Bulk and interface Al 2*p* core excitons in GaAs/AlAs/GaAs heterostructures

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Aluminum 2*p* soft-x-ray emission and absorption spectra (XES and XAS) of a GaAs/AlAs/GaAs heterostructure semiconductor have been measured with high-energy resolution. The Al 2*p* XES shows a similar feature to that of $Al_xGa_{1-x}As$ alloys. Strong Al 2*p* core excitons have been observed in XAS, and attributed to the *X*- and *L*-like states in the conduction band. The XAS profile has changed depending on the incident angle of the excitation x rays. This dependence may relate to the symmetry of the exciton transitions. [S0163-1829(99)01208-4]

Excitons in multilayer semiconductors have been investigated during the last decade. Recently, much attention has been focused on the electronic and optical properties of the core exciton in heterostructure systems,[1–6] since progress in the molecular-beam epitaxy (MBE) technique has led to the possibility of making superlattice semiconductors. GaAs/AlAs superlattices have been studied intensively because of their interesting quantum-well effects.[7–10] Both AlAs and GaAs have a cubic zinc-blende crystal structure, and various band-structure calculations have been carried out for them.[11,12] The valence-band structure of AlAs and GaAs are similar, although the conduction-band minima occur at the Brillouin zone center (Γ) along the (100) and (111) axes near the *X* and *L* points, respectively. Elements of tetravalent semiconductors such as these have a valence configuration of s^2p^2, and form sp^3 hybridization. Knowledge of the electronic structure of internal layers and their interface is a key concept for understanding the properties of semiconductor devices.

The intense Al 2*p* core excitonic structure of AlAs was first observed in total electron yield (TEY) spectrum measured by Kelly *et al.*[13] Since the surface of AlAs is unstable in the atmosphere, the surface should be covered with a stable layer such as GaAs. Thus it was difficult to obtain good photoelectron signals from the AlAs layers through the overlayers, and the Al 2*p* core excitons of bulk AlAs under overlayers have not been well understood.

Owing to the longer mean free paths of soft x rays in solids, the soft-x-ray emission and absorption spectra (XES and XAS) are more bulk sensitive than any electron spectra. For instance, Nilsson *et al.*[14] studied the electronic structure of buried Si layers in GaAs using synchrotron radiation, and showed the possibility of detecting a signal from the buried layer due to the appreciable penetration of soft x rays.

In this paper, we report on the Al 2*p* XES and XAS in a GaAs/AlAs/GaAs heterostructure semiconductor to provide information about electronic structure and core excitons states. The experimental measurements of GaAs/AlAs/GaAs were performed at a revolver undulator beamline BL-19B at the Photon Factory at the National Laboratory for High Energy Physics with a varied-line space-grating monochromator (VLS19) (Ref. 15) without an entrance slit. The XES were recorded using a soft-x-ray emission spectrometer[16] which consisted of an input slit, a spherical grating, and a CsI-coated microchannel detector. The XAS were measured by total photon yield (TPY) mode. The energies of incoming photons were calibrated by photoelectron emission spectra of Au 4*f* levels and the Fermi edge and the energy scale of XES was calibrated by the reflection of x rays. The energy resolutions of XAS and XES were about 0.02 and 0.5 eV, respectively.

The GaAs (60 Å)/AlAs (400 Å)/GaAs (3000 Å) heterostructure specimen was fabricated on a GaAs(100) substrate by the MBE method.[17] The sample rotation axis stood at right angle to the incoming x rays which were plane-polarized light, and the experimental geometry is shown in the inset of Fig. 3, where α and β indicate the incident angle and the exit angle, respectively, so that a larger α means the greater amount of grazing incidence. The arrangement of the experimental system fixed $\alpha + \beta = 105°$.

Figure 1(b) shows the Al 2*p* XES measured at an excitation energy of 74.66 eV, and the XAS of AlAs, and they are clearly observed in spite of the GaAs overlayers. Figures 1(a) and 1(c) show the results of the band calculation[11] to compare with the present experimental spectra. The Al 2*p* XES (XAS) provided information on the valence (conduction) band having *s*- and *d*-like orbitals with respect to the Al site. The excitation energy of XES was high enough so that the spectrum showed a nonresonant normal-emission spectrum. The band-gap energy of AlAs has been reported to be about 2.2 eV.[12] An arrow put between the valence- and conduction-band edges serves as a guide for the eye.

The Al 2*p* XES from an $Al_xGa_{1-x}As$ alloy system for various values of *x* have been reported.[18–20] However, the Al 2*p* XES from the $x=1$ sample remain unknown because of experimental difficulties. As one expects, the Al 2*p* XES of AlAs look similar to that of a high Al concentration $Al_xGa_{1-x}As$ alloy. Peak *A* is attributed to *s* orbitals located on the As site, and here it can be observed in this energy region as well. Peak *B* is attributed to a hybridized state of *s* orbitals on the Al site with *p* orbitals on the As site. Bands *C* and *D* are *p*-like bands rather than *s*-like bands on the Al site.

