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X-ray standing-wave study of monolayers of Sb on GaAs(110)

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The x-ray standing-wave technique has been used to determine the geometrical structure of Sb on GaAs(110). Using the back reflection diffraction geometry from (220) and (400) planes, we find the average vertical distance of Sb atoms from the GaAs surface to be 2.27 ± 0.05 Å in agreement with theoretical calculations for the epitaxial continued layer structure. Other models of buckled zigzag chains are found inconsistent with our results. Additionally, our data indicate less than 10% disorder in the Sb overlayer.

One monolayer of Sb on GaAs(110) is the most studied compound semiconductor interface.[1-13] This emphasis arises because while most metallic overlayers either react or cluster, Sb forms an ordered epitaxial structure. The near ideal morphology of this system makes it tractable for both theoretical calculations and structural studies.[2-7] However, until now experimental structural information has been available only from elastic low-energy electron diffraction[2,3] (ELEED) and scanning tunneling microscopy (STM).[8] Despite a consensus that Sb grows as a nondisruptive and relatively ordered overlayer, several questions on the exact geometry of the epitaxy exist. While STM pictures show the presence of Sb zigzag chains at the Sb/GaAs(110) interface,[8] recent calculations of LaFemina, Duke, and Mailhiot indicate that several energetically favorable structures exist within this class of models.[5] Here we will discuss the theoretical models in the context of our x-ray standing-wave (XSW) data. We will also address the intercorrelated issue of the Sb overlayer buckling and disorder.

XSW has recently emerged as a powerful tool for the study of adsorption geometry on single-crystal surfaces.[14-21] Specifically, XSW allows the direct determination of the position of adsorbed atoms relative to a selected subset of substrate planes. This information is of particularly importance since precise information on vertical distances from surface planes is not readily available from STM.[8] ELEED, another technique which in principle provides similar information, involves complex theoretical model-dependent analysis which employs a complex multiple-scattering theory.[2,3,13]

The theory behind the XSW measurement is based on the dynamical description of x-ray diffraction from crystals.[14] Conceptually, as the angle or photon energy is swept through a Bragg condition, a standing wave is formed within and in front of the substrate. The change of the phase within the total reflection width causes the spatial movement of the nodes and antinodes of the electric field intensity relative to the diffracting planes. Since photoabsorption is proportional to the electric field intensity at the atom core, this spatial movement of the standing-wave produces a modulation in the absorption of the overlayer atoms. Analysis of the variation in absorption allows a precise determination of the vertical adatom position.

In our study, the XSW signal is detected by sweeping not sample angle, as applied in most prior work (see for example Refs. 15–17), but the incident photon energy in the back reflection diffraction configuration.[18-21] In this way the energy scanning capability of the synchrotron radiation beam line[22] is utilized. Using the back reflection geometry also reduces sensitivity to crystalline imperfection and beam divergence. Additionally, we employ electron rather than fluorescent yield to measure the absorp-

tion. This detection mode is often utilized in surface-extended x-ray absorption fine-structure (SEXAFS) studies,[23] but it is rarely used in the XSW research.[18,21]

Experiments were performed in a standard cylindrical mirror analyzer equipped ultrahigh-vacuum chamber on the National Institute of Standards and Technology beam line X-24 A at the National Synchrotron Light Source (NSLS).[22] The data from the 1-monolayer (ML) Sb/GaAs(110) interface were collected in a fixed-angle normal-incidence diffraction geometry by scanning a pair of Si(111) monochromator crystals through energies corresponding to the GaAs(220) and (400) Bragg back reflection conditions. The samples were prepared by evaporating slightly greater than 1 ML of Sb, as measured by a quartz crystal oscillator, onto outgassed and then cleaved thick GaAs single crystals. After evaporation the interfaces were lightly annealed (10–15 min at ~330 °C) to desorb Sb in excess of 1 ML and to further enhance their order. This procedure is known to reproducibly provide well-ordered epitaxial interfaces.[9,13]

