OPTOELECTRONICS AND ADVANCED MATERIALS – RAPID COMMUNICATIONS Vol. 4, No. 11, November 2010, p. 1705 - 1708

Optical band gap studies on *Cu*-doped *Zinc-Borate* glassy thin films

G. KILIC*, S. PAT, M. Z. BALBAG, S. TEMEL, S. KORKMAZ, N. EKEM
Eskisehir Osmangazi University, Science and Art Faculty, Physics Department, 26480, Eskisehir, Turkey

In this study, optical properties of *Cu*-doped *Zinc-Borate* glassy thin films (GTFZs) were investigated. The glassy thin films of bulk glasses were grown onto SiO_2 substrates with argon gas plasma under vacuum with RF sputtering technique. As a result of XRD analysis of obtained glassy thin films, they are observed to have amorphous structure. From absorbance and transmission data obtained from Uv-Vis spectra of thin films, optical band gaps for direct and indirect transitions and also Urbach energies were calculated. Not only the fundamental absorption edge and cut-off wavelength shift towards red with the increase in V_2O_5 content, but also ZnO narrows the optical band gaps.

(Received October 4, 2010; accepted November 10, 2010)

Keywords: Vanadium, Borate, Glass, Thin film, Semiconductors

1. Introduction

The physical properties, electrical, optical mechanical and magnetic properties of pure and various transition and rare earth metal ions doped borate glasses have been under investigation in recent years. Semiconducting glasses can be generally divided into two groups, chalcogenide glasses and oxide glasses, containing transition metal ions. Oxide glasses containing transition metals such as vanadium, copper, etc. exhibit semiconducting properties [1-8]. These glasses are potential candidates for electrical memory and optical switching devices [9-11], cathode materials for making solid devices and optical fiber [12-14]. Very few studies have been carried out on glasses containing both B_2O_3 and V_2O_5 [15]. Glasses containing high concentration of transition metal ions are electronic conductors [16-18]. This classifies them as a form of amorphous semiconductors.

We report here some significant structural results obtained from x-ray diffraction analysis and optical properties of semiconducting glassy thin films that were prepared from borate-based glasses.

2. Experimental

Glass samples of compositions as presented in Table 1, were prepared from the reagent grade chemicals. These chemicals in the appropriate amounts were thoroughly mixed. The mixtures were then melted in a platinum crucible in an electrical furnace at 1400 °C for one hour. The melts were occasionally stirred for homogenization and were finally poured into a graphite mould for giving a cylindrical shape. The sample was taken out of the mould and put in an annealing oven that has been adjusted to 350 °C. This process is applied to avoid the cracking, breaking of the sample and also to provide the internal tension. The sample kept in 350 °C for an hour was left to cool down at room temperature.

Glassy thin films were grown onto SiO_2 glasses by using these glass samples as raw material with RF sputtering technique in 100% Argon environment. The thicknesses of the glassy thin films, produced under 4.10^2 Torr pressure in approximately 180 minutes are about 400 nm. X-ray diffraction (XRD) patterns of the glassy thin film samples were recorded in an X-ray diffractometer (Shimadzu XRD-6000). The optical absorption and transmission spectra of the glassy thin films were recorded in the wavelength range 300-1200 nm at room temperature using UV-vis spectrophotometer (Hitachi 150-20).

Table 1. Structures of glassy thin film samples.

Code	Glassy thin film structure
GTF Z1	$80\ \mathbf{B_2O_3}+15\ \mathbf{Na_2O}+4\ \mathbf{ZnO}+1\ \mathbf{V_2O_5}$ **: 0.5 Cu**
GTF Z2	$80\ \mathbf{B_2O_3}+15\ \mathbf{Na_2O}+4.5\ \mathbf{ZnO}+0.5\ \mathbf{V_2O_5}$ **: 0.5 Cu**

3. Results and discussion

3.1. X-ray diffraction spectra

X-ray diffraction (XRD) patterns were recorded with CuK_α radiation at a scanning step of 0.1 in the 2θ range 0-70. Fig. 1 shows XRD patterns for two of the glassy thin film samples. Each pattern exhibits a broad diffuse scattering especially at low angles, instead of crystalline peaks, confirming a long range structural disorder characteristic of amorphous network [19]. Two humps at $2\theta=22^o$ and $2\theta=45^o$ were also observed in previous studies of borate glass samples [20].