Figure 2 shows the Al 2*p* XES of AlAs measured at various excitation energies indicated on the left side. The solid curves show the recombination peak of the incident x rays and, the intensity is at a reduced scale of $\frac{1}{15}$. The excitation

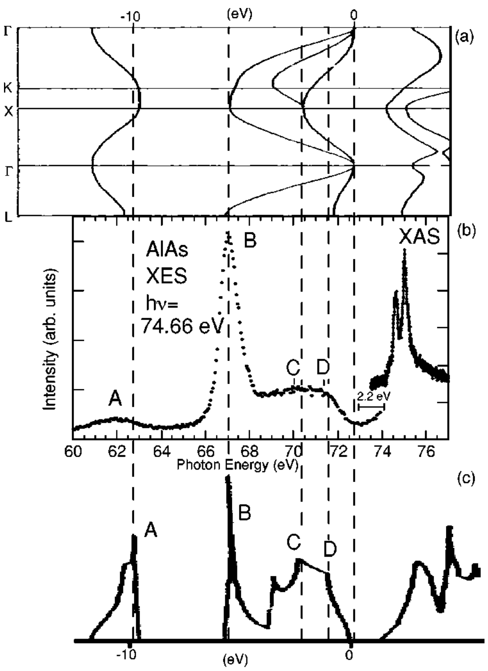

FIG. 1. (a) The band dispersion curves of AlAs taken from Ref. 11. (b) The Al 2p XES of GaAs/AlAs/GaAs and the XAS. (c) The total density of states of AlAs taken from Ref. 11.

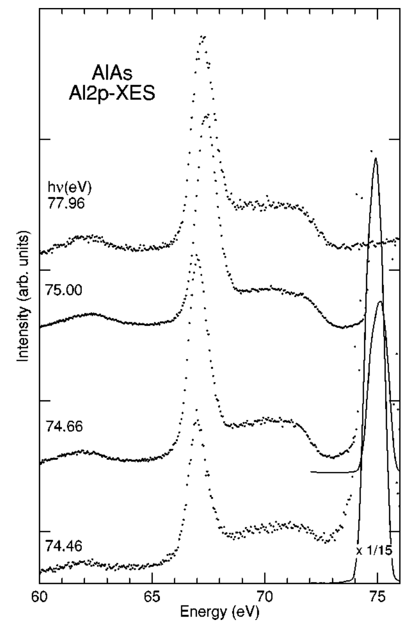

FIG. 2. The Al 2p XES of GaAs/AlAs/GaAs measured at various photon energies in the Al 2p core exciton region. The solid lines are the recombination peaks of the incoming x rays. The intensity is in factor of $\frac{1}{15}$. The numbers on the left side of the spectra indicate the excitation energies.

energies of 77.96 and 75.00 eV can produce both the Al $2p_{3/2}$ and the Al $2p_{1/2}$ core holes, while the excitation energies of 74.66 and 74.46 eV create only the Al $2p_{3/2}$ core hole. When the incident photon creates only the $2p_{3/2}$ core hole, only the transitions from the valence band to the $2p_{3/2}$ component contribute to the spectra, so that structure B is sharper at 74.66 and 74.46 eV. On the other hand, when incident photons create both Al $2p_{3/2}$ and Al $2p_{1/2}$ core holes at 75.00 and 77.96 eV, structure B becomes broad and shifts to the higher-energy side. XES excited at high energy do not show the core-exciton-like structure at around 75 eV which was reported by Nithianandam and Schnatterly,[19] but at low energy the spectrum has a very intense direct recombination peak which is related to existence of core exciton states.

Two intense peaks are observed in the XAS which correspond to the Al $2p_{1/2}$ and Al $2p_{3/2}$ core excitonic peaks with the Al 2p spin-orbit splitting $\zeta_{2p}=0.44$ eV. The present XAS, which were recorded by the TPY mode, reproduced very well the results of the TEY experiment by Kelly *et al.*[13] However, remarkable structures corresponding to the conduction band were not found in the present results, but a low-intensity broadband was found in the higher-energy region. If the structural difference between the samples of the XAS and TEY experiments is not important, this difference could be attributed to the difference between the decay processes, that is, photons (XAS) and electrons (TEY). The present result, that strong exciton structures are observed in XAS, suggests that the x-ray emission processes is dominant under the core-exciton excitation as compared with the photoemission processes. Taking advantage of the relatively weak contribution of the conduction band in the XAS, we can simplify the line-shape fitting procedure described below, where we deal with the continuum transition as a part of the background.

