

The interactions of metallic and semiconducting adsorbates with Si(100)

This article has been downloaded from IOPscience. Please scroll down to see the full text article.

1994 J. Phys.: Condens. Matter 6 8141

(<http://iopscience.iop.org/0953-8984/6/40/006>)

View [the table of contents for this issue](#), or go to the [journal homepage](#) for more

Download details:

IP Address: 171.66.16.151

The article was downloaded on 12/05/2010 at 20:41

Please note that [terms and conditions apply](#).

The interactions of metallic and semiconducting adsorbates with Si(100)

G S Khoo† and C K Ong‡

† Division of Physics, School of Science (National Institute of Education), Nanyang Technological University, 469 Bukit Timah Road, Singapore 1025, Singapore

‡ Department of Physics, National University of Singapore, Lower Kent Ridge Road, Singapore 0511, Singapore

Received 10 May 1994

Abstract. We have investigated the interactions of several adsorbates, Al, C, Ge and Mg, with the Si(100) 2×1 surface using a semiempirical molecular orbital method. Our results show that elements with a smaller electronegativity than that of the substrate (Si), such as Al and Mg, lose charge to the substrate, whereas C and Ge, which both have a higher electronegativity, gain charge. These findings are compatible with the experimental studies on the phenomena of electromigration on the Si(100) 2×1 surface where different adsorbates migrate in different directions with respect to the electron flow on the surface. A more detailed study is made on the adsorption and diffusion properties of Al on the Si(100) surface. Al is found to be highly mobile with a preferred diffusion path perpendicular to the dimer rows. For diatomic Al, our calculations favour the parallel ad-dimer model rather than the orthogonal model, in agreement with the findings of Northrup *et al* and Itoh *et al*. In addition, for Al adsorption in the vicinity of a missing dimer, the atomic configuration of the terminating Al atom at the end of the Al dimer line is compatible with that observed under the STM.

1. Introduction

Previous work has shown that the interactions of adsorbates, particularly metallic atoms in thin-film conductors of electronic devices, tend to deteriorate the performance of the conductors, causing them to be electrically defective [1–3]. One such influence of these metals is on the phenomenon of electromigration or current induced mass transport. This is believed to arise from a momentum exchange between conducting electrons and ions, producing atomic diffusion [1]. However, there is still controversy regarding the direction of electromigration as different metals migrate in different directions with respect to electron flow [4].

Recently, Ichinokawa *et al* [4] investigated the electromigration of metallic islands formed by vapour deposition on the Si(100) 2×1 surface with an ultra-high-vacuum scanning electron microscope. In their experiment, they heated the Si substrate to temperatures higher than the melting points of the islands while passing a direct current through the Si substrate. The direction of the island migration was found to be dependent on the type of metal. The authors proposed that the charge transfer between the semiconductor substrate and the metal gives a rough indication to predict the direction of electromigration. For instance, they found that Au islands migrate in the same direction as the electron flow whereas Al migrates in the opposite direction. They attributed this conflicting observation to the different electronegativities of the metals with respect to that of Si. The electronegativity of

Au is larger than that of Si while that of Al is smaller. Thus, the sign of the charge transfer between the Si substrate and the metal atom determines the direction of the electromigration [4].

Presently, we will demonstrate that the above proposal to account for the observed contrasting directions of electromigration for different adsorbates on the Si(100) surface based on their different electronegativities with respect to that of Si is consistent with theoretical calculations supporting the charge transfer model. For convenience and familiarity with the parameters we have used in our previous investigations, we take as model atoms C and Ge, which are in the same group as Si in the periodic table and whose electronegativities are higher than that of Si, while Al and Mg are the model atoms with electronegativities lower than that of Si. Our results show that when these metallic and semiconducting atoms are deposited on the Si(100) surface, the sign of the charge transfer between the Si substrate and the adsorbates is influenced by their electronegativities with respect to that of Si, consistent with the experimental results described above [4].

