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High-resolution photoemission study of Co/Si(111) interface formation

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We have examined the formation of the Co/Si(111) interface at room temperature using high-resolution core-level photoemission spectroscopy. Two chemically shifted Si 2*p* core-level components have been identified. The evolution of these components with Co coverage makes it possible to model the development of this interface. Heterogeneous $CoSi_2$-like cluster formation is observed for nominal Co coverages of less than ≈ 4 Å. Continued reaction to form $CoSi_2$ becomes diffusion limited when the clusters coalesce, and a solid solution forms with Si atoms in a Co matrix. For Co coverages of more than 8–10 Å, the interfacial region is buried by a metallic Co film.

INTRODUCTION

Investigations of the nature of metal-semiconductor interfaces are important for both technological and scientific reasons.[1] Recent studies of interface morphologies have shown that metal-semiconductor junctions are generally not abrupt on the atomic scale and that atomic intermixing can produce a variety of different boundary-layer profiles.[2] These include thin silicide layers which form for Ce/Si(111) following cluster-induced reaction,[3] nearly perfect silicide-silicon interfaces for $NiSi_2$/Si,[4] and asymmetries of formation for metals on semiconductors compared to semiconductors on metals.[5] Important objectives in such studies include the characterization of the properties and physical extent of the (metastable) reaction products which form when metal atoms are deposited onto semiconductor surfaces under controlled conditions.

For the Co-Si and Ni-Si systems, it has been shown that annealed interfaces exhibit epitaxial disilicide growth.[4] For Co/Si(111) the disilicide structure is rotated 180° about the surface normal, forming the so-called *B*-type silicide, while both the rotated and unrotated types exist for Ni/Si(111). There has been a great deal of excellent characterization of these lattice-matched interfaces, including correlations between the structure type and the Schottky barrier.[6] Further, transistor-like devices have been fabricated based on Si/$CoSi_2$/Si layers.[7] In our own laboratory, we have used angle-resolved Auger electron spectroscopy to examine the structure of very thin $CoSi_2$ layers formed by Co deposition onto Si(111) and annealed according to the recipe of Tung.[6] Those results indicated that *B*-type $CoSi_2$ clusters form at very low coverage and are terminated by a Si(111) bilayer.[8] These clusters are 2–3 unit cells in thickness. For nominal Co depositions of 1 monolayer (ML), we found a heterogeneous surface of Si(111) decorated with *B*-type $CoSi_2$.

The present study was undertaken to examine the boundary layer that forms at room temperature, with particular interest in the growth of the silicide when the reaction itself is impaired by kinetics and diffusion limitations. Although less is known about room-temperature growth than about the formation of the interface at higher temperature, two interesting studies have been reported. Pirri *et al.*[9] used angle resolved photoemission to study the valence bands, low-energy electron diffraction (LEED) to investigate ordering, and x-ray photoemission to follow changes in the core-level signatures. Chainet *et al.*[10] used surface electron-energy-loss fine-structure spectroscopy (SEELFS) to determine Co—Si bond lengths at the evolving interface. These authors noted the similarities of Co/Si with the more extensively studied Ni/Si system.[11]

In this paper, we present high-resolution core-level photoemission results for the room temperature formation of the Co/Si(111) interface. Observed binding energy shifts for the Si 2*p* core levels are used to reveal changes in chemical environment at the interface, and line shape analysis provides insight into the nature and extent of these environments.[12] We have found that a very thin layer of $CoSi_2$ forms during the early stages of deposition at room temperature. When the formation of the silicide is limited by kinetics, a solide solution phase of Si in Co forms over the silicide layer. The solution phase ultimately yields to an overlayer of pure Co for thick films grown at room temperature.

EXPERIMENT

Photoemission experiments were performed at the Wisconsin Tantalus storage ring using synchrotron radiation that was monochromatized by the Grasshopper Mark V monochromator. Photoelectrons were energy analyzed using a double-pass cylindrical mirror analyzer in an ultra-high vacuum system having an operating pressure of $\sim 5\times 10^{-11}$ Torr. High purity Ames Laboratory cobalt was evaporated by resistive heating of a degassed 5-mil tungsten boat. The source to sample distance was ~ 30 cm and the evaporation rate, as measured with a quartz crystal oscillator, was approximately 1 Å/min. Evaporations were done at pressures of less than 3×10^{-10} Torr. Submonolayer depositions were done by timed exposures of the sample to the evaporation source. The Si crystals were *n* type and were oriented for cleavage along the (111) plane. The quality of the cleaved surface was judged visually and with valence band and 2*p* core level spectra.

