Reflectivity spectra of structurally pure wurtzite-type ZnS in ultraviolet and vacuum-ultraviolet regions

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There has been a significant discrepancy among the reflectivity spectra of wurtzite-type ZnS reported previously. The spectrum measured by Baars with structurally pure wurtzite-type ZnS is different from the other spectra which are very close to that of the cubic phase. In addition, the one by Baars shows a distinct polarization dependence, while the others show a very weak or no polarization dependence. From our reflectivity study on structurally pure wurtzite-type ZnS, we are confident that the discrepancy is caused by the structural difference of the samples. The spectrum measured in this work is in good agreement with that of Baars and appreciably different from that of the cubic phase. The energy positions of peaks in our spectrum are consistent with the values deduced from reflectivity data on ZnS-CdS alloys.

Reflectivity spectra of wurtzite-type ZnS reported previously[1-3] exhibited both energies and magnitudes very similar to those of the zinc-blende phase except for the spectrum reported by Baars.[4] The spectrum closely related to that of the zinc-blende phase has also been reported recently.[5] The spectrum of Baars is referred to as type I and the others as type II, hereafter. Contrary to these results the data on ZnS-CdS alloys by Drew, Davis, and Leiga[6] (DDL) have indicated that the spectrum of wurtzite-type crystals does not resemble that of the cubic phase. The spectrum of wurtzite-type $Zn_{0.92}Cd_{0.08}S$ is very similar to type I, and that of rotation-twinned-cubic $Zn_{0.92}Cd_{0.08}S$ is similar to type II. The alloys $Zn_xCd_{1-x}S$ have been reported to have wurtzite structure when x is less than 0.92 and to have rotation-twinned-cubic structure when x is larger than 0.92.[6] The purpose of this work is to determine which spectrum of the two types corresponds to wurtzite-type ZnS.

We examined the reflectivity spectra of structurally pure wurtzite-type ZnS at photon energies from the lowest gap energies to 11 eV at room temperature. Single crystals were grown from the melt using ZnS powder with 10^{-3}-mol Al per mol ZnS. A spectroscopic analysis showed the Al content to be of the order of 100 ppm in the as-grown crystals. From x-ray patterns of the oscillation and Weissenberg photographs we were confident that the grown crystals are structurally pure wurtzite. The x-ray photographs about the $\langle 00.1 \rangle$-axis precession showed two-layer stacking ($2H$), and in addition, all diffraction spots were sharp without measurable broadening due to stacking faults. Broadened spots were often observed in cubic ZnS with stacking faults.[7] It is noted that melt-grown ZnS without Al has three-layer-cubic structure ($3C$) with broadened spots

on the n layer with $n \neq 3m$ (m is an integer) in the $\langle 111 \rangle$-axis x-ray photographs. The crystals with 10^{-4}-mol Al per mol ZnS are mixtures of $6H$ and $3C$ polytypes. The cubic crystals with growth faults or rotation twins give rise to back-reflection Laue patterns which have a sixfold symmetry about the $\langle 111 \rangle$ axis and thus are often misinterpreted as being the hexagonal phase. They also show a birefringence banding in the easy cleaving face when observed under a polarizing microscope. X-ray diffraction studies using powdered samples indicate that the lattice constants of our wurtzite-type ZnS are $a = 3.81$ Å and $c = 6.23$ Å, to be compared with $a = 3.811$ Å and $c = 6.234$ Å given in Ref. 8.

A McPherson 225 monochromator served as the light source from 4.5 to 11 eV. A McPherson 665-L reflectometer with a sodium-salicylate coated rotatable light pipe was used with an incident angle less than 10°. The light incident on the sample was partially polarized because of our instrument setup. In the lowest gap region, a Shimazu 40R spectrophotometer with an attachment for reflectivity measurements was used with or without a polacoat polarizer. The cleaved ($10\bar{1}0$) face was used. The face was not so specular as the cleaved face of cubic crystals and parallel running microsteps were observed in the face. The microsteps are often seen in the cleaved face of wurtzite-type CdS or of wurtzite-type $Zn_xCd_{1-x}S$. For a comparison measurements were also performed on naturally grown zinc-blende-type ZnS and melt-grown $3C$-type ZnS, where cleaved ($1\bar{1}0$) faces were used.

