Interband transitions in gallium sulfide layered single crystals by ellipsometry measurements

3 authors, including:

Mehmet Isik
Atilim University
42 PUBLICATIONS **110** CITATIONS

SEE PROFILE

Nizami Mamed Gasanly
Middle East Technical University
235 PUBLICATIONS **1,579** CITATIONS

SEE PROFILE

Interband transitions in gallium sulfide layered single crystals by ellipsometry measurements

M. Isik [a,*], N.M. Gasanly [b], R. Turan [b]

[a] Department of Electrical and Electronics Engineering, Atilim University, 06836 Ankara, Turkey
[b] Department of Physics, Middle East Technical University, 06800 Ankara, Turkey

ARTICLE INFO

ABSTRACT

Spectroscopic ellipsometry measurements on the GaS single crystals are presented in the energy range of $1.2-6.2$ eV at room temperature. Optical constants; pseudorefractive index, pseudoextinction coefficient, real and imaginary parts of the pseudodielectric function were determined. Analysis of the second derivative of real and imaginary parts of the pseudodielectric constant revealed five transitions with critical point energies of 3.95, 4.22, 4.51, 4.75 and 5.50 eV. These energies were assigned to interband transitions according to theoretical study of GaS band structure available in literature.

© 2012 Elsevier B.V. All rights reserved.

1. Introduction

Gallium sulfide (GaS) crystal belongs to the family of III–VI layered semiconductors. It crystallizes in the hexagonal structure with lattice parameters of $a=0.3578$ and $c=1.547$ nm [1]. Each layer in the crystal structure is composed of two gallium and two sulfur atoms stacked along the c-axis with a repeating unit of S–Ga–Ga–S [2]. In GaS crystals, weak Van der Waals forces dominate the interlayer interactions, while strong covalent bonds are effective on the intralayer forces. GaS has an importance position in the fabrication and application of optoelectronic devices due to its significant structural, electrical and optical properties. Many experimental and theoretical studies on the characterization of GaS crystals and thin films have been accomplished to view its application areas and to set light to new possible technological areas. Optical absorption measurements on GaS crystals at room temperature revealed the presence of indirect transitions with 2.59 eV energy and direct transitions at approximately 0.45 eV higher in energy [3]. These optical properties make GaS a promising material in the fabrication of near-blue-light emitting devices [4]. GaS exhibits photoluminescence and electroluminescence in the green-blue region [5]. Other some publications were about photoconductivity [6] and temperature-dependent absorption and piezoreflectance measurements [7,8]. The characterization of GaS thin films have also been reported in Refs. [9,10].

Previously, we have performed the low-temperature photoluminescence (PL) [11] and Raman scattering [12] on GaS layered crystals.

Three bands at energies of 2.22, 2.02 and 1.59 eV have been observed from PL measurements. In the same work, temperature and excitation intensity dependencies of the observed bands have revealed that all bands originate from donor-acceptor pair recombination processes.

Researches carried out to get any information about the optical properties of GaS contribute to the appropriate application areas of the crystal. For this purpose, in the present work, we introduce the spectral dependencies of the optical constants; real and imaginary parts of the pseudodielectric function, pseudorefractive index and pseudoextinction coefficient, and interband transition energies using ellipsometry measurements. Previously, Ho and Lin [7], Schlüter et al. [13] and Grandolfo et al. [14] studied the optical constants of gallium sulfide crystals. Piezoreflectance measurements carried out in the energy range of $2-5$ eV at $T=15$ K showed the presence of three interband transitions with energies around 3, 4 and 4.5 eV [7]. In Ref. [13], interband transition energies have been found using reflectivity and wavelength modulated reflectivity measurements at $T=5$ K temperature and in the $3-6$ eV energy range. Grandolfo et al. [14] reported the real and imaginary parts of the dielectric constant using Kramers–Kronig transformation of the reflectivity ($T=300$ K) and thermally modulating reflectivity ($T=77$ K). But they did not give any analysis on the dielectric function to represent the interband transition structures. As distinct from these works, we give the real and imaginary parts of the pseudodielectric function, pseudorefractive indices and pseudoextinction coefficients by means of room temperature ellipsometry meaurements in the $1.2-6.2$ eV spectral range. Besides, the obtained spectra of the real and imaginary parts of the pseudodielectric function have been analyzed using the second

* Corresponding author. Tel.: +90 312 5868715; fax: +90 312 5868091.
E-mail address: misik@atilim.edu.tr (M. Isik).

derivative analysis method to find the interband transition critical point energies.

