Local valence-band densities of states of Al$_x$Ga$_{1-x}$As

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Aluminum $L_{2,3}$ soft-x-ray emission (SXE) spectra measured for Al$_x$Ga$_{1-x}$As in the range $0 < x < 0.8$ show changes due to modifications of the s-like local density of states (DOS) as the Al concentration is varied from $x = 0.05$ to $x = 0.8$. Differences in SXE data and x-ray photoemission spectra with alloy composition are attributed to the difference between the local DOS measured by SXE spectroscopy and the global DOS measured by photoemission spectroscopy. These measurements show a nonlinear shift of the top of the valence band and slope change near $x = 0.4$ may be explained in part by the role of cation d orbitals and other hybridization effects which correlate with the direct-band-gap–indirect-band-gap transition.

I. INTRODUCTION

The alloy semiconductor compounds Al$_x$Ga$_{1-x}$As have been extensively studied because of their importance in semiconductor technology[1] and because they are also interesting theoretically since random substitutional alloys occur on a zinc-blende lattice that contains chemical, but very little structural disorder; the lattice constant changes by only 0.1% for all compositions.[1] These materials form an ideal model system for theoretical calculations which as an approximation typically assume random compositional disorder on an ideal lattice,[2] and this system constitutes an important limiting case for calculations that seek to accommodate disorder in both chemical species and bond length[3] since the lattice constants and bond lengths are nearly the same for AlAs, for GaAs, and for intermediate alloys Al$_x$Ga$_{1-x}$As.

Soft-x-ray emission (SXE) spectra are produced by dipole transitions from extended valence-band states to essentially atomic core levels. They provide density-of-states (DOS) information that is both spatially localized ($r \sim 0.2$ Å) and weighted by the ($\Delta l = \pm 1$) dipole selection rule on angular momentum. We discuss here Al $L_{2,3}$ data which are produced by transitions to the ($2p$) core levels of Al. These spectra provide a measure of the partial density of states (PDOS) with s and d character localized on the Al cation. Since Al has no occupied atomic (d) states initially, we expect our data to represent primarily the s-like occupied state density. A detailed analysis of both $L_{2,3}$ and $M_{4,5}$ spectra of the Al$_x$Ga$_{1-x}$As and GaAs$_x$P$_{1-x}$ alloy systems ($0 < x < 0.8$) will be presented elsewhere.

In contrast to SXE, photoelectron spectroscopy (PES) measures a more global density of states, averaged over all chemical species and all space, but weighted by matrix elements which for this system are nearly equal for both s and p occupied states. In this paper we concentrate on the important differences between the local PDOS information provided by SXE spectra and the more global DOS data provided by PES for the Al$_x$Ga$_{1-x}$As system, which approximates the theoretical local DOS averaged over the periodic unit cell and weighted by atomiclike matrix elements. The only existing local DOS information for III-V compound semiconductors is that from Auger transitions ($M_1 M_{4,5} V$ spectra of GaAs) which were calculated by Feibelman et al.[4] and measured by Davis et al. in 1981.[5] Auger-electron spectroscopy (AES) has a similar local DOS sensitivity as SXE due to the core-level transitions, but generally has a much poorer resolution since now two core levels are involved, with the deeper level usually having a much greater energy width than the upper level. Thus it would be much more difficult for AES to detect the relatively small changes in band structure with alloy composition that are observed by PES and SXE for Al$_x$Ga$_{1-x}$As.

As a local and chemically sensitive probe, our SXE study monitors changes occurring on the Al site as the atomic concentration at other sites is changed. Since the four nearest neighbors are As atoms and therefore remain unchanged as composition is varied, the changes in our data that result from changing the ratio of Ga to Al are due to compositional changes on the 12 sites of the second shell and on more remote cation sublattice neighboring shells. The changes we observe in the PDOS should provide a stringent test of the importance of these second- and higher-nearest-neighbor interactions in

theoretical models of the band structures of this system.[2,3,6]

