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Formation of WSi_2 at the Si-W(110) interface

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Photoemission, Auger, and work-function measurements of room-temperature deposition of Si on W(110) show that Si interacts strongly with W and forms WSi_2 at the interface. As the formation of WSi_2 continues with increasing coverages of Si, silicon oxide species accumulate gradually on top of the surface due to the presence of O impurities. These species eventually form a thin oxide layer and hinder the formation of WSi_2 in the interfacial region.

There has been considerable interest in the studies of transition-metal/Si interfaces and interfacial silicide formations due to their potential application in integrated circuits and devices.[1] Substantial progress has been made in the understanding of interfacial reaction, chemical bonding, and compound formation between silicon substrates and near-noble-metal overlayers.[1-10] It has been observed[1-10] that, in general, deposition of near-noble metals on Si surfaces results in the formation of metal-rich silicides such as Ni_2Si, Pd_2Si, and Pt_2Si in the interfacial region even at room temperature, and that compound formation in the first few layers of metal coverage dominates the electronic properties of these interfaces. Within the first few layers of the metal/Si interface, however, compounds with structures or properties deviated from these metal-rich silicides have always been found.[2-10]

The past few years have also witnessed an increasing interest in the studies of refractory-metal/Si interfaces and silicides. In contrast to near-noble-metal/Si interfaces, however, less is known about the chemical interaction and the microscopic structure associated with the refractory-metal/Si interfaces. Several systems that have been studied[11-13] reveal different interaction behaviors between the deposited metals and the Si substrates, ranging from noninteracting[11] for V/Si to interdiffusing[12] for Cr/Si, and to reactive compound formation[13] for Mo/Si.

In this Rapid Communication we present both photoemission and Auger measurements on the interaction between evaporated Si atoms and clean W(110) surfaces. The results show that Si interacts strongly with W and gives rise to electronic structure identical to WSi_2 at the interface. The formation of this WSi_2 microscopic structure persists up to ten monolayers of evaporated Si. Its gradual disappearance is found to correlate with the gradual appearance of silicon oxide species on top of the surface, suggesting that impurities such as O are most likely responsible for the disruption of further WSi_2 formation in the Si/W(110) interfacial region.

The experiments were performed *in situ* in an ultrahigh vacuum system[14,15] which comprises a Si evaporator, a double-pass cylindrical mirror analyzer (CMA), a single-pass Auger spectrometer, a quadrupole gas analyzer, and an energy-resolving mass spectrometer used previously for electron stimulated desorption studies.[14,15] Si atoms were evaporated from a small Si crystal sitting in a Ta wire basket which can be resistively heated. The deposition rate was kept at a constant value of approximately 2 Å/min, as estimated repeatedly from many deposition tests. The photons were generated from a homemade resonance lamp which provided photons with an energy of 21.2 eV/(HeI) in this study. The photoemission spectra were collected via a computer-assisted data-acquisition system. Both photoemission and Auger spectra were taken before and after each deposition. For photoemission, angle-integrated energy distribution curves (EDC's) were taken by keeping the sample surface normal 42° with respect to the axis of the CMA.

