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Thermally induced Si accumulation onto Pd$_2$Si surfaces has been studied for the first time with synchrotron radiation photoemission. Evidence is given of the formation of strong bonds between Si and Pd in the transition region between Pd$_2$Si and Si. The results are discussed in view of the Pd-Si interfaces prepared by annealing in device technology.

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The electron states in silicon $d$-metal systems (silicides and Si $d$-metal interfaces) have been studied extensively, and a general picture of the nature of the chemical bond between Si and last column transition metals (Ni, Pd, and Pt) is now available.[1-14] This knowledge is a prerequisite for understanding the experimental results reported in this letter. The present paper deals with the electron states of a silicide surface (Pd$_2$Si) enriched in Si owing to thermal treatment. The accumulation of Si on the Pd$_2$Si surface has already been reported in Refs. 6–8, but this is the first photoemission work with synchrotron radiation (SR). This paper includes also results from conventional Auger measurements taken in a separate experiment. The present paper emphasizes the understanding of the accumulation mechanism and its importance for the annealing procedures often used in device technology. A thin Pd silicide layer (6–7 monolayers) was prepared *in situ* by evaporating Pd from a Pd coated, W-Ohmic filament, onto an ultrahigh vacuum (UHV) cleaved Si (111) surface at room temperature (RT). All the stages of the sample preparation were done in a vacuum better than $2 \times 10^{-10}$ Torr. It is known that at these coverages the reaction at RT proceeds with a formation of a Pd$_2$Si-like phase. Minor differences[9] with respect to bulk Pd$_2$Si are not relevant in the present context. The photoemission experiments were carried out at photon energies giving a very short escape depth ($\sim 4$ Å) so that the contribution from the Si (111) substrate could be neglected. It should be recognized that the work here on *thin* layers, reacted at RT, avoids the risk of Si enrichment during the formation of *thick* Pd$_2$Si layers which require elevated temperatures to be prepared.

The experimental setup for the SR photoemission measurements is the same as that reported earlier.[10] We have measured the Si $2p$ core lines (at $h\nu = 160$ eV) and the valence band photoemission spectra at $h\nu = 80$ eV and $h\nu = 130$ eV. The angle integrated photoelectron energy distribution curves were obtained with a double-pass cylindrical mirror analyzer. At $h\nu = 80$ eV, the $d$-band photoemission is dominant while it is strongly suppressed at $h\nu = 130$ eV, due to the Cooper minimum effect, and information on the Si contribution to the density of states can be obtained as

was shown, for the first time, in earlier experiments.[2,3]

The main experimental results are summarized in the figures. The valence band photoemission spectra taken at $h\nu = 80$ eV are shown in Fig. 1(a) for samples prepared at RT and then annealed. All the distribution curves were recorded at RT after five minutes of annealing at the quoted temperatures. The most notable effect of the thermal treatment (above 350 °C) is the increase in intensity of the shoulder around — 6 eV (shaded in the figure). In Fig. 1(b), we present photoelectron energy distribution curves (EDC's) taken at the Cooper minimum ($h\nu = 130$ eV) at RT and after annealing at 350 °C. The Si contribution to the photoemission spectra is enhanced at this photon energy. We can observe very strong modifications in the electronic structure due to annealing. This is of crucial importance and we note that it is the first observation of this kind. Earlier photoemission work has been restricted to $h\nu = 21.2$ eV, He$_I$ radiation,[8]
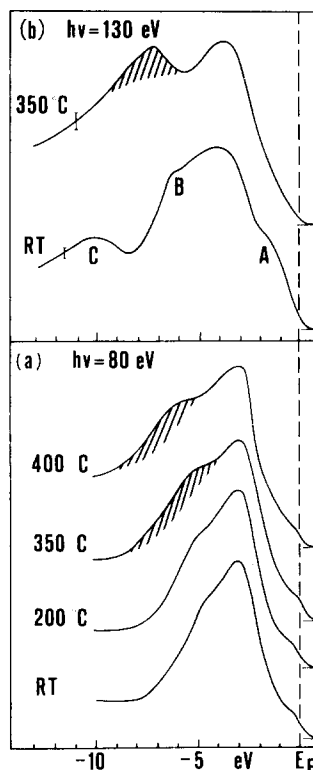


FIG. 1. Angle integrated photoemission spectra from Pd$_2$Si prepared at RT and then annealed at increasingly higher temperatures. The EDC's are for two different photon energies:(a) 80 eV and (b) 130 eV and all normalized to the same height.

where the $d$-band photoemission from Pd is masking the Si contribution [compare to the EDC's at $hv = 80$ eV, Fig. 1(a)].

The accumulation of Si on the $Pd_2Si$ surface is evident from the Si $2p$ and Pd $4d$ core level spectra summarized in Fig. 2(a). The intensities of the core lines are shown as a function of temperature. The solid lines (with the indicated error bars) are the best fit not only to the SR photoemission measurements but also to an extensive set of Auger measurements (AES) of the Si and Pd concentrations obtained in a separate experiment. In the latter case, the Auger intensities were scaled to the escape depths of the SR measurements, [11,12] i.e., the different degrees of surface sensitivity in the AES and photoemission data were normalized to an escape depth value of 4 Å in order to make a meaningful comparison between the two sets of data possible. The Auger line shapes are not reported here but are in agreement with the results reported earlier by Oura *et al.*[6,7] The concentration of the accumulated Si is also in agreement with previous results. After correcting for the differences in escape depths,[11,12] we found that 1.6–1.9 monolayers of Si are accumulated in the surface region. This does not imply that a monolayer of pure Si is present in the topmost layer since a small Pd concentration (below 10%) with negligible effect on Auger line shape would be compatible with our results. The layer below the topmost surface layer could contain as much as 25% of Pd. The presence of Pd in the top layers would also be consistent with the changes of the Si $2p$ core line binding energy as a function of temperature [Fig.2(b)]. As is shown in Fig. 2(b), the Si $2p$ lines are shifted towards the value of clean Si(111) (indicating Si enrichment) with increasing temperature, but a residual difference of 0.15–0.2 eV in binding energy still exists. We note that a number of other factors can also contribute, for instance, the morphology of the overlayer. The present measurements provide information on the electronic structure of the Pd/Si interface when Si enrichment is obtained at the surface.