The electronic structure of $Al_xGa_{1-x}As$ compounds have been studied using both optical[7-10] and photoemission methods.[11-14] The optical measurements[7] have established the variation of the optical band gap as a function of Al concentration with high precision, and confirm theoretical calculations that indicate a crossover from a direct Γ_{15}-Γ_1 band gap in the range $0 < x < 0.4$ to an indirect Γ_{15}-X_1 band gap in the range $0.4 < x < 1.0$.[7] Photoemission studies of these compounds reveal essentially linear shifts of the global DOS features with Al concentration.[14] In our SXE studies of these compounds we find a monotonic but nonlinear shift of the top of the valence band with composition and a change of slope near $x = 0.4$. This differs from PES and may possibly be due to the fact that published PES measurements have lower instrumental resolution (~ 0.5 eV) than that of our SXE data (0.07–0.13 eV for photon energy from 55 to 80 eV).

Wei and Zunger found that it is necessary to include cation-d-orbital contributions to correctly describe the valence-band discontinuity in heterojunctions.[15] The inclusion of cation-d-orbital hybridization can effectively lower the top of the valence band with respect to the average inner potential. From our data we find that a larger contributions of d orbitals than suggested by Wei and Zunger would be necessary to explain our observed shift of the valence-band edge.

The remaining parts of this paper are organized as follows. In Sec. II the experimental procedures are described. Section III gives the experimental results for various alloy compositions and Sec. IV contains the discussion of results and conclusions.

II. EXPERIMENTAL PROCEDURE

Measurements were made with a high-resolution and high-efficiency SXE spectrometer which has been described in detail elsewhere and is currently installed at the National Synchrotron Light Source (NSLS),[15] Brookhaven National Laboratory (Upton, NY). A 600-(lines mm) grating and an input slit of 80 μm width were used for the present experiments. The instrumental resolution is 0.13 eV at a photon energy of 75 eV. The spectra reported here were excited with 200 μA of 2-keV electrons during a 5-month shutdown of the vuv light source at the NSLS. Electrons were incident on the sample at 30° and the average photon exit angle was 50°. Measurements were made in an ion-pumped UHV chamber at a pressure of $\sim 6 \times 10^{-9}$ Torr.

Samples were grown at AT&T Bell Laboratories using a liquid-phase-epitaxy technique. The sample thicknesses were about 2 μm and the quoted concentrations are accurate to $\pm 1\%$ Al atomic fraction. Prior to mounting in the SXE apparatus, the samples were stripped of their protective oxide layer in NH_4OH solution for 3 min and then etched in a 0.5% solution by volume of Br_2 in methanol for 2 min immediately before they were mounted for measurement. Remaining surface oxide layers are estimated to be less than ~ 20–40 Å, and thus are much smaller than the electron-excitation depth (600–800 Å)

and photon-escape depth (1500–3000 Å).

Emission spectra were taken and processed as described elsewhere.[16] The bremsstrahlung background was subtracted after fitting a straight line to the baseline data near 50 and 80 eV, and this baseline was used for all spectra independent of Al composition. Self-absorption effects were investigated by varying the electron-excitation energy from 1–3 keV and no observable changes in our spectra were detected. This indicates that the self-absorption effects are negligible over the energy range that we used. Such effects would be much more important with photon excitation or with higher-energy-electron excitation. Some small surface and host-lattice features in the spectra were subtracted using data taken on pure GaAs, which was from samples that were prepared in the same way and measured at the same time as the $Al_xGa_{1-x}As$ samples. Emission spectra were significantly distorted by surface contributions at low Al concentration, $x < 0.1$, and therefore a more detailed study of this dilute composition range will be made using monochromatized photon excitation at a later time.

