Electronic states and atomic structure at the Pd$_x$Si–Si interface

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(Received 15 September 1980; accepted 17 December 1980)

Electronic states and atomic structure at the Pd$_x$Si–Si interface have been investigated using AES and UPS in conjunction with transmission electron microscopy (TEM). By following the core and valence spectra from submonolayer to several atomic layers of Pd coverage, the changes in the partial state density of the Pd and Si atoms during interface formation have been observed. Stoichiometry calibration based on relative variation of Auger intensities reveals extra Si states existing within a few Å of the interface. Analysis of the spectral shapes and peak shifts shows that these Si states are derived from a Si-rich environment at the interface and are located mostly near the Si bandgap region. TEM lattice images reveal a structurally sharp Pd$_x$Si–Si [111] interface with misfit dislocations and atomic steps present within several Å of the interface. Combining the spectroscopy and TEM results, we infer that the interface states originate from chemical bonds associated with the atomic defect structures produced by silicide formation.

PACS numbers: 73.40. − c, 73.20. − r, 73.40.Sx, 85.30.Hi

I. INTRODUCTION

Recently there has been considerable interest in studying the electronic properties of the silicide–Si interface because of the potential of such interfaces as contacts in semiconductor devices. Such studies are also important for the basic understanding of Schottky barrier formation. One aspect distinguishing the silicide–Si interface from other metal–semiconductor interfaces is its strong chemical reactivity, which causes the formation of the silicide compound. The formation of the silicide alters not only the stoichiometry of the interface but the atomic structure and the chemical bonding as well. This gives rise to an interface with electronic properties distinctly different from those of the abrupt, noninteracting metal–semiconductor interfaces. Therefore, a meaningful study of the electronic properties of the silicide–Si interface should take into account the effects of material reactions on the atomic structure and chemical bonding.

Surface spectroscopy studies, notably those using UV photoemission (UPS) and Auger (AES) spectroscopics, have been carried out on several silicide systems. The results observed at the interface after several monolayers of silicide coverage showed spectral features reflecting substantial changes in the metal and Si valence electronic structure. While these studies demonstrate the strong influence of silicide formation on interface characteristics, many details concerning the nature of the electronic states are still lacking. This is because most of these studies have relied mainly on one particular spectroscopic technique, which restricts the information that can be extracted on the electronic properties of a reactive interface where extensive intermixing of metal and Si atoms occurs.

We have investigated a number of silicide–Si interfaces using UPS and AES conjunction with transmission electron microscopy (TEM). The UPS and AES spectra are complementary in providing information on the valence density of states for metal and Si atoms. In addition, the intensity of the Auger transitions, being atom-specific and having electron escape distances of 10–20 Å, can be used to calibrate the stoichiometry within a few Å of the interface region. TEM observations, particularly those made with lattice imaging techniques in a cross section of the interface, provide not only phase identification but also the lattice microstructure of the interface. Among the silicides, the Pd$_x$Si–Si interface is the most studied and the results enable us to correlate the stoichiometry and microstructure with the electronic states at the interface. This paper summarizes the results for the Pd$_x$Si–Si interface with discussions emphasizing the implication of our stoichiometric and structural results on the nature of the electronic states.

II. EXPERIMENTAL

Experiments were carried out on atomically clean Si(111) and Si(100) surfaces in ultrahigh vacuum. The Si surface was cleaned and restructured by heating to 1250°C and slowly cooled over a period of 1 h. Pd was evaporated at room temperature by in situ sublimation from a Pd wire and the rate was controlled to provide metal coverage from submonolayer to tens of atomic layers. A crystal monitor was used to measure the Pd thickness, which was calibrated by the He backscattering technique. A beam chopping technique was used with a double-pass CMA to obtain the undifferentiated Auger N(E) spectra directly.