The XSW spectra were recorded by monitoring the Sb MNN Auger yield (~450 eV) as a function of photon energy around the Bragg condition. The photon energy scans were also taken with the analyzer energy set 50 or 100 eV above the Auger peak for background subtraction. This is necessary because the Sb Auger peak rides on top of the background of inelastically scattered electrons which are also strongly modulated by the standing-wave field. The peak to background ratios were approximately 35% and 100% $[(S-B)/B]$ for the (220) and (400) reflections, respectively. Although the higher-energy (400) data (~4386 eV) were obtained with degraded monochromator performance, their analysis yielded results quantitatively identical to those obtained from the (220) reflection (~3101 eV) which is within the optimal energy range for the Si(111) monochromator crystals. Simultaneous with the XSW signal, the reflectivity spectra were measured with a Ni grid and a channeltron upstream of the sample. 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 reflectivity from the (220) planes together with the best fit using the Darwin-Prins intrinsic line convolved with a Gaussian of 0.91 eV full width at half maximum (FWHM). The same Gaussian broadening, which approximates the monochromator response function, was also used while fitting of the Sb yield which is presented in Fig. 2. These data were fitted to the formula which describes absorption in the field of the standing wave.[14,18]

$$Y(E)/Y_0 = 1 + R(E) + 2\sqrt{R(E)} \sum_i \{F_i \cos[\varnothing(E) - 2\pi D_i]\} . \quad (1)$$

Here, D_i are the adsorbate-substrate distances in units of the reflecting plane spacing, and F_i are the coherent fractions which correspond to the fraction of total atoms at the coherent distances. $R(E)$ and $\varnothing(E)$ are the energy-dependent reflectivities and phases which are given by the dynamical theory of diffraction.[14]

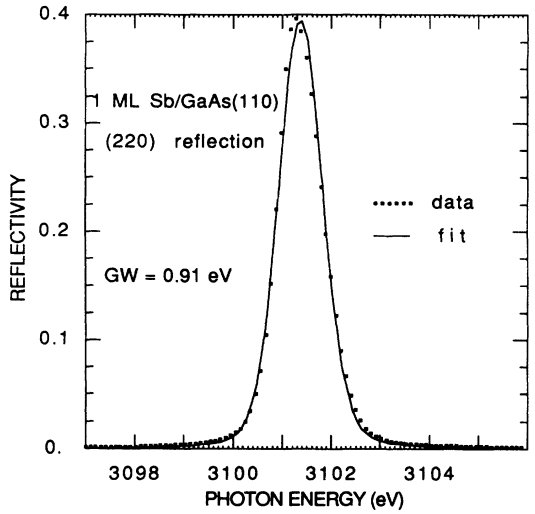

FIG. 1. Energy dependence of the reflectivity for (220) Bragg diffraction from GaAs(110). The experimental data and the theoretical curve have been convolved with a Gaussian of 0.91 eV FWHM.

To specify the tentative model and the meaning of the fitting parameters, Fig. 3 shows the side view of the epitaxial continued layer structure (ECLS in Ref. 5) of the 1-ML Sb/GaAs(110)$p1\times1$ interface. Here Sb atoms occupy positions close to the next layer of As and Ga atoms as if they were grown epitaxially on the surface. The saturation of the dangling bonds by the Sb is expected to remove the clean surface relaxation yielding a bulklike termination of the GaAs(110) substrate. However, since Sb atoms are larger than either As and Ga, an upward displacement of the Sb overlayer is expected. Additionally, due to the geometric and electronic inequivalence of the substrate As and Ga atoms, one expects a difference in the height of the two inequivalent Sb atoms. This overlayer buckling is often expressed in the literature[2-6] as the

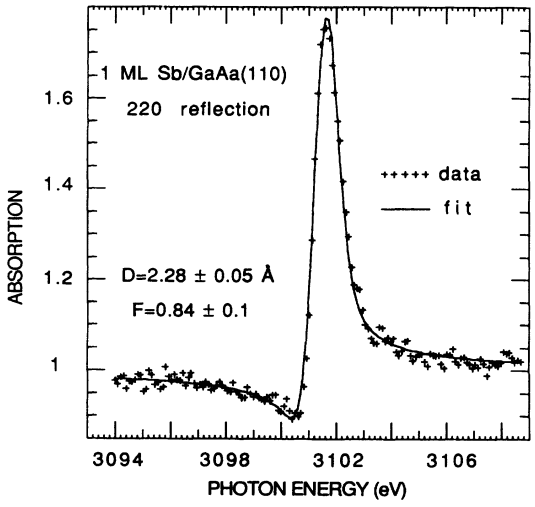

FIG. 2. Energy dependence of the background corrected Sb MNN yield from the 1-ML Sb GaAs(110)$p1\times1$ interface (crosses) and theoretical fit (solid line).