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Evaporated Co thicknesses are expressed here in angstroms, as measured with the quartz crystal oscillator. The conversion to monolayer-equivalent coverage is given by the Si(111) surface atom density, 7.8×10^{14} atom cm^{-2} and 1 Å Co = 1.17 ML or 9.1×10^{14} atoms cm^{-2}.

RESULTS AND DISCUSSION

In the left panels of Figs. 1 and 2 we show background-subtracted Si $2p$ photoelectron energy distribution curves (EDC's) taken at photon energies of 108 and 135 eV as a function of overlayer thickness Θ. These photon energies provided Si $2p$ photoelectrons with mean free paths of $\sim$24 and 4.4 Å, respectively, for bulk and surface sensitive measurements.[13] The experimental resolution (monochromator + analyzer) was 190 meV for the spectra taken at 108 and 250 meV for those at 135 eV.

The results of Figs. 1 and 2 show significant changes in the Si $2p$ core-level line shapes as the Co coverage is in-

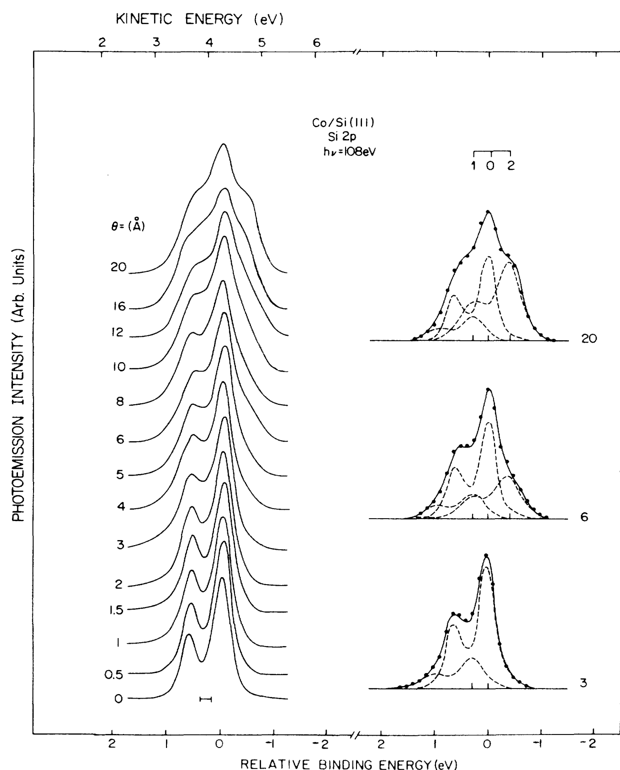

FIG. 1. Background subtracted Si $2p$ energy distribution curves (EDC's) taken at a photon energy of 108 eV showing changes in line shape as a function of Co coverage. Decompositions such as those on the right identify two chemically shifted components. Component 1 is shifted 0.3 eV to higher binding energy and component 2 is shifted 0.4 eV to lower binding energy relative to the substrate. Both have line shapes equal to that of the substrate convoluted by a Gaussian of FWHM equal to 0.4 eV. The horizontal line indicates our resolution, 190 meV. The spectra on the right panel have been rigidly shifted to align the substrate peak, correcting for a 50 meV change in band bending upon Co deposition.

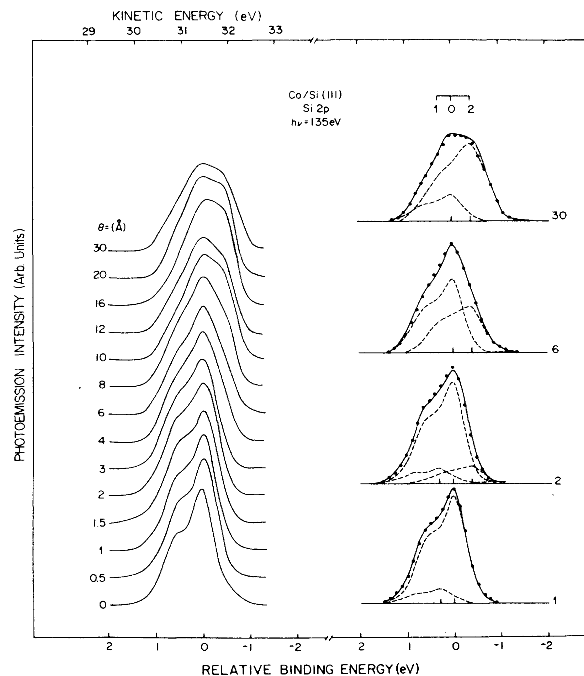

FIG. 2. Si $2p$ EDC's and decomposition, analogous to Fig. 1 but with $h\nu = 135$ eV to maximize surface sensitivity. The total resolution (monochromator plus electron energy analyzer) is 250 meV.

