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Surface atomic structure of $c\ 2\times2$ -Si on Cu 110

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The technological importance of Schottky barriers has led to many experiments of metal-on-semiconductor systems. Here we present an example of the inverse case by depositing a semiconductor on a metal, studying the very early stages of the metal-semiconductor interface formation. We show that 0.5 monolayers of Si on Cu(110) form an ordered $c(2\times2)$ overlayer and resolve its geometrical structure. Using full-hemispherical x-ray photoelectron diffraction, we find that Si atoms form an almost coplanar layer, replacing one out of two Cu surface atoms.

I. INTRODUCTION

Due to the important technological applications of Schottky barriers,[1] many metal-semiconductor interfaces have been studied in the past. Many electronic devices are actually based on the rectification properties of such interfaces. Most of the work carried out until now has been performed by depositing metal films on semiconductor surfaces (M/S). For low coverage, which is the concern of the present study, this leads to ordered structures and many different combinations of metals and semiconductors have been studied.[2,3] However, when a semiconductor is deposited on a metal surface (S/M), poorly ordered alloys are usually formed from the very beginning on the growth, rendering interface studies by surface techniques difficult.[4,5] It has been reported[6] that M/S deposition leads to the formation of interfaces much wider than the ones for S/M systems. The variation of the deposition sequence not only affects the interface morphology but also the chemistry of the interface and thus different compounds can be formed when the deposition order is reversed.[4] Thus, the study of ordered interfaces formed by the inversion of the deposition sequence can shine light on the understanding of the fundamental mechanisms of the interfaces' formation. Particularly, the understanding of the inequivalence between the sequences of deposition (M/S and S/M) is of great interest for the comprehension of the initial stages of Schottky barrier formation and, therefore, more fundamental information about the structural properties at the very early stages of S/M deposition is required.[7]

Very little about S/M interfaces has been reported in literature. As far as we know, there is only one example of ordered surface structures obtained by S/M deposition.[6] There, Si and Ge were deposited on Cu(111) and the electronic structure was studied by angle-resolved direct and inverse photoemission. Ordered structures were found upon annealing the deposited films. The aim of the present work is to report on the existence of a nonpreviously reported ordered surface crystalline phase that appears for submonolayer Si deposition on Cu(110) at room temperature, and to present an atomic model for the surface termination.

II. EXPERIMENT

Experiments were performed using a VG-ESCALAB MK II spectrometer modified for motorized sequential angle-scanning data acquisition and with a base pressure in the lower 10^{-11} mbar region. Photoelectron spectra were recorded using Mg $K\alpha$ radiation ($h\nu=1253.6$ eV). The Cu(110) surface was prepared by the standard method of repeated cycles of Ar^+ sputtering and annealing at 600 °C. Si was evaporated in the low 10^{-10} mbar range from a liquid-nitrogen-cooled electron-bombardment evaporation cell that was calibrated before and after experiments with a quartz microbalance. Also, the Cu to Si x-ray photoelectron spectroscopy intensity ratios matched the ones expected for the coverages.

After deposition of around 0.2 Si monolayers (ML), a $c(2\times2)$ low-energy electron diffraction (LEED) pattern can be observed. At this coverage, the fractional spots from the superstructure are wide and elongated along the $\langle\underline{1}10\rangle$ surface direction. These half order spots become narrower with coverage and they reach a maximum of intensity for a Si coverage of 0.5 ML. After this coverage the spots become strikes along the $\langle001\rangle$ direction. The experiments presented hereafter were performed for a total Si coverage of 0.4 ML, just before the saturation coverage, in order to avoid the presence of the stroked high coverage phase, which could affect the experimental results.

The clean Cu(110) surface consists of rows of Cu atoms running along the $\langle\underline{1}10\rangle$ direction and presenting a (1×1) LEED pattern. In this work, 1 ML will be considered to be the number of Cu atoms present on these $\langle\underline{1}10\rangle$ rows (i.e., 1.09×10^{15} atoms/cm^2).