In order to have more insight into the interaction between the adsorbates, especially the metallic atoms, and the substrate, the Si(100) surface, we also investigate in more detail the adsorption and diffusion properties of Al on the Si(100) surface to compare to recent findings from scanning tunnelling microscopy (STM) experiments by Nogami *et al* [5], who reported the growth of several well ordered phases for low coverage of Al on Si(100). In particular, the 2×2 phase is complete at 0.5 ML (monolayer), without disruption of the surface Si-Si dimer bonds. Nogami *et al* [5] put forward two models of the 2×2 structure that may account for their STM results: the Si(100) 2×2 orthogonal ad-dimer and the Si(100) 2×2 parallel ad-dimer. For the former, Al atoms are adsorbed on the surface as dimers between the Si dimer rows, oriented perpendicularly to the Si-Si dimer bond. In the latter model, each Al dimer is now rotated through 90° so that it is parallel to the adjacent Si dimers, similar to the findings of Steele *et al* [6] for the Si(100) 2×2 -In surface. While experimentally [5] these two forms of Al ad-dimers were never conclusively distinguished, recent theoretical calculations [7, 8] tend to favour the parallel ad-dimer configuration. Very recently, Itoh *et al* [9] also reported that their STM results for the 2×2 and 2×3 structures of the Al/Si(100) surface appear to support the parallel ad-dimer structure proposed by Northrup *et al* [7]. Additionally, they investigated the atomic arrangement at the end of the Al-dimer lines, i.e. when the neighbouring Si dimers are missing [9].

Our findings for the more detailed study of Al on Si(100) will be shown to consolidate the ad-dimer model for the Si(100) 2×2 -Al surface established from theory [7, 8] and experiments [9] thus far. Al is highly mobile on the Si(100) surface with a low-energy channel in the direction perpendicular to the dimer rows, between two adjacent dimers in a dimer row. Our calculations also favour the parallel Al ad-dimer model, in agreement with the findings of Northrup *et al* [7] and Itoh *et al* [9]. In addition, we also investigate the adsorption of an Al atom in the vicinity of a missing Si dimer and find that the Al atom prefers a bonding site different from the case for the perfect surface. This site is similar to the atomic configuration of the terminating Al atom at the end of the Al dimer line where a neighbouring Si dimer is missing, observed under the STM [9].

2. Theoretical method

We use a well established semiempirical self-consistent molecular orbital method: the complete neglect of differential overlap (CNDO) method [10] to investigate the adsorption of Al, C, Ge and Mg atoms on the Si(100) surface. In this method, the Hartree-Fock-Roothaan equations are solved via the introduction of semiempirical parameters. The CNDO

method can be derived either as a systematic approximation of the Hartree–Fock theory [11] or a systematic approximation of density functional theory [12]. It has been especially successful in defect studies where geometries and charge densities are concerned as well as total energies [13, 14]. Recently, it has also been employed to investigate the adsorption properties of metals on stepped and unstepped semiconductor surfaces [15]. We have also simulated the enhancement of emission of Si atoms from the Si(100) and (110) surfaces by deposition of Cl atoms on the surface [16]. In the present work, the CNDO parameters for C, Si [17] and Ge [14] yield calculated values of their bulk properties in good agreement with experimental data while the parameters for Al and Mg are from Pople and Beveridge [10]. We implement the MOSES code [18] and calculations are performed on a 63-atom (100) surface cluster to depict the Si(100) surface, details of which have been provided previously in [19]. A larger simulation cluster is used for the case of the adsorption of Al atoms on the Si surface with a missing dimer.