In order to investigate the character of the exciton states, the incident angle dependence of Al 2p XAS has been measured. Figure 3 shows the incident angle dependence of XAS of AlAs normalized by the incident photons. The solid lines, called CE1, CE2, and CE3, are guides for the eye, and CE1′(CE2′ and CE3′) refers to the spin-orbit splitting of CE1 (CE2 and CE3). To decompose the components of the spectra, line-shape fitting analyses were carried out using a least-squares fit method, adopting the superposition of the six Lorentzian functions and one straight line. Three different exciton states on each 2p orbital were assumed, and they

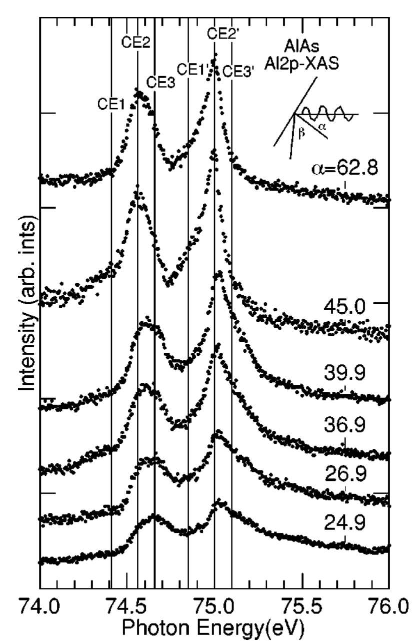

FIG. 3. The XAS of GaAs/AlAs/GaAs measured at various incident angles. α is the incident angle. β is the exit angle.

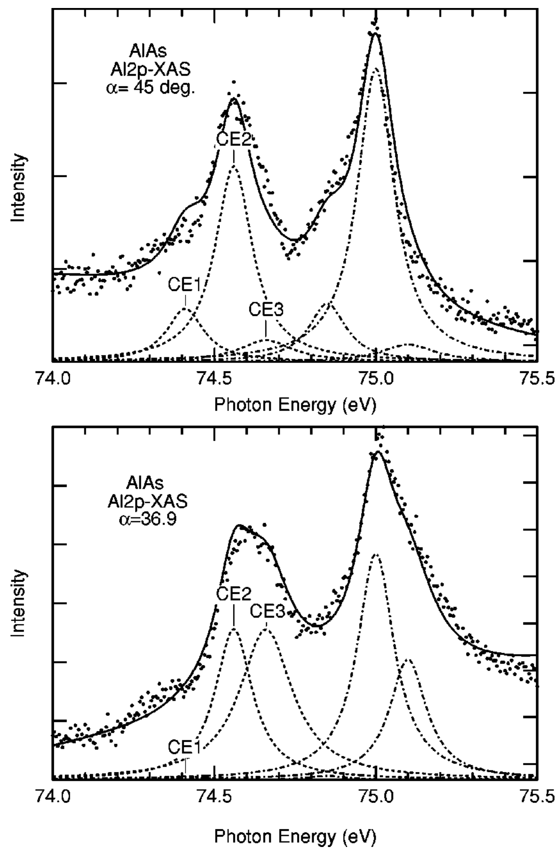

FIG. 4. Fitted Al $2p$ XAS of GaAs/AlAs/GaAs spectra measured at the incident angle $\alpha = 45°$ and 39.9°. The solid curve shows the calculated spectrum using a superposition of six Lorentzian functions (dashed curves) and one straight line (not shown).

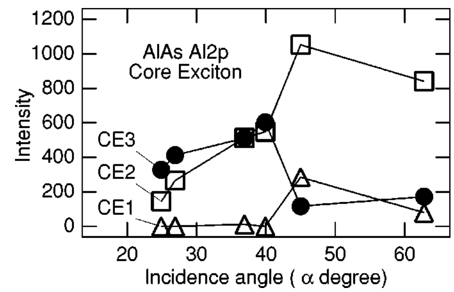

FIG. 5. The incident angle dependence of the intensity of each exciton.

were represented by Lorentzian functions; in addition, one straight line was for background signals including the conduction band state. The full width at half maximum intensity ratio, by the spin-orbit splitting, and the energy positions for each incident angle, were fixed; in the present study, the intensity ratios were fixed to be CE1:CE1′ $=1{:}1.1$, CE2:CE2′ $=1{:}1.5$, and CE3:CE3′ $=1{:}0.8$. Figure 4 displays the typical fitting spectra of the Al $2p$ XAS at $\alpha = 45°$ and 39.9°. The solid curve and dashed curves show the fitted spectrum and six Lorentzian functions, respectively.

