Physica B 406 (2011) 418–420

Contents lists available at ScienceDirect

Physica B

journal homepage: www.elsevier.com/locate/physb

Photoreflectance study of $AgGaTe_2$ single crystals

T. Raadik [a,*], J. Krustok [a], M.V. Yakushev [b]

[a] Department of Materials Science, Tallinn University of Technology, Ehitajate tee 5, 19086 Tallinn, Estonia
[b] Department of Physics, Strathclyde University, Glasgow G4 0NG, UK

ARTICLE INFO

Article history:
Received 17 June 2010
Received in revised form
30 September 2010
Accepted 2 November 2010

Keywords:
Solar energy materials
Photoreflectance
Semiconductors
Ternary chalcopyrite $AgGaTe_2$

ABSTRACT

The optical properties of ternary chalcopyrite $AgGaTe_2$ were studied by photoreflectance spectorscopy (PR). Due to the optimal direct energy gap and high absorption coefficient $AgGaTe_2$ is a promising material for solar energy conversion. Single crystals used in this work were grown by the vertical Bridgman technique. The PR temperature dependent spectra were measured in the range of 25–300 K. At room temperature two energy gaps in $AgGaTe_2$ were detected: $E_g^A = 1.320$ eV and $E_g^B = 1.425$ eV, with temperature coefficients $dE_g^A/dT = -2.1 \times 10^{-4}$ eV/K and $dE_g^B/dT = -3.4 \times 10^{-4}$ eV/K. At low temperature ($T=25$ K) these bandgap energies were $E_g^A = 1.355$ eV and $E_g^B = 1.466$ eV. Temperature dependence of bandgap energies is maximum at about $T=90$ K.

1. Introduction

Despite the fact that optical properties of $AgGaTe_2$ (AGT) have been studied for over 30 years, there are still some open questions. It is known that AGT is a member of chalcopyrite ternaries and the reported direct energy gap is suitable for solar energy conversion. At the same time there is wide variation in the actual value of this bandgap energy and the electronic band structure has different interpretations. The most common method to measure bandgap energy is optical absorption. However, it is known that in chalcopyrite ternaries usually large potential fluctuations are present and therefore the density of states function near band edges is quite complex [1–4]. This is why absorption spectra greatly depend on the depth of these potential fluctuations. Deeper fluctuations usually give additional absorption at lower energies and thus the absorption tail is formed. The shape of this tail is not always known and therefore the bandgap energy calculated from the absorption spectrum could be incorrect. Another approach to obtain the bandgap energy is to use various modulation methods like electroreflectance, photoreflectance or thermoreflectance. Tell et al. [5] measured the electroreflectance spectra of an $AgGaTe_2$ single crystal at 77 and 300 K. At room temperature they found the lowest bandgap energy $E_g=1.316$ eV, while at 77 K the bandgap energy was $E_g=1.356$ eV. Due to valence band splittings they also measured higher energy bandgaps at 77 K: $E_g^B = 1.472$ eV and $E_g^C = 2.26$ eV. Very similar results were published by Bodnar et al. [6] on AGT thin films using absorption measurements. At room temperature they found $E_g^A=1.32$ eV, $E_g^B=1.43$ eV, and $E_g^C=2.14$ eV. Thermoreflectance spectroscopy was also recently used for single crystals of AGT by Arai et al. [7] at $T=20$–300 K. The lowest direct bandgaps determined from thermoreflectance spectra were $E_g^A=1.36$ eV, $E_g^B=1.19$ eV, and $E_g^C=2.00$ eV at $T=20$ K. As can be seen the lowest bandgap in this paper has an energy $E=1.19$ eV. At the same time the low temperature ($T=15$ K) bandgap energy determined using optical absorption from the same single crystals was about 1.25 eV. It is interesting that different methods give different bandgap energies. In this paper we will present the photoreflectance data of Bridgman grown AGT measured in a wide temperature range.

2. Experimental

An ingot of AGT was grown by the vertical Bridgman technique often used for fabrication of $CuInSe_2$ and other chalcopyrite ternary compounds [8]. A pseudobinary phase diagram for $AgGaTe_2$ has been determined by Palatnik and Belova [9], establishing the melting point to be 725.7 °C [10]. At first a near stoichiometrical mixture of high (99.999%) purity Ag, Ga, and Te was sealed in vacuum of 10^{-5} mbar in a thick walled (3 mm) quartz ampoule of 10 mm inner-diameter. Then this mixture was prereacted at 900 °C for 2 h in a rocking furnace and solidified in a horizontal position. After cooling down the ampoule was introduced into the upper (hot) zone of a two-zone vertical furnace. The material was melted again and held at a temperature of 900 °C for 6 h. Then the temperature in the upper part of the furnace was reduced to 800 °C and that in the lower part to 700 °C. The furnace was slowly moved up, translating the ampoule into the lower (cold) zone at the

* Corresponding author. Tel.: +372 620 3210.
E-mail address: taavi.raadik@ttu.ee (T. Raadik).

