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Photoemission studies of $Al_xGa_{1-x}As(100)$ surfaces grown by molecular-beam epitaxy

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An As-stabilized $Al_{0.7}Ga_{0.3}As(100)$ surface grown by molecular-beam epitaxy was studied using photoemission techniques. Core-level shifts and relative emission intensities at the surface were used to deduce the surface structure. High-energy-electron-diffraction and surface-contamination-rate measurements were also made. The results indicate that this surface is very similar to the As-stabilized GaAs(100)-$c(2\times 8)$ surface in structure with complete depletion of Al at the surface.

Using photoemission techniques, we have studied an $Al_{0.7}Ga_{0.3}As(100)$ surface grown by molecular-beam epitaxy (MBE). $Al_xGa_{1-x}As$ is an important material used in the electronic and optoelectronic industries, and its (100) surface is usually the device face. Studies of the intrinsic properties of this surface are important steps toward understanding the physics and chemistry of interface formation involving $Al_xGa_{1-x}As$. There have been in the past many investigations of pure elemental and binary compound semiconductor surfaces, such as those of Si and GaAs.[1-3] But much less has been done for compound semiconductor alloys such as $Al_xGa_{1-x}As$. This is largely related to the complexities involved in preparing well-characterized samples suitable for ultrahigh vacuum studies. Using MBE techniques[4] we have been able to prepare *in situ* atomically smooth surfaces of $Al_xGa_{1-x}As$. This system is fundamentally more complex than GaAs and AlAs. It is known that GaAs(100) has many surface phases with the As-stabilized $c(2\times 8)$ structure being one of the most stable and easiest to prepare. On the other hand, the related AlAs(100) surface usually shows a (3×2) reconstruction.[4,5] Our aim is to study the surface structure and composition of the alloy system $Al_{0.7}Ga_{0.3}As$ using photoemission techniques.

Core-level binding energies associated with surface atoms are usually shifted relative to the bulk due to differences in the atomic environment. This effect has been observed before using the photoemission techniques for many systems including the cleaved GaAs(100)-(1×1) surface.[1-3] These shifts are related to the surface structure, but the actual determination of surface structure from the measured shifts is rather difficult. In the present investigation, the measured shifts are used as fingerprints to deduce structural information. Furthermore, the relative photoemission intensities from the bulk and surface are used to deduce the surface composition. Our results show that a stable $Al_{0.7}Ga_{0.3}As$ surface grown under high As partial pressure has a structure very similar to the GaAs(100)-$c(2\times 8)$ surface, with a complete depletion of Al in the surface atomic layer.

The experiment was done at the Synchrotron Radiation Center at Stoughton, Wisconsin. $Al_xGa_{1-x}As$ samples about 2000 Å thick were grown on GaAs(100) substrates in a MBE chamber. The sample growth was monitored and the resulting surfaces were characterized using high-energy-electron-diffraction (HEED) techniques. After growth, the samples were transferred under ultrahigh vacuum conditions to a photoemission chamber in which the core-level measurements were made. Many samples of $Al_xGa_{1-x}As(100)$ were prepared with different x's under high As partial pressure $\sim 10^{-6}$ torr. The growth rate was typically about 1 Å/sec, and the growth temperature was about 520–700 °C depending on x. The growth was terminated by turning off Ga and Al beams simultaneously and leaving the sample annealed in As vapor before cooling down. No changes in HEED patterns were observed during annealing. All samples with $0 < x < 1$ showed a fuzzy (2×8) pattern nearly identical to that observed for a somewhat disordered GaAs(100)-$c(2\times 8)$ surface.[6] This fuzziness was reproducible and most likely intrinsic due to disorder by alloying. For simplicity, we will discuss only the results in detail for $x \simeq 0.7$. At this relatively large x value, the (2×8) phase was invariably produced with the quarter-order reconstruction relatively fuzzy and barely discernible in the HEED pattern. The growth was quite stable with a substrate temperature of about 570 °C. A few attempts to prepare other surface phases by using lower or higher substrate temperatures were not successful, and the surface became rough or faceted after growth of a thick layer ($\gtrsim 500$ Å).

