Charging mechanism of AlGaN/GaN open-gate pH sensor and electrolyte interface

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Abstract- The charging mechanism of the interface between an AlGaN/GaN based open-gate ion-sensitive field-effect transistor and electrolyte is studied theoretically. Density functional theory calculations are performed to obtain the energy minimum structure of the surface oxide and electrolyte interface. Thermodynamics based relations are employed to obtain the double layer parameters. An analytical model is applied to study the carrier density modulation of the AlGaN/GaN heterostructure by the influence of the surface charge.

keywords— **AlGaN, GaN, Electrical Double Layer, Gallium Oxide, pH sensor, Density Functional Theory**

I.   INTRODUCTION

AlGaN/GaN open gate sensors have attracted significant interest for measuring the pH of electrolytes. The adsorption of the H^+ ions on the device native oxide surface results in surface charge accumulation that modulates the carrier density in the channel. However, the impact of the surface adsorption processes on the sensitivity of the sensor is not well understood. This study provides more insight into the charging mechanism of the sensor-surface and provides accurate estimation of the Ga_2O_3 protonation properties such as the number of surface sites and dissociation rates. Fig. 1, depicts the charging mechanism of the sensor-surface through protonation and deprotonation of the surface adsorption sites.
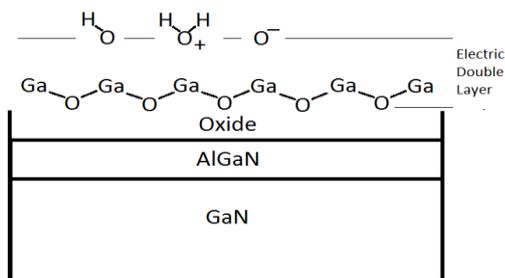

Fig. 1. Surface charging mechanism. Electrical double layer is used to model the interfacial charge distribution.

II.   METHODOLOGY

The atomic coordinates, energetics of the relaxed structure and the surface site density are calculated through *ab initio* simulations. The relaxed atomic coordinates are then used to calculate the surface reaction rates and interfacial capacitance. These parameters are used to derive the surface potential and charge density. Finally an analytical model is used to obtain the sensitivity of the sensor.

A. ab Initio Calculations

Electronic structure calculations of neutral α-gallium oxide slabs in the [0001] direction were performed using Quantum Espresso [5]. Norm-conserving pseudo-potentials and Local Density Approximation (LDA) exchange and correlation functions as proposed by Pedrew-Zunger [5] were employed. A kinetic energy cutoff of 156 Rydbergs and a convergence threshold of 1×10^{-7} was applied to limit the error to within 5%. The Brillouin zone was sampled by Monkhorst-Pack [7, 8] k-point meshes centered at the Γ point. A mesh size of 4×4×4 for the bulk structure calculations and a mesh size of 4×4×1 for the surface calculations were used. A super-cell with 4 layers consisting of 120 atoms from the relaxed bulk structure with 10 Å of vacuum space was created to study the surface properties.
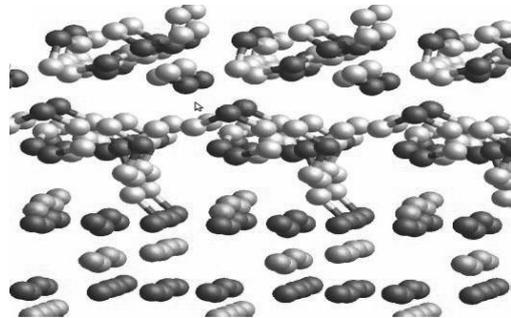

Fig. 2.   Snapshot of the relaxed structure. Both molecular and dissociative adsorption processes are present. Ga, O, and H atoms are represented by grey, black and silver, respectively.

The hydration radius of a Na cation was calculated by finding the number of water molecules that relaxed within the first hydration sphere of the cation. The number of reactive surface sites on the oxide was obtained by minimizing the energy per absorbed water molecule. It was observed that the distance between the O-plane of the oxide and the first and second layers of adsorbed water was in close proximity of those of Al_2O_3 [3, 9]. Lattice parameters of the α-Ga_2O_3 that

were calculated in this study are summarized in Table 1. The relaxed bond lengths and the average distance of the first and second layer of water to the oxide surface are summarized in Table 2. Fig. 2, depicts the energy minimum structure of the interface between the Ga_2O_3 surface and the first and second layer of water molecules.