The bottommost curve in Fig. 1 shows the photoemission EDC of the clean W(110) surface. It reveals a main *d*-band peak at -1.5 eV below the Fermi level (E_F) and a weak *s-p* band peaked at -6.2 eV. After deposition of Si on W(110), the main *d*-band peak shifts gradually toward -2.0 eV with coverage, and three new peaks appear in the EDC's. The corresponding difference curves, obtained by subtracting the weighted W(110) EDC from the observed EDC's, are also shown in Fig. 1 (designated as curve 1 through curve 12) for a variety of Si thicknesses x (Å). All these different curves, regardless of x (Å), exhibit identical structures, namely, with four peaks occurring at -1.8, -3.0, -4.7, and -6.7 eV, respectively. If Si forms an unreacted layer over W, we would expect the EDC's, especially of the thicker samples, to resemble that of either an amorphous Si or a bulk Si such as Si(100) [which, structurally speaking, fits more closely to the W(110) substrate surface lattices]. Neither is true as can be seen from Fig. 1 which also shows the photoemission EDC's of an amorphous[16] Si and a Si(100) surface.[5] In fact, we find that these structures are identical to those of 50-Å Si/W(110) after annealing[17] to about 700 °C (see Fig. 1), which, according to previous studies,[1] results in the formation of W disilicides (WSi_2). This clearly shows that room-temperature deposition of Si on W(110) results in the formation of WSi_2 at the interface. Based on the calculation[18] concerning $MoSi_2$, we interpret the peaks at -1.8 and -3.0 eV in both the difference curves and the WSi_2 EDC shown in Fig. 1 as being due to the bonding between the W-*d* and the Si-*p* orbitals, with the peak at -1.8 eV being mainly *d* derived and the peak at -3.0 eV *p* derived. The other two peaks at -4.7 and -6.7 eV, respectively, are derived from the Si-*p* orbitals mainly. These interpretations can also be roughly predicted from the spectra shown in Fig. 1 where we find that the three peaks at -3.0, -4.7, and -6.7, eV coincide with the *p*-derived peaks shown in the Si spectra, and that the -1.8-eV peak is closely related to the W(110) *d*-band peak. The substantial peak intensity near E_F and the sharp Fermi edge observed in both the difference curves and the WSi_2 spectra reveal strong metallic characters of W disilicides.

The Auger results are also consistent with the formation

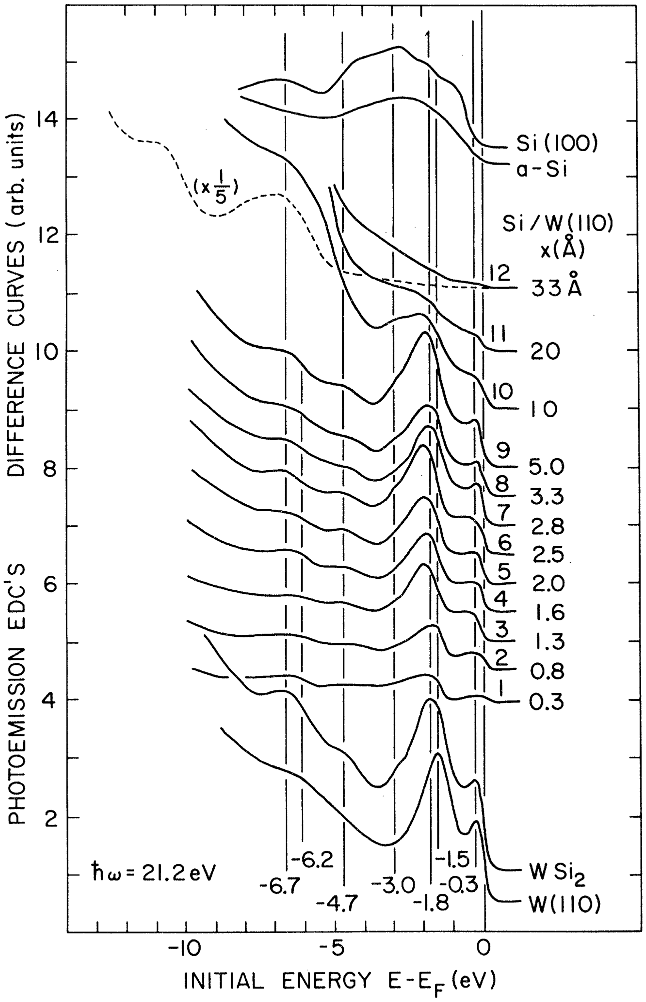

FIG. 1. Bottommost and the topmost four curves show the photoemission EDC's of clean W(110), annealed WSi_2, *a*-Si, and clean Si(100) surfaces. Curves 1 through 12 show the photoemission difference curves of Si on W(110) for a variety of evaporated Si thickness x (Å).