III. EXPERIMENTAL RESULTS

Figure 1 shows Al $L_{2,3}$ spectra for $x = 0.05$, 0.1, 0.2, 0.3, 0.4, 0.6, and 0.8 alloys with all spectra normalized at the maximum intensity height. Except for the 5% atomic concentration alloy, which shows some distortion that we believe results from emission of near-surface Al atoms, all of the spectra are qualitatively similar. The designations $P1$, $P2$, and $P3$ locate the three major characteristic peaks that typically occur in the DOS of zinc-blende semiconductors.[2,11-14,17-23] Peak $P3$ is at
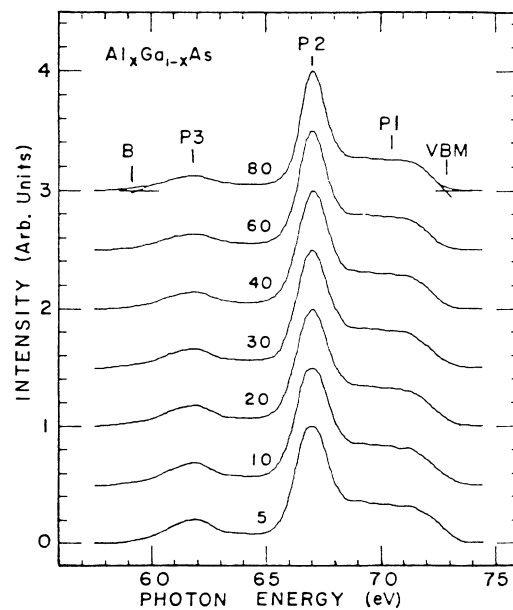

FIG. 1. Background-subtracted labeled soft-x-ray $L_{2,3}$ emission spectra of Al in $Al_xGa_{1-x}As$. Curves are labeled with Al concentrations in percent. The main spectral features VBM, $P1$, $P2$, $P3$, and B are designated on the 80% curve and are identified in the text. Spectra are normalized to $P2$-peak intensity maximum.

the position of the lowest band (band 1 in the usual nota-
tion), which is due to s orbitals centered mainly on the As
anion. A small remnant of this state overlaps onto the Al
cation site and gives the overlap with the Al core levels
resulting in SXE data. Peak $P2$ is due to band 2, which is
locally mainly the s orbitals on the cation site, and thus
peak $P2$ is the major feature of the Al $L_{2,3}$ spectrum.
The s-like and p-like valence electrons make about equal
contributions to this $P2$ peak in the transition DOS mea-
sured by PES. Peak $P1$ labels the broadbands 4 and 5,
which actually consist of several overlapping peaks in the
DOS associated with the mainly p-like covalent bonds.
The s-like and d-like PDOS's form a broad weak shoulder
in this region which extends close to the top of the
valence band. We will discuss the changes in these spec-
tra with changing Al composition, especially changes
occurring in the major peak $P2$ and changes near the
valence-band maximum (VBM). The VBM and the bot-
tom of the valence band are located in the conventional
way by linearly extrapolating the upper and lower edges
of the spectra to the baseline from the point of maximum
slope.

Changes occurring with Al concentration may be seen
more clearly in Figs. 2 and 3, where the emission spectra
are plotted together with $x=0.1$, 0.2, 0.4, and 0.8 alloys,
with the areas of the curves normalized to unity. The
qualitative changes are the following.

(1) No changes occur in peak $P3$ in either position or
magnitude.

(2) Peak $P2$ narrows with increasing Al content and in-
creases in amplitude so that its area is unchanged.

(3) The position of the $P2$ peak maximum is un-
changed, but the peak broadening is asymmetric with the
changes in width occurring almost entirely on the low-
energy side of the peak.

(4) The high-energy peak $P1$ is unchanged except that
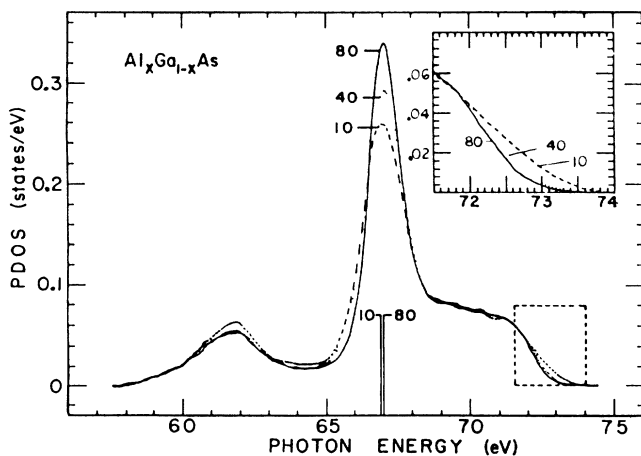the energy position of the valence-band maximum de-