creased. These are due to the development of reaction products in which the Si atoms are in different environments than crystalline Si and there is valence charge redistribution of the sort discussed elsewhere in the context of band calculations for silicides.[14] Although the positions, widths, and intensities of these components will be analyzed in greater detail in the following, some trends are apparent. First, the 135-eV spectrum for the clean Si surface shows a low binding energy (high kinetic energy) tail which is reduced by the deposition of 0.5 Å of Co. This tail is due to the surface core level component[15] and is not apparent in the 108-eV spetrum due to the greater escape depth. Upon deposition of a few angstroms of Co, a filling in of the region between the $2p_{1/2}$ and $2p_{3/2}$ components occurs and a higher-binding-energy tail appears. At higher coverage a low binding energy shoulder also appears and develops fully. These results indicate the presence of both high *and* low binding energy Co-induced Si $2p$ components.

In addition to the core-level studies described above, we also followed the evolution of the valence bands. Our results, taken at a photon energy of 60 eV, are in good agreement with those of Pirri *et al.*[9] and are not reproduced here. The dominant valence band feature is a broad peak $\sim$1 eV below E_F which is characteristic of the disilicide. This shifts toward E_F to reach the position characteristic of Co metal at a coverage of 8 Å. In the early stages of reaction, this peak is associated with the nonbonding d states of the interface silicide[14] and, with increasing coverage, it evolves as the Co-rich layer grows on the silicide.

A more quantitative discussion of the reaction products is aided by decompositions of the Si 2p core-level EDC's, as shown in Figs. 1 and 2. To do so, the inelastic background was first subtracted and the spectra were normalized to the incident photon flux. For the EDC's at 135 eV, the surface component was empirically subtracted and the resulting lineshape was used for fitting of subsequent EDC's. Analysis showed that the low coverage results could be decomposed into two components, one being the substrate (labeled 0) and the other shifted to higher binding energy by 0.3 eV and broadened (labeled 1). The broadening was equivalent to the convolution of the substrate line shape with a Gaussian of full width at half maximum (FWHM) equal to 0.4 eV. Decomposition at higher coverages required the introduction of a third component (labeled 2) with the same line shape as component 1 and shifted 0.4 eV to lower binding energy with respect to the substrate. This procedure is equivalent to what has been discussed in detail in Ref. 12 and citations therein. Representative decompositions are shown on the right panels of Figs. 1 and 2. These EDC's have also been rigidly shifted so as to align the substrate peaks, thus correcting for a 50-meV band bending change induced by the deposition of the first 0.5 Å of Co. This change is toward lower binding energy and indicates an increase in the energy separation between the Fermi level and conduction band minimum. No further change is observed after 0.5 Å.

In Figs. 3 and 4 we summarize the coverage-dependent Si 2p integrated emission obtained by normalizing the emission at coverage Θ to that of the clean surface, $\ln[I(\Theta)/I(0)]$. The uppermost curve corresponds to the total emission. By decomposing the core level EDC's, it was also possible to construct the component-specific attenuation curves, as shown. Such a procedure makes it possible to characterize the growth and attenuation of each reaction product. For Co/Si, there are two different coverage regimes, each identified by the growth and decay of one of the two shifted components. The attenuation curves and the behavior of each component, together with differences due to the use of different escape depths, will be discussed in the next section.