2. Experimental details

Gallium sulfide polycrystals were synthesized using high-purity elements (at least 99.999%) taken in stoichiometric proportions. GaS single crystals were grown by the Bridgman method. The samples were prepared by easy cleavage an ingot parallel to the crystal layer (perpendicular to the **c**-axis).

The spectroscopic ellipsometry measurements of the crystal were carried out at room temperature in the $1.2-6.2$ eV spectral range using SOPRA GES-5E model ellipsometry with high resolution of 0.01 eV. The measurements were performed on the layer-plane (0 0 1) crystal surfaces with light polarization $\boldsymbol{E} \perp \boldsymbol{c}$, where $\boldsymbol{c}$ is the optical axis. Since the crystal has layered structure, it is very difficult to perform measurements on any other than the sample natural layer-plane surfaces. For measurements the samples with thickness about 1 mm were used. Since the freshly cleaved platelets (along the layer plane (0 0 1)) were mirror-like, no further polishing and cleaning treatments were required.

3. Theoretical model

As a non-destructive optical measurement technique, ellipsometry characterizes the light reflected from the samples after a linearly polarized light beam is irradiated onto the sample. Two values ψ and Δ are measured as an ellipsometric data. ψ and Δ represent the amplitude ratio and phase shift of the parallel (p) and perpendicular (s) components of the reflected light, respectively. Depending on the reflection and transmission principles of the light, ψ and Δ are given in terms of the Fresnel coefficients (r_p and r_s) of the polarized light as

$$\rho = r_p/r_s = \tan(\psi)e^{i\Delta} \tag{1}$$

where ρ defines the complex reflectance ratio of the polarized light. A simple two phase (ambient-substrate) optical model gives the pseudodielectric constant of the bulk, flat samples as [15–18]

$$<\varepsilon> = <\varepsilon_1> + i<\varepsilon_2> = \sin^2(\phi)\left[1 + \left(\frac{1-\rho}{1+\rho}\right)^2 \tan^2(\phi)\right], \tag{2}$$

where φ is the angle of incidence. Once the complex pseudodielectric function is obtained from Eq. (2), the pseudorefractive index ($<n>$) and pseudoextinction coefficient ($<k>$) are calculated using the relations

$$<n> = [\left(<\varepsilon_1> + (<\varepsilon_1^2> + <\varepsilon_2^2>)^{1/2}\right)/2]^{1/2}, \tag{3}$$

$$<k> = [\left(-<\varepsilon_1> + (<\varepsilon_1^2> + <\varepsilon_2^2>)^{1/2}\right)/2]^{1/2} \tag{4}$$

After the pseudodielectric function of the sample is obtained using the convenient optical model, this spectral data can be used to find the critical point (CP) energies of the interband transitions from the second derivative analysis of the pseudodielectric constant. The theoretical expression giving the relation between second derivative spectra, photon energy (E), amplitude (A), critical point energy (E_{cp}), broadening parameter (Γ) and phase angle (ϕ) is [15–18]

$$\frac{d^2<\varepsilon>}{dE^2} = m(m-1)A\exp(i\phi)(E-E_{cp}+i\Gamma)^{m-2} \quad (m \neq 0) \tag{5}$$

$$\frac{d^2<\varepsilon>}{dE^2} = A\exp(i\phi)(E-E_{cp}+i\Gamma)^{-2} \quad (m = 0) \tag{6}$$

The values of parameter m depend on the dimensions of the wave vectors having a part in the optical transitions. The m values are equal to -1, $-1/2$, 0 and $+1/2$ for excitonic, one-, two- and three-dimensional lineshapes, respectively.

