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Pseudopotential Density-Functional Energy Study of Sub-Nano Li, Be and Al Layers on the Si (100) Surface: Band Gaps and Ordering

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Abstract

Within the framework of the density functional theory and the pseudopotential method, the electronic structure calculations of the systems "metal-Si (100)" systems with Li, Be or Al coatings of one to three monolayers thickness, were carried out. Band gaps in the densities of states were observed in the one monolayer Li-Si (100) and Be-Si (100) systems (1.02 eV and 0.36 eV, respectively). In the Li-Si (100) system, the gap disappears with increasing thickness of the metal coating to two monolayers, and in the Be-Si (100) system it increases to 0.40 eV for two monolayer and disappearing when three monolayers are deposited. No gap was found in the Al-Si (100) system. This behavior of the band gaps can be explained by the passivation of the substrate surface states and the peculiarities of the electronic structure of the deposited metals.

Keywords: Density functional theory; Modelling; Density of electronic states; Band gap; Total energy

Introduction

Metal layers on silicon have long attracted attention of researchers. However, this mainly refers to layers of refractory 3d transition metals that form stable silicides. Layers of low-melting metals on silicon have not been studied enough. The most indicative include works, where the atomic and electronic structure of the ultra-thin layers on Si (100) and Si (111) surfaces were studied. In the work of Kotllyar et al [1]. The high-temperature interaction of Al with Si (100) surface at low Al coverages was studied using low-energy electron diffraction, Auger electron spectroscopy and STM. At low Al coverages (≈0.05-0.2 ML), interaction of Al atoms with a top Si (100) substrate layer proceeds by two competitive mechanisms. First mechanism prevails at the Si (100) surface with a low density of missing-dimer defects and resides in the formation of the specific Al–Si clusters. The second mechanism is stimulated by the presence of missing-dimer defects and resides in substitutional incorporation of Al atoms in the top Si (100) substrate layer. Both mechanisms result in the liberation of the surface Si atoms which agglomerate into flat islands. The Si mass transport and Al incorporation have been treated quantitatively, the composition of the Al–Si clusters has been estimated and the cluster structural model has been constructed. In the work of Cocoletzi and Takeuchi [2]. The first principles total energy calculations of the Al induced Si (001)- (3×4) reconstruction are presented; local density of state images were calculated for that model and compared with the experimental STM measurement. Northrup [3]. Have studied the adatom-induced reconstruction the the Si (111) surface using first-principles pseudopotential total-energy and force calculations. He proposed a new adatom model of this reconstruction wherein each Al adatom sits in a threefold-symmetric site with three first-layer Si neighbors and one second-layer Si neighbor directly below. For this model, the calculated dispersion of the adatom-induced surface states is in good agreement with experiment. Work of KO Young-Jo et al [4]. Is of particular interest to us, since it describes in detail first-principles calculations of the electronic structure of the Li-Si (100) system, which is one of the objects of our work. They find that Li adatoms interact mainly with the dangling-bond orbitals of

