

Above bandgap optical properties of ZnS grown by hot-wall epitaxy

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Abstract – The real (ϵ_1) and imaginary (ϵ_2) parts of the dielectric function of ZnS have been measured by spectroscopic ellipsometry (SE) in the 3.7-6.0 eV photon-energy range at room temperature. The obtained dielectric function spectra reveal distinct structures at energies $E_0 / (E_0 + \Delta_0)$ and E_1 critical points. The spectrum after chemical treatment to remove surface oxide overlayer showed that these data seem to be the best representation of the dielectric function of ZnS, having the largest ϵ_2 value at E_1 peak region reported so far by SE. Dielectric-related optical constants of ZnS, such as the complex refractive indices ($n^* = n + ik$), absorption coefficient, and reflectance, are also presented.

I. Introduction

A knowledge of the optical response of II-VI compounds over a wide range of photon energies is of great importance for device applications. However, for ZnS, only a few studies have been reported in the visible-to-ultraviolet spectral region [1, 2]. The Spectroscopic Ellipsometry (SE) is known to be highly suitable for measuring dielectric functions (or refractive indices) of semiconductors [3-7], a quantity directly related to the band structure over a wide energy range, which can be determined without the need of Kramers-Kronig transformations.

In this paper we present the dielectric-function spectra of zincblende-type ZnS at room temperature between 3.7-6.0 eV obtained by SE measurements. Using proper chemical etching treatment to remove the oxide overlayer on ZnS, we obtain the best results of the dielectric function spectra of ZnS reported so far by SE. Dielectric-related optical data, such as the complex refractive indices, absorption coefficients, and reflectances, are also presented, which are helpful for the design and analysis of optoelectronic devices.

II. Experimental Details

ZnS epilayers were grown on Cr-doped semi-insulating GaAs (100) substrates by hot-wall epitaxy (HWE) [8]. The source material was 5N poly-crystalline ZnS powder. The GaAs substrates were ultra-sonically cleaned by trichloroethylene, acetone, and methanol in sequence. They were etched in 50-60°C 3H₂SO₄ : H₂O₂ : H₂O for 1 min and rinsed with deionized water. After drying with Ar gas, they were put on the substrate holder in the HWE set-up. The GaAs substrates were preheated at 600°C for 20 min to remove the remaining impurities and the oxide layer on the substrate surfaces. Following the preheating, the substrates were cooled at a rate of 5°C/min to the growth temperature. The growth temperatures for the source, the walls, and the substrate were 700°C, 570°C, and 400°C, respectively. The growth rate was maintained at about 1~2 Å/s during the growth of the epilayers.

Pseudodielectric function spectra $\langle \epsilon(\omega) \rangle = \langle \epsilon_1(\omega) \rangle + i \langle \epsilon_2(\omega) \rangle$ were measured at room temperature between 3.7 eV and 6.0 eV using an automatic spectroscopic rotating analyzer ellipsometer of the type developed by Aspnes [4, 9, 10]. (The pseudodielectric function $\langle \epsilon \rangle$ is defined as the measured or apparent dielectric function obtained by reducing the ellipsometric data with the two-phase (ambient-substrate) model [11], ignoring the presence of possible surface overlayers and microscopic roughness layer.) After being dispersed by a Cary 14 R monochromator, the light from a 75 W Xenon lamp is linearly polarized with a Rochon-quartz prism. Upon

reflection from the sample the linearly polarized light becomes elliptically polarized. The reflected light is modulated by means of a rotating analyzer (Rochon prism) and detected by a photomultiplier. The output of the photomultiplier is digitized and the signal is analyzed with the aid of a personal computer. The measurements were generally performed at an incident angle of 67.08° .

III. Results and Discussion

3.1. Chemical Etching

It is well known that overlayers complicate efforts to obtain the intrinsic dielectric response of a material by ellipsometry because of the surface sensitivity of this technique. A wet chemical etching procedure as described in Ref. 4 was carried out while the ellipsometric data were taken in a windowless cell in flowing purified N_2 to minimize surface contamination. The general procedure for obtaining the dielectric response of the pure material is to chemically treat the sample until the E_2 peak is maximized. However, since the E_2 peak of ZnS is out of our spectral range ($E_2 \sim 7.0$ eV [1]), the chemical treatment was repeated until real-time ellipsometric spectra showed no more changes, and