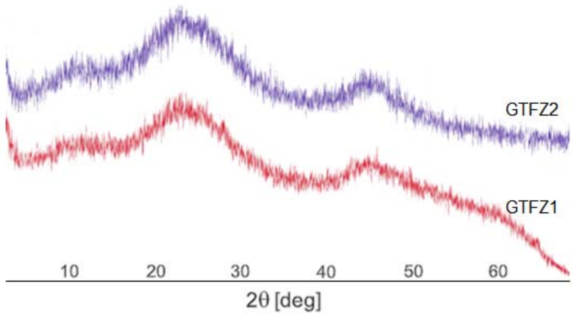

Fig. 1. X-ray diffractograms of prepared glassy thin film samples.

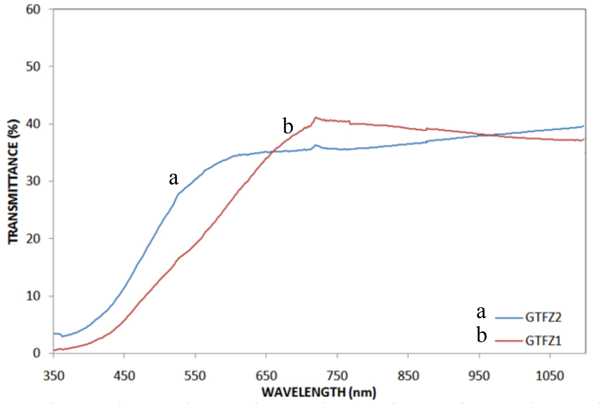

Fig. 2. Transmittance spectra of glassy thin film samples.

3.2. Optical absorption spectra

The optical absorption and transmission spectra of the glassy thin film samples including Cu^{2+} ions are recorded at room temperature. Similar studies on alumino borate glasses, the absorption spectra show a single broad band centered at 784 nm [21]. It is well known that this band is attributed to the $^2B_{1g} \rightarrow {}^2B_{2g}$ transition of Cu^{2+} ions in the distorted octahedral sites. The transmission, the absorption spectra of both samples are shown in Figs. 2 and 3, respectively. The absorption spectra of the two samples show a slightly narrow peak at about 784 nm.

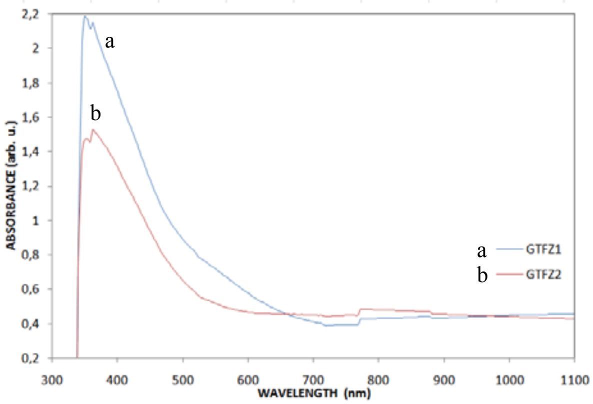

Fig. 3. Absorbance spectra of glassy thin film samples.

3.3. Optical band gap and Urbach energy

The study of fundamental absorption edge in the UV region is a useful technique to investigate optical transitions and electronic band structure in glasses. The main feature of the absorption edges of amorphous substances, particularly at lower values of absorption coefficient, is an exponential increase of absorption coefficient, $\alpha(\nu)$ with photon energy $h\nu$ in accordance with the empirical relation.

$$\alpha(\nu) = \alpha_0 exp\left(\frac{h\nu}{\Delta E}\right) \quad (1)$$

here, α_0 is a constant and ΔE is the Urbach energy which indicates the width of the band tails of the localized states. The broadening of the exciton levels at the absorption edge is dominated by the random electric fields due to either the lack of long range order or the presence of defects [21].

For the optical band gap the equation takes the form:

$$\alpha h\nu = [A(h\nu - E_g)]^r, \quad (2)$$

where r is the index which can have different values; 2, 3, 1/2 and 1/3 corresponding to indirect allowed, indirect forbidden, direct allowed and direct forbidden transitions, respectively. This law for amorphous materials the optical absorption at higher value of $\alpha(\nu)$ $(\geq 10^4 cm^{-1})$ above the exponential tail given by Davis and Mott [22]. B is a constant called band tailing parameter, E_{opt} is the optical band gap energy $h\nu$ is the incident photon energy and "A" is a constant.

