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Ab Initio Studies of Al and Ga Adsorption on 4H-SiC{0001} Surfaces

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Changes in the atomic and electronic structure of Si- and C-terminated 4H-SiC{0001} surfaces resulting from aluminium and gallium adsorption have been studied within density functional theory framework. Al and Ga coverages ranging from a submonolayer to one monolayer were considered. Our results show that Al binds more strongly to both surfaces than Ga. The binding is stronger to the C-terminated surface for both metals. The sites occupied by Al and Ga atoms at 1 monolayer are different and it is due to a different charge transfer from metal to the substrate.

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1. Introduction

Thin nitride films are still attracting much interest because of their potential applications in opto- and microelectronics. An important substrate for epitaxial growth of AlN and GaN layers is SiC, since it is nearly lattice matched with AlN and has relatively low misfit with GaN. Nitride heterostructures are mainly grown on the 4H- and 6H-SiC with the growth direction along the hexagonal c-axis. Such heterovalent heterostructures exhibit the built-in macroscopic electric fields [1] that originate from (i) the heterovalent character of the interface, and (ii) piezo- and pyroelectric character of the constituent bulk materials. In spite of considerable experimental [1, 2] and theoretical efforts [3–8], the physical understanding of these intriguing interfaces is still incomplete. Presented paper aims at understanding the first step of creation of such interfaces, i.e. the adsorption of Ga and Al on 4H-SiC{0001} surfaces. We examined the differences in the behaviour of the two metals on studied surfaces as well as the influence of the surface termination on Al and Ga adsorption.

2. Method

Our calculations have been performed using density functional theory (DFT) as implemented in Siesta program package [9]. The electron exchange-correlation effects were treated within the generalized gradient approximation (GGA) using the PBE form of the exchange-correlation functional [10]. The electron ion-core interactions were represented by pseudopotentials of the Troullier–Martins type [11] and the electron wave-functions were expanded into the atomic-orbital basis set using the double-ζ polarized set. The cutoff of 120 Ry was used for the real space mesh. The Brillouin zone integrations were performed applying the (8,8,2) and (8,8,1) k-points meshes for bulk and surface calculations, respectively. The 4H-SiC crystal was represented by a hexagonal supercell containing eight atoms that was repeated periodically in space. The calculated lattice parameters for 4H-SiC polytype ($a = 3.113$ Å, $c = 10.205$ Å) are in good agreement with experimental data ($a = 3.073$ Å, $c = 10.053$ Å [12]) and with results of recent plane-wave-basis calculations [13] performed by applying the projector-augmented wave method and the GGA-PBE functional. The determined lattice parameters were applied to construct slabs of 12 Si–C double-layers representing the (0001) and (000$\bar{1}$) surfaces of the 4H-SiC crystal, terminated with Si and C atoms, respectively. For brevity, in the following these surfaces will be referred to as Si(0001) and C(000$\bar{1}$). The dangling bonds on the bottom layer atoms of the slabs were saturated by hydrogen atoms. The slabs of such thickness which were separated from their periodic replicas in neighbouring cells by a vacuum region of ≈ 20 Å proved to be sufficient for reproducing surface properties [13]. The atomic positions of the four topmost double Si–C layers of the slab, and of the terminating H atoms on the backside were relaxed until forces acting on atoms converged to less than 0.02 eV/Å. The positions of atoms of the remaining double Si–C layers have been held fixed.

The adsorption energy E_{ad} of adsorbed atoms was calculated from the equation

$$E_{\mathrm{ad}} = E_{\mathrm{Me/SiC}} - E_{\mathrm{SiC}} - E_{\mathrm{Me}}, \qquad (1)$$

where $E_{\mathrm{Me/SiC}}$ and E_{SiC} represent the total energy of

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a slab with adsorbed atom Me (Al or Ga) and a clean surface, respectively, while E_{Me} is the total energy of a corresponding isolated atom Me.

3. Results

We studied different coverages of Al and Ga adsorbed on the 4H-SiC{0001} surfaces by considering single adsorbed atom in supercells built of equal number of Si and C atoms, and different surface dimensions: 1×1, 2×1, 2×2, and 3×3, containing in total: 25, 50, 100, and 225 atoms, respectively. A single atom placed in one of the above supercells corresponds respectively to a monolayer (ML), 1/2, 1/4, and 1/9 ML of adsorbate atom. Several high-symmetry on-surface sites either on Si- or C-terminated 4H-SiC{0001} surface were considered for adsorption. These included adsorption on-top of the Si/C atom of the topmost surface layer, in H_3 or in T_4 site or in the bridge between two neighbouring topmost substrate atoms (Fig. 1). Studies of 0.5 and 1 ML were performed in 2×2 supercell to take into account possible interaction of adsorbates on the surfaces. Thus, either two or four adsorbate atoms were placed in various also inequivalent high-symmetry sites at the surface.

