Al $2p$ core exciton in $Al_xGa_{1-x}As$

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Al $L_{2,3}$ x-ray emission spectra from $Al_xGa_{1-x}As$ of varying aluminum concentration are presented. The nature of the Al $2p$ core exciton observed in these spectra is discussed. Some comments are also made on the effects of anion disorder in these alloys.

$Al_xGa_{1-x}As$ is a single-phase, random-alloy semiconductor system with an essentially constant lattice parameter for all compositions. This ternary-alloy semiconductor is closely lattice matched to GaAs and it has properties which are important in high-frequency and optoelectronic applications. Yet, despite the fundamental importance of this compound-semiconductor alloy system, there have been few theoretical and experimental studies regarding its electronic structure as a function of aluminum concentration.

Soft-x-ray emission spectroscopy (SXES) provides information on the occupied valence-electron states. In this paper we report our results from a study of the Al $L_{2,3}$ x-ray-emission spectra of $Al_xGa_{1-x}As$ for different compositions x. The transitions from the valence-band electron states to the Al $2p$ core level are governed by dipole selection rules and, hence, these L x-ray-emission bands provide information on the valence-electron states having s- and d-like symmetry with respect to the Al sites.

Valence-exciton states of $Al_xGa_{1-x}As$ have been studied extensively using optical-absorption and photoluminescence measurements.[1] Optical-absorption studies of $Al_xGa_{1-x}As$ as a function of composition show that the valence-exciton binding energy changes sharply at 25% AlAs mole fraction. We observe for the first time in these Al L x-ray-emission spectra a feature near the bottom of the conduction band which we attribute to the radiative decay of the Al $2p$ core exciton. The nature of core exciton in semiconducting alloys like Si_xGe_{1-x} (Ref. 2) and $Ga_xAs_{1-x}P_x$ (Ref. 3) has been investigated experimentally. Excitons are usually described either by a Wannier or a Frenkel[4] model. Theoretical investigations on the nature of the core exciton in semiconductors and semiconductor alloys have also been made.[5,6] Recently, the relationship between the binding energy and intensity of core excitons of different materials was investigated using soft-x-ray–emission spectroscopy by our group[7] and a Wannier model was found to explain the observed intensity–binding-energy relationship of core excitons in these materials. Since there is no previous work on the nature of Al $2p$ core excitons in $Al_xGa_{1-x}As$, we concentrate on these and other related electronic properties in this paper.

The soft-x-ray–emission spectrograph used in this work is described in detail elsewhere.[8] $Al_xGa_{1-x}As$ epi-

taxial layers of different Al concentrations were grown on (100)-oriented single-crystal GaAs substrates by the metal-organic chemical-vapor-deposition (MOCVD) process. The thickness of the $Al_xGa_{1-x}As$ epitaxial layers were about 2 μm. The $Al_xGa_{1-x}As$ epitaxial layers were not doped and they had smooth and shiny surfaces. An electron beam of 3 kV energy was used to ionize the Al $2p$ core levels in the $Al_xGa_{1-x}As$ samples. The x-ray photons emitted due to electronic transitions from occupied valence- or conduction-band states to the vacancy in the Al $2p$ core levels were energy-dispersed by a holographically-aberration-corrected toroidal grating. The soft-x-ray photons were detected by a photodiode-array detector. The temperature of each of the samples was about 195 K during the electron-beam excitation, and pressure in the sample ultrahigh-vacuum chamber was better than 2×10^{-9} Torr. The energy resolution of the spectrometer in the Al $L_{2,3}$ x-ray-emission range was about 0.1 eV and the energy uncertainty was about 0.07 eV.

