



Electronic Structure of Li, Be, and Al Ultra Thin Coverings on the Si(100) Surface

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Abstract

Within the framework of density functional theory and the pseudopotential method, calculations of the density of electronic states of the system “Si(100) substrate plus disordered two-dimensional metal layers (Li, Be or Al)” with a thickness of one to four single-atomic layers were carried out during growth at 0°K. It is shown that the electronic structure of the first single-atomic layers of these metals on Si(100) has band gaps. The maximum band gap was found in the Be-Si system (1.03 eV for a single-atomic layer). In this system, the band gap disappears when four single-atomic layers are deposited. In the Li-Si system (0.98 eV for a single-atomic layer) it disappears for two single-atomic layers. In the Al-Si–system (0.50 eV with four single-atomic layers), the band gap disappears for three single-atomic layers. This behavior of the band gap can be explained by the passivation of the substrate surface states and the peculiarities of the electronic structure of the adsorbed metals.



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Introduction

Metal layers on silicon have long attracted the attention of researchers. However, this mainly refers to layers of refractory 3d transition metals that form stable silicides. (See for example recent publications.¹⁻³ Layers of low-melting metals on silicon have not been studied enough. The most indicative include works,⁴⁻¹⁷ where the atomic and electronic structure of the ultra-thin layers on Si(100) and Si(111) surfaces was studied. Work⁷ 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. Unfortunately, we were unable to find similar publications concerning the electronic structure of the Be-Si(100) and Al-Si(100) systems.

This work is devoted to computer modeling of ultra thin (one to four single-atomic layers thick) disordered coatings of Al, Be and Li on the Si(100) surface using

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the Kohn-Sham method¹⁸ within the framework of the density functional theory¹⁹ and the pseudopotential method.²⁰

Research Methodology

All calculations were performed using the FHI96md package.²¹ Pseudopotentials were found using the FHI98pp package.²⁰ To calculate the exchange-correlation energy, the local electron density approximation was used^{22,23} In all cases, the cutoff energy of a set of plane waves was taken to be 14 Ry; calculations were carried out with the five k-points: (0.5; 0.5; 0.5), according to the 3x3x1 scheme, in a supercell with dimensions 14.54x14.54x40 (all values are given in atomic units, 1 atomic unit = 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 four single-atomic layers (SAL), in which each SAL contained four atoms, and the lower SAL 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 (40 atomic units) for the supercell ensures that there is no interaction between the virtual plates in Z dimension.

The atoms of the lower SAL of silicon were fixed; the atoms of the remaining layers, as well as the atoms of the studied metals, could shift under the action of quantum mechanical interatomic forces.

Each metal SAL also contained four atoms. Their deposition was carried out in a disordered manner using a special program developed by us based on a random number generator. At the same time, bringing the system to a state of local minimum total energy was carried out at a temperature of 0°K. Therefore, the behavior of metal layers on a cold silicon substrate was actually studied.

To make sure that the band gap arises precisely during the interaction of silicon with metal, we also calculated the DOS for metal layers taken separately from the silicon substrate.

Results and Discussion

Calculations showed that for all the metals studied, despite the randomness of the initial deposition of their atoms in the forming layers, the structures obtained after atomic relaxation turned out to be very similar. As an example, Figure 1 shows the arrangement of Li, Be and Al atoms when the first single-atomic layers of metals are deposited on the Si(100) surface.