3. Surface reconstruction and calculations

Before investigating the adsorption and charge transfer of the metal atoms on the Si(100) surface, we first carry out the various kinds of surface reconstruction as outlined in [19] and obtain the minimum-energy configuration for the 2×1 dimer structure on Si(100), where two adjacent atoms on the surface bend towards each other to form a third covalent bond, so that this pair of atoms constitutes a dimer. The calculated dimer bond length for the Si(100) 2×1 surface is greater than the bulk bond length by 1.92%. This is consistent with low-energy ion scattering spectroscopy results [20], which determine the dimer bond length to be 2.4 ± 0.1 Å. Charge transfer polarization is also treated in our self-consistent calculations and the minimum total energy found will also include terms that allow net charges on atoms and place these charge entities at the appropriate positions. The charge transfer obtained for the 2×1 reconstruction is about $0.15e$. Other surface relaxations such as the 4×1 , 4×2 and 2×2 Å yield total energies per dimer reasonably close to each other, which have already been described in detail in [19]. After obtaining the minimum-energy configuration for Si(100) 2×1 surface, we introduce the adsorbates with different electronegativities compared with that of Si on the surface to investigate the possibility of charge transfer between them and the Si surface. More detailed calculations are subsequently performed for the case of the Al atoms on Si(100) to correlate to experimental results for the Si(100) 2×2 -Al surface [5, 9]. The results of our calculations for these systems are described below.

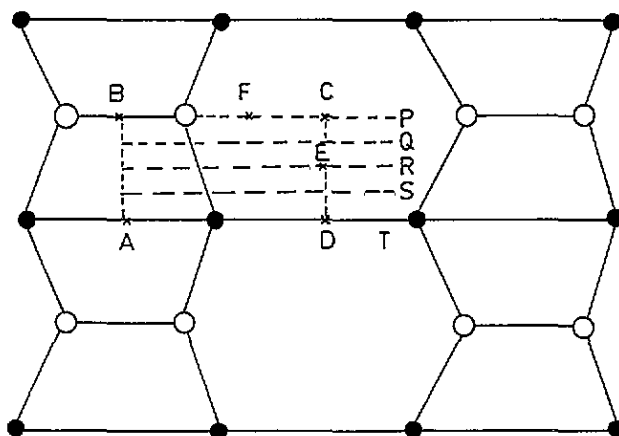
4. Results and discussion

4.1. Adsorption and charge transfer on Si(100) 2×1

We investigate the interactions of the metallic and semiconducting atoms with each pair of dimers where subsequent relaxations are then taken into account for the adsorbates and the pair of dimers involved. We pay special attention to the possible adsorption sites, A, B, C, D and E, as shown in figure 1. Three of the adsorbates, C, Ge and Mg, prefer to occupy the usual epitaxial site (B) between two surface Si atoms, saturating their dangling bonds (see figure 1). Table 1 illustrates the Si–X bondlengths for the three cases where X = C, Ge and Mg. For C especially, adsorption leads to further penetration of the C atom, with the C atom displaced by 0.46 Å vertically downwards from the usual epitaxial site, where it

Table 1. Adatom-substrate bond lengths (Si-X, where X = Al, C, Ge and Mg) for adsorption on the Si(100) surface.

Element, X	Si-X bond length (Å)
Al	2.68
C	1.99
Ge	2.37
Mg	2.36

**Figure 1.** The top view of the Si(100) 2×1 surface. Surface Si atoms are shown as open circles and second-layer Si atoms as dark circles. Total energy calculations are performed for the adsorbate atoms at different points along five traverses, P, Q, R, S and T within the rectangular grid ABCD. A, B, C, D, E and F are possible adsorption sites.

saturates the dangling bonds of two of the surface Si atoms, yielding an Si-C bond length of 1.99 Å, quite close to the bulk bond length of SiC (2.03 Å). Thus, all three break the dimer, but they differ in the extent of penetration on the surface.

C appears to have the most interaction with the Si surface, possibly because they are both group IV elements and alloying and intermixing lead to stable binary compounds such as SiC. C is more penetrating because of its smaller size whereas the Ge atom, which is slightly bigger than Si, has less or no penetration. The calculated Si-Ge bond length is however in good agreement with the sum of their atomic radii, while that for the Si-C is quite close to the bulk bond length of SiC. Thus, the Si(100) surface shows promise as a substrate for the growth of SiC crystals as C atoms are deposited on the clean Si(100) surface.

In contrast, Al has less reactivity with the Si(100) 2×1 surface, preferring to adsorb at site A, right at the centre, midway on the axis between two neighbouring dimers on the same row (see figure 1). The calculated Si-Al bond length for Al at this site is 2.68 Å, the extended bond length reflecting its lack of reactivity with the Si surface as is the case with III-V surfaces [15].

