Stoichiometric and Structural Origin of Electronic States at the Pd_2Si-Si Interface

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Extra Si density of states has been observed within about 3–4 Å of the Pd_2Si-Si(111) interface. Spectral analysis indicated that most of these states exist near the Si band-gap region and originate from an atomic environment more Si rich than Pd_2Si. Transmission-electron-microscopy lattice images showed a structurally sharp Pd_2Si-Si interface with misfit dislocations and atomic-step imperfections. It is suggested that the interfacial bonding in such a structure can account for the observed interface states.

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Knowledge on the nature of the electronic properties at the metal-semiconductor interface is important for the basic understanding of Schottky-barrier formation. Recent experiments show that the effects of interfacial reactions, such as atomic diffusion[1] and defect generation,[2] are important for determining the interfacial electronic properties. The interface between a transition metal and Si forms a distinct class by itself because of the strong reactivity of these systems, which causes the formation of silicide compounds. During silicide formation, the reaction front proceeds into the Si, resulting in a silicide-Si interface with bonding and structural characteristics basically different from those of nonreacting metal-Si interfaces. Recent spectroscopy studies,[3-7] which use ultraviolet photoelectron spectroscopy (UPS), Auger-electron spectroscopy (AES), and x-ray photoemission spectroscopy (XPS) on the interfaces of Pd, Pt, and Ni on Si, revealed that silicide formation in the first few layers of metal coverage indeed dominates the electronic properties of such interfaces.

Among the silicides, the Pd-Si system has attracted the most interest. In bulk Pd_2Si, the electronic structure has been investigated with use of UPS and AES,[8] where an analysis of the spectroscopic data based on the calculated partial densities of states showed that the filled Pd $4d$ band shifted 2.75 eV below the Fermi level ($E_F \equiv 0$) and the bonding in the Pd_2Si lattice is primarily due to the hybridization of the Pd $4d$ and Si $3p$ electrons which form separate groups of bonding (at about -5 eV) and antibonding states (near E_F). At the Pd_2Si-Si interface, UPS observation during the initial formation stage revealed a valence-band structure similar to the bulk silicide but with the major peak in the d band starting from -3.5 eV and then shifting to the bulk value of -2.75 eV. This peak shift and the corresponding surface work-function change were attributed to a stoichiometry gradient with Si enrichment near the interface.[3] Similar conclusions have been suggested for the Pt-Si and Ni-Si interfaces. Indeed, it has been proposed that a Si-rich stoichiometry gradient with the MSi_4 composition at the interface can be used as a basis to confirm the Schottky model for silicide-Si interface.[9]

Several relevant questions concerning the interfacial stoichiometry gradient have to be resolved. First, since transmission electron microscopy (TEM) revealed only the Pd_2Si phase at the initial (~5 Å) Pd/Si interface,[5] it is difficult to justify thermodynamically a large stoichiometry variation within a single phase layer of a few angstroms; so far there has been no direct stoichiometry measurement within, e.g., 10 Å of the interface. Second, since surface spectroscopy techniques sense only the local atomic environment, the data alone do not reveal the overall atomic structure of the interface. And third, there remains an important, yet unanswered, question on the nature of the electronic states associated with the stoichiometry variation. In an attempt to resolve these questions, we have carried out a direct composition and structure determination for the Pd_2Si-Si(111) interface using Auger-intensity calibration and cross-sectional TEM. For these studies, the Pd-Si(111) interface is well suited. First, the difference in the line shapes of the Si $L_{2,3}VV$ Auger transition is sufficient for separating the silicide intensity from that of the Si substrate, a condition required for composition calibration. And second, the Pd_2Si formed is epitaxial to the substrate, making it possible to observe the interfacial structure with use of lattice-imaging techniques. Experimental details have been previously published.[3,5,8]

The composition calibration is based on the variation of the integrated intensities for Si $L_{2,3}VV$,

