Atomic Geometry of GaAs(110)-$p(1\times1)$-Al

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An ordered (1×1) structure is formed by evaporating approximately one-half monolayer of Al on GaAs(110) and subsequently annealing at 450 °C for 30 min. Both a dynamical analysis of the low-energy electron-diffraction intensities from the resulting half-monolayer of GaAs(110)-$p(1\times1)$-Al structure and soft–x-ray photoemission spectroscopy indicate that the Al replaces the Ga in the *second* atomic layer beneath the surface. The uppermost layer retains the structure of clean GaAs(110) but is relaxed 0.1 Å toward the second AlAs layer.

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Although the properties and stability of metal-semiconductor interfaces are of enormous importance in the fabrication and life of microelectronic circuits, no determinations of their microscopic atomic geometries have yet been accomplished. In this Letter we report the first step in this process for Al contacts on GaAs: the determination of the atomic geometry of the $p(1\times1)$ structure formed by one-half monolayer (M.L.) of Al on GaAs(110). Room-temperature deposition of up to two M.L. of Al evaporated on GaAs(110)—either vacuum cleaved or ion bombarded and annealed—leads to disordered overlayers which form $p(1\times1)$ ordered structures upon annealing at 450°.[1] Herin we describe the dynamical analysis of the elastic low-energy electron-diffraction (ELEED) intensities for Al coverages, $\theta \leq 1$ M.L. [i.e., one to two Al for each Ga in the uppermost layer of GaAs(110)]. This analysis indicates that after annealing *the Al replaces the Ga species in the second and deeper atomic layers from the surface.* Moreover, these ELEED results are confirmed by soft–x-ray photoemission spectroscopy (SXPS) which reveals the movement of Al away from the surface to bulk bonding sites. Not only is this analysis the first step in the determination of the microscopic atomic geometry of Al-GaAs interfaces, but also it reveals the considerable difference between the atomic geometry determined experimentally via ELEED/SXPS and the hypothetical geometries used in a variety of calculations of the electronic properties of group-III metals adsorbed on GaAs(110).[2-6]

The experimental procedures for sample preparation, acquisition of the ELEED intensity data, and comparison with earlier measurements are described elsewhere.[1] The data shown here were obtained from ion-bombarded and annealed (IBA) substrates, although comparable results are obtained from cleaved substrates. The intensity profiles of ten beams associated with normally incident electrons, i.e., those with the beam indices $(10)=(\bar{1}0)$, (01), $(0\bar{1})$; $(11)=(\bar{1}1)$, $(1\bar{1})=(\bar{1}\bar{1})$; (02), $(0\bar{2})$; and $(21)=(\bar{2}1)$, $(2\bar{1})=(\bar{2}\bar{1})$, and $(1\bar{2})=(\bar{1}\bar{2})$, were measured at $T=295$ K for several values of the Al coverage, θ. These are the experimental ELEED intensities on which our structure analysis is based.

The calculations of the ELEED intensities were performed utilizing multiple-scattering models.[7,8] The electron–ion-core scattering factors were calculated from an overlapping atomic potential embodying Slater exchange.[9] The propagation of the incident electrons between scattering events was described with use of a complex inner potential.[7,9] The inner potential was chosen to minimize the x-ray R factors[10,11] associated with the description of the measured intensities by the calculated ones. This procedure yielded $\lambda_{ee}=8$ Å for the value of the inelastic collision damping length and different values of the real inner potential, V_0, for each structural model. The use of only six phase shifts and five atomic bilayers provided adequately converged dynamical calculations for

TABLE I. Candidate structures for GaAs(110)-*p*(1×1)-Al(0.5 M.L.). The coverages θ are as-deposited, prior to annealing. R_x and R_{ZJ} designate the x-ray and Zanazzi-Jona reliability factors defined in Ref. 10. ω_1 is the angle defining the rotational relaxation of the uppermost layer and $\Delta d_{12,\perp}$ is the change in the spacing between this layer and that beneath it relative to the unreconstructed surface. Both symbols are defined precisely in Ref. 8.

Structure	ω_1	$\Delta d_{12,\perp}$(Å)	V_0(eV)	Prior GaAs(110)[a]		$\theta = 0$ M.L.		$\theta = 1/2$ M.L.		$\theta = 3/4$ M.L.		$\theta = 1$ M.L.	
				R_x	R_{ZJ}	R_x	R_{ZJ}	R_x	R_{ZJ}	R_x	R_{ZJ}	R_x	R_{ZJ}
(*a*) Relaxed Al → Ga in second layer	27.34°	−0.15	11	0.32	0.24	0.38	0.35	0.31	0.34	0.25	0.30	0.25	0.24
(*b*) Relaxed Al → Ga in top layer	16.44°	−0.15	13	0.33	0.23	0.39	0.35	0.35	0.38	0.39	0.37	0.39	0.32
(*c*) Mele and Joannopoulos[b]	⋯	⋯	6	0.46	0.28	0.48	0.35	0.49	0.40	0.43	0.35	0.47	0.34
(*d*) Swarts *et al.*[c]	⋯	⋯	11	0.51	0.36	0.57	0.43	0.47	0.45	0.52	0.40	0.52	0.39
(*e*) Reconstructed GaAs(110)[a]	27.34°	−0.05	5	0.17	0.24	0.21	0.29	0.29	0.35	0.29	0.36	0.42	0.36

[a] Ref. 8.

