JOURNAL OF NANO- AND ELECTRONIC PHYSICS
Vol. **9** No 5, 05025(6pp) (2017)

ЖУРНАЛ НАНО- ТА ЕЛЕКТРОННОЇ ФІЗИКИ
Том **9** № 5, 05025(6cc) (2017)

Spectroscopic Ellipsometry Studies and Temperature Behaviour of the Dielectric Function of $TlInS_2$ Layered Crystal

O.O. Gomonnai[1,*], O. Gordan[2], P.P. Guranich[1], P. Huranich[1], A.G. Slivka[1], A.V. Gomonnai[1,3], D.R.T. Zahn[2]

[1] *Uzhhorod National University, 46, Pidhirna Str., 88000 Uzhhorod, Ukraine*
[2] *Semiconductor Physics, Technische Universität Chemnitz, 70, Reichenhainer Str., D-09107 Chemnitz, Germany*
[3] *Institute of Electron Physics, Ukr. Nat. Acad. Sci., 21, Universytetska Str., 88017 Uzhhorod, Ukraine*

(Received 30 June 2017; revised manuscript received 11 August 2017; published online 16 October 2017)

Real and imaginary parts of the dielectric function of $TlInS_2$ single crystals in the spectral range from 1 to 5 eV were determined within a temperature range of 133–293 K from spectroscopic ellipsometry measurements. The energies of interband transitions (critical points) for $TlInS_2$ were obtained from the second derivatives of the dielectric function. Temperature dependent features observed in the temperature range of the structural phase transition (190–220 K) and at lower temperatures are discussed.

Keywords: Dielectric function, Optical transitions, Structural phase transitions.

DOI: 10.21272/jnep.9(5).05025 PACS numbers: 78.67. – n, 78.90. + t

1. INTRODUCTION

Layered semiconductors are interesting objects for research due to their characteristics resulting from the quasi-two-dimensionality and structural anisotropy which are important for applications, in particular, in optoelectronics and sensorics. This class of materials includes $A^{III}B^{III}C^{VI}$ chalcogenides (A = Tl, B = In, Ga, C = S, Se), among them $TlInS_2$ being of special interest, possessing not only semiconducting, but also ferroelectric properties in a certain temperature range [1, 2]. It should be mentioned that in $TlInS_2$ crystals a series of successive phase transitions (PTs) involving an incommensurate phase in the temperature range of 190-220 K are observed. A phenomenological approach applied for the description of the phase transitions in $TlInS_2$ enabled qualitative agreement with the experimental dependence of thermodynamical functions on temperature to be obtained [3-5]. For these materials extensive temperature studies of acoustic [6], electrical [7-12], and optical [13-16] properties were carried out while ellipsometric studies of $A^{III}B^{III}C^{VI}$ (A = Tl, B = (In, Ga), C = (S, Se)) chalcogenides were subject of several publications [17-26].

In particular, an analysis of the second derivative spectra of the dielectric function for $TlGaS_{2x}Se_{2(1-x)}$ [17], $TlGa_xIn_{1-x}S_2$ [18], and $TlGa_xIn_{1-x}Se_2$ [19] solid solutions was performed. Note that for $TlInS_{2x}Se_{2(1-x)}$ the analysis was carried out only for set of compositions (x = 0.25, 0.5, and 0.75) at room temperature [20]. Recently study of dielectric functions and interband critical points of $TlIn(S_{1-x}Se_x)_2$ (x = 0.05, 0.08, 0.25) solid solution crystals were performed within a temperature interval 140-293 K [21]. Interband transitions for $TlGaSe_2$ [22, 23], $TlGaS_2$ [23, 24], $TlInSe_2$ [25], and $TlInS_2$ [24, 27] were determined. Ellipsometric measurements in the photon energy range 1.5-4.2 eV were performed for $TlInS_2$ in the temperature interval of 100-400 K [26]; however, the behaviour of the real and imaginary parts of the $TlInS_2$ dielectric function was analysed in detail only within the energy range of 2-2.7 eV, *i.e.* in the range of direct and indirect transitions. Moreover, the temperature dependence of the exciton transition energy was analysed [26]. To our knowledge, in the literature available no analysis of the $TlInS_2$ dielectric function second derivative spectra, neither its amplitude A, critical point energy E_{cp}, broadening parameter Γ, and phase angle φ were reported for various temperatures, including the phase transition range.