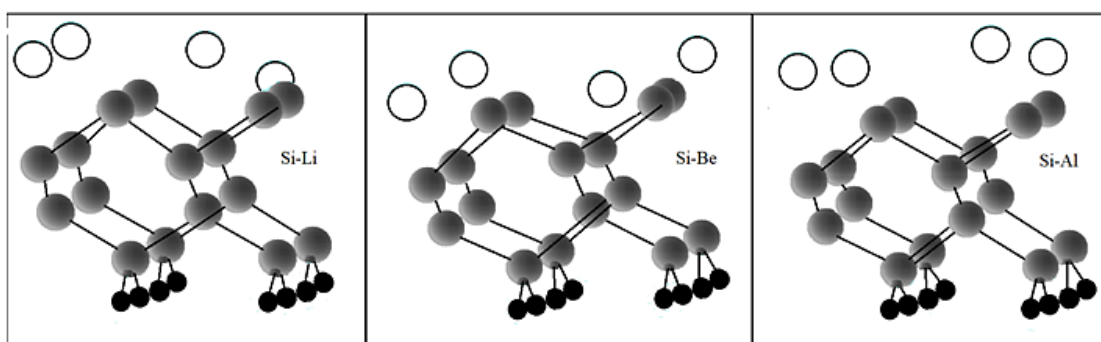


Fig. 1: Arrangement of atoms in the Si-Li, Si-Be and Si-Al systems when the first disordered metal single-atomic layers are deposited on the Si(100) surface. White circles are metal atoms, gray circles are silicon atoms, black circles are hydrogen atoms.

It can be seen that, under the influence of the structure of the silicon surface, some ordering of the arrangement of metal atoms occurred, but in all cases the structure of the metal single-atomic layers

was still far from epitaxial. The structure of systems with a greater number of single-atomic layers than one became increasingly disordered with increasing thickness.

Figure 2 shows the distribution patterns of the density of states (DOS) formed when the first single-atomic layers of Li, Be and Al are deposited on the surface. The DOS for a clean Si(100)- 2x1 surface with the gap of 0.35 eV is also shown

there. Note that the reconstruction of the structure of the Si(100)→Si(100)-2x1 surface occurred spontaneously during the relaxation of the free Si(100) surface, and during calculations with adsorbed metal layers, the reconstruction disappeared

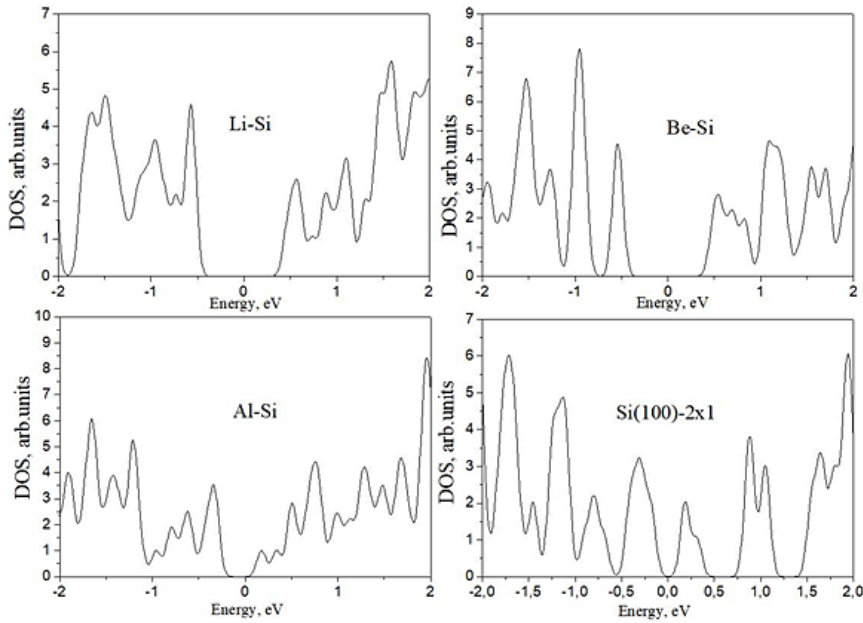


Fig. 2: Density of electronic states formed when the first single-atomic layer of Li, Be and Al is deposited on the Si(100) surface in comparison with the density of states for a clean Si(100)-2x1 surface. The Fermi level corresponds to zero energy.