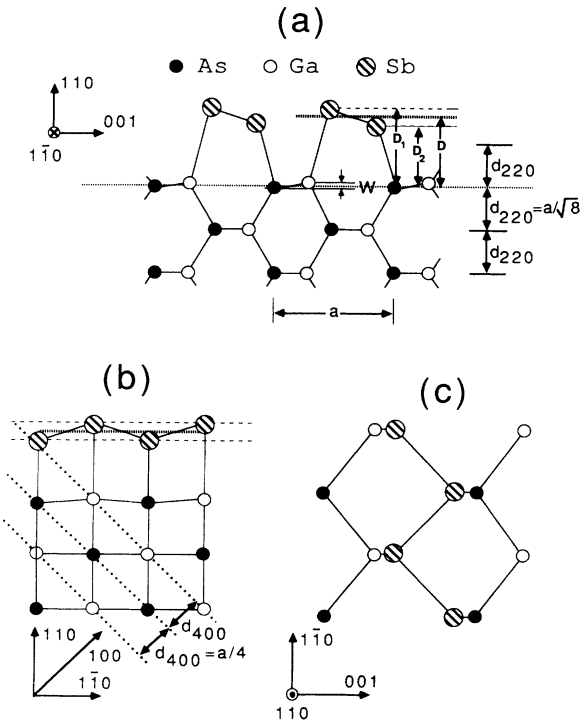

FIG. 3. Diagram of the surface geometry determined in this work for 1-ML Sb on GaAs(110) surfaces: (a) side view along the 110 direction, (b) side view along the 100 direction, (c) top view.

vertical shear parameter $\Delta_\perp = D_1 - D_2$. Additionally, Fig. 3 implies some buckling, W, of the topmost substrate layer, although all theoretical calculations[4-6] indicate that W is small. These calculations also indicate that the contraction of the topmost substrate layer is negligible (2.5% in Northrup's calculation[6]). Therefore in our analysis we consider all substrate atoms to be in their truncated bulk positions.

There are two mathematically equivalent ways to analyze the XSW data from the Sb overlayer. First, if one assumes an ideal overlayer morphology (as implied in Fig. 3) two distances, D_1 and D_2, of the two half-layers ($F_1 = F_2 = 0.5$) may be presumed. Equivalently one may determine one distance, D, and one coherent fraction, F. In the latter case D is an average distance $(D_1 + D_2)/2$, and the effective coherent fraction is given by $F = \cos[\pi(D1 - D2)] = \cos(\pi\Delta_\perp)$. Note that if the real morphology were ideal (i.e., free of disorder) the vertical shear, $\Delta_\perp$, may be explicitly obtained from F. However, in the general case F includes effects of structural and vibrational disorder, which result in a lower F value than $\cos(\pi\Delta_\perp)$. The presence of structural disorder therefore precludes the quantitative determination of the buckling from the available data and gives only an upper bound of the vertical shear. In principle this ambiguity can be resolved by additional XSW data. The presence of disorder, however, does not affect the reliability of the coherent distance determination, for it adds only an incoherent signal to the yield. Table I compares our results for two sets of (220) data taken on different samples with predictions

TABLE I. Comparison of distances determined from the (220) back-reflection data for the Sb-GaAs(110)$p1\times1$ interface with theoretical calculations for the ECLS model and ELEED determinations. (For comparison with other models, see text.) Notice that the distances are given here in angstroms while all formulas in the text employ units of diffracting plane spacing.