0921-4526/$ - see front matter © 2010 Elsevier B.V. All rights reserved.
doi:10.1016/j.physb.2010.11.002

speed of 2 cm a day through a temperature gradient. The solidified material was cooled at a rate of 3 °C/h down to 200 °C. In the middle part the grown ingot had a 2 cm long cylindrical shaped single grain of $AgGaTe_2$. The elemental composition of the resulting single crystals was confirmed by EDX and RBS measurements. The elemental composition varied along the ingot, gradually becoming Ag rich close to the end of the freeze (top) zone.

Single crystal surfaces with a size of about 2×2 mm were freshly cleaved from the ingot for PR measurements.

Before PR measurements Raman measurements were made at room temperature with a micro-Raman spectrometer Horiba Yobin Yvon HR800; a Nd–YAG laser with $\lambda=532$ nm was used for excitation. Photoreflectance (PR) measurements were made with a traditional setup, where an $f=40$ cm grating monochromator together with a 250 W halogen bulb was used for the primary beam and the 50 mW He–Cd laser ($\lambda=441$ nm) as a secondary beam. The reflectance signal at 225 Hz was detected using a Si detector and a lock-in amplifier. The crystals under study were glued with cryogenic grease on the cold finger of the closed-cycle He cryostat.

3. Results and discussion

From the Raman measurements in Fig. 1, 4 main peaks are clearly seen; the most intensive is at 130 cm^{-1} and the others are at 94, 201, and 221 cm^{-1}. These peaks are typical for an $AgGaTe_2$ crystal [11] and according to these spectra we can be sure that we have a pure $AgGaTe_2$ single crystal without additional phases. Photoreflectance spectra at two different temperatures are shown in Fig. 2. Despite our efforts we detected only two signals originating from A and B bandgaps. Even at low temperatures the C bandgap reported by Tell et al. [5] and Bodnar et al. [6] could not be detected.

Each PR spectrum has been analyzed by the low-field electroreflectance line-shape function, the third derivative functional form [12]

$$\Delta R/R = \mathrm{Re}\{Fe^{i\theta}(E-E_g)+i\Gamma\}^m, \quad (1)$$

where E is the photon energy and F, θ, E_g, and Γ are the amplitude, phase, energy, and broadening parameter of the spectrum, respectively; m is a parameter that depends on the critical point type and $m=5/2$ (the three-dimensional critical point) has been used in this study. Results of this analysis are also presented in Fig. 2 as continuous lines.

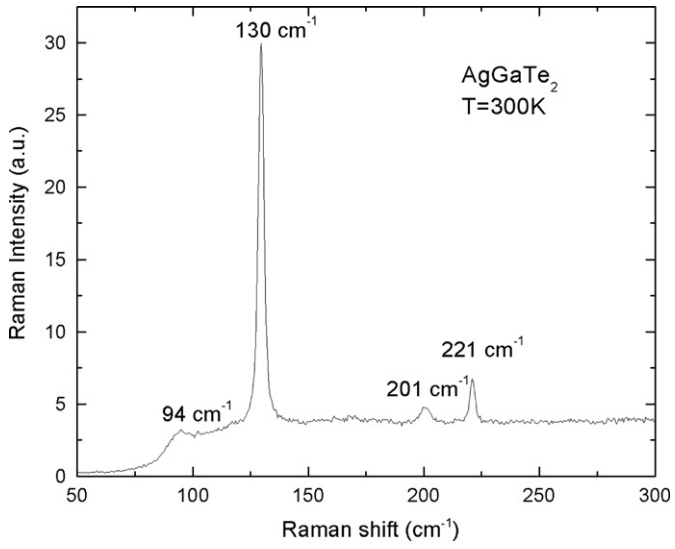

Fig. 1. Room temperature Raman spectrum of $AgGaTe_2$ crystal.

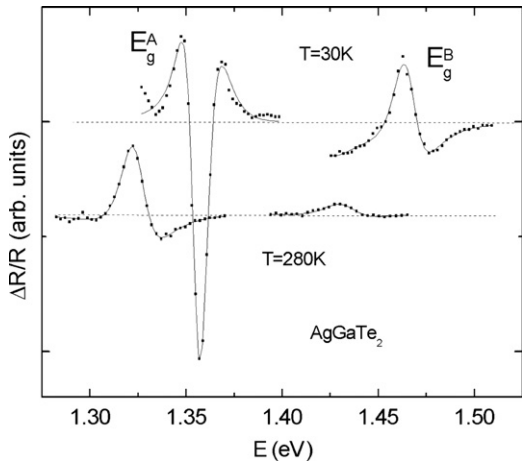

Fig. 2. Photoreflectance spectra of $AgGaTe_2$ crystal at different temperatures. Continuous lines represent the fitting results. A and B bandgaps are clearly resolved.