In various glass systems, Eq. (2) depicts a straight line for r = 2 (Fig. 4(b)). Figs. 4(a) and (b) represents the Tauc's plot $\{(\alpha h\nu)^2 \text{ vs. } h\nu\}$ and $\{(\alpha h\nu)^{1/2} \text{ vs. } h\nu\}$, respectively, for the glassy thin film samples. Optical band gaps for direct and indirect transitions obtained according to the linear regions of the curves in Fig. 3 are seen in Table 2. Optical band gaps for direct transitions of the samples are 2.2 eV, 2.5 eV and 1.1 eV, 1.4 eV for indirect transitions. In another similar study of ours, optical band gaps were found to be 2.963-3.228 eV and 2.592-2.807 eV for direct transmissions and indirect transmission, respectively when the samples were in the form of bulk glass [23]. Also in our similar studies on glassy thin films including MgO, optical band gaps were found to be 2.6-3.0 eV and 1.7-1.95 eV for direct transmissions and indirect transmission, respectively.

Fig. 5 shows a plot of $\ln\alpha(\nu)$ and $h\nu$ of the glassy thin film samples. The reciprocal of the slope of the linear region of the curve gives the Urbach energy of the corresponding samples. The values of the Urbach energies also listed in Table 2.

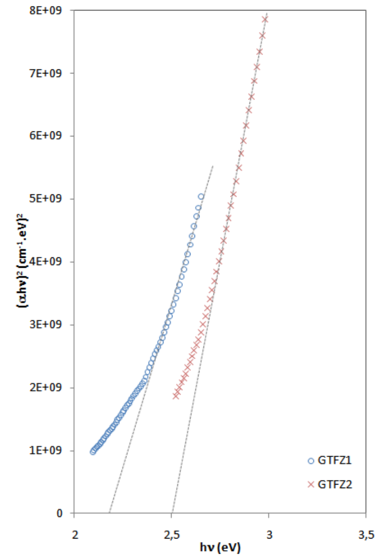

Fig. 4(a). Band gaps for direct transitions of glassy thin film samples.

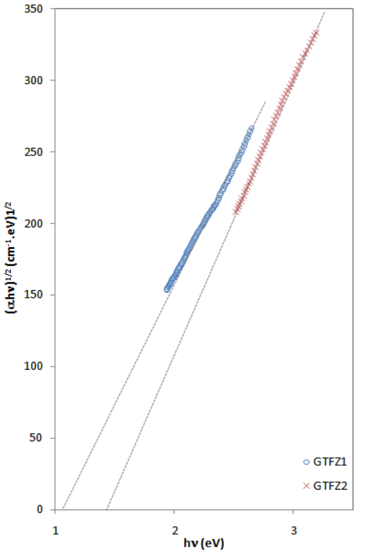

Fig. 4(b). Band gaps for indirect transitions of glassy thin film samples.

Table 2. Optical band gaps of glassy thin films.

Code	E_g(direct) (eV)	E_g(indirect) (eV)	Urbach en. ΔE (eV)
GTFZ1	2.2	1.1	0.82
GTFZ2	2.5	1.4	0.76

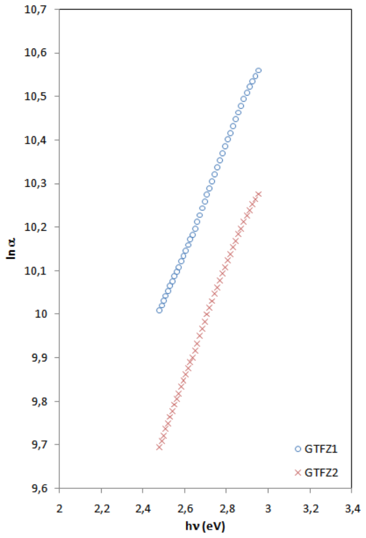

Fig. 5. $\ln\alpha(\nu)$ as a function of $h\nu$ for the glassy thin film samples.