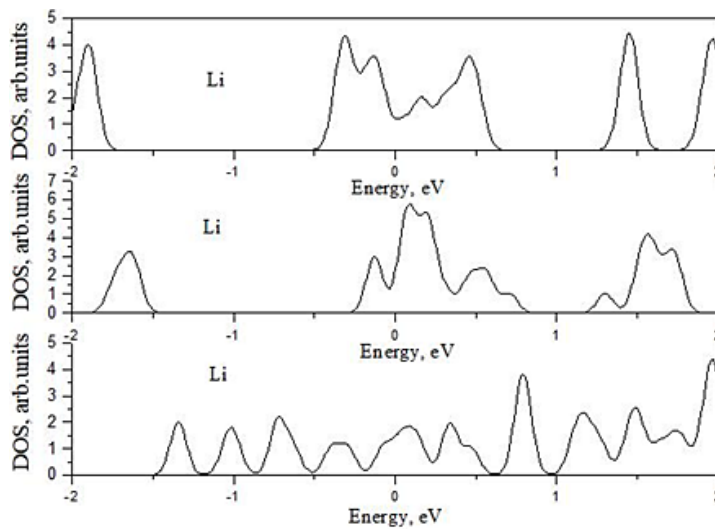


Fig. 3: DOS corresponding to single-atomic layers of Li, Be and Al taken separately from the silicon substrate.

From this figure it is clear that in all cases there is an energy gap near the Fermi level: 0.98 eV for Li-Si, 1.03 eV for Be-Si and 0.50 eV for Al-Si. For the clean Si(100)-2x1 surface, we obtained 0.35 eV in good agreement with the known data given in published works²⁴ - 0.4 eV (electron energy loss spectroscopy method);²⁵ - 0.5 eV (scanning tunneling spectroscopy method); and²⁶ - 0.2-0.3 eV (calculations from first principles). At the same time, we did not detect an energy gap in the electronic structure of Li, Be and Al single-atomic layers without a silicon substrate (Figure 3).

The deposition of the second single-atomic layer led to the fact that in the Li-Si system the gap in the density of states disappeared (which is consistent with the results of),²⁶ in the Be-Si system it decreased to 0.61 eV, and in the Al-Si system it increased to 0.62 eV, which is illustrated in Figure 4 - (top panels). In contrast, the density of states of two single-atomic layers of Li, Be and Al without a substrate has a metallic character, as can be seen in the same figure (lower panels), as in the case of a single-atomic layer,