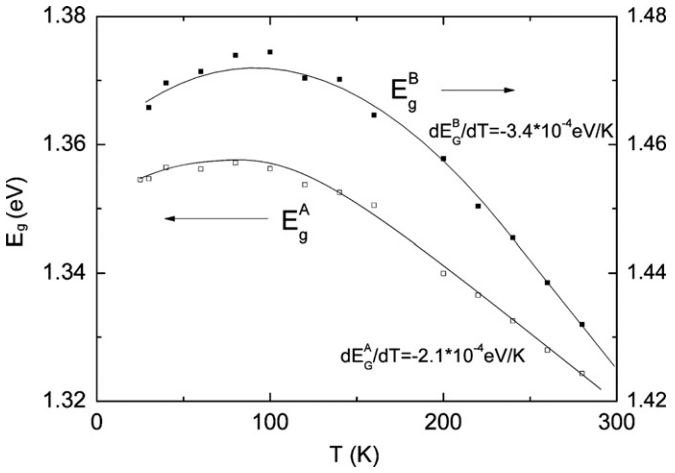

Fig. 3. Temperature dependence of A and B bandgap energies of $AgGaTe_2$ crystal obtained from photoreflectance spectra. At higher temperatures nearly linear dependence can be observed.

All PR measurements were made at $T=25$–295 K. From these measurements, after fitting with Eq. (1), E_g^A and E_g^B were found and the results are presented in Fig. 3. It can be seen that both bandgap energies have a maximum at about $T=90$ K. This behavior is typical for ternary compounds containing Ag and the same kind of behavior in AGT was also observed by Bodnar et al. [13]. It is suggested that this trend can be due to the effects of lattice dilation and electron–phonon interaction. At the same time the temperature dependence of bandgap energies found by Arai et al. [7] did not show any maximum. At higher temperatures the temperature dependence of bandgap energies shows a nearly linear trend, but the rate of this trend is different for different bandgaps (see Fig. 3). The lowest bandgap shows a temperature coefficient $dE_g^A/dT=-2.1\times10^{-4}$ eV/K and this value is very close to the value -2.02×10^{-4} eV/K found by Bodnar et al. [13]. The temperature coefficients found by Arai et al. [7] for their A–C bandgaps are all in the range $dE_g/dT=-(2.4\text{–}2.6)\times10^{-4}$ eV/K. Thus our results support the findings made by Tell et al. [5] and Bodnar et al. [6,13].

4. Conclusion

$AgGaTe_2$ crystals were studied at different temperatures using photoreflectance spectroscopy. The lowest bandgap energy at

room temperature was found to be $E_g^A = 1.320$ eV and the temperature coefficient was $dE_g^A/dT = -2.1 \times 10^{-4}$ eV/K. The next bandgap energy was $E_g^B = 1.425$ eV and temperature coefficient $dE_g^B/dT = -3.4 \times 10^{-4}$ eV/K. The bandgap energy maximum was around $T = 90$ K with values $E_g^A = 1.357$ eV and $E_g^B = 1.474$ eV.

Acknowledgements

This work was supported by the Estonian Science Foundation Grant G-8282 and by the target financing by HTM (Estonia) no. SF0140099s08.

References

[1] J. Krustok, H. Collan, M. Yakushev, K. Hjelt, Phys. Scr. T 79 (1999) 179.
[2] J. Krustok, J. Raudoja, M. Yakushev, R.D. Pilkington, H. Collan, Phys. Status Solidi 173 (1999) 483.
[3] B.I. Shklovskii, A.L. Efros, Electronic Properties of Doped Semiconductors, second ed., Springer, Berlin, 1984.
[4] J. Krustok, A. Jagomägi, M. Grossberg, J. Raudoja, M. Danilson, Sol. Energy Mater. Sol. Cells 90 (2006) 1973.
[5] B. Tell, J.L. Shay, H.M. Kasper, Phys. Rev. B 9 (1974) 5203.
[6] I.V. Bodnar, V.F. Gremenok, I.A. Viktorov, O.N. Obraztsova, J. Appl. Spectrosc. 60 (1997) 809.
[7] S. Arai, S. Ozaki, S. Adachi, Appl. Opt. 49 (2010) 829.
[8] R.D. Tomlinson, Sol. Cells 16 (1986) 17.
[9] L.S. Palatnik, E.K. Belova, Izv. Akad. Nauk SSSR Neorg. Mater. 3 (1967) 2194.
[10] A. Burger, J.O. Ndap, Y. Cui, U. Roy, S. Morgan, K. Chattopadhyay, X. Ma, K. Faris, S. Thibaud, R. Milers, H. Mateen, J.T. Goldstein, C.J. Rawin, J. Cryst. Growth 225 (2001) 505.
[11] C. Julien, I. Ivanov, A. Khelfa, F. Alapini, M. Guittard, J. Mater. Sci. 31 (1996) 3315.
[12] D.E. Aspnes, in: M. Balkanski (Ed.), Handbook on Semiconductors II, North-Holland1980, p. 109.
[13] I.V. Bodnar, V.F. Gremenok, R.W. Martin, M.V. Yakushev, Opt. Spectrosc. 88 (2000) 377.