4. Conclusions

GTFZ1 and GTFZ2 glassy thin films are observed to be far from amorphous structure. This situation is consistent with the literature results of borate based bulk glasses. When transmission and absorption spectra of both samples were examined, characteristic peaks of vanadium doped glass that are seen in the literature could not be found [24], but the absorption spectra of the two samples showed a slightly narrow peak at about 784 nm, belonging to CuO. While the increase in V_2O_5 ratio carries the transmission margin to the long wavelength, it also narrows the optical band gap. While direct optical band gap and indirect optical bad gap of GTFZ1 sample having 1% vanadium ratio were found to be 2.2 eV and 1.1 eV, respectively, it was calculated to be 2.5 eV and 1.4 eV respectively for GTFZ2 sample having a vanadium ratio of 0.5%. In our similar study, when magnesium is doped instead of zinc, the optical band gaps were found to be wider. Accordingly, the presence of zinc in the structure instead of magnesium plays an important role in the narrowing of the optical band gap. Like optical band gaps, Urbach energies of the glassy thin film samples were found to depend on vanadium concentrations. As a result, both of the samples demonstrate the characteristics of an amorphous semiconductor. Our studies on different doping ratios and optical and magnetic works on glassy thin films of various compositions continue.

Acknowledgements

I would like to thank Prof. Ertunç ARAL whom we have prepared in previous studies similar bulk glass samples, however with different structures than these glassy thin films.

References

[1] S. Sindhu, S. Sanghi, A. Agarwal, Sonam, V. P. Seth, N. Kishore, Physica B **365,** 65 (2005).

[2] M. Toderaş, S. Filip, I. Ardelean, J. Optoelectron. Adv. Mater. **8**(3), 1121 (2006).

[3] Aloka Ghosh, S. Bhattacharya, A. Ghosh, J Alloy Compd. **490**, 480 (2010).

[4] N. F. Mott, E. A. Davis, Electronic Processes in Non-Crystalline Materials, Clarendon Press, Oxford (1979).

[5] N. F. Mott, J. Non-Cryst. Solids 1 (1968).

[6] M. Sayer, A. Mansingh, Phys. Rev. B **6**, 4629 (1972).

[7] G. D. Khattak, A. Mekki, L. E. Wenger, J. Non-Cryst. Solids **355,** 2148 (2009).

[8] E. R. Shaaban, M.Y. Hassan, A. G. Mostafa, A. M. Abdel-Ghany, J. Alloys Compd. **482,** 440 (2009).

[9] J. Livage, J. P. Jollivet, E. Tronc, J. Non-Cryst. Solids **121**, 35 (1990).

[10] A. Ghosh, J. Appl. Phys. **64,** 2652 (1988).

[11] P. Pascuta, G. Borodi, E. Culea, J. Non-Cryst. Solids **354,** 5475 (2008).

[12] G. D. Khattak, A. Mekki, J Phys. Chem. Solids **70**, 1330 (2009).

[13] R. A. Montani, M. Levy, J. L. Souquet, J. Non-Cryst. Solids **149**, 249 (1992).

[14] A. Ghosh, B. K. Chaudhuri, J. Non-Cryst. Solids **103**, 83 (1988).

[15] V. Kundu, R.L. Dhiman, D. R. Goyal, A. S. Maan, J. Optoelectron. Adv. Mater. **10**(10), 2765 (2008).

[16] I. Kashif, S. A. Rahman, A. A. Soliman, E. M. Ibrahim, E. K. Abdel-Khalek, A. G. Mostafa, A. M. Sanad, Physica B **404,** 3842 (2009).

[17] L. Murawski, C. H. Chung, J. D. Mackenzie, J. Non-Cryst. Solids **32**, 91 (1979).

[18] M. Sayer, A. Mansingh, M. Pollak (Ed.), Non-crystalline Semiconductors, vol. III, CRC Press, USA, (1987).

[19] S. Sen, A. Ghosh, J. Non-Cryst. Solids **258**, 29 (1999).

[20] M. P. Medda, A. Musinu, G. Paschina, G. Piccaluga, J. Non-Cryst. Solids, **150**, 76 (1992).

[21] V. R. Kumar, J. L. Rao, N. O. Gopal, Mater Res Bull, 40, 1256 (2005)

[22] N. F. Mott, E. Davis,Electronic processes in Non-Crystalline Materials, second ed., 289 (1979).

[23] G. Kılıc, E. Aral, GU J Sci. **22**(3), 129 (2009).

[24] C. R. Bamford, Colour Generation and Control in Glass, Elsevier Scientific Publishing Company, New York (1977).

---

*Corresponding author: gkilic@ogu.edu.tr