In Fig. 1 we present the reflectivity spectra of wurtzite-type ZnS measured for the orientations of the c axis (a) parallel and (b) perpendicular to the polarized direction. Although the light is partially polarized, we denote the two orientations as
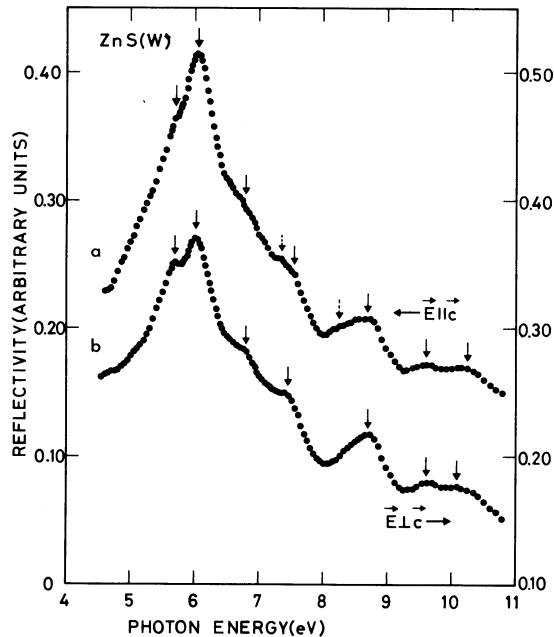
FIG. 1. Reflectivity spectra of structurally pure wurtzite-type ZnS with orientations of the c axis (a) parallel and (b) perpendicular to the polarized direction at room temperature from 4.5 to 11 eV. Arrows indicate the peak positions. We emphasize that the light is partially polarized.
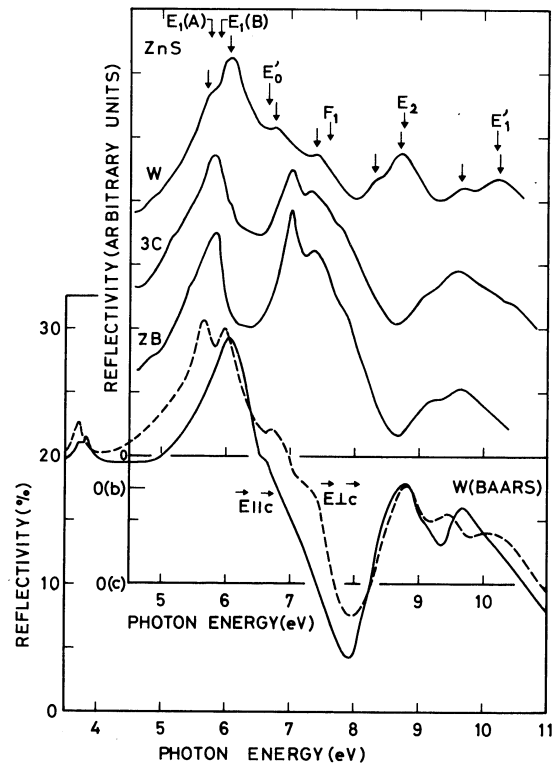

FIG. 2. Reflectivity spectra of wurtzite-type (W), naturally grown zinc-blende type (ZB), and melt-grown-cubic (3C) ZnS at room temperature from 4.5 to 11 eV. Arrows indicate the peak positions. The energy positions accompanied by the notation indicated on the curve of wurtzite-type ZnS are the extrapolated values of DDL (Ref. 6). For a comparison, the spectra of wurtzite-type ZnS are reproduced from Baars (Ref. 4).

$\vec{E} \parallel \vec{c}$ and $\vec{E} \perp \vec{c}$ in the figure. Arrows in the figure indicate the peak positions. In Fig. 2 we compare the spectrum of wurtzite-type ZnS taken on the unknown orientation of the c axis with respect to the polarized direction with those of structurally pure zinc-blende-type and structurally impure 3C-type ZnS. In addition the spectra of type I or structurally pure wurtzite-type ZnS are reproduced from the data of Baars[4] in the figure. The arrows in the curve of wurtzite-type ZnS indicate the peak positions. The notations such as $E_1(A)$, $E_1(B)$, and E_2 with respective energy positions are the ones given by DDL.[6] It is noticed that the spectra of our wurtzite-type ZnS are very similar to those of type I and are dissimilar to those of cubic ZnS. The spectra in the lowest gap region are given in Fig. 3 for crystals of the wurtzite, zinc-blende, 3C types.