Photoemission spectra from core levels of the Al 2*p*, Ga 3*d*, and As 3*d* core levels for $Al_{0.7}Ga_{0.3}As(100)$ are shown in Figs. 1–3, respectively. These three figures are presented differently in order to emphasize different points. Two different photon energies are used in each case. The lower (higher) photon energy was chosen to emphasize the bulk (surface) contribution: the photoelectron kinetic energy is ~5(40) eV, and the escape depth is ~20(6) Å.[3] These spectra will be referred to as bulk sensitive (lower photon energy) and surface sensitive (higher photon energy) in the following. Since the chemical environments of Al and Ga atoms are nearly identical for this alloy semiconductor, the core-level shifts for surface Al and Ga atoms should be similar for similar sites. The relative photoemission intensity ratios between different atomic species and between surface and bulk contributions can be used to deduce the composition. The deconvolution of photoemission spectra into bulk and surface contributions were done with a nonlinear least-squares fitting procedure taken into account the instrumental Gaussian broadening, inhomogeneous broadening due to alloying, lifetime broadening, spin-orbit splitting, branching ratios, and the background (approximated by a third-order polynomial). Details will be published elsewhere, and the main results are summarized in Table I. Here by surface atoms, we mean those atoms near the surface whose chemical environments are sufficiently different from the bulk such that the differences should be readily detectable whether these atoms are on or just below the surface.

The solid curves in Fig. 1(a) are the experimental Al 2*p* core-level spectra. The bulk-sensitive spectrum ($h\nu = 82$ eV) clearly shows the spin-orbit splitting. The surface-sensitive spectrum ($h\nu = 112$ eV) is broader not due to any surface shift but because of larger instrumental broadening (the instrumental broadening is ~0.28 and 0.49 eV at $h\nu = 82$ and 112 eV, respectively, determined from measured Fermi-edge widths). The results of a theoretical fit assuming no surface shifts are shown as closed and open circles in Fig. 1(a). The data, after background subtraction and proper normalization to give the same

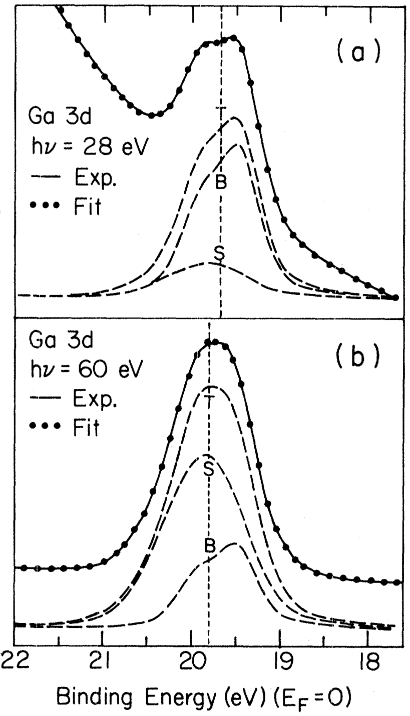

FIG. 2. In (a) and (b) the solid lines are photoemission spectra for Ga 3*d* core levels of $Al_{0.7}Ga_{0.3}As(100)$ taken with $h\nu = 28$ eV (bulk sensitive) and 60 eV (surface sensitive), respectively. The decomposition into the surface (S) bulk (B), and total ($T \equiv S + B$) contributions is shown by the long dashed lines. The centers of gravity for these two spectra are indicated by the vertical short dashed lines. The binding energy is referred to the Fermi level E_F.

