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Compound formation and bonding configuration at the Si-Cu interface

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Joint photoemission and Auger LVV line-shape spectroscopies on the Si-Cu interface show the existence of a silicidelike compound with bonding characteristics similar to those of the near-noble-metal silicides. This makes the Si-Cu interface different from the other noble-metal–Si interfaces where alloylike phases (Si-Au) or narrow interfaces with concentration gradients (Si-Ag) are formed. The Si-Cu compound is metal-rich with a stoichiometry close to the eutectic composition Cu_3Si and is stable over a wide range of temperatures.

INTRODUCTION

The nature of the chemical bond in noble-metal–elemental-semiconductor interfaces has been the subject of an extensive investigation, theoretical and experimental, with particular attention to the Au-Si and Ag-Si systems. Those two systems present quite different interface formation processes; the Si-Au interface is very broad and is characterized by an alloy phase with variable composition[1-3] and a concentration gradient–the Si-Ag interface is conversely narrow[4] with intermixing limited to the very top layers of Si.[5] The Si-Cu case has been much less studied[6] because it is a less favorable case for photoemission studies. In fact, the Cu $3d$ valence electrons have a considerably higher cross section for photoionization than the Si $3sp$ states over the entire range of photon energies of interest for surface spectroscopic studies, therefore making impossible the detection of the valence structures due to the substrate. In the case of Si-Au photoemission at the Cooper minimum for the $5d$ subshell experimental results have been compared with valence-band (VB) density-of-states (DOS) calculations, allowing for a final assignment of all the contributions to the energy distribution curves (EDC's) structures.[3] Nevertheless, some difficulty remains in defining an ultimate bond configuration since, in the alloylike Si-Au mixture, no preferential coupling of Si p states and Au d states is found. This led Bisi *et al.*[3] to conclude that rehybridization of Si p and Au $5d$ electrons is much less important in the Si–Au bonding than it is in the case of the corresponding $5d$ near-noble-metal silicide Pt-Si.[7] The Si-Ag interface has also been investigated with photoemission at the Cooper minimum, and the evidence of a chemical reaction was found.[5] The interface is nevertheless very different with respect to the corresponding near-noble-metal silicide Si-Pd, which is a highly mixing and reactive system with stable stoichiometries (Pd_2Si, PdSi).[10,11,14]

EXPERIMENT

We have adopted a new approach to the study of the Si-Cu interface using two different techniques to probe the valence electronic structure with high sensitivity to the different orbital contributions: photoemission spectroscopy with high sensitivity to the Cu $3d$ states and Si $L_{2,3}VV$ line-shape analysis to probe the Si p DOS.[8,9] Only the combination of these two techniques, used in such a way to give information about the same sampled area of the sample (kinetic energies of the Auger and photoelectrons in the range 55–95 eV, corresponding to 5–7 Å of escape depth), made this study and the following discussion meaningful, proving itself as an alternative method of investigation of valence states at interfaces for $3d$ metals (which do not have Cooper minimum). Our experimental work on the Si-Cu interface allows us to discuss in detail the bonding configuration between Cu and Si and make precise assignments of the orbital contributions to the total DOS. The samples were prepared by cleaving Si(111)-oriented bars in UHV (pressure $\sim 5 \times 10^{-11}$ Torr) and evaporating Cu from a Cu bead on a Pt wire at pressures below 1×10^{-10} Torr, under control of a quartz-crystal thickness monitor. All the spectra were obtained in the $N(E)$ (retarding) mode with use of a cylindrical mirror analyzer perpendicular to the sample surface and, as an excitation source, grating incidence monochromatic synchrotron radiation at $h\nu = 80$ eV (VB), $h\nu = 160$ eV (Si $2p$), and $h\nu = 150$ eV (LVV) in order to obtain escape depths for the emitted electrons at the (same) maximum value of surface sensitivity.