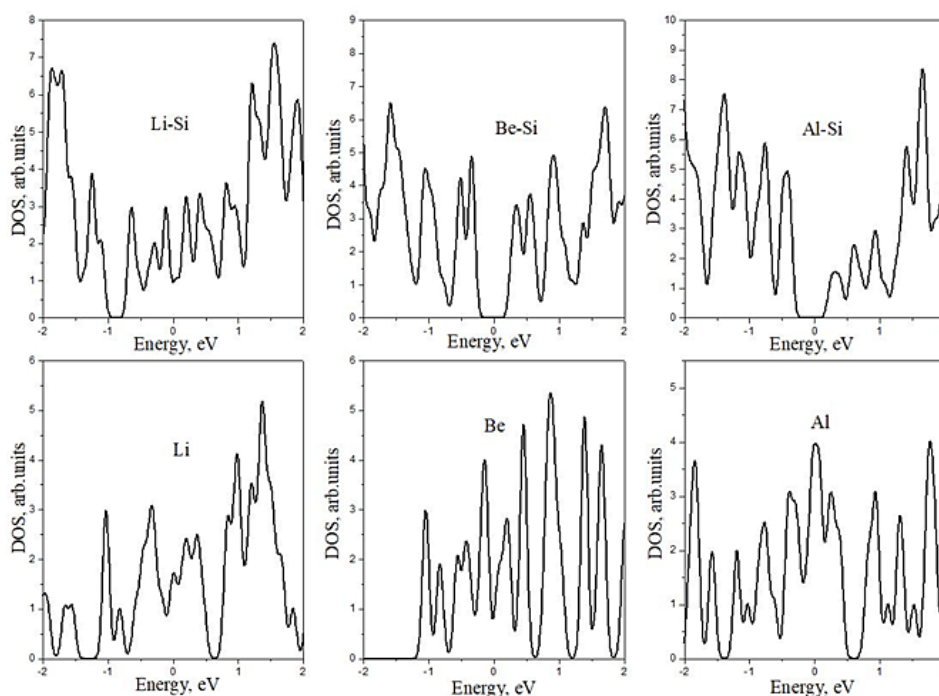


Fig. 4: Densities of states of Li-Si, Be-Si and Al-Si systems with two metal single-atomic layers. On the lower panels there is a DOS for two single-atomic layers of Li, Be and Al, taken separately from the silicon substrate.

We did not examine the Li-Si system during the deposition of the third single-atomic layer, since we were interested in the presence of the energy gap, and in this system the gap disappeared already with two metal single-atomic layers. The DOS for the Be-Si and Al-Si systems are shown in Figure 5 (top panels). In the Be-Si system, the gap decreased to 0.27 eV, and in the Al-Si system it completely disappeared. Calculation of three single-atomic

layers of beryllium and aluminum separately from silicon demonstrated the metallic nature of their DOS (see Figure 5, bottom panels).

To find out whether the energy gap in the Be-Si system will disappear when another (fourth) Be single-atomic layer is deposited on the silicon surface, we carried out the corresponding calculations and plotted the density of states in Figure 6.

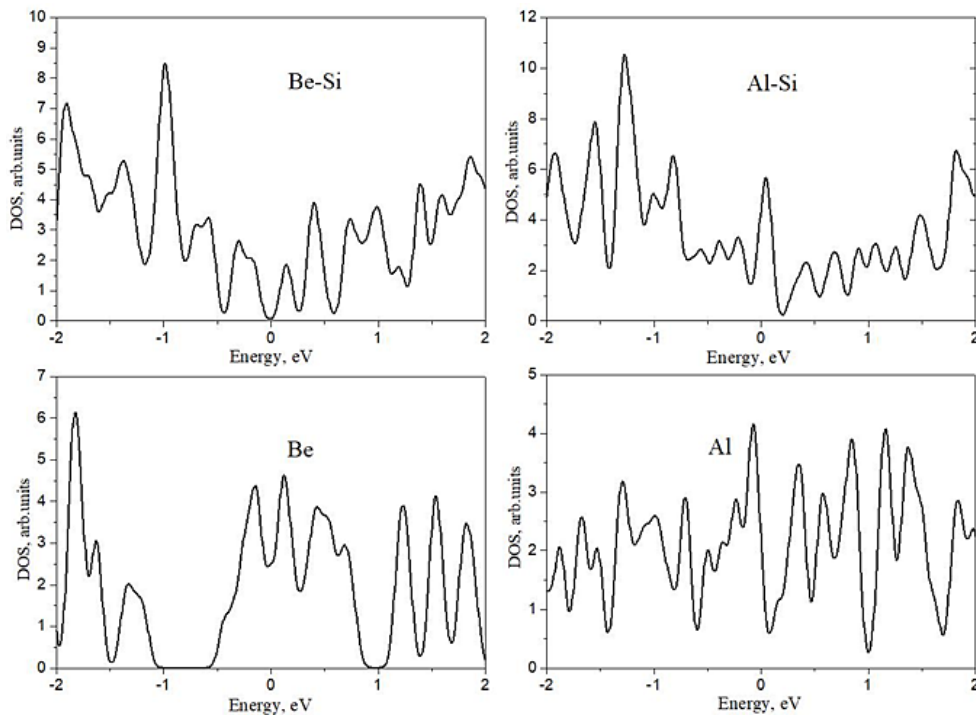


Fig. 5: DOS for Be-Si and Al-Si systems with three metal single-atomic layers. Here (on the lower panels) is a DOS for three single-atomic layers of Be and Al, taken separately from the substrate.

