

## Atomic Intermixing and Electronic Interaction at the Pd-Si(111) Interface

O. Bisi<sup>(a)</sup> and K. N. Tu

*IBM T. J. Watson Research Center, Yorktown Heights, New York 10598*

(Received 23 August 1983)

We present a theoretical study of electronic properties of the Pd-Si(111) interface in the early stages of interaction. Three models are considered: a chemisorbed Pd layer on Si, an epitaxial Pd<sub>2</sub>Si layer on Si, and a near-surface Si layer containing interstitial Pd atoms. By comparing the results of our calculations with the spectroscopic data, we find that the model of mixing interstitial Pd atoms in Si is the most appropriate one. This suggests an interpretation of the interfacial reaction in terms of a precursor state of formation of Pd silicide.

PACS numbers: 73.20.Hb, 71.45.Nt

Because of the multiple applications of thin-film silicides as contacts,<sup>1</sup> gates,<sup>2,3</sup> and high-resolution infrared detectors<sup>4-6</sup> in microelectronic devices, the atomic and electronic structures and properties of metal-silicon and silicide-silicon interfaces are attracting wide attention. Transition metals form silicides with Si upon annealing.<sup>7,8</sup> In the cases of near-noble metals, they can even react with single-crystal Si near liquid-nitrogen temperature. How the covalent bonds in Si can be broken at such a low temperature is an intriguing question; the atomic processes involved in the chemical reaction must be considered.

Currently, many experimental studies of interfacial interaction begin by a controlled deposition of a submonolayer to several monolayers of metallic atoms on a well characterized Si surface, then followed by a combination of surface techniques to measure atomic position and chemical bonding.<sup>9-18</sup> However, no modeling of interfacial structure has been attempted to see if it correlates well with experimental results. The aim of this work is to investigate the electronic structure of three different models of reacted interfaces between Si(111) and Pd and to answer the question where are the Pd atoms after a monolayer or so of them have been deposited onto the Si(111) surface. The first model is a monolayer of Pd atoms chemisorbed on top of a Si(111) surface. The second is a monolayer (or two layers) of Pd<sub>2</sub>Si epitaxially grown on a Si(111) surface. The last is a model of Pd atoms below the Si surface, occupying interstitial sites in Si. We have selected the Pd-Si system because microscopic chemical interaction and properties of the interface have been studied.<sup>10-12,17</sup>

Our calculation of these complex models was carried out using the linear combination of atomic orbitals method in the extended Hückel approximation (EHT). The approach has been successfully

applied to the electronic structure of bulk silicides.<sup>19-22</sup>

In the EHT scheme the Coulomb integrals  $\alpha_i$  are set equal to the negative of the valence orbital potential  $I_{is}$  for the  $i$ th orbital of the  $s$ th atom. The resonance integral is approximated by the expression

$$\beta_{is,jr} = K_{ij} \left[ \frac{1}{2} (I_i + I_j) \right] S_{is,jr}, \quad (1)$$

where  $S_{is,jr}$  is the overlap integral. The orbital-dependent parameters  $K_{ij}$  and the wave-function Slater exponents have been adjusted to reproduce the electronic bands of Si, Pd, and Pd<sub>2</sub>Si.<sup>23</sup> An iterative procedure was set up by allowing the  $I_{i,s}$ 's to vary as a function of the excess charge found on the same atom ( $q_s$ ) and on the different atoms ( $q_r$ ):

$$I_{i,s}(q_s, q_r) = I_{i,s}(0, 0) + \mu_{is} q_s + \sum_{jr \neq is} \gamma_{is,jr} q_r, \quad (2)$$

where  $\mu_{is}$  and  $\gamma_{is,jr}$  are the intra-atomic and interatomic (Madelung) contribution per unit charge, respectively. Because of the nonorthogonality of our basis, the charge  $q_s$  is calculated through a Mulliken population analysis.<sup>24</sup>

The first model investigated is a monolayer of Pd on top of a Si(111) surface. This model has already been studied by Ihm, Cohen, and Chelikowsky<sup>25</sup> by a self-consistent pseudopotential method. In agreement with these authors, we find a sharp Pd  $d$  peak between  $-1$  and  $-2$  eV below  $E_F$ , and two hybridization peaks straddling the Si band edges.