Si dimers. The analysis of charge densities demonstrates a large charge transfer from the Li adatom to a dangling-bond orbital of a Si dimer, which is responsible for a large decrease of work function at submonolayer coverages. We will present their results in more detail below in comparison with ours. The work of Morikawa et al [5]. Is devoted to the theoretical support to the double-layer model for potassium adsorption on the Si (001) surface. Haye et al [6]. Nave studied sodium-doped dimer rows on Si (001). The stability and electronic structure of a nanowire were studied by first-principles calculations. The wire consisted of a single depassivated silicon dimer row on the hydrogen passivated Si (001)-2×1 surface. In the work of Jeong and Kang [7]. The atomic and electronic structure of the Na/Si (111) – (3×1) surface was studied using the pseudopotential density-functional total-energy method. Authors predicted that sodium atoms evaporated onto this surface stick preferentially at the depassivated row and partially fill the empty one-dimensional states of this row. This leads to a thin metallic wire of atomic size dimensions. At room temperature the sodium atoms are mobile along the depassivated row; they become immobile at temperatures below 120ºK. Based on the calculated electronic structures, authors proposed that a saturation Na coverage is 1/3 monolayer. This model can explain the experimental results: the semiconducting ground state, double-row scanning-tunneling-microscopy image, chemical passivation for oxidation. Rysbaev et Al [8]. Studied the formation of silicide films of metals (Li, Cs, Rb, and Ba) during ion implantation in Si and subsequent thermal annealing. Hite, Tang and Sprunger [9]. Used scanning tunneling microscopy and photoelectron spectroscopy to investigate the nucleation, growth, and structure of beryllium on Si (111)-(7×7). They indicated that a chemical reaction occurs at temperatures as low as 120ºK, resulting in a nano-clustered morphology, presumed to be composed of a beryllium silicide compound. Upon annealing to higher temperatures, their data indicate that beryllium diffuses into the selvage region. Saranin et al [10]. Studied ordered arrays of Be-encapsulated Si nanotubes on Si (111) surface using scanning tunneling microscopy. Gordeev, Kolotova and Starikov [11]. Investigated the formation of metastable aluminum silicide as intermediate stage of Al-Si alloy crystallization. They noted that the mechanism of Al-Si alloy crystallization from an amorphous state is still unclear. Despite the absence of equilibrium compounds for this binary system, there are several experimental evidences confirming the formation of metastable silicide at annealing of amorphous Si mixed with Al. Authors considered the properties of aluminum silicide Al2Si structure, which is a probable candidate for the role of the observed metastable compound. Their investigation was based on the atomistic simulations with the interatomic potential and density functional theory approach. Terekhov et al [12]. Have studied a possibility of the metastable Al3Si phase formation in composite Al-Si films obtained by ion-beam and magnetron sputtering. Endo et al [13]. Made an elementary analysis of each metal atoms on the Si (001) surface by scanning tunneling microscopy and spectroscopy; the result was evaluated with the first principles calculations of quantum mechanics. As metallic contaminations, sub-monolayer of aluminum is evaporated on Si (001)2×1. The local density of states on the Al/Si (001)-2×1 was measured by scanning tunneling spectroscopy at room temperature. Experimental results are in good agreement with that obtained from the calculations. Our work is devoted to computer modeling of sub-nano (of one to three monolayers thickness) layers of Al, Be and Li on the Si (100) surface using the Kohn-Sham approach within the framework of the density functional theory [14-15] and the pseudopotential method [16].

Research Methodology

All calculations were performed using the FHI96md package [17]. Pseudopotentials were found using the FHI98pp package. To calculate the exchange-correlation energy, the local electron density approximation was used [18-19]. In all cases, the energy cutoff of a set of plane waves was taken to be 10 Ry; calculations were carried out with the five k-points: (0.5; 0.5; 0.0), according to the $3\times3\times1$ Monkhorst scheme [20]. In a supercell with dimensions 14.54×14.54×50 (all values are given in atomic units, one atomic unit is equal to 0.529 Å). The electronic structure was studied by calculating the density of electronic states (DOS), for which each electronic level was smeared using a Gaussian function with a half-width of 0.05 eV. As a silicon substrate with a Si (100) surface, we took a Si slab consisting of 12 monolayers (ML), in which each ML contained four atoms, and the lower ML was terminated with eight hydrogen atoms. Thus, due to the periodic boundary conditions in the X and Y directions, we studied a thin infinite plate, and the large value of the parameter C (50 atomic units) for the supercell ensures that there is no interaction between the virtual plates in Z dimension. The atoms of the lower ML of silicon were fixed; the atoms of the remaining layers, as well as the atoms of studied metals, could move under the action of quantum mechanical interatomic forces. Each metal ML also contained four atoms.

Results and Discussions

One metal monolayer

Our calculations showed that for studied metals, the arrangement of their atoms on the Si (100) surface turned out to be very different. Schemes of the optimized arrangement of atoms in the "metal monolayer + Si (100)" systems are presented in (Figure 1). It can be seen from this figure that on the clean Si (100) surface, asymmetric (skewed in different directions) dimers with a length of 2.32 Å and a bevel angle of 13.5° are formed and p(2×2)

symmetry is established, which is consistent with the conclusions of works [23-24]. When applying a monolayer of Li, silicon dimers lose their asymmetry and increase their length to 2.78 Å, and in the case of beryllium and aluminum, silicon dimers as such disappear, their length is compared with the distance between the underlying silicon atoms (2.90 Å). Note also that beryllium atoms are immersed in the silicon substrate and are installed between the first and second layers.

