

Anisotropic empty electron-band states at the pseudo- 5×5 Si(111)/Cu interface

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The partial (s - d) density of empty states at the Cu site in the pseudo- 5×5 Si(111)/Cu interface has been investigated by polarization-dependent x-ray absorption spectroscopy at the Cu $L_{2,3}$ edges. The absorption spectra are strongly dichroic showing a metallic edge in the interface plane and a quasigap in the perpendicular direction. The *two-dimensional* nature of the electron-band states at the pseudo- 5×5 interface layer is therefore directly probed.

Interfaces are intrinsically low-dimensional systems whose properties are extensively investigated because of the large impact that interface control has on technology. The electronic states at epitaxial interfaces can be studied either in thick epitaxial layers with probes allowing for depth sensitivity, or by reducing the epitaxial layer to minimal thickness, often down to one monolayer, and probing the entire density of states.^{1,2}

Both approaches lead to shortcomings either due to the difficult resolution of true interface states or to the difficult generalization from monolayer phases to bulk epitaxy. The Cu-Si system is noteworthy since a well-defined, albeit little understood, incommensurate phase is formed when amounts of Cu in the range 5×10^{14} – 1.5×10^{15} atoms/cm² are deposited on Si(111) 7×7 surfaces and annealed at temperatures of the order of 600°C.²⁻⁹ This phase cannot be grown at larger thicknesses and therefore is a prototype of true interface compound, whose atomic and electronic structure is entirely determined by the low-dimensionality condition.

A renewed interest in this system has therefore occurred as surface structural probes like scanning tunneling microscopy have acquired the necessary reliability for attacking this incommensurate interface phase.⁵⁻⁸

In this paper we show results that allow us to discuss in a direct way the anisotropy in the electron states of the pseudo- 5×5 Cu-Si phase (hereafter called p - 5×5). Experiments with linearly polarized soft x rays have recently allowed the probing of the crystal-field asymmetry at the metal sites in epitaxial interfaces between rare earths and silicon by resolving the ground-state splitting along the field direction when measuring atomiclike $3d$ to $4f$ transitions.¹⁰ When probing $2p$ to $(3d-4s)$ transitions in the d metals the final state carries the band-structure information which is therefore reflected in the line shape and width of the x-ray absorption-edge resonance.¹¹

If anisotropies exist in the energy distribution and density of the states in the empty bands, these are reflected in polarization-dependent line shapes (dichroism) when the

relevant directions are probed by a searchlight excitation. The searchlight effect of linearly polarized x rays has been long established.¹²

Si(111) substrates were cleaned by Ar⁺-ion sputtering and thermal flashing (1150°C). The Si(111) 7×7 reconstruction was achieved after slow cooling, and sharp 7×7 diffraction patterns of low-energy electrons (LEED) were reproducibly obtained. Cu was Ohmically evaporated at very low rates (1 Å/min) from W filaments and the coverages calibrated with a quartz microbalance. We define one monolayer on the basis of the surface density of Si(111) = 7.8×10^{14} atoms/cm². Each coverage reported herein corresponds to freshly prepared substrates. The base pressure was $\approx 2 \times 10^{-10}$ mbar, rising up to $\approx 5 \times 10^{-10}$ mbar during the evaporation. Heating of the samples (1 min at 600°C) was done subsequent to the Cu deposition by circulating an electric current across the wafers. The temperature was measured by an optical pyrometer. The x-ray absorption-spectra (XAS) measurements were performed at the beamline SA-22 of the 800-MeV positron-storage ring SuperACO of LURE at Orsay. A photon-energy resolution of about 300 meV was achieved at the Cu $L_{2,3}$ threshold energy by using a double-crystal ultrahigh-vacuum (UHV) monochromator with a mounting of beryl(10-10) crystals. All the spectra were collected in total-electron-yield mode.

We have also measured Cu $2p$ XAS spectra from polycrystalline fcc Cu and from some Cu-(Si,Ge) alloys which belong to the class of "electron phases" or Hume-Rothery phases: Cu₃Si, Cu_{82.5}Si_{17.5}, Cu₈₅Ge₁₅, Cu₃Ge.

The p - 5×5 phase was obtained after annealing at 600°C for one minute of coverages of 0.5, 1, and 2 ML of Cu on Si(111) substrates that displayed sharp 7×7 LEED patterns before the deposit. The sharpness of the p - 5×5 pattern decreases at 2 ML and is not observed at higher coverages, in agreement with the recent literature. The dichroism of the Cu L_3 XAS spectra can be easily appreciated in Fig. 1 where the row data are aligned for the three coverages considered here. All the spectra are nor-