RESULTS AND DISCUSSION

In Fig. 1, we show the Si $L_{2,3}VV$ spectra for Si + 15 Å Cu (~ 12 monolayers). To better point out the structures, we

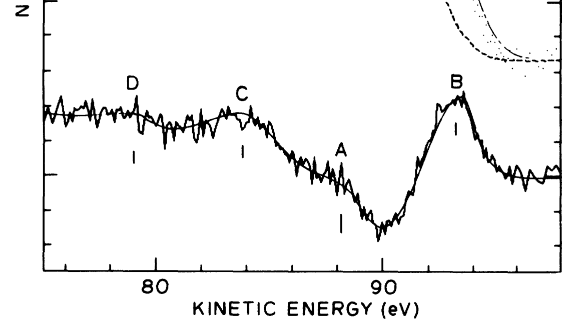

FIG. 1. Si $L_{2,3}VV$ line shape [$N(E)$] for Si + 15 Å Cu (dots), for clean Si(111) (dashed line), and difference curve (solid line).

compare it with the Si $L_{2,3}VV$ spectrum for the clean as-cleaved Si(111)-(2×1) surface and show the difference curve obtained by subtracting the clean spectrum from the one for Si-Cu having artificially set the amplitudes of the two spectra equal so as to cancel out the experimental background in the subtraction. The difference curve clearly shows four peaks at ~79.2, 84, 88.3, and 93.5 eV of kinetic energy. Those peaks have a one-to-one correspondence to those obtained from a similar analysis of the Si-Pd interface and of Pd$_2$Si (shown for comparison in Fig. 2).[10,11] These peaks are interpreted as due to a redistribution of the p states of Si into two main structures separated by ~5 eV which give rise to the four Auger peaks according to a scheme proposed first by Ho *et al.*[10] for Pd$_2$Si. The two Si p peaks in the DOS were assigned to bonding Sip-Pdd hybrids centered around ~ −5.5 eV below E_F and the corresponding antibonding states around E_F. Those assignments were independently achieved by photoemission at the Cooper minimum in the case of Pd-Si (Ref. 12) and by DOS calculations by Ho, Schmidt, and Foll[11] and by Bisi and Calandra.[13]

This bonding scheme is typical for all the near-noble-metal silicides as was demonstrated by Cooper minimum photoemission for Pd-Si,[14] Pt-Si,[7] by x-ray photoemission spectroscopy[13] and photoelectron spectroscopy[15] for Ni-Si, and by theoretical DOS calculations.[12] In particular, the 3d near-noble-metal silicide Ni-Si presents a bonding hybrid structure (Ni3d-Si3p) between −4 and −6 eV below E_F, which is stable over changes in stoichiometry from NiSi$_2$ to Ni$_2$Si.[15]

The valence-band photoemission spectra dominated by the Cu3d emission are collected in Fig. 3. The Cu3d peak lies at −3.7 eV below E_F for $\theta=2$ Å and $\theta=4$ Å, and undergoes a small energy shift (~0.2 eV) towards the position of the bulk Cu signal (given for reference in the top panel of the figure) for $\theta=15$ Å. From the corresponding Si $L_{2,3}VV$ line-shape spectra collected in Fig. 4, it seems that Si is at least partially mixed and reacted with Cu for all coverages. In fact, by subtracting an estimated amount of

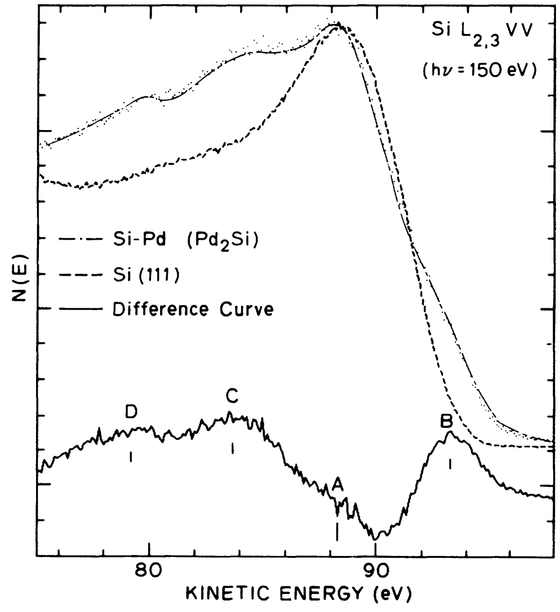

FIG. 2. Si $L_{2,3}VV$ line shapes [$N(E)$] for Si-Pd (Pd$_2$Si) (dots), pure Si(111) (dashed line), and difference curve.