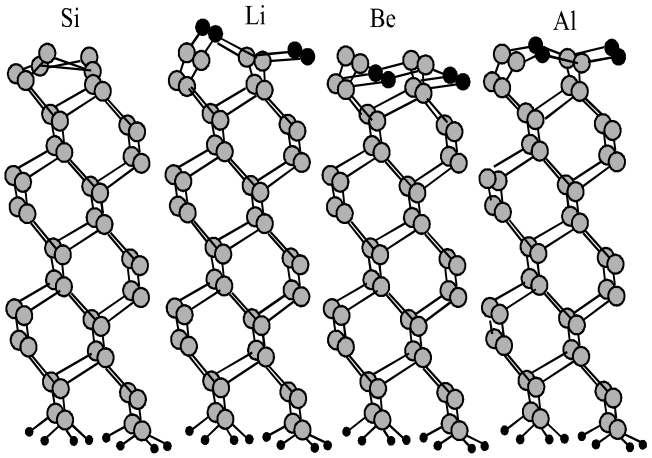

Figure 1: *Arrangement of Li, Be and Al atoms on the Si (100) surface in the case of deposition of 1 ML. The gray circles are Si atoms, the small black circles are hydrogen atoms, and the big black circles are metal atoms. The clean structure on the Si (100) surface is also shown.*

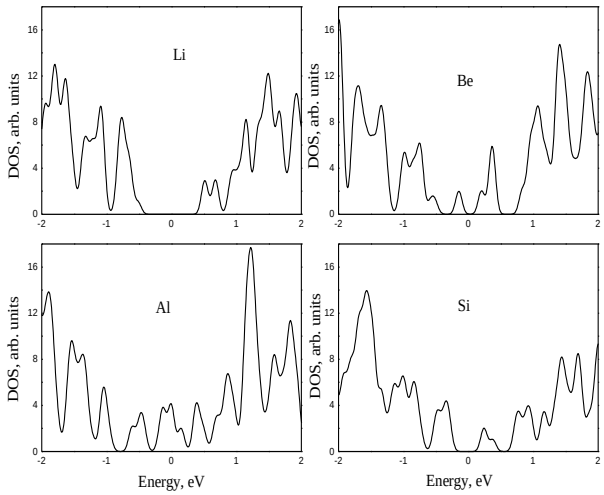

Figure 2: *Density of electronic states formed when the first monolayer of Li, Be and Al is deposited on the Si (100) surface in comparison with the density of states for the clean Si (100)- (2×1) surface. The Fermi level corresponds to zero energy.*