Energy-band-structure calculations, x-ray-photoemission-spectroscopy (XPS), and SXES measurements of the valence-band electronic structure of $Al_xGa_{1-x}As$ have been reported.[9-17] The Al L x-ray-emission spectra of $Al_xGa_{1-x}As$ are shown in Fig. 1 for different Al concentrations, and they show that the valence x-ray-emission bands are qualitatively similar. The broad peak at about 62 eV in the lower valence subband is due to s orbitals centered on the As atoms. The prominent peak at 67 eV in the upper valence subband is due to s orbitals centered on the Al and Ga cation atoms. The intensity of this peak increases with the increase of the Al concentration, but its width decreases with increasing Al concentration. The shoulder region near the valence-band edge is due to the As p hybrid orbitals. Changes in the strength of the shoulder region in these spectra with x are negligible, as the As atom is the nearest neighbor to Al for all concentrations. There is a small peak at about 65 eV in the L x-ray spectra of $Al_xGa_{1-x}As$ samples with $x = 0.5$ and 0.6, and this weak feature lies in the valley between the upper and lower valence subbands. The origin of this weak feature in our x-ray spectra is not clear. The valence-band XPS spectrum of $Al_xGa_{1-x}As$ with $x = 0.55$ also shows some extra intensity at about 7.5 eV below the valence-band maximum (VBM).[15] Further detailed band-structure and electronic density-of-state (DOS) cal-
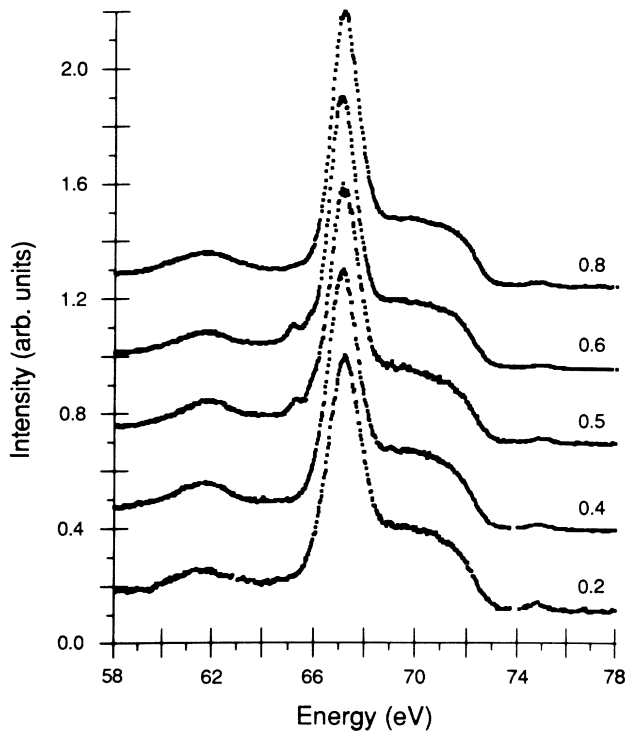

FIG. 1. Aluminum $L_{2,3}$ x-ray-emission spectra from Al$_x$Ga$_{1-x}$As with different aluminum concentrations.

culations for Al$_x$Ga$_{1-x}$As of different compositions are necessary to understand the origin of this weak feature.

In our measured Al $L_{2,3}$ x-ray-emission spectra of Al$_x$Ga$_{1-x}$As, we observe a small but significant x-ray emission above the valence-band edge and near the bottom of the conduction band. By analogy with other materials, we identify this emission feature at about 74 eV in these spectra as being due to the Al 2p core exciton.[4] In order to obtain useful information regarding the Al 2p core exciton and other related electronic properties, we used a simple model to describe the energy region in our x-ray spectra that includes the valence-band edge and the emission in the gap region. Visual inspection of the valence-band x-ray-emission spectra in Fig. 1 suggests a straight-line shape for the valence-band edge. We often observe a linear onset in the valence-band SXE which we take to be a superposition of $(E_t - E)^{1/2}$ (allowed) and $(E_t - E)^{3/2}$ (forbidden) shapes. Accordingly, we fitted the data points in the region 72–78 eV of our x-ray spectra with a convolution of a linear function $A_t(E_t - E)$ with a Gaussian and a line-shape function for the Al 2p core exciton. A_t is a constant and E_t is the position of the valence-band maximum. An E^3 factor that is present in the expression for the intensity of the emitted soft-x-ray photons[18] was included in the model. The full width at half maximum (FWHM) of the Gaussian broadening function probably represents alloy disorder and phonon coupling.[19–21] A Voigt line-shape function was used for the core exciton. The physical origin of the width of the exciton is not, at present, understood. We included the $I(L_2)/I(L_3)$ emission intensity ratio of 0.5 and the Al 2p spin-orbit splitting of 0.4 eV in the nonlinear least-