III. RESULTS AND DISCUSSION

Full-hemispherical x-ray photoelectron diffraction (XPD) is by now a well-established technique for obtaining structural information of surface overlayers.[8,9] A visual inspection of XPD patterns already allows us to distinguish the strong emission directions that can be associated with forward scattering directions and thus, allows us to identify the main bond directions. More details about the XPD technique can be found in Ref. 10. Figure 1(a) displays the experimental Si $2p$ XPD pattern for approximately 0.4 ML of Si/Cu(110). The pattern has been azimuthally averaged according to the twofold rotational symmetry of the system, and normalized with respect to the mean intensity for each polar emission angle. The angular distribution of the Si $2p$ photoelectron

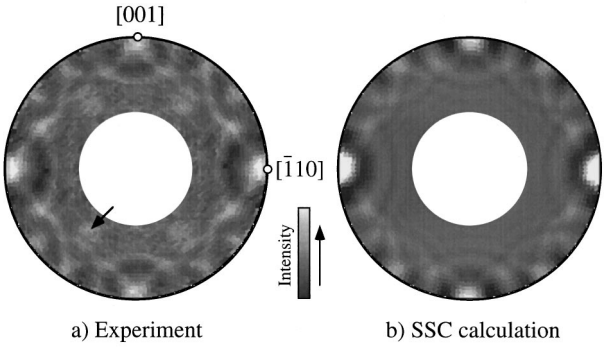

FIG. 1. XPD patterns of the Si $2p$ emission from the $c(2\times2)$-Si-Cu(110) structure at a kinetic energy of 1156 eV. (a) Experiment, (b) SSC calculation. The main surface directions are indicated. The small arrow indicates a forward scattering direction related to a higher coverage structure (see text for details).

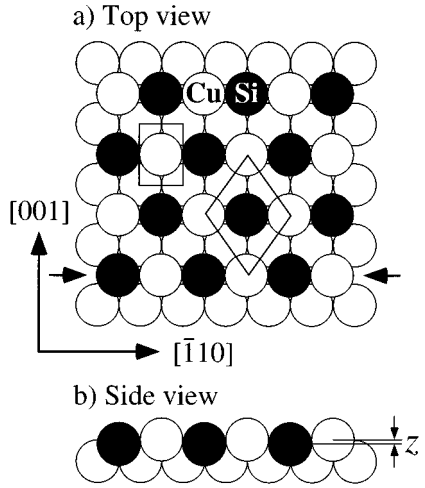

FIG. 2. Top and side views of the atomic model for the $c(2\times2)$-Si-Cu(110) structure. Si and Cu atoms are represented as filled and open circles, respectively. The surface unit cells of the (1×1) surface and of the $c(2\times2)$ reconstruction are indicated.

intensity is plotted using the stereographic projection. The center of the plot corresponds to the surface normal and the outer circle represents grazing emission along the surface (90° off-normal emission). In all patterns shown the $\langle\underline{1}10\rangle$ azimuth corresponds to the horizontal direction. Due to the low Si coverage (around 0.4 ML) and the low photoionization cross section for Si $2p$ emission using Mg $K\alpha$ radiation, the signal is rather weak. In order to shorten the measuring time and since intensities at angles from the surface normal up to 50° did not show anisotropy, intensities were only collected on an outer circle (angles from 88°–50° off normal). The lack of anisotropy for nongrazing emission angles is a clear indication for the absence of Si diffusion towards the bulk that would lead to forward scattering intensity maxima at nongrazing angles.

In the experimental XPD pattern shown in Fig. 1(a), four strong peaks of enhanced intensity appear at very grazing emission angles. These peaks correspond to the forward focusing directions along the $\langle\underline{1}10\rangle$- and $\langle001\rangle$-type directions. These maxima are surrounded by high intensity fringes that are due to the first-order interference maxima of the photoelectron diffraction process.[11] Such first-order interference fringes contain direct information about the emitter-scatterer distance. All the strong forward focusing peaks appear at emission angles as high as 88 degrees off the surface normal, indicating a planar or nearly-planar Si overlayer. Similar XPD patterns, exhibiting first-order interference fringes surrounding the forward scattering peaks at grazing emission angles, have been reported for Na adsorbed on Al(100).[12] This kind of pattern represents the atomic environment of the Si atoms at the surface, and thus, it is possible to conclude that Si atoms have neighboring coplanar atoms along $\langle\underline{1}10\rangle$ and $\langle001\rangle$ directions. As a complement to the XPD experiments, low-energy ion-scattering spectroscopy spectra ($E_{\mathrm{kin}} = 1$ keV) at grazing incidence angle (data not shown) indicate the coexistence of Cu and Si atoms in the topmost layer.