A Kelvin probe driven by an acoustic transducer was incorporated into the vacuum chamber for in situ measurements of surface work function. After each Pd evaporation, the work function was measured together with the Si L$_{2,3}\text{VV}$, KLL, and Pd MVV Auger spectra, so that changes in work function can be correlated to the spectroscopy results. In addition, UPS measurements are now completed for Si(111) and (100) surfaces during in situ evaporation of Pd overlayers. The
III. RESULTS AND DISCUSSION

A. Electronic structure

Upon silicide formation the changes in the density of states (DOS) give rise to distinct shapes for the UPS and Si L_{2,3}VV spectra. The spectra have been interpreted based on partial state densities calculated for Pd-Si compounds of several stoichiometries. In Fig. 1 we show the valence DOS calculated for PdSi and Pd_{2}Si together with the UPS spectrum observed for Pd_{2}Si. Because of their high photoionization cross section, the Pd(4d) states dominate the valence DOS as seen in UPS. From Fig. 1, the shape of the experimental Pd_{2}Si spectrum shows good qualitative agreement with the overall features of the DOS calculated for the two Pd-Si compounds. One key feature in the spectrum is that the d band is almost completely shifted below $E_F$ as a result of silicide formation; the main d peak in the silicide occurs near $-2.75$ eV. These results are consistent with the calculated DOS in the Pd-Si compounds, as evident from the position of the d peak in Fig. 1. The calculation also reveals that the amount of peak shift varies with the compound stoichiometry, or in other words with the number of nearest-neighbor Si atoms surrounding each Pd atom. This peak shift has been observed during initial formation of the interface which will be used to infer the stoichiometry at the interface.

UPS experiments have been carried out on Si(111) and (100) surfaces at room temperature with increasing Pd coverage from the submonolayer range to study the electronic properties of the interface. The results were very similar for these two surfaces, with the incremental difference spectra revealing interface features very close to those of Pd_{2}Si except for the position of the d peak. Thus the electronic properties of the interface are dominated by a Pd_{2}Si-like compound which was found to form at room temperature upon Pd deposition. The d peak was observed to shift from $-3.5$ eV at lowest coverage to $-2.75$ eV in Pd_{2}Si, with most of it occurring in the first 4 Å.

Similar UPS results have also been observed for Pd-Si metallic glasses within a 10% range of the Pd_{2}Si composition. Specifically, spectral features similar to Pd_{2}Si were observed and the d peak shifted with composition as well. Thus, it appears that these shifts are general characteristics associated with the chemical bonding in the Pd-Si system. In Fig. 2, the experimental and calculated d shifts are summarized for the Pd-Si system. The overall trend clearly indicates that the d shift observed during initial formation of Pd_{2}Si reflects a Si-rich environment for the interfacial Pd atoms. Indeed, if a similar stoichiometry dependence of the d shift is assumed in our study, the Si concentration would vary from about 50 at. % at the interface to the 93 at. % of Pd_{2}Si within about 4-5 Å.

In addition to the d shift observed in UPS spectra, a corresponding peak shift to reflect the Si-rich environment for interfacial Pd atoms has been observed in the Pd M_{4,5}VV Auger spectrum. We show in Fig. 3(a) a set of the M_{4,5}VV spectra observed on the Si(111) surface as a function of silicide...
coverage. Overall this quasi-atomic Auger line shows little change in its spectral features but starting from the low coverage (about 1 Å for the second bottom spectrum), the main peak gradually shifts toward higher energies. When the spectrum becomes that of Pd$_2$Si, the total shift amounts to 1.4 eV. An additional 1.2 eV shift is observed when pure Pd metal is observed on the untreated surface of a thick overlayers film. A similar shift of 1 eV has been observed by Riley et al.\textsuperscript{10} between the Pd$_2$Si glass and Pd. By measuring the energy shift of the 3d$_{5/2}$ (M$_4$) core level (using XPS), these authors concluded that about half of the shift comes from energy change of the 4d valence states due to Pd-Si bonding. Using a similar reasoning, we attribute the peak shift observed in AES for the low coverages to larger binding energies of the 4d states. This is consistent with the UPS results, thus reflecting a Si-rich environment for the interfacial Pd atoms. Interestingly, if the peak shift is plotted for increasing surface coverage as shown in Fig. 3(b), then most of the peak shift can be seen to occur within 4–5 Å of the interface. This range of the Si-rich environment agrees well with UPS observations.

