Electrical conductivity, photoconductivity and gas sensitivity of Ge-Se-Te thin films

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Abstract. Films of Ge$_x$Se$_{y}$Te$_{z}$ ($x\approx33$) with a thickness of 0.8 µm and four different compositions were prepared by thermal evaporation of preliminary synthesized glasses. The glass and film compositions were determined by Energy-Dispersive X-ray Spectroscopy. X-ray diffraction measurements have confirmed the amorphous structure of both bulk and thin film samples. The temperature dependence of the dark conductivity has been measured in the range 20 – 110 °C. No significant change of the room temperature conductivity (around 5x10⁻⁷ S/cm) and the dark current activation energy (around 0.7 eV) have been observed with increasing $z$. Spectral photocurrent measurements have revealed that the increase of Te content results in: (i) a photoconductivity decrease and (ii) a red shift of the low-energy side of the spectrum which indicates an optical band gap decrease. Resistive chemical sensing tests carried out at room temperature with ammonia, acetone, ethanol or water vapours in air as carrying gas have shown that the Ge$_{32}$Se$_{55}$Te$_{13}$ films are sensitive to ammonia but not to water vapour and hence they are suitable for selective ammonia sensors operating at room temperature. The observed sensitivity is related to the specific lattice structure of the region nearest to the film surface.

1. Introduction
Amorphous chalcogenides show a unique set of photoinduced effects which makes them very interesting for optical fabrication and performance [1,2]. Besides, these glasses have attracted much attention for the development of active and passive infrared devices. A great variety of alloys such as Ge-Sb-Te, In-Sb-Te, Te-Ge-Sb-S, Ge-Sb-Se-Te and many others have been suggested for use as the active material in non-volatile memories [3-5]. Intensive investigations in the field of ion-selective electrodes on the basis of chalcogenide glass materials have been carried out during the last two decades [6-8].

Today, there is an increasing demand for gas sensors with selectivity for specific gases in different fields of applications, e.g. industrial tasks like process control, challenges in homeland security,
detection of chemical or biological hazardous substances, pollution control etc. Compared to metal oxide devices, chalcogenide-based sensors appear superior as they can be readily operated at ambient temperatures. Also, in comparison to their crystalline counterparts, amorphous chalcogenides exhibit useful advantages which originate from their good long-term stability and resistance to chemical reaction. In a series of works [9,10] a class of gas sensors using thin films from pure tellurium or its alloys from the As–Ge–Te system has been proposed to detect some pollutants in ambient air. Such films show very good sensing properties to NO\textsubscript{2} even at room temperature. Results on the interaction of Te-based thin films with different gas species such as propylamine, carbon oxide [11] and ammonia [12] have also been reported. Also, a relevant study has been performed on Te\textsubscript{1}:Ge\textsubscript{x}-based binary, ternary and quaternary alloys of Te, Ge, Se, As, Mg, I and S [13] in an attempt to find appropriate material compositions for use in future NO sensors operating at room temperature. All these results have motivated further studies to find appropriate materials for each separate analyte. A way to obtain suitable sensing properties is the development, preparation and characterization of complex chalcogenide glasses.

In this study, Ge\textsubscript{x}Se\textsubscript{y}Te\textsubscript{z} thin films with four different compositions have been prepared by thermal vacuum evaporation of preliminary synthesized glassy materials. Their structure, electrical and photoelectrical properties have been studied and their sensitivity to various vapours such as ammonia, alcohol, acetone, water and isopropanol has been tested.

2. Experimental details

Selected complex glasses of the (GeSe\textsubscript{2})\textsubscript{x}(GeTe)\textsubscript{y}(PbTe)\textsubscript{z} system (\(x = 54 - 90\), \(y = 9 - 36\), \(z = 0, 10\)) at four different compositions (see table 1) were synthesized by the conventional melt quenching technique. The synthesis was performed with step-wise heating up to 773, 1073 and 1248 K, at rates 3 - 4, 2 - 3 and 2 - 3 K.min\textsuperscript{-1}, respectively. Homogeneous annealing of the melts was carried out at these temperatures for 0.5, 0.5 and 2.0 h, respectively, combined with continuous vibration stirring at the highest temperature. The samples were quenched in melting ice and at a cooling rate of 15 K.sec\textsuperscript{-1}. The glassy state was verified by XRD and electron microscopy analyses [14].

