic properties of an interface buried well below the upper surface of the material are exploited which potentially leads to a longer device lifetime.

Another point to consider is that the sensitivity of conventional sensors based on measurements of electrical conductivity of Pd films increases with an increased film thickness [35]. There, buckling of Pd films Pd clamped to rigid substrates while exposed to H\textsubscript{2} will severely limit the maximum possible Pd thickness, since the probability of irreversible deformations due to buckling increases with increasing film thickness [35]. On the contrary, similar to other interface effects, the overall effect of PMA on macroscopic material parameters (e.g. on its FMR response) does not noticeably
depend on $Pd$ thickness above some critical thickness for the onset of $PMA$ (on the order of several atomic layers), and increases with a decrease in $Co$ thickness. Thin $Pd$ layers can withstand huge compressive stresses without buckling [70]. Hence, by exploiting an interface effect instead of a bulk one the problem of irreversible deformations can be naturally avoided. It should be also noted that the functionality of our sensor is based on variation of frequency of an eigen-excitation in a material instead of a change in its static parameters such as electric conductivity [35, 149], hence one may expect potentially smaller noise and the absence of a level drift.

Sensors for concentrations 0.01-10% are required for ensuring hydrogen safety, and ones capable to operate in a broad range 1-100% are needed in fuel-cell technology [153]. Given the result in figure 4.7, our concept, as of now, is more appropriate for fuel-cell applications, as in a separate study (section 4.2) we showed that the upper limit of concentration resolution range is determined solely by device settings [106] (in the present case it is given by the driving microwave frequency for a fixed nanowire width). Hence, by combining two devices tuned to two complementary concentration ranges on the same microchip it will be possible to cover the whole required concentration range 1-100%. For the present geometry, the tuning may be achieved by fabricating two nanowire arrays with wires of slightly different widths and driving both arrays at the same microwave frequency, i.e. from the same microwave generator.

4.1.5: Conclusion

In conclusion, we have demonstrated clear advantages of nanopatterned $Pd/Co$ films over continuous $Pd/Co$ films as candidates for future hydrogen gas sensing devices with fast response times. The nanopatterning results in higher sensitivity and much faster hydrogen desorption rate and removes the need for an external applied magnetic field for operation. A wide range of hydrogen gas concentrations has been
detected with the nanopatterned material - from 0.1% to 50%, in nitrogen as a carrier gas and from 0.3% in air. Dramatic enhancement of performance – zero-applied field operation, much faster response and recovery times, and a very wide range of detectable hydrogen gas concentrations – was demonstrated compared with our earlier work [22].

4.2: Demonstration of wide range hydrogen gas detection by adjustable m-HGS

4.2.1: Introduction

The result presented in this Section is the first demonstration of wide-range hydrogen detection (<0.01 to 100%) with an m-HGS. The text below closely follows the recent paper [106]. Also the introduction to that paper is included for completeness.

In Chapter 3 we demonstrated that the sensitivity of the m-HGS strongly depends on the direction of a magnetic field applied to the sample during the experiment: in the configuration when the field was applied perpendicular to the film plane (PP configuration) the films’ FMR response was almost 10 times more sensitive to the presence of \( H_2 \) than when the field was applied in the film plane (IP configuration) (Section 3.3.1). In this section, we use this advantageous PP configuration to demonstrate a functional, wide-concentration-range hydrogen gas sensing method.
4.2.2: Experimental Section

A Silicon wafer is used as a substrate for the bi-layer structure. The silicon substrates are cleaned with acetone, ethanol and finally de-ionized water. The substrate is then blow-dried and put on the substrate holder for thin film sputtering. The $Co$ and $Pd$ layer thicknesses are approximately 5 nm and 13 nm respectively. These thicknesses were measured from high resolution TEM (Transmission Electron Microscopy) imaging and STEM-EDS elemental maps (Scanning Transmission Electron Microscopy Energy-dispersive X-ray spectroscopy) (Figure 4.8a & b). A thin native $SiO_x$ layer is seen on the upper surface of the Si substrate in Fig. 1a. The STEM-EDS results in Figure 1b are suggestive of some interface alloying between $Co$ and $Pd$. Figure 4.8c shows the X-Ray diffraction trace ($2\theta$ scan) for the sample. There is reasonable agreement with expected peak position for cubic $Pd$ and $Co$ and hcp $Co$. The peak at 64.6° corresponds closely to that expected for $Co_3O_4$ and is thus potentially suggestive of some oxidation of the $Co$ layer, perhaps at the interface with $Si/SiO_2$. Both TEM and X-ray characterizations of the film were carried out after the exposure of the sample to $H_2$. 
Figure 4.8: (a) Cross-sectional high resolution TEM image of the //Co/Pd bilayer obtained using a FEI Titan G2 80-200 TEM/STEM with ChemiSTEM technology. The upper region is a Carbon layer deposited for film protection during TEM sample preparation. The latter was carried out using a FEI Helios Nanolab G3 CX DualBeam FIB/SEM. (b) Elemental mapping of Co and Pd across the film’s thickness using STEM-EDS. (c) Background-subtracted X-ray diffraction (XRD) trace of the sample. Expected peak positions for diffraction from the shown cubic Co, Pd and Co$_3$O$_4$ planes as well as hcp Co are shown as labelled, vertical lines. (d) Schematic showing the film which is placed face-down on a microwave stripline which forms the bottom panel of an air-tight chamber. Mixtures of $H_2$ and $N_2$ enter and exit the chamber through the two shown ports. SMA connectors (orange) interface to the receiver which is shown in a simplified block diagram with the microwave (MW) source and the lock-in amplifier, the latter being used to measure the differential FMR absorption signal. In this view, the dc magnetic field is perpendicular to the plane of the page. (e) Schematic showing the chamber during measurement, mounted between the poles of the electromagnet and the modulation coils which are driven at 220 Hz. The SMA ports are shown for reference. The electromagnet is used to generate a dc magnetic field.
All the results shown below have been obtained under a constant flow rate of 800 sccm at atmospheric pressure by the standard gas blending setup (Section 2.3.1). As the measurements have been taken in a very broad range of concentrations across the threshold of hydrogen flammability in air, nitrogen is utilized as a carrier gas for fire safety. This is also done for hydrogen gas concentrations below 4%, in order to compare that data with data taken at higher concentrations. For the specific purpose of the present work this arrangement is fully appropriate. Furthermore, in our recent work [105] (refer to the preceding section 4.1) we demonstrated that the responses in air and nitrogen converge when approaching the 2% concentration point from below.

4.2.3: Experimental Results

Time resolved FMR traces are the main basis of this work and are obtained as discussed in section 2.2.2.2 [22, 105]. A fixed dc magnetic field (13 kOe; 1 Oe ~ 80 A/m) is applied perpendicular to the sample plane. Application of a field is needed because for a continuous film, the FMR frequency for a zero internal field is zero [20]. Upon application of a 13kOe external magnetic field however, the FMR frequency shifts to 8.2 GHz. In order to maximize the signal to noise ratio of FMR measurements, “lock-in with field modulation” (section 2.2.1.1) and “interferometric detection” techniques (section 2.2.1.2) are employed.

Figure 4.9 illustrates the time resolved FMR traces method. To obtain the traces shown in the figure, a c.w. (continuous wave) microwave signal at a frequency of 8.2 GHz was applied to the sample. First field-resolved FMR traces were obtained for two atmospheres - pure nitrogen gas and 50% hydrogen and 50% nitrogen gas (Panel (a)). Then the applied magnetic field was set to a value corresponding to some specific point within the field-resolved FMR trace (shown by the red vertical line in Panel (a)). The chamber was then purged with 800 sccm of pure nitrogen for 5 minutes while
CHAPTER FOUR: Demonstration of functional prototypes of hydrogen gas sensors

keeping both microwave frequency and the applied field constant. The atmosphere was then changed to 50% hydrogen and 50% nitrogen gas for 5 minutes. This time has been found to be sufficient to complete the transient process associated with hydrogen intake by Pd. Finally, the chamber is flushed with pure nitrogen gas leading to FMR signal recovery to (almost) the same level.