4. Results and discussion

Fig. 1 shows the experimental ellipsometric spectra of the real ($<\varepsilon_1>$) and imaginary ($<\varepsilon_2>$) parts of the pseudodielectric constants of the GaS crystal in the energy range of $1.2-6.2$ eV. The spectrum of the imaginary part indicates three peaks which can be referred to strong absorption of photon energy at the corresponding critical points. Moreover, there is a decrease in the spectrum of $<\varepsilon_2>$ between the energy values of 2.42 and 2.49 eV. This decrease can be attributed to the energy band gap transition occurring in this energy interval. Theoretically, $<\varepsilon_2>$ values should be zero below the band gap energy. However, this condition is not satisfied in our measurements and there exist residual absorptions below the band gap energy of the studied sample. At present time the origin of this below-band gap feature for GaS crystals is not clear. Earlier, the absorption tails below the fundamental gap edge were also observed in the study on optical properties of $CuIn_5Se_8$ and $CuGa_5Se_8$ [19] and $CuAl_xIn_{1-x}Se_2$ [20] crystals by ellipsometric measurements. According to the authors, these tails result from intrinsic contributions (alloy disorder) and deviation from stoichiometry. In our sample, one of the possible reasons may be the deviation from stoichiometry during the crystal growth process. Fig. 2 represents the spectra of pseudo-refractive index and pseudoextinction coefficient calculated from
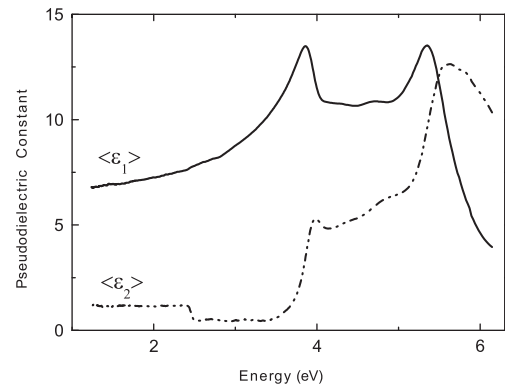

Fig. 1. Spectra of the pseudodielectric function of the GaS crystal. Solid and dot-dashed curves represent the real and imaginary part spectra, respectively.
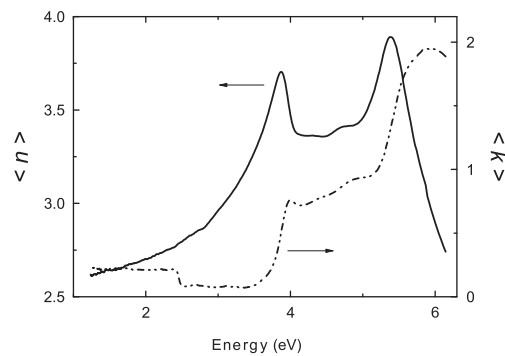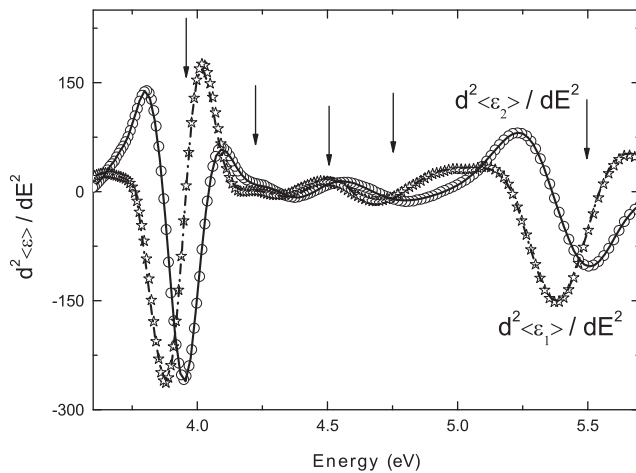

Fig. 2. Spectra of the pseudorefractive index and pseudoextinction coefficient of the GaS crystal. Solid and dot-dashed curves represent the pseudorefractive index and pseudoextinction coefficient spectra, respectively.

Fig. 3. Second-energy derivative of the pseudodielectric function of the GaS crystal. Stars and open circles represent the second-energy derivative spectra of the real and imaginary components, respectively. The solid and dot-dashed curves show the fit to the experimental data. The arrows indicate the positions of critical point energies.

Eqs. (3) and (4). The pseudorefractive indices of the GaS crystal vary between 2.65 and 3.05 in the visible spectral range.

The critical point analyses of the GaS crystals have been performed using the second derivative of the $<\varepsilon_1>$ and $<\varepsilon_2>$ spectra shown in Fig. 3. Throughout the process of obtaining the second derivative spectra, we have smoothed the each graph using low binomial filtering. Smoothing process was applied without giving any distortion to the main experimental curves. Then the spectra of the GaS crystal are fitted using Eq. (5) for the value of $m = -1$ (excitonic optical transition). This value of parameter m was chose due to its lowest mean square deviation demonstration. We have observed some deviations of the spectra of real and imaginary parts in some energy ranges during the process of smoothing. Therefore, we have carried out the critical point analysis method in the energy ranges of $3.6 - 5.7$ eV which do not have any smoothing problem. Five interband transitions at CP energies of 3.95, 4.22, 4.51, 4.75 and 5.50 eV were found as a result of least square fitting program. The arrows in Fig. 3 indicate the positions of these energies.