As shown in Fig. 1, the distinct peak observed at 5.7 eV in the curve b appears to become simply a shoulder in the curve a. The difference in magnitude between these two curves can be explained by the polarization dependence observed by Baars. Also the structures at 6.8 and 7.45 eV in the curve b are more distinct than the corresponding ones in the curve a, being consistent with the polarization dependence. The significant features in the spectrum of wurtzite-type ZnS are the absence of

the pronounced peaks at near 7 eV which are seen in zinc-blende-type ZnS and the appearance of the E_2 peak at 8.7 eV. The E_0 gap of wurtzite-type ZnS was observed at 3.78 and 3.87 eV, in good agreement with 3.75 and 3.83 eV given in Ref. 4, or with 3.76 and 3.86 eV given in Ref. 6, respectively. It is also consistent with the previous data with structurally pure wurtzite-type ZnS taken at 77 K,[9] but is slightly larger than that of cubic ZnS measured in this work or reported previously.[4,5] There is a good one-to-one correspondence between the observed feature in this work and the one predicted by DDL.[6] These results indicate that the present reflectivity spectrum, which is dissimilar to that of type II, corresponds to that of structurally pure wurtzite-type ZnS.

From the fact that the reflectivity spectrum of structurally pure wurtzite-type ZnS is appreciably different from that of cubic ZnS and our spectrum of the wurtzite phase is similar to that of type I, we conclude that the spectrum of type I corresponds to structurally pure wurtzite-type ZnS. It is noted that the ZnS crystals of structurally pure
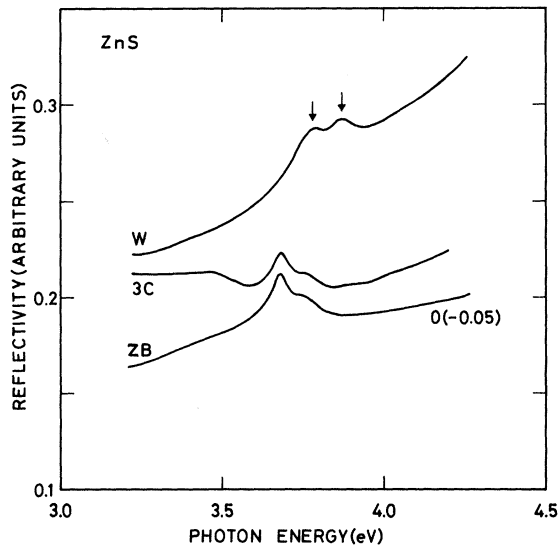
FIG. 3. Reflectivity spectra of wurtzite-type (W), naturally grown zinc-blende type (ZB), and melt-grown-cubic (3C) ZnS at room temperature in the E_0 gap region. Arrows indicate the peak positions.

the vapor-phase and chemical transport techniques. It provides a large-size single crystal in a rather short growth time with good reproducibility. In general, melt-grown crystals are rotation-twinned cubic, while our growth technique is the first one which produces structurally pure wurtzite-type ZnS from the melt.

We emphasize that consideration of the differences in the reflectivity spectra of wurtzite- and zinc-blende-type ZnS may be of importance for a better understanding of the structural stability of ZnS. These may be correlated with such properties as ionicity, electronic charge density, deviation of the lattice-constant ratio c/a from the ideal value of $(\frac{8}{3})^{1/2}$, and lattice-constant variation with impurity contents.[10] The correlation between ionicity and bonding charge derived from the charge density has been reported,[11] with the charge density being calculated theoretically in terms of the energy band for typical semiconductors[11] including ZnS.[12] Unfortunately, the calculations have been based on empirically refined energy bands without nonlocal effects, while recent photoemission studies using x rays[13] and far-ultraviolet (vacuum) radiations[14] have indicated that calculations of the valence-band width with local-pseudopotential approximations lead to a narrower width than that deduced from photoemission measurements. Also, the difference between calculations with local pseudopotential approximations and optical data becomes appreciable at photon energies larger than about 8 eV.[5] These discrepancies can be removed by including nonlocal potentials in the local approximations.[15] The calculation of the electronic charge distribution for the zinc-blende and wurtzite phases in terms of the nonlocal band scheme is needed for the analysis of the structural stability of ZnS.

wurtzite type can be distinguished from the crystals of pure zinc-blende type or the rotation-twinned-cubic type by the reflectivity spectra. The cleaving habit may be also used for the distinction of the wurtzite-type crystals from the cubic type: The cleavage face with nonspecular surface corresponds to the pure wurtzite phase and the easy cleavage face with specular surface corresponds to the cubic type including pure zinc-blende, rotation-twinned, and probably polytype structures.

It is noted that the melt-grown technique has several advantages over other techniques such as

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