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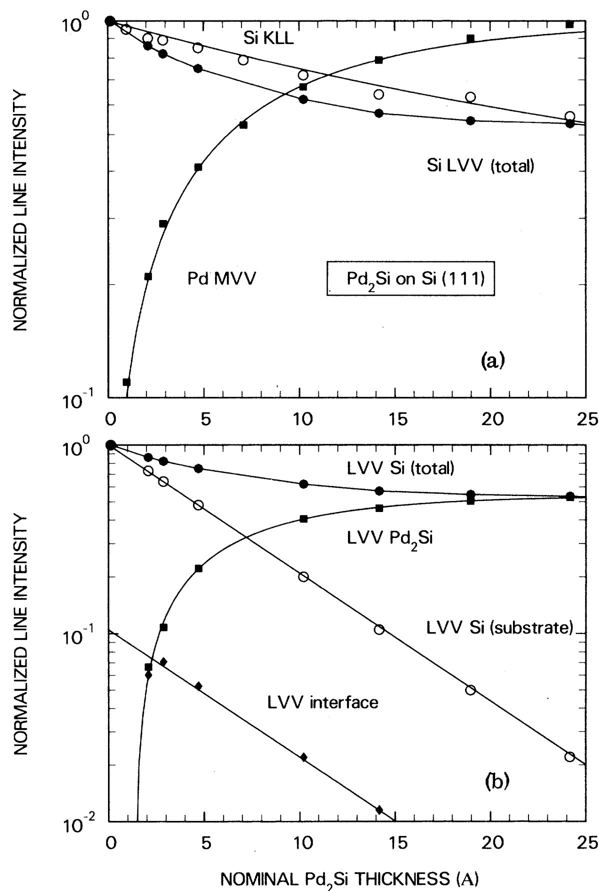


FIG. 1. (a) Variations of the integrated intensities of Pd *MVV* and Si *KLL* and *LVV* Auger lines for increasing coverages of Pd_2Si; (b) intensity variations of the substrate Si, silicide, and interface portions of the Si *LVV* spectrum for increasing coverages of Pd_2Si ($\lambda = 8.4$ Å).

KLL, and Pd $M_{4,5}VV$ as a function of silicide coverage and the depth sensitivity comes from the different escape distances (λ) of these Auger transitions. The intensity variations are first formulated for various types of surface coverage,[10] e.g., uniform or island coverage of the substrate by a silicide of a certain composition. Then a match between the predicted and the observed intensity variations determines the composition and the escape distances.

Figure 1(a) shows the variations of the Auger intensities observed in one experiment as a function of thickness. The *MVV* and *KLL* intensity variations (normalized to bulk silicide and Si, respectively) indicate an overall composition of Pd_2Si with characteristic λ of 11.7 and 28 Å, respectively. The analysis of the *LVV* intensity variation is carried out by first subtracting the