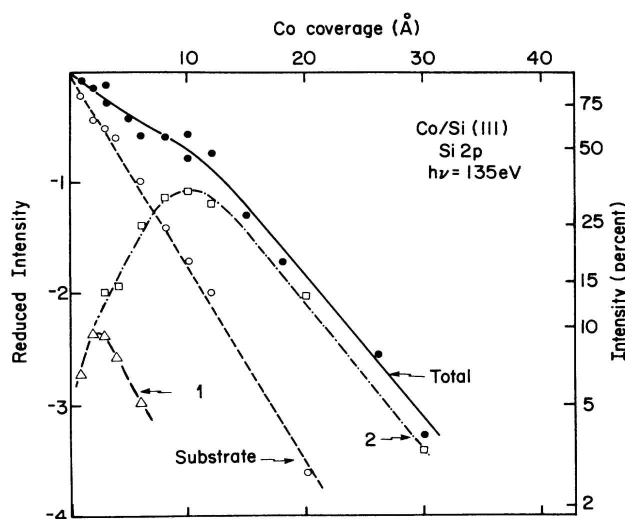

FIG. 4. Attenuation results $\ln[I(\Theta)/I(0)]$ analogous to Fig. 3 but with a greater surface sensitivity because of the higher photoelectron kinetic energies. Differences in the attenuation of the two components as a function of escape depth help in formulating a model for the interface. Component 1 is associated with a thin interface $CoSi_2$-like phase while component 2 arises from the emission of Si atoms in solution in the Co overlayer. The concentration of these dissolved Si atoms diminishes with distance from the interface.

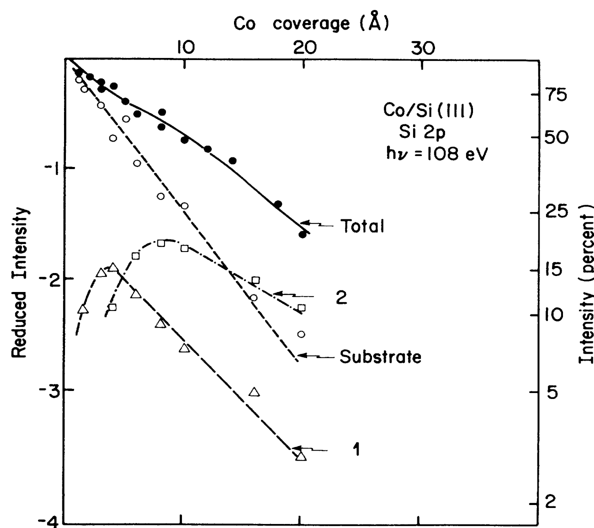

FIG. 3. Attenuation curves defined as $\ln[I(\Theta)/I(0)]$ showing the reduction in the Si 2p emission as a function of Co coverage for spectra taken at $h\nu = 108$ eV. The relative contribution of the two shifted components has been plotted as a function of coverage.

Prior studies of room temperature Co/Si(111) interface formation have been reported by Pirri *et al.*,[9] and their results favored the formation of the $CoSi_2$-like layers at low coverages. The SEELFS results of Chainet *et al.*[10] indicated that the Co-Si nearest-neighbor distance was equal to that of $CoSi_2$, to within their experimental error, for 2 Å of Co on Si. They observed spectra resembling those of CoSi at 4 Å and those of Co_2 Si at 6 Å, concluding that sequential silicide formation is likely—or at least that the Si environment becomes increasingly Co coordinated. Our high-resolution core-level photoemission results are compatible with the former results, and we find no evidence for sequential silicide formation.

During the deposition of the first few monolayers of Co, component 1 grows in relative intensity in both the high and low escape depth attenuation curves. The peak intensity is reached at an equivalent Co coverage of only 3–5 Å, indicating a very narrow interface phase is present. At this coverage, further production of phase 1 stops and emission from it is attenuated by the phase formed on top of it, as can be seen on both attenuation curves. The appearance of component 1 is accompanied

by valence band spectra suggestive of $CoSi_2$, as discussed by Pirri *et al.* Further support for assigning a $CoSi_2$-like composition to the first reaction product comes from studies of the Si $2p$ levels in Ni_2Si, NiSi, and $NiSi_2$,[16] which showed the Si $2p$ binding energy in NiSi to be greater than in elemental Si by 0.33 ± 0.15 eV. This is comparable to the shift we observed for component 1 at the Co/Si interface.

From the attenuation curves, we see that the low binding energy component 2 can already be resolved when production of phase 1 ceases. At this coverage, component 2 has approximately the same intensity as component 1 for our surface sensitive measurements (135 eV); it is somewhat lower for the more bulk sensitive measurements (108 eV). We conclude that interface phase 1 is already covered by significant amounts of phase 2 at nominal depositions of 3–4 Å, indicating that the initial interface growth does not occur in a layer by layer mode but is more heterogeneous. This process can be visualized by assuming that Co atoms initially deposited on Si diffuse to reaction sites where the nucleation of $CoSi_2$-like islands begins and phase 1 forms. Further Co depositon leads to the lateral growth of these islands. When the supply of Si on the surface of the islands is insufficient to continue the formation of $CoSi_2$, then we see the growth of phase 2 over phase 1. This heterogeneous growth continues until the clusters have coalesced to form a continuous layer.

