Direct observation by reflection high-energy electron diffraction of amorphous-to-crystalline transition in the growth of Sb on GaAs(110)

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Direct evidence, using reflection high-energy electron diffraction, is found for a transition, at a specific thickness, from an amorphous to a crystalline state in Sb deposited on GaAs(110). After crystallization, Sb exists as small, 30–40 Å crystallites with a (0001) contact plane but randomly azimuthally oriented. A new surface phase, GaAs(110) $p(3\times2)$-Sb, is found and appears to be a consequence of the crystallization transition.

The initial stage of growth of thin films has historically been divided into three limiting-case modes: layer-by-layer (Frank–van der Merwe), 3D cluster growth (Volmer–Weber), and monolayer followed by 3D cluster growth (Stranski–Krastanov).[1] These modes are established on the basis of a comparison of adatom-adatom and adatom-substrate interactions and relative lattice constants of adsorbed-layer phase and substrate, and represent equilibrium situations.[1] Although many overlayer-substrate systems fit easily into one of these categories, many others do not and represent some intermediate situation.

One such example is the growth of Sb on GaAs(110), which we discuss here. We present direct crystallographic evidence that Sb, when deposited at room temperature on GaAs(110), undergoes an amorphous-to-crystalline transition at a dose of $\sim$20 ML. There has been indirect evidence for this phenomenon from ultraviolet photoelectron spectroscopy (UPS) measurements,[2] in which a transition from a semiconductorlike to a metal-like state was observed, and from Raman spectroscopy measurements,[3] in which the sudden appearance of an optical phonon indicative of a crystalline state was observed. We have made reflection high-energy electron diffraction (RHEED) measurements as a function of dose and observe the transition directly through the appearance of a transmission diffraction pattern. We are able to demonstrate that the substrate influences this crystallization transition, in that the Sb crystallites have a preferred contact plane relative to the substrate, which we determine to be the Sb(0001) plane. We can furthermore show that the Sb crystallites have a random azimuthal orientation with respect to the substrate, and can estimate the average size of the crystallites from the broadening of the angular profiles of diffracted beams.[4]

Our measurements are performed in an ultrahigh vacuum system operating at a base pressure of 5×10^{-11} Torr. RHEED is performed at energies between 5 and 10 kV and grazing angles of incidence of 2–6°. GaAs samples are cleaved *in situ* to produce (110) surfaces. The structural perfection of these surfaces is verified with RHEED. A flat surface, free of steps and other extended defects, will give a RHEED pattern consisting of sharp spots lying along arcs.[4,5] An example is shown in Fig. 1(a). Sb is deposited from an MBE source; the deposition rate is measured with a quartz crystal microbalance. As Sb is deposited, the following observations are made. For doses from 0 to 0.5 ML, the diffracted beams from the substrate elongate [Fig. 1(b)], indicating the formation of 2D domains with finite size. From 0.5 to 1 ML, the elongation reduces again to the point

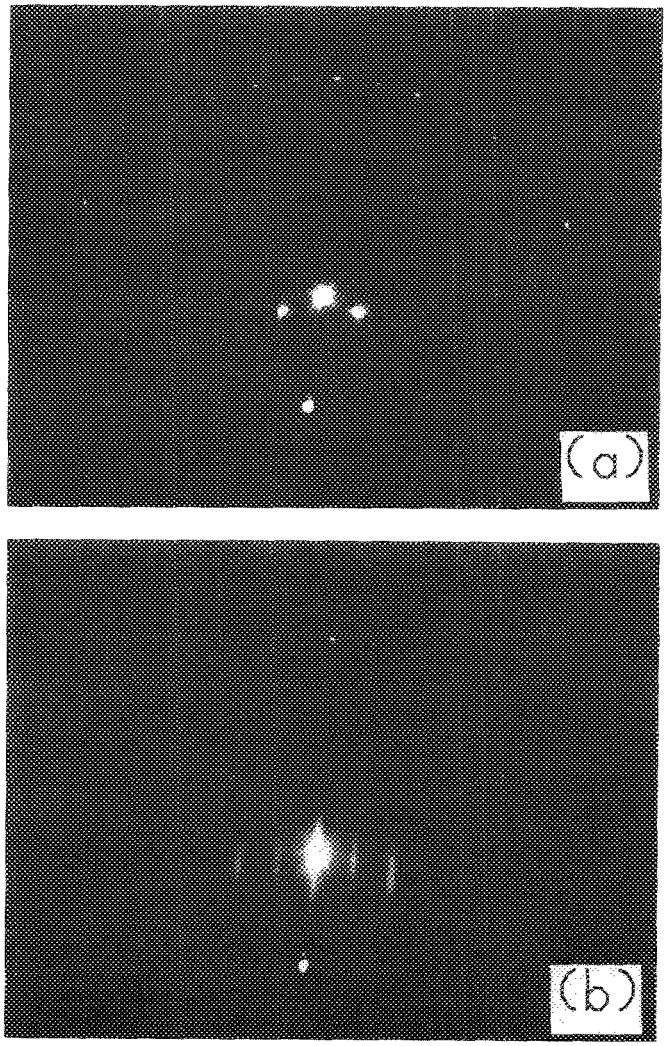

FIG. 1. RHEED patterns from (a) clean cleaved GaAs(110) and (b) cleaved GaAs (110) with half a monolayer of Sb adsorbed. The absence of superlattice beams and the elongation of fundamental beams indicates that a 2D $p(1\times1)$ Sb layer with an island structure is formed. From the elongation of the streaks at $\theta=0.5$, the average size of Sb islands is estimated to be $\sim$50 Å. At $\theta=1$, the streaks have nearly disappeared again, indicating the completion of the monolayer.

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where the initial sharpness of the substrate beams is almost recovered. These observations are consistent with the formation of a 2D $p(1\times1)$ Sb layer, as has been previously observed with low-energy electron diffraction.[6,7] A remaining diffuse intensity is indicative of point disorder or two-dimensional voids in the layer or extra Sb atoms on top of the first layer. This result is consistent with the recent observation[8] that energy-loss spectroscopy spectra become much sharper if the (1×1) Sb phase is annealed, probably desorbing the second-layer atoms.

Continued deposition results in the gradual disappearance of the substrate pattern until only a diffuse intensity remains, indicative of a random arrangement of atoms. At a dose of 20 ± 3 ML (1 ML is defined to be equal to the number of Ga or As atoms per unit area) a transmission diffraction pattern suddenly appears, as shown in Fig. 2. This indicates the transformation to a crystalline structure. Figure 2 shows an interesting feature, namely, the existence of elongated spots that lie on lines that curve inward. It can be shown[5] that such a pattern is produced by an arrangement of crystals that all have the same contact plane with respect to the substrate but have a random azimuthal orientation. By indexing the diffraction pattern, using the separation of the streaked spots, it can be shown that the crystallites have the lattice constants of Sb and that they are oriented such that the (0001) basal plane (Sb is rhombohedral, which can be described by a larger, nonprimitive hexagonal cell) is in contact with the GaAs(110) substrate, i.e., that the c axis of the Sb unit cell is normal to the surface. The preferential orientation with the substrate indicates that the substrate influences the crystallization of the Sb, presumably through the introduction of strain which then is at least partially relieved by the transformation to the crystalline state.

The mean size of the 3D Sb crystallites can be estimated from the angular profile of the diffraction pattern streaks in a cut across a streak.[5] The average size is of the order of 30–40 Å.

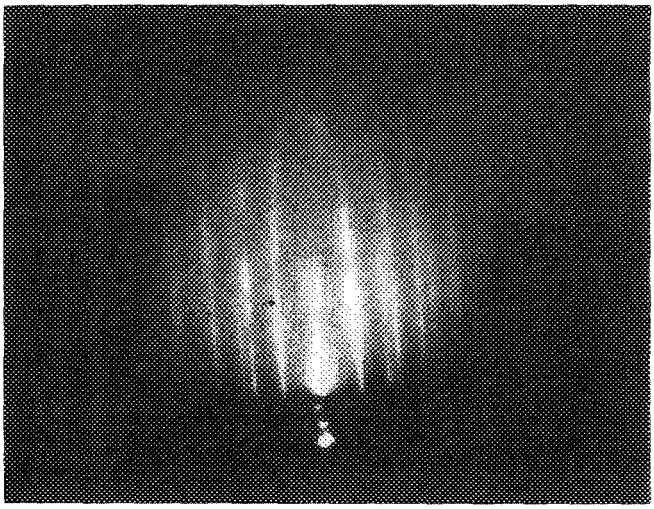

FIG. 2. RHEED pattern of ~20 ML Sb on GaAs(110) after crystallization. Curved streaks (actually elongated spots overlapping and lying along curves) are characteristic of small crystallites that have one axis fixed [the (0001) contact plane] but have azimuthal randomness. The spacing of the diffraction features can be indexed to give the orientation. The widths of the streaks can be interpreted in terms of the mean size of crystallites.