Table I
lattice parameters

Phase	Space group	This work	DFT[a]	Experiment[a]
α	$R\bar{3}c$	a = 4.981 c = 13.431	a = 5.059 c = 13.618	a = 4.983 c = 13.433

Space groups and lattice parameters in Å of the α-Ga_2O_3 structure.
[a]Reference[1]

Table II
Relaxed bond length

Bond Length	This study	Other study	Experiment
$R_{Ga_s - O_s}$	1.84	1.845[b]	1.921±0.010
$R_{Ga_s - O_w}$	1.848	2.099[b]	
$R_{O_w - H_w\ first\ layer}$	1.022	0.986[b]	
$R_{O_w - O_w\ first\ layer}$	1.559		
$R_{O_s - O_w\ first\ layer}$	2.6539	2.3[d]	
$R_{O_s - O_w\ second\ layer}$	5.4308	5.278[d]	
Hydration Radius Na coordination number 6	2.8	3.06[c]	

Relaxed bond length in Å. Values are obtained by averaging over 12 water atoms in the first and 12 water molecules in the second layer.
[b]Reference [2], [c]Reference[6] , [d] Al_2O_3 parameters are mentioned for comparison [8, 9] ,

Sverjensky et al. [3] used the surface site density, N_s, obtained by isotopic exchange methods. In this study, it was observed that molecular adsorption of 4 water molecules on the gallium oxide surface minimized the energy of the system. Therefore, it is assumed that 4 sites are available on average per unit cell surface area of $4.31 \times 10^{-19}\ m^2$, which gives a surface site density of 9.28 site per nm^2. Fig. 3, depicts the changes of the surface adsorption energy against the number of adsorbed water molecules.
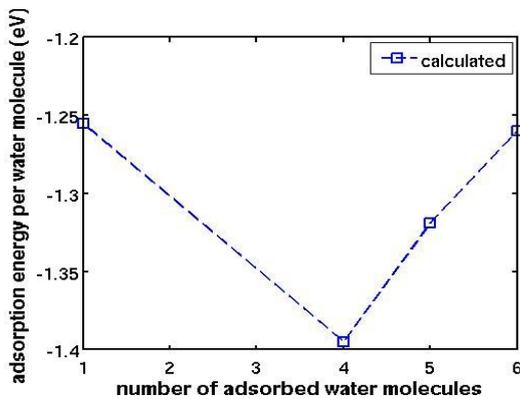

Fig. 3. Surface adsorption energy against the number of adsorbed water molecules

B. Surface Dissociation Rates

The oxide surface-electrolyte interface is approximated by an electrical double layer (DL) model. The surface complexation processes can be described as [3, 10]

$$> SOH +\ H^+_{aq}\ \Leftrightarrow\ > SOH^+_2 \tag{1}$$

$$K_{s,1} =\ \frac{a_{>SOH^+_2}}{a_{SOH}\ a_{H^+_{aq}}}\ 10^{F\psi_0/2.303RT} \tag{2}$$

$$> SO^- + > H^+_{aq} \Leftrightarrow\ > SOH \tag{3}$$

$$K_{s,2} =\ \frac{a_{>SOH}}{a_{>SO^-}\ a_{H^+_{aq}}}\ 10^{F\psi_0/2.303RT} \tag{4}$$

where $> S$ represents the surface site which is bonded to the underlying bulk material, a_j represents the activity of the jth surface species, F represent Faraday's constant, R is the ideal gas constant, and T is the temperature. The power term in the equilibrium constant for equations 2 and 4 describes the electrostatic work required to bring the ion from the bulk to the relevant charged surface. The equilibrium process at the pH of the pristine point of zero charge (pH$_{ppzc}$) is described by

$$pH_{ppzc} = 0.5(logK_{s2} +\ logK_{s1}) \tag{5}$$

The difference between the surface protonation constants is defined as

$$\Delta pK =\ logK_{s2} -\ logK_{s1} \tag{6}$$

Born solvation theory of surfaces along with the electrostatics can be used to obtain the following relations to calculate pH_{ppzc} and ΔpK [11]