	D	F
XSW GaAs1(220)	2.28 ($\pm$0.05) Å	0.84 ($\pm$0.1)
XSW GaAs2(220)	2.26 ($\pm$0.06) Å	0.86 ($\pm$0.1)
Theory 1 (Ref. 4)	2.29 Å	
Theory 2 (Ref. 5)	2.35 Å	
Theory 3 (Ref. 6)	2.30 Å	
ELEED 1 (Ref. 2)	2.39 ($\pm$0.1) Å	
ELEED 2 (Ref. 3)	2.34 Å	

of energy minimization calculations and for the ECLS model ELEED results. Experiments using the (400) reflection yielded $D' = 1.60$ Å and $F' = 0.86$. Although these values are established with less precision, they are quantitatively consistent with the (220) determination, for the (400) planes are inclined 45° from the surface [see Fig. 3(b)]. The distance determined from the (400) planes should then correspond to the (220) value divided by $\sqrt{2}$(2.27 Å/$\sqrt{2}$ = 1.60 Å). This finding lends additional support of our structural determination.

Our determination of the average distance is in quantitative agreement with calculations based on the ECLS, which is perhaps surprising considering that theories which utilize the tight-binding scheme[4,5] arbitrarily choose bond lengths as input parameters. The distances obtained from ELEED (Refs. 2 and 3) (Table I) are larger than the XSW ones, but they are within the combined experimental error. Our upper bound of the vertical shear of 0.34 Å as calculated $\Delta_\perp = (1/\pi)\cos^{-1}(F)$ appears to be excessively large, but it may be brought into quantitative agreement if one assumes a finite amount of structural disorder ($\sim$10%). The structural disorder may be in fact even smaller if the vertical thermal vibrations of the overlayer atoms are large. The effect of thermal disorder will be a subject of our future investigation. We should note that structural disorder was recently found in Raman studies of the surface vibrations[10] and may result from Sb atoms residing on cleavage steps or in clusters. Additionally, disorder was observed as small protrusions which lie on top and within the first layer in large scale STM images.[8] In LEED studies it results in an increase of the inelastic background.[2]

Clearly these results support the epitaxial continued layer structure depicted in Fig. 3. Comparisons with other structures considered by LaFemina, Duke, and Mailhiot[5] are significantly less favorable, (EOCS, epitaxial overlapping chain structure; $D = 2.11$ Å), or they can be firmly ruled out (EOTS, epitaxial on top structure; $D = 2.93$ Å). In these models the top layer of Sb forms zigzag chains which differ in the registry from the 110 substrate chains. Although, the presence of chains is consistent with the STM results of Mårtensson and Feenstra,[8] STM does not

provide an accurate distance normal to the surface and therefore cannot differentiate between the ECLS and EOTS models (a rough estimate of 2.8 and 2.4 Å for negative and positive bias voltages is reported in Ref. 8). In fact the EOTS model, which corresponds to an energy optimized p^3 model originally proposed by Skeath *et al.*,[1] was found by LaFemina to be in best agreement with the STM image analysis.[5,8] Moreover, the EOTS model is consistent[5] with angle-resolved photoemission[11] and inverse photoemission data.[12] Thus knowledge of the vertical distance is critical to discriminate between the two structures. In particular, the EOTS, which overestimates the vertical distance by as much as 0.5 Å, can be rejected on the basis of our data. Qualitatively, EOTS, which consists of Sb zigzags commensurate with but on top of the substrate chains, is expected to yield a larger vertical distance than the ECLS in which Sb atoms lie along the inclined substrate dangling bonds. As for the EOCS model,[5] all experimental evidence so far, including our data, indicate that this model should be rejected as the minimum energy structure for the Sb overlayer. LaFemina, Duke, and Mailhiot[5] point out that this model may be favorable theoretically due to an inadequate treatment of the Coulomb repulsion in their tight-binding code.[5]

In conclusion, the x-ray standing wave technique has been used to establish the vertical distance of a Sb monolayer to the GaAs(110) surface. This structural parameter, 2.27 ± 0.05 Å, distinguishes between the theoretical zigzag chain models of surface reconstruction and strongly supports the epitaxial continued layer structure. Although the EOTS model in which Sb zigzag chains ride directly on top of the substrate atoms is consistent with most other experimental evidence, it can be conclusively eliminated by our data. Unfortunately, quantitative determination of the buckling of the Sb layer is hampered by the presence of structural disorder which we estimate to be $\sim 10\%$.

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