of WSi_2 upon deposition of Si on W(110). First, the Auger line shapes for as-deposited Si/W(110) are similar to those of annealed WSi_2, but different from that of bulk Si. Examples are shown in Fig. 2 where we have plotted several Auger differentiated spectra corresponding to the clean W(110) surface, two as-deposited Si/W(110), and one annealed [from the 50-Å Si/W(110) sample] WSi_2 surface, respectively. The Si (92 eV) Auger line shape of the 3.3-Å Si/W(110) is identical to that of the annealed WSi_2, and is different from that of a bulk Si, such as the 50-Å Si/W(110) sample. Second, the thickness dependences of both W and Si Auger intensities follow the predictions assuming the formation of WSi_2 upon deposition. This result is shown in Fig. 3 where we have plotted the peak-to-peak heights of both W (169 eV) and Si (92 eV) Auger lines as a function of evaporated Si thickness x (Å). The three pairs of solid curves correspond to the predictions in which an unreacted Si overlayer, a metal-rich W_5Si_3, and a silicon-rich WSi_2 are assumed. The data are evidently consistent with the formation of WSi_2 upon deposition of Si onto W(110).

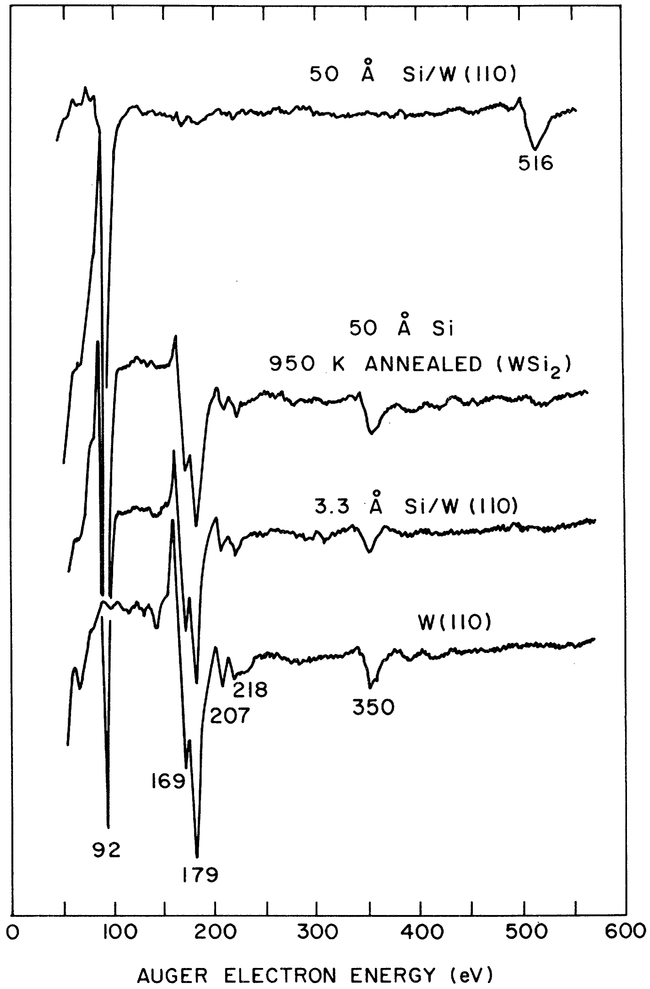

FIG. 2. Auger differentiated spectra for four different samples.

Work-function changes associated with the deposition of Si on W(110), which are shown in Fig. 4, are also consistent with the formation of WSi_2. It is found that, within 0.1 eV, all the work functions of the as-deposited Si/W(110) (especially for x less than about 8 Å where O impurities are insignificant in both photoemission and Auger spectra) are equal to that of WSi_2.

It is interesting to note that the deposited Si atoms have been shown[19] to sit above the twofold horrow sites of the W(110) surface. This geometry is similar to that of $WSi_2(100)$, where two Si layers locate above the (1×1) square W lattice, with the first layer of Si atoms sitting directly above the fourfold horrow sites.