FIG. 3. Background-subtracted and spin-orbit-stripped
($2p_{3/2}$ component) $L_{2,3}$ emission spectra of Al in $Al_xGa_{1-x}As$
for Al concentrations of 20 and 80%. The area of the curves
are normalized to 1. The inset shows the valence-band maxima
on an expanded scale.

creases with increasing Al composition.

It is clear from Figs. 1–3 that the PDOS effects ob-
served are rather subtle and, therefore, that it is very im-
portant to understand the resolution inherent in these
measurements. In addition to the experimental resolu-
tion of 0.07–0.13 eV, there are intrinsic width contribu-
tions to the core-level and valence-band state energies
that broaden our SXE data. These are phonon broaden-
ing and finite lifetime widths of the Al $L_{2,3}$ shell core lev-
els, which are 0.11 ± 0.02 and 0.04 ± 0.02 eV, respectively,
for Al metal.[24] The valence-band hole state is expected to
have a much smaller width than the $L_{2,3}$ core level and
thus can probably be neglected. If we assume that these
values hold for $Al_xGa_{1-x}As$ alloys, then the total
effective energy resolution at the top of the valence band,
VBM, is $\sim0.02\pm0.04$ eV.

The measured $L_{2,3}$ SXE spectrum consists of overlap-
ping, independent components from the L_2 and L_3 shells
which are separated by the spin-orbit splitting of 0.40 eV
for Al and weighted by the branching ratio of $\frac{1}{2}$. If we
assume these components are identical in shape, then it is
straightforward to "strip out" this spin-orbit width as is
shown in Fig. 3 for the $x=0.2$ and 0.8 data. The average
valence-band energy given by the first moment of the
spectra in Figs. 2 and 3 is shown by vertical lines near 67
eV. The inset also shows an expanded view of the data
near the VBM, which is more clearly resolved than in the
unstripped data shown in Fig. 2. In addition, both sets of
data curves in Figs. 2 and 3 have been scaled by a factor
of E^3 in order to account for the energy variation of the
dipole matrix elements in the SXE process.

IV. DISCUSSION AND CONCLUSIONS

The zinc-blende structure of this system implies that
variations in alloy concentration have an effect only on
the second- and higher-nearest neighbors. Thus, the
small variation of the peak positions and the rather small

FIG. 2. Background-subtracted soft-x-ray $L_{2,3}$ emission spec-
tra of Al in $Al_xGa_{1-x}As$ for Al concentrations of 10, 40, and
80%. The area of the curves are normalized to 1. Note the in-
creased broadening of peak $P2$ with decreasing Al concentra-
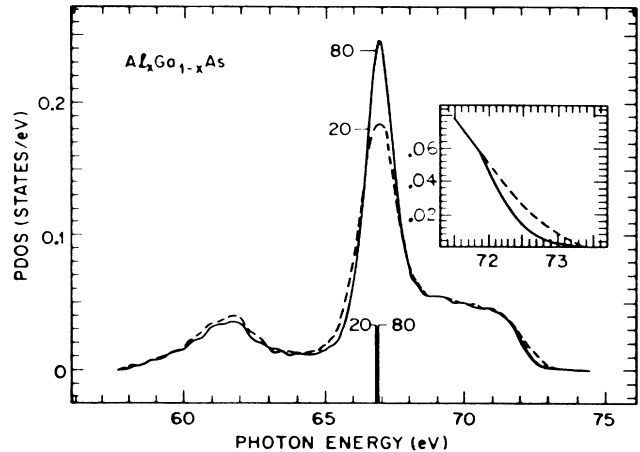tion. The inset shows the valence-band maxima on an expanded
scale.