squares program used to fit the data. A fit based on this model to the spectrum of Al$_x$Ga$_{1-x}$As with $x = 0.4$ for states at the top of the valence band and in the gap region is shown in Fig. 2. The values of the parameters of the fits to our data are given in Table I. Figures 3–6 show the variations of these fit parameters with composition x.

Al$_x$Ga$_{1-x}$As is a substitutional alloy semiconductor with its atoms located at the lattice sites of a zinc-blende crystal structure. However, in contrast to ideal crystals, Al and Ga cation atoms are randomly distributed on one face-centered-cubic (fcc) sublattice, and each of these is bonded tetrahedrally to four As anion atoms on the other fcc sublattice of the zinc-blende structure. Therefore there is alloy disorder in Al$_x$Ga$_{1-x}$As. There are two kinds of alloy disorder in semiconductor alloys, namely anion and cation disorder produced by the fluctuation of potentials at the anion and cation sites, respectively. Cation disorder in common-anion semiconductor alloys has been studied extensively.[19,20] The problem of anion disorder has been recently studied in alloys like Hg$_{1-x}$Cd$_x$Te using x-ray-photonemission spectroscopy.[21]

Figure 3 shows the valence-band-maximum (VBM) position (L_3) obtained from fits to the Al L x-ray-emission spectra of Al$_x$Ga$_{1-x}$As as a function of composition. This energy value actually represents the position of the Al $2p_{3/2}$ core level below the VBM of Al$_x$Ga$_{1-x}$As. In common-anion alloys like Al$_x$Ga$_{1-x}$As, the nearest neighbors of cation atoms are always the same anion atoms. Hence, we expect the cation core-level shifts and

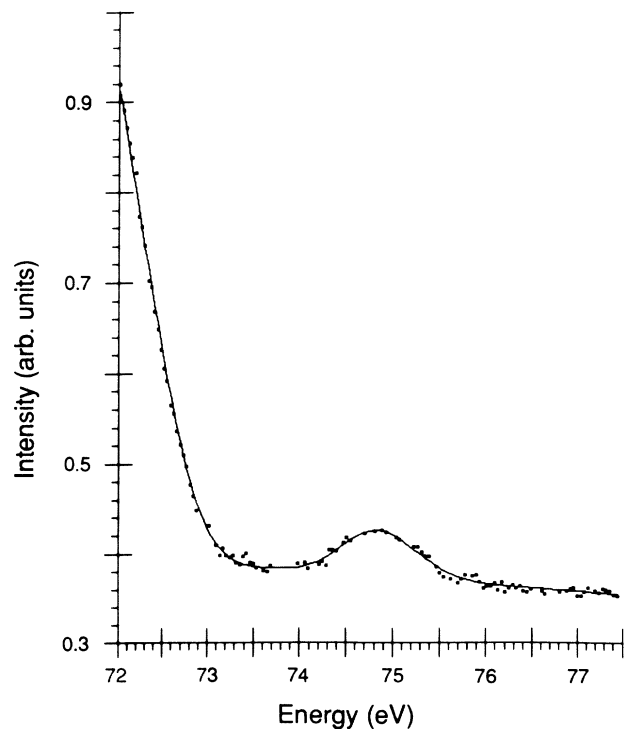FIG. 2. Upper valence-band edge and gap-region parts of the Al L x-ray-emission spectrum of Al$_{0.4}$Ga$_{0.6}$As. Squares represent emission data and the line represents a fit based on a model described in the text.