To construct the second model, we note that lattice imaging of the cross section of Pd<sub>2</sub>Si/Si(111) interfaces show that the interface is crystallographically sharp and there are atomically flat portions. It implies that we can begin to construct these interfaces by joining a plane of Pd<sub>2</sub>Si to Si(111). In the model, we use a slab of twelve Si(111) planes hav-

ing on each surface one or two planes of  $\text{Pd}_2\text{Si}$ . These two planes are shown in the inset in Fig. 1. In the case of 1 monolayer (mL) of  $\text{Pd}_2\text{Si}$  our supercell contains 40 Si and 6 Pd atoms. Adding the second plane of  $\text{Pd}_2\text{Si}$  to form the 2-mL model we have 42 Si and 12 Pd atoms. The distance between the Si surface layer and the first  $\text{Pd}_2\text{Si}$  layer has been taken to be  $1.64 \text{ \AA}$ , intermediate between the  $\text{Pd}_2\text{Si}$  and the average Si(111) interlayer separation. At present, no experimental measurement of this distance is available.

The results for the interfaces between  $\text{Pd}_2\text{Si}$  and

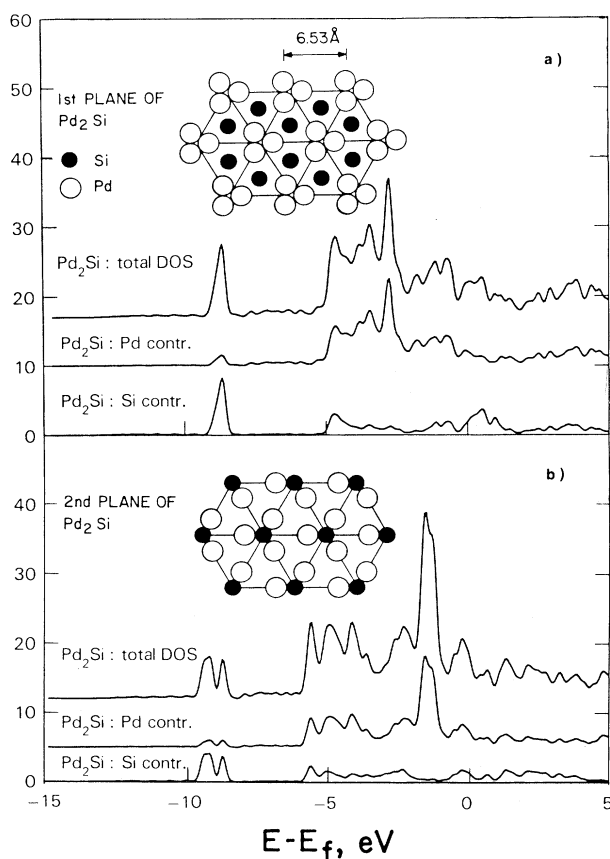


FIG. 1. Theoretical partial and total densities of states for (a) 1 mL of  $\text{Pd}_2\text{Si}$  on Si(111). The inset is the first plane of  $\text{Pd}_2\text{Si}$  and it is used as the 1-mL model in the calculation. The inset in (b) is the second plane of  $\text{Pd}_2\text{Si}$ , and by adding it to the first plane, we form the 2-mL model. The crystal structure of bulk  $\text{Pd}_2\text{Si}$  can be represented by stacking these two planes alternately. In the first plane of  $\text{Pd}_2\text{Si}$ , if we replace each of the three clustered Pd atoms by one Si atom and expand the distance of  $6.53$  to  $6.56 \text{ \AA}$ , we obtain a bulk Si(111) plane. The good crystallographic match allows an epitaxial growth of  $\text{Pd}_2\text{Si}$  on Si(111) surface. (b) 2 mL of  $\text{Pd}_2\text{Si}$  on Si(111).

Si(111) [Figs. 1(a) and 1(b)] show that the chemical bond in the interfacial compound is mainly due to Si  $p$  and Pd  $d$  interaction. We found a charge transfer towards every silicide's Si atom of  $0.09$  (1 mL),  $0.13$  (2 mL, first layer), and  $0.35$  (2 mL, second layer) electron. These values are to be compared with the corresponding bulk  $\text{Pd}_2\text{Si}$  value:  $0.17$  electron towards every Si atom.