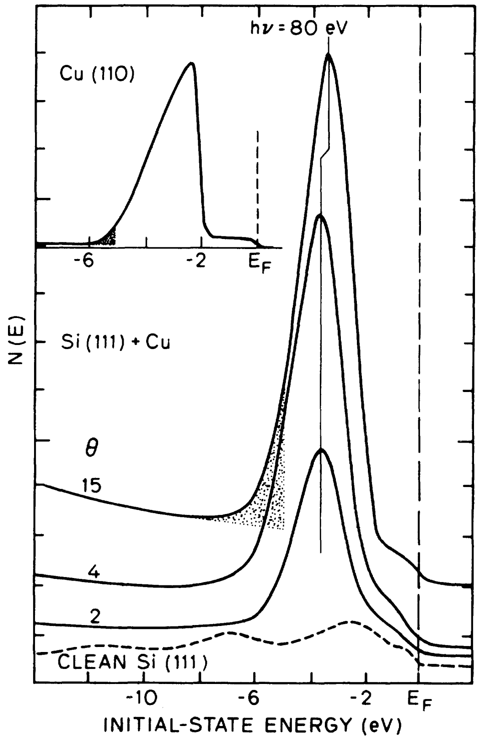

FIG. 3. Partially angle-intergrated photoelectron energy distribution curves (EDC's) for Cu(110) (top curve) (Ref. 16), clean Si(111) (dashed line), and Cu overlayers onto Si(111). The shaded areas show the DOS at Cu3d around −5.5 eV in pure Cu and in mixed Si-Cu. The coverages θ are in angstroms.

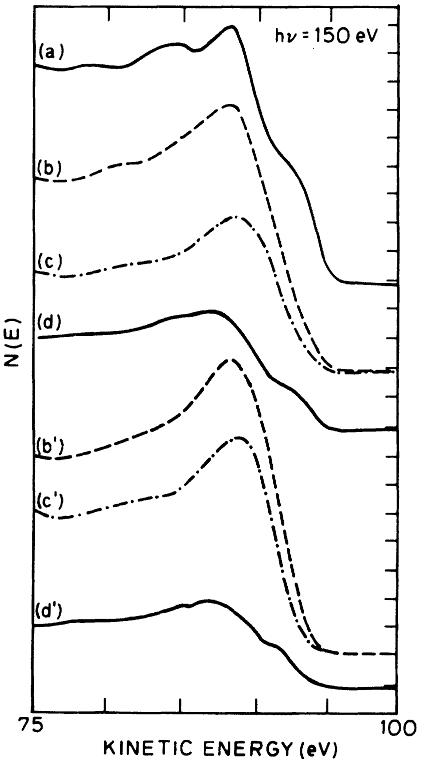

FIG. 4. Si $L_{2,3}$ line shapes for Si(111) and Si+Cu. (a) Si+15 Å Cu, fully mixed. (b) Line shape for Si+4 Å Cu. (b′) Line shape for Si+2 Å Cu. (c) (c′) Line shape for pure Si attenuated. (d),(d′) Difference curve-s: line-shape contribution from Si mixed reacted with Cu at $\theta=4$ Å and $\theta=2$ Å.

pure Si signal from the background (assuming an approximately constant escape depth of ~7 Å), we obtain a line-shape contribution from the residual Si signal which strongly resembles the final line shape for Si entirely mixed with Cu at $\theta = 15$ Å, shown in the top curve.[17]