TABLE I. E_t is the position of the valence-band maximum (L_3), Γ_G is the FWHM of the Gaussian broadening function of the upper valence-band edge, E_c is the position of the Al $2p$ core exciton, and Γ_V is the FWHM of the Voigt function representing the Al $2p$ core-exciton feature.

Sample composition x	E_t	Γ_G	E_c	Γ_V	χ^2
0.2	72.86	0.62	74.64	0.63	10.5
0.4	72.77	0.47	74.75	0.81	5.7
0.5	72.80	0.47	74.87	0.60	11.2
0.6	72.71	0.61	74.83	0.64	12.3
0.8	72.68	0.77	74.66	0.78	6.8

corresponding inhomogeneous broadenings to be small. Photoemission studies on $Al_xGa_{1-x}As$ by three different groups[15-17] also show that, as the Al concentration is changed, the binding energy of the Al $2p$ core level does not change to within 0.1 eV. Thus the measured changes in the Al $2p$ core level relative to the VBM of $Al_xGa_{1-x}As$ as a function of composition in our Al L x-ray-emission spectra primarily reflect the movement of the VBM.

Band-structure calculations of $Al_xGa_{1-x}As$ (Ref. 9) show that the electronic states near the VBM of $Al_xGa_{1-x}As$ are primarily As hybrid p states. These, as wave functions, are different depending on whether As atoms are bonded to Al or Ga atoms. The anion disorder in $Al_xGa_{1-x}As$ results from the difference in As levels when an As atom is bonded to different cations that are distributed randomly. The VBM decreases slightly with the increase in Al concentration because of the presence
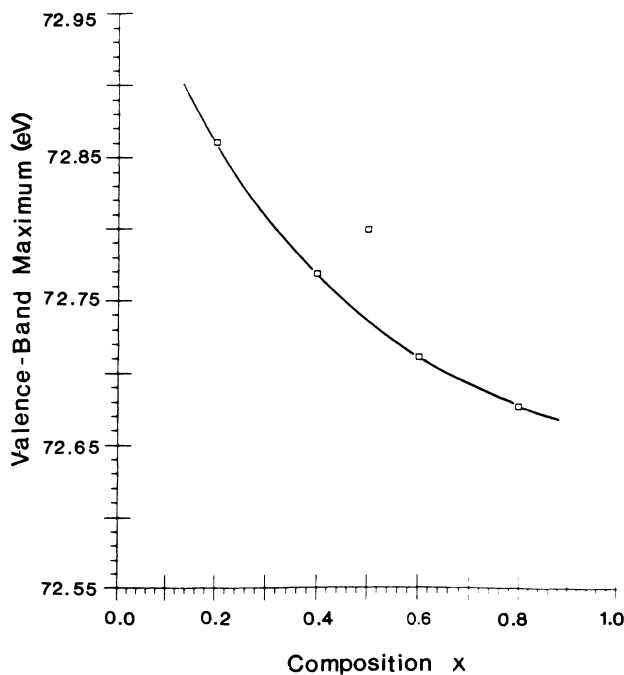

FIG. 3. Position of valence-band maximum of $Al_xGa_{1-x}As$ as a function of aluminum concentration. The energy uncertainty of each point is ±0.05 eV.

of anion disorder in $Al_xGa_{1-x}As$.[11]

Shih and co-workers[21] introduced the concept of "natural valence-band offset" (NVBO) in the common-anion alloy $Hg_{1-x}Cd_xTe$, which plays an important role in the electronic properties of these alloys. Shih and co-workers explain this offset as an energy shift when one places the band structure of two separate binary compounds like AlAs and GaAs on the same absolute energy scale. The heterojunction offset will be this natural offset plus the contribution from the dipoles across the interface.[21] The natural valence-band offset obtained from Fig. 3 (the vertical range of the data) is 0.31 eV. The valence-band discontinuity of the AlAs/GaAs heterojunction measured by XPS (Ref. 22) for different growth sequences and crystal orientations ranges from 0.36 to 0.55 eV. Thus the interface dipole has a non-negligible effect on the valence-band discontinuity in the AlAs/GaAs heterostructure.

