

## MULTICOMPONENT GERMANIUM CHALCOGENIDE GLASSES

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Thin films of the glassy systems Ge-Se-Y (where Y is Ga, Tl or B) were prepared by vacuum evaporation. The kinetics of the processes of the evaporations and condensation are investigated. From electrical investigations some basic electrical characteristics of the investigated semiconductor films were calculated applying the Christov's theory for injected electron currents. Effective electron mass ( $m_e/m$ ) in the conduction band and work function of the films ( $\chi$ ) as a function of boron, gallium, and thallium content were determined.

(Received July 8, 2002; accepted July 22, 2002)

*Keywords:* Germanium chalcogenides, Thin films, Evaporation kinetics, Electrical properties

### 1. Introduction

The intensive development of modern technologies has led to the synthesis of new materials. In recent years there has been a great deal of interest in the study of chalcogenide glasses from the point of view of basic physics [1] as well as of device technology [2]. It is well known that Se rich chalcogenide glasses exhibit high resistivity values implying certain limitation in their application. It is worth then to add more than one component into selenium matrix in order to produce considerable changes in the properties of new complex glasses.  $\text{Ge}_x\text{Se}_{1-x}$  is probably one of the best glass former in the chalcogenide family and forms glasses for  $x < 43\%$  [3]. Chalcogenide glasses in Ge-Se system are interesting materials for infrared optics. They have a large range of transparency and good mechanical properties such as hardness, adhesion, low internal stress and water resistance. The addition of third element in tetrahedral structure of Ge-Se glass make the glass interesting material and new, promising properties of the material are expected.

This paper is an attempt to summarize the results obtained during investigation of thin films from Ge-Se-Y system (where Y = B, Ga or Tl).

### 2. Experimental

Bulk glasses with compositions  $\text{GeSe}_5\text{-Y}$  (Y is 5, 10, 15 20 at.% of B, Ga or Tl) were obtained by direct single temperature synthesis followed by rapid quenching of melts with a rate higher than 50 K/s. Thin films were prepared by thermal vacuum evaporation on different substrates from previous obtained bulk glass. Thickness and composition of the films were controlled and morphology was monitored by transmission electron microscope.

Electrical measurements were performed on sandwich samples with two metal electrodes deposited on the bottom and top of the films. Capacitance and dielectric losses were measured at room temperature using a precise RLC bridge at 8 kHz frequency. Current-voltage characteristics were investigated at room temperature by applying a linearly increasing voltage on the samples. The experimental data were processed with a high accuracy by a special computer program.

From the volt-ampere characteristics of the structures some basic electrical characteristics were obtained by applying the Christov's theory.

### 3. Christov's theory

Christov has proposed the most general theory of electron emission from metal in vacuum [4]. According to the theory, the total injected current  $j$  as a function of electrical field  $E$  and temperature  $T$  is:

$$j(E,T) = j_1' + j_2' + j'' = Q_1'(T/T_c)j_{FN} + Q_2'(E,T)j_{MG} + Q''(T_k/T)j_{RS} \quad (1)$$

where  $j_{FN}$ ,  $j_{MG}$ ,  $j_{RS}$  are defined by the well-known formula of Fowler-Nordheim, Murphy-Good and Richardson-Schottky for the regions of field, thermo-ionic field and thermo-ionic emission, respectively.  $Q_1'$ ,  $Q_2'$  and  $Q''$  are determined as a function of field and temperature.

The dependence of the thermo-ionic emission component  $j''$  ( $j'' \sim \exp E^{1/2}$ ) of the current density, the thermo-ionic-field emission component  $j_2'$  ( $j_2' \sim \exp E^2$ ) and their sum  $j = j'' + j_2'$  on the field intensity in Schottky co-ordinates reach an intersection point of the curves for which  $j'' = j_2'$ . This point corresponds to transition of the characteristics  $\ln j(E^{1/2})$  from linear to nonlinear shape. The point lies at a field intensity  $E_k$  and is defined by the condition  $T_k/T = 1.76$ . Using the value of  $E_k$  one can determine the ratio  $m_c/m$  by the expression

$$m_c/m = [h(e \epsilon)^{1/4} / 1.76 \pi^2 kT] E_k^{3/2} \quad (2)$$

where  $m$  is the free electron mass,  $h$  is Planck constant,  $k$  is Boltzmann constant,  $e$  is the electron charge,  $\epsilon$  is the relative permittivity of the material. The relation is valid for any temperature if only the critical field  $E_k$  is reached. Vodenicharov has proposed a method for the determination of the ratio  $m_c/m$  (effective electron mass) using the general theory of Christov for metal/semiconductor/metal systems [5, 6].

From the above defined emission regions the electron work function of the "metal-semiconductor" interface can be calculated. For the thermionic emission region it is obtained

$$\chi = -kT \ln(j^*/AT^2 m_c/m) \quad (3)$$

where  $A$  is the Richardson's constant and  $j^*$  is a current density at  $E = 0$ , deduced from the  $\ln j(E^{1/2})$  graphical dependence.