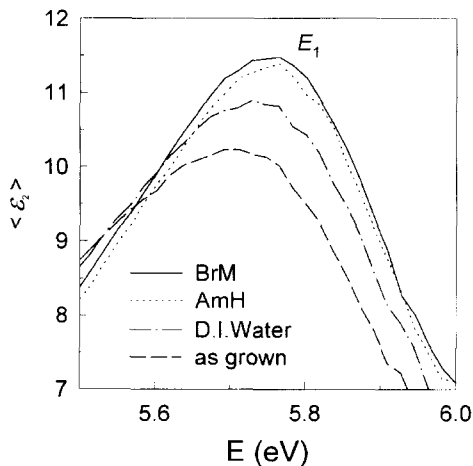


Fig. 1. Effect of chemical treatment on the imaginary part $\langle \epsilon_2 \rangle$ of a ZnS film grown by HWE on a GaAs(100). The results of no treatment (as grown) (dashed line), deionized water and methanol (line-dot-line) treatment, diluted NH_4OH solution with methanol (AmH) (dot) treatment, and Br_2 in methanol (BrM) treatment (solid line) are shown.

the highest values of ϵ_2 at the E_1 band-gap energy region were obtained. Figure 1 shows the imaginary (ϵ_2) part of the pseudodielectric function after the successful removal of the oxide overlayer on ZnS. We first etched with deionized water and methanol (line-dot-line), followed by diluted NH_4OH solution [6] with methanol (dot), and then finally with Br_2 in methanol (BrM : less than 0.1%) (solid line) [7]. The chemical treatment was repeated until real-time ellipsometric spectra showed no more changes, and the highest values of $\langle \epsilon_2 \rangle$ at the E_1 (or the highest values of $\langle \epsilon_1 \rangle$ of E_1) band gap energy region were obtained.

3.2. Dielectric function and refractive index

The final spectra after chemical treatment are

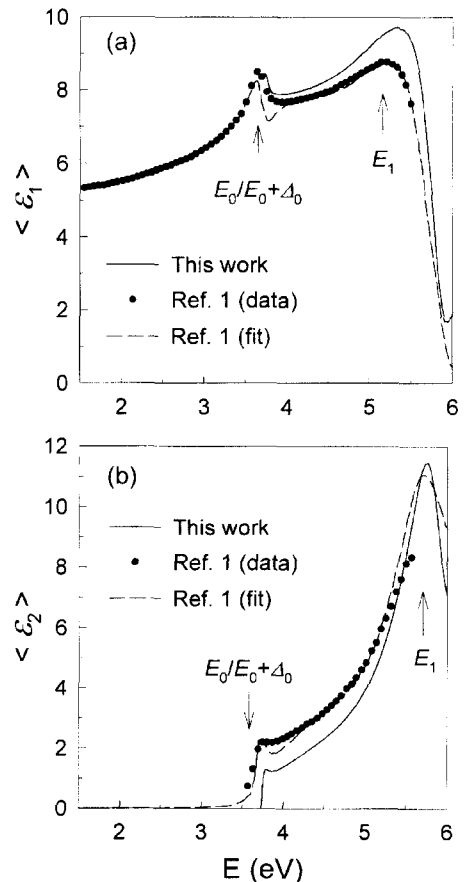


Fig. 2. (a) Real $\langle \epsilon_1 \rangle$ and (b) imaginary $\langle \epsilon_2 \rangle$ parts of the $\langle \epsilon \rangle$ spectra of ZnS. The solid lines represent the data of this work. The solid circles are data of Ref. 1 and the dashed line is the fitted curve of Ref. 1.

compared with those reported by Adachi *et al.* [1] who presented their results as a smooth curve fit to their data. Figures 2(a) and (b) show the real and imaginary part of the pseudodielectric function $\langle \epsilon \rangle$ of this work (solid line) along with the data of Ref. 1 (solid circles) and the fitted curve in Ref. 1 (dashed line). Identification of $E_0/E_0 + \Delta_0$ and E_1 peaks in Fig. 2(b) followed after that of Ref. 1. Since the value of $\langle \epsilon_2 \rangle$ in the region of E_1 we obtained in this work is higher than the fitted curve by Adachi *et al.*, we concluded that Adachis data seem to contain information of surface layers such as natural oxide overlayers or any kind of contamination [12]. This analysis should be reasonable because Fig. 2(b) shows that Adachis data points start to deviate clearly from its fitted curve at 5.3 eV. In other words the real data points of Adachi *et al.* should have much smaller $\langle \epsilon_2 \rangle$ values than those of this work at the E_1 peak region. Therefore we believe that current dielectric function values of this work best represent those of ZnS.