According to "common-anion rule,"[23] two semiconductors sharing the same anion would have a very small valence-band offset ΔE_v, and thus heterostructures like AlAs/GaAs and CdTe/HgTe are expected to have negligible band offset. However, XPS measurements show that ΔE_v for these heterostructures are not negligible. Wei and Zunger have recently shown that,[24] in tetrahedral symmetry, the anion p states and cation d states both have the Γ_{15} representation at the top of the valence band, and they can couple to each other and produce a significant pd repulsion energy, E_{pd}, at the VBM. In AlAs the unoccupied Al $3d$ orbitals are above the As $4p$ states, and so its pd repulsion energy is negative. They also found that cation d orbitals provide the most important discriminating factor between a pair of common-anion semiconductors like AlAs/GaAs and CdTe/HgTe in that they control the valence-band discontinuities. The calculated pd repulsion-energy contributions to the valence-band offsets of AlAs/GaAs and CdTe/HgTe heterojunctions are 0.31 and 0.34 eV, respectively. These calculated values are in excellent agreement with the "natural-valence-band-offset" values obtained from SXES and XPS studies of the variations of the VBM of $Al_xGa_{1-x}As$ and $Cd_xHg_{1-x}Te$, respectively. Further theoretical work is necessary to study the relationship between pd repulsion energy and the offset in $Al_xGa_{1-x}As$.

The nonlinear least-squares fits to the valence-band edges of the L x-ray spectra of $Al_xGa_{1-x}As$ yield values of the FWHM, Γ_G, of the Gaussian broadening function, and Fig. 4 shows the variation of Γ_G with alloy composi-
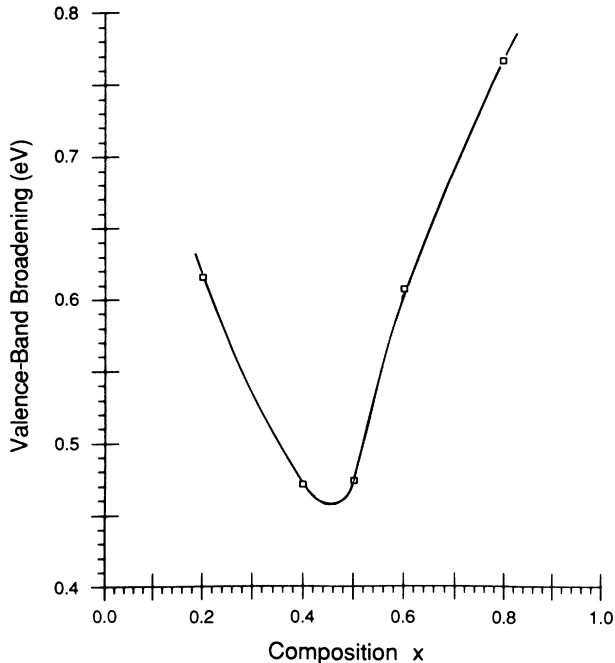
FIG. 4. FWHM of Gaussian broadening function of upper valence-band edge of Al$_x$Ga$_{1-x}$As as a function of composition x.