$$pH_{ppzc} = -0.5(\frac{\Delta\Omega_{r,z}}{2.303RT})\left(\frac{1}{\epsilon_k}\right) - B_z\left(\frac{s}{r_{>s-OH}}\right) + logk''_{H^+,z} \tag{7}$$

$$\Delta pK =\ (\frac{\Delta\Omega_{r,n}}{2.303RT})\left(\frac{1}{\epsilon_k}\right) - B_n\left(\frac{s}{r_{>s-OH}}\right) + logk''_{H^+,n} \tag{8}$$

where ϵ_k is the permittivity of the bulk oxide and $\frac{s}{r_{>s-OH}}$ is the Pauling bond strength per unit bond length for the oxide bulk cation, $\Delta\Omega_{r,z}$ is the interfacial Born solvation coefficient and represents the contribution from solvation to the free energy of surface protonation, B_z is the electrostatic constant, and $k''_{H^+,z}$ is related to intrinsic contribution. Sverjenski et al. fitted experimental points of zero charge from literature to the equations 7 and 8 to obtain

$$pH_{ppzc} = 21.1158\left(\frac{1}{\epsilon_k}\right) - 429148\left(\frac{s}{r_{>s-OH}}\right) + 14.4866 \tag{9}$$

$$\Delta pK = 12.692\left(\frac{s}{r_{>s-OH}}\right) + 3.537 \tag{10}$$

Equations 5−10 are used to derive the point of zero charge and the surface dissociation constants. In calculating the Pauling bond strength per unit bond length, the valency of the Ga can be calculated using Shannon's equation [12]

$$s = s_0 \left(\frac{R}{R_0}\right)^{-N} \qquad (11)$$

C. Surface Capacitance

The distance of the first layer of water to the O_s − surface i.e. $R_{O_s - O_{w\,first\,layer}}$ and the cation hydration radii that were calculated through DFT calculations are used to calculate the interfacial capacitance ($\mu F.cm^{-2}$) between the surface and the first layer of water

$$\frac{1}{C} = \frac{R_{hydrated\,cation}}{8.854\varepsilon_{int}} + \frac{R_{O_s - O_{w\,first\,layer}}}{8.854\varepsilon_{int}} \qquad (12)$$

Table 3, summarizes the calculated parameters and lists experimental and simulated values for comparison, where available. The atomic coordinates from the relaxed surface-water interface are used to calculate four out of the five parameters that are required to calculate surface speciation which are the surface dissociation constants, number of surface sites and the capacitance of the first layer. The second layer is considered as a constant capacitance [3]. The values of the calculated point of zero charge, and surface dissociation constants were in close agreement with the experimental values .

Table III
Calculated parameters of the surface adsorption

	Ga_2O_3	other study	$Al_2O_3^\dagger$
$r_{>s-O}$ [Å]	2.6539		1.913
$r_{>s-OH}$ [Å]	2.6539+1.01		1.913+1.01
S	0.75		0.5
$S/r_{>s-OH}$	0.2047		0.1710
ε_k	10.2		10.43
ε_{int}	53*		53
C [$\mu F.cm^{-2}$]	86.0415		99
pH_{ppzc}	7.7721	$8^+, 9^\ddagger$	8.6
ΔpK	6.1351		6
$logK_2$	4.7046	6^+	5.5
$logK_1$	10.8396	10^+	11.5
N_s [sites. nm^{-2}]	9.28	9^+	8

† Reference [2, 3], Al_2O_3 parameters are mentioned for comparison,
*Interfacial permittivity of Ga_2O_3 is assumed to be equal to that of Al_2O_3. Capacitance is calculated for NaCl solution,
‡ Reference [4], Experiment, $^+$ Reference[8], Simulated ,

D. Surface Charging Mechanism

Despite the heterogeneous nature of the oxide surfaces, for simplification purposes, it can be assumed that all surface sites are equivalent [3]. Any surface atom capable of adsorbing or desorbing a proton is considered a surface site [2]. Therefore, mass balance on surface sites requires

$$N_T = \left(c_{>SOH_2^+} + c_{>SOH} + c_{>SO^-}\right) \qquad (13)$$

where N_T represents the total number of surface sites. Surface charge ($C.m^{-2}$) at O-plane is calculated through

$$\sigma_0 = \frac{F}{AC_s}\left(c_{>SOH_2^+} - c_{>SO^-}\right) \qquad (14)$$

It can be assumed that the oxide-electrolyte interface behaves like a parallel plate capacitor where the charge and potential are related through