Dielectric-related optical constants, such as the complex refractive indices ($n^* = n + ik$), absorption coefficients (α), and reflectances (R) are obtained from the measured dielectric function. The real refractive index $n(E)$ and extinction coefficient $k(E)$ can be determined by the formula,

$$n(E) = \left[\frac{[\epsilon_1(E)^2 + \epsilon_2(E)^2]^{1/2} + \epsilon_1(E)}{2} \right]^{1/2} \quad (1a)$$

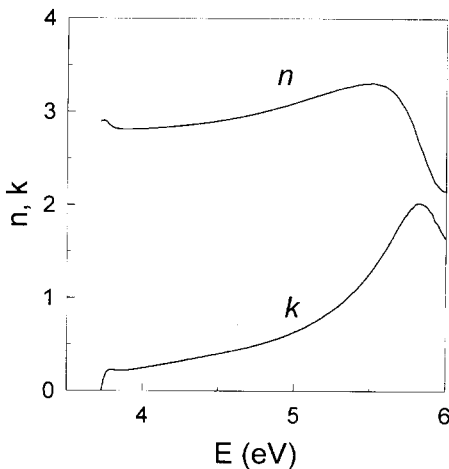


Fig. 3. Numerically calculated spectral dependence of $n(E)$ and $k(E)$ for ZnS.

$$k(E) = \left[\frac{[\epsilon_1(E)^2 + \epsilon_2(E)^2]^{1/2} - \epsilon_1(E)}{2} \right]^{1/2} \quad (1b)$$

Figure 3 shows the numerically calculated spectral dependence of $n(E)$ and $k(E)$ for ZnS, which are obtained from Eq. (1a) for n and Eq. (1b) for k .

The absorption coefficient $\alpha(E)$ and reflectance $R(E)$ can be given by

$$\alpha = \frac{4\pi}{\lambda} k(E) \quad (2a)$$

$$R(E) = \frac{[n(E)-1]^2 + k(E)^2}{[n(E)+1]^2 + k(E)^2} \quad (2b)$$

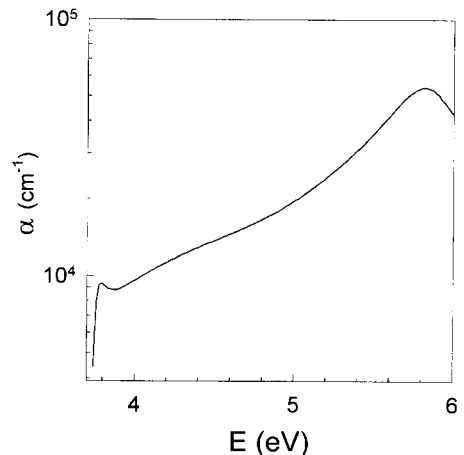


Fig. 4. Numerically calculated spectral dependence of $\alpha(E)$ for ZnS.

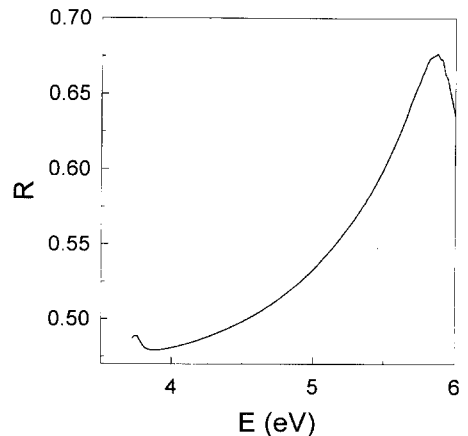


Fig. 5. Numerically calculated spectral dependence of the reflectance $R(E)$ for ZnS.

Numerically calculated spectral dependence of the absorption coefficient $\alpha(E)$ and reflectance $R(E)$ for ZnS by above equations are also shown in Fig. 4 and Fig. 5, respectively, which are helpful for optoelectronic device applications.

IV. Conclusion

We have measured the dielectric function of zinc-blend ZnS film grown on GaAs substrate by Hot-Wall Epitaxy, using spectroscopic ellipsometry in the 3.7-6.0 eV region at room temperature.

After proper chemical etching treatment to remove the oxide overlayer on ZnS, we obtained the best results of the dielectric function spectra of ZnS reported so far by SE, confirmed by the fact that our experimental data of $\langle \epsilon_2 \rangle$ at the E_1 peak region have much bigger values than those of theoretical and experimental results reported so far. Dielectric-related optical data, such as the complex refractive indices and absorption coefficients, are also presented, which are helpful for the design and analysis of optoelectronic devices.

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