From the contrast of the Auger line shapes with the photoemission, we conclude that the Cu $3d$ signal observed originates from Cu mixed with Si. At $\theta = 2$ Å, the Cu $3d$ peak appears narrower and symmetric. This indicates that Cu is more diluted at this low θ than at higher coverages, and therefore, for $\theta = 2$ Å, the Si-Cu mixed phase does not have the metalliic character that determines the broadening of the $3d$ peak in bulk Cu. We want to notice that in the absence of the parallel Auger LVV analysis the Cu $3d$ peak at this low coverage could have been interpreted as due to semi-isolated Cu atoms in weak interaction with the substrate.[18,19] Rather, the rearrangement of the valence states of Si upon condensation of Cu at the surface requires the Cu atoms to be involved in a strong chemical reaction. The $3p$ DOS of Si, in fact, is not affected at low coverages when the only consequence of the deposition of submonolayers of metal is the disruption of the surface. In the case of Ag, for example, the removal of the sp^3 coordination of the surface Si atoms has been proved; nevertheless, the Si LVV line shape of Si for Si + 1 monolayer. Ag does not show evidence of strong rehybridization of the Si $3p$ states. This demonstrates the difficulty a pure photoelectron spectroscopy investigation encounters when the interfaces between elements with large differences in cross section of the valence states are studied in regard to the bonding character. The small evolution of the shape and binding energy of the Cu $3d$ peak over the coverage range investigated and the final full width at half maximum (FWHM) of the d-band signal at $\theta = 15$ Å rule out the possibility of Cu islands or the presence of very different stoichiometries (concentration gradient) at the Si-Cu interface. The binding energies of the Cu$3d$ states are the same as those of Pd $4d$ in Pd_2Si. In particular, we notice that in the region of the valence band around -5.5 to -5 eV there is a strong increase of the Cu $3d$ emission which becomes ~20% of the total Cu $3d$ intensity, with respect to the ~5% in pure Cu, as indicated by the shaded areas in Fig. 3.

The rehybridization scheme discussed for the Si $3p$ states has its counterpart in this increased d density of states around -5.5 eV, which therefore strongly indicates the presence of a silicidelike bonding contribution for Si-Cu, a peak of bonding hybrids at energies centered around -5.5 eV, and the corresponding density of antibonding states in the E_F region. The Cu $3d$ states not involved in the rehybridization determined a nonbonding peak at -3.5 eV below E_F with a rather symmetric peak shape and FWHM equal to that of the d band in bulk copper—this marks a difference between Si-Cu and the other noble-metal–silicon interfaces which do not show strong silicidelike behavior. This point deserves some discussion. In fact, it is known that at high Si dilution the LVV line shape changes to a structure (double peaked in the most common derivative spectra) similar to that for Pd_2Si and Si-Cu: This is found in the Au-Si alloys and also for diluted Si in Ag-Si alloys. As a consequence, it might appear safer to simply state that our measured LVV line shape is characteristic of Si atoms in a metal environment. From our results on Si-Cu, though, the Cu $3d$ band appears to be distributed according to the redistribution of the Si $3p$ states and the fact that such electronic structure develops from the very beginning of the interface formation, i.e., submonolayer coverages of Cu give a marked silicidelike character to this system in analogy to the reactive near-noble-metal–silicon systems. Such silicide bonding structure has been disproved in the case of the Au-Si alloys[3] and is also inappropriate for the Ag-Si system where only a thin mixed region is formed which does not develop into an extended reacted phase. From an extensive Auger electron spectroscopy–low-energy-electron diffraction experiment on the intermixing and temperature dependence of the Si-Cu interface formation (80 to 1300 K), we found that the electronic configuration for the Si-Cu interface described above for the $\theta = 15$ Å case is *very stable* over a large interval of Cu coverages at room temperature and that the composition (Auger intensity ratio) that corresponds to that Si $L_{2,3}VV$ line shape is also fairly stable over a large range of temperatures (RT → 350 °C).