From this figure one sees that the device-prototype response time, as measured at 90% of the steady amplitude (relative to the original level), is 20 seconds. The recovery time (the time needed to recover 90% of the total change in signal, once H₂ has been removed from the atmosphere in the chamber) is noticeably larger – 120 seconds.

Figure 4.9: Diagram illustrating the physical principle underlying the time-resolved FMR measurements. (a) Conventional field-resolved FMR traces obtained in pure nitrogen gas (black line) and 50%/50% hydrogen/nitrogen gas mix (blue dashed line). The microwave frequency is kept constant at 8.2 GHz. (b) Black solid line: amplitude of the FMR response as a function of time, when the applied field has been set to a constant value 12988 Oe [see red vertical line in (a)] with the frequency at 8.2 GHz. The atmosphere in the chamber is originally pure nitrogen gas, constantly flowing through the chamber. It is replaced with the constantly flowing gas mix at time = 300 seconds. The chamber is then flushed with pure nitrogen at time = 600 s. This pure remains
constantly flowing afterwards. The red dashed line shows the hydrogen concentration in the chamber (right-hand axis).

Now we use the time scan method to demonstrate the possibility to tune sensitivity of the device-prototype to particular hydrogen gas concentration ranges. The experiment is carried out as follows. The atmosphere in the chamber is cycled between pure nitrogen gas and a $H_2/N_2$ gas mix, with $H_2$ concentration increasing from cycle to cycle. The variation in the FMR amplitude is recorded with time resolution while the microwave frequency and applied dc magnetic field are kept constant at $f_0=8.2$ GHz and $H_0=12988$ Oe respectively. At each step we wait sufficiently long to allow the FMR response to stabilize (with accuracy 10%). Then, in order to verify the time-resolved data, field resolved FMR traces are recorded for the same $f_0$ and $H_0$ and the same hydrogen gas concentrations. From the latter traces FMR amplitudes corresponding to the particular $H_0$ are extracted and compared to the amplitudes of the respective peaks in the time resolved scan.

In figure 4.10 (a) we show PP FMR field-resolved traces taken for $H_2$ concentration ranging from 2% to 100%. One sees that the FMR peak shifts to a higher magnetic field with an increase in the concentration. The shift is consistent with a decrease in the perpendicular magnetic anisotropy (PMA) for the sample (section 3.3.1). Panel (b) of the same figure shows the FMR resonance field vs. $H_2$ concentration, as extracted from the set of the raw FMR traces in figure 4.10(a). To produce these points, the raw traces were fitted with a first derivative of a Lorentzian (see [157] for details). One sees that the higher the hydrogen concentration, the more the PP FMR peak shifts upwards in field. Importantly, the shift does not saturate with an approach to the 100% concentration. This demonstrates that a sensor based on this FMR principle can operate over a very large range of $H_2$ concentrations.
CHAPTER FOUR: Demonstration of functional prototypes of hydrogen gas sensors

Figure 4.10: (a) PP field-resolved field-modulated FMR traces under different hydrogen gas concentrations (2% to 100%). (b) Resonance peak shift as a function of $H_2$ concentration as extracted from the experimentally obtained FMR traces in (a).

Based on figure 4.10, one may suggest three candidates for a future working sensor’s output. The first is via the shift in the FMR frequency as a function of hydrogen gas concentration, measured while keeping the applied magnetic field constant. However, measuring the resonant frequency in the microwave range is not a trivial task in practical terms. Alternatively, one can have a measure of the shift of the maximum of the FMR peak as a function of the applied field (as done in Figure 4.10(b)), while keeping the frequency of the microwave signal constant. This method of “field detection” is easier, however its implementation requires application of a magnetic field to the sample and hence electronics to control the magnetic field. In our recent paper [105], we demonstrated that by laterally
nanostructuring Pd/Co films it is possible to shift the FMR frequency from zero and thus to enable functionality of the magnetic $H_2$ sensor without applying a magnetic field at all ("shape-anisotropy bias"). If the field detection method is chosen, the advantage of the shape-anisotropy bias is largely lost. Given this, the most obvious method of measuring the FMR absorption amplitude for fixed frequency and fixed applied field turns out to be the most practical way to detect $H_2$ concentration. It will be used below.

Note that each field bias point will not necessarily represent an optimised working point for the full concentration range. For example, when going from 0% to 100% $H_2$, the signal at the first bias point, “Bias 1” (Figure 4.10 (a)), will first decrease and then increase, preventing a one-to-one mapping between voltage levels and $H_2$ concentrations (this non-monotonic behavior is explicitly seen below). Although working at bias point “Bias 3” will enable a monotonic decrease in the signal with increasing $H_2$ concentration, the sensitivity will be reduced near 0% $H_2$ and near 100% $H_2$, as the field-resolved differential absorption curves in figure 4.10(b) for these particular concentrations show extrema for this bias value. Note also that while the FMR peak shift is approximately equal to the peak-to-peak resonance linewidth here, an increased sensitivity or reduced linewidth would result in a peak shift that clearly exceeds the linewidth, again preventing the one-to-one concentration to voltage mapping, even when working at Bias 3.

To remedy this, we will demonstrate a feature of the magnetic hydrogen gas sensor (m-HGS) based on the amplitude method. It exploits the fact that the detection range can be adjusted by controlling the magnetic field applied to the sample. We will show that one simply needs to set the field to some particular value, in order to make the device-prototype operational in some particular concentration range. This is of course easier than sweeping or stepping the field. Furthermore, altering the external actual magnetic field may be replaced by a sensor dependent shape-anisotropy bias.
We now look at three different biasing fields in order to cover a hydrogen gas detection range from 0.2% to 100%. These fields are: Bias 1 (equal precisely to the FMR resonance field in the absence of $H_2$); Bias 2 & 3: within the resonance line but not precisely at the resonance field; and, Bias 4: outside the FMR resonance line. Note again that these field values are marked on figure 4.10(a) as vertical lines. Below, we will show that Bias 1 is suitable for measuring lower hydrogen gas concentrations (less than 5%); Bias 2 is appropriate for the low to middle concentration range (1~10%); Bias 3 is suitable for measuring middle concentration range (10~80%) and Bias 4 can be employed when the $H_2$ concentration is expected to be between 80% and 100%.

Measuring the smallest concentrations requires the highest sensitivity. As such, the bias point should be set to the position where the FMR trace slope is at its maximum. Recall that we employ the Field Modulated FMR method. Accordingly, the highest slopes of the differential absorption traces shown in figure 4.10(a) correspond to the respective maxima of the underlying FMR (Lorentzian) peaks. Based on the traces in figure 4.9(a), to enable measurements of the smallest concentrations, we choose the applied field value equal to Bias 1. The respective vertical line in this panel cuts the differential FMR trace for 100% $N_2$ very close to the midpoint between the maximum and the minimum of the trace, i.e. very close to the maximum of the underlying Lorentzian. The red open squares in figure 4.11(a) show the vertical co-ordinates of the points where this line crosses all the traces in figure 4.10(a). One sees a very steep slope for concentrations below 10%, enabling the measurement of $H_2$ concentrations in this range with high accuracy. The graph also predicts that at 10% of $H_2$ the output signal of the device will saturate and then roll off for yet larger concentrations.