In this study, we present the temperature dependence of the dielectric function spectra of $TlInS_2$ from 133 to 293 K in the photon energy range of 1-5 eV. The critical points (CPs) for interband optical transitions were obtained from the dielectric function. From the temperature behaviour of the dielectric function and the CPs, we discuss the effect of structural phase transitions in the 190-220 K region on the electronic band structure of $TlInS_2$.

2. EXPERIMENTAL

$TlInS_2$ single crystals were grown by the Bridgman technique [27]. Spectroscopic ellipsometry measurements were carried out using a Variable Angle Spectroscopic Ellipsometer J.A. from Woollam Co., Inc. The angle of the incident light beam was adjusted to 70°. The measurements were performed on the layer-plane (001) crystal surfaces perpendicular to the optical axis ***c***. The real (ε_1) and imaginary (ε_2) parts of the effective dielectric function of the $TlInS_2$ single crystals were obtained in the spectral range from 1 to 5 eV. The temperature dependent measurements of ε_1 and ε_2 were performed in the temperature range of 133-293 K using a THMS600 Linkam stage. The measurements were performed at atmospheric pressure. At low temperatures the samples were subjected to nitrogen flow in order to avoid water condensation on the surface.

* gomonnai.o@gmail.com

The spectral dependence of ε_1 and ε_2 built based on the ellipsometric measurements exhibit several features related to interband transition critical points. Their energies were determined by analysing the calculated second energy derivatives of the effective dielectric functions obtained from the spectroscopic ellipsometry data.

3. RESULTS AND DISCUSSION

$TlInS_2$ crystals possessing a monoclinic layered structure are optically biaxial. However, its biaxiality at room temperature is very small according to conoscopic interference pattern data. As follows from the study of the temperature dependence of the orientation of the optical axes plane and the angle between the optical axes in $TlInS_2$, this crystal can be regarded as an uniaxial material with the optical axis ***c*** normal to the layer plane.

Spectroscopic ellipsometry enables one to measure the change in the polarization state undergone by the incident linearly polarized light after reflection from a surface. This change is characterised by the ratio of the complex reflection coefficients corresponding to the polarization within (r_p) and normal to (r_s) the plane of incidence. The measurements are described by the ellipsometric angles ψ and Δ as functions of the photon energy. Construction of a physical model for the reflection coefficients r_p and r_s enables several parameters to be determined by fitting the spectra calculated using Eq. (1) to the experimental measurement data [28]:

$$\rho = \frac{r_p}{r_s} = \tan(\psi)\exp(i\Delta). \qquad (1)$$

The dielectric functions of crystals, thin films, and their materials are obtained using different theoretical optical models. A simple ambient-substrate optical model was used to determine the dielectric function of bulk flat crystals expressed as [27]

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

where ϕ is the angle of incidence.

The spectral dependence of the dielectric function of $TlInS_2$ at temperatures being reduced from 293 K down to 133 K are shown in Fig. 1. As can be seen from the figure, with decreasing temperature the spectra shift towards higher energies in agreement with the data of Ref. [26]. Note that a detailed analysis of the real and imaginary parts of the $TlInS_2$ dielectric function in the energy range of 2-2.7 eV, *i.e.* in the range of direct and indirect transitions was carried out in Ref. [26], therefore we will concentrate our discussion mostly beyond this spectral interval.

However, the ε_2 values for photon energies below 2.4 eV are nearly 2 and it may seem rather strange. One should mention that earlier ellipsometry studies of $TlInS_2$ reported by other authors [23, 26] show controversial data with regard to the ε_2 values below 2.4 eV. While the authors of Ref. [26] report much lower ε_2 close to zero for this spectral range, the value shown in Ref. [23] is practically the same as ours. Moreover, similar ε_2 values (close to 2 and even higher) were reported as well for other materials of $TlInS_2$ type [20, 23]. The origin of this below-bandgap feature is not clear yet. Similarly to the data reported for other selenoindates [29, 30], the authors of Ref. 23 relate this feature to the absorption tails resulting from intrinsic contributions and deviations from stoichiometry which could appear during the crystal growth process.

