The theoretical study of Cs/O absorption on Ga$_{0.9375}$Mg$_{0.0625}$N (0001) surface: A first principle calculation

S S Ren$^1$, J Ma$^1$, X Q Fu$^{1,2,*}$, M Z Yang$^3$, H Zhao$^1$

$^1$ School of Information Science and Engineering, University of Jinan, China
$^2$ Shandong Provincial Key Laboratory of Network based Intelligent Computing, University of Jinan, China
$^3$ School of Physics and Optoelectronic Engineering, Nanjing University of Information Science and Technology, China

ise_fuxq@ujn.edu.cn

Abstract. In order to theoretically study the adsorption process of GaN photocathode, the adsorption model on Ga$_{0.9375}$Mg$_{0.0625}$N is established. Then, the adsorption energy, work function, Mulliken charge distribution and density of states on the surface of (2×2) Ga$_{0.9375}$Mg$_{0.0625}$N(0001) are calculated by first principle on CASTEP. By comparing the adsorption energy of Cs on N atom, surface centrality and Mg atom, the result shows that adsorption is the most stable on Mg atom. The Cs/O adsorption model on Mg atom is mainly researched, according to analysis the properties of different computing results for different adsorption models, it is found that they are in accordance with the changing trend of the experiment. This provides a theoretical basis for the study of the experiment.

1. Introduction

GaN UV photocathode is a semiconductor material with wide direct band gap, corrosion resistance, high temperature resistance, radiation resistance, solar blind response and high quantum efficiency [1-7]. It has a broad application prospect in the field of blue light-emitting diode, blue light activator, ultraviolet detector and other optoelectronic devices [8-13]. With the development of human beings in aerospace, electron beam printing, UV communication, ozone monitoring and other fields, higher requirements are put forward for wide band gap semiconductor photoemission materials with UV response, and the excellent performance of negative electron affinity photocathode makes it the focus of research. The most ideal one is GaN photocathode with negative electron affinity whose band gap reaches 3.4eV[14-17]. In this paper, Ga$_{0.9375}$Mg$_{0.0625}$N model is established by doping Mg atoms in GaN and adsorbing Cs and O on the surface. This model was proposed before and its formation mechanism was studied. However, the surface adsorption energy, work function and electronic structure need to be further studied. Further study of adsorption energy, work function and electronic structure play an important role in understanding the formation mechanism of negative electron affinity.

In this paper, the first principle of DFT is used to calculate and analyse the adsorption energy, work function, population charge distribution and electronic structure of Ga$_{0.9375}$Mg$_{0.0625}$N(0001) surface which provides a theoretical basis for the study of Ga$_{0.9375}$Mg$_{0.0625}$N(0001) surface.
2. Method of calculation
The calculation of this paper is based on the DFT ab-initio quantum mechanics program CASTEP[18]. The lattice constants are all experimental values. BFGS algorithm is used to optimize the lattice model. The valence electron wave function in the primitive cell is expanded by the plane wave basis vector, and the plane wave truncation energy is set. The convergence accuracy in the iterative process is \(2 \times 10^{-6}\) eV/atom. The convergence criterion of the interatomic interaction is 0.005 eV/nm, and the convergence criterion of the single atom energy is \(1.0 \times 10^{-5}\) eV/atom. The convergence criterion of the internal stress of crystal is 0.05 GPa, the convergence criterion of the maximum displacement of atom is 0.001 nm, and the plane wave super soft pseudopotential method under the generalized gradient approximation (GGA) of DFT is used[19-20]. The Brillouin area integration adopts the high symmetry special k-point method in the form of Monkho-rs-pack[21]. The k-point network is set to \(4\times 4\times 1\), and the energy calculation is carried out in the reciprocal space. The valence electrons involved in the calculation are Ga:3d\(^{10}\)4s\(^{2}\)4p\(^{1}\), N:2s\(^{2}\)2p\(^{3}\), Mg: 2p\(^{6}\)3s\(^{2}\), Cs:5s\(^{2}\)5p\(^{6}\)6s\(^{1}\), H:1s, O:2s\(^{2}\)2p\(^{4}\).

