RAPID COMMUNICATIONS

PHYSICAL REVIEW B VOLUME 32, NUMBER 8 15 OCTOBER 1985

# Core-excitonic lines at the Al 2$p$ surface optical-absorption threshold of AlAs and AlP

M. K. Kelly, D. W. Niles, P. Perfetti,* E. Colavita,† A. Savoia,‡ and G. Margaritondo§
*Department of Physics and Synchrotron Radiation Center,*
*University of Wisconsin, Madison, Wisconsin 53706*

M. Henzler
*Institut für Festkörperphysik, Universität Hannover,*
*Appelstrasse, 3000 Hannover 1,*
*Federal Republic of Germany*

(Received 2 July 1985)

The optical-absorption spectra of AlAs and AlP exhibit unusual features—strong Al 2$p$ core-excitonic lines. The data were obtained with synchrotron-radiation photoemission in the partial-yield mode. The analysis was based on the approach proposed by Johnson, Fock, Ley, and Cardona for AlSb and on Onodera and Toyozawa's exciton theory.

Core excitons in semiconductors have been an interesting and often controversial problem of solid-state physics for many years.[1-3] There now seems to be a general agreement that the core-exciton binding energies are much larger than the valence-exciton binding energies. For example, very large binding energies were recently reported for the Si 2$p$ exciton of amorphous semiconducting materials containing silicon.[2] The large core-exciton binding energies in semiconductors cannot be treated with an effective-mass approach.[1] Several alternate theories have been proposed to explain them.[4-6] Another general feature of core excitons in semiconductors is that they manifest themselves as shifts in photon energy of the core optical-absorption threshold with respect to the energy that one would expect in the single-particle approximation. Ordinarily, one does not observe resolved core-excitonic lines in semiconductors. This has been attributed to the short lifetime of these excitonic states.

The normal absence of core-excitonic lines in semiconductors enhances the interest in exceptional cases for which lines are visible. We report here the observation of core-excitonic lines at the Al 2$p$ threshold for two semiconducting Al compounds, AlAs and AlP. Evidence of similar lines for a third Al compound, AlSb, was independently reported by Johnson, Fock, Ley, and Cardona.[7] In all cases, a single-particle interpretation of the optical transitions would put the final states below the bottom of the conduction band. The splitting between the $j=\frac{1}{2}$ and $j=\frac{3}{2}$ components of the excitonic doublet is modified by the exchange interaction between the electron and the hole, which also determines their intensity ratio.

The experiments were performed at the University of Wisconsin Synchrotron Radiation Center. The optical-absorption coefficient in the spectral region of the Al 2$p$ threshold was measured with the partial-yield photoemission technique.[8] The photons were emitted by the storage ring Tantalus and filtered in energy by its Mark II "Grasshopper" grazing-incidence grating monochromator. The experiments also involved extensive characterization of the surface, e.g., by low-energy electron diffraction (LEED) analysis and by synchrotron-radiation photoemission studies of the density of states in the energy regions of the valence band of the Al 2$p$ level and of several other core levels of interest. The experimental system was described in detail elsewhere.[9]

One important component of these experiments was the preparation of the clean AlAs and AlP surfaces. The method of cleaving under vacuum used for other III-V compounds cannot be implemented for these materials. AlAs has been prepared by many authors using molecular-beam epitaxy. We used instead a method originally proposed by Huijser, Van Laar, and van Rooy,[10] i.e., the deposition of a thin Al overlayer on a freshly cleaved GaAs (110) surface and subsequent activation of the Al-Ga exchange reaction. We extensively characterized the quality of the AlAs surfaces obtained with this method, in particular using LEED and valence-band photoemission.[11] Figure 1 shows, for example, the valence-band photoemission spectrum of AlAs obtained with our procedure, compared to that of the GaAs substrate.