Figure 4.11(e) demonstrates the result of a time-resolved measurement of the differential FMR absorption amplitude when the applied field magnitude is set to Bias 1 value (12822 Oe). During this measurement, the atmosphere in the chamber is cycled between pure $N_2$ and different concentrations of $H_2$ - from 0.2% to 30%. One
sees that for this bias it is indeed possible to measure gas concentrations in the range 0.2% to 10%. Overall, there is a good agreement with that predicted from the FMR traces (see the blue filled circles in figure 4.11(a) which show the amplitudes of maxima of the negative peaks in figure 4.11(e)). Namely a steep slope at concentrations below 10% and an approach to saturation above 10% are observed.

In order to measure hydrogen gas concentrations spanning from 1% to 40% we set the bias field to 12940 Oe (Bias 2 in figure 4.10(a)). The respective time resolved trace is displayed in figure 4.11(f) and the amplitudes of the negative maxima from this panel are displayed in figure 4.11(b) where they are overlaid with the respective predictions. It is clearly visible that for Bias 2 the best concentration resolution is achieved for this concentration range and that the output FMR signal starts to approach saturation at 40% of $H_2$.

Similarly, moving the bias point further towards larger fields (13108Oe, Bias 3 in figure 4.10(a)) we are able to measure $H_2$ concentration in the range from 10% to 80% with the response rolling off above 80% (Figures 4.11(c) and (g)). Finally, we attempt to resolve $H_2$ concentrations in the range 80% to 100%. Given that for concentrations close to 100% the FMR peak shift is equal to the resonance linewidth, to enable this measurement it is useful to set the bias field outside the high-slope portion of the differential FMR trace obtained in pure $N_2$. This value of the field (13615 Oe) is shown as Bias 4 in figure 4.10(a). Figure 4.11(d) predicts that the slope of the concentration dependence of the differential absorption amplitude will then be of the opposite sign with respect to the data in Panels (a) and (b) of the same figure. This is confirmed by the recorded time resolved data (Figure 4.11(h)). Quite a linear dependence of the differential absorption amplitude on the $H_2$ concentration for this concentration range is observed in this trace and the respective processed data in figure 4.11(d).
Figure 4.11: (a-d): Comparison of predicted FMR response amplitudes with experimentally measured ones. Red open squares: predictions from Figure 2(a). Blue circles: extracted from the respective time-resolved FMR traces. Small filled black squares: sensitivity (right-hand axis). (e-h): Black solid lines (left-hand axis): time-resolved differential FMR traces taken at a constant applied field. Positive peaks in (e), (f) and (g) and negative ones in (h) correspond to pure $N_2$ gas atmosphere in the chamber. Negative peaks in (e), (f) and (g) and positive ones in (h): established FMR responses in the presence of $H_2$ in concentrations shown by the respective peaks in the red dashed line (right-hand axis). Steep slopes of the black line: transient processes between the two steady states. The heights of the negative peaks from (a), (b) and (c) and of positive ones in (d) are shown in Figure 4.11 with blue circles. (a) and (e): Applied field is 12822 Oe (Bias 1); (b) and (f): 12940 Oe (Bias 2); (c) and (g): 13108 Oe (Bias 3); (d) and (h): 13615 Oe (Bias 4).
4.2.4: Discussion

Let us now discuss sensitivity of the proposed method. We may define the sensitivity $S$ as the slopes of the curves in figure 4.11 - $S = dA/dC$, where $A$ is absorption amplitude and $C$ is the $H_2$ concentration. The sensitivity extracted from the experimental points in figure 4.11 (a)-(d) is also shown in these panels. One sees that the maximum of $S$ is achieved for Bias 1, as originally expected, the smallest sensitivity being for Bias 4.

For each of the bias value the sensitivity is not constant for the whole respective concentration range, but for each bias there is a range where it is nearly constant. These ranges of constant sensitivity are displayed in figure 4.12(a). Figure 4.12(b) shows the respective response amplitudes for comparison. One sees that indeed the four biases combined cover the whole concentration range from 0.2% to 100% with constant sensitivity within each of the sub-ranges. The absolute sensitivity drops while moving from Bias 1 to Bias 2 and then to Bias 3. The smallest one is for Bias 4 – its mean value is 0.01 (see figure 4.12(a)).

This may be understood by looking at figure 4.10. The maximum sensitivity for a particular bias is achieved for a specific $C$ value, for which the vertical line in figure 4.10(a) corresponding to this bias cuts the respective differential absorption curve right in the middle between curve’s maximum and minimum (where its slope is maximized). For Bias 1 it is achieved for $C=0$%; for Bias 2 for 6% and for Bias 3 for $C=40$%. These values are in agreement with the middles of the respective constant-sensitivity ranges from figure 4.12. From figure 4.10(b) one sees that the slope of the curve shown in it decreases with a decrease in $C$. This is the reason why the sensitivity drops with an increase in the concentration – the resonance peak shift decreases with an increase in $C$ which leads to a smaller $dA/dC$. The smallest peak shift is for $H_2$ concentrations close to 100%; therefore the
sensitivity is smaller for Bias 3, which enables covering the highest concentration range with constant sensitivity.

Figure 4.12: (a) Sensitivities for all bias fields (same as black filled squares in Figure 4.12 (a-d) but only for concentration ranges where the sensitivity is nearly constant). Dots: experimental values. Lines: mean values of the sensitivity. Numerical values (xxx) in the figure show the mean sensitivity values. (b) Response amplitudes for all bias fields, given here for comparison with Panel (a) (same as blue filled circles in Figure 4.12 (a-d), but only for concentration ranges where the sensitivity is nearly constant).

4.2.5: Conclusion

Here, it has been demonstrated that measuring FMR response amplitude of Pd/Co bilayer films in the presence of hydrogen gas enables the determination of hydrogen gas
concentration over a very broad concentration range. The range probed here was from 0.2 to 100%, with the lowest concentration limited not by the sensitivity of the method but by the capability of our gas mixture preparation equipment. Across this broad concentration range the sensitivity varies by 80 times - from 0.45 μV/% (at small concentrations) to 0.01 μV/% (for concentrations close to 100% with no signal saturation). The numerical values of the sensitivity are not critical however since they largely depend on the details of the experimental fixture and apparatus employed. In this study, they were not optimized to achieve the absolute maximum of sensitivity. What is critical however is the extent of the variation of the sensitivity across the concentration range which is underlain by the physics of the variation in the FMR resonance frequency or field due to exposure of the material under study to hydrogen gas. Suppose that an apparatus allows one to reliably discriminate between 99% and 100% of $H_2$. Then our result implies that at the lower end of the concentration range explored in the present work it will be possible to discriminate between 2000 and 2025 ppm of hydrogen gas concentration. Similarly, optimization of the response at the lower end such that the values of 2000 and 2025 ppm are well resolved will also allow discrimination between 99% and 100%.

In order to enable this broad-range operation of the device prototype, the gas concentration range was divided into four sub-ranges. A value of a bias magnetic field specific to each sub-range was applied to the sample in order to detect hydrogen gas concentration in this sub-range. We claim that in real-world applications, instead of applying the bias magnetic field one will be able to employ shape-anisotropy bias obtained through film lateral nanostructuring [105]. The real sensor will then contain several nanostructured films each tuned to a particular concentration range and the amplitudes of FMR response for those films will be probed in parallel to enable the broad-range measurement of hydrogen gas concentration with constant sensitivity across each of the sub-ranges.
4.3: Demonstration of a wide-range hydrogen gas detection by \textit{CoPd} alloy as an active m-HGS sensor medium

4.3.1: Introduction

In the preceding section we found that our concept can cover a very large range of $H_2$ concentrations – from 0.2% to 100%. To this end, the whole concentration range was divided into four sub-ranges and the magnetic field applied to our device-prototype was adjusted to maximise the device sensitivity to one of those sub-ranges [106]. We speculated that the whole range could then be covered by employing three or four sensors operating in parallel, each tuned to its own concentration sub-range.