The characteristics of the bonding for a Si-rich layer interfacing a $Pd_2Si$-like phase at the surface (region A in Fig.

3) is probably similar to that at the $Si$-$Pd_2Si$ interface in the bulk (region B in Fig. 3) where a concentration gradient is present between the Si substrate and the silicide overlayer. We also believe that the information reported here is a complement to the understanding of the Si/Pd interface which so far has been studied only for the Pd-rich side (region C in Fig. 3).[1,2,4,5,14] It is noteworthy that the SR photoemission measurements with a short escape depth (4 Å) integrate over the transition region between $Pd_2Si$ and Si. The crucial point is that the EDC's cannot be interpreted as *the sum* of a silicide and a top layer of silicon. (For a photoemission of pure Si, see Ref. 3.) The modification of the shape of the EDC's as a function of temperature (shaded areas in Fig. 1) indicates the presence of a $d$ contribution (enhanced and seen at $hv = 80$ eV) and of a Si contribution (enhanced and seen at $hv = 130$ eV). This observation is taken as the direct spectroscopic evidence for the formation of new hybrid bonds due to the accumulation of Si on top of $Pd_2Si$. These bonds are typical of the transition from a silicide to a phase very rich in Si. They appear at higher binding energies than the $p$-$d$ hybrids[3] in $Pd_2Si$ [peak B in Fig. 1(b)]. At the same time, peaks A and C, present in $Pd_2Si$-like situation, disappear or are strongly reduced which is consistent with Si enrichment. As was discussed in detail elsewhere,[3] peak C is basically nonbonding in $Pd_2Si$.

The new Si-Pd bonds localized in the Si-rich overlayer provide evidence that the system gains energy when the surface is enriched in Si. This result is important in at least two respects:

(1) The new bond formation gives a substantial contribution to the driving force responsible for the thermal accumulation of Si; in this sense, our results give the first spectroscopic evidence for the accumulation process.

(2) The interface between the Silicide and the Si-rich overlayer has very stable bonds. This fact is expected to be typical also of the bulk-Si-rich side of the $Si/Pd_2Si$ interface and explains how this part of the interface acts as a membrane against interdiffusion, giving the high concentration gradient. This is also consistent with previous results[4,13] showing a small concentration gradient in the metal-rich
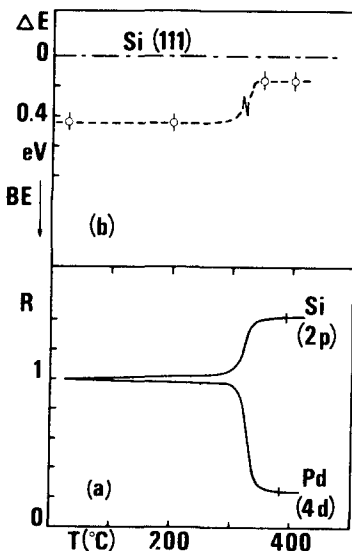


FIG. 2.(a) Photoemission intensities of Pd and Si as a function of temperature. $R$ denotes the ratio $I_T/I_{RT}$, where $I_{RT}$ is the intensity at room temperature and $I_T$ the intensity after heat treatment. (b) Si $2p$ core line binding energy shift as a function of treatment temperature (dashed line). The horizontal line (dash-dotted) represents the Si(111) surface before Pd deposition.
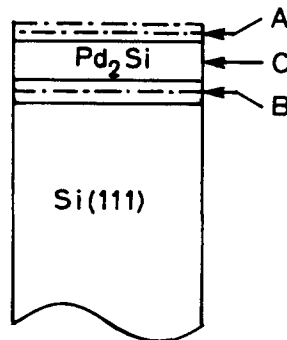


FIG. 3. Schematics of the Si/Pd interface formed at room temperature and then annealed at high temperature, resulting in Si accumulation of the surface. Region A is the Si-rich, thermally induced overlayer; region B is the Si-rich matching phase betwen Si and the reacted $Pd_2Si$, where a concentration gradient is present. Region C is the $Pd_2Si$ region with a small Pd concentration gradient.

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side of the interface. We believe that the strong bonds are the microscopic explanation to the stability observed for the Si-Pd interfaces prepared by annealing in device technology.

The photoemission data can also give a limited amount of structural information. We observed that the thermal treatment caused a chemical shift of the Si $2p$ core line *without* introducing any broadening as would have been the case if two or more Si species were present in the region explored with the photoemission techniques. This rules out an agglomeration due to the thermal treatment which was also confirmed independently by electron microscopy analysis of the samples after completion of the photoemission measurements.

In conclusion, we have shown that new electronic states are formed at the interface between $Pd_2Si$ and Si when Si is accumulated at the surface due to thermal treatment. The high binding energy of the new electronic states suggests that the bonds at this junction are strong.

In our discussion we used this direct evidence of strong bonds at the "surface $Pd_2Si$-Si interface" to suggest that a similar situation probably exists in the "bulk Si-$Pd_2Si$ interface," and proposed that this is a reasonable explanation of the high concentration gradient known to be present in this system.

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