As shown in Figure 1, the Ga\(_{0.9375}\)Mg\(_{0.0625}\)N(0001) surface model consists of 6 surfaces, each layer has Ga and N atoms, and Mg atoms exist on the GaN (0001) surface as impurity atoms. They replace Ga atom in 1, 3 and 5 layers to form a Ga\(_{0.9375}\)Mg\(_{0.0625}\)N surface model. In order to avoid mirror interaction between the plates, a 2.6nm vacuum layer along the z-axis is established, the lower three layers are fixed to simulate the internal of GaN, and the upper three bimolecular layers are free relaxation. In order to avoid the surface electron transfer, the pseudopotential H atom is added to the bottom layer. The calculation model mainly establishes three models of Cs atoms adsorbed on the Mg atom, in the middle, and on the N atom, namely T1, T2 and T3. The position is shown in Figure 2.

3. Result and discussion
3.1. Adsorption energy
As an important indicator to measure the adsorption capacity of atoms, surface adsorption energy reflects whether atoms are easy to adsorb on the surface. In this paper, \(E_{\text{ads}}\) is used to represent adsorption energy. Its expression is

\[
E_{\text{ads}} = \frac{(E_{\text{Cs/surface}} - E_{\text{clean/surface}} - nE_{\text{Cs}})}{n}
\]
Where \( n \) is the number of adsorbed atoms, \( E_{\text{clean/surface}} \) and \( E_{\text{Cs/surface}} \) represent the total energy of the system without adsorption and with adsorption, respectively. The total energy of isolated Cs atom is \(-548.9466\) eV. The adsorption energy of each model is shown in Table 1.

### Table 1. The adsorption energy of different surface adsorption models

|                  | Cs-T1          | Cs-T2          | Cs-T3          |
|------------------|----------------|----------------|----------------|
| \( E_{\text{Cs/surface}} \) | -53169.70276037 | -53169.29629706 | -53169.15864622 |
| \( E_{\text{ads}} \)       | -1.45           | -1.04           | -0.97           |

By calculation, the adsorption energy of Cs atom in N atom, positive middle atom and Mg atom is 0.97, 1.04 and 1.45eV respectively. According to the analysis of the results, the most stable adsorption site of Cs atom on \( \text{Ga}_{0.9375}\text{Mg}_{0.0625}\text{N}(0001) \) surface is Mg atom.

#### 3.2. Mulliken charge distribution

The surface of \( \text{Ga}_{0.9375}\text{Mg}_{0.0625}\text{N} \) (0001) will inevitably cause the transfer of surface electronic structure and charge after adsorption of Cs/O. Through the analysis of the distribution of surface charge number before and after adsorption of Cs/O, the interaction between Cs/O and \( \text{Ga}_{0.9375}\text{Mg}_{0.0625}\text{N} \) (0001) surface is further observed.

### Table 2. Mulliken charge distribution

|                  | Mulliken charge distribution | First bilayer | Second bilayer |
|------------------|-----------------------------|---------------|----------------|
|                  |                             | Ga(average)   | Mg(average)    | Ga(average) | N(average) |
| clean            |                             | 0.77          | -1.14          | 1.62        | 0.74       | -1.04       |
| Cs               |                             | 0.60          | -1.13          | 1.65        | 0.86       | -1.05       |
| 2Cs              |                             | 0.57          | -1.13          | 1.64        | 0.86       | -1.04       |
| 2Cs+O            |                             | 1.25          | -1.00          | 1.8         | 0.88       | -1.05       |
| 2Cs+O+Cs         |                             | 0.60          | -1.13          | 1.63        | 0.90       | -1.04       |

The table 2 shows the change of surface Mulliken charge distribution before and after Cs/O adsorption. The Mulliken charge distribution of Ga and N in the table are average. From table 2, it can be seen that the Mulliken charge distribution of Ga atom in the first layer decreases, among which, the decrease is the largest after adsorption of two Cs; The Mulliken charge distribution of Ga atom in the second layer increases slightly, the increase is the most after adsorption of two Cs and one O and the increase is the largest after adsorption of another Cs. The Mulliken charge distribution of N atom in the first layer and the second layer is basically the same before and after adsorption. Through analysis, we can know that Cs and O mainly interact with Ga atom. The main reason for this result is that the electronegativity of O atom is 3.5, that of Ga atom is 1.81, and that of Cs atom is 0.79, so the order of electronegativity is \( O > Ga > Cs \). According to the theorem, the greater the electronegativity of an atom, the stronger the ability to get electrons; on the contrary, the smaller the ability to get electrons.