In the 2-mL case the free surface of our system is constituted by the metal-rich  $\text{Pd}_2\text{Si}$  plane and a sharp peak of nonbonding  $d$  states at  $\sim 1.5 \text{ eV}$  is seen in the calculation which is not dissimilar to the peak in the top chemisorption case.

The geometry of a Pd interstitial atom in a slab of 12 Si layers which we have investigated is shown in Fig. 2(a). The interstitial is positioned on top of an atom of a  $B'$  plane, delineated by three atoms, one from each of the planes  $A$ ,  $A'$ , and  $B$ . The inter-

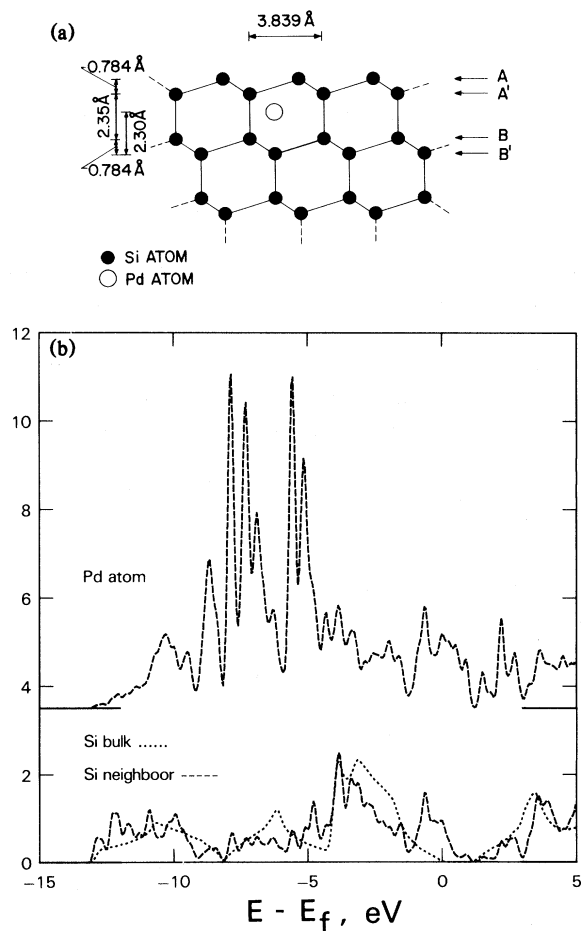


FIG. 2. (a) Pd interstitial in Si(111) geometry. Black circles, Si atoms; open circles, Pd atoms. (b) Theoretical partial densities of states for a Pd atom interstitial in Si(111).

tomic distance between the interstitial and the  $B'$  atom and the three neighboring atoms of  $A$ ,  $A'$ , and  $B$  are assumed to be 2.30, 2.74, 2.37, and 2.69 Å, respectively. The closest Pd-Pd distance is 6.65 Å, indicating that the Pd-Pd interaction is negligible.

Figure 2(b) shows the density of states for the Pd atom and for a Si neighbor (atom of plane  $A'$ ). The densities of states for other Si atoms surrounding the Pd are indistinguishable from the curve shown. On comparing the Si-neighbor density of states (DOS) with the Si bulk DOS, we see the strong modification of the former by the disruption of the tetrahedral symmetry and by the Pd-Si interaction. The Pd  $d$  electrons are also strongly perturbed and various peaks emerge as a result of this interaction. We note the existence of a broad peak just around  $E_F$ , indicating that the system which consists of the interstitial Pd and surrounding Si atoms has become a metallic cluster.