[b] Ref. 2.

[c] Ref. 6.

$E \leq 180$ eV.

Our structure searches were performed with use of R-factor programs developed for InP(110).[12] The x-ray R factors, R_x, and the newer "Zanazzi-Jona" ones, R_{ZJ}, both as defined by Zanazzi and Jona,[10] provided quantitative measures of the comparison between the calculated and measured structures. The values of both R factors resulting for various candidate structures are given in Table I.

In order to identify probable structures we calculated the ELEED intensities for over fifty hypothetical model geometries selected from four broad classes. All structures were characterized by half-monolayer coverage of Al, a fact indicated by labeling the structure GaAs(110)-*p*(1×1)-Al($\frac{1}{2}$ M.L.). Interstitial positions were examined by inserting an extra Al species at the center of each of the two hexagons normal to the (110) surface indicated as sites "1" and "2" in Fig. 1. The vertical positions of the Al were varied from 1.0 Å above to 2.0 Å below the outermost As species. Otherwise the GaAs surface was taken to exhibit its clean-surface reconstruction.[8] Two comparable minima of $R_x \simeq 0.35$ result from this process. Since these minimal R factors are much larger than those characteristic of the description of clean GaAs, i.e., $R \simeq 0.2$ as indicated in Table I, such interstitial structures are not compatible with the measured ELEED intensities from annealed GaAs(110)-*p*(1×1)-Al($\frac{1}{2}$ M.L.).

The second class of geometries which we examined consists of "Ga-on-top" structures derived from the geometry predicted by Mele and Joannopoulos (MJ) on the basis of their analysis of photoemission and band-bending measurements.[2] These structures are obtained by replacing the Ga in the top layer by Al (site "3," Fig. 1) and placing this Ga above the As in the top layer

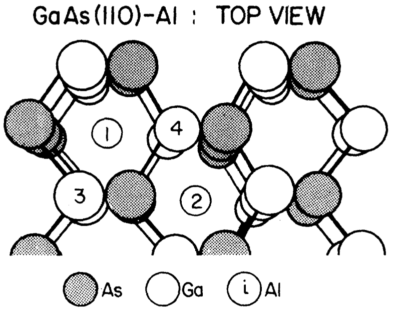

FIG. 1. Schematic indication of adsorption sites for Al on GaAs(110). The preferred site for GaAs(110)-*p*(1×1)-Al($\frac{1}{2}$ M.L.) is the one labeled 4.

near the position which it would have occupied in the bulk GaAs. The structure preferred by MJ gives $R_x \geq 0.43$ as noted in line *c* of Table I. The lowest R_x of ten related structures was 0.36, still outside the range $0.2 \leq R_x \leq 0.3$ needed for consideration as a "probable" model geometry.[10,12]

The third class of structures considered was that obtained by replacing the Ga in the top layer by Al (site "3," Fig. 1), if we presume that the Ga either evaporated[13] or segregated on top in clumps[14] during the anneal cycle. These correspond to the type of structures originally inferred from analyses of photoemission measurements,[15] although later photoemission studies[16] suggested disordered overlayers at low Al ($\theta < 1$ M.L.) coverages for room-temperature deposition. Minimization of R_x with a grid of nine such structures led to the "best-fit" structure indicated in line *b* of Table I. While this structure constitutes a discernible improvement over the MJ structure, it still yields R_x, $R_{ZJ} > 0.3$ and hence does not constitute a probable geometry.

The final class of structures examined was that based on second-layer Al-for-Ga replacement reactions (site "4," Fig. 1). Values of $R_x = 0.28$ and $R_{ZJ} = 0.30$ are achieved for a deposited Al coverage of $\theta = 0.75$ M.L., even if no other change is made in the clean GaAs(110) geometry. Refining this structure with use of a grid of nine model geometries led to the best-fit structure given in line *a* of Table I which yields R_x, $R_{ZJ} \leq 0.3$, i.e., lying in the range of "probable" structures. This structure provides a description of the $\theta = 1$ M.L. intensity data comparable to that of the $\theta = 0$ data afforded by the clean-surface structure.[8] Therefore, the R-factor fitting criteria indicate that a second-layer Al-for-Ga replacement structure for as-deposited Al coverages of $0.5 \leq \theta \leq 1$ M.L. (i.e., a nominal Al coverage of $\theta = \frac{1}{2}$ M.L.) is as firmly established as the surface structure of clean GaAs(110).[8,17] The accuracy of the structure specified in line *a* of Table I is approximately ±0.05 Å for distances normal to the surface and ±0.15 Å for distances parallel to the surface.