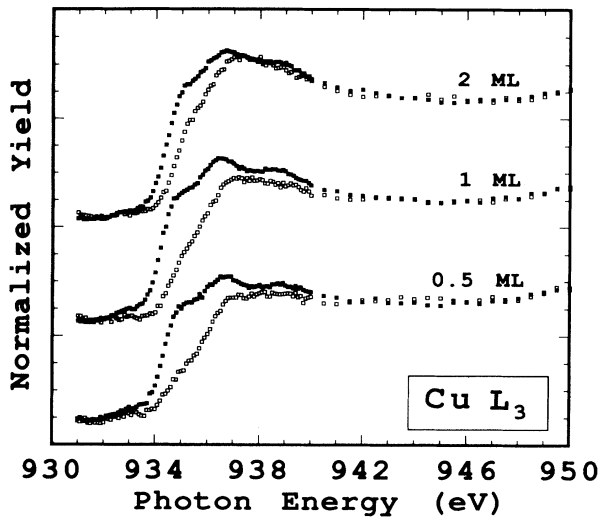


FIG. 1. Cu L_3 absorption edges for the p - 5×5 interfaces at different Cu coverages. ■: polarization vector in the surface plane (normal incidence of the photons). □: polarization vector 10° off the surface normal (grazing incidence). All the spectra are as collected.

malized at 925 eV (before the L_3) and 985 eV (after the L_2). It can be observed that the sharpness of the spectral features decreases at the highest coverage, while remaining qualitatively identical, in connection with the weakening of the LEED pattern. The sharp features in the XAS spectra are associated with the well-defined order of the p - 5×5 structure and therefore reflect the empty band structure of the interface layer.

The comparison between the absorption spectra of the interfaces and those of the electron-phase compounds (Fig. 2) excludes any correlation of the p - 5×5 reconstruction with a three-dimensional alloying. The electron-phase alloys have very large unit cells,^{13,14} but the detailed structures so far are unrefined; these unit cells contain several unequivalent local environments for the Cu atoms, all amounting to average electron densities

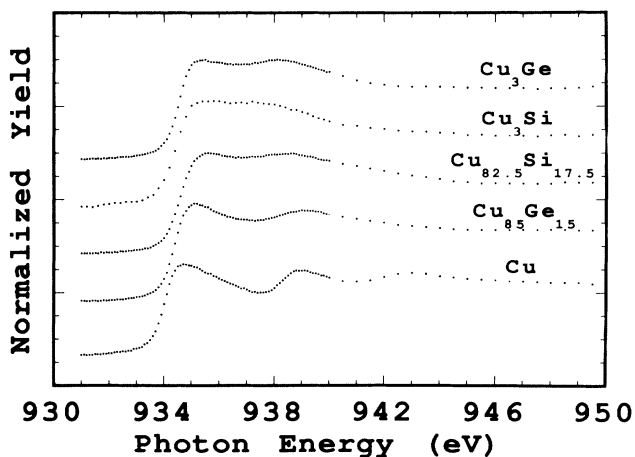


FIG. 2. Cu L_3 edge for polycrystalline Cu metal, Cu-Si, and Cu-Ge alloys.

which are thought to stabilize these compositions. On the other hand, the projections on the Cu site of the empty s - d states at the p - 5×5 interface show sharp peaks at characteristic energies which imply a high degree of bond order.

The development of the discussion is done with reference to Fig. 3 where the sharpest L_3 data, obtained for 0.5-ML Cu, at the two polarization orientations are expanded and compared with the (isotropic) L_3 spectrum of fcc Cu.

The dichroism of the L_3 edge for the p - 5×5 interface is very clear and is represented by the difference spectrum. The absorption at normal incidence, i.e., with the E vector lying in the interface plane, shows a sharp rise at 934(0.1) eV and two prominent peaks at 934.6 and 936.4 eV, while the absorption measured at glancing incidence, i.e., with E almost perpendicular to the interface plane, shows a delayed onset with a shoulder at 935 eV and weaker peaks at 936.6 and 939.3 eV. An overall quantitative difference of the absorption is also quite clearly observed. The delayed onset of the absorption at glancing incidence can be understood if an extended quasigap exists for the conduction states perpendicular to the interface layer. Alternatively, states of lesser localization may be probed at a threshold in the perpendicular direction and the relative weakness of the absorption can be attributed to matrix-element effects. In all cases the spectra show an extraordinary large anisotropy for the band states of a metal-silicon phase, which is striking proof of the two-dimensionality of the pseudo- 5×5 interface compound.

The difference spectrum shows characteristic peaks near the edge which can be compared to the features of the fcc Cu spectrum.

The single-particle picture of the Cu L_3 edge associates the absorption peaks to the Cu-projected $3d$ - $4s$ density of states, as dictated by the electric-dipole selection rule along the $l \rightarrow (l+1)$ [$l \rightarrow (l-1)$] optical channels. The

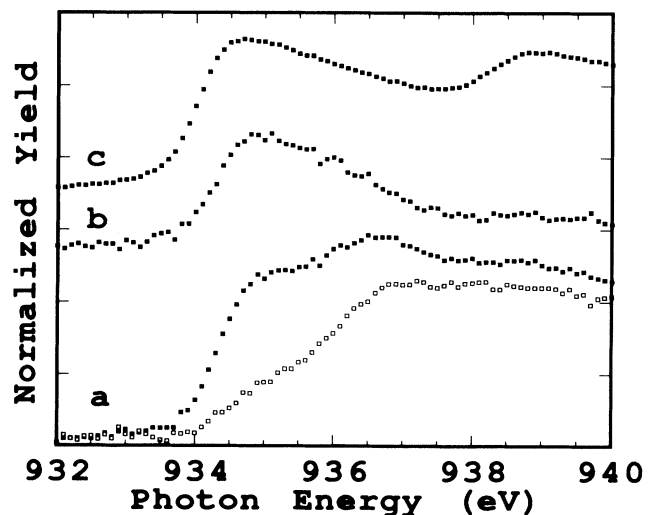


FIG. 3. *a*: 0.5 ML Cu/Si(111), as Fig. 1. The same linear background has been subtracted from both spectra. *b*: Difference of the spectra in *a*. *c*: fcc Cu L_3 edge.