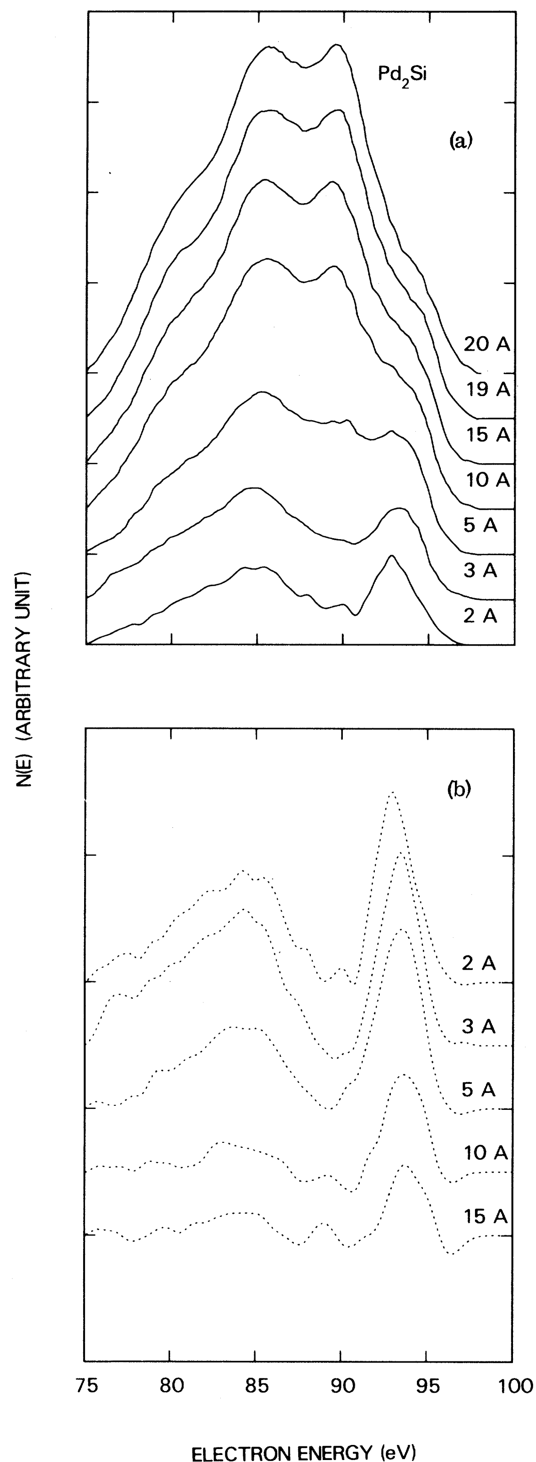


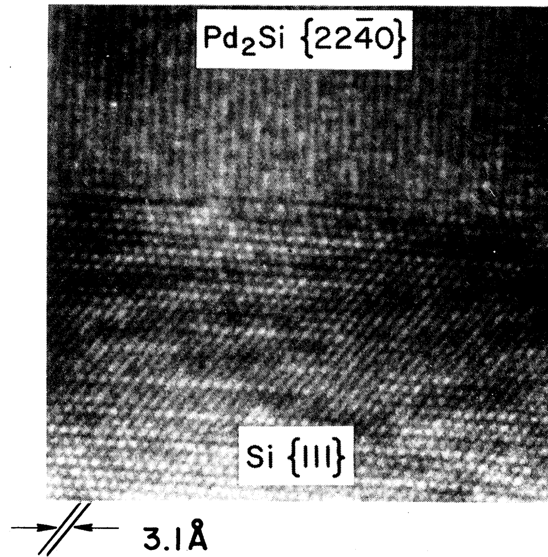
FIG. 2. (a) The silicide portion of the Si $L_{2,3}VV$ Auger spectrum for increasing Pd_2Si coverage; (b) the interface portion of the Si *LVV* spectrum as a function of coverage.

Si-substrate contribution. In Fig. 2(a), the variation of the *LVV* spectrum after subtraction is displayed for increasing coverages. At 20 Å, the spectrum is essentially that of bulk Pd_2Si, but for low coverages the overall feature is different, particularly for the portion in 91–96 eV. In addition, the integrated intensities consistently exceed those predicted for a Pd_2Si layer. Further decomposition[10] by subtracting the Pd_2Si contribution in these spectra reveals extra features [Fig. 2(b)] which seem to be invariant for all coverages but characteristically different from those of the substrate and Pd_2Si. Moreover, the intensity of these spectra decreases with coverage in a manner similar to that of the substrate [Fig. 1(b)], and therefore we attribute this to an interface contribution. The coverage dependence of the extra intensity (note the maximum at about 3 Å) is consistent with a depth distribution of the additional states within about 3 Å from the interface.[11]

There are two other pieces of experimental evidence indicating an interface layer within a few angstroms in the silicide.[10] First, measurements of the surface work function by a Kelvin-probe technique indicated that the increase of the work function from that of the Si surface to the Pd_2Si value was saturated after about 3 Å of coverage. And second, the energy shift observed for the *MVV* peak was consistent with the presence of Pd atoms in a Si-rich interface layer of about 4–5 Å wide.

The interface spectrum [Fig. 2(b)] is dominated by a peak at 94 eV which has been shown to originate from the antibonding states.[8] Since the antibonding states locate mostly within the band gap, and so a major portion of the observed interface states are most probably band-gap states derived from Si atoms. Furthermore, the shift of the 94-eV interface peak toward higher energy for increasing coverage can be related to a decreasing occupation of the antibonding states caused by shifts in E_F. Based on the calculated stoichiometry dependence of the density of states, this reflects a Si-rich environment at the interface.[12] We note that the extra states occur with relatively high density of about 0.1 of the interface Si atoms, which is insufficient, however, to account for an interfacial silicide layer of high silicon concentration, e.g., $PdSi_4$.

In Fig. 3(a) we show the TEM lattice image of the Pd_2Si-Si(111) interface as obtained from a sample where Pd_2Si was formed by evaporating ~100 Å of Pd on a chemically cleaned surface. In Si the image shows the {111} and {220} planes which are interwoven to yield the ⟨110⟩ channels, while in Pd_2Si the {22$\bar{4}$0} planes are observed. These lattice images clearly extend from both sides to the interface, indicating that the lattice structures of Pd_2Si and Si reach the interface with no evidence for a different interface compound. However, even for a structurally sharp Pd_2Si-Si (111) interface, there is a transition region in general consisting of approximately one Si and



(b)