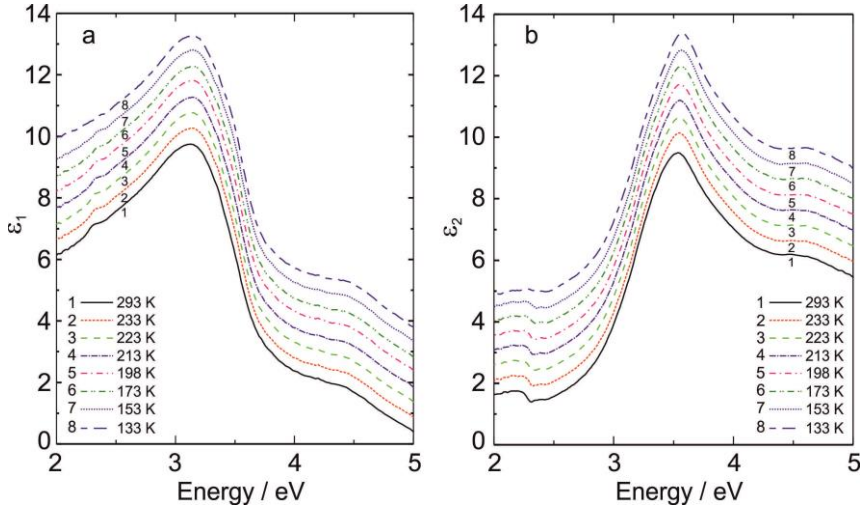

Fig. 1 – Spectral dependence of the real (a) and imaginary (b) parts of the complex dielectric function of $TlInS_2$ at different temperatures. The ε_1 and ε_2 plots for 293 K correspond to the actual values shown at the vertical axes; the corresponding plots for the subsequent temperatures are offset upward by value of 0.5 each in order to avoid the strong superimposement of the curves

Detailed information about the energies of the interband transitions (critical points) for $TlInS_2$ can be obtained from the analysis of the dielectric constant as a function of energy. The critical point analysis can be performed using the second derivative spectra of the dielectric function. The corresponding theoretical expression is given by [28, 31]:

$$\frac{d^2\varepsilon}{dE^2} = m(m-1)A\exp(i\varphi)\left(E - E_{cp} + i\Gamma\right)^{m-2}, \ (m \neq 0), \quad (3)$$

$$\frac{d^2\varepsilon}{dE^2} = A\exp(i\varphi)\left(E - E_{cp} + i\Gamma\right)^{-2}, \ (m=0), \qquad (4)$$

where E is energy, A is the amplitude, E_{cp} is the critical point energy, Γ is the broadening parameter, φ is the phase angle, and m is related to the dimensions of wave vectors taking part in the optical transitions. Each critical point is classified into one, two, and three dimensions according to the dimensions of the wave vectors participating in the optical transition, and the actual m values are equal to – 1/2, 0, and +1/2 for one-, two-, and three-dimensional cases, respectively [28]. Furthermore, when an optical transition exhibits excitonic behaviour, $m = -1$ [28].

Second derivative spectra of the dielectric constant in the energy range 2.5-5 eV for the temperatures T=293 K and T=133 K obtained from those shown in Fig. 1 using Savitzky-Golay filtering are shown in Fig. 2. As can be seen from the figure, the calculated dependence agree with the experimental data. The calculations were performed using a model with 4 CPs, *i.e.* interband transitions with energies E_{c1} = (3.24 ± 0.01) eV, E_{c2} = (3.33 ± 0.01) eV, E_{c3} = (3.59 ± 0.01) eV, and E_{c4} = (4.52 ± 0.05) eV. These second derivative spectra of the dielectric function were analysed in the temperature range 133-293 K. The corresponding amplitude A, critical point energy E_{cp}, broadening Γ, and phase angle φ parameters were determined, their temperature dependence is shown in Figs. 3 and 4.

The temperature dependences of the amplitude A and broadening Γ parameters are shown in Fig. 3. As can be seen from the figure, with a temperature decrease from 293 to 223 K the parameter values remain practically the same. With cooling from 223 down to 133 K the A_1 parameter increases from 0.01 to 0.03 and A_3 from 0.20 to 0.46 while A_2 decreases from 3.10 to 1.83 and A_4 decreases from 0.23 to 0.17. A variation of the broadening parameter Γ is also observed in the phase transition range below 223 K, namely with the temperature decrease down to 133 K Γ_2 and Γ_4 decrease from 0.49 and 0.33 to 0.40 and 0.29, respectively, while Γ_1 and Γ_3 increase from 0.08 and 0.17 to 0.11 and 0.19, respectively.