**B. Interface states**

The analysis of the Auger data regarding interface electronic properties is focused on the band-like Si L$_{2,3}$VV transition, which provides information on the Si-specific valence DOS (i.e., the Si partial DOS) and thus complements the UPS results (which give mainly Pd DOS). To obtain the true spectral features associated with silicide formation in the first few Å of the Si substrate, the contribution from the Si substrate has to be subtracted. With distinctly different L$_{2,3}$VV lineshapes for the silicide vs Si, this is relatively straightforward from knowledge of the electron escape distance and the overlayers thickness (see details in next section). Figure 4(a) shows a series of the silicide L$_{2,3}$VV spectra (after subtracting the substrate contribution) observed on the Si(111) surface with increasing Pd$_2$Si coverage. At 20 Å coverage, the spectrum is essentially that of bulk Pd$_2$Si. However, as the coverage decreases toward the interface, the spectral features become increasingly different. At low coverages, the magnitude of the integrated intensity consistently exceeds that of a Pd$_2$Si layer. Further decomposition of these spectra by subtracting the Pd$_2$Si contribution reveals the extra intensity to have the spectral shape shown in Fig. 4(b). These spectra exhibit basic features which are invariant with coverage but characteristically different from those of either the Si substrate or bulk Pd$_2$Si. In addition, the coverage dependence of the extra intensity varies in a manner similar to that of the substrate (details shown in next section). Based on these results, we attribute these spectra to additional Si states associated with the interface.

The interface L$_{2,3}$VV spectra are dominated by those of the high-energy peak at 94 eV, which shifts 1 eV toward lower energy at lowest coverage. According to the schematics of the L$_{2,3}$VV transitions in Pd$_2$Si\textsuperscript{10} the 94 eV peak is originated from the antibonding states near the bandgap region (see peak A in Fig. 1. The splitting of the Si 3p states into two groups, antibonding (A) and bonding (B) with about 5 eV separation, is a common feature obtained in all the DOS calculations of Pd-Si compounds.\textsuperscript{10,13,14} Auger transitions involving these two groups of p states and a group of 3s states at 10 eV below the Fermi energy $E_F$ account satisfactorily for the silicide L$_{2,3}$VV line shape. In Fig. 1, one can see that an increase of Si concentration in the compound enhances the occupation of the antibonding states by moving peak A further below $E_F$, causing a shift of the 94 eV Auger peak toward

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**Fig. 3.** (a) A series of Pd M$_{4,5}$VV Auger spectrum observed for increasing Pd$_2$Si coverage on the Si(111) surface. (b) Shift of the main MVV peak as a function of Pd$_2$Si coverage.
lower energy. On this basis, the coverage-dependent shift of the 94 eV peak is an indication of a Si-rich stoichiometry for Si atoms at the interface. As shown in Fig. 4(b), most of the peak shift occurs below 5 Å surface coverage. This is another chemical shift evidence, in this case associated with the chemical environment of the Si atoms instead of the Pd atoms, which indicates a range of 4-5 Å for the Si-rich environment at the interface.

Summarizing the results from the spectral analysis of AES and UPS data, we conclude that extra interfacial DOS exists primarily near the bandgap region and that these states are derived from Si atoms with a Si-rich environment as compared to that in the bulk silicide. The range of the interfacial Si-enrichment is limited to about 4-5 Å.

C. Interfacial stoichiometry

So far the information regarding the interfacial stoichiometry has been inferred from the peak shifts (chemical shifts) observed in the valence AES and UPS spectra. To determine directly the stoichiometry distribution of the interface, we have carried out an Auger composition calibration. The method is based on calculation of the relative intensity variations of the Si LVV and KLL and Pd MVV Auger lines as a function of silicide coverage. The depth sensitivity of the calibration comes from the different escape distances associated with these Auger electrons. For the PdSi-Si interface, the difference in the spectral feature is sufficient to decompose the observed LVV spectrum into contributions from the Si substrate and the silicide overlayer. As shown in Fig. 4, the spectrum from the overlayer can be further decomposed into silicide and interface portions. By separating the LVV intensity into contributions from elemental Si, silicide and the interface region, we are able to calibrate the depth distribution of different Si valence states in the sample within the range of the electron escape distance (about 8 Å, see below).