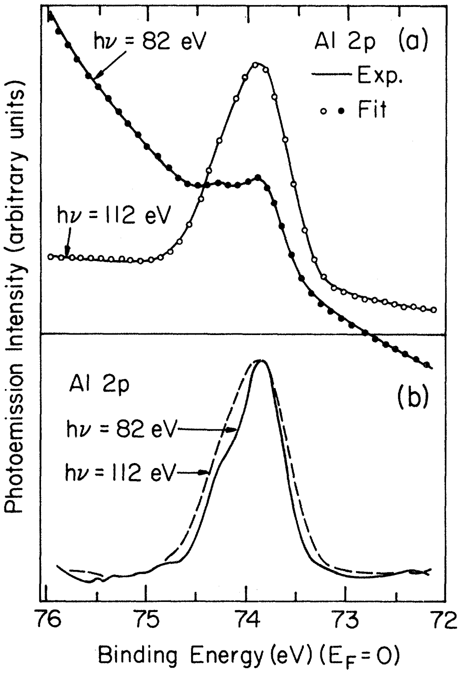

FIG. 1. (a) Solid lines are photoemission spectra for Al 2*p* core levels of $Al_{0.7}Ga_{0.3}As(100)$ taken with $h\nu = 82$ eV (bulk sensitive) and 112 eV (surface sensitive), respectively. Closed and open circles are the results of theoretical fitting. (b) Solid and dashed lines are the spectra in (a) with background subtracted and normalized to have the same peak intensity. The binding energy is referred to the Fermi level E_F.

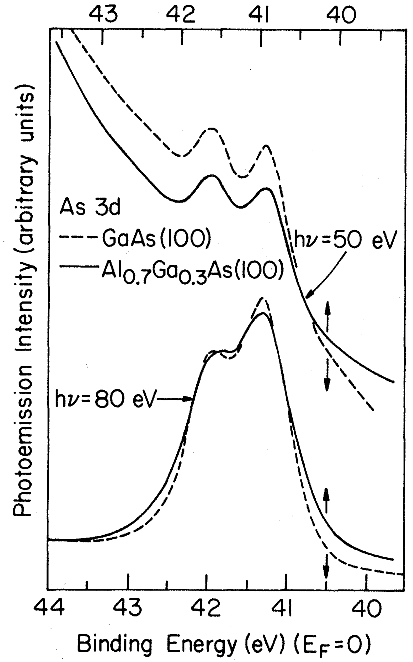

FIG. 3. The solid and dashed lines are photoemission spectra for As $3d$ core levels of $Al_{0.7}Ga_{0.3}As(100)$ and GaAs(100)-$c(2\times 8)$, respectively, taken with $h\nu = 50$ eV (bulk sensitive) and 80 eV (surface sensitive) as indicated. The binding energy is referred to the Fermi level E_F, and the two scales are relatively shifted such that the bulk peaks are lined up vertically.

peak intensity, are shown in Fig. 1(b). The centers of gravity for these two curves almost coincide with a small shift due to about 10% change in the spin-orbit branching ratios.[9] The theoretical fit shown in Fig. 1(a) is excellent, and indicates two possibilities: (1) there are no surface Al atoms (complete surface depletion during growth), or (2) the surface Al atoms happen to show little core shifts. The second possibility is ruled out since surface Ga atoms (which should show similar shifts) do show large shifts.

Figures 2(a) and 2(b) show the experimental spectra (solid curves), fit (closed circles), and theoretical decompositions into bulk (B), surface (S), and total ($T \equiv B + S$) contributions for Ga $3d$ core levels in the bulk- and surface-sensitive regimes, respectively. In the fit, the surface contribution was allowed to have a wider width (Table I) to account for possible extra inhomogeneous broadening due to the possible presence of different sites. This seems to work well and does illustrate that there is a surface shift ~ 0.22 eV to a higher binding energy (the centers of gravity for the two spectra in Fig. 2, indicated by short dashed lines, differ by 0.11 eV). The intensity ratio between surface and bulk contributions R is 2.6 for the surface-sensitive spectrum, much larger than expected for homogeneous systems.[3] We have also performed similar analysis for GaAs(100)-$c(2\times 8)$, and found that the same surface core shift and a much smaller value of $R = 0.78$ fit the surface-sensitive spectrum well (not shown here).[10] The ratio between

TABLE I. Physical quantities for $Al_{0.7}Ga_{0.3}As(100)$ determined from theoretical fit unless otherwise noted. B and S refer to the bulk and surface core levels, respectively. E is the binding energy of $3d_{5/2}$ (for Ga and As) or $2p_{3/2}$ (for Al) referred to the Fermi level. Δ is the spin-orbit splitting. BR is the branching ratio ($d_{3/2}/d_{5/2}$ for Ga and As and $p_{1/2}/p_{3/2}$ for Al) for the bulk-sensitive (BS) or surface-sensitive (SS) spectra. δE is the Gaussian width (most likely due to crystal field; the instrumental width is not included). Γ is the Lorentzian width (due to lifetime; negligible for Al). $I(S)/I(B)$ is the intensity ratio between surface and bulk contributions.