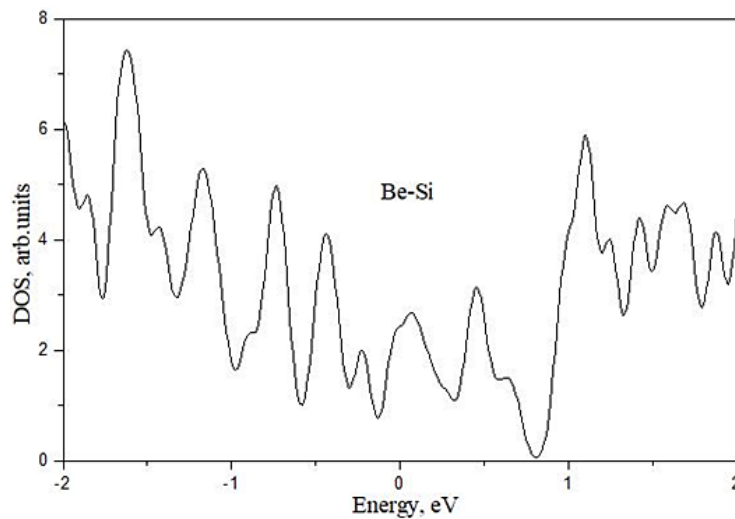


Fig. 6: DOS for the Be-Si system with four metal single-atomic layers

From this figure it is clear that the DOS for the Be-Si system with four single-atomic layers of beryllium has a metallic character.

Thus, the results obtained show that in disordered Li-Si(100), Be-Si(100) and Al-Si(100) systems with metal single-atomic layers, electronic structures with

band gaps, usually wider than that of the substrate, are formed, and the bands disappear with increasing thickness of the deposited metal layers. Moreover, they disappear most quickly for Li (with two SAL), then for Al (with three SAL) and last of all for Be (with four SAL).

We can compare our results with published data only for the Li-Si system ⁷ where a band gap with a width of about 1.3 eV was discovered when a single-atomic layer of Li was deposited on the Si(100) surface, and where it disappeared for two single-atomic layers. These data correlate with ours, and the more small gap value we obtained with a SAL (0.98 eV) is apparently associated with the disorder of our metal SAL: in⁷ Li atoms were placed in symmetrical positions corresponding to the absolute minimum of the total energy.

Conclusion

Electronic structure calculations by the Kohn-Sham method using pseudopotentials showed that in the densities of electronic states of two-

dimensional "metal-Si(100)" systems with Al, Li and Be disordered layers of the single-atomic thick, band gaps with widths of 0.5 eV, 0.98 eV and 1.03 eV appear, respectively. These gaps disappear with increasing thickness of the metal layers: first in the Si-Li system (for two SAL), then in the Si-Al system (for three SAL) and then in the Si-Be system (for four SAL).

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Conflict of Interest

The authors have no conflict of interest with anyone.