Table 2 gives the electronegativities of the adsorbate atoms and Si, together with the sign of the charge transfer between them and the Si(100) 2×1 surface. As can be seen, the trend of the charge transfer is consistent with the values of their electronegativities relative to that of Si. Both the Al and Mg atoms lose charge to the Si surface while both C and Ge gain charge, although the gain for Ge is the smallest (the electronegativity of Ge is also

Table 2. The electronegativities of adsorbates and the sign of the charge transfer between these adsorbates and the Si(100) surface ('+' sign for a loss of charge to Si substrate, '-' sign for a gain in charge).

Element	Electronegativity	Charge transfer
Al	1.61	+0.23e
C	2.55	-0.20e
Ge	2.01	-0.04e
Mg	1.31	+0.30e
Si	1.90	—

the closest to that of Si). C and Mg exhibit the greatest values in the charge transfer, a reflection of the greater disparity between their electronegativities and that of Si (refer to table 2).

Our findings appear to support the proposal by Ichinokawa *et al* [4] that the relative electronegativities of the metallic adsorbates with respect to that of Si can influence the sign of the charge transfer between adsorbate atoms and the Si(100) 2×1 surface and, hence, predict the direction of the electromigration of the metallic islands on an Si surface as observed from UHV-SEM experiments [4]. Adsorbates with higher electronegativities (C and Ge) appear to gain charge from the Si substrate while those with lower electronegativities (Al and Mg) seem to lose charge, rendering them either positively or negatively charged on the Si substrate. Therefore, the sign of the charge transfer between the adsorbates and the Si substrate may influence how these adsorbates will move when a direct current is passed through the Si substrate, consistent with the experimental observations [4]. Presumably, the induced charge on the adsorbate interacts with the current, giving rise to the observed electromigration. Understanding of the origin of this phenomenon will have great implications in the semiconductor industry for interpreting the process of electromigration of integrated circuits.

4.2. Al diffusion and ad-dimer on Si(100)

We now turn to the calculations for different locations of the Al atom with the rectangular grid ABCD along five traverses, P, Q, R, S and T, perpendicular to the dimer rows, as shown in figure 1, to investigate the diffusion profile of Al on Si(100). At each location, the Al atom is moved perpendicularly to the surface to obtain the local minimum. When the results of the calculations are repeated over the whole surface, we obtain the total energy surface for Al on Si(100). There appears to be a low-energy channel perpendicular to the dimer rows, midway between adjacent dimers belonging to the same row. The global minimum is at site A along traverse T, centrally located midway between two neighbouring dimers in the same dimer row as shown in figure 1. The binding energy of the Al adatom at this location is 3.92 eV. The next lowest minimum-energy site is at E (in figure 1), 0.19 eV higher than at A. There also appears to be a shallower trough parallel to the surface Si dimer rows, between adjacent rows, along which site B lies. These results are compatible with those of Brocks *et al* [8].

Next, we introduce another Al atom on the surface and minimize the total energy for several configurations of two Al atoms on the Si(100). Figure 2 illustrates the two lowest-energy configurations, with the parallel ad-dimer (figure 2(a)) being lower than the orthogonal ad-dimer (figure 2(b)) by 0.68 eV. Table 3 summarizes our findings in comparison with the calculations of Brocks *et al* [8] and Northrup *et al* [7]. In terms of the geometric properties of the Al ad-dimer configuration on Si(100), our findings are more