tion x. To our knowledge, no calculation has been made on the effects of intrinsic and alloy broadening on the x-ray spectra of Al$_x$Ga$_{1-x}$As, but there are theoretical[5,6] and experimental absorption[2] studies on the nature of Si 2p core excitons in Si$_x$Ge$_{1-x}$ alloys. The results of these studies are useful in understanding the nature of the Al 2p core exciton in Al$_x$Ga$_{1-x}$As. Calculations by Krishnamurthy and collaborators[6] show that the competition between an intrinsic broadening due to screening and extrinsic alloy broadening in Si$_x$Ge$_{1-x}$ alloys could result in a minimum in the total broadening at $x = 0.15$. The conduction-band minimum in the Si$_x$Ge$_{1-x}$ alloys changes from the X to the L region of the Brillouin zone at the critical composition $x_c = 0.15$. The variation of Γ_G with composition x shown in Fig. 4 for Al$_x$Ga$_{1-x}$As has a minimum value at about $x = 0.4$ which corresponds to the critical composition at which the bottom of the conduction band changes from Γ to X.[10,11] The broadening effects in the core spectra of Si$_x$Ge$_{1-x}$ alloys exhibit similar behavior at the critical composition,[2] and this clearly suggests that both intrinsic broadening due to screening and alloy broadening are important in the Al L x-ray-emission spectra of Al$_x$Ga$_{1-x}$As.

The nature of core-exciton states in ternary alloy semiconductors have been of considerable interest recently. The electron-hole interaction via energy-derivative reflectance spectra of transitions from the shallow Ga 3d core levels to lower conduction-band final states in Al$_x$Ga$_{1-x}$As (Ref. 25) and GaAs$_{1-x}$P$_x$ (Ref. 3) alloys has been studied. These experimental studies show that the core excitons associated with the Ga 3d core hole and the conduction electron around the lowest L- and X-symmetry points are coupled with each other through in-

tervalley electron-hole interaction. We present, for the first time, the results on the intervalley electron-hole interaction in excitations from the Al 2p core level to the conduction band of Al$_x$Ga$_{1-x}$As studied with soft-x-ray–emission spectroscopy.

Figure 5 shows the positions of the Γ, L, and X conduction-band minima relative to the top of the valence band as a function of aluminum concentration. The conduction-band structure of Al$_x$Ga$_{1-x}$As is characterized by a change from the sequence Γ-L-X to X-L-Γ with increasing energy as the alloy composition x is varied. This shows that Al$_x$Ga$_{1-x}$As is a direct-band-gap semiconductor (Γ_{1c} conduction band) below the crossover concentration $x_c = 0.4$ and an indirect-band-gap (X_{1c} conduction band) semiconductor at high x. Studies on the valence exciton in Al$_x$Ga$_{1-x}$As show that its position follows the lowest conduction band, like the usual Wannier exciton, as the composition is varied.[1]

Positions of the Al 2p core exciton above the VBM obtained from Al L x-ray-emission spectra of Al$_x$Ga$_{1-x}$As for different aluminum concentrations are also shown in Fig. 5. In contrast to the Wannier-type valence exciton, the energy positions of the Al 2p core excitons do not simply follow the lowest conduction-band minimum. The Al 2p core excitons for $x = 0.2$ and 0.3 lie above the lowest Γ_{1c} conduction-band minimum, but below the L conduction-band minimum. Such behavior has been anticipated theoretically.[26] It is clear from Fig. 6 that the Al 2p core exciton is of mixed character for all concentrations. We conclude that the central-cell part of the po-
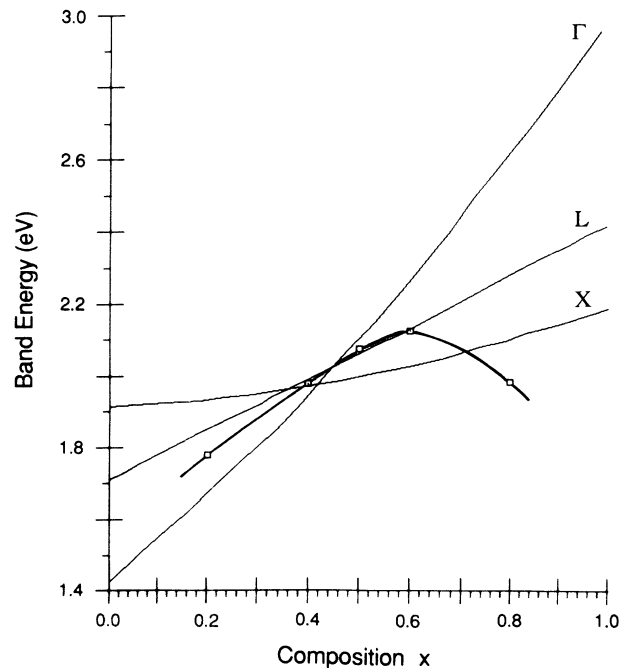