### 4. Results

The deposition from alloys composed by elements with different pressure in gas phase is an important problem of practical meaning. The deposition of the films obtained by vacuum sublimation at substrate temperatures  $T_s \ll T_m/3$  is generally assumed to proceed in the sequence vapor phase-liquid phase-solid (amorphous) phase. The process of film preparation is described thermodynamically by kinetic gas theory, and the specific evaporation rate  $v_e$  is given by

$$v_e = 0.584 \alpha_e p_0 \sqrt{\frac{M}{T_e} \exp\left(-\frac{Q_e}{RT_e}\right)} \quad (4)$$

where  $\alpha_e$  is the evaporation coefficient,  $p_0$  is the residual gas pressure,  $M$  is the molar mass,  $R$  is the universal gas constant,  $T_e$  is the evaporation temperature, and  $Q_e$  is the evaporation energy. This equation refers to the free evaporation in vacuum from an evaporizer of small area. The dependence of the evaporation rate versus  $Y$  content of the investigated glasses is presented in Fig. 1.

The condensation process can be considered as a superposition of three mass flows: flow of condensed particles, flow of particles arriving at the substrate and flow of reevaporated particles. The specific condensation rate  $v_c$  is determined by a formula similar to the one for evaporation. Evaporation and condensation energies of the processes are determined from the slope of graphical dependencies  $(v_e T^{1/2}) = f(1/T_e)$  and  $(v_c T_s^{1/2}) = f(T_s^{1/2})$ . The energy values increase fast for multicomponent glasses. The relation for the condensation energies versus composition of the films is presented in Fig. 2. The results for binary Ge-Se system investigated by us [7] are shown in Fig. 2 (the

small graph). Our experiments of GeSe vapor deposition illustrate the possibility of obtaining polycrystalline films at substrate temperatures lower than  $2T_m/3$  [8]. Thin films of the multicomponent glasses prepared under same conditions (pressure and temperature of the substrate) are found to be amorphous in the whole concentration region of investigated glasses [9, 10]. The addition of any of the three different elements into Ge-chalcogenide host material, causes exactly the same effects on the  $Q_e$  values.

Current density dependence on field intensity in Schotky coordinates is presented in Fig. 3. The amplitude of applied voltage to the samples varied as a function of the film thickness in order to cover the thermo-ionic emission region. The electrical transport in the M-Chalcogenide films-M under these conditions shows only the thermo-ionic emission. At higher voltages break-down and irreversible processes occurred occasionally in some samples. The average value of work function of the films calculated for thermo-ionic and thermo-ionic-field emission regions is  $\chi = (0.85 \pm 0.02)eV$ . The results presented in Fig. 3 show that the replacement of thallium atoms (with relative large atomic radii) by gallium and boron (with relative small atomic radii) has a weak effect on the electrical parameters. The values of  $m_e/m$  as a function of composition are given in Fig. 4. Obviously, the structure and electrical properties of the films are determined by a dominant role of the selenium matrix.

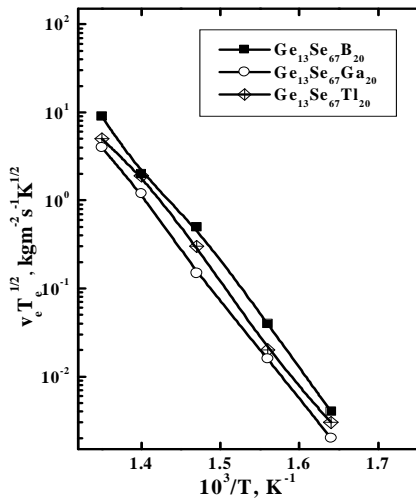


Fig. 1. Dependence of the evaporation rate on the evaporation temperature in the Ge-Se-Y systems.

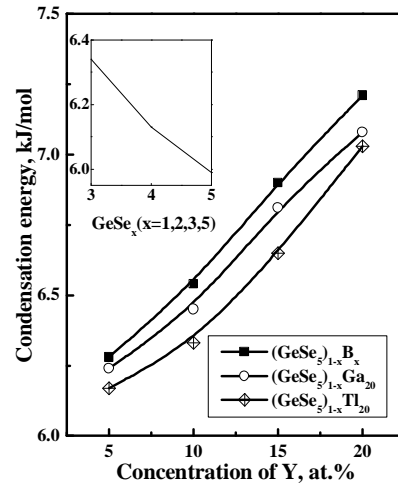


Fig. 2. Condensation energy variations versus B, Ga and Tl content.

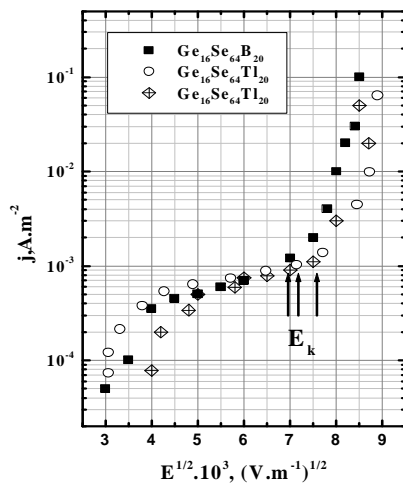


Fig. 3. Current-voltage characteristics  $\ln j = f(E^{1/2})$  for the films from Ge-Se-Y systems.