A detailed investigation of the atomic geometries (including Si atom relaxation) is out of the scope of the present paper, since it would require a total energy minimization procedure. Rather we are interested in discriminating among the three models on the basis of a comparison with the spectroscopical data. To this end we note that Rubloff *et al.* (see Figs. 3 and 4 of Ref. 11) using UPS found the  $d$  band for submonolayer coverage at  $\sim -3.5$  eV, to be compared with the  $-2.75$  eV value found in bulk  $\text{Pd}_2\text{Si}$ . In the experiment the photon energy used was 21.2 eV and the Pd  $4d$  photoionization cross section was dominant. In Fig. 3 we show a comparison between our calculated  $4d$  projected densities of states and the bulk  $\text{Pd}_2\text{Si}$   $d$  densities of states. Clearly, the ultraviolet photoelectron spectroscopy (UPS) finding of the low-energy position of the  $d$  band at a low coverage and the direction of  $d$ -band shift from  $-3.5$  to  $-2.75$  eV on going from a low coverage to bulk cannot be interpreted in terms of the theoretical DOS for an epitaxial  $\text{Pd}_2\text{Si}$  layer; in particular the sharp peak of nonbonding  $d$  states found in the Pd-rich silicide layer at  $\sim -1.5$  eV [see Fig. 1(b)] grossly disagrees with the experimental data.

In the interstitial case the  $d$  states are found at low energies between  $\sim -4.5$  and  $\sim -9.0$  eV with two main peaks at  $\sim -5.5$  and  $-7.5$  eV, respectively. The formation of a band  $\sim 4.5$  eV wide is due to strong interactions between the Pd atom and Si neighbors in this geometry. The energy position of the  $d$  states is determined by the large number of Si neighbors, each one receiving a charge of  $\sim 0.07$  electron. By introducing some geometrical relaxation and by increasing the con-

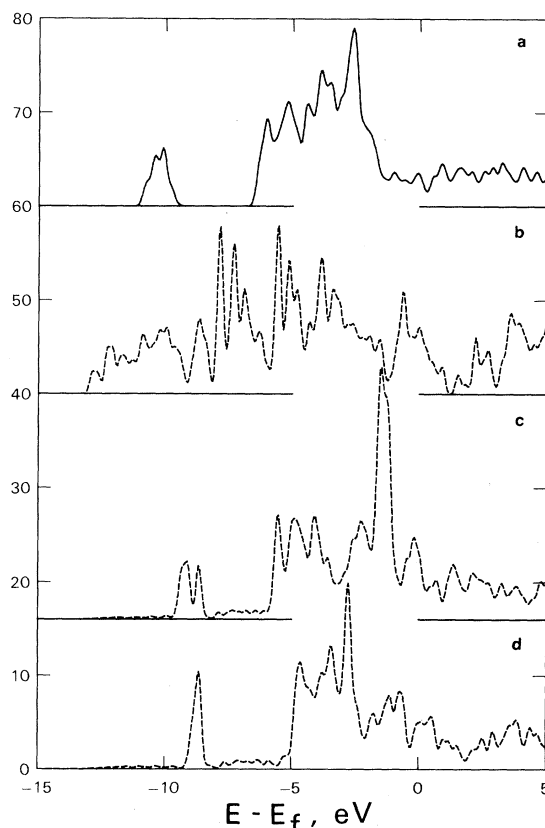


FIG. 3. Theoretical  $l=2$  projected densities of states for (a)  $\text{Pd}_2\text{Si}$  bulk; (b) Pd atom interstitial in Si (111); (c) 2 mL of  $\text{Pd}_2\text{Si}$  on Si (111); (d) 1 mL of  $\text{Pd}_2\text{Si}$  on Si (111).

centration of interstitials we would expect a better agreement with the experimental data. For example, if we increase the Pd-Si  $B'$  atom distance [in the (111) direction] and the Pd-Si  $A'$  atom distance [in the (111) plane] by 0.2 Å we obtain the relaxed result shown in Fig. 3. However, the significance of our result is that the right direction of the  $d$ -band shift comes out only in the interstitial geometry case.

We believe that in deposition, Pd atoms approaching the Si surface and having a closed-shell configuration  $4d^{10}$  do not bond with the reconstructed Si(111) dangling bonds and prefer instead to occupy the interstitial sites in Si, producing metallic clusters near the surface. When the concentration of the metallic clusters is sufficiently high, a transition to a full metallic system may take place leading to the formation of a  $\text{Pd}_2\text{Si}$ -like intermetallic compound. The detection of a silicelike UPS spectra in the very early stage of interfacial reaction between Pd and Si should not necessarily be taken to indicate the formation of  $\text{Pd}_2\text{Si}$  compound; rather

it may indicate just the formation of Pd interstitials in Si, which is a crucial kinetic precursor state needed for the low-temperature compound formation. Because of their metallic nature, the clusters may play a key role in Schottky behavior of Pd and Pd<sub>2</sub>Si on Si.