#### 3.3. The change of work function induced by adsorption

According to the three-step model of negative electron affinity photocathode proposed by W.E.Spicer the three-step model of negative electron affinity photocathode is photon absorption, electron migration to the surface and electron escape from the surface to the vacuum\[22\]. The third step is mainly affected by the surface environment. For example, adsorption of Cs and O on the surface can change the work function of the surface. The work function is the minimum energy that makes the surface electron escape to vacuum. The formula is
Φ=E_{vac}-E_{F}

Where $E_{vac}$ is the vacuum level, $E_{F}$ is the Fermi level of the system.

According to the calculation results of adsorption energy, the best adsorption is obtained on Mg atom, so we only carry out Cs and O adsorption on Mg atom, and analyse the change of work function. We have established four adsorption models including Mg - Cs, Mg - 2Cs, Mg -2Cs -O, Mg - 2Cs - O -Cs, calculated and analysed their work functions, as shown in Table 3.

| Table 3. The energy function of different surface adsorption models |
|------------------|--------|----------|--------|---------|
| clean            | Mg-Cs | Mg-2Cs   | Mg-2Cs-O | Mg-2Cs-O-Cs |
| Φ               | 2.405eV | 1.223eV  | 1.312eV  | 6.899eV  |
| ΔΦ              | 1.182  | 1.093    | 4.494    | 1.48     |

The table 3 shows the calculation results of each model in which the work function of Mg - 2Cs - O increases and the rest decreases. The work functions of Mg - CS, Mg - 2Cs model and Mg - 2Cs - O - Cs model vary by 1.182, 1.093 and 1.48ev respectively. Therefore, the work function of Mg - 2Cs - O - Cs model is the lowest. The decrease of work function is mainly due to the formation of dipole moment on the surface due to electronegativity O > Ga > Cs.

3.4. Electronic structures of clean Ga$_{0.9375}$Mg$_{0.0625}$N (0001) and the Cs-O/ Ga$_{0.9375}$Mg$_{0.0625}$N (0001) adsorption system

The PDOS diagram of clean Ga$_{0.9375}$Mg$_{0.0625}$N (0001) can be seen in Figure 3. Figure 4 shows the DOS of clean Ga$_{0.9375}$Mg$_{0.0625}$N (0001) and the Cs-O-2Cs/ Ga$_{0.9375}$Mg$_{0.0625}$N (0 0 0 1) model. In every Figure, the line indicates the Fermi level. As is depicted in Fig.3, it can tell that Ga4p, N2p and Mg2p states play the major role for the top of the valence band for Ga$_{0.9375}$Mg$_{0.0625}$N (0001) surface, Ga4s and Mg2p states make a chief contribution for the bottom of conduction band for Ga$_{0.9375}$Mg$_{0.0625}$N (0001) surface. In addition, Ga4s, Ga4p, Mg2p and a small numbers of N2p states conform the surface state between the conduction and valence bands. It can be seen from the Fermi level that the Ga$_{0.9375}$Mg$_{0.0625}$N (0 0 0 1) surface has the property for metal conductivity. This is consistent with the calculation results of Du et al [23]. After Cs and O adsorption, the model of Cs-O-2Cs Ga$_{0.9375}$Mg$_{0.0625}$N can be obtained. From the Figure 4 and Figure 5 we can know that the maximum peak increases and moves to the right. The reason is that Cs5p and O2p states make a chief contribution.

![Figure 3. The PDOS of Ga$_{0.9375}$Mg$_{0.0625}$N (0001) surface model](image-url)


4. Conclusion
The adsorption energy, work function and population charge distribution of Cs and O adsorption system on GaN (0001) surface were calculated by the first principle density functional theory plane wave super soft pseudopotential method. The adsorption energy of Cs atom on N atom, positive middle atom and Mg atom is analysed and calculated. The result shows that the adsorption on Mg atom is the most stable. After Cs and O adsorption on Mg atom, the work function of Mg - 2Cs - O - Cs is the lowest. Cs and O atoms mainly interact with Ga atoms after adsorbing on Ga$_{0.9375}$Mg$_{0.0625}$N (0001) surface.

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