Figure 5 shows the incident angle dependence of the intensities of CE2 (open squares) CE3 (closed circles), and CE1 (open triangle) excitons obtained by the fitting. Using Fresnel's formula and x-ray interaction coefficients table,[23] the attenuation lengths[24] of GaAs and AlAs at 75.5 eV were estimated to be over 180 and 300 Å. Also, when sweeping $\alpha = 20-60°$, the values do not vary rapidly with angle change. Indeed the penetration depth of soft x rays is deeper than the thickness of the overlayer GaAs in the region of the Al $2p$ core exciton.

It is difficult to know the radius of excitons of indirect semiconductors such as AlAs; however, the effective-mass approximation succeeds well in many cases. The Al $2p$ core exciton of an $Al_xGa_{1-x}As$ alloy system has been discussed in a Wannier exciton model.[19] In the case of the Wannier exciton model, the excitonic Bohr radius is represented by $a = a_B \epsilon m_0/\mu$, where $a_B = 0.53$ Å is the Bohr radius. Fern and Onton[21] reported that the dielectric constant ϵ was 8.16, and Rheinlander *et al.*[22] reported that the effective mass perpendicular to the principal axis of the mass tensor at the X point was 0.19. Thus the calculated radius is about 20 Å . In the same model, the exciton binding energy is estimated to be about 0.4 eV. Since a larger binding energy was suggested in the later discussions, the exciton radius may be smaller than the estimated value, but at least one can say that the core-exciton radius is smaller than the thickness of AlAs in this sample. It is consistent that CE2 and CE3 are assigned to the bulk components.

What is the origin of CE2 and CE3? At large incidence angle, these intensities drastically change toward opposite inclinations as shown in Fig. 5. This strongly suggests the symmetry difference between CE2 and CE3 transitions. In Fig. 5, the CE2 and CE3 components have comparable intensities, less than $\alpha \approx 40°$, near normal incidence. Both components should be bulk components of AlAs. It is well known from band calculations that the lowest conduction band is located at the X point, and the second lowest, at the L point.[11,18,19] Therefore, we tentatively assign CE2 to the X-point core exciton, and CE3 to the L-point core exciton. The energy difference between CE2 and CE3 is about 0.1 eV, which is smaller than the value by the band calculations, typically 0.2 eV. This discrepancy is probably caused by the exciton binding energy difference between the X- and L-point core excitons. If this assignment is correct, it suggests that the core-exciton binding energy should be the order of 0.1 eV, and such a large binding energy means that some wave-function mixing effects exist between the X and L points in the core-exciton states. Even in the case when X and L states are mixed, two exciton states can be still observed in the absorption spectra; for example, Ga $3d$ core excitons attributed to the L and X points in $Al_xGa_{1-x}As$ mixed crystal are observed near the L-X crossover composition, $x \approx 0.4$.[25] Therefore we call these core excitons X-like (CE2) and L-like (CE3) core excitons.

Roughly speaking, the Al $2p$ XAS show $2p \rightarrow 3s$ and $2p \rightarrow 3d$ transitions. Though s- and d-character wave functions are allowed to appear at both the X and L points of Al sites,[26] d character is stronger at the X point, while s character is dominant at the L point. According to this, the X-like core exciton may enhance the character of the $2p \rightarrow 3d$ transition, while the L-like core exciton may enhance the character of the $2p \rightarrow 3s$ transition. The different incident angle dependences of the CE2 and CE3 intensities can be related to the difference of the transition characters, though a full understanding of this will be left for further investigations.

The incident angle dependence of CE1 is analogous to that of CE2, though the intensity of CE1 is considerably weak. Therefore, CE1 may have an X-like character in the above meaning. We tentatively assign CE1 to the X-like core exciton at the GaAs-AlAs interfaces. It has been known that GaAs/AlAs heterostructures caused by MBE have abrupt interfaces without a mixing of the compositions. However the Al 2p core-exciton wave function at the interfaces can penetrate into the GaAs layer in the exciton radius. Taking into account the fact that the Γ point of GaAs is located below the X point of AlAs, we can expect the core-exciton energy near the interfaces to be reduced by the penetration, though a theoretical examination will be necessary to evaluate the energy quantitatively.

To summarize, we have investigated the electronic structure of AlAs covered with GaAs by x-ray emission and absorption spectroscopy. Al 2p XES show s and d partial densities of states which are similar to those in $Al_xGa_{1-x}As$ alloys. Two strong Al 2p core excitons were observed in XAS, and the components were attributed to the X- and L-like excitons in the conduction band. Further, a weak core exciton was observed at the lower-energy side, which was tentatively attributed to the interface exciton. The XAS intensity dependence on incident angles may be due to the difference between the symmetries of the excitons.

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