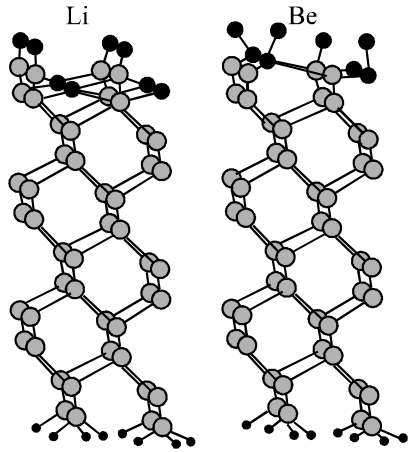

Figure 3: *Arrangement of Li and be atoms on the Si (100) at the 2 ML coatings.*

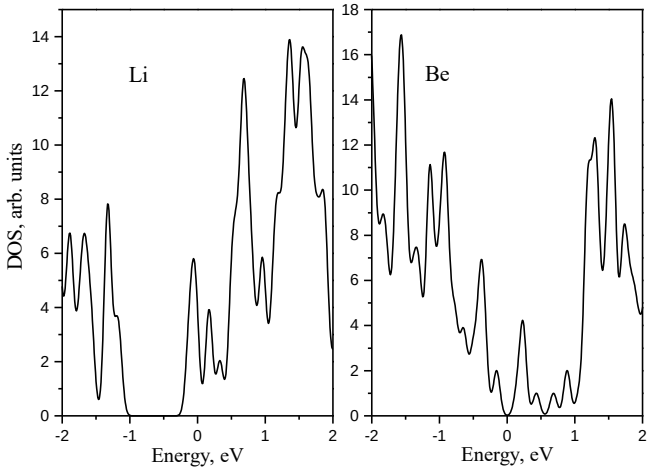

Figure 4: *DOS calculated for 2 Li and 2 be nonolayers on the Si (100) surface.*

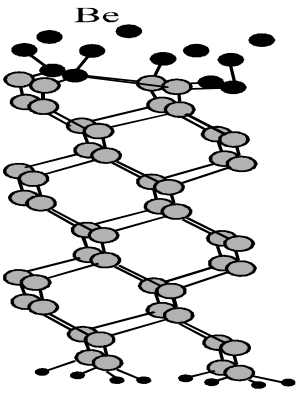

Figure 5: *Arrangement of be atoms on the Si (100) surface at 3 ML coating.*

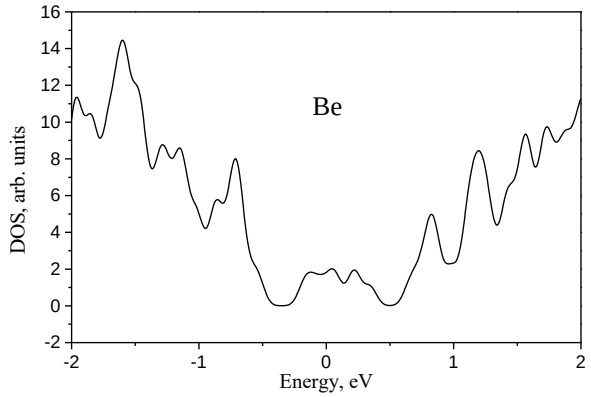

Figure 6: *DOS for three beryllium ML on the Si (100) surface.*

In (Figure 2) we plot the densities of states calculated for the first ML of lithium, beryllium and aluminum. The DOS for the clean Si (100) surface is also shown there for comparison. From this figure it is clear that in the Li-Si (100) and Be-Si (100) systems a forbidden gap Egap presents. Namely, for Li Egap = 1.02 eV, for B-Si (100) Egap = 0.36 eV. In the Al-Si (100) case there is no band gap. For the clean Si (100) surface we obtained Egap = 0.54 eV. We were able to make a comparison with literature data only for lithium and pure silicon. In theoretical work [4], with an arrangement of lithium atoms close to ours, but with eight layers of silicon, an energy gap width of 1.35 eV was obtained. In the work, using electron energy loss spectroscopy Egap = 0.4 eV was determined. The authors of have found Egap = 0.5 eV using scanning tunneling spectroscopy. Those results are close to ours, so we have reason to believe that our results obtained for me and Al monolayers on Si (100) are also quite reliable.

Two monolayers of metal

Due to the fact that we were interested in the formation of a band gap in electronic states, in this section we studied only the Li-Si (100) and Be-Si (100) systems, since in the Al-Si (100) system the band gap did not appear already at deposition of one ML of metal. The energetically favorable arrangement of Li and be atoms on the Si (100) surface with a two-layer coating is shown in (Figures 3-4). Shows the DOS for these two systems. From this figure it follows that in the Li-Si (100) system the ordering of the arrangement of metal atoms does not disappear, but becomes different compared to a monolayer case. Li atoms penetrate deep into the silicon substrate and occupy positions between the first and second silicon layers. In the Be-Si (100) system a half of metal atoms are situated practically at the same lever with the first silicon layer. From this figure it can be seen that in the electronic structure of the 2ML Li-Si (100) system there is no energy gap, but in the 2ML Be-Si (100) system there is a gap with a width of 0.40 eV, a little larger than in the 1 ML case.

Three metal monolayers

We studied this case only for the Be-Si (100) system. The optimized structure of this system is shown in (Figure 5). From which it can be seen that the arrangement of metal atoms has become practically disordered. Shows the DOS for this system. It is easy to see that with a coating 3 ML thick, some mixing of be and Si atoms is occur, and the disordered arrangement of metal atoms becomes obvious. The DOS for this system is shown in (Figure 6). We see that when three beryllium ML are deposited on the Si (100) surface, the energy gap in the density of states disappears.

Local densities of states

In the case of systems with layer-by-layer atomic structure (and composition), it is very important to understand how the electronic structure changes from layer to layer. This also applies to the case of pure silicon, with the surface that undergoes structural restructuring. To clarify this issue, we performed calculations, layer-by-layer, local densities of electronic states (LDOS). In order not to clutter the paper with many similar results, we limited ourselves to pure silicon with the Si (100)-p (2×2) surface and systems of 1 and 2 ML Li on Si (100). The first case is interesting due to the presence of dimers on the silicon surface, which leads to a band gap significantly smaller than in bulk silicon; the second case demonstrates a sharp increase in the Egap width and its sharp disappearance. Local densities of states for pure silicon with the Si (100)-p (2×2) surface are shown in (Figure 7).

