Dielectric function of cubic and hexagonal CdS in the vacuum ultraviolet region

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The dielectric function of cubic CdS films grown epitaxially on InP(110) has been determined by spectroscopic ellipsometry in the photon energy range 4.5–18 eV. Structures in the imaginary part of ϵ below 9.5 eV are assigned to transitions at critical points of the Brillouin zone and are compared with our measurements on hexagonal CdS performed in the same energy range. Structures in ϵ_2 above 12 eV are assigned to transitions from cadmium $4d$ and sulfur $3s$ states into the conduction band.

In contrast to many tetrahedral semiconductors the stable modification of cadmium sulfide has a hexagonal wurtzite structure and the cubic zinc-blende structure is metastable under normal conditions. In both crystal structures the arrangement of first and second neighbors is nearly the same.[1] There is considerable interest in the electronic structure of CdS, especially of the cubic modification, because of its promising properties in heterogeneous solar cells.[2]

In the past most experimental work on CdS has been confined to the hexagonal phase because of the difficulty in obtaining cubic CdS samples. However, by using the technique of molecular-beam epitaxy and suitable substrates it is possible to grow CdS relatively easily in the cubic modification. Wilke, Seedorf, and Horn obtained high-quality single-crystal films, as confirmed by Raman scattering and x-ray diffraction, by depositing CdS on cleaved InP(110) surfaces.[3,4] Note that the lattice parameter of InP (5.87 Å) is close to that of cubic CdS (5.82 Å).

In contrast, the calculation of the electronic band structure is easier for the cubic structure because its unit cell contains only half as many atoms as that of the hexagonal phase. Several band-structure calculations can be found in the literature, both for the cubic[5–8] and hexagonal[8,9] modifications. An important question in the past has been to what extent the cation d states participate in the bonding. Photoemission studies place the Cd $4d$ states in CdS about 9.5 eV below the valence-band maximum.[10,11] Because of the interaction of these states with the p-derived bands they should not be treated as core levels, but rather considered explicitly as part of the valence band.[7,8,11,12] An optical spectroscopic technique such as ellipsometry can provide detailed information on the electronic properties of solids and in particular the energies of interband transitions. The imaginary part of the dielectric function ϵ_2, which is measured in a straightforward way by ellipsometry, shows features which are directly related to transitions at critical points of the Brillouin zone. In general, for the interpretation of these structures some knowledge of the band structure is required. However, once assigned, the measured transition energies provide a good test for the accuracy of band-structure calculations.

Since the fundamental band gap of CdS is about 2.4 eV many of the interband transitions lie in the vacuum ultraviolet (VUV) region. Many years ago Cardona and co-workers measured the VUV reflectivity of hexagonal CdS (Ref. 13) and also performed measurements on cubic CdS samples grown on GaAs(111) and GaP(111) surfaces using a chemical vapor-phase transport technique.[14] The optical constants were then calculated using Kramers-Kronig analysis. Inspection of these results shows a considerable degree of similarity between the spectra of the cubic and hexagonal modifications. This suggests that the cubic samples may have been of inferior crystal quality with large amounts of the hexagonal phase. We have therefore repeated these optical measurements using a well-characterized preparation technique for the cubic films and the more powerful method of spectroscopic ellipsometry. In this paper we present data on *in situ* grown cubic CdS films between 4.5 and 9.5 eV, i.e., the interband transition region, and between 12 and 18 eV, where transitions from the Cd $4d$ and S $3s$ states into the conduction band occur. The dielectric function of hexagonal CdS was also measured in the same energy regions, both for the c axis parallel and perpendicular to the polarization vector of the incoming light.

Films of CdS were grown at 470 K by molecular-beam epitaxy following the method described by Zahn *et al.*[4]

on InP(110) single-crystal substrates cleaved *in vacuo*. CdS was evaporated from a Knudsen cell mounted in the main vacuum chamber of the ellipsometer. The cell was kept at a constant temperature of either 838 or 857 K which gave evaporation rates of 0.8 and 1.6 nm/min. The evaporation rate was determined with a quartz-crystal monitor and the films investigated were 50 and 450 nm thick. For comparison spectra of hexagonal CdS were recorded from a polished single crystal with the c axis in the plane of the surface. The measurements were performed with the VUV ellipsometer on the 2-m Seya-Namioka monochromator using synchrotron radiation from the Berlin electron storage ring, BESSY; the instrument has been described previously.[15] The ellipsometric data were recorded in two energy regions, between 4.5 and 9.5 eV using a MgF_2 Rochon polarizer and between 12 and 18 eV with a triple-reflection gold-coated polarizer. Because of the high degree of linear polarization of the synchrotron light from the monochromator, an additional polarizer before the sample was not necessary. Measurements between 9.5 and 12 eV could not be performed reliably because of second-order light from the monochromator. The normal incidence reflectivity of the CdS films and the hexagonal CdS were measured directly. All spectra were recorded both at room temperature and at 90 K.