Thin films (of around 0.8 μm thickness) were prepared by thermal evaporation of the synthesized and powdered glasses in a high vacuum of 6×10\textsuperscript{-6} Torr at evaporation rate of 0.8 - 1.0 nm.sec\textsuperscript{-1}. The films were deposited on crystalline silicon or glass substrates at room temperature for investigations of composition/surface morphology and for electrical measurements, respectively.

The composition of both bulk samples and thin films was determined by a scanning electron microscope with an X-ray microanalyzer Jeol Superprobe 733 (Japan) at an electron accelerating voltage of 20 kV and a current of 1.4 nA. The results from the X-ray microanalysis show (table 1) that no Pb has been detected in the films produced from source material with 10 mol % of PbTe. Thus ternary Ge\textsubscript{x}Se\textsubscript{y}Te\textsubscript{z} films have been produced with near stoichiometric Ge content (the atomic concentration has been determined with an accuracy of ± 1%) and four different Se/Te compositions.

Table 1. Source glass and thin film compositions determined by X-ray microanalysis.

| Sample No | Source materials (mol %) | Glasses (at %) | Thin films (at %) |
|-----------|--------------------------|----------------|------------------|
| 1.        | (GeSe\textsubscript{2})\textsubscript{90}(GeTe)\textsubscript{10} | Ge\textsubscript{34}Se\textsubscript{56}Te\textsubscript{4} | Ge\textsubscript{34}Se\textsubscript{56}Te\textsubscript{4} |
| 2.        | (GeSe\textsubscript{2})\textsubscript{81}(GeTe)\textsubscript{9}(PbTe)\textsubscript{10} | Ge\textsubscript{32}Se\textsubscript{57}Te\textsubscript{7}Pb\textsubscript{4} | Ge\textsubscript{32}Se\textsubscript{57}Te\textsubscript{7}Pb\textsubscript{4} |
| 3.        | (GeSe\textsubscript{2})\textsubscript{67.5}(GeTe)\textsubscript{22.5}(PbTe)\textsubscript{10} | Ge\textsubscript{34}Se\textsubscript{50}Te\textsubscript{12}Pb\textsubscript{4} | Ge\textsubscript{34}Se\textsubscript{50}Te\textsubscript{12}Pb\textsubscript{4} |
| 4.        | (GeSe\textsubscript{2})\textsubscript{51}(GeTe)\textsubscript{18}(PbTe)\textsubscript{10} | Ge\textsubscript{35}Se\textsubscript{45}Te\textsubscript{18}Pb\textsubscript{4} | Ge\textsubscript{35}Se\textsubscript{45}Te\textsubscript{18}Pb\textsubscript{4} |

The surface morphology of the films was studied by means of a Scanning electron microscope Philips SEM 515 operating in a regime of secondary electrons and at an accelerating voltage of 20 kV. The angle between the electron beam and the normal to the film surface was varied between 0° and
The obtained images showed quite smooth film surface with no distinct grains larger than 100 nm (that is the image resolution). Stokes Raman spectra in a pseudo-backscattering geometry were recorded using a system of a SPEX 1403 double monochromator (operated at a spectral slit width of ~ 3 cm⁻¹) and a cooled photomultiplier connected to photon counting equipment. The 488 nm (2.54 eV) line of an Ar⁺ laser was used for the excitation in a line focusing configuration (cylindrical lens) in order to avoid degradation of the films. The Raman spectra were obtained at 293 K in air.

Dark current dc measurements were carried out by means of a Keithley 6487 Picomammeter using co-planar aquadag contacts on the top surface of the layers; the contacts produce a gap cell with an active area of ~ (1×10) mm². Current-voltage (I-V) characteristics were measured in dark at applied electric fields in the range 1 - 10² V cm⁻¹ which showed Ohmic-like behaviour of the contacts. The temperature dependences of the dark and photocurrent were determined in the 293 – