RAPID COMMUNICATIONS

PHYSICAL REVIEW B VOLUME 43, NUMBER 17 15 JUNE 1991-I

Potassium-induced unrelaxation of the GaAs(110) surface

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(Received 17 December 1990; revised manuscript received 25 February 1991)

A low-energy electron-diffraction (LEED) *I-V* study of the K/GaAs(110) interface has been performed to explore structural changes during the initial stages of metal-semiconductor interface development. Analysis of LEED background intensities as a function of coverage indicates that there is no long-range ordering of the K overlayer at any coverage up to a saturated monolayer. Preferential attenuation of multiple-scattering peaks at partial K coverages permitted a kinematic LEED intensity analysis of the scattered intensities from the underlying GaAs substrate. This analysis suggests that the relaxed GaAs surface undergoes a K-induced bond rotation towards the unrelaxed position at $\sim\frac{1}{2}$ saturation K coverage.

The interrelation between geometric and electronic structure of surfaces is fundamental to the study of physical and chemical properties of semiconductor surfaces and interfaces.[1] For GaAs(110), As- and Ga-derived states would exist in the bulk band gap for the clean unrelaxed surface if that structure existed. However, the observed surface bond rotation sweeps the states away from the gap. The question arises whether the clean-surface relaxation is removed or modified upon growth of a metal layer atop the surface. Removal of the surface relaxation might induce an As-derived interface state in the gap which could strongly affect the Schottky-barrier height at the interface.[2] We note that alkali-metal-induced electronic structure (for submonolayers) has been observed just below the valence-band maximum with angle-resolved photoemission.[3] It was speculated that the state originates from an unrelaxation of the bulk.[3] Indications of metal-induced unrelaxation of III-V (110) surfaces have been reported for Co clusters on GaAs(110) studied by core-level spectroscopy[4] and for Ag clusters on InP(110) as studied by photoemission extended x-ray-absorption fine structure (PEXAFS).[5] Low-energy electron-diffraction (LEED) studies for ordered overlayers of the semimetals Sb and Bi have also suggested unrelaxation of GaAs(110).[6]

We report a LEED *I-V* study of K/GaAs(110) interface to address the question of substrate structural unrelaxation upon the development of a metal-semiconductor interface. K and GaAs(110) have several unique properties that allow this system to be considered as a model metal-semiconductor interface. K has a relatively simple electronic structure—a lone 4*s* electron in its outer shell and no inner *d* electrons. K is the smallest alkali metal that does not intermix with or diffuse into the GaAs(110) substrate. The GaAs(110) surface is characterized by a bond angle rotation which has been studied extensively[7] and is well understood. Our analysis indicates that the K overlayer deposited at room temperature is disordered which, with a few exceptions, is characteristic of many metal–III-V-semiconductor interfaces. Due to the difficulty in directly incorporating disorder[8] into either a kinematic or multiple scattering LEED calculation, we have approached this problem by comparing our data, which we assume represents a disordered K layer atop an ordered GaAs(110) surface structure, with calculations for an ordered GaAs(110) surface. We have found experimentally that it is appropriate to consider electron diffraction from the K/GaAs(110) interface by a kinematic LEED analysis, at least to first order, since multiple-scattering features are preferentially attenuated due to the presence of a disordered overlayer. Following this approach, the results of a kinematic LEED analysis suggest that the K/GaAs(110) interface involves a bond rotation of the GaAs(110) surface structure towards the unrelaxed geometry.

The LEED measurements were performed with a video-LEED system which consists of a standard front-viewing Varian LEED optics and a COHU Model 4400 video camera interfaced to a Digital Equipment Corporation PDP-11 computer. All beam intensities were measured in 0.5-eV increments and all spot intensities were background subtracted. K depositions were made at room temperature with a well-outgassed SAES getter source. The base pressure in the chamber was 7×10^{-11} Torr and did not exceed 1.5×10^{-10} Torr during K depositions. Preparation of the GaAs(110) surface (Si doped, $n_{\mathrm{Si}}\sim10^{18}$ cm^{-3}) was achieved by cycles of argon-ion bombardment (~550 eV) for ~20 min followed by annealing at $T\sim515\,^\circ\mathrm{C}$ for ~10 min. Cleanliness and structural homogeneity of the clean surface were confirmed by comparing *I-V* profiles with previously published results.[9] Sample alignment was established by careful comparison of the *I-V* spectra of equivalent diffracted beams. Since the work-function change ($\Delta\Phi$) is relatively large (a few eV) for a saturated alkali-metal monolayer deposited on a semiconductor surface, $\Delta\Phi$ was chosen as the method of determining relative K coverage. $\Delta\Phi$ was measured with the LEED gun by the retarding field method. A $\Delta\Phi$ versus exposure plot, exhibiting a typically large decrease in work function due to alkali-metal adsorption, is presented in Fig. 1. While the absolute coverage is unknown, saturation coverage at room temperature (Θ_{sat}), obtained after an ~8 min dose, represents a K monolayer, as was later confirmed by thermal desorption spectroscopy (TDS) and electron-energy-loss spectroscopy (EELS).[10]

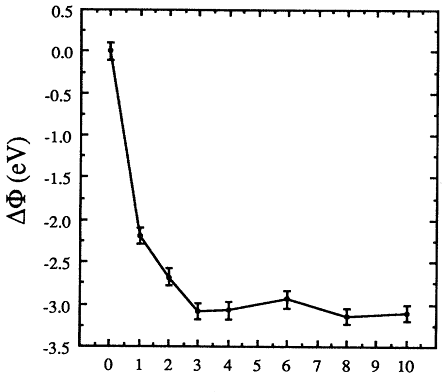

FIG. 1. $\Delta\Phi$ vs exposure time for K on GaAs.

The LEED pattern for the clean GaAs surface exhibited sharp diffraction spots with little diffuse background for energies up to $\sim$260 eV at $T\sim$300 K. However, at saturation K coverage a large diffuse background intensity was observed, and no diffraction spots were visible. To determine the onset of disorder, a series of line scans were performed at partial K coverages. A representative line scan performed at an electron-beam energy of 120 eV (Fig. 2) shows a uniform increase of diffuse background with very weak spot intensities at $\sim\frac{1}{2}\Theta_{\rm sat}$. It was also noted that no streaking of the spot intensities was observed for these coverages which would be characteristic of linear chain formation which occurs for the Cs/GaAs(110) interface.[11] Cooling the sample to $\sim$150 K resulted in no visible change in the LEED pattern or in the diffuse background. In addition, annealing the saturated surface at several intermediate temperatures up to $\sim$200 °C provided no visible diffraction spots. Partial desorption of K began at higher temperatures which eventually resulted in the return of the original GaAs diffraction pattern. These observations provide strong evidence that no long-range order exists for the K overlayer at all coverages up to saturation in contrast to a recent report.[12]