The measurements on cubic CdS were performed on films with a thickness of about 50 nm. This value was chosen to avoid any contributions from the InP substrate. Figure 1(a) shows the dielectric function of cubic CdS at 90 K between 4.5 and 9.5 eV. The spectral features are somewhat sharper and slightly shifted by ~ 0.1 eV to higher energy compared to the corresponding room-temperature spectra. The structures in ϵ_2 have been tentatively assigned to critical points in the Brillouin zone and their energies determined by differentiating the spectra. Figure 2 explains the standard nomenclature for optical transitions in semiconductors with zinc-blende structure. The assignment is based on a visual examination of the calculated bands and does not take into account excitonic effects or transitions at non-high-symmetry points. In Table I our results for the maxima in ϵ_2 are compared with the eigenvalue differences from three different band-structure calculations. Chang, Froyen, and Cohen[8] have calculated the effect of the Cd $4d$ bands on the occupied bands of cubic CdS using a self-consistent local-density (SC-LD) formalism. To obtain values for the energies of the optical transitions we have taken the conduction-band states from the same calculation (not including the d states) and adjusted their separation to the valence bands so as to fit the experimental value of 2.4 eV for the band gap (scissors operator).[3] The inclusion of the d states enhances the required adjustment without giving substantially better agreement with the experimental values. Kurganskii, Farberovich, and Domashevskaya[7] also include the d states in their modified orthogonalized-plane-wave (OPW) calculation, but the agreement with experiment (and indeed with the other calculations) is so poor that we have not included these values in Table I. Stukel *et al.*[5] have calculated the imaginary part of the dielectric function for cubic CdS

from their self-consistent orthogonalized-plane-wave (SC-OPW) band structure. Due to the approximate nature of the calculation of the transition matrix elements there is only qualitative agreement with the presented results, as was also found for other II-VI semiconductors. The order of the structures, however, agrees with our assignment.

For the ellipsometric measurements the hexagonal CdS sample was mounted on the manipulator with either the c axis nearly perpendicular or nearly parallel to the polarization vector of the incident light. Small contributions of the $\mathbf{E} \perp \mathbf{c}$ spectrum in the $\mathbf{E} \parallel \mathbf{c}$ spectrum and vice versa are to be expected. However, comparison of the normal incidence reflectivity calculated from the dielectric function measured ellipsometrically and the normal incidence reflectivity measured directly indicates that these contributions are small. Figures 1(b) and 1(c) show the dielectric function of hexagonal CdS at 90 K between 4.5 and 9.5 eV for $\mathbf{E} \perp \mathbf{c}$ and $\mathbf{E} \parallel \mathbf{c}$, respectively. Note that both spectra differ from that of the cubic form in Fig. 1(a) which reflects the significantly different band structure.
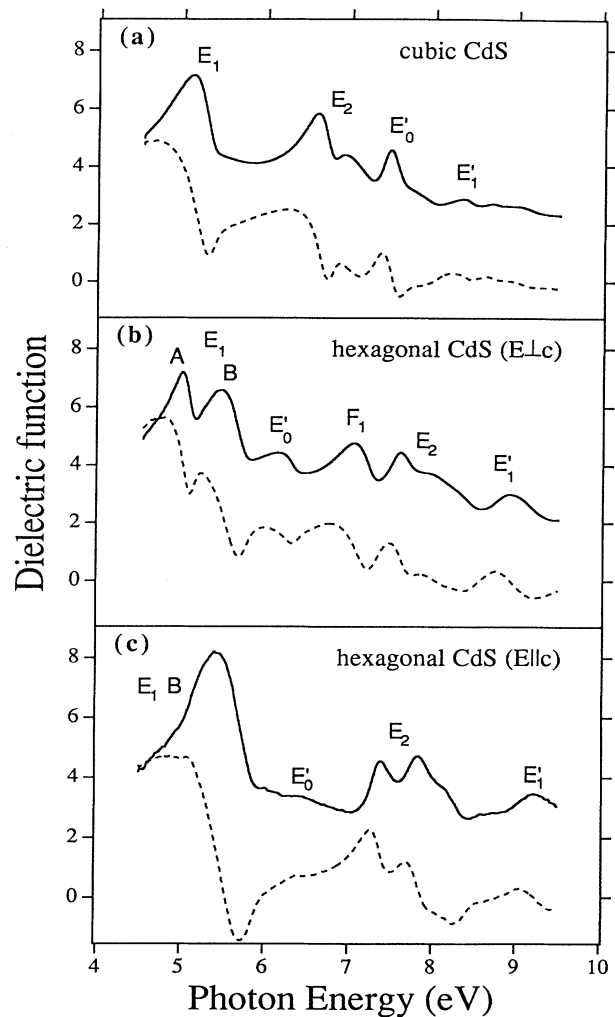

