Journal of the Korean Vacuum Science & Technology; JKVST
Vol.5, No.2, 2001, pp.52～55

Study on the optical properties of ZnS and its natural oxide by spectroscopic ellipsometry

T. J. Kim, Y. D. Kim*, and Y. D. Choi*

Department of Physics, Kyung Hee University, Seoul 130-701
**Department of Physics, Mokwon University, Taejon 302-729*
(Received November 15, 2001)

Abstract

We report best dielectric function of ZnS by spectroscopic ellipsometry in the 3.7 - 6.0 eV photon energy range at room temperature. Using proper wet chemical etching procedure, natural overlayer was removed to obtain the pure dielectric function of ZnS, which had a higher $\langle \varepsilon_2 \rangle$ value at the E_1 band gap peak than that previously reported. We also determined the dielectric property of the natural overlayer on ZnS by following the evolution of $\langle \varepsilon \rangle$ with chemical etching. We found that the optical property of the overlayer was well described by amorphous semiconductor model.

1. Introduction

Spectroscopic ellipsometry (SE) is an excellent technique for investigating the bulk dielectric response $\langle \varepsilon \rangle = \langle \varepsilon_1 \rangle + \langle i\varepsilon_2 \rangle$ of semiconductors and semiconductor alloys [1]. (The pseudodielectric function $\langle \varepsilon \rangle$ is defined as the measured or apparent dielectric function obtained by reducing the ellipsometric data with the two-phase (ambient-substrate) model, [2] ignoring the presence of possible surface overlayers and microscopic roughness layer.) A knowledge of the optical properties 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 performed to determine the intrinsic bulk dielectric response ε [3-5]. In this paper we present dielectric function spectra of zincblende-type ZnS and its oxide overlayer at room temperature between 3.7-6.0 eV obtained by SE measurements.

It is well known that overlayers complicate efforts to obtain pure dielectric functions [6]. There are two basic methods of minimizing overlayer effects; one is the direct approach of removing overlayers as much as possible by chemical etching, and the other is indirect approach of correcting the $\langle \varepsilon \rangle$ data by mathematically removing the overlayer with assumed overlayer dielectric function ε_o and thickness d within the three-phase (substrate-overlayer-ambient) model [2]. In this work, we first used direct chemical etching to remove overlayer to obtain intrinsic dielectric function of ZnS, and then used indirect method to extract overlayer dielectric function ε_o.

2. Experimental Details

ZnS epilayer was grown on Cr-doped semi-insulating GaAs (100) substrate by hot-wall epitaxy(HWE) [7]. The source material was 5N poly-crystalline ZnS powder. The GaAs substrate was ultra-sonically cleaned by trichloroethylene, acetone, and methanol in sequence, and then etched in 50-60℃ $3H_2SO_4 : H_2O_2 : H_2O$ for 1 min and rinsed with deionized water. After drying with Ar gas, it was put on the substrate holder in the HWE set up, and then was preheated at 600℃ for 20

※ E-mail : ydkim@khu.ac.kr

min to remove the remaining impurities and the oxide overlayer on the substrate surface. Following the preheating, the substrate was cooled at a rate of 5℃/min to the growth temperature. The growth temperatures for the source, the wall, and the substrate were 700℃, 570℃, and 400℃, respectively. The growth rate was maintained at about 1~2 Å/s during the growth of the epilayer.

Pseudodielectric function spectra $\langle \varepsilon(\omega) \rangle = \langle \varepsilon_1(\omega) \rangle + i\langle \varepsilon_2(\omega) \rangle$ 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 [1,8,9]. 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°. A wet chemical etching procedure was carried out while the ellipsometric data were taken in a windowless cell in flowing purified N_2 to minimize surface contamination.

3. Results and Discussion

SE measurement is very sensitive to the existence of overlayers, so we have performed an in-situ chemical etching procedure as described in Ref. 8 to obtain the most abrupt interrupt interface. Under this condition $\langle \varepsilon \rangle$ can be considered to be as the best representation of the true bulk dielectric response of ZnS. Even if the E_2 band gap peak is most commonly used as the indicator of abruptness, it is out of our spectral range. Accordingly, we maximized the value of $\langle \varepsilon_1 \rangle$ value at the E_1 peak instead. We used deionized water, methanol, and NH_4OH(30%):methanol mixture solution to remove overlayer. Fig. 1 shows the final spectrum(solid line) of the chemical etching along with the initial spectrum