With the temperature decrease from 293 to 223 K the phase angle φ parameter gradually decreases; however, though practically for all CPs the temperature dependences reveal kinks at the phase transition temperature near 220 K, other features of the temperature behaviour are somewhat different for different critical points. Namely, the $\varphi(T)$ dependence seems to have more features in the case of the first CP, though the data available are not sufficient to provide an unambiguous explanation for the features observed. Unfortunately, in the earlier ellipsometry studies for $TlInS_2$ [23, 26] no data regarding the $\varphi(T)$ dependence were published which at the moment makes the comparison of our results with those of other authors impossible.

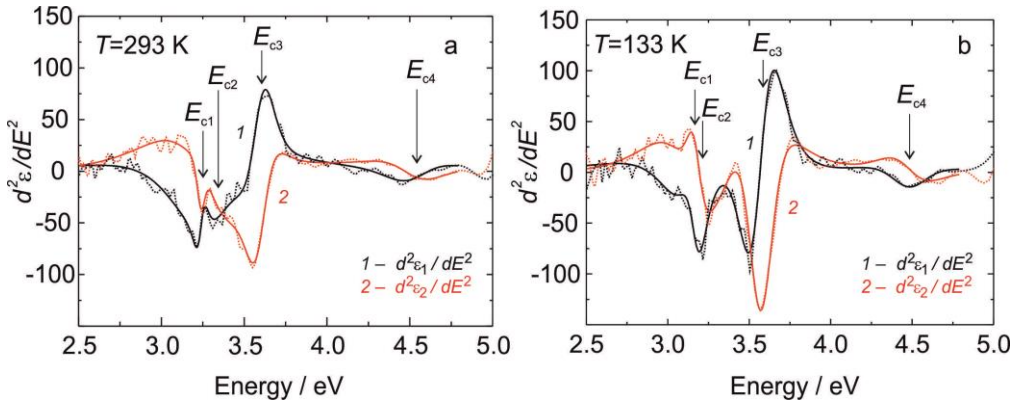

Fig. 2 – Second energy derivative spectra of the dielectric function for $TlInS_2$ at T = 293 K (a) and T =133 K (b). Dotted curves show the experimental data. Solid lines represent fitting by the second-energy derivative spectra of the real and imaginary parts of the dielectric function, respectively

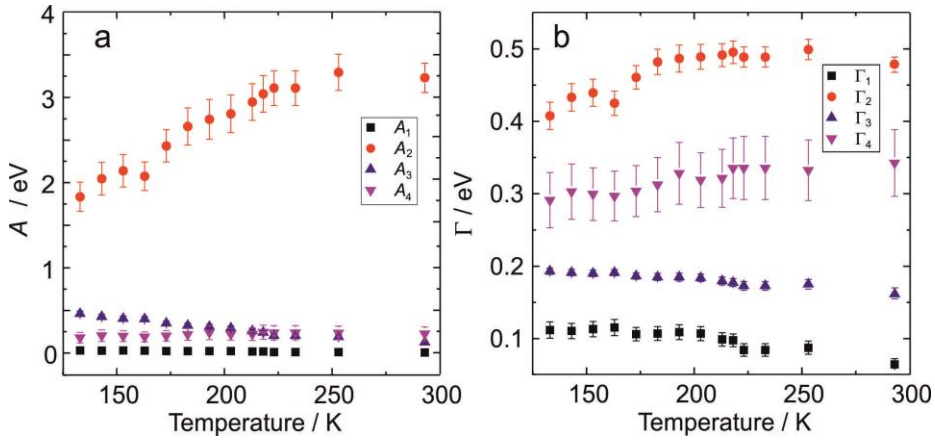

Fig. 3 – Temperature dependences of the amplitude A and broadening Γ parameters for $TlInS_2$

The temperature behaviour of the critical point energies E_{cp} corresponding to interband transitions in $TlInS_2$ was also analysed. At room temperature their values are as follows: $E_{c1} = (3.24 \pm 0.01)$ eV, $E_{c2} = (3.33 \pm 0.01)$ eV, $E_{c3} = (3.59 \pm 0.01)$ eV, and $E_{c4} = (4.52 \pm 0.05)$ eV. The E_{c3} and E_{c4} energy values are in agreement with earlier data of $E_{c3} = 3.50$ eV and $E_{c4} = 4.50$ eV [23] while E_{c1} and E_{c2} values were not reported. However, it is interesting to note that the compositional dependence of the transition energies determined from ellipsometric measurements performed for $TlInS_{2x}Se_{2(1-x)}$ mixed crystals [20, 21] clearly reveals the presence of the two lower transition energies E_{c1} and E_{c2} for the solid solutions in a broad interval of x which can be extrapolated for $TlInS_2$ as 2.8 and 3.15 eV, the second one being in fair agreement with our data.