Two characteristics of the FMR response of the films are important for the mHGS functionality. One is the magnitude of the FMR peak (field or frequency) shift induced by $H_2$. The second important parameter is the absolute value of the FMR peak height (“FMR absorption amplitude”); the larger the amplitude, the simpler the electronics is which is needed to detect the FMR absorption for a sample.

Obviously, in order to maximise the sensor response, the \textit{PMA} strength should be maximised. This is because the stronger is \textit{PMA}, the larger absolute variation of its strength one can expect in the presence of the same amount of $H_2$ in the environment. In FMR measurements, the interface \textit{PMA} is seen as an effective bulk-like field whose strength scales as $1/L$, where $L$ is the thickness of the ferromagnetic layer [138]. Accordingly, one may expect reduction of the $H_2$-induced FMR peak shift with an increase in $L$. Indeed, our recent experiment confirmed that the sensitivity of the bilayer film based mHGS to hydrogen gas is inversely proportional to the thickness of the film’s cobalt layer [104].
On the other hand, the FMR absorption amplitude scales as the volume of the resonating material and, consequently, as $L$. Accordingly, a decrease in $L$ leads to a decrease in the signal-to-noise ratio at the HGS output. Hence a more complicated electronics to detect the FMR signal is required for thinner samples. In our previous work we found that $L=5\text{nm}$ is an optimum thickness. On one hand, it enables a significant FMR field shift in the presence of $H_2$; on the other hand, the strength of the FMR absorption is still large enough in order to detect it with a lock-in based FMR setup [84].

A further improvement in the amplitude of the FMR absorption is needed to make our HGS concept interesting for real world applications. In this chapter we report one possible approach to solving this problem—based on using an alternative $H_2$-sensitive material.

Recently it has been demonstrated that the strength of PMA in CoPd alloy films is sensitive to the presence of $H_2$ [43, 52, 158]. As in this case one deals with bulk PMA instead of the interface one, one may expect that its effect on the FMR field or frequency does not drop with an increase in the thickness of the film. This idea lifts the limitation for the upper limit for the thickness of the ferromagnetic layer, thus allowing an increase in the FMR absorption amplitude without sacrificing material’s sensitivity to $H_2$ (i.e. the magnitude of the $H_2$-induced FMR peak shift). In this section we put this idea under test by investigating FMR response of CoPd alloy films in the presence of $H_2$.

4.3.2: Experimental Section

$Co_xPd_{1-x}$ alloys films with different Co concentrations $X$ were prepared with co-sputtering. All the films represent 15nm-thick in-plane continuous layers. In total, four
samples were fabricated, $X=65, 39, 24 \& 14$. These films could not be produced at UWA and had to be ordered elsewhere. For a technical reason, it was important to minimise the number of ordered films and to maximise the number of good films in the ordered batch. Therefore, four CoPd alloy compositions from a recently published paper by W.C. Lin’s team [43, 52, 158] were chosen which previously showed a good optical response to hydrogen gas.

To carry out the FMR characterisation of the films in the presence of hydrogen gas, a pressure-tight chamber with 0.3mm-wide microstrip line forming its floor is used [22, 104, 107]. During the measurements, the film is facing the microstrip line (i.e. the film’s substrate is facing away from the line). This is done in order to maximize the microwave absorption signal. A static magnetic field is applied to the film plane in order to shift the resonance frequency from zero and thus to enable the FMR characterisation of the sample. The field is applied perpendicularly to the film plane (PP configuration). This is done for convenience, as we previously found that the $H_2$-induced FMR field shift is maximised in the PP configuration [107] (refer to a thesis section 3.3). A field-modulated FMR method is employed to improve the signal to noise ratio [84]. A microwave interferometric receiver is also employed to further improve the signal to noise ratio [102].

To prepare the gas, the same custom-built gas mixing setup is employed. All the FMR measurements are carried out under a constant gas flow rate of 800 sccm and atmospheric pressure. Because a very wide range of hydrogen gas concentrations is probed (0.1% to 100%), nitrogen is used as carrier gas for the mix. As before, this is done to ensure fire safety of our experiment.
4.3.3: Experimental Results

The PP FMR configuration is also convenient for extraction of magnetic parameters for the samples. This is because, following Kittel Equation for the PP configuration (Section 2.2.1, Eq 2.3)

\[
\omega = \gamma(H - 4\pi M_{\text{eff}})
\]

the FMR frequency \(\omega\) scales linearly with the effective magnetisation \(4\pi M_{\text{eff}} = 4\pi M_s - H_{\text{PMA}}\) which is the difference between the saturation magnetisation \(4\pi M_s\) and the effective field of PMA. The slope of the \(\omega(H)\) dependence is given by the gyromagnetic ratio for the material under test. The intercept of the straight line with the vertical axis gives the value of \(4\pi M_{\text{eff}}\) for it. From figure 4.13 one sees that the lower the Co concentration in the alloy, the lower \(4\pi M_{\text{eff}}\). Also, the gyromagnetic ratio grows with the decrease in \(X\).

Figure 4.13: FMR frequency as a function of FMR field.
CHAPTER FOUR: Demonstration of functional prototypes of hydrogen gas sensors

<table>
<thead>
<tr>
<th>Sample</th>
<th>Co content</th>
<th>Pd content</th>
<th>gamma</th>
<th>eff 4piMs</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sample1</td>
<td>65</td>
<td>35</td>
<td>0.00284</td>
<td>9518.6</td>
</tr>
<tr>
<td>Sample2</td>
<td>39</td>
<td>61</td>
<td>0.00299</td>
<td>2050.4</td>
</tr>
<tr>
<td>Sample3</td>
<td>24</td>
<td>76</td>
<td>0.00315</td>
<td>922.3</td>
</tr>
<tr>
<td>Sample4</td>
<td>14</td>
<td>86</td>
<td>0.00610</td>
<td>36.6</td>
</tr>
</tbody>
</table>

Table 4.2: Magnetic parameters for the films extracted from the data in figure 4.13.

All the four CoPd alloy samples were then characterised with IP FMR. It was found that except the sample with the highest Co content (i.e. sample 1) an FMR peak could not be found for any other sample in the reasonable field range +/- 10 kOe. This result implies that those CoPd alloy samples have their hard magnetisation axis in the film plane. This evidences that they exhibit strong PMA. This result also matches one from the paper by WC Lin’s group [43].

One important observation is that the resonance fields for the alloys are smaller than for pure cobalt films and decrease with a decrease in Co content. As seen from table 4.2, this translates into smaller effective saturation magnetization values for the alloys with smaller cobalt concentrations. This property of the decrease in the FMR field may be beneficial for applications of these materials in the mHGS sensors. In Ref. [107] we showed that the sensitivity of the FMR response of ferromagnetic films to a change in PMA strength is significantly larger for the static field applied perpendicular to the film plane than parallel to it. Furthermore, it does not depend on the saturation magnetization value. Hence the PP FMR probing of PMA strength could be very beneficial for future applications in H₂ sensors. However, this configuration also possesses an important drawback – application of large magnetic fields is required in order to magnetically saturate a film perpendicular to its plane and thus to create conditions for existence of a PP FMR response. The decrease in the saturation magnetization with the decrease in Co content translates in the smaller applied fields.
CHAPTER FOUR: Demonstration of functional prototypes of hydrogen gas sensors

From figure 4.13 one sees that the FMR fields for Samples 2 to 4 are already small enough such that compact permanent magnets can be used to generate them.

