Surface-sensitive x-ray standing-wave study of Si(111)$\sqrt{3}\times\sqrt{3}$-Ag

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By combining the surface sensitivity of low-energy elastic photoelectrons with the position sensitivity of the x-ray standing-wave technique, we have determined both the Ag and Si atomic heights at the Si(111)$\sqrt{3}\times\sqrt{3}$-Ag interface. Our data give evidence that the Si(111)$\sqrt{3}\times\sqrt{3}$-Ag surface consists of a missing Si top-layer reconstruction, with Ag adatoms terminating the structure. The perpendicular height of the Ag layer and the first Si layer supports the honeycomb-chained-trimer model proposed for this interface. [S0163-1829(96)02624-0]

Despite intensive investigation since its discovery in 1967 by low-energy electron diffraction (LEED),[1] a consensus concerning the structure of the Si(111)$\sqrt{3}\times\sqrt{3}$-Ag surface has only recently begun to form.[2] The ambiguity had arisen, in part, because of the complex arrangement of the Ag and Si atoms within the near surface.

Early scanning-tunneling-microscopy (STM) studies found the Ag-Si surface to consist of a honeycomb array with two bright protrusions per $\sqrt{3}\times\sqrt{3}$ surface-unit cell.[3,4] These protrusions were, however, attributed to Si (Ref. 3) or Ag (Ref. 4) atoms in back-to-back studies. This confusion was propagated in other investigations utilizing Auger electron spectroscopy which concluded that the Ag saturation coverage for this surface is either $\frac{2}{3}$ or 1 ML.[5,6] In a STM reexamination,[7] the lateral registry of the protrusions relative to the clean Si(111)7×7 adatom structure were determined, and the protrusions were again attributed to Ag atoms, although it was argued that the full double-layer structure of the Si(111) surface remained intact.

In a later x-ray standing-wave (XSW) study, Vlieg, Fontes, and Patel[8] determined the position of the Ag atoms relative to the Si-bulk-diffracting planes. This study supported an earlier proposed honeycomb-chained-trimer (HCT) model which was based on x-ray-diffraction (XRD) data[9–12] and consists of a missing-top Si layer. One of these studies also included termination of the $\sqrt{3}\times\sqrt{3}$-Ag structure with Si atoms rather than Ag.[9] Unfortunately, typical XSW data determine only the impurity or adatom positions relative to the diffracting planes of the host crystal; hence no information on the arrangement of the Si atoms within the near surface was determined, and the idea that the Ag-Si surface may be terminated with Si atoms in a honeycomb arrangement persisted.[8,12]

A reanalysis of the XRD data[10] indicates that the structural refinement of the HCT structure is very sensitive to the fitting parameters assumed in the calculations, including the Debye-Waller parameters for the nine topmost Si planes, and that better quality data may be required to obtain accurate parameters.[12] These results, however, are in agreement with x-ray photoelectron diffraction[2] and coaxial impact-collision ion scattering,[13] which indicate that the very topmost surface layer is Ag and not Si.

Due to the lack of chemical specificity in STM, and because STM simultaneously measures topography and electronic density of states, interpretation of the STM images for this system was complicated. A recent theoretical work[14] illustrated that an unoccupied surface state close to the Fermi level, for the HCT model terminated by a full monolayer of Ag atoms, could account for the honeycomb array observed in STM. Likewise, the theoretical charge distributions for the occupied states for this model resemble the atomic arrangement of the Ag atoms in this model. Recent experimental STM images obtained from tunneling into the empty states and out of the occupied states have confirmed these conclusions.[15]

Additionally, a prior low-energy electron-diffraction study suggested that Ag is not required for the formation of the $\sqrt{3}\times\sqrt{3}$ structure, and that when Ag is present it forms a

diffuse interface with no long-range order.[16] However these results contradict studies by STM (Refs. 3, 4, 7, and 15) and XSW,[8] which indicate that Ag atoms in this structure do have both short-range and long-range order. Also, more recent LEED analyses indicate that the I-V data are consistent with the HCT model with long-range order.[17,18]

Although there appears to be a consensus on the structure of this surface, most of the techniques used to date require a complex modeling of the experimental data by varying fitting parameters. Further investigation of this system is warranted by a technique which is not dependent upon fitting the experimental data to assumed structural models. In this work, we utilize the recently developed surface-sensitive XSW technique[19] to study the position of the Si atoms within the near surface at the Si(111)$\sqrt{3}\times\sqrt{3}$-Ag interface. Combined with conventional back-reflection XSW data, we independently determine both the Ag and Si atomic positions within the near surface. Our findings give compelling evidence that the structure consists of a missing-top Si layer which is terminated with Ag atoms. A relatively large reduction in the perpendicular height of the top-layer Si atoms from their ideal-bulk position suggests that they are trimerized, in accord with the HCT model.