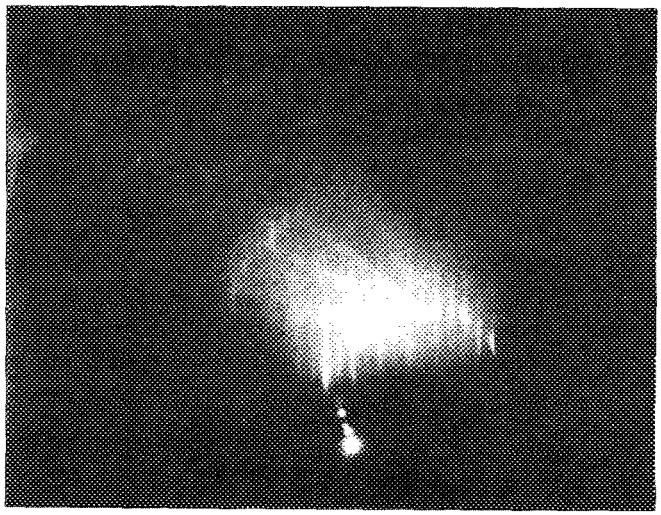

FIG. 3. RHEED pattern of the $p(3\times2)$-Sb phase formed at the Sb-GaAs interface as a consequence of Sb crystallization. The pattern is observed after all but ~1ML of Sb has been desorbed.

Finally, we have found that a new GaAs/Sb monolayer superstructure, GaAs(110) $p(3\times2)$-Sb, is created in the growth sequence we have described above. Its existence appears to be correlated with the crystallization transition of Sb above a 20 ML dose. We find this phase consistently if we evaporate all but the last monolayer of Sb. A RHEED pattern is shown in Fig. 3. It is known[6,7] that Sb can be removed from GaAs(110) by heating, but that the first monolayer adheres more tightly than subsequently deposited Sb. Previous investigators have not considered doses high enough to observe the amorphous-to-crystalline transition and thus also did not observe the $p(3\times2)$ phase.

Although we cannot prove it conclusively, we postulate that the $p(3\times2)$ is formed as a consequence of the energy release in the crystallization transition. We cannot prove it because we can observe the phase only after evaporating the majority of Sb, and it is conceivable that the evaporation causes the formation of the phase. However, the thermal energy involved in heating the film is much less than the crystallization energy, and furthermore, the phase is not observed for films that are not first crystallized.[9] The appropriate measurement to demonstrate conclusively that the phase is formed during crystallization would be grazing-angle x-ray diffraction through the ~20 ML of Sb to look for the new surface phase.

The $p(3\times2)$ phase occurs at a coverage of 0.9 ± 0.1 ML of Sb. It is therefore probably a defect phase, with an ordered arrangement of vacancies causing the diffraction pattern. It is more stable than the $p(1\times1)$ phase that forms first. Once the $p(3\times2)$ phase has been made, it is impossible to return to the $p(1\times1)$ phase without first completely removing all Sb. Doing so restores a GaAs(110) surface that is not as good as the original cleaved surface, but contains a higher density of steps.[9] At the process conditions and temperatures used here there is no evidence of formation of Ga-Sb or As-Sb compounds.

In conclusion, we have found direct structural evidence

for an amorphous-to-crystalline transition in a thin film of Sb deposited on GaAs(110) at room temperature, supporting earlier indirect evidence.[3,4] The transition occurs at a dose of ~ 20 ML. The resulting crystallites of Sb have a bulk Sb structure, but are oriented with respect to the substrate in that they all have the same contact plane, the (0001) plane. The crystallites have a random azimuthal orientation and an average size of 30–40 Å. The preferred orientation indicates that the substrate influences the crystallization. Finally, a new submonolayer phase, GaAs(110) $p(3\times 2)$-Sb, has been identified and appears to be correlated to the crystallization reaction of the Sb.

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