The next step of our experimental study is characterising the samples in the presence of hydrogen gas. We found that the exposure of the $Co_{65}Pd_{35}$ alloy sample to $H_2$ led to irreversible changes to its FMR response – upon exposure of the sample to 50% of $H_2$ and then to pure $N_2$ the FMR peak did not return to the same position as for the virgin state of the sample. Furthermore, we could not find an FMR response for $X=14$ in the presence of hydrogen gas. Therefore these two samples were excluded from further experiments and below we focus on the two remaining samples - with $X=39\%$ (Sample 2) and 24\% (Sample 3). Importantly, the resonance linewidths for the two samples as measured in their virgin states are quite different. The linewidth for Sample 3 is 252 Oe, whereas it is almost 3 times bigger for Sample 2 (692 Oe).

The two samples with the $X$ values in the middle of the available range showed well-repeatable FMR responses while cycled between pure nitrogen and hydrogen containing atmospheres. Panels (a) and (b) of figure 4.14 display families of raw FMR traces for the samples taken for different hydrogen gas concentrations. The magnitudes of the peak shifts extracted from the raw traces are shown in Panel c). Panel (d) demonstrates the shift magnitudes relative to the respective resonance linewidths.
Figure 4.14 FMR profiles for different concentrations of hydrogen gas for a) the sample 2 (Co$_{39}$Pd$_{61}$) and b) the sample 3 (Co$_{24}$Pd$_{76}$) alloy sample. Figure 4.14 c) shows the comparison of the FMR peak shifts for the two samples. While figure 4.14 d) shows the comparison of the ratio of the FMR peak shift to the respective linewidth for the two samples.
These data show that the absolute values of the hydrogen induced peak shift are much larger for Sample 3 than for $\text{Co}_{39}\text{Pd}_{61}$ for the same hydrogen gas concentrations. The shift exceeds 10 times the linewidth for the highest $H_2$ concentration and remains larger than the linewidth for the opposite end of the concentration range - 0.1%. On the other hand, the peak shift is always smaller than the linewidth for Sample 2.

Let us first discuss one important feature of the data for Sample 3. From figure 4.14b one sees that the sample response amplitude is 4+ microvolt. This magnitude is practically the same as for the bi-layer Pd/Co film with Co layer thickness of 5 nm studied in Ref. [106] (5 $\mu$V). However, the concentration of cobalt in this alloy is just one quarter (24%). Hence, accounting for the 3 times larger thickness (15nm) of the alloyed film, the FMR response per one Co atom is

\[
\frac{1}{(3 \cdot 0.24)} \frac{4\mu V}{5\mu V} = 1.1
\]

times larger for the alloyed sample than for the bi-layer film (if we neglect potential differences in crystal lattices for the two materials). This implies that one way to further increase the FMR absorption amplitude is by employing yet thicker films. This is possible with the alloyed samples.

The absorption amplitude for Sample 2 is almost the same – 6 $\mu$V. However, this sample is characterised by an about three times larger resonance linewidth $\Delta H$. Furthermore, the Co content in this alloy is 1.5 times larger than for Sample 3. It is known that, for the same amplitude of the microwave driving field, the absorption amplitude scales as $1/ \Delta H$. Given the latter fact, relative to the reference Pd/Co film, the FMR absorption amplitude per one Co atom for the alloyed film is
CHAPTER FOUR: Demonstration of functional prototypes of hydrogen gas sensors

\[
\frac{1}{(3\cdot0.39)} \frac{6\mu V}{5\mu V} = 1.1.
\]

This is the same as for Sample 2. However, if we correct for the 3-times larger linewidth, the absorption amplitude for Sample 2 becomes 3 times larger than for the reference Pd/Co bi-layer film. So, reducing FMR linewidth for this sample to the level of Sample 2 will be very beneficial. However, this is out of scope of the present study. Furthermore, below we will show that having a material with a large \( \Delta H \) and relatively strong FMR response (6 \( \mu V \), as for Sample 2) can be useful for magnetic \( H_2 \) sensing.

But before we proceed to this demonstration, let us first discuss the response time to exposure of the sample to hydrogen gas (“response time”) and the time of its recovery to the original state upon \( H_2 \) evacuation from the environment (“recovery time”). These two parameters are also very important for hydrogen-gas sensitive materials. We will discuss this aspect on the example of Sample 2. In order to measure the response and recovery times, the “FMR Time Scan” method [106] is employed in the present work. Figure 4.15 shows an FMR time scan taken at 10GHz with a bias magnetic field of 4160 Oe. In order to get this trace, the FMR frequency and the bias field were kept constant throughout the experiment and the FMR absorption amplitude was measured as a function of time. The black line in the plot shows the sample environment as a function of time. Originally it was pure \( N_2 \); at 480 seconds into the experiment the atmosphere was replaced with one containing 0.1% \( H_2 \). At 1800 seconds the chamber was flushed with pure nitrogen gas which was then kept flowing through it till the end of the measurement.

The main observations from this figure are that there is a sharp response of the film to the presence of hydrogen gas in the environment and a slow recovery of the system, once hydrogen has been removed from the chamber. The response and recovery times are on the order of hundreds and thousands seconds respectively (\( \sim \)280minutes are...
CHAPTER FOUR: Demonstration of functional prototypes of hydrogen gas sensors

needed to recover to 90% of the origin signal level). These large times are typical for continuous films [43, 52, 105, 158]. Also our observation is that the response and recovery for this sample are much faster than for Sample 2 (not shown).

Figure 4.15. Responses and recovery time of sample 3 which is measured at 10 GHz and 4160 Oe. It takes around 10 minutes to achieve 90% of signal saturation (hydrogenation) and around 280 minutes to return to 90% of the original signal level (dehydrogenation). (Remark: The jump in the signal happened at ~12500 second is due to re-tuning of the microwave receiver.)

Let us now turn to the role of the resonance linewidth in the functionality of a film as an efficient m-HGS. In Ref. [106] (see the preceding section of the thesis, Section 4.2) we showed how to cover a wide range of hydrogen gas concentrations with a single sensor device-prototype by consequently tuning sensor sensitivity to different narrower sub-ranges of that wide concentration range. The sensor tuning proceeds by adjusting a static magnetic field applied to the film. The tuning was needed because the hydrogen gas induced FMR field shift exceeded the resonance linewidth. This implies that if a material is found which demonstrates the same absorption amplitude
and the same $H_2$-induced FMR peak shift but possesses an $\Delta H$ value which is equal or larger than the maximum shift no field adjustment will be needed in order to cover a broad $H_2$ concentrations range.

This is actually the case of Sample 2. Figure 4.16 shows a time scan for this sample taken while cycling the atmosphere in the chamber between pure $N_2$ and different concentrations of $H_2$. One sees that the material responds to a change in the gas environment within minutes, which shows much faster hydrogenation responses than sample 3. Figure 4.16(a) displays the time scan profile for the concentration range from 1% to 100%, while figure 4.16(b) shows one for smaller concentrations - from 5% to 0.1%. The maxima of the negative peaks in figure 4.16(a) and (b) correspond to $H_2$-containing environments and the baseline is for pure nitrogen. Figure 4.16(c) displays the peak height with respect to the baseline. From this figure one sees that hydrogen concentrations as low as 0.1% can be detected with Sample 2 and the sensitivity to hydrogen does not saturate all the way up to 100%.
Figure 4.16: (a) Time scan for 1% to 100% of hydrogen in the gas mix. (b) The same but for 1% to 0.1% hydrogen gas. Applied field is 5809 Oe and the frequency is 10 GHz. (c) Variation of the FMR absorption amplitude as a function of hydrogen gas concentration for sample 2 (i.e. Co$_{39}$Pd$_{61}$).
4.3.4: Discussion

In figure 4.17 we compare the sensitivity $S$ to $H_2$ for different materials extracted from the data in figure 4.16. We define $S$ as variation in the absorption amplitude per unit of concentration (measured in $\mu$V/%). Two samples are considered – Sample 2 and the $Pd/Co$ bilayer film from Ref. [106] (Section 4.2). From this figure one sees that Sample 2 may cover the whole range accessible with the bi-layer film with the level of sensitivity across the range which is the same as for the bi-layer film. However, the applied field had to be re-adjusted 2 times in order to cover this concentration range with the bi-layer film, but with the alloyed film no field re-adjustment is needed. This is because the alloyed sample possesses combination of a strong FMR absorption, relatively large $H_2$-induced peak shift, and a large FMR linewidth.