The calibration is carried out by obtaining first the integrated intensity of the Auger lines as a function of silicide coverage. Before integrating the spectral intensity, the background contribution has to be subtracted. Then the observed intensity variations of the Auger lines are matched to those predicted for certain surface coverages, whereby layer composition and escape distances can be determined. For example, in the case of a uniform coverage of the Si substrate by a PdSi compound, the integrated line intensities as a function of layer thickness $x$ can be expressed as:

$$I_{LVV}/I_{LVV} = \exp(-x/\lambda_{LVV} \cos \theta),$$

$$I_{LKV}/I_{LVV} = 1 - \exp(-x/\lambda_{MVV} \cos \theta),$$

$$I_{MVV}/I_{MVV} = 1 - \exp(-x/\lambda_{MVV} \cos \theta),$$

and

$$I_{KLL}/I_{KLL} = \left(1 - \frac{n}{m}\right) + \frac{n}{m} \exp(-x/\lambda_{KLL} \cos \theta),$$

where for convenience, the intensities from the substrate (superscript s) and compound (c) are normalized with respect to the bulk Si (si) and silicide (sc) respectively, and $\cos \theta$ is a factor correcting for the beam-detecter geometry.

Intensity variations for other types of surface coverages can be similarly formulated; in fact, overlayers with inhomogeneous in-depth composition distribution can be readily treated. Among the possibilities, the situation of a partial

coverage with islands of uniform thickness or a complete coverage by islands with random size and thickness is particularly worth consideration. We have analyzed both these cases. A partial coverage leads to intensity variations different from Eq. (1), the extent of which depends upon the amount of surface coverage. Therefore, the occurrence of such a surface coverage can be checked according to the observed intensity variations with coverage. The other case is difficult to discern by a similar reasoning because the predicted intensity variations are quite similar to those of a uniform coverage. Fortunately, however, the analysis of Eq. (1) is still valid provided that the values of $x$ and $\lambda$ be replaced by the proper statistical averages. For the Pd$_x$Si-$\text{Si}$ interface, work function data are available also for assessing the extent of island formations.

In Fig. 5, we present the results from one of the experiments carried out on a Si(111) surface at room temperature. For simplicity, the total $LVV$ intensity is used and the observed intensity variations, expressed in terms of two ratios, indicate that the stoichiometry throughout the overlayer is essentially that of Pd$_x$Si. This is consistent with previous TEM observations revealing Pd$_x$Si to be the only phase present at the initial (~5 Å) Pd-$\text{Si}$ interface. In Fig. 6(a), we show the intensity variations of individual Auger lines as a function of coverage. These variations can be accounted for by the analysis given in Eq. (1) on the basis of an overlayer with the Pd$_x$Si composition. The good overall agreement rules out the possibility of having a partial island coverage in the thickness range of the experiment since a partial coverage up to about 90% can be detected because of the different overall intensity variations. Values of the electron escape distances are determined to be 8.4 Å for LVV, 11.7 Å for MVV and 28 Å for KLL. Results of the analysis for the three LVV components are plotted in Fig. 6(b) where the intensity variation of these components again can be characterized by a single $\lambda$ of 8.4 Å. It is significant to note that the variation of the interface intensity is similar to that of the substrate and its maximum intensity occurs at about 3 Å coverage. We have attempted to model the distribution of such interface states based on various forms of in-depth distributions. However, with the range of the observed intensity being comparable to the electron escape distance we found it difficult to distinguish some of these model distributions, e.g. localized states at the interface vs an exponential gradient from the interface. In spite of this difficulty, the results of the calculation show that most of the extra interfacial states responsible have to be located within a few Å of the interface.

