Ab-initio study of the structural and electronic properties of Zr adsorption on the AlN(0001) surface

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We have performed spin-polarized first-principles calculations to explore the Zr adsorption and diffusion on the AlN(0001)-(2x2) surface. The calculations were performed using the generalized gradient approximation (GGA) with ultrasoft pseudopotential within the density functional theory (DFT). We found that the most energetically favorable structure corresponds to the Zr-T4 reconstruction or the Zr adatom located at the hcp-hollow (T4) site, while the Zr adsorption on-top of a aluminium atom (T1 position) is energetically unfavorable. The Zr diffusion on surface shows an activation energy of 0.473 eV (T4 to H3). The resultant reconstruction of the Zr adsorption on AlN(0001)-2x2 surface presents a lateral relaxation of some hundredth of Å in the most stable site. The comparison between the electronic structure of the AlN(0001) clean-surface and with Zr adatom is also examined. The clean surface aluminium-terminated has one Al dangling-bond in the top layer. We found that the clean AlN(0001) surface layer have metallic behavior, due to the partial occupation of the Al dangling-bond band by 0.75 of an electron, disappearing the existing gap in the bulk AlN. The existence of a partially filled state means that this state gives rise to a metallic surface with the Fermi energy crossing the surface state. The Zr adsorption saturates some dangling bonds of the clean surface and the system presents a metallic behavior in both spin components.

1. Introduction

The group-III-nitride semiconductors (AlN, GaN and InN) and their alloys are recognized as very promising materials for many optoelectronic device applications such as blue-green and UV light-emitting diodes (LEDs), laser diodes (LDs), and high-temperature/high-power electronic devices. For the fabrication of alloys and interfacial compounds between AlN and the TM contacts it is critical to be able to control the high-quality crystal growth, and this makes that an understanding of the fundamental growth mechanisms indispensable. In this work, we perform first-principles spin polarized calculations to investigate the adsorption, diffusion and electronic properties of Zirconium atoms on the AlN(0001) surface using density functional theory (DFT) within a plane-wave pseudo-potential framework.

2. Methodology

The total energy and electronic structure calculations were performed using the first principles pseudopotential method in the framework of the spin density functional theory (DFT). Exchange and correlation effects were treated with generalized gradient approximation (GGA) implemented in the Perdew-Burke-Ernzerhof functional (PBE). The calculations were performed using the "Quantum-Espresso" simulation package. The electron wave functions were expanded in plane waves up to a cutoff energy of 50Ry and a cutoff of 500Ry for the charge density. For the analysis of Zirconium adsorption and diffusion on the AlN(0001) surface, the calculations were performed employing a slab model with a 2x2 surface unit cell consisting of four Al-N bilayers and a vacuum thickness of ~15Å separating the slabs. The two lowest AlN bilayers were fixed in the bulk optimized configuration, while the two uppermost AlN bilayers as well as the Zirconium adatom were allowed to relax. The dangling bonds at the bottom layer were saturated with pseudo-hydrogens atoms, each one with a fractional charge of 0.75*e* in order to prevent unphysical charge transfer between the top and bottom slab surfaces.

3. Results

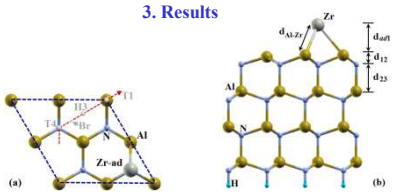

Figure 1: (a) Top view of the AlN(0001) surface with adsorbed Zr, showing high symmetry surface adsorption sites *T4*, *H3* and *T1*. The dashed line indicates the path corresponding to energy profile. (b) Top view of the AlN(0001) slab with adsorbed V, showing notation used for the interlayer distances. The dark gray balls represent Al atoms, the light gray balls represent N atoms and the black ball represent Zr adatom.

	d_{Al-Zr}(Å)	d_{ad1}(Å)	d_{12}(Å)	d_{23}(Å)	E_{ads}(eV)	ΔZ_{Al} (Å)	ΔZ_N (Å)
Limpia			0.650	1.910			
Zr-T_4	2.796	2.153	0.679	1.885	-4.767	0.115	0.048
Zr-H_3	2.863	2.241	0.697	1.905	-4.401	0.342	0.106
Zr-T_1	2.669	2.669	0.552	1.905	-3.266	0.102	0.069

Table. Calculated structural parameters .

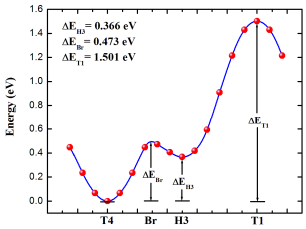

Figure 3: Total energy surface (in eV) for Zirconium adatom at different sites on AlN(0001) surface. The energy zero corresponds that of the Zr-*T4* reconstruction.

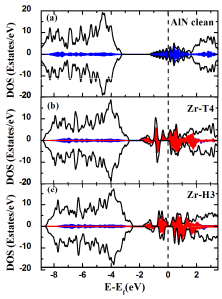

Figure 4: Density of states (DOS) of the (a) relaxed clean AlN(0001) surface, (b) Zr-*T4* reconstruction, and (c) Zr-*H3* reconstruction. The black lines are the total DOS. The dark (blue) and dark (red) shared areas indicate Al-surface atoms and Zr adatom partial DOS contributions, respectively.

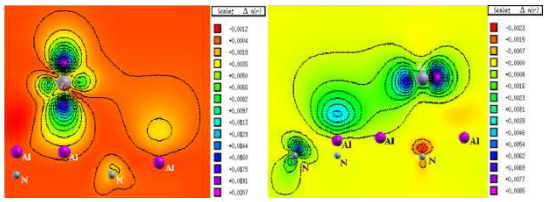

Figure 5: Charge density differences Δn(r)[n↑(r) - n↓(r)], (a) Zr-*H3* reconstruction and (b) Zr-*T4* reconstruction.

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5. Conclusions

In this study the Zirconium adsorption and diffusion on AlN(0001)-(2x2) surface was analyzed using density functional theory. The Zirconium adsorption was found to be most stable at *T4* site, while on *T1* site the adsorption energy is weak producing an unstable system. The small barrier energy is an indicative of a significant diffusion of the Zirconium adatom on the surface. The Zirconium adsorption induce changes on the electronic structure of the clean AlN(0001) surface introducing localized states of both spin orientations around the Fermi level. This is an additional feature of the electronic structure of a metallic surface with a transition metal adatom and is of interest in technological applications as well as from the theoretical point of view.

We thank to Universidad del Norte and Universidad del Magdalena for their financial support during the realization of this work. The calculations were carried out in the Hiperlab cluster of Basic Sciences in Universidad del Norte-Barranquilla.

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