Figure 4.17 Sensitivity to hydrogen gas for $CoPd$ alloyed film (Sample 2) and $Pd/Co$ bi-layer film from Ref [106] (Section 4.2).
Figure 4.18 displays the same sensitivities but plotted on a logarithmic scale. One sees that the $S$ vs. concentration traces are perfectly linear on that scale. The solid lines in the figure are respective linear fits. One sees that the intercepts of these lines with the horizontal axis is located at very low concentrations, especially for Sample 2. This suggests that the alloyed samples are prospective candidates for detection of low hydrogen gas concentrations as well. However, this is out of scope of this work, as reaching the small concentrations will require considerable modifications to our gas preparation setup.

Figure 4.18. Films’ FMR peak shift / linewidth vs hydrogen concentration plotted on a logarithmic scale. Dots: experiment; lines: linear fit to the experimental data. Squares and solid line: Sample 3. Circles and dashed line: Sample 2. Triangles and dotted line: bi-layer sample from Ref. [106].
CHAPTER FOUR: Demonstration of functional prototypes of hydrogen gas sensors

4.3.5: Conclusion

In this study, it has been demonstrated that by measuring the FMR differential signal of \( \text{Co}_{39}\text{Pd}_{61} \) alloy continuous film in the presence of hydrogen gas, it is possible to determine a wide range of hydrogen gas concentrations (<0.1% to 100% hydrogen) by only applying one bias field value. It makes the wide range HGS much simpler than a combined sensor from Ref. [153] and even our field-adjustable sensor concept [106] (Section 4.2. of the thesis). This advantage originates from a combination of the wider FMR linewidth and a larger FMR peak shift due to hydrogenation. Furthermore, the out-of-plane magnetic field needed to bias the \( \text{Co}_{39}\text{Pd}_{61} \) alloy (15nm) is much lower than for the bi-layer Co 5nm/Pd 10nm film - 5809 Oe vs 12800 Oe respectively. This is one more important benefit because this bias field level can be easily reached with an inexpensive permanent magnet, through exchange bias or nano-patterning. Also, we anticipate that by nanostructuring the \( \text{Co}_{24}\text{Pd}_{76} \) film it may become possible to detect ultra-low hydrogen gas concentrations.
4.4 Chapter Summary

Table 4.3 shows a summary table of the significance of the three demonstration approaches. By summarizing the demonstration results, some important configuration parameters for the m-HGS will be easily found out. CoPd alloy is so far the best sample composition in terms of both sensitivity and wider detection range. Furthermore, nanostructuring a film by lithographically forming an array of parallel nanostripes not only enhances the sensitivity and shortens the hydrogen response times, but also eliminates the need of a bias field in the FMR measurement. Finally, PP FMR configuration provides much higher sensitivity and shortens the de-hydrogenation time.

<table>
<thead>
<tr>
<th>Demo</th>
<th>sample composition</th>
<th>special features</th>
<th>FMR geometry</th>
<th>(H_2) detection range</th>
<th>Significances</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Tri-layer structure</td>
<td>with nano-wires structure</td>
<td>IP</td>
<td>0.1 - 50%</td>
<td>no bias field is needed</td>
</tr>
<tr>
<td>2</td>
<td>Bi-layer structure</td>
<td>a) in-situ annealing, b) adjustable detection range</td>
<td>PP</td>
<td>0.1% - 100% (by 4 bias field)</td>
<td>adjustable (H_2) detection range</td>
</tr>
<tr>
<td>3</td>
<td>Co\textsubscript{39}Pd\textsubscript{61} alloy</td>
<td>alloy film by co-sputtering</td>
<td>PP</td>
<td>&lt;0.1% - 100% (by 1 bias field)</td>
<td>(Co_{39}Pd_{61}) alloy is superior for m-HGS</td>
</tr>
</tbody>
</table>

Table 4.3: Details of the three mHGS demonstrations described in the thesis.
Chapter 5: Conclusions, outlook and further actions

5.1 Conclusions and outlook

The concept of a FMR based m-HGS was suggested and experimentally verified [22]. However, most of details of the physics underlying the functionality of m-HGS were still missing at the time of the start of the present PhD project. Since the m-HGS concept was novel at the time of the start of the present PhD study and is magnetism related, the physics behind operation of other palladium based sensors cannot be directly applied to the m-HGS. Therefore, a large volume of work described in the present thesis concerned the most basic parameters, for examples, optimisation of the thickness of the active magnetic layer, selection of optimal detection configuration and samples’ geometry, etc. Finally, based on a number of investigations and optimisations, successful demonstration of a number of functional prototypes of HGS was carried out.

Below we will discuss significant results / outcomes of the project. Moreover, important conclusions and limitations of the obtained results will be presented. Finally, some directions for the future work will be suggested aimed to further improving the m-HGS performance and understanding of the physics underlying it.

5.1.1 The m-HGS concept is realised and demonstrated

The first important achievement of the project is the detailed verification of the m-HGs concept: all the advantages of the m-HGS concept could be realised and demonstrated. Moreover, a wide range of hydrogen gas concentration detection (<0.1% to 100%) could be
demonstrated with m-HGS. (At least two methods can achieve this, one is employing CoPd alloyed films (Section 4.3) and the other one is by adjusting the bias magnetic field applied to a bi-layer Co/Pd film (Section 4.2)). This result is very important, because so far only a limited number of competing HGS concepts were able to demonstrate a similar performance. Therefore, in order to increase the range of hydrogen gas concentrations detection, most of the device prototypes reported in the literature combines two different types of HGS in one device [153]. Furthermore, multiple m-HGS demonstrations were performed in this project; by applying different approaches in order to achieve the functionality of magnetic films as m-HGS. In the thesis, we highlighted three different approaches to achieve the functionality which are based on sensor materials (cobalt and palladium or their alloy), structures (single-layer to tri-layers, with or without nano-patterning) and FMR configurations (IP and PP). Also, multiple aspects of physics underlying the functionality were revealed potentially allowing further performance enhancement of m-HGS.