The authors would like to thank Dr. P. S. Ho and Dr. A. R. Williams for helpful comments.

---

(a)Permanent address: Institute of Physics, Modena, Italy.

<sup>1</sup>C. J. Kircher, *Solid State Electron.* **14**, 507 (1971).

<sup>2</sup>B. L. Crowder and S. Zirinsky, *IEEE Trans. Electron Devices* **26**, 369 (1979).

<sup>3</sup>S. P. Murarka and D. B. Fraser, *J. Appl. Phys.* **51**, 342 (1980).

<sup>4</sup>H. Elabt, T. Villani, and W. Kosonocky, *IEEE Trans. Electron. Devices Lett.* **3**, 89 (1982).

<sup>5</sup>C. Y. Wei, W. Tantraporn, W. Katz, and G. Smith, *Thin Solid Films* **93**, 407 (1982).

<sup>6</sup>T. R. Harrison, A. M. Johnson, P. K. Tien, and A. H. Dayem, *Appl. Phys. Lett.* **41**, 734 (1982).

<sup>7</sup>K. N. Tu and J. W. Mayer, in *Thin Films—Interdiffusion and Interactions*, edited by J. M. Poate, K. N. Tu, and J. W. Mayer (Wiley, New York, 1978), p. 359.

<sup>8</sup>G. Ottaviani, *J. Vac. Sci. Technol.* **16**, 1112 (1979).

<sup>9</sup>I. Abbati, L. Braicovich, B. De Michelis, and U. del Pennino, *J. Vac. Sci. Technol.* **17**, 1303 (1980).

<sup>10</sup>J. L. Freeouf, G. W. Rubloff, P. S. Ho, and T. S. Kuan, *Phys. Rev. Lett.* **43**, 1836 (1979).

<sup>11</sup>G. W. Rubloff, P. S. Ho, J. F. Freeouf, and J. E. Lewis, *Phys. Rev. B* **23**, 4183 (1981).

<sup>12</sup>P. S. Ho, P. E. Schmidt, and H. Föll, *Phys. Rev. Lett.* **46**, 782 (1981).

<sup>13</sup>N. W. Cheung and J. W. Mayer, *Phys. Rev. Lett.* **46**, 671 (1981).

<sup>14</sup>J. H. Weaver, V. L. Moruzzi, and F. A. Schmidt, *Phys. Rev. B* **23**, 2916 (1981).

<sup>15</sup>P. J. Grunthaner, F. J. Grunthaner, A. Madhunkar, and J. W. Mayer, *J. Vac. Sci. Technol.* **19**, 649 (1981).

<sup>16</sup>Y. J. Chang and J. L. Erskine, *Phys. Rev. B* **26**, 4766 (1982).

<sup>17</sup>G. Rossi, I. Abbati, L. Braicovich, I. Lindau, and W. E. Spicer, *Solid State Commun.* **39**, 195 (1981).

<sup>18</sup>F. Comin, J. E. Rowe, and P. H. Citrin, *Phys. Rev. Lett.* **51**, 2403 (1983).

<sup>19</sup>O. Bisi, C. Calandra, L. Braicovich, I. Abbati, G. Rossi, I. Lindau, and W. E. Spicer, *J. Phys. C* **15**, 4707 (1982).

<sup>20</sup>A. Franciosi, J. H. Weaver, D. G. O'Neill, Y. Chabal, J. E. Rowe, J. M. Poate, O. Bisi, and C. Calandra, *J. Vac. Sci. Technol.* **21**, 624 (1982).

<sup>21</sup>O. Bisi and C. Calandra, *J. Phys. C* **14**, 5479 (1981).

<sup>22</sup>O. Bisi and L. W. Chiao, *Phys. Rev. B* **25**, 4943 (1981).

<sup>23</sup>O. Bisi, unpublished.

<sup>24</sup>R. S. Mulliken, *J. Chem. Phys.* **23**, 1833 (1955).

<sup>25</sup>J. Ihm, M. L. Cohen, and J. R. Chelikowsky, *Phys. Rev. B* **22**, 4610 (1980).