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changes in the Al SXE spectra are not too surprising. However, the dependence of peak position on composition is not the same as that observed in PES experiments or that expected from typical band-structure calculations. One significant change is in peak $P2$, which has a maximum intensity that increases linearly with increasing Al concentration and narrows linearly with increasing Al concentration by 0.75 eV, such that the area of peak $P2$ remains unchanged (see Fig. 4). The broadening that is observed on the lower edge of $P2$ may be directly associated with changes in the GA concentration on the second and more remote neighbors. The local s-like PDOS for Al should be readily obtainable from theoretical band-structure models and the effects of second-nearest-neighbor interactions tested against our results. We note that the observed linear broadening with increasing Ga concentration does not agree with calculations of the total DOS which show maximum broadening at Al-to-Ga ratios near 1:1.[3] Presumably, the total DOS is broadest when peaks in the local DOS of Al and Ga are separated in energy and combine to form a broadened $P2$ peak, while the SXE peak $P2$ is broadest when all second-nearest neighbors are Ga rather than Al. Other examples of the important distinction between local SXE spectra and more global DOS's are discussed below.

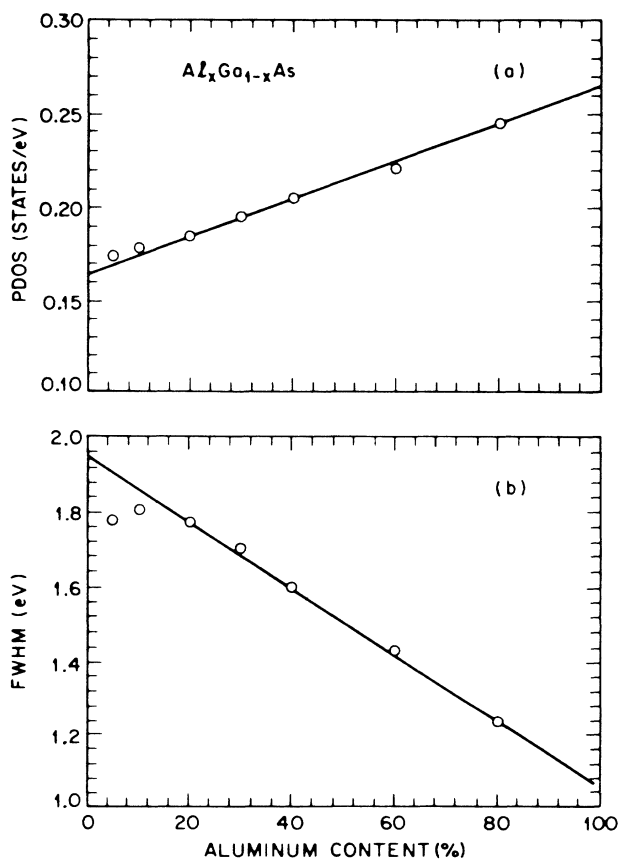Changes in the observed spectra near the top of the

valence band (VBM) with Al composition are very surprising since here band states are thought to be quite extended and characteristic of p-like states on the As atoms. We expected to find almost no variation in the VBM with alloy composition. The observed change in the position of the VBM is plotted in Fig. 5. A total shift of about 0.75 eV is observed, which may be fitted by two straight-line curves that intersect at about $x=0.38$ near the composition of the direct-indirect band-gap transition. This result is not simple to correlate with band effects because the changes in the band gap result from a crossing of two nearly linear band-gap curves with different slopes, while we measure a local VBM which is presumably just the Γ_{15} band state. For reasons that are not understood, our data imply that the lowest conduction-band edge maintains a constant energy separation from the Al $2p$ core level and from peak $P2$ and from peak $P3$, while the VBM position adjusts accordingly.