We have obtained another piece of experimental evidence for an interface layer within a few Å in the silicide. Measurements of the surface work function by the Kelvin probe technique indicate that the increase of the work function from that of the Si surface to the Pd$_x$Si value saturates after about 3–4 Å coverage (Fig. 7). The saturation range of the work function is also an indication that there is no partial surface coverage due to island formation beyond a few Å.

D. Microstructure

The spectroscopy results presented so far concern mainly the electronic properties of the interface but give little information on the overall atomic structure of the interface, which is important for understanding the structural origin of the interface states. For microstructure studies, the Pd₃Si/Si(111) interface is well-suited because the basal plane of the hcp Pd₃Si lattice matches the Si(111) surface to within 2%, so that an epitaxial interface is formed.¹⁵

In Fig. 8(a) we show the TEM lattice image of the Pd₃Si/Si(111) interface as obtained from a sample where Pd₃Si was formed by evaporating ~100 Å of Pd on a chemically cleaned surface.¹⁶ The lattice images in Si show the (110) channels formed from intersections of the [111] and [220] planes while in Pd₃Si the [2240] plane images are observed. The observed images indicate clearly that the Pd₃Si and Si crystal structures extend from opposite sides to form a structurally sharp Pd₃Si-Si interface. For this epitaxial interface, there is no evidence within the resolution limits of about 3 Å for the presence of an interfacial compound with stoichiometry different from Pd₃Si. (As indicated, the separation of the lattice fringes is 3.1 Å. From the image contrast, the interfacial structure can be resolved to one lattice fringe, so the direct structural evidence is limited to about 3 Å.) Further detailed exploration of the interface structure will have to rely on image contrast calculations based on atomic models.

While such studies are presently in progress, one can illustrate the general characteristics of the interface by schematic models. One such model is shown in Fig. 8(b) where the fine lines indicate the observed lattice fringes. The interface as outlined contains two types of structural imperfections. The first is the misfit dislocation, which can be detected by counting the difference in the numbers of lattice fringes on the two sides of the interface; the second is the atom step, ranging from monolayer to several atomic layers. Even at the ideal interface there is a structural transition region in general consisting of one Si and two Pd₃Si layers due to the Al-type stacking of the Pd₃Si hcp lattice planes on the Si(111) plane. Within this region of 3–4 Å for two Pd₃Si and one Si lattice planes, the environment is Si-rich compared to the bulk Pd₃Si and the chemical bonding is characteristically distinct from that of the bulk silicide lattice.

Thus it seems that the interfacial bonds in such a structure may have the proper characteristics to account for the additional electronic states observed at the interface. In addition, both types of structural defects can change the local bonding configuration without varying the overall lattice structure. These defects should also induce interface states, but with characteristics probably different from those associated with microscopically flat portions of the interface. The relative contributions from different types of interface states vary with the degree of perfection of the interface structure, which is
determined by the extent of interfacial reaction and the misfit between the silicide and Si lattices. While such problems are extremely interesting for future studies, the range of the interface layer and its Si-rich environment are general characteristics which provide a satisfactory explanation for the extra Si DOS observed at the Pd$_2$Si-Si(111) interface. For this interface there is no evidence for extensive stoichiometry variations other than those of special bonding configurations required at the atomically abrupt epitaxial Pd$_2$Si/Si(111) interface.

IV. SUMMARY

In summary, our results show directly the existence of Si interface states derived from an Si-rich environment within a range of about two to three atomic layers at the Pd$_2$Si-Si interface. The origin of these states can be qualitatively accounted for by the local bonding configuration of a structurally sharp silicide-Si interface. Since a major portion of these interface states lies near the Si bandgap region, they are expected to be important for understanding Schottky barrier formation at the silicide-Si interface.

ACKNOWLEDGMENTS

We wish to thank J. Clabes, J. L. Freerof, T. Y. Tan, and K. N. Tu for stimulating and useful discussions, and to J. E. Baglin for his assistance in backscattering calibration.