Considering all the information gathered from the inspection of Fig. 1(a), an atomic model for the $c(2\times2)$-Si/Cu(110) surface can be drawn. The only possible way of arranging Si and Cu atoms within the (1×1) Cu(110) surface to form a $c(2\times2)$ structure, respecting the forward scattering directions with meaningful interatomic distances in the lattice, is schematically shown in Fig. 2. In this model, Si atoms replace substitutionally one out of two Cu atoms in the $[\underline{1}10]$ surface rows.

Interestingly, this kind of atomic structure has also been found in metallic epitaxial films on different fcc metals, forming the so-called magnetic surface alloy.[9,13–15] Particularly, many studies have been carried out for the $c(2\times2)$-Mn/Cu(100) interface, where it has been reported that Mn atoms replace Cu surface atoms. The Mn atoms are at a slightly different vertical position. It has been proposed recently that the buckling of the Mn atoms may be magnetically driven[14] and that local interactions stabilize the surface reconstruction.[15] Analogously, a complete determination of the atomic positions of a nonmagnetic surface alloy may be important for the understanding of the basic mechanisms for surface alloy formation.

In order to accurately determine atomic distances in the structural model proposed above, calculations have been performed using the single scattering cluster (SSC) formalism.[16] The results of the calculations have been compared with the experiment by means of an R factor (R_{MP}) based on the space of multipole coefficients.[17] Besides the distance z between the topmost Cu layer and the plane containing the Si atoms, the effective mean-free-path Λ of the Si $2p$ photoelectrons, the surface vibrational amplitude $\langle u_j^2\rangle$ and the effective inner potential V_0[17] responsible for refraction at the surface potential step have been refined in the R-factor analysis. Figure 3 shows the R-factor value as a function of the Si-Cu layer spacing z.[18] The minimum of the curve corresponds to $z = -0.05 \pm 0.1$ Å, which means that the Si atoms are located slightly below the topmost Cu layer. It is worth noting that Si atoms are around 0.06 Å smaller than Cu atoms,[19] and a geometrical replacement of the Cu atoms by Si is thus sensible. The experimental XPD pattern [Fig. 1(a)] is very nicely reproduced by the SSC calculation shown in Fig. 1(b), which has been done using the structural model presented above (Fig. 2) and uses the best-fit parameters. All the experimental features and particularly the interference fringes that contain information about the interatomic distances are well reproduced in the calculation.

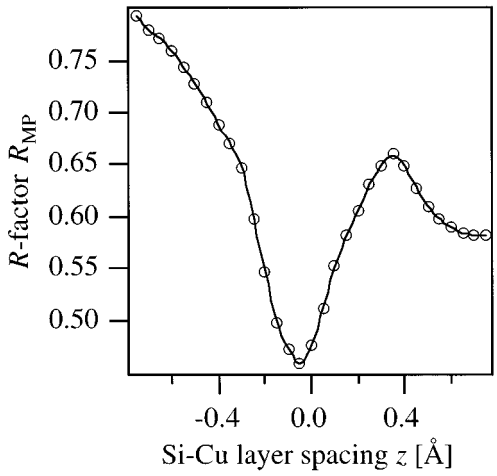

FIG. 3. R factor curve obtained by comparing SSC calculations with the experimental Si $2p$ XPD pattern as a function of the distance z between Cu and Si layers indicated in Fig. 2.

However, looking closer to the experimental XPD pattern of Fig. 1(a), we notice four very weak forward scattering peaks at polar emission angles of 60°, which are not reproduced in the SSC calculation. One of these four symmetry-related weak maxima is indicated by a small arrow in Fig. 1(a). These four little peaks become stronger with increasing coverage (data not shown).[20] Therefore, they may be related to the (2×2) structure that we find for higher coverages.[20] They correspond to the $\langle 011\rangle$ crystallographic directions of the clean Cu crystal and thus, a small number of Si atoms has an atomic environment similar to that of a Cu atom in the second layer. This either indicates Si diffusion towards the second Cu layer or, more likely, that some Si atoms are adsorbed in hollow sites on top of the $c(2\times2)$ Si-Cu layer. Then, the maxima are due to electrons from Si emitters within the $c(2\times2)$ layer scattering from Si atoms in hollow sites.[20]

In conclusion, we have shown that 0.5 ML of Si deposited on Cu(110) forms an ordered $c(2\times2)$ superstructure by substituting one out of two Cu atoms in the first Cu layer. The position of the substitutional $c(2\times2)$ Si layer is slightly below the top Cu layer. Si-Cu(110) thus represents the first example where the atomic structure of an *ordered* semiconductor-on-metal interface is resolved.

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