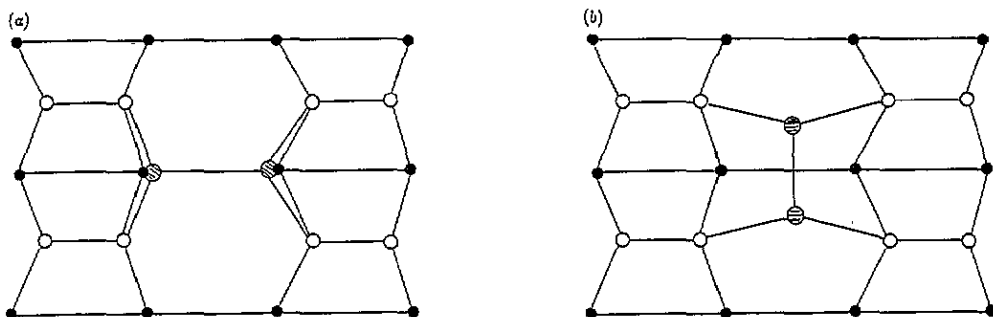


Figure 2. The minimum-energy configurations for two Al atoms on the Si(100) 2×1 surface: (a) the parallel ad-dimer and (b) the orthogonal ad-dimer. Surface Si atoms are shown as open circles and second-layer Si atoms as dark circles. Shaded circles denote the adsorbed Al dimer.

Table 3. A comparison of the calculated bond lengths in ångströms of the Si dimer, the Al ad-dimer and the separation (Δz) between the planes containing the Si dimer and the Al ad-dimer in the present work (a) with those of Northrup *et al* [7] (b) and Brocks *et al* [8] (c).

	Parallel			Orthogonal		
	a	b	c	a	b	c
Si-Si dimer	2.46	2.44	2.36	2.68	2.69	2.36
Ad-dimer	2.71	2.69	2.67	2.60	2.58	2.62
Δz	0.98	1.10	1.35	0.76	0.71	—

consistent with those of Northrup *et al* [7], although qualitatively, all three findings agree that the parallel ad-dimer is preferred to the orthogonal ad-dimer model.

Recent STM observations of the structures of low-coverage phases of Al on the Si(100) surface by Itoh *et al* [9] also verify this result that the parallel ad-dimer model proposed by Northrup *et al* [7] is the more stable. In addition, Itoh *et al* [9] also examine the atomic arrangement at the end of Al dimer lines, where neighbouring Si dimers are missing. Supplementary calculations are performed firstly for a single Al atom in the vicinity of a missing Si dimer, and secondly, for three Al atoms to simulate the work of Itoh *et al* at the end of the Al dimer line. For the case of the single Al atom, its equilibrium bonding site is no longer site A in figure 1, but site T in figure 3(a), between two Si dimer rows (R_1 and R_2), but closer to the Si dimer row (row R_1) without any missing dimer. For the three-atom case, two of the Al atoms originally form a parallel ad-dimer as in figure 2(a), while the third is then introduced at locations in the region bordering the edge of the Si dimer rows and in the vicinity of the missing Si dimer. This third atom is moved along the axis of the parallel Al ad-dimer, perpendicular to the Si dimer rows as well as along the channel parallel to the Si dimer rows, between the two neighbouring dimer rows R_1 and R_2 (which has a missing Si dimer). The equilibrium site of this third Al atom is illustrated in figure 3(b), corresponding to site T in figure 3(a); displacements of this Al atom in directions either parallel or perpendicular to the Si dimer rows from this site result in higher energy. This site is equivalent to one end of the Al ad-dimer in the parallel configuration, except that the Al is now displaced towards the surface, compared with its neighbouring counterparts constituting the ad-dimer.