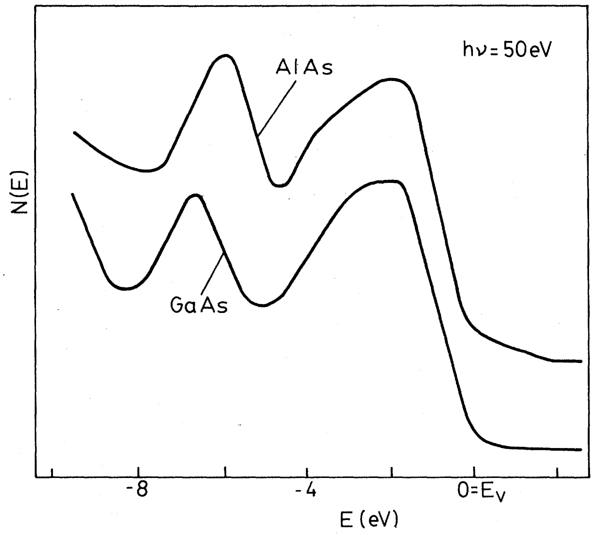

FIG. 1. Valence-band photoemission spectra taken at a photon energy $h\nu=50$ eV on cleaved GaAs (110) and on AlAs (110) obtained with the method discussed in the text.

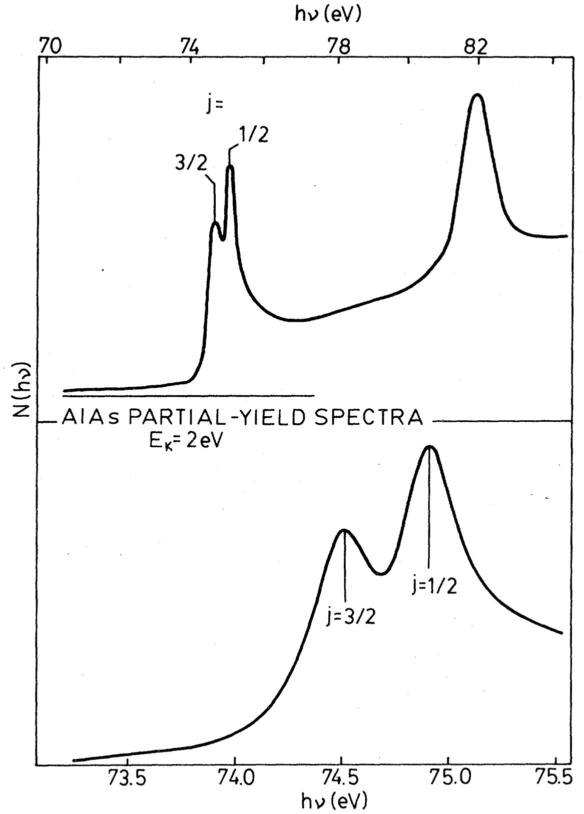

FIG. 2. (Top) AlAs optical-absorption spectrum obtained with the partial-yield photoemission technique in the region of the Al $2p$ threshold. The kinetic-energy window was centered at 2 eV. The high-energy peak is not an absorption feature but the constant-final-state spectrum of the Al $2p$ core level (Ref. 8). Notice the two sharp core-excitonic peaks at the threshold. (Bottom) The spectral region near the Al $2p$ threshold, with the two well-resolved core-excitonic peaks.

The conclusion of our study was that high-quality AlAs substrates can be reliably obtained by deposition of 2-4 monolayers of Al and annealing at 450 °C for 10 min. The only problem in the substrates obtained with this method was the presence of a separate phase of metallic Ga—probably macroscopic droplets—produced by the exchange reaction. This separate phase, however, did not interfere with the present experiments nor with other interface-formation studies performed on AlAs substrates.[11] Another delicate point was the possible presence of reacted Ga in the AlAs, i.e., the formation of $Ga_{1-x}Al_xAs$ instead of AlAs. Core-level photoemission provided only a partial answer to this question. In fact, the interpretation of the data on the Ga $3d$ and the Al $2p$ photoemission intensities depends on the model adopted for the structure of the system in the region near the surface. Our data were consistent with a sharp interface between pure GaAs and pure AlAs or, alternatively, with a very small fraction of reacted Ga inside the AlAs region. Taking all uncertainties into account, a very conservative estimate of the upper limit for the reacted Ga gave $1-x<0.15$. Reacted Ga in that amount does not modify our data analysis.