The experiment was performed on the ''Jumbo'' double-crystal monochromator at the Stanford Synchrotron Radiation Laboratory in a standard ultrahigh-vacuum chamber equipped with a double-pass cylindrical mirror analyzer (CMA) and low-energy electron-diffraction (LEED) optics. Clean Si(111)7×7 surfaces were prepared by flashing degreased and degassed Si(111) wafers to 1050 °C. The Si(111)$\sqrt{3}\times\sqrt{3}$-Ag surfaces were prepared by depositing approximately 1 ml (calibrated by a quartz-crystal balance) of Ag from a thoroughly degassed W coil followed by heat treatment to 575 °C for 15 min. This procedure produced sharp $\sqrt{3}\times\sqrt{3}R30°$ LEED patterns with no residual 7×7 spots of the clean Si surface.

Back-reflection x-ray standing-wave data were collected in a fixed-angle normal-incidence diffraction geometry by scanning a pair of InSb(111) monochromator crystals through the Si(111) Bragg back-reflection condition, which occurs near 1977 eV. Data from the Ag overlayer were recorded in the constant-final-state mode both at the Ag MNN Auger line (350-eV kinetic energy) and 50 eV above it at background. Surface-sensitive Si 1s data were recorded from the overlayer covered surface in the constant-initial-state mode both at the Si 1s photopeak (around 130-eV kinetic energy) and 5 eV above it at background by scanning the CMA kinetic energy and the monochromator simultaneously. The reflectivity spectra were measured by the incident flux monitor, which consisted of an 80% transmitting Ni grid and a channeltron upstream of the sample. As the energy is swept through the Bragg condition, the back-reflected beam intensity from the crystal at normal incidence is observed on top of the signal from the incident flux. The detection of the reflectivity peak is critical for the analysis because it provides fiducial information on the energy resolution and energy calibration as well as control of the sample alignment.

Figure 1 shows the Si(111) reflectivity along with the best fit to the data points. The fit is the result of convoluting the theoretical reflectivity[20] with a Gaussian of width 0.70 eV

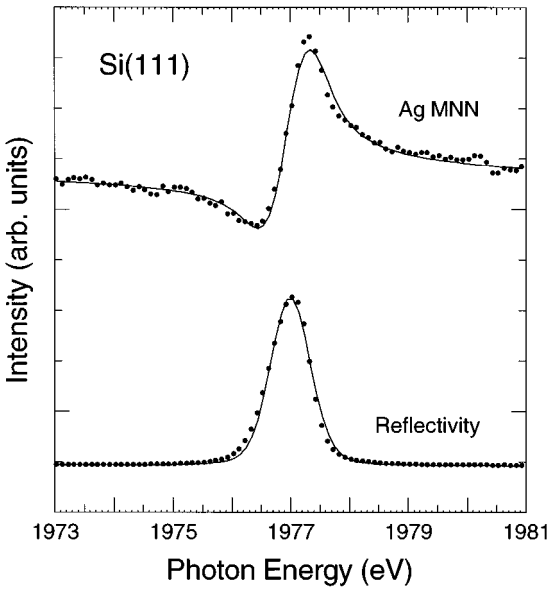

FIG. 1. Photon-energy dependence of the reflectivity and the background-corrected Ag MNN x-ray standing wave near the Si(111) Bragg back-reflection condition for the Si(111)$\sqrt{3}\times\sqrt{3}$-Ag surface. The lines are the best fits to the data points (see text).

and adjusting it for a small energy offset. Shown also is the photon energy dependence of the background-corrected Ag MNN (350 eV) Auger yield. This signal is compared to a least-squares fit by the function[20]

$$Y=1+R+2\sqrt{R}F\cos(\phi-2\pi\nu).$$

The pertinent fitting parameters for the standing-wave pattern are ν, the coherent distance in units of the reflecting plane spacing, and F, the coherent fraction of atoms at ν. R is the reflectivity and ϕ is the phase of the standing wave. The best fit to the Ag standing-wave pattern determines $\nu=1.07\pm0.02$ and $F=0.94\pm0.1$ These numbers are indistinguishable (within the experimental uncertainty) from those reported by Vlieg, Fontes, and Patel[8] for the same surface, and they support the HCT model as previously described.[8]

Although these data very accurately determine the position of the Ag atoms relative to the Si[111] bulk-diffraction planes, they contain no information on the position of the Si atoms within the near surface. Note that the HCT model is unique to most other surface structures[21] in that it consists of a missing-top Si layer. Further analysis[8] of [111] and [220] reflections found the Ag atoms to be laterally reconstructed, and the data consistent with a Ag-Ag bond length of 3.5 Å; however, the termination of the Ag-Si surface remained an open issue, and the standard XSW technique alone is not sensitive to surface relaxation.