$l \rightarrow (l+1)$ path is about 50 times more probable than the $l \rightarrow (l-1)$ path. Thus, the signal for Cu L_3 absorption should essentially mimic a Cu $3d$ -derived character spread out above the Fermi level, apart from possible matrix-element-effect modulations. Linear-augmented-plane-wave (LAPW) calculations by Müller and others¹⁵ confirm this expectation. The feature at 934.6 eV is assigned to a Cu $3d$ -derived character which is pulled up above the Fermi level due to $3d$ - $4s$ hybridization, in contrast to the "closed $3d$ subshell" nature of the Cu atom. This peak is thus reminiscent of the intense $2p \rightarrow 3d$ white lines measured in the $3d$ transition metals which have a large unoccupied density of $3d$ states. The higher energy structures have been ascribed by Müller and others¹⁵ to the tails of the Cu $4p$ wave functions, extending from the nearest-neighboring atoms onto the core-hole excited Cu atom and exhibiting a certain degree of $3d$ character when developed at the central site.

A detailed description of the chemical bonding of the p - 5×5 phase cannot be drawn simply from the XAS measurements. Nevertheless, several points can be positively addressed.

The transitions to s final states are not only much weaker, but also spatially symmetric. The dichroism of the p - 5×5 interface shown in Fig. 3 must then originate from the anisotropic hybridization of the Cu d levels. The existence or absence of empty d states is in this case a very direct and highly sensitive probe of the hybridization: When the d band is almost entirely filled, small variations in the electron occupation lead to large relative differences in the d -hole counting.

The presence of d holes in the interface plane (normal-incidence spectra) is related to the hybridization of the Cu d levels and forms the 5×5 layer structure: an empty band above the Fermi level carrying a certain d character must correspond to the filled bonding states. On the other hand, when probing 10° off the surface normal, the d -hole contribution is strongly depressed, suggesting that Cu d levels are not implied for the perpendicular bonding.

The observed dichroism implies the $d_{x^2-y^2}$ symmetry of the antibonding d component, and suggests a two-dimensional metallic character of the p - 5×5 interface with a covalent (semiconducting) coupling to the substrate.

Indirect evidence of two-dimensional d -band structure has been recently reported by Chambliss and Rhodin.¹⁶ Their angle-resolved photoemission data showed dispersion and symmetry of the d bands allowing to attribute $d_{x^2-y^2}$ character to deep-lying states at 3.8-eV binding energy and d_{z^2} character to states at shallower energies

around 3 eV below the Fermi level. In a bonding scheme for the p - 5×5 that implies hybridization of the Cu $3d$ states with $3p$ and $3d$ states derived from neighboring Si and Cu atoms, the deeper states will have bonding character implying an empty antibonding counterpart. Both these structures (occupied and empty) are experimentally found to have $d_{x^2-y^2}$ character, i.e., to lie in plane, both by the photoemission¹⁶ and by the present absorption data. The lack of hybridization perpendicular to the plane is established by our grazing-incidence data. A non-energy-dispersive peak in the empty density of states was measured by angle-resolved inverse photoemission at 2.5 eV above the Fermi level and tentatively attributed to Cu-Si surface states.⁹

The present results have noteworthy implications for the general understanding of the p - 5×5 interface. The strong bonds involving the Cu d band are oriented in the plane, while only Cu s -like states are implied for the perpendicular bonds. This reflects a weak coupling of the p - 5×5 layer to the substrate and accounts for the incommensurability^{4,6} and the recently suggested frustration of the p - 5×5 layer.⁸ The empty d states in the p - 5×5 plane are measured at identical photon energies as in fcc Cu. If the core-hole effect on the threshold energy is similar in the two materials, then one should conclude that the antibonding $d_{x^2-y^2}$ states are partially occupied and that the bonding scheme for the p - 5×5 resembles in two dimensions the transition-metal-silicide bonding scheme.^{1,2,17}

A number of remarkable anisotropies must be connected to the bidimensionality, including anisotropic metallicity, electron-transport properties, electron mean-free path. These quantities deserve careful experimental determination and are likely to lead to increased information on interfaces between semiconductors and low-dimensional metals.

In conclusion, we have directly probed the two-dimensional hybridization of the $3d$ band in the pseudo- 5×5 interface of Cu on Si(111) 7×7 . The results indicate that the pseudo- 5×5 Cu-Si interface phase is a prototypical two-dimensional interface compound whose further study will most probably lead to improved understanding of metal-semiconductor interfaces.

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