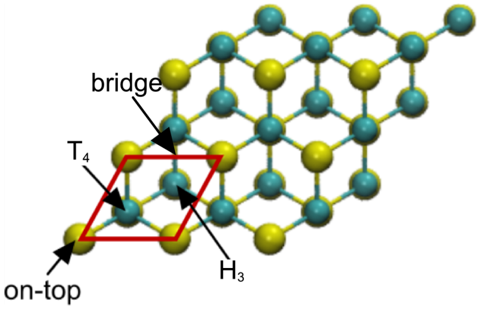

Fig. 1. Adsorption sites indicated by arrows taken into account for Al or Ga adsorption on 4H-SiC{0001} surfaces. Top view of the surface with 1×1 supercell indicated in red. Blue/yellow balls represent Si or C atoms depending on the termination considered.

Our study shows that there are only two stable sites, namely H_3 and T_4, for Al or Ga adsorption at coverages below 0.5 ML. The adsorption energies E_{ad} for 0.25 ML coverage are summarised in Table. In general, for both metals adsorption on the Si(0001) surface is more favourable in T_4 position. Hence, when Al is adsorbed four bonds are created with three surface Si atoms and one C from the layer below the topmost one. In case of Ga they have equal length of 2.55 Å. However, the bond length between adsorbed Al and C atom is slightly shorter than those between Al and Si and they amount to 2.47 Å and 2.49 Å, respectively. On the C(000$\bar{1}$) surface it is more favourable for both metals to adsorb at H_3 position. Then, the three bonds with the nearest surface C atoms are created. These bonds are shorter than at Si(0001) surface and equal to 2.05 Å and 2.21 Å for Al and Ga, respectively. These shorter bonds are reflected in lower adsorption energies at C-terminated than at Si-terminated surface. Moreover, Al binds stronger to examined surfaces than Ga. In case of the C(000$\bar{1}$) surface the difference between Al and Ga adsorption energies is especially large and amounts to more than 1.5 eV.

TABLE

Adsorption energy E_{ad} in eV/atom for stable adsorption sites at 0.25 ML of Al and Ga adsorbed on 4H-SiC{0001} surfaces.

Adsorption site	Si(0001)		C(000$\bar{1}$)	
	Al	Ga	Al	Ga
H_3	−5.78	−5.12	−7.19	−5.52
T_4	−6.13	−5.39	−6.23	−4.92

At adsorbate coverage of 0.5 ML the interaction between metal atoms becomes meaningful. At Si-terminated surface both metals create a Me_2 molecule lying along (10$\bar{1}$0) direction tilted with respect to the surface (Fig. 2). Atom closer to the surface is placed in the most favourable for lower coverages T_4 position. The distance to the nearest Si atoms is similar for both metals and slightly bigger than at 0.25 ML. It equals 2.58 Å and 2.60 Å for Al and Ga, respectively. On the contrary, the distance between Al–Al and Ga–Ga atoms differs meaningfully and amounts to 1.80 Å and 2.72 Å, respectively. At C-terminated surface, one of the Al atoms is bound at the most favourable H_3 position to three surface C atoms with Al–C distance 2.07 Å which is almost the same as for 0.25 ML. The second Al binds to the remaining surface C atom tilted towards the other Al. The Al–C distance is again 2.05 Å while Al–Al is 2.78 Å. The charge density distribution for 0.5 ML Al adsorbed at 4H-SiC{0001} surfaces is given in the bottom row of Fig. 2. It displays the electron charge density difference between the valence charge density and the sum of atomic valence charges. It can be seen that in both cases there is a charge accumulation in the regions between adsorbed Al and its nearest neighbour from the surface: either Si or C at the expense of Al atom. At Si-terminated surface there is some additional charge between adsorbed metal atoms.

Interestingly, at coverage of 1 ML the examined metals behave differently, although opposite to the 0.5 ML they are uniformly spread over the surface. Al atoms, regardless of the surface termination adsorb on top of the topmost surface atoms (Fig. 3). On the other hand, Ga atoms adsorb in the most favourable H_3 position at C(000$\bar{1}$) surface. However, at Si(0001) the adsorption takes place not exactly at T_4 site but Ga atom is slightly shifted towards the H_3 site. There exist also differences in the charge density distribution in case of those two metals adsorption. When Al is adsorbed some of the electronic charge is transferred from above the Al atom to the region between adsorbate and surface atom. For Ga adsorption, transfer is mainly from just below the metal atom to region above the topmost surface atom. This should lead to different surface dipole moments for either Al or Ga monolayer on 4H-SiC{0001} surfaces.