Figure 2 shows the optical-absorption threshold measured by partial-yield photoemission at a kinetic energy of 2 eV. The top curve shows an extended spectral region including the Al $2p$ threshold and the constant-final-state Al $2p$ signal.[8] The bottom curve shows the region close to the Al $2p$ threshold. Notice the two intense peaks corresponding to the Al $2p_{1/2}$ and Al $2p_{3/2}$ excitations. No comparably intense structure has been observed at other III-V compound partial-yield absorption thresholds, with the exception of the Al $2p$ threshold in AlSb.[7] Similar to those in AlSb, these peaks appear insensitive to contamination.

Figure 3 shows a similarly strong structure at the Al $2p$ threshold of AlP. This material was obtained with a method similar to that used for AlAs, i.e., by thermally stimulating the Al-Ga exchange reaction for a thin Al film deposited on

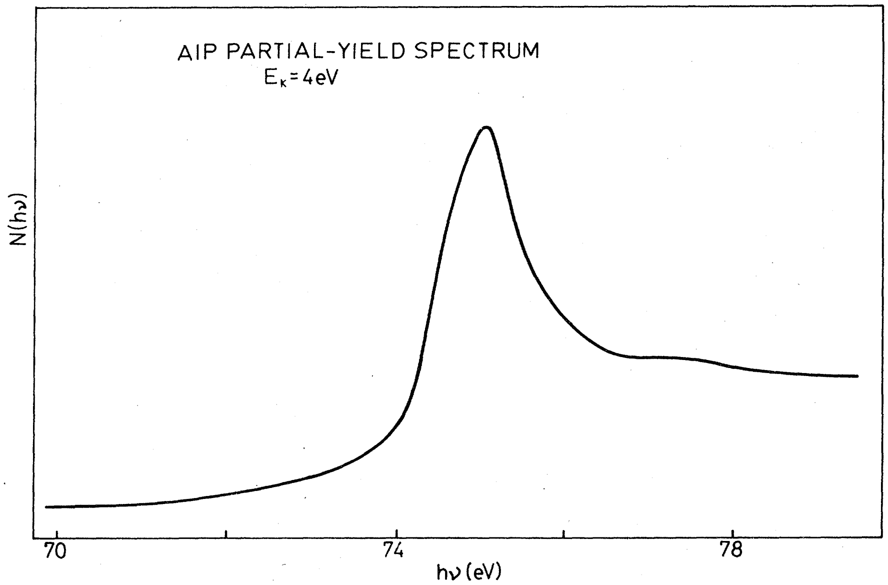

FIG. 3. Partial-yield spectrum showing the (unresolved) Al $2p$ core-excitonic doublet of AlP. The kinetic-energy window is centered at 4 eV.

GaP. The overall quality of the AlP films was somewhat lower than that of the AlAs films obtained with this method. Notice, in particular, that the two spin-orbit components are not resolved in the absorption spectrum of AlP.

Two features are particularly important in the analysis of the above data—the position in energy of the excitonic peaks and their relative intensity ratio. We used the conventional approach to estimate core-excitonic binding energies.[1] In particular, we estimated the single-particle absorption thresholds for the two Al 2*p* spin-orbit components from the AlAs gap and from the binding energy of Al 2*p* measured with photoemission. We experimentally obtained for Al $2p_{3/2}$ a binding energy of 73.15 ±0.15 eV measured from the top of the valence band. Combined with the room-temperature gap from Ref. 12, 2.16 eV, this gives a single-particle threshold of about 75.3 eV. The corresponding peak in Fig. 1 occurs instead at a photon energy $h\nu = 74.5$ eV. A conservative estimate of the experimental uncertainty gives ±0.25 eV for the single-particle threshold, and ±0.02 eV for the position of the absorption peak. Therefore, the discrepancy between the measured positions of the $j = \frac{3}{2}$ peak in Fig. 2 and the single-particle threshold is much larger than the experimental uncertainty. The ±0.25 eV uncertainty for the single-particle threshold includes a ±0.1 eV uncertainty for the gap, which is primarily due to the possible presence of reacted Ga. All things considered, we estimate a core-excitonic binding energy of 0.8 ±0.3 eV.