The obtained CP energies were assigned to interband transitions according to theoretical study of GaS band structure [13]. In this study, Schlüter et al. presented the calculated interband transition energies using reflectivity and wavelength modulated reflectivity measurements at $T = 5$ K temperature and in the $3 - 6$ eV energy range. Our CP energies show a good consistency with the corresponding energy values in Ref. [13] (Table 1). An energy difference of nearly 0.08 eV was observed between the results. This deviation comes from the variation of energy values with temperature. In accordance with Ref. [13], the first main peak $GS2$ (3.95 eV) corresponds to the transition between the topmost valence band and the lowest conduction band along the lines T, S and their connecting line in $\boldsymbol{k}$ space. For designation of the observed peaks we used the notations of Ref. [13]. The peak

Table 1
Critical point energies for GaS single crystals.

Ref.	Temp. (K)	GS2	G1	S1	S2	S3
This work	300	3.95	4.22	4.51	4.75	5.50
Ref. [13]	5	4.03	4.30	4.61	4.82	5.57

$G1$ (4.22 eV) is assigned to transitions between the topmost valence band and the lowest conduction band near the point H in the hexagonal Brillouin zone. The peak $S1$ (4.51 eV) corresponds to the transitions from the lower lying valence band to the bottom of lowest conduction band at the point Γ of hexagonal Brillouin zone. The peak $S2$ (4.75 eV) and the second main peak $S3$ (5.50 eV) originate mainly from transitions between the lower lying valence band and the upper conduction band at the point M and along the line Σ, respectively.

5. Conclusion

Using the spectroscopic ellipsometry measurements for light polarization $\boldsymbol{E} \perp \boldsymbol{c}$ in the $1.2 - 6.2$ eV spectral range at room temperature, the complex pseudodielectric function, pseudorefractive index and pseudoextinction coefficient of the GaS single crystals were obtained. The critical point energies of interband transition structures have been found from the analysis of second derivative spectra of the pseudodielectric constant. These energies were assigned to interband transitions according to theoretical study of GaS band structure available in literature.

References

[1] O.Z. Alekperov, M.Z. Zarbaliev, Inorg. Mater. 10 (1971) 971.
[2] A. Gouskov, J. Camassel, L. Gouskov, Prog. Cryst. Growth Charact. 5 (1982) 323.
[3] E. Aulich, J.L. Brebner, E. Mooser, Phys. Status Solidi 31 (1969) 129.
[4] T. Aono, K. Kase, A. Kinoshita, J. Appl. Phys. 74 (1993) 2818.
[5] A. Cingolani, A. Minafra, P. Tantalo, C. Paorici, Phys. Status Solidi A 4 (1971) K83.
[6] G.A. Gamal, M.I. Azad, J. Phys. Chem. Solids 66 (2005) 5.
[7] C.H. Ho, S.L. Lin, J. Appl. Phys. 100 (2006) 083508.
[8] C.H. Ho, K.W. Huang, Solid State Commun. 136 (2005) 591.
[9] M.R. Lezell, P. O'Brien, D.J. Otway, J.H. Park, Chem. Mater. 12 (1999) 3430.
[10] S. Suh, D.M. Hoffman, Chem. Mater. 9 (2000) 2794.
[11] A. Aydinli, N.M. Gasanly, K. Goksen, J. Appl. Phys. 88 (2000) 7144.
[12] N.M. Gasanly, A. Aydinli, H. Ozkan, C. Kocabas, Solid State Commun. 116 (2000) 147.
[13] M. Schlüter, J. Camassel, S. Kohn, J.P. Voitchovsky, Y.R. Shen, M.L. Cohen, Phys. Rev. B 13 (1976) 3534.
[14] M. Grandolfo, F. Somma, P. Vecchia, Phys. Rev. B 5 (1972) 428.
[15] M. Cardona, Modulation Spectroscopy, Academic, New York, 1969.
[16] D.E. Aspnes, Handbook on Semiconductors, North-Holland, Amsterdam, 1980.
[17] J.W. Garland, C. Kim, H. Abad, P.M. Raccah, Phys. Rev. B 41 (1990) 7602.
[18] S.G. Choi, D.H. Levi, C. Martinez-Tomas, V.M. Sanjose, J. Appl. Phys. 106 (2009) 053517.
[19] L. Duran, J. Castro, J. Naranjo, J.R. Fermin, C.A. Durante Rincon, Mater. Chem. Phys. 114 (2009) 73.
[20] M.I. Alonso, M. Garriga, C.A. Durante Rincon, M. Leon, Appl. Phys. Lett. 88 (2000) 5796.