	Ga $3d$	As $3d$	Al $2p$
E(B) (eV)	19.46	41.23	73.82
E(S) (eV)	19.68	. . . [a]	
Δ (eV)	0.44[b]	0.70[b]	0.42[c]
BR(BS)	0.62[b]	0.57[b]	0.44
BR(SS)	0.62[b]	0.57[b]	0.50
δE(B) (eV)	0.26	0.25	0.36
δE(S) (eV)	0.69	. . . [a]	
Γ(B, S) (eV)	0.29[b]	0.40[b]	~ 0[d]
$I(S)/I(B)$(BS)	0.29	0.26	0
$I(S)/I(B)$(SS)	2.58	1.66	0

[a] Complex, at least two surface components.
[b] Reference 3.
[c] Reference 7.
[d] Reference 8.

the two R values $0.78/2.6 = 0.3$ equals the value of atomic percentage of Ga in $Al_{0.7}Ga_{0.3}As$! From all of the above evidence, we conclude that the $Al_{0.7}Ga_{0.3}As(100)$ surface is very similar to GaAs(100)-$c(2 \times 8)$ in structure *and* composition. Evidently, the deposited Al atoms tend to diffuse from the surface into the subsurface region during growth. Furthermore, the depletion of Al is confined *only* to the surface layer, and this accounts for the observed R value larger (3.3 times) in $Al_{0.7}Ga_{0.3}As$ than in GaAs(100).

The results on As core levels (Fig. 3) also support our conclusions. The As core levels show significant surface components shifted to both lower and higher binding energies (the deconvolution is not shown here)[10] for GaAs(100)-$c(2 \times 8)$ and $Al_{0.7}Ga_{0.3}As(100)$. In Fig. 3, the bulk peaks for these two crystals are lined up by shifting the energy scales as shown, and this can be seen clearly by examining the two bulk-sensitive (upper) spectra. The two surface-sensitive (lower) spectra then appear very similar, except that the spectrum for $Al_{0.7}Ga_{0.3}As$ is somewhat broader (most likely due to broadening introduced by alloying).[11] Therefore the two surfaces are very much alike as far as As core shifts are concerned.

Residual gas contamination rate for the sample surface is also a good qualitative probe for surface composition. The $Al_{0.7}Ga_{0.3}As(100)$ surface is as inert as the GaAs(100) surface (no detectable contamination in several days), while the related AlAs(100)-(3×2) surface, with Al atoms on the surface, is considerably more reactive (similar to the metallic Al surfaces) with contamination detectable in about an hour. This is consistent with the conclusion of an absence of Al atoms on the $Al_{0.7}Ga_{0.3}As(100)$ surface.

In summary, the As-stabilized $Al_{0.7}Ga_{0.3}As(100)$ surface is very similar to GaAs(100)-$c(2 \times 8)$ in structure and composition. The depletion of Al on $Al_{0.7}Ga_{0.3}As(100)$ surface is not extended into the bulk. The above conclusions are based upon measurements of (1) HEED, (2) surface core-level shifts and relative photoemission intensities, and (3) contamination rates. This is also consistent with the fact that sharp GaAs-$Al_xGa_{1-x}As$ interfaces can be formed by MBE.[6]

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[9] This change in branching ratio is most likely due to the final-state effects.

[10] T.-C. Chiang, R. Ludeke, and D. E. Eastman (unpublished).

[11] The widths of bulk Ga and As 3*d* core levels are also wider in $Al_{0.7}Ga_{0.3}As$ than in GaAs.