$$\sigma_0 = C(\psi_0 - \psi_d) \qquad (15)$$

where ψ_0 represents the surface potential and ψ_d represents the Stern potential. For a 1:1 (M^+L^-) electrolyte, electrical charge at the hypothetical parallel planes can be obtained using the modified Grahame equation [10]

$$\sigma_0 = (8\varepsilon_0\varepsilon_w K_B T C^0)^{1/2}\sinh\left(\frac{qz\psi_d}{2K_B T}\right) \qquad (16)$$

where ε_0 and ε_w represent the permittivity of the free space and the aqueous medium respectively, K_B is the Boltzmann's constant, z is the ion valence number and C^0 is the bulk concentration of the solution (particles.m^{-3}). The surface charge density can be connected to the surface dissociation reactions by [13]

$$\sigma_0 = qN_s\left(\frac{10^{-2pH}\exp\left(\frac{-q\psi_0}{K_B T}\right) - K_{s1}K_{s2}\exp\left(\frac{q\psi_0}{K_B T}\right)}{K_{s1}10^{-pH}+10^{-2pH}\exp\left(\frac{-q\psi_0}{K_B T}\right) + K_{s1}K_{s2}\exp\left(\frac{q\psi_0}{K_B T}\right)}\right) \qquad (17)$$

Equations 15-17 can be solved numerically to obtain the surface potential. Fig. 4, depicts the experimental and calculated surface potential on the O-plane using equations $1 − 17$. It can be observed that the simulated values are in close agreement with the experiment
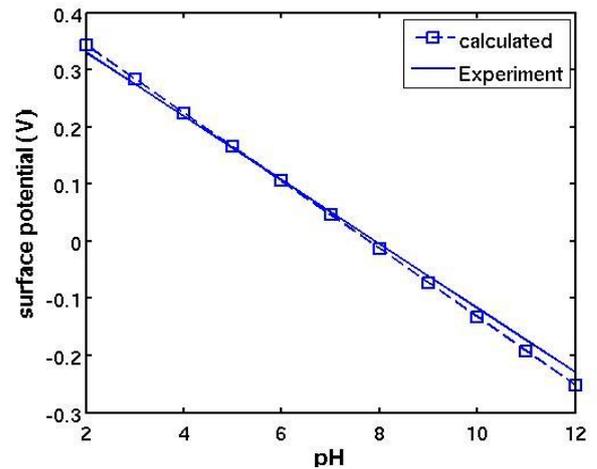

Fig. 4. Calculated surface charge as a function of pH

E. Sensitivity

An analytical model [14] is used to simulate the sensitivity of the device to the changes of pH. The device characteristics are the same as those of the device studied in reference [10, 15]. The AlGaN/GaN heterostructure is grown on sapphire by metal-organic vapor phase epitaxy with aluminum composition of 0.23 and AlGaN thickness of 22nm. The gate length is 1 μm and the gate width is 6 μm. The electron mobility and density of the two dimensional electron gas are 950 cm^2/V and 8.0×10^{12} cm^{-2}, respectively. The doping concentration is 0.5×10^{18} cm^{-3}. The contact resistance and the saturation velocity are assumed to be 10 Ω and 1×10^7 $cm.s^{-1}$ respectively. Fig. 5, depicts the calculated and experimental values. An offset value of 8 mA is present between the simulated and experimental data. The experimental and simulated results show a sensitivity of 37 μA per pH unit and 41 μA per pH unit respectively when V_{ds} = 0.2 V and V_{gs} = -0.5 V.
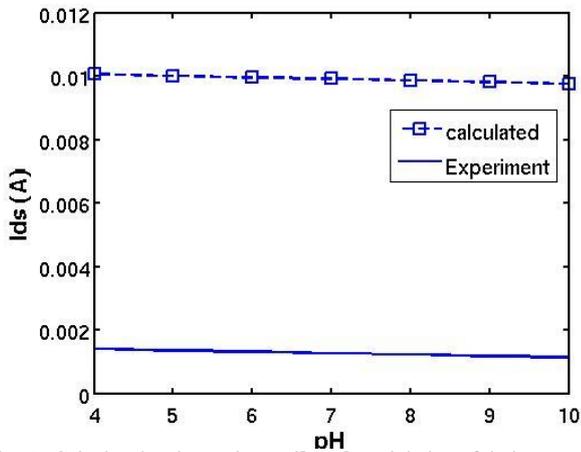