It can be seen from Fig. 4 that the two higher transition energies E_{c3} and E_{c4} reveal only a slight monotonous red shift with cooling in the whole temperature range. Meanwhile, the two lower transition energies E_{c1} and E_{c2} do not undergo considerable changes upon a temperature decrease from 293 to 223 K, but decrease much more rapidly at cooling from 223 down to 133 K. Note that this red shift of E_{c1} and E_{c2} reveals a rather stepwise than a constant-rate temperature behaviour, the temperature positions of its features being in agreement between each other as well as with the temperature behaviour of the phase $\varphi(T)$ for the lowest-energy critical point observed in Fig. 3. It is worth mentioning that a noticeably similar stepwise-like behaviour was observed for the temperature dependence of the CP parameters in $TlGaS_2$ [32] and $TlGaTe_2$ [25].

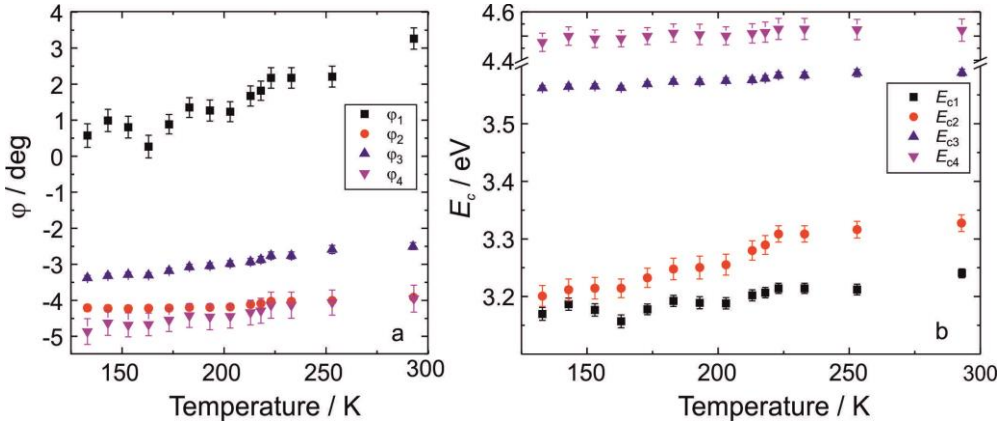

Fig. 4 – Temperature dependences of the phase angle φ parameter (a) and interband critical point energies E_c (b) for $TlInS_2$

It should be noted that the temperature dependence of important critical points in the band structure of semiconductors can be explained by taking into account thermal expansion and electron-phonon interaction. The bandgap variations for ferroelectric and dielectric systems are usually explained by the thermal expansion of the lattice, the renormalization of the band structure by electron-phonon interaction, and phase transitions [33].

The situation can get even more complicated since in $TlInS_2$ due to crystal imperfections (impurities, structural defects) the PT between the incommensurate and commensurate phases can be split in two close transitions at $T_{c1} = 204$ K and $T_{c2} = 201$ K. In accordance with this model, the anomaly at $T_{i2} = 206$ K observed earlier [2] corresponds to the formation of a new incommensurate structure. The anomalous behaviour of $\varepsilon(T)$ at 190-195 K is explained [5] by the coexistence of polar commensurate domains which appear at $T_{c1} = 204$ K and $T_{c2} = 201$ K, and the transitions at these temperatures correspond to incommensurate-commensurate phase transitions to improper and proper ferroelectric phases [5]. The PTs at $T_i = 216$ K and $T_{i2} = 206$ K are treated as transitions to an incommensurate phase of type I and II, respectively [5].