References

1. A.A. Monyak G.S. Grebenyuk, E.Yu. Lobanova, M.V. Kuzmin. *St. Petersburg Polytechnic University Journal. Physics and Mathematics*. 16(1.3). 55–61 (2023). DOI: <https://doi.org/10.18721/JPM.161.309>.
2. I.V. Chepkasov, V.S. Baidyshev, E.V. Sukhanova, M.A. Visotin, P. Süle, Z.I. Popov. *Appl. Surf. Sci.*, 527, 15, 146736 (2020), doi: <https://doi.org/10.1016/j.apsusc.2020.146736>.
3. N.I. Plusnin. *Tech. Physics*, Vol. 68, No. 1 13. 146-155. (2023) DOI: 10.21883/TP.2023.01.55449.191-22.
4. V.G. Kotlyar, A.A. Saranin, A.V. Zotov, V.G. Lifshits, O. Kubo, H. Ohnishi, M. Katayama, K. Oura. *Surf. Sci.*, 506, 80 (2002).
5. G.H. Coccoletzi, N. Takeuchi. *Surf. Sci.*, 504 101 (2002).
6. J.E. Northrup. *Phys. Rev. Lett.* 53(7) 683 (1984).
7. Young-Jo Ko, K.J. Chang, Jae-Yel Yi. *Phys. Rev.*, 56(15), 9575 (1997).
8. Y. Morikawa, K. Kobayashi, K. Terakura, S. Blugei. *Phys. Rev. B*, 44(7), 3459 (1991).
9. M.J. Haye, P.M.L.O. Scholte, A.F. Bakker, S.W. de Leeuw, F. Tuinstra, G. Brocks. *Phys. Rev. B*, 56(4), R1708 (1997).
10. Sukhim Jeong, Myung-Ho Kang. *Phys. Rev. B*, 51(24), 17635 (1995).
11. A.S. Rysbayev, M.T. Normurodov, Zh.B. Khuzhaniyozov, A.A. Rysbayev, D.A. Normurodov. *Poverkhnost'. Rentgenovskiy, Sinkhrotronnyy i Neytronnyy Issledovaniya*, 6, 75 (2021) (in Russian).
12. D. Hite, S. Tang, P. Sprunger., *Chem. Phys. Lett.*, 367, 129 (2003; DOI:10.1016/S0009-2614(02)01637-8).
13. A.A. Saranin, A.V. Zotov, V.G. Kotlyar, T.V. Kasyanova, O.A. Utas, Hideaki Okado, Mitsuhiro Katayama, Kenjiro Oura. *Nano Lett.* 4(8):1469 (2004).
14. I. Gordeev, L.N. Kolotova, V. Starikov. *Scripta Materialia*, 210, 114481 (2022); doi/ 10.1016/j.scriptamat.2021.114481.
15. V.A. Terekhov, D.S. Usoltseva, O.V. Serbin, I.E. Zanin, T.V. Kulikova, D.N. Nesterov, K.A. Barkov, A.V. Sitnikov, S.K. Lazaruk, E.P. Domashevskaya. *Cond. Matter Interphases*,

- 20(1), 135 (2018). <https://doi.org/10.17308/kcmf.2018.20/485>.
16. Endo, K., Arima, K., Kataoka, T. et al. *Appl Phys A* 66(1), S145–S148 (1998). <https://doi.org/10.1007/s003390051118>.
17. I. Jum'h, H.H. Abu-Safe, M.E. Ware, I.A. Qattan, A. Telfah, C.J. Tavares. *Nanomaterials*, 13, 970. (2023) <https://doi.org/10.3390/nano13060970>
18. W. Kohn, J.L Sham. *Phys. Rev.*, 40, A1133 (1965).
19. P. Hohenberg, W. Kohn. *Phys. Rev.*, 136, B864 (1964).
20. M. Fuchs, M. Scheffler. *Comp. Phys. Commun.*, 119, 67 (1999).
21. M. Beckstedte, A. Kley, J. Neugebauer, M. Scheffler. *Comp. Phys. Commun.*, 107, 187 (1997).
22. J.P. Perdew, A.S. Zunger. *Phys. Rev.*, 23, 5048 (1981).
23. D.M. Ceperley, B. J. Alder. *Phys. Rev.*, 45, 566 (1980).
24. L. Gavioli, M.G. Betti, A. Cricenti, C. Mariani. *J. Electron. Spectrosc.*, 76, 541 (1995).
25. Kenji Hata, Yasunori Shibata, Hidemi Shigekawa. *Phys. Rev. B*, 64, 235310 (2001).
26. J. Fritsch, P. Pavone. *Surf. Sci.*, 344, 159 (1995).