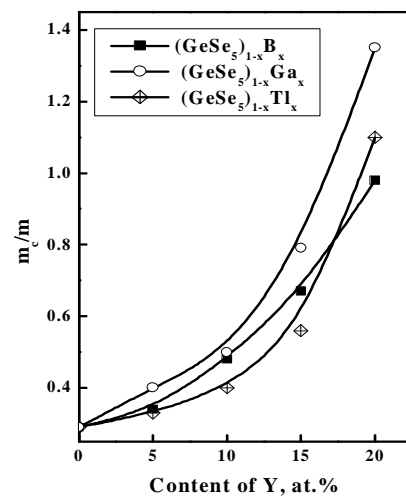


Fig. 4. Relation of effective electron mass versus B, Ga and Tl content.

#### 4. Discussion

For thin films production from complicated bulk glasses consisting of elements very different in their atomic mass and behavior it is of great importance to study the kinetics of the process. The problems in evaporation caused by the differences in the atomic mass and temperatures of evaporation are avoided by utilizing special evaporizer constructed by Vodenicharov [11]. According to the band model for amorphous semiconductors proposed by Ovshinsky [12] in covalently bonded alloy all atoms have their valence bond requirements locally satisfied. Amorphous materials should be viewed as being composed of an interactive matrix whose electronic configurations are generated by free energy forces and can be defined by the chemical nature and coordination of the constituent atoms. The valence band states must be considered neutral when they are occupied whereas the conduction band states are neutral when they are empty. Some overlap of the valence band tail and conduction band is believed to take place in the center of the mobility gap. The resultant charge transfer creates positively charged states above and negatively charged states below the Fermi level. The additives of B, Ga and Tl incorporated in Ge-Se matrix influence the electronic structure of the material. These elements of the III group of periodic table are most often positive charged and their bands are located at the upper half of the mobility gap. The introduction of a charged additive disturbs the concentration of the native charged defects, but keeps the charge neutrality. As a consequence the Fermi level shifts in direction to the conduction band and electronic properties of the multicomponent glasses alter.

High field current seems to be associated with a deviation of the electrons and holes from their equilibrium distribution, they are easily disequilibrated among localized states in the mobility gap. The only way to reach an equilibrium distribution is by thermal excitation of carriers into extended states and subsequent trapping and recombination. Flexibility of the glassy matrix could decrease the energy barrier and assist the electron motion.

#### 5. Conclusions

The incorporation of high concentration of various additives in the amorphous chalcogenide semiconductors can affect their electronic properties. The comparison of the experimental data obtained from current voltage characteristics with Christov's equation shows a better coincidence than with Richardson-Schottky equation. This fact confirms the validity of Christov's theory on thin chalcogenide films in the thermionic emission region and intermediate emission region.

From the performed studies the following parameters of the GeSe-Y glasses have been determined:

- (i) condensation energies of these chalcogenides increase with increasing of the third component;
- (ii) effective electron mass in the conduction band  $m_c/m$ , increases up to 1.35 with the increase of Y concentration up to 20 at.%;
- (iii) average value of the electron work function at the Al-(Ge-Se-Y) interface,  $\chi = (0.85 \pm 0.02)$  eV, calculated from both emission regions is practically independent on the Y content.

#### References

- [1] M. Abdel-Aziz, E. El Metwally, H. Labib, M. Fadel, M. Afifi, *Thin Solid Films* **386**, 99 (2001).
- [2] R. Tomova, G. Spasov, R. Stoycheva-Topalova, A. Buroff, *J. Non-Cryst. Solids* **266-269**, 985 (2000).
- [3] S. S. Fouad, *Physica B*, **293**, 276 (2001).
- [4] S. G. Chistov, *Phys. Stat. Sol. (a)* **15**, 655 (1973).
- [5] C. Vodenicharov, *Phys. Stat. Solidi (a)*, **29**, 233 (1975).
- [6] C. Vodenicharov, *Phys. Stat. Sol. (a)* **42**, 785 (1977).
- [7] C. Vodenicharov, P. Petkov, *Thin Solid Films* **190**, 335 (1990).
- [8] A. Feltz, C. Kaps, *Thin solid Films* **70**, 17 (1980).
- [9] P. Petkov, C. Vodenicharov, C. Kanasirski, *Phys. Stat. Sol. (a)*, **168**, 447 (1998).
- [10] P. Petkov, S. Parvanov, Y. Nedeva, E. Kashchieva, *Phys. Chem. Glas.* **41** 781 (2000).
- [11] A. Stanchev, C. Vodenicharov, Bulgarian Patent No 31375, 1975.
- [12] S. R. Ovshinsky, *Proc. of IX Int. Conf. On Amorphous & Liquid Semiconductors*, Ed. B. Chakraverty and D. Kaplan, Grenoble, France, 1095 (1981).