5.1.2 Conclusions from fundamental studies on m-HGS

The work described in Chapter 3 represents investigation of details of physics underlying the functionality of m-HGS. It also serves as a basis for the functionality demonstrations reported in Chapter 4. A number of important results are presented in that chapter. The active layer thickness investigation section, reports on the results for three types of structures named bi-layers, tri-layers and super-lattices. For the bi-layer structures, the hydrogen sensitivity is found to be inverse proportional to the cobalt thickness. This implies that the interfacial alloying of Co with Pd is the key to sensing hydrogen gas. This conclusion translates into a dilemma for the bi-layer structures. On one hand, a decrease in the thickness of the cobalt layer enhances hydrogen sensitivity. On the other hand, the FMR signal level depends on the volume of FM material: a decrease in the thickness of the cobalt layer will lower down the overall FMR signal amplitude. This study revealed that the optimal
CHAPTER FIVE: Conclusions, outlook and further actions

thickness of cobalt for sensing hydrogen with our bi-layer films is 5nm. Although there is no room for further thinning down the cobalt layer of the bi-layers structure, some methods can be applied to boost up hydrogen sensitivity. They will be discussed below. As for the tri-layers structures, the initial idea was that this structure has two $Co/Pd$ interfaces. If both interfaces are hydrogen sensitive, this should increase the hydrogen sensitivity. However, unlike the monotonic decrease in the hydrogen sensitivity with Co thickness found for the bi-layers, an optimal cobalt thickness of 20nm was found for the tri-layers. At the moment we have no clear explanation for the finding. Several experiments were performed in order to understand the physics behind the difference. Firstly, the study in section 3.3.1 (figure 3.12a, b) found that the effective saturation magnetisation for IP and PP are same; hence, the difference in the de-hydrogenation scenarios may not be due to a difference in effects of hydrogen on the effective saturation magnetisation. Moreover, the de-hydrogenation time is also not related to the magnitude of the applied magnetic field (as shown in section 3.3.2 with figure 3.14-15). Furthermore, it is not due to the magnetostriction, since from the study in section 3.6 it follows that the effect of magnetostriction is negligible when a thin film is clamped to its substrate. Thus, we were able to eliminate a number of factors potentially causing the difference, but the explanation is still in pending. Repeatable occurrence of the effect was observed, independently from sample’s origin – deposited with our groups’ sputtering machine or elsewhere. It will be a good simulation work of Density Functional Theory for understanding the physics in the tri-layers structure. However, the empirical results we obtained for the tri-layer structures still are a very important contribution to the development of m-HGS.

Since the optimal thickness for the cobalt layer of the tri-layers is large - 20nm, the tri-layer structure turns out to be very suitable for the investigation of the effect of nanopatterning on the response of the layered materials to exposure to hydrogen gas. The nano-patterned structure designed in the framework of this thesis represents a periodic array of 300nm-wide nano-wires. The structure period is 600nm (i.e. the total volume of the magnetic material in the nano-wire structure is just one half of that for a
continuous film of the same thickness). Therefore, observing a good-quality FMR response for nano-pattered bi-layer films with the optimal thickness [5nm] of the cobalt layer is problematic, in the first place because the volume of the magnetic phase is small. On the contrary, because of the larger optimal Co thickness, the tri-layer nanopatterned structures have a cobalt volume which is sufficient to produce a strong FMR response (the optimal cobalt thickness of 20nm, results in a volume of the magnetic phase which is equivalent to a 10 nm thick continuous cobalt film).

Based on this consideration, a tri-layered nano-wire structure with the optimal cobalt thickness of 20nm was proposed and designed. It was fabricated by Prof. Adeyeye’s team at NUS. Functionality of the m-HGS was demonstrated based on these samples which have very good sensing properties (Section 4.1). A number of super-lattice samples were also investigated as potential hydrogen sensors, including samples sputtered with our sputter machine and at NUS. However, all of them showed much lower hydrogen sensitivity, we therefore dropped the idea of super-lattices structure as an active sensor medium already in the initial stage of the project.

While investigating the effect of FMR configuration (IP vs PP) on the response of the films to hydrogen, we focussed on hydrogen sensitivity and response times. Regarding the hydrogen sensitivity, FMR measurements taken in the PP configuration demonstrated a factor of eight improvements over the IP configuration. An analysis based on the Kittel equation for FMR frequencies was carried out to understand the mechanism of sensitivity enhancement: It was found that the sensitivity of the FMR method to small changes of an effective anisotropy field is larger (or significantly larger, depending on the strength of the anisotropy) for the static magnetic field applied along the anisotropy axis. This fact was confirmed in this work both experimentally and theoretically. Furthermore, significantly shorter de-hydrogenation times (around 15 times shorter) were also repeatedly found for the PP configuration. Although we were able to experimentally rule out the hypothesis that this effect can originate from a
CHAPTER FIVE: Conclusions, outlook and further actions

stronger bias field required to magnetise a film PP, no more plausible explanation of the differences in hydrogen desorption times between IP and PP FMR configurations could be suggested. Finding this explanation will be a good topic for a follow-up study. In conclusion, the FMR configuration studies provide a huge step forward to practical implementation of m-HGS, because the PP FMR configuration provides significant improvement in both hydrogen sensitivity and response times. However, there is also one potential drawback of the FMR PP configuration. This is a stronger magnetic field needed to saturate the sample in the PP direction. One way to eliminate the drawback is by using a magnetic material with lower situation magnetisation. We demonstrated this experimentally by employing CoPd alloy films as an active sensor medium (Section 4.3). This result will be discussed later on in the conclusion.

The sample orientation with respect to the microstrip line (sample facing up compared with facing down) is an effective way to reduce the hydrogen response times by one half. This was experimentally verified in the framework of this thesis. However, one drawback of this method is that the FMR amplitude drops due to significantly weaker electromagnetic coupling the film to the stripline because the distance between them becomes large with respect to the stripline width. There are some ways to reduce the drawback of this, for example, much thinner silicon substrate, or by lithographically forming the micro stripline on the back side of the film or nanostructure.

Another important way for hydrogen sensitivity enhancement is the in-situ annealing. Based on the study of the bi-layer Co/Pd continuous films carried out as a part of the present thesis, the sensitivity can be improved by 30% in the case of IP FMR and by a factor of 2.5 in the PP case. The sensitivity enhancement is due to the promotion of CoPd alloy formation at the interface leading to enhancement of the interface PMA. Also, the lattice constant of Pd [112] is increased (by the XRD result shown at Section 3.5) which allows more hydrogen stored at the vacancy sites [78]. The importance of this study consists not only in suggestion of a method to enhance sensitivity of bi-layer
structures to hydrogen, but also in providing an insight into the importance of CoPd alloys as an active sensor medium.

Our investigation of the role of the elastic strain in the sensor response to hydrogen through combined FMR measurements under two different stimuli - strain and hydrogenation effect was aimed at finding the main reason for the \( H_2 \) induced change in PMA at the interfaces of Pd layers with Co layers. It was found that this is modification of the electronic structure of the interface. This electronic contribution to PMA is reduced by absorption of hydrogen gas by palladium. In the literature, it has been shown that a hydrogen atom partially attracts electron charge from a nearby Pd-Co chemical bond. This reduces the overlay of orbitals of Co with Pd leading to reduction in the exchange coupling of Co to Pd and hence reduction in PMA [23]. On the contrary, the study shows no noticeable magneto-elastic (magnetostriction) contribution to the hydrogen induced change in the PMA for films grown on silicon substrates because these substrates are highly rigid. However, this contribution cannot be excluded for the films grown on flexible Kapton substrates. If it is present, it should be of the opposite sign with respect to the electronic one and hence the two contributions partially compensate each other. As a conclusion, a highly rigid substrate is necessary to maximise sensitivity of m-HGS.

Sample nano-patterning is an important way to improve functionality of the magnetic films as active media of m-HGS. Nanopatterning not only leads to improvement of both hydrogen sensitivity and response times, but also, more importantly, it eliminates the need in a magnetic bias field. The latter is because nano-patterning induces a strong shape anisotropy field which is able to completely replace the real field applied to the sample. As a result, no magnetic field will be necessary in order to obtain an FMR response from the material. On top of this, we found a huge performance enhancement originating from the nanopatterning, - about a factor of 3 improvement in sensitivity and a 24 times shorter de-hydrogenation time with respect to a reference
CHAPTER FIVE: Conclusions, outlook and further actions

continuous film sample. It is an impressive improvement for m-HGS. A minor contributor to the performance enhancement is an increase in the surface area to volume ratio [the smaller, the better]. However, the observed effect is much bigger than expected from this contribution. Therefore, there should be other reasons for the observed strong enhancement. This will be a good topic for a follow-up study.