A common difficulty in the study of mixed phases by means of surface-sensitive techniques is the lack of direct quantitative information on the composition and/or stoichiometry of surfaces and interfaces. Here, we attempt a determination of the average composition at the intermixed Si-Cu interface on the basis of our capability of measuring true relative photoemission intensities[16] for electron orbitals of the two elements and using the calculated values for the (atomic) cross sections for photoionization of the Si $2p$ and Cu $3d$ subshells[20] to calibrate, on a relative scale, the experimental intensities. This follows a relative quantitative analysis within regions of the sample, the volume resolution being determined by the escape depth of

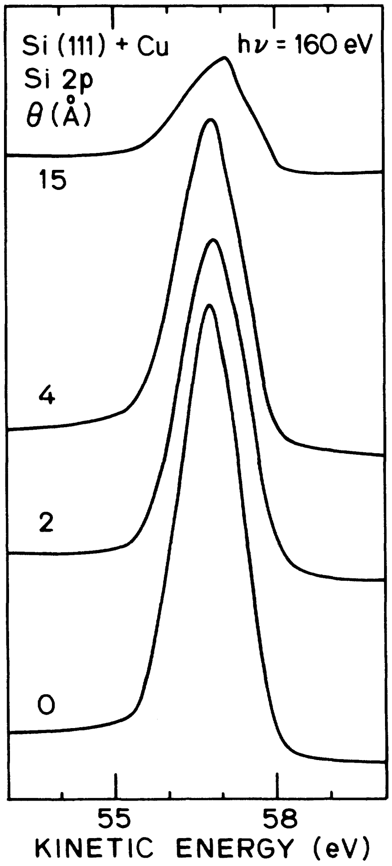

FIG. 5. Si $2p$ core photoemission at the escape depth minimum (obtained with $h\nu = 160$ eV). A small shift, ~150 meV, is seen in the fully reacted $\theta = 15$ Å sample.

the electrons and the accuracy in the composition determination being limited by the approximation inherent in adopting calculated values for the atomic cross sections for photoionization to the solid state. This approximation is, in general, good for core levels, while it can be inaccurate for valence states[16] due to the fact that overlapping bandlike wave functions may be severely distorted from the atomic correspondent wave functions so that the overlap between the initial and final state in the photoionization process is poorly reproduced in atomic calculation. For example, radial wave functions that present nodes in the overlap region (like the 4*d* and 5*d* transition metals) are greatly distorted and this largely affects the singularities in the cross section, i.e., the Cooper minimum effect. In the present case, though, the Cu 3*d* states are relatively localized and the wave function does not have radial nodes.

Attempting such analysis, by reducing the normalized photoemission counting rates (peak areas) for Si 2*p* and Cu 3*d* to internally comparable intensities and using the cross-section values, we obtain, for the sample with 15 Å of Cu, a proportion of Cu vs Si atoms within the top 7 Å of the sample of 2.8:1 to 3.05 ratios.[21] A consistent value is also obtained from the attenuation profile of the Si 2*p* photoemission versus Cu coverage (Fig. 5) which shows a reduction of a factor of 3.6 in going from the clean Si(111) to Si + 15 Å Cu.[22] This consistency of the cross-section determined composition with the measured reduction of the Si 2*p* photoemission intensity gives support to our analysis and to the composition values suggested for the top layers of the samples.

It thus appears that Cu_3Si is the average composition of the mixed Si-Cu phase whose electronic structure and chemical bonding has been discussed in this paper. Also, it results that Cu_3Si is the dominant stoichiometry at the Cu-Si interface in a wide range of Cu coverages. The Cu_3Si composition corresponds to the eutectic for Si-Cu. This explains thermodynamically the favorite formation of this phase at the interface and its stability over a large temperature range.

CONCLUSIONS

We have shown the peculiar character of the Si-Cu interface which gives a silicidelike stable phase with approximately the eutectic composition Cu_3Si, which therefore appears different from the other Si–noble-metal systems. This important result was obtained on a pure experimental basis by exploiting jointly photoelectron and Auger line-shape spectroscopies and by use of the values for the cross sections for photoemission to determine the approximate average stoichiometry.

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