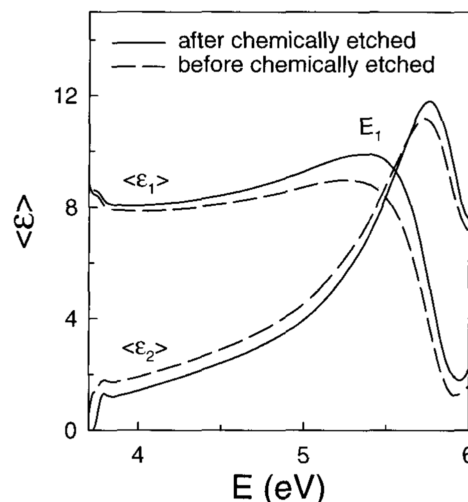

Fig. 1. $< \varepsilon >$ spectra of ZnS before(dashed line) and after(solid line) chemical etching. The latter is our best approximation to the intrinsic bulk dielectric response ε of ZnS.

measured prior to the chemical etching(dashed line). We found that the highest value of $\langle \varepsilon_2 \rangle$ at E_1 peak was 11.83, which was 11.47 in our previous report [5]. The-biggest-is-the-best rule [10] tells that the final spectrum in this work should represent the best intrinsic dielectric response of ZnS reported so far. We conjecture that the previous experiment could not remove the overlayer completely.

In Fig. 2 we compare our best spectrum(solid lines) with those reported by Adachi *et al.* [3] who have presented their results as a model lineshape fit(dashed line) to their experimental data(solid circles). Since the value of $\langle \varepsilon_2 \rangle$ in the region of E_1 band gap obtained in this work is higher than the fitted curve of Adachi *et al.*, we conclude that Adachi's data seem to contain information of surface overlayers such as natural oxide layers or any kind of contaminations [11]. This interpretation should be reasonable because Fig. 2 shows that Adachi's $\langle \varepsilon_2 \rangle$ data points start to deviate clearly from its fitted curve at 5.3 eV. In other words the experimental data points of Adachi *et al.* should have much smaller $\langle \varepsilon_2 \rangle$ values than those of this work at the E_1 peak region. Therefore we believe that our current

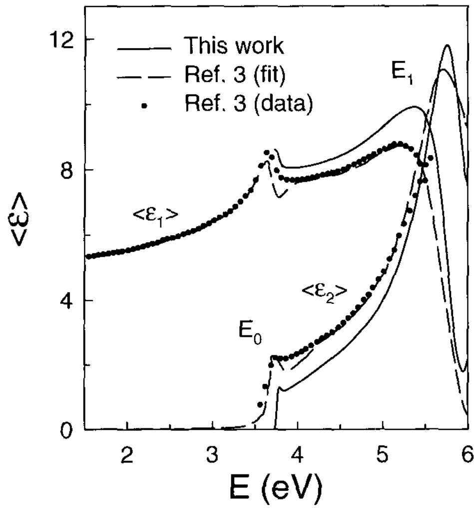

Fig. 2. < ε > spectra of ZnS. The solid line represents the data of this work. The solid circles are data of Ref. 3, and the dashed lines are the fitted curves of Ref. 3.

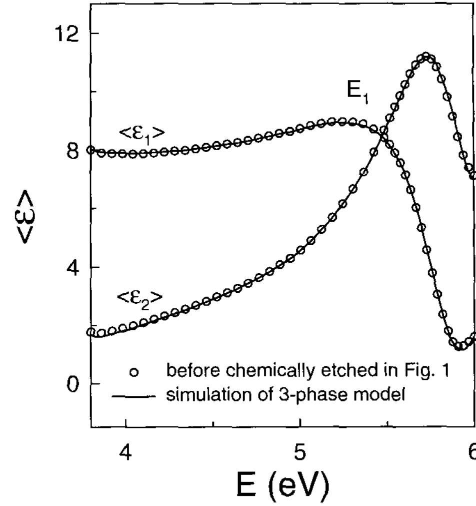

Fig. 3. Open circles : < ε > spectrum of Fig. 1 before chemical etching. Solid lines : simulation of 3-phase model with amorphous semiconductor model for overlayer.

dielectric function values in this work best represent those of ZnS.

To obtain dielectric function of oxide overlayer on ZnS, we have investigated specifically the possibility of representing overlayer dielectric function ε_o by an amorphous semiconductor model [12] which is given as,

$$\varepsilon(\omega)=1+\frac{2D}{\pi}\left[-\frac{E_g^2}{(\hbar\omega+i\Gamma)^2}\ln\left(\frac{E_c}{E_g}\right)+\frac{1}{2}\left(1+\frac{E_g}{\hbar\omega+i\Gamma}\right)^2\ln\frac{\hbar\omega+i\Gamma+E_c}{\hbar\omega+i\Gamma+E_g}+\frac{1}{2}\left(1-\frac{E_g}{\hbar\omega+i\Gamma}\right)^2\ln\frac{\hbar\omega+i\Gamma-E_c}{\hbar\omega+i\Gamma-E_g}\right]$$