In order to determine the structure of the Si atoms within the near surface, we turn to the standing-wave data collected by monitoring the surface-sensitive Si 1s signal. Much success has been achieved recently in the application of the XSW technique to the study of clean surface reconstructions through the use of surface-sensitive electron detection to-

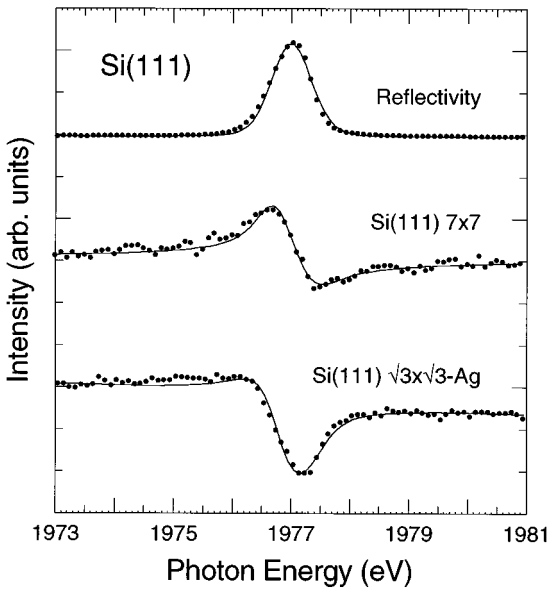

FIG. 2. Photon-energy dependence of the reflectivity and the Si 1*s* normalized x-ray standing wave for the clean Si(111)7×7 and Si(111)$\sqrt{3}\times\sqrt{3}$-Ag surfaces near the Si(111) Bragg back-reflection condition. The lines are the best fits to the data points (see text).

gether with low photon energies;[19,21] this study further extends these investigations to overlayer-induced reconstructions.

Figure 2 shows the normalized Si 1*s* photoelectron yield for the clean Si(111)7×7 surface and for the Si(111)$\sqrt{3}\times\sqrt{3}$-Ag surface plotted with the Si(111) reflectivity. Also shown are the best fits to the data points. Note the significant difference between the two wave patterns from the clean and overlayer-covered surfaces. The signal from the clean surface was attributed to adatoms of the 7×7 structure.[21] Their position, 0.54 ± 0.1, agreed well with recent theoretical predictions,[22] although it differed somewhat from the x-ray-diffraction determination.[23] On the other hand, the wave form from the Si(111)$\sqrt{3}\times\sqrt{3}$-Ag surface gives a position of 0.77 ± 0.1.

Let us now explore the structural consequences of this position. It is clear that the Si arrangement does not correspond to a bulklike geometry. Had it, the surface- and bulk-standing-wave patterns would be indistinguishable, and their resulting normalization would consequently be independent of photon energy. The position determined is consistent with a single layer of Si atoms displaced away from the position of a bulk double layer, i.e., $1(=3.13$ Å). Note, however, that the position corresponding to the atoms of the bottom half of a double layer is 0.875. The significant reduction observed experimentally from this position, nearly 0.1 Si(111) lattice spacing or 0.31 Å, is too large to attribute only to

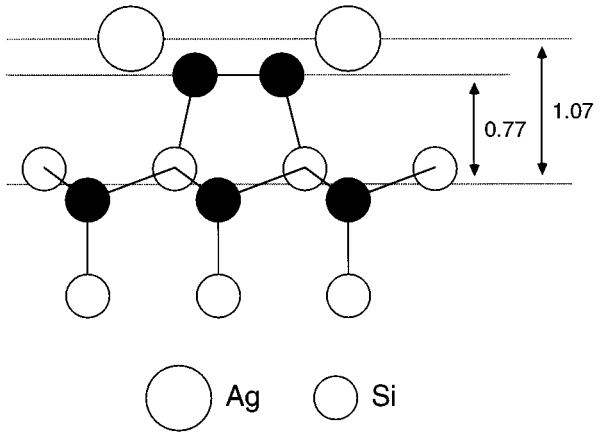

FIG. 3. Side view of the Si(111)$\sqrt{3}\times\sqrt{3}$-Ag HCT model with Si and Ag perpendicular distances [in units of the Si(111) reflecting-plane spacing] as determined from this work.

relaxation.[24] It has been noted that a trimerization of the first Si layer exists for the HCT model in which the Si-Si near-neighbor distances in the Si trimers are close to the bulk value of 2.35 Å.[2] In this case, the perpendicular height of this layer is significantly reduced from its unrelaxed position because the bonds no longer are oriented perpendicular to the surface. For ideal trimers (i.e., those with the bulk Si-Si near-neighbor distance of 2.35 Å), the corresponding height would be 0.82, which is within the experimental uncertainty of our result. Additionally, theoretical calculations[14] find a relaxation of the deeper layers, which would likely bring our result into even closer quantitative agreement. Figure 3 shows the side view of the HCT structure with our determination of the Ag and Si positions.

In conclusion, by exploiting the surface sensitivity of low-energy elastic photoelectrons and the x-ray standing-wave field, we have determined the positions of both the Ag and Si atoms at the Si(111)$\sqrt{3}\times\sqrt{3}$-Ag interface independently. While our data for the Ag position are consistent with earlier XSW results,[8] the Si position gives compelling evidence that the structure is terminated by Ag and not Si atoms. Our combined results for both the Ag and Si atomic positions are consistent with a missing-top Si layer, and imply Si trimerization in support of the HCT model.

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