FIG. 1. The dielectric functions of (a) cubic and (b),(c) hexagonal CdS in the energy region of the interband transitions at 90 K (ϵ_1, dashed line; ϵ_2, solid line).
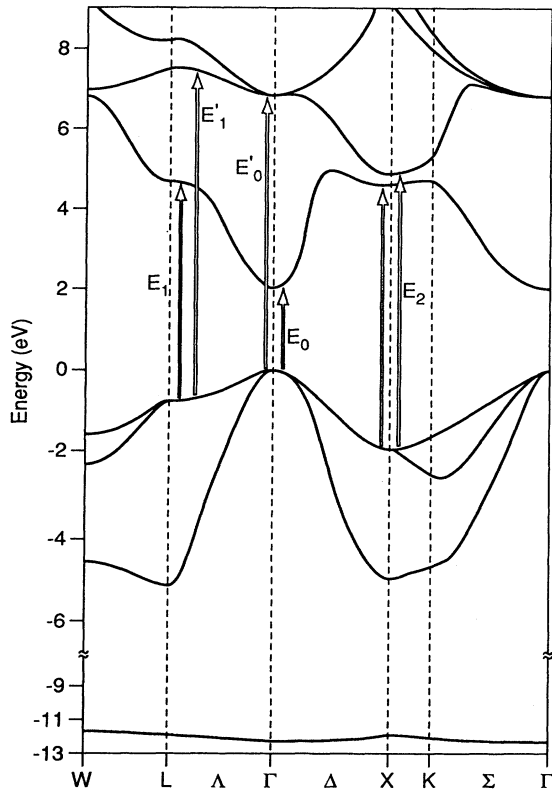
FIG. 2. Nomenclature for optical transitions in semiconductors with wurtzite structure and the band structure of cubic CdS from Zunger and Freeman (Ref. 6).
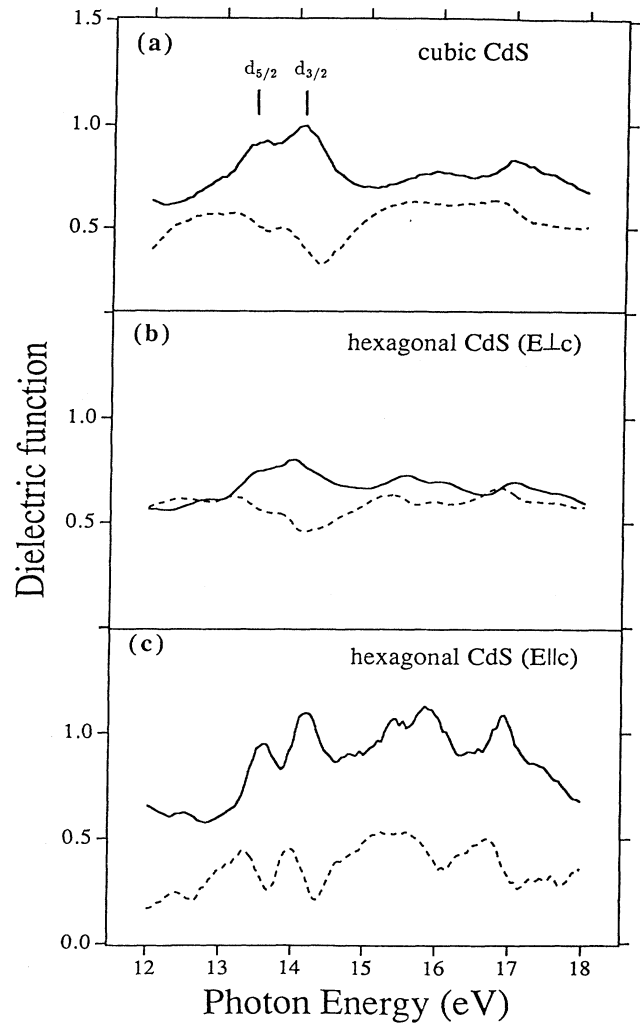