In order to convey the flavor of these R-factor results we present a visual comparison between calculated and measured intensities both for clean GaAs(110) and for as-deposited coverages

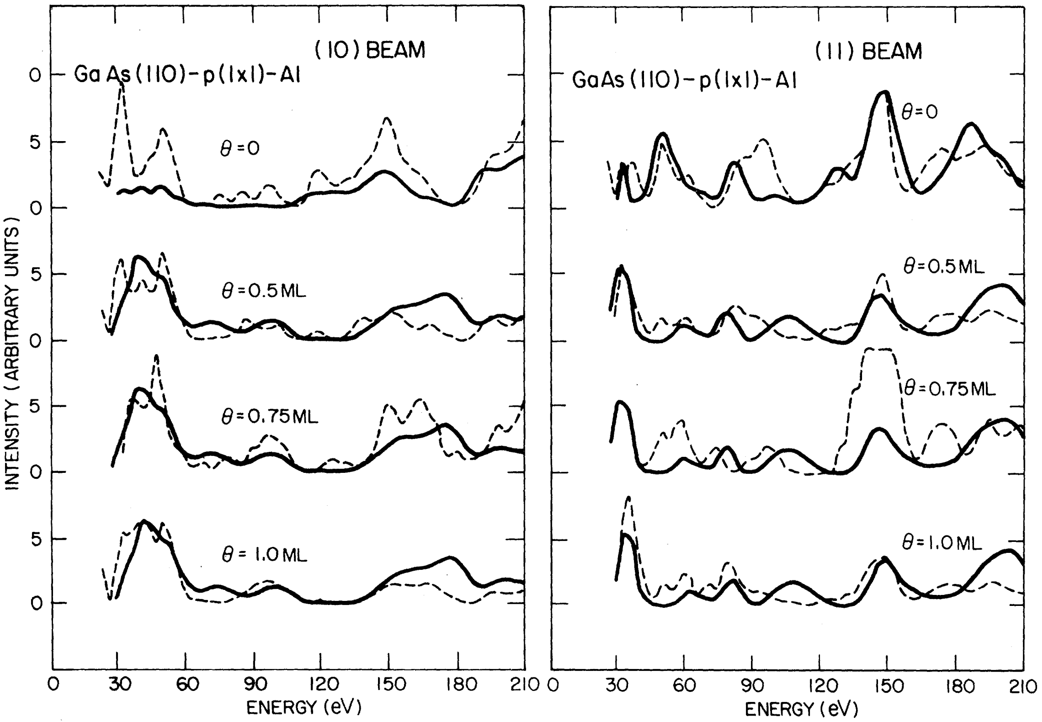

FIG. 2. Calculated (solid lines) vs measured (dashed lines) ELEED intensities for normally incident electrons on GaAs(110)-$p(1\times1)$-Al(θ) diffracted into the (10) and (11) beams. Top panels show the comparison of the intensities calculated with use of the best-fit structure (Ref. 8) [line *e*, Table I] and the clean room-temperature ELEED intensities from clean GaAs(110). The lower three panels of each compare our best-fit nominal $\theta = \frac{1}{2}$ M.L. structure [line *a*, Table I] with room-temperature ELEED intensities prepared by Al deposition followed by annealing at 450 °C. The Al coverage *prior* to annealing is indicated in each panel.

of $\theta=0.5$, 0.75, and 1.0 M.L. in Fig. 2 for two typical low-index beams, the (10) and the (11), respectively. The correspondence between the measured and calculated intensities improves with increasing coverage because the deposited Al does not move uniformly into the second layer upon annealing, but also penetrates somewhat into the third and deeper layers. Thus, the second-layer Ga sites become fully occupied by Al only for as-deposited coverages of about $\theta=1$ M.L.

Finally, to test these conclusions and relate the results obtained via our annealing process to those obtained earlier by room-temperature deposition,[15,16] we performed SXPS studies on annealed samples as well. Annealed $p(1\times 1)$ surfaces exhibit substantial intensity decreases of the Al $2p$ vs As $3d$ or Ga $3d$ core-level features. Furthermore, the Al $2p$ core exhibits a 0.5–0.65 eV chemical shift to higher binding energy upon annealing. Both results indicate that Al moves to a more highly coordinated bonding site *below* the surface. This substitution reaction upon annealing also is implied by shifts in the Al *LMM* Auger line from 67 eV prior to annealing to 65 eV after annealing, a value characteristic of AlAs.[1] Thus, SXPS confirms explicitly the ELEED results that, at low coverages $\theta<1$ M.L., the Al replaces the Ga in layers *beneath* the surface, rather than in the surface layer itself.

We conclude that upon annealing for $\theta<1$ M.L. the vacuum-deposited Al species move from their (disordered) overlayer positions into the *second* and deeper layers of the GaAs(110) structure, replacing the Ga. Not all of the Al species go simply into the second layer but some occupy other lattice sites as well. Second-layer Ga sites are thermodynamically more favored than top-layer sites while exhibiting smaller net kinetic barriers to the replacement reaction than third and deeper layers. Thus, the microscopic picture of this process afforded by the ELEED structure analysis reveals the interplay between replacement and diffusion chemical processes which determine the structure and stability of microelectronic devices as well as of idealized model systems like GaAs(110)-$p(1\times 1)$-Al.

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