5.1.3 Outlook from the three m-HGS demonstrations

Functionality of three different m-HGS sensor concepts has been demonstrated. These concepts are based on the results of investigations presented in Chapter 3. For each of the demonstrations, a different approach was employed in order to achieve the functionality. Firstly, the HGS functionality demonstration is done with a tri-layer nano-wire sample and a IP FMR configuration [105]. The significance of the demonstration is the elimination of the need for an external applied bias field for sensor operation. This is an important milestone in bringing the m-HGS concept closer to real-world applications. The demonstrated detection range of hydrogen gas concentrations is < 0.1% to 50%. The demonstrated range is large, but still limited, the latter being possibly due to limited hydrogen sensitivity in the FMR IP configuration. The second demonstration employed three new ideas aimed to increasing the range of detected hydrogen gas concentrations - in-situ annealing of the sample, PP FMR configuration and adjustability of the detection range. As discussed above, the in-situ annealing provides higher hydrogen sensitivity and the PP FMR configuration leads to enhancement of hydrogen sensitivity and faster hydrogen response times. However, this measure alone cannot extend the detection range till its natural boundaries – 0% and 100%. Therefore, in addition to the annealing we introduced one more novelty which is the adjustable detection range technique. It is the unique advantage of magnetic hydrogen gas sensing that one can tune the hydrogen detection range by changing the bias field of the active sensor. By combining both techniques, a wider detection range (<0.2% to 100%) could be demonstrated whereby the whole
detectable concentration range was divided into 4 different “bias applied magnetic field” sub-ranges and the applied magnetic field was optimised in order to maximise sensor sensitivity to one of those sub-ranges. However, there is a drawback associated with this method, which is a need in a strong bias magnetic field (12.8 ~13.6 kOe) applied to the active medium of the sensor. The third demonstration involved a simple single-layer CoPd alloyed film as an active medium and turned to be the most important demonstration. CoPd alloys possess intrinsic bulk PMA which leads to higher hydrogen sensitivity when compared with Co/Pd bi-layers without in-situ annealing. We found that together with much wider FMR linewidth this produces a wider hydrogen detection range (<0.1~100%) which can be achieved with just one value of the bias field. The drawback of this concept is the same as for the second demonstration - a bias field is still needed. However, because the saturation magnetisation and the PP saturating field for the of CoPd alloy are much lower than for the Co/Pd bi-layers samples, the needed bias field (around 5800 Oe) is smaller than half of that for the bi-layer Co/Pd sample. It may be easier to be producing this bias, for instance by either applying of nano-patternning or exchange-biasing the ferromagnetic layer, or even by combining of both.

5.2 Further Actions

All of the demonstrations results suggest that there are still rooms for further improvement of the three most important characteristics of the m-HGS: the hydrogen response times, the FMR signal level (not to confuse with hydrogen sensitivity, of CoPd alloyed films in the PP FMR configuration is large enough) and bias scheme for the active sensor medium.
CHAPTER FIVE: Conclusions, outlook and further actions

5.2.1 Improvement on the hydrogenation response times

The hydrogen absorption response time is around 20 sec while the desorption time is around 120 seconds. A further hydrogen desorption time reduction is required, as for some applications, for example, in HGS used in stationary system, the required hydrogen desorption time should be less than 60 second [154]. As discussed in the above section, three measures shorten efficiently the response times. These are nano-patterning of the active medium, employing the PP FMR configuration, and orienting the sample face-up. At the moment, we can only confirm each of those measures separately. Unfortunately, we could not detect an FMR signal from the nanostripes in the PP configuration, which is often the case experimentally and can be explained by the fact that the PP direction is a hard axis direction and it is difficult to magnetise a material uniformly along a hard axis. The non-uniformity of magnetisation will lead to inhomogeneous line broadening making the FMR response amplitude vanishing. Moreover, we could not detect an FMR resonance from the nano-patterned sample in the face-up orientation, as the signal amplitude drops a lot. Therefore further experiments are suggested aimed on investigation of a combined effect of several measures from the list above on hydrogen response times. Firstly, in order to take FMR measurements for nano-patterned samples in the IP configuration and the face-up orientation, one can try to deposit the active sensor medium on top of a micro-stripline (that will allow the sample to face up without a loss in signal amplitude). Moreover, one can combine nano-patterning with exchange biasing the active sensor medium in the PMA direction in order to facilitate PP magnetisation of the sample. To be more aggressive, one can combine the above two suggestions to produce a joint effect of all three measures. Furthermore, one more hydrogen response time improvement way may be possible, as discussed in the Chapter 1, which is purposely inducing defects, voids, cracks or dislocations in the palladium layer that allow hydrogen easier to be absorbed or desorbed by palladium [44, 50, 51].
CHAPTER FIVE: Conclusions, outlook and further actions

5.2.2 Increment on the FMR signal level

All the demonstration results were obtained in FMR measurements employing a microwave receiver. As discussed in Chapter 2, the microwave receiver helps to significantly reduce the noise level of the FMR measurements. However, if the m-HGS sensor has a larger signal to noise ratio than currently achieved, one can simplify the detection circuitry by using a simple microwave diode instead of the receiver. This will further reduce the cost of the m-HGS. Some further works are suggested to address the amplitude of the FMR signal. One can try thicker CoPd alloy films, because the amplitude of the FMR response is proportional to the FM material volume. In other words, an investigation of the impact of the thickness of the CoPd alloy film on the performance of the film as a hydrogen gas sensor is suggested. Similarly, a large sample area overlapped with the micro-stripline may help to enhance the FMR signal as well. Moreover, there is one more effective way to boost the FMR signal which is by narrowing the micro-stripline, and even integrating the micro-stripline into the active medium of m-HGS by lithography and cleanroom processes that minimise the separation between the stripline and the active sensor.

5.2.3 Improvement on bias scheme for the active sensor medium

In a real-world device, no external magnetic field is expected to be applied to the magnetic layer. In order to achieve this, the magnetic layer has to be magnetically saturated in the PMA direction. Bias schemes for the active sensor thus may become an important area to be developed. In one of the demonstration results, it was already successfully demonstrated that nano-patterning (in the form of nano-wires) helps to achieve FMR at zero applied magnetic field in FMR IP configuration. This eliminates the requirement to apply a magnetic field during the FMR measurement. However, in the case of the PP FMR configuration, a much stronger demagnetising field is present.
Therefore the bias provided to the active sensor needs to be significantly enhanced in order to saturate the sample. Some suggestions for nano-patterning may be to try different patterned shapes, for example, dots and anti-dots, which may help to decrease the demagnetising field in the PMA direction. One can even try to add exchange bias to the magnetic layer in order to saturate it in the PMA direction. Furthermore, CoPd alloys may have much lower saturation magnetisation in the PMA direction (since they demonstrate tilted magnetisation even for a 15nm thick continuous thin film) and may be easier saturated than the bi-layer Co/Pd films. Figure 5.1 shows a possible optimal structure of an m-HGS. It could combine some advantages of the design concepts obtained from the fundamental studies in this thesis.

Figure 5.1: A possible optimal structure of m-HGS. The active sensor for m-HGS is “patterned” CoPd alloy (The picture shown here is anti-dots structure). An IrMn layer is inserted under patterned CoPd alloy which provides perpendicular exchange coupling to the active sensor (if patterned structure provides not enough anisotropic field to active sensor to saturate it at PMA direction). Moreover, Micro-stripline is integrated with the m-HGS by lithography and cleanroom processes to maximise the coupling.
between micro-stripline and the active sensor. This structure possibly combines some advantages of the design concepts obtained from the fundamental studies.

The last but not least, it will be an important study to investigate the effect of temperature / pressure / humidity on the m-HGS, in order to find the optimal ranges of the individual parameters for the m-HGS operation conditions.


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