FIG. 3. The dielectric functions of (a) cubic and (b),(c) hexagonal CdS in the energy region of the core-level transitions at 90 K (ϵ_1, dashed line; ϵ_2, solid line).

The designation of the structures in ϵ_2 follows the assignment of Cardona and Harbeke.[13] Mojumder[16] has calculated the selection rules for optical transitions for the nonsymmorphic space group of the hexagonal structure and has suggested an interpretation for the optical spectra of hexagonal CdS. However, the complexity of the band structure leads to some uncertainty in the assignment and more theoretical work is necessary: the obvious way of obtaining a more reliable assignment of the structures would be by comparison with a theoretically calculated ϵ_2 curve.

Other than the lowest direct gap (E_0) the best established assignment[13] is that of the E_1 peak of the cubic

modification which splits into two for wurtzite [peaks A and B in Fig. 1(b)] in the $\mathbf{E} \perp \mathbf{c}$ polarization although only one (peak B) is visible for $\mathbf{E} \parallel \mathbf{c}$. This peak appears in all materials with zinc-blende structure[17] and has been assigned to transitions with critical points along the four equivalent $\{111\}$ directions between the top of

TABLE I. Comparison of the structures in ϵ_2 with the predictions of various band-structure calculations (in eV).

Transition	SC-OPW (Ref. 5)	SC-LD (Ref. 6)	SC-LD (Ref. 8)	SC-LD including d states (Ref. 8)	Ellipsometry
E_0	2.7	2.0	1.8	2.4	
E_0'	7.6	6.8	6.9	7.5	7.4
E_1	4.9	5.5	4.2	5.4	5.0
E_1'	8.5	8.3	8.1	9.1	8.3
E_2	6.3	6.5	5.6	7.1	6.4
	7.1	6.8	6.7	8.2	6.9

the valence band and the bottom of the conduction band. These directions split into one along **c** (*A*) and three perpendicular to **c** (*B*) in wurtzite; the selection rules shown in Fig. 1 follow. The E'_1 transitions should also be related to {111} critical points but between the top valence bands and the second lowest set of conduction bands (see Fig. 2).

The results for the hexagonal phase are in good agreement with the early reflectivity measurements of Cardona and Harbeke,[13] whereas our spectra for the cubic modification differ significantly from those of Cardona, Weinstein, and Wolff.[14] The spectra for the hexagonal modification with **E** ∥ **c** resemble strongly the results for the cubic modification presented by Cardona, Weinstein, and Wolff[14] and we may conclude that their samples had substantial admixtures of the hexagonal phase.

Figure 3 shows the dielectric functions of both cubic and hexagonal CdS at 90 K for photon energies between 12 and 18 eV. There is a certain degree of similarity between the main features in the spectra for both crystal modifications, in contrast to the low-energy spectra, which reflects the smaller dispersion of the more core-like initial states. The structures in ϵ_2 originate from transitions between Cd 4*d* and S 3*s* states and the conduction band. Taking the experimental values for the energy of the Cd 4*d* bands and the band gap one would expect the onset of the transitions from the *d* bands to the conduction-band minimum (CBM) to be at about 12 eV. The features between 13.0 and 14.5 eV therefore originate primarily from the Cd 4*d* levels (note in Fig. 3 the splitting of about 0.65 eV between the first two peaks of the family. It corresponds to the $d_{5/2}$-$d_{3/2}$ spin-orbit splitting of the Cd 5*d* core levels[18]). Reflectivity measurements on other II-VI semiconductors suggest that structures caused by core excitons with binding energies of several hundred meV (relative to the CBM) may be found at the edge of the *d*-band transitions.[19,20] At higher energies transitions at other high-symmetry points of the Brillouin zone occur. The band-structure calculations place the S 3*s*–derived band about 11 eV below the valence-band maximum. For the 3*s* states transitions to the CBM are forbidden for **E** ⊥ **c** in the hexagonal and cubic structures and are only allowed for **E** ∥ **c** in the hexagonal modification. Thus, transitions from the S 3*s* states are only to be expected in the region 13–14 eV in the wurtzite structure for **E** ∥ **c**. As pointed out by Zunger and Freeman,[6] a further complication for transitions involving semicore states is that the observed transition energies are not equal to the differences in the energy eigenvalues. This effect is similar to the usual "gap" problem of band-structure calculations based on the local-density approximation which tend to underestimate the size of the band gap.[21] It is not to be expected that the "scissors operator" used here to correct the "gap problem" will also correct the corresponding effects of semicore states.