It should be noted that in an earlier study of the temperature dependence of $TlInS_2$ single crystal thermal expansion coefficient in the direction perpendicular to the layers [34], an expected intense peak observed in the PT temperature range (190-200 K) is accompanied by distinct shoulders near 140 and 170 K. This correlates well with our present data reporting the anomalies in the temperature behaviour of $TlInS_2$ physical properties below the known PT range.

We expect that anticipated calculations of the band structure of $TlInS_2$ which, to our knowledge, have not been published yet, will provide additional information for the discussion of the data obtained in the present work.

4. CONCLUSIONS

The real and imaginary parts of the dielectric function of $TlInS_2$ crystal were determined in the spectral range of 1-5 eV and in the temperature interval of 133-293 K from spectroscopic ellipsometry measurements. The energies of interband transitions (critical points) of $TlInS_2$ were obtained from the second derivative of the dielectric function real and imaginary parts. In the phase transition range, a variation of all the fitting parameters (amplitude A, critical point energy E_{cp}, broadening parameter Γ, and phase angle φ) describing the second derivative spectra of the dielectric constant is observed.

ACKNOWLEDGEMENT

The first author gratefully acknowledges Deutscher Akademischer Austauschdienst for the financial support of his research stay at Technische Universität Chemnitz (project No. A/12/85971).

Спектроскопічні еліпсометричні дослідження та температурна поведінка діелектричних функцій шаруватого кристалу $TlInS_2$

О.О. Гомоннай[1], О. Гордан[2], П.П. Гуранич[1], П. Гуранич[1], О.Г. Сливка[1], О.В. Гомоннай[1,3], Д.Р.Т. Цан[2]

[1] *Ужгородський національний університет, вул. Підгірна, 46, 88000 Ужгород, Україна*
[2] *Кемніцький технічний університет, D-09107 Кемніц, Німеччина*
[3] *Інститут електронної фізики НАН України, вул. Університетська, 21, 88000 Ужгород, Україна*

Дійсну та уявну частини діелектричної функції кристалу $TlInS_2$ визначено в спектральному діапазоні від 1 до 5 еВ в інтервалі температур 133-293 К із спектроскопічних еліпсометричних досліджень. Енергії міжзонних переходів (критичних точок) отримано для $TlInS_2$ з других похідних від діелектричних функцій. Обговорюються особливості в області структурних фазових переходів (190-220 К) та при нижчих температурах.

Ключові слова: Діелектрична функція, Оптичні переходи, Структурні фазові переходи.

Спектроскопические эллипсометрические исследования и температурное поведение диэлектрических функций слоистого кристалла $TlInS_2$

А.А. Гомоннай[1], О. Гордан[2], П.П. Гуранич[1], П. Гуранич[1], А.Г. Сливка[1], А.В. Гомоннай[1,3], Д.Р.Т. Цан[2]

[1] *Ужгородский национальный университет, ул.Пидгирна, 46, 88000 Ужгород, Украина*
[2] *Кемницкий технический университет, D-09107 Кемниц, Германия*
[3] *Институт электронной физики НАН Украины, ул. Университетська, 21, 88017 Ужгород, Украина*

Из спектроскопических эллипсометрических исследований определена действительная и мнимая части диэлектрической функции кристалла $TlInS_2$ в спектральном диапазоне от 1 до 5 эВ в интервале температур 133–293 К. Энергии между зонных переходов (критических точек) получено для $TlInS_2$ из вторых производных от диэлектрических функций. Обсуждаются особенности в области структурных фазовых превращений (190–220 К) и при меньших температурах.

Ключевые слова: Диэлектрическая функция, Оптические переходы, Структурные фазовые превращения.