Fig. 5. Calculated and experimental[7,11] modulation of drain current as a function of pH at Vds =0.2 V

III. CONCLUSION

A complete description of the surface charging mechanism has been given. The relaxed bond-lengths that were obtained through *ab initio* calculations were used to calculate the surface reaction rates, interfacial capacitance and surface site density and all these characteristics were in close agreement with experimental values. A double layer model was used to calculate the surface charge and potential. The calculated surface potential was in close agreement with the experiment. An analytical approach was used to calculate the device current - voltage sensitivity to the changes in pH. There was an offset value observed between the simulated results and the experiment that needs to be further investigated. However, the calculated sensitivity of the sensor was in close agreement with the experiment.

REFERENCES

[1] S. Yoshioka, H. Hayashi, A. Kuwabara, F. Oba, K. Matsunaga, and I. Tanaka, "Structures and energetics of Ga2O3 polymorphs," *Journal of Physics: Condensed Matter,* vol. 19, p. 346211, 2007.

[2] X. Zhou, E. J. Hensen, R. A. van Santen, and C. Li, "DFT Simulations of Water Adsorption and Activation on Low-Index α-Ga2O3 Surfaces," *Chemistry-A European Journal,* vol. 20, pp. 6915-6926, 2014.

[3] D. A. Sverjensky, "Prediction of surface charge on oxides in salt solutions: Revisions for 1: 1 (M^+L^-) electrolytes," *Geochimica et Cosmochimica Acta,* vol. 69, pp. 225-257, 2005.

[4] M. Kosmulski, "Pristine points of zero charge of gallium and indium oxides," *Journal of colloid and interface science,* vol. 238, pp. 225-227, 2001.

[5] J. P. Perdew and A. Zunger, "Self-interaction correction to density-functional approximations for many-electron systems," *Physical Review B,* vol. 23, p. 5048, 1981.

[6] S. B. Rempe and L. R. Pratt, "The hydration number of Na^+ in liquid water," *Fluid Phase Equilibria,* vol. 183, pp. 121-132, 2001.

[7] H. J. Monkhorst and J. D. Pack, "Special points for Brillouin-zone integrations," *Physical Review B,* vol. 13, p. 5188, 1976.

[8] M. Bayer, C. Uhl, and P. Vogl, "Theoretical study of electrolyte gate AlGaN∕ GaN field effect transistors," *Journal of applied physics,* vol. 97, p. 033703, 2005.

[9] M.-P. Gaigeot, M. Sprik, and M. Sulpizi, "Oxide/water interfaces: how the surface chemistry modifies interfacial water properties," *Journal of Physics: Condensed Matter,* vol. 24, p. 124106, 2012.

[10] S. Rabbaa and J. Stiens, "Validation of a triangular quantum well model for GaN-based HEMTs used in pH and dipole moment sensing," *Journal of Physics D: Applied Physics,* vol. 45, p. 475101, 2012.

[11] D. A. Sverjensky and N. Sahai, "Theoretical prediction of single-site enthalpies of surface protonation for oxides and silicates in water," *Geochimica et cosmochimica acta,* vol. 62, pp. 3703-3716, 1998.

[12] I. t. Brown and R. Shannon, "Empirical bond-strength-bond-length curves for oxides," *Acta Crystallographica Section A: Crystal Physics, Diffraction, Theoretical and General Crystallography,* vol. 29, pp. 266-282, 1973.

[13] R. Van Hal, J. Eijkel, and P. Bergveld, "A general model to describe the electrostatic potential at electrolyte oxide interfaces," *Advances in Colloid and Interface Science,* vol. 69, pp. 31-62, 1996.

[14] H. Morkoç, *Handbook of Nitride Semiconductors and Devices, Materials Properties, Physics and Growth* vol. 1: John Wiley & Sons, 2009.

[15] T. Kokawa, T. Sato, H. Hasegawa, and T. Hashizume, "Liquid-phase sensors using open-gate AlGaN/GaN high electron mobility transistor structure," *Journal of Vacuum Science & Technology B: Microelectronics and Nanometer Structures,* vol. 24, pp. 1972-1976, 2006.