A similar analysis was also performed for AlP, but the estimate of the core-excitonic binding energy was severely affected by the lower quality of the sample with respect to the AlAs sample and by the consequent experimental uncertainty. In fact, the discrepancy between the single-particle threshold and the measured threshold, 0.5 eV, was similar to the experimental uncertainty.

One interesting feature of the spectra of Fig. 2 is the intensity ratio between the two spin-orbit components. This ratio clearly deviates from its statistical value, 2:1—as reported in Ref. 13 for the Ga 3*d* absorption edge of GaP. Johnson *et al.*[7] proposed for a similar effect exhibited by the Al 2*p* exciton in AlSb an interpretation based on the mixing of the excitonic states due to exchange interaction. The theoretical basis for this interpretation is provided by the classic theory of alkali halide excitons by Onodera and Toyozawa.[14] The theory links the spin-orbit intensity ratio $R$ to the exchange energy $J$ and to the spin-orbit splitting $\approx 0.4$ eV:

$$J = [1 - (2R)^{1/2} + (2/R)^{1/2}]\Delta/3 \ . \tag{1}$$

For statistical ratio $R = 2$, Eq. (1) gives, of course, $J = 0$. In our case $R \approx 0.75$ and $J \approx 0.19$ eV. The exchange interaction also reduces, with respect to $\Delta$, the distance in energy between the two spin-orbit excitonic peaks. Calling $\Delta_0$ the measured distance, one can derive from Onodera and Toyozawa's theory the following equation:

$$\Delta_0/\Delta = [(2/R)^{1/2} + (2R)^{1/2}]/3 \ . \tag{2}$$

In the present case, we obtain $\Delta_0/\Delta = 0.95$, i.e., $\Delta_0 = 0.38$ eV. The experimental value $\Delta_0 \approx 0.38$ is consistent with this prediction—but the difference between $\Delta_0$ and $\Delta$ is comparable to the experimental uncertainty. A similar agreement between theory and experiment was found for AlSb.

In summary, all III-V compounds containing Al examined until now exhibit sharp core-excitonic peaks at the Al 2*p* threshold. The excitonic binding energies range from 0.14 eV for AlSb to 0.8 for AlAs. The properties of these core-excitonic peaks are well described by the theory developed by Onodera and Toyozawa for alkali halide excitons.

The following question remains: Why are core-excitonic lines present in these Al compounds? This question can be reformulated: Why is the lifetime of the excitonic states longer in these compounds than in other III-V compound semiconductors? These questions remain unanswered at present. One interesting point is that measurements of the AlAs valence-band photoemission intensity at photon energies near this threshold did not reveal strong changes like those found at the Ga 3*d* threshold in GaAs.[15,16] In the latter material those changes are due to photoemission resonance, i.e., to the quantum interference between the direct photoemission process and a process involving core excitation and direct recombination. A limited role of direct recombination in our Al compounds could explain the behavior of the valence-band photoemission intensity. The limited role of direct recombination, however, would not be sufficient to guarantee a long excitonic lifetime,[13] which depends on all possible recombination mechanisms.

This study was supported by NSF Grants No. DMR-84-21292 and No. INT-81-22013. We are indebted to the entire staff of the University of Wisconsin Synchrotron Radiation Center for their expert technical support.

---

[*] On leave from the Istituto di Struttura della Materia, Consiglio Nazionale delle Ricerche, Frascati, Italy.