REFERENCES

1. G.D. Guseinov, E. Mooser, E.M. Kerimova, R.S. Gamidov, I.V. Alekseev, M.Z. Ismailov, *phys. status solidi* **34**, 33 (1969).
2. A.M. Panich, *J. Phys.: Condens. Matter* **20**, 293202 (2008) (Topical Review).
3. S. Kashida, Y. Kobayashi, *J. Phys.: Condens. Matter* **11**, 1027 (1999).
4. B.R. Gadjiev, Preprint cond-mat/0403667 http://xxx.lanl.gov/pdf/cond-mat/0403667 Los Alamos Nat. Lab. (2004).
5. F.A. Mikailov, E. Basaran, T.G. Mammadov, M.Y. Seyidov, E. Senturk, R. Currat, *Physica B: Condens. Matter* **334**, 13 (2003).
6. A.D. Belyaev, Yu.P. Gololobov, V.F. Machulin, K.R. Allakhverdiev, T.G. Mamedov, *Ukr. J. Phys.* **34**, 582 (1988).
7. A.F. Qasrawi, N.M. Gasanly, *phys. status solidi A* **199**, 277 (2003).
8. O.Z. Alekperov, A.I. Nadjafov, *Inorganic Materials* **40**, 1248 (2004).
9. R.M. Sardarly, O.A. Samedov, A.I. Nadzhafov, I.Sh. Sadykhov, *Phys. Solid State* **45**, 1137 (2003).
10. E. Senturk, L. Tumbek, F.A. Mikailov, F. Salehli, *Cryst. Res. Technol.* **42**, 626 (2007).
11. A.F. Qasrawi, N.M. Gasanly, *Cryst. Res. Technol.* **39**, 439 (2004).
12. N.S. Yuksek, N.M. Gasanly, H. Ozkan, O. Karci, *Acta Phys. Polonica A* **106**, 95 (2004).
13. J. Grigas, E. Tolik, E.S. Gagarina, *Physica Status Solidi B* **237**, 494 (2003).
14. T.D. Ibragimov, *J. Appl. Spectroscopy* **70**, 99 (2003).
15. Y.G. Shim, N. Uneme, S. Abdullayeva, N. Mamedov, N. Yamamoto, *J. Phys. Chem. Solids* **66**, 2116 (2005).
16. A.F. Qasrawi, N.M. Gasanly, *J. Mat. Science* **41**, 3569 (2006).
17. M. Isik, N.M. Gasanly, *Opt. Commun.* **285,** 4092 (2012).
18. M. Isik, N.M. Gasanly, *J. Alloys and Compounds* **581**, 542 (2013).
19. M. Isik, S. Delice and N.M. Gasanly, *Phil. Mag.* **94**, 2623 (2014).
20. I. Guler, *J. Appl. Phys.* **115**, 033517 (2014).
21. O.O. Gomonnai, O. Gordan, P.P. Guranich, A.G. Slivka, A.V. Gomonnai, D.R.T. Zahn, *Appl. Surf. Sci.*, 424, 383 (2017).
22. Y. Shim, Y. Itoh, K. Wakita, N. Mamedov, *Appl. Surf. Sci.*, 421, 788 (2016).
23. M. Isik, N.M. Gasanly, R. Turan, *Physica B* **407**, 4193 (2012).
24. T. Kawabata, Y.G. Shim, K. Wakita, N. Mamedov, *Thin Solid Films* **571**, 589 (2014).
25. Y. Shim, H. Aoh, J. Sakamoto, K. Wakita, N. Mamedov, *Thin Solid Films* **519,** 2852 (2011).
26. N. Mamedov, Y. Shim, W. Okada, R. Tashiro, K. Wakita, *phys. status solidi B* **252**, 1248 (2015).
27. A.V. Gomonnai, I. Petryshynets, Yu.M. Azhniuk, O.O. Gomonnai, Yu.I Roman, I.I. Turok, A.M. Solomon,

R.R. Rosul, D.R.T. Zahn, *J. Cryst. Growth* **367**, 35 (2013).
28. H. Fujiwara, *Spectroscopic ellipsometry principles and applications* (John Wiley & Sons, NewYork, 2007).
29. L. Duran, J. Castro, J. Naranjo, J.R. Fermin, C.A. Durante Rincon, *Mater. Chem. Phys.* **114**, 73 (2009).
30. M.I. Alonso, M. Garriga, C.A. Durante Rincon, M. Leon, *Appl. Phys. Lett.* **88**, 5796 (2000).
31. S. Adachi, *Optical properties of crystalline and amorphous semiconductors: Materials and fundamental principles* (Springer Science & Business Media, 2012).
32. . Y.G. Shim, T. Kawabata, K. Wakita, N. Mamedov, *phys. status solidi B* **252**, 1254 (2015).
33. X.L. Zhang, J.J. Zhu, G.S. Xu, J.Z. Zhang, L.P. Xu, Z.G. Hu, J.H. Chu, *Opt. Mat. Express* **5**, 2478 (2015).
34. N.A. Abdullaev, T.G. Mamedov, R.A. Suleimanov, *Low Temp. Phys.* **27**, 676 (2001).