This figure shows that in the LDOS corresponding to the top layer, the band gap has a small width (0.54 eV) and is limited on both sides by high peaks of occupied and unoccupied states. Next, we see that gradually, from layer to layer, the relative intensities of the nearby free states, marked by arrows, decrease and go to zero towards the last layer, thereby opening an approximately twice wider gap (≈1.0 eV), satisfactorily corresponding to the value of Egap in bulk silicon (1.12 eV) (Figure 8). Shows the LDOS for systems of 1 and 2 monolayers of Li on Si (100). This figure shows that in the case of 1 ML Li coating (A panels) densities of states near the Fermi level are very similar in the top, middle and bottom of the silicon slab, and the band gap remains practically the same everywhere. On contrary, 2 ML Li coating (B panels) leads to disappearing of the band gap, and metal-induced unoccupied states present at the Fermi level up to the bottom of the silicon slab.

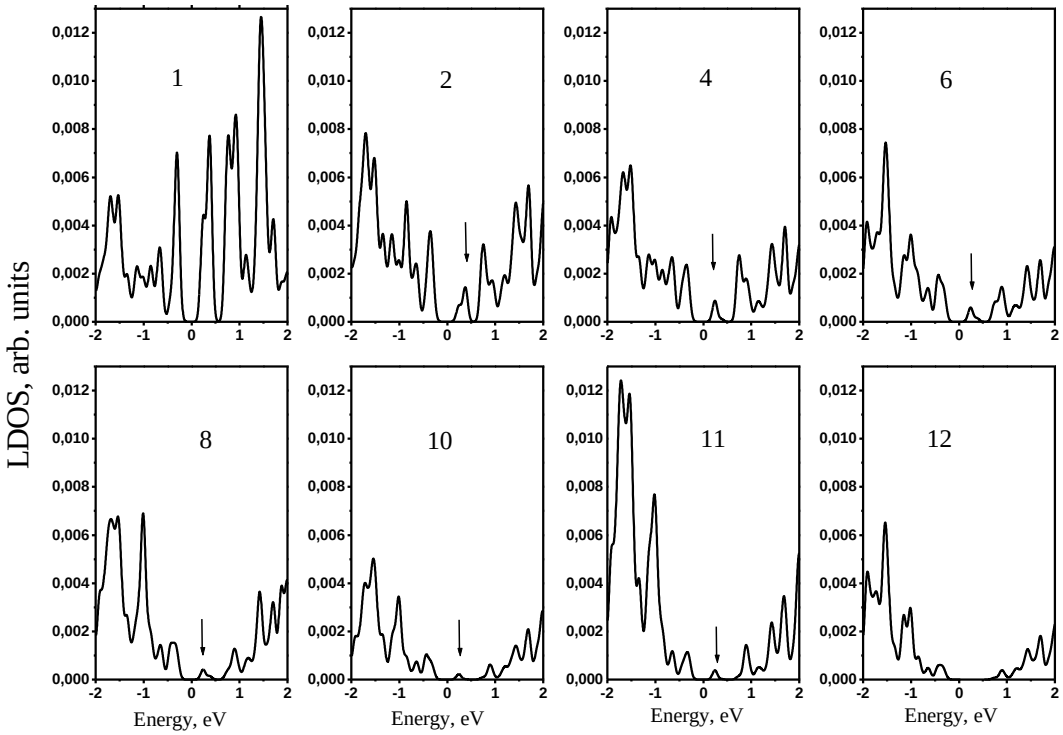

Figure 7: *Local densities of states for pure silicon with the Si (100)-p (2× 2) surface. The numbers show the numbers of layers, starting from the surface where the dimers are formed.*

Conclusions

Our calculations showed that in the Li-Si (100) system there is a noticeable mixing of the metal and silicon layers. In the cases of beryllium and aluminum the ordered and disordered structures are formed without signs of significant mixing with silicon. As for the electronic structure, in the 1 MC Li-Si (100) and 1 MC Be-Si (100) systems, the energy gap is observed, while in the Al-Si (100) system there is no gap. When deposited the second monolayer, the gap in the Li-Si (100) system disappears, but in the Be-Si (100) system the gap remains. When three monolayers of beryllium are deposited, the gap disappears. Calculations of local densities of states have shown that when computer studying the electronic structure of near-surface regions of silicon, one need to be very careful because the metal-induced states penetrate even at the twelve-atomic layer deep.

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