The measured dielectric function of a thick (450 nm) film of CdS on InP(110) between 4.5 and 9.5 eV resembles the spectrum from hexagonal CdS for **E** ∥ **c**. The spectral features were at the same positions and had the same relative intensities, but were broadened. This implies that at a critical value of the film thickness a phase transition into the stable hexagonal structure occurs. Further investigations of this effect are in progress.

[1] J. L. Birman, Phys. Rev. **115**, 1493 (1959).

[2] A. Yoshikawa and Y. Sakai, Solid State Electron. **20**, 133 (1977).

[3] W. G. Wilke, R. Seedorf, and K. Horn, J. Vac. Sci. Technol. B **7**, 807 (1989).

[4] D. R. T. Zahn, Ch. Maierhofer, A. Winter, M. Reckzügel, R. Srama, A. Thomas, K. Horn, and W. Richter, J. Vac. Sci. Technol. B **9**, 2206 (1991).

[5] D. J. Stukel, R. N. Euwema, T. C. Collins, F. Herman, and R. L. Kortum, Phys. Rev. **179**, 740 (1969).

[6] A. Zunger and A. J. Freeman, Phys. Rev. B **17**, 4850 (1978).

[7] S. I. Kurganskii, O. V. Farberovich, and E. P. Domashevskaya, Fiz. Tekh. Poluprovodn. **14**, 1315 (1980) [Sov. Phys. Semicond. **14**, 775 (1980)].

[8] K. J. Chang, S. Froyen, and M. L. Cohen, Phys. Rev. B **28**, 4736 (1983).

[9] A. Kobayashi, O. F. Sankey, S. M. Volz, and J. D. Dow, Phys. Rev. B **28**, 935 (1983).

[10] L. Ley, R. A. Pollak, F. R. McFeely, S. P. Kowalczyk, and D. A. Shirley, Phys. Rev. B **9**, 600 (1974).

[11] N. G. Stoffel, Phys. Rev. B **28**, 3306 (1983).

[12] S. H. Wei and A. Zunger, Phys. Rev. B **37**, 8958 (1988).

[13] M. Cardona and G. Harbeke, Phys. Rev. **137**, A1467 (1965); M. Cardona, Solid State Commun. **5**, 109 (1963).

[14] M. Cardona, M. Weinstein, and G. A. Wolff, Phys. Rev. **140**, A633 (1965).

[15] R. L. Johnson, J. Barth, M. Cardona, D. Fuchs, and A. M. Bradshaw, Nucl. Instrum. Methods A **290**, 606 (1990).

[16] M. A. Mojumder, Solid State Commun. **43**, 13 (1982).

[17] M. L. Cohen and J. R. Chelikowsky, *Electronic Structure and Optical Properties of Semiconductors* (Springer, Heidelberg, 1989).

[18] T. C. Chiang and F. J. Himpsel, in *Electronic Structure of Solids: Photoemission Spectra and Related Data*, edited by A. Goldmann and E. E. Koch, Landolt-Börnstein, New Series, Group X, Vol. 23, Pt. a (Springer, Heidelberg, 1989), p. 93.

[19] M. Krause, H.-E. Gumlich, and U. Becker, Phys. Rev. B **37**, 6336 (1988).

[20] E. Flach, H.-E. Gumlich, Ch. Jung, and M. Krause, Phys. Status Solidi B **155**, 317 (1989).

[21] X. Zhu and S. G. Louie, Phys. Rev. B **43**, 14 142 (1991).