The WSi_2 structure disappears gradually from both photoemission and Auger spectra with increasing x. Concurrently, both spectra show the gradual formation of SiO_2 or SiO_x on the surface, as evidenced from, e.g., the two characteristic energy levels (-7 and -11 eV; see Fig. 1) associated with the adsorption of O on Si surfaces.[20] The implication of this result is that the deposited Si atoms, albeit reacting strongly with W atoms and forming WSi_2, are captured by O impurities first and form SiO_2 or some kind of silicon oxides. These oxides species are probably left on the top of the surface as most of the free Si atoms continue,

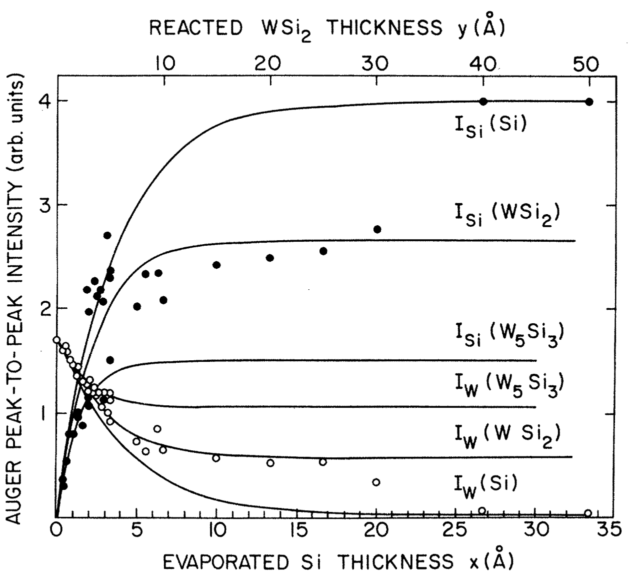

FIG. 3. Open and closed circles are the measured intensities of the W and Si Auger lines, respectively, plotted as a function of evaporated Si thickness x. The three pairs of solid curves represent the predicted intensities of both W and Si Auger lines as a function of x assuming three different compound structures for the Si layers, namely, an unreactive Si layer and two types of W silicides.

via interdiffusion, to react with W and form WSi_2. These oxide species gradually accumulate on the surface and eventually form an oxide layer which prevents further reaction between the incoming Si atoms and the W atoms. It is seen from Fig. 4 that the work function increases initially as a result of oxide formation and decreases gradually to a value of 4.83 eV as more and more unreacted Si layers are deposited onto the surface. It is interesting to note that the work function of a clean Si(100) surface[5] is also 4.8 eV. This suggests that the unreacted Si layers, although being amorphous, may have local ordering similar to that of Si(100).

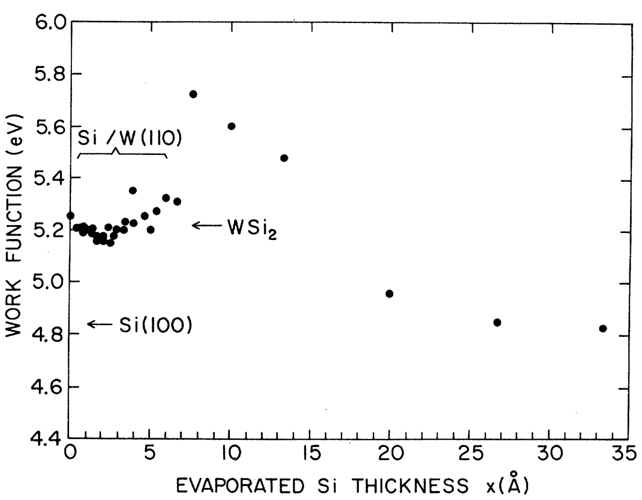

FIG. 4. Measured work functions (from photoemission EDC's) of Si/W(110) as a function of evaporated Si thickness x. The arrows indicate the work functions of the annealed WSi_2 and the Si(100) face, respectively.

In conclusion, we have shown that room-temperature deposition of Si on W(110) results in the formation of WSi_2 at the interface. Although the present results suggest that this effect may have already occurred at submonolayer coverages, further studies are obviously needed to obtain a more definite conclusion. The present results also show that, as the formation of WSi_2 continues with increasing coverages of Si, a silicon oxide layer gradually accumulates on top of the surface as a result of the presence of O impurities. This oxide layer eventually hinders the formation of WSi_2 in the interfacial region.

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