Cluster formation is compatible with the LEED results of Pirri *et al.*[9] It has been suggested for the related Ni/Si system based on surface extended x-ray-absorption fine structure (SEXAFS) and ion scattering results.[11] The heterogeneous nature of the interface phase is also suggested by the 0.4 eV broadening of component 1, implying the existence of a number of inequivalent Si environments.

The restricted thickness of the $CoSi_2$ layer can be explained by diffusion-limited processes since reaction of Co and Si to produce a silicide occurs spontaneously at room temperature at the Co/Si interface. Indeed, diffusion-limited reaction is a general phenomena for interface growth. Variations in thickness can then be related to the ease with which substrate and deposited atoms diffuse through the reaction product to reach a region where reaction can continue. In turn, this is dependent on the morphology of the reacted layer since grain boundary diffusion is faster than bulk diffusion and a perfect crystal can tolerate a greater concentration gradient than a polycrystalline array. Increasing the temperature greatly enhances Co and Si diffusion through the silicide region and allows a thicker layer to grow.

The attenuation curves show that emission from the second shifted component grows, reaches a maximum, and then falls once the growth of the $CoSi_2$-like phase is impeded. After the maximum is reached, the attenuation curves show that the amount of Si in the probed region diminishes. We associate component 2 with a solid solution phase of Si in polycrystalline Co in which Si becomes diluted with coverage. The line-shape broadening of the second reacted component again points to inhomogeneities or to inequivalent atomic environments for Si. The identification of phase 2 as a solid solution is further supported by the relatively slow attenuation of this component relative to component 1 or the substrate (which both decay at approximately the same rate). This is due to a concentration gradient in the solution phase and is less apparent on the low escape depth data because of the reduced probing distance.

In Fig. 5 we schematically summarize our observations for the Co/Si interface. We have found that in the 2–6 Å Co coverage range, $CoSi_2$ clusters are covered by a solid solution of Si in Co. Hence, a probe which averages over all emitting Co atoms will detect decreasing Si coordination for Co, as observed.[10] Finally, we obtain a Schottky-barrier height (SBH) which is in reasonable agreement with previously reported data for Si interfaces with $CoSi_2$ or CoSi.[1] Since we observe no evolution of the SBH after the initial deposition of 0.5 Å of Co, we conclude that the initial nucleation and clustering determines the electrical properties of the interface. It is not possible, however, for us to identify the mechanism of SBH formation, but we draw attention to interesting work by Tung and co-workers and Ho and co-workers[6] for $CoSi_2$/Si and $NiSi_2$/Si.

Our model as sketched in Fig. 5 indicates that silicide formation begins at very low coverage and is heterogeneous across the surface. Based on our angle resolved Auger structural results, we suspect that the silicide is 2–3 layers in thickness where it forms. With further Co deposition, there is competition between (i) continued disilicide reaction as Co atoms arrive on the Si surface and (ii) the formation of a solution phase when Co atoms arrive on the silicide and diffusion restricts the number of Si atoms available for reaction. This morphology is, of course, dependent on temperature since evolution at elevated temperature would show thicker films of silicide. This is consistent with what has been reported for the growth of thick disilicide layers on Si and with temperature dependent studies of other interfaces.

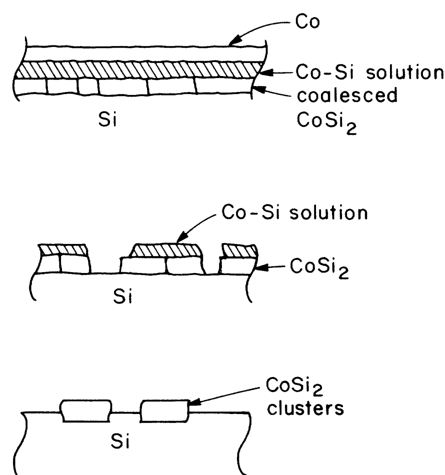

FIG. 5. Sketch of the evolving Co/Si interface showing silicide clusters at low coverage, their coalescing and effective regulation of the thickness of the silicide layer, the formation of a thin solid solution of Si in Co, and the convergence to pure Co at higher coverage.

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