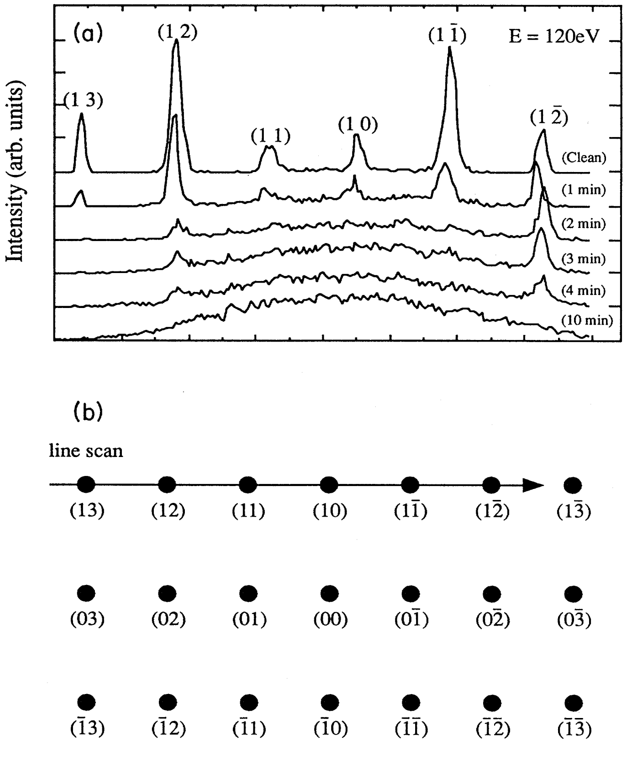

FIG. 2. (a) Series of line scans showing the coverage dependence of the diffuse background and the spot intensities at $E=120$ eV. (b) Reciprocal lattice of GaAs(110) surface indicating the line scan section. Note that $(hk)=(\bar{h}k)$.

From analysis of relative spot intensity as a function of coverage for several line scans, it was observed that certain diffraction spots attenuate more rapidly than others. In Fig. 2, for example, the $(1\bar{2})$ diffraction spot remains visible beyond $\sim\frac{1}{2}\Theta_{\rm sat}$, yet the $(1\bar{1})$ spot, which is approximately three times as intense initially, is totally attenuated after only $\sim\frac{1}{4}\Theta_{\rm sat}$. At this energy, kinematic calculations show that a maximum in intensity should occur at 120 eV only for the (12) and the $(1\bar{2})$ spots. From observations at this and other energies, it was assumed that the dominant scattering mode for the GaAs substrate with a partial K overlayer is kinematic in origin. This assumption is justified since elastic scattering from the GaAs substrate is weak in comparison with the absorption caused by the disordered K overlayer which is the condition for dominance of kinematic scattering phenomena.[13]

A kinematic analysis of diffracted beam intensities as a function of electron energy was undertaken for coverages up to $\sim\frac{1}{2}\Theta_{\rm sat}$ to determine the K-induced modifications of the structure of the underlying GaAs(110) surface. Beam intensities for energies less than 85 eV were not analyzed due to the large angular dependence of the forward scattered intensities in this range.[14] Kinematic scattering intensities for the unrelaxed surface were calculated and compared with those for the relaxed surface. The dimensions for the relaxed surface (Fig. 3) were taken from the calculation of Duke *et al.*[7] An inner potential of 10 eV was assumed for the clean surface, and this potential was adjusted by the appropriate work-function change when

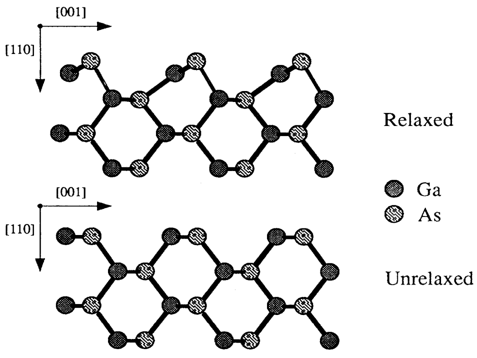

FIG. 3. Side views of GaAs(110) showing relaxed and unrelaxed surface structures.

treating the adsorbed K layer. Since the Debye temperature for GaAs is 345 K, no correction for temperature effects was made in the calculations.

Fifteen beams with indices (03), (02), (0$\bar{2}$), (0$\bar{3}$), (13), (12), (11), (10), (1$\bar{1}$), (1$\bar{1}$), (1$\bar{2}$), (1$\bar{3}$), (21), (20), and (2$\bar{1}$) were analyzed for this study. Energies between 85 and 225 eV for the lower-order spots and between 100 and 265 eV for the higher-order spots were analyzed. Figures 4–6 present the results of experimental and calculated I-V scans for the (12), (1$\bar{2}$), and (1$\bar{1}$) beams, respectively. These are the strongest diffracted beams which also exhibit the most pronounced differences in the calculated kinematic intensities for the relaxed and unrelaxed structures. In Fig. 4(a) features A, B, C, and D of the clean GaAs data correspond to features A', B', C', and D' of Fig. 4(b) for the relaxed kinematic scattering calculation, while the other features of the clean surface diffraction data are attributed to multiple-scattering processes.[15] With increased K exposures, features A, C, and the multiple-scattering features attenuate more rapidly than features B and D (see Fig. 2). Features A' and C' are not present for the unrelaxed structure which is consistent with a K-induced bond rotation towards this structure. Figures 5(a) and 5(b) show similar effects for the (1$\bar{2}$) beam where feature E and the multiple-scattering features