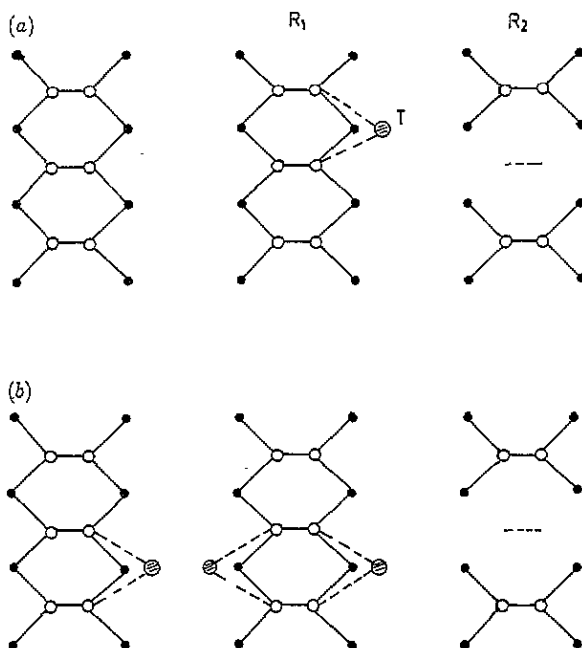


Figure 3. The minimum-energy configuration for (a) a single Al atom and (b) three Al atoms adsorbed on the Si(100) 2×1 surface with a missing dimer. Surface Si atoms are shown as open circles and second-layer Si atoms as dark circles. Shaded circles denote adsorbed Al atoms and --- is the site of the missing Si dimer.

5. Conclusion

Our present results suggest that adsorbate atoms on the Si(100) surface can appear as either positively or negatively charged ions, depending on their relative electronegativities with respect to the Si substrate. The results support the electromigration experiments of Ichinokawa *et al* [4]. Our calculations of the adsorbed Al dimer on Si(100) consolidate the 2×2 parallel ad-dimer model. The preferred adsorption site for a single Al atom on the perfect surface is different from that on the surface with a missing dimer. The Al atom prefers site A (figure 1) on the perfect surface whereas site T (figure 3(a)) is favoured on the surface with the missing dimer. This finding corresponds well with the experimental observation of the atomic configuration of the terminating Al atom at the end of the Al dimer line.

References

- [1] Huntington H B 1975 *Diffusion in Solids (Recent Development)* ed A S Nowick and J J Burton (New York: Academic) ch 6
- [2] Zhou J M, Baba S and Kinbara A 1982 *Thin. Solid Films* **98** 109
- [3] Yasunaga H and Sasuga E 1990 *Surf. Sci.* **231** 263
- [4] Ichinokawa T, Izumi H, Haginoya C and Itoh H 1993 *Phys. Rev. B* **47** 9654
- [5] Nogami J, Baski A A and Quate C F 1991 *Phys. Rev. B* **44** 1415
- [6] Steele B E, Lian Li, Stevens J L and Tsong I S T 1993 *Phys. Rev. B* **47** 9925
- [7] Northrup J E, Shabel M C, Karlsson C J and Uhrberg R I G 1991 *Phys. Rev. B* **44** 13799

- [8] Brocks G, Kelly P J and Car R 1993 *Phys. Rev. Lett.* **70** 2786
- [9] Itoh H, Itoh J, Schmid A and Ichinokawa T 1993 *Phys. Rev. B* **48** 14663
- [10] Pople J A and Beveridge D L 1970 *Approximate Molecular Orbital Theory* (New York: McGraw-Hill)
- [11] Sadlej J 1985 *Semi-Empirical Methods in Quantum Chemistry* (Winchester: Ellis Horwood)
- [12] Lynholm E and Lundquist S 1985 *Phys. Scr.* **T 32** 220
- [13] Hayes W and Stoneham A M 1985 *Defects and Defect Processes in Non-Metallic Solids* (New York: Wiley)
- [14] Khoo G S and Ong C K 1987 *J. Phys. C: Solid State Phys.* **20** 1385; 1990 *J. Phys. Chem. Solids* **51** 1177; 1993 *J. Phys.: Condens. Matter* **5** 3917; 1993 *Phys. Rev. B* **47** 9346
- [15] Khoo G S and Ong C K 1993 *J. Phys.: Condens. Matter* **5** 6507; 1993 *Phys. Rev. B* **48** 11936
- [16] Khoo G S, Ong C K, Itoh N and Kanasaki J 1994 *J. Appl. Phys.* **75** 255
- [17] Harker A H and Larkins F P 1979 *J. Phys. C: Solid State Phys.* **12** 2497
- [18] Harker A H and Lyon S B 1979 AERE-R8598
- [19] Ong C K and Chan B C 1989 *J. Phys.: Condens. Matter* **1** 3931
- [20] Aono M, Hou Y, Oshima C and Ishizama Y 1982 *Phys. Rev. Lett.* **49** 567