where E_g is optical energy gap, E_c is high-energy cutoff, D is nondirect-transition strength, and Γ is phenomenological damping energy. In short, this model is an extension of that of Tauc *et al.* [13,14], and assumes nondirect optical transitions between the valence and conduction bands. The 3-phase model(substrate-overlayer-ambient) was used to represent the original spectrum (dashed line) of Fig. 1. The overlayer dielectric function ε_o was modeled as described by above equation, and the substrate dielectric function ε was taken to be the final spectrum(solid line) in Fig. 1. The overlayer thickness and the 4 parameters in the model equation were used as fitting parameters in least-square analysis. The best fit was obtained with a thickness d=10.7 Å, E_g=5.09, E_c=15.15, D=8.52, and Γ=0.565. The result of the fitting is shown as solid lines in Fig. 3 showing excellent agreement with the open circle data which is the original spectrum(dashed line) in Fig. 1.

Figure 4 shows the resulting ZnS overlayer dielectric function yielded by above 4 parameters. The fit resulted in the proper values for each parameters to be able to describe the behavior of typical amorphous materials, having broad peak at $\langle\varepsilon_1\rangle$ spectrum and slow increase in higher energy region with long tail in lower energy region at $\langle\varepsilon_2\rangle$ spectrum. Natural oxide overlayers are mostly amorphous crystals. The disappearance of a sharp band gap structure in Fig. 4 is due to the break down of crystal periodicity in typical amorphous materials. Since the oxide dielectric function of Fig. 4 was not obtained by inversion calculation of multilayer model but by modelization of an analytic equation, we believe that the dielectric function can be extended

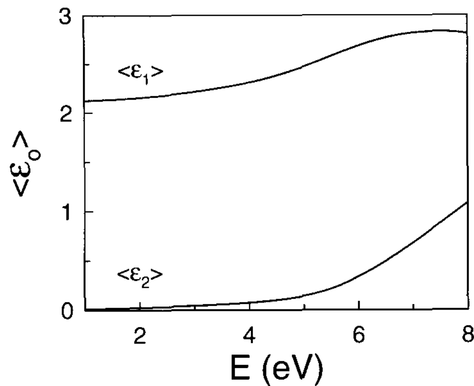

Fig. 4. ZnS overlayer dielectric function ε_o described by amorphous semiconductor model.

over its energy range of fitting. We concluded that the natural oxide overlayer on ZnS was well described by a typical amorphous semiconductor model, and our first report on oxide dielectric function of ZnS should be an appropriate starting point for further study on the oxide overlayer of ZnS.

4. Conclusions

We report room-temperature dielectric function spectra from 3.7 to 6.0 eV for ZnS films grown on GaAs substrates. The most abrupt interrupted surface was prepared with proper chemical etching, which removed oxide overlayers on the top. Using the three-phase model, we extracted the dielectric function ε_o of the overlayer. We found that the oxide overlayer of ZnS was well explained by amorphous semiconductor model.

Acknowledgments

This work was supported by BK21 program. The work at Mokwon University was supported by Korea Research Foundation Grant(KRF-2000-015-DP0158).

References

[1] D. E. Aspnes and A. A. Studna, Appl. Opt. **14**, 220 (1975).

[2] R. M. Azzam and N. M. Bashara, *Ellipsometry and Polarized Light* (North-Holland, Amsterdam, 1977).

[3] S. Ozaki and S. Adachi, Jpn. J. Appl. Phys. **32**, 5008 (1993).

[4] S. Lee, B. Park, and S. Oh, Jpn. J. Appl. Phys. **36**, 5346 (1997).

[5] M. S. Lee, M. S. Koo, T. J. Kim, Y. D. Kim, Y. M. Yoo, B. O, and Y. D. Choi, J. Kor. Vac. Soc. **3**, 112 (1999).

[6] D. E. Aspnes and A. A. Studna, Phys. Rev. B **27**, 985 (1983).

[7] S. Nam, B. O, K. S. Lee, and Y. D. Choi, J. Cryst. Growth. **194**, 61 (1998).

[8] D. E. Aspnes and A. A. Studna, Appl. Phys. Lett. **39**, 316 (1981).

[9] D. E. Aspnes, Opt. Commun. **8**, 222 (1973).

[10] D. E. Aspnes and H. Arwin, J. Vac. Sci. Thchnol. A **2**, 1309 (1984).

[11] D. E. Aspnes, J. Vac. Sci. Technol. **17**, 1057 (1980).

[12] S. Adachi, J. Appl. Phys. **70**, 2304 (1991).

[13] J. Tauc, R. Grigorovici, and A. Vancu, Phys. Status Solidi **15**, 627 (1966).

[14] J. Tauc, in *Optical Properties of Solids*, edited by F. Abeles (North-Holland, Amsterdam, 1972), p.277.