FIG. 5. Positions of Γ, L, and X conduction-band minima of Al$_x$Ga$_{1-x}$As relative to top of the valence band as a function of aluminum concentration. Circles represent positions of the Al 2p core exciton above the valence-band maximum of Al$_x$Ga$_{1-x}$As for different compositions x.
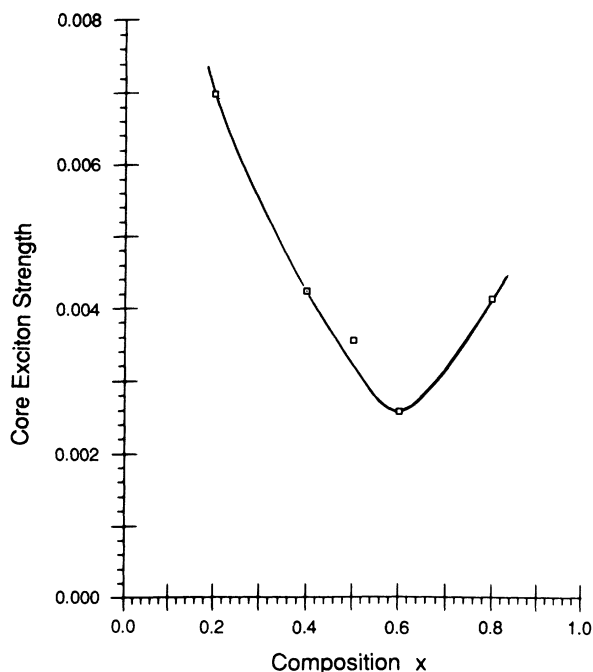
FIG. 6. Ratio of the area of the Al $2p$ core exciton with respect to the area of the valence x-ray-emission band of $Al_xGa_{1-x}As$ as a function of x.

troscopic measurements by Carson and Schnatterly[7] on diamond, BN, B_2O_3, LiF, and crystalline- and amorphous-silicon samples showed that the intensity of the core exciton is an intrinsic feature of the x-ray-emission spectrum of a solid. They also observed that the intensity of core excitons in the x-ray-emission spectra of these solids vary as the square of the core-exciton binding energy. They interpreted the observed core-exciton intensity–binding-energy relationship in these solids using a Wannier exciton model.

The area of the Al $2p$ core-exciton peak observed in the x-ray-emission spectrum of $Al_xGa_{1-x}As$ represents the intensity of the core exciton. Figure 6 shows the area of the Al $2p$ core-exciton peak normalized to that of the Al $L_{2,3}$ x-ray valence-band emission band of $Al_xGa_{1-x}As$ as a function of x. It shows that the intensity of Al $2p$ core exciton of $Al_xGa_{1-x}As$ smoothly varies with x and it has a minimum at $x = 0.6$. This variation does not lend itself to a simple explanation. Further theoretical work is necessary to understand the variation of Al $2p$ core-exciton intensity with composition x, and the conduction-band electronic-structure calculations of $Al_xGa_{1-x}As$ for different x will be useful in explaining the observed properties of the Al $2p$ core exciton and other related electronic properties.

tential of the Al $2p$ core level is strong enough to mix the electron states at different conduction-band minima of $Al_xGa_{1-x}As$ for all x. Since the exciton lies at most about 0.1 eV above the conduction-band edge, and since its width is much more than this, we do not expect and do not observe a strong variation in width with exciton position relative to the conduction-band edge.

As mentioned earlier, several studies on the nature of core excitons in solids observed by core-level spectroscopies have been made. Recent soft-x-ray–emission spec-

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