[†] On leave from the Department of Physics, University of Calabria, Italy.

[‡] On leave from Programma per l'Utilizzazione della Luce di Sincrotrone, Laboratori Nazionali di Frascati, Istituto Nazionale di Fisica Nucleare, Italy.

[§] Corresponding author.

[1] A. Quattropani, F. Bassani, G. Margaritondo, and G. Tinivella, Nuovo Cimento **51B**, 335 (1979); G. Margaritondo, A. Franciosi, N. G. Stoffel, and H. S. Edelman, Solid State Commun. **36**, 297 (1980).

[2] F. Evangelisti, F. Patella, R. A. Riedel, G. Margaritondo, P. Fiorini, P. Perfetti, and C. Quaresima, Phys. Rev. Lett. **53**, 2504 (1984).

[3] M. Altarelli and D. L. Dexter, Phys. Rev. Lett. **29**, 1100 (1972); M. Altarelli, *ibid.* **46**, 205 (1981); L. Resca and R. Resta, *ibid.* **44**, 1340 (1980); F. C. Brown and O. P. Rustgi, *ibid.* **28**, 497 (1972); R. S. Bauer, R. Z. Bachrach, D. E. Aspnes, and J. C. McMenamin, Nuovo Cimento **39B**, 408 (1977); B. A. Bunker, S. L. Hulbert, J. P. Stott, and F. C. Brown, Phys. Rev. Lett. **53**, 2157 (1984); S. M. Kelso, D. E. Aspnes, C. G. Olson, D. W. Lynch, and D. Finn, *ibid.* **45**, 1032 (1980); F. C. Brown, R. Z. Bachrach, and M. Skibowski, Phys. Rev. B **15**, 4781 (1977); W. Eberhardt, G. Kalkoffen, C. Kunz, D. E. Aspnes, and M. Cardona, Phys. Status Solidi (b) **88**, 135 (1978).

[4] G. Strinati, Phys. Rev. Lett. **49**, 1519 (1982); Phys. Rev. B **29**, 5718 (1984).

[5] H. P. Hjalmarson, M. Bütner, and J. D. Dow, Phys. Rev. B **24**, 6010 (1981).

[6] A. Zunger, Phys. Rev. Lett. **50**, 1215 (1983).

[7] R. L. Johnson, J. H. Fock, L. Ley, and M. Cardona, in *Proceedings*

*of the Seventeenth International Conference on the Physics of Semiconductors, San Francisco, 1984,* edited by D. J. Chadi and W. A. Harrison (Springer, New York, 1985), p. 1239.

[8] W. Gudat and C. Kunz, Phys. Rev. Lett. **29**, 196 (1972); for a discussion of this technique and of other synchrotron-radiation photoemission techniques, see G. Margaritondo, Solid-State Electron. **26**, 499 (1983).

[9] G. Margaritondo, J. H. Weaver, and N. G. Stoffel, J. Phys. E **12**, 662 (1979).

[10] A. Huijser, J. Van Laar, and T. L. van Rooy, Surf. Sci. **102**, 264 (1981).

[11] M. K. Kelly, D. W. Niles, E. Colavita, G. Margaritondo, and M. Henzler, Appl. Phys. Lett. **46**, 768 (1985).

[12] B. R. Pamplin, in *Handbook of Chemistry and Physics,* edited by Robert Weast (CRC Press, Boca Raton, 1981), p. E-103.

[13] F. Sette, P. Perfetti, C. Quaresima, F. Patella, M. Capozi, and A. Savoia, Phys. Rev. B **28**, 4882 (1983).

[14] Y. Onodera and Y. Toyozawa, J. Phys. Soc. Jpn. **22**, 833 (1967).

[15] G. J. Lapeyre and J. Anderson, Phys. Rev. Lett. **35**, 117 (1975).

[16] F. Cerrina, A. Bommannavar, R. Benbow, and Z. Hurych (unpublished).