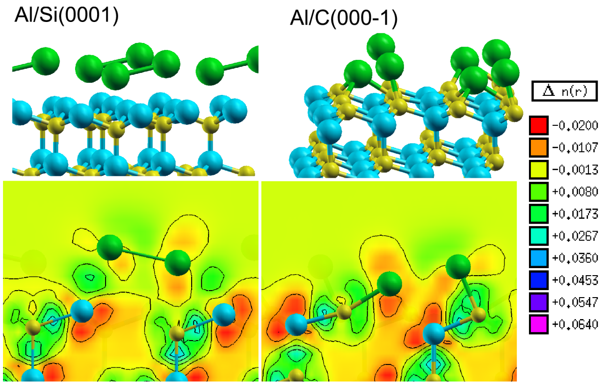

Fig. 2. Top: final atomic structure for 0.5 ML of Al adsorbed on 4H-SiC{0001} surfaces Si-terminated (left part) and C-terminated (right part). Bottom parts show corresponding charge density distribution (in electron/Å^3). Blue, yellow and green balls represent Si, C and Al, respectively.

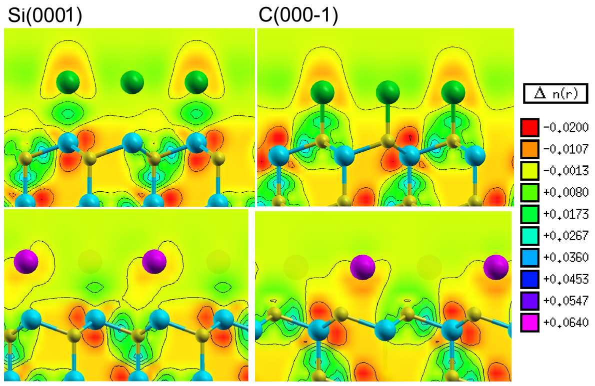

Fig. 3. Charge density distribution for 1 ML of Al (top) or Ga (bottom) adsorbed at 4H-SiC{0001} surfaces (in electron/Å^3).

The dependence of the adsorption energy on the metal coverage is summarised in Fig. 4. For both metals and both terminations the E_{ad} is the smallest for the smallest coverage. The adsorption energy increases meaningfully for coverages larger than 0.5 ML by around 1.5 eV. It may indicate the existence of some additional stress on the surface yielded by Al or Ga adsorption at 4H-SiC{0001} surfaces. In general, Al is bound more strongly to the examined surfaces than Ga. Moreover, adsorption at C(000$\bar{1}$) surface is more favourable than that at Si(0001) by ≈ 1 eV for Al. In case of Ga adsorption the biggest difference is between more favourable adsorption at C(000$\bar{1}$) surface than that at Si(0001) surface for 1 ML which is ≈ 0.5 eV. The calculated adsorption energy for Ga/Si(0001) agree well with the results of temperature programmed desorption (TPD) experiment performed by King et al. [14]. They measured Ga desorption energy from (3×3) 6H-SiC(0001) surface and obtained 6.2 ± 0.3 eV.

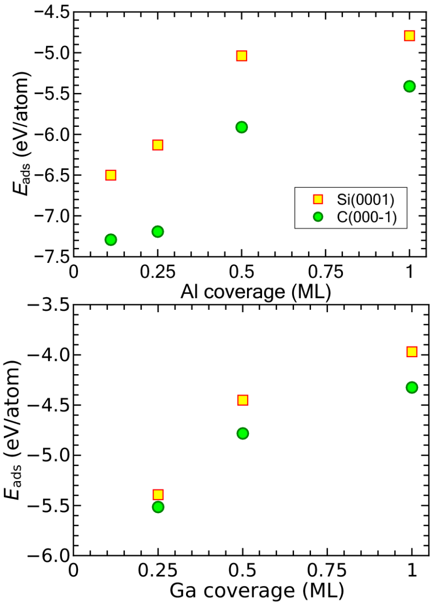

Fig. 4. Adsorption energy E_{ad} as a function of Al (top) and Ga (bottom) coverage on 4H-SiC{0001} surfaces.

4. Summary

We examined adsorption of Al and Ga atoms at 4H-SiC{0001}. We found that in general Al atoms bind more strongly to considered surfaces than Ga ones. Moreover, the adsorption energy at C-terminated surface is lower than that at Si-terminated for both metals. Although the same type of adsorption sites is the most favourable at coverages below 1 ML, Al and Ga occupy different places at the surface. This is accompanied by a different mechanism of spatial charge transfer from metal towards substrate.

Acknowledgments

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