The direct band gaps and the high-symmetry band positions are expected to vary nearly linearly with alloy composition based on the theoretical parameters of Van Vechten and Bergstresser.[25] The inclusion of cation–d-orbital contributions as suggested by Wei and Zunger may partially explain our VBM data since the mixing of empty Al $3d$ states (which have Γ_{15} symmetry) is expected to be more important at the VBM for Al-rich alloys and this may shift the measured VBM position. Relative to the mean internal crystal potential, recent heterojunction studies[26] have shown that the VBM of the alloys of $Al_xGa_{1-x}As$ should shift by $\sim 0.5\Delta E_g$, where ΔE_g is the change in band gap. The measured shift in our SXE data is twice this value, which means that the Al $2p$ core level shifts also by $\sim 0.5\Delta E_g$ in approximate agreement with PES results.[14] We calculated the average spectra position of the data shown in Figs. 1–3 and found this value to be independent of Al composition, similar to the peak position $P2$; thus, the shift of the VBM seems to be an effect that depends on a small number of states and is not an

FIG. 4. (a) Normalized intensity of the peak $P2$ in units of states per eV and (b) width of peak $P2$ as a function of Al concentration.
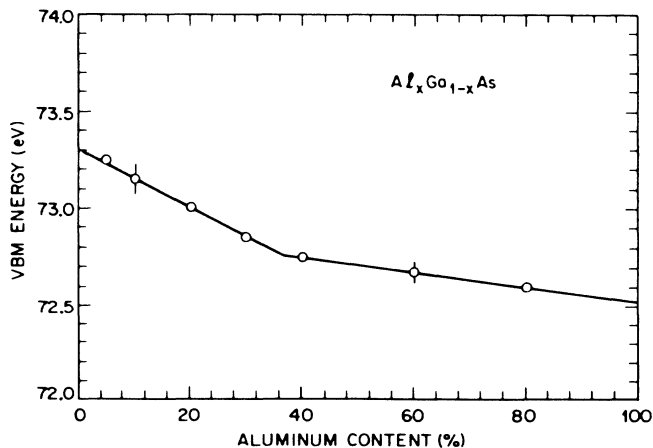

FIG. 5. Energy position of valence-band maximum as a function of Al concentration. The relative energy position measured closely follows the change in the width of the band gap as determined from optical measurements.

average quasiatomic property of this system. We note that a published calculation for the $Ga_xIn_{1-x}As$ system shows a similar near invariance of the conduction-band levels.[3]

The PES experiments of Ludeke et al., who measured the positions of both valence-band features and core levels,[14] differ from our SXE measurements of the VBM if we assume one-electron-like values for the PES binding energies and subtract them to get relative VBM-to-core energies. Since SXE energy positions measure separations between the core and valence-band levels, these values can be compared to the separations measured using PES. In the SXE data no change is observed in the $P2$ and $P3$ peak positions. In PES very large linear shifts of about 0.9 and 0.6 eV are measured for peaks $P2$ and $P3$, respectively, in going from $x=0.2$ to 0.8, with the spacing between the peaks changing by about 0.3 eV.

These differences are much larger than the experimental uncertainties and should be understood in terms of the difference between the spectroscopies. Experiments using PES measure a global DOS which is an average over contributions from all constituents. In contrast, SXE data show that the contributions to the total DOS from each Al site changes little with changing Al-to-Ga ratios. Thus, the large shifts observed for peaks $P2$ and $P3$ in the PES data represent an average of the contributions from the Ga and Al sites to the total DOS which do not occur in the SXE measurement.

We have measured the local PDOS for the $Al_xGa_{1-x}As$ alloy system by x-ray emission spectroscopy with an experimental resolution of ~ 0.2 eV. The major features seen in our data agree with the expected DOS peaks, but the peak energies vary with alloy composition

somewhat differently than the corresponding peaks in photoemission results which are not site specific to the Al atomic positions as are the SXE results. We have shown that the large changes in the SXE spectral function occur for the peak $P2$, which is localized most strongly on the Al sublattice. However, important shifts are also measured for the VBM (Γ_{15}), which are not in agreement with PES results. This may be due to the fact that SXE measures spectral positions relative to the core-level local site, while PES measures states relative to the Fermi energy and therefore spectral differences in PES, giving approximately the same one-electron energies as in SXE, do not agree quantitatively with SXE data. We believe that the SXE technique will prove to be useful in further semiconductor alloy band-structure studies and will provide results that are complementary to those from photoemission spectroscopy.

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