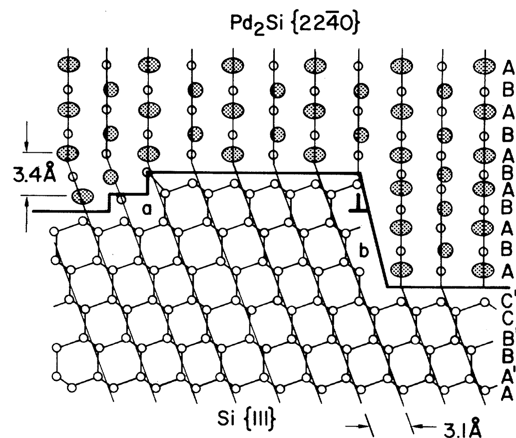


FIG. 3. (a) TEM lattice images observed in a vertical cross section of the Pd_2Si-Si(111) interface; (b) schematic illustration of the lattice structure in a Pd_2Si-Si(111) interface.

two Pd_2Si layers because of the AB-type stacking of the hcp Pd_2Si lattice as shown schematically in Fig. 3(b). Within this interface region of 3–4 Å, the atomic environment is Si rich compared to bulk Pd_2Si and the chemical bonding is different as well. Thus, it appears that the chemical bonding contained in such an interface structure should have the necessary characteristics to account for the electronic states observed at the interface. In addition, one can distinguish two types of structural imperfections at the interface: the misfit dislocation and the atom steps [shown at sites a and b in Fig. 3(b), respectively]. Both types of defects can change the local bonding configuration without varying the overall lattice structure, thereby inducing interface states different from those associated with the flat interface. While the electronic properties of the different interfacial bonds are interesting for future studies, qualitatively the range of the interface layer and its Si-rich environment as indicated in Fig. 3(b) provide a satisfactory explanation for the extra Si density of states observed at the Pd_2Si-Si(111) interface.

In summary, our results show directly the existence of Si interface states derived from a Si-rich environment within a range of about two to three atomic layers at the Pd_2Si-Si interface. The origin of these states can be qualitatively accounted for by the atomic structure of the silicide-Si interface. The fact that a major portion of the interface states lies in the band-gap region show that they are important for an understanding of Schottky-barrier formation at the silicide-Si interface. This report appears to be the first correlation between stoichiometry, microstructure, and electronic states at a silicide-Si interface.

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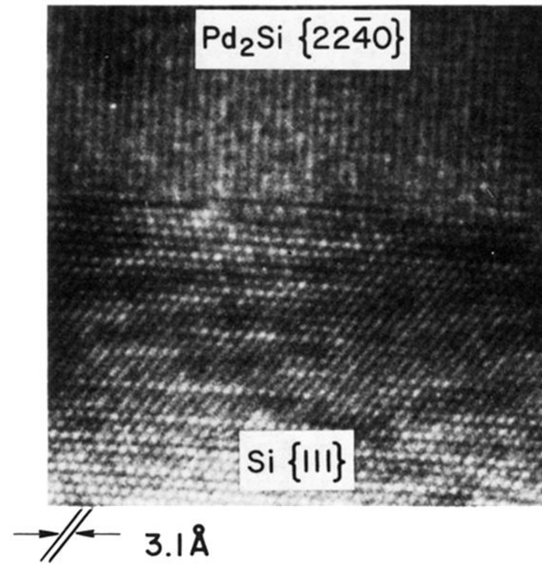
[11]Complications due to nonuniform surface coverages have been considered. While a partial coverage with islands of uniform thickness can be ruled out readily, it is difficult to rule out a complete coverage by islands with random size and thickness. For this case, the analysis based on a uniform coverage is still valid, provided that the layer thickness and λ are replaced by the proper statistical averages. We have attempted to model the stoichiometry distribution within the interface layer but found it difficult to ascertain the uniqueness of such calculations; so the results are not reported.

[12]V. L. Moruzzi and A. R. Williams, private communication.



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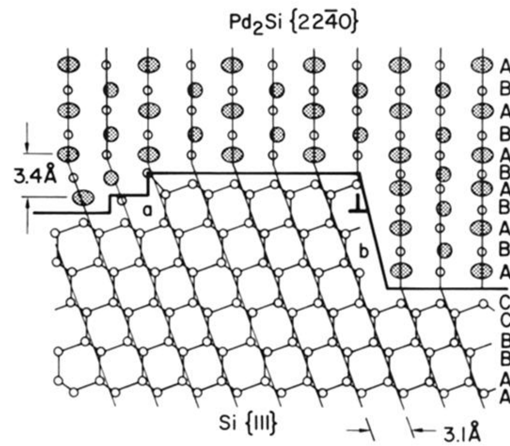

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