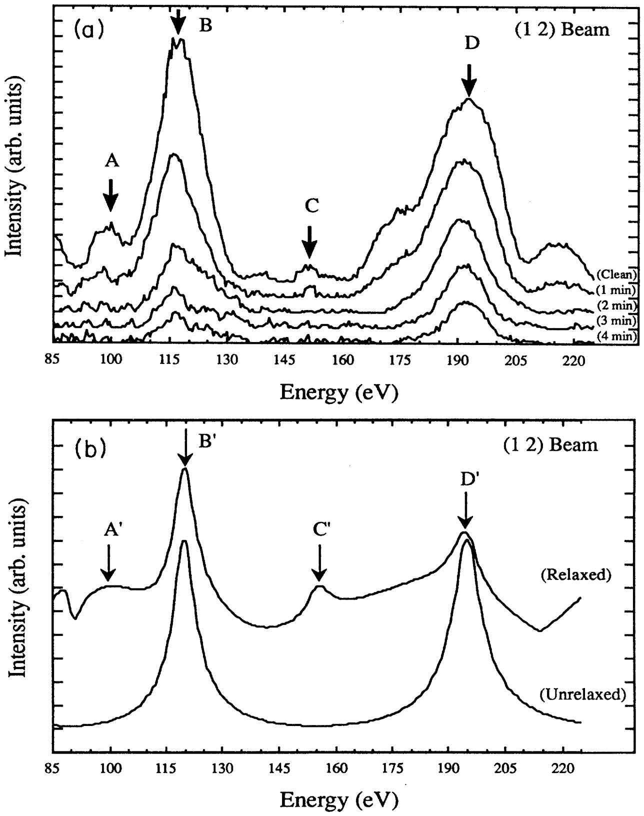

FIG. 4. (a) Measured I-V curves for the (12) beam as a function of K coverage for electrons normally incident on the GaAs(110) surface. (b) Calculated I-V curves for the (12) beam for the relaxed and unrelaxed GaAs(110) surface geometries using kinematic LEED analysis.

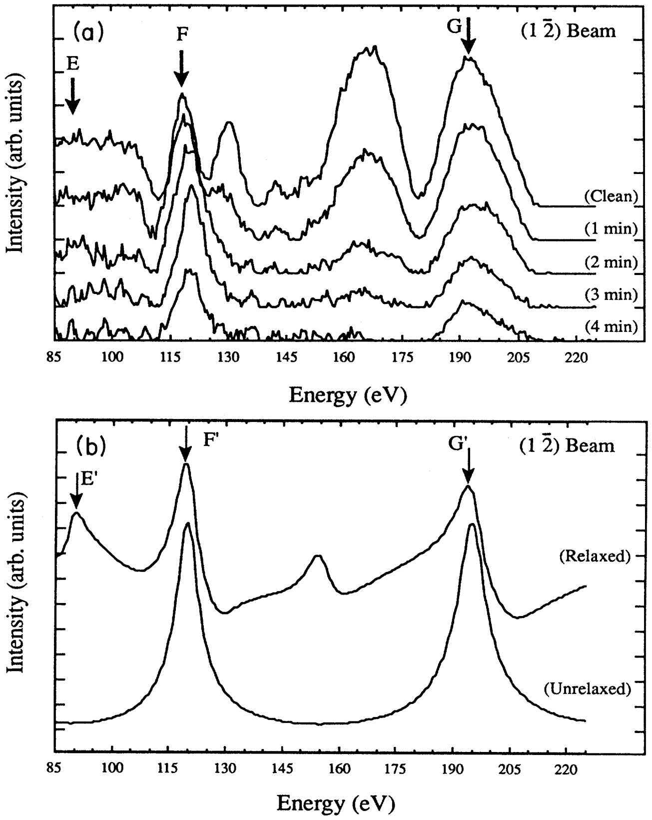

FIG. 5. Same as Fig. 4 for the (1$\bar{2}$) beam.

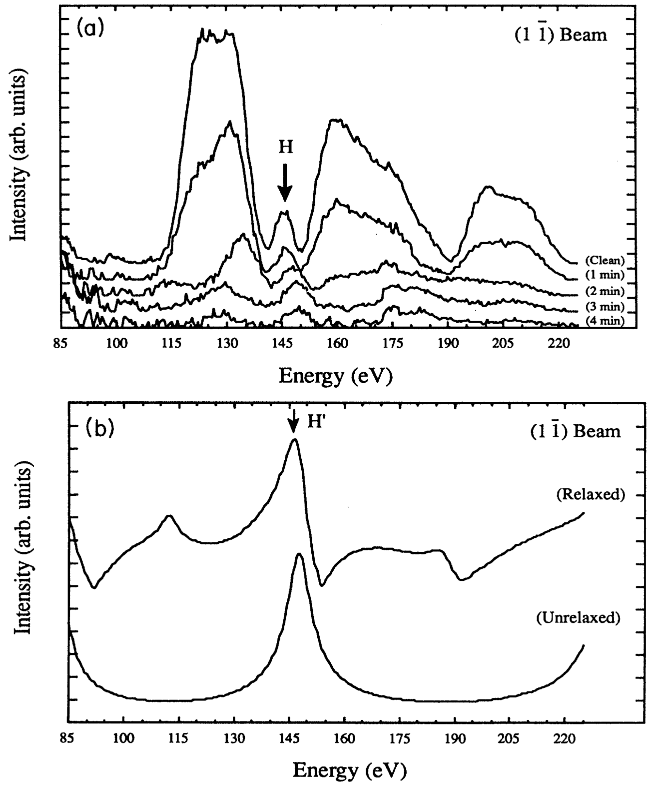

FIG. 6. Same as Fig. 4 for the (1$\bar{1}$) beam.

again attenuate more rapidly than the other features. In addition, a shift of ~3 eV is observed for peak H in Fig. 6(a). This is in qualitative agreement with the calculated shift of ~1.4 eV for bond rotation to the unrelaxed GaAs(110) structure as seen in Fig. 6(b).

Only two geometries, the relaxed and unrelaxed GaAs(110) structures, beneath a disordered K layer have been considered in these calculations since the kinematic analysis is not sensitive enough to distinguish small deviations from either geometry. The observation that disorder occurs in the K overlayer is supported by calculations of alkali-metal adsorption on the (unrelaxed) GaAs(110) surface[16] which conclude that multiple sites have comparable adsorption energies. Therefore, no strong site preference is expected, particularly as the density of the K layer increases. While it is conceivable that additional disordering in the uppermost GaAs layer might occur, it is reasonable to attribute the disorder exclusively within the K layer. The observation that thermal desorption of K at ~250 °C produces the 1×1 LEED pattern of the clean surface and the result of valence and core-level photoelectron spectroscopy which indicate that K does not react strongly with GaAs(110) (Ref. 17) give strong evidence that the K does not intermix with the GaAs. In addition, the observed rate of attenuation of the kinematic peaks is not in agreement with the rate that would be expected for disordering in both the K and GaAs layers.

The agreement between the kinematic calculations and the experimental data provides evidence for a bond rotation of the surface GaAs atoms towards the unrelaxed structure. The data also suggests the dominance of the kinematic scattering phenomenon for scattering through disordered K overlayers which, to first order, justifies the use of kinematic scattering theory for the structural analysis. As a complement to this study, a study with a short-ranged probe such as photoemission extended PEXAFS may be performed to further access the degree and extent of the alkali-metal-induced unrelaxation.

We gratefully acknowledge Professor E. W. Plummer for the use of the LEED *I-V* apparatus in his laboratory as well as his valuable comments. The expert technical assistance of Mr. Wolfgang Nadler and the contributions of Mr. Thomas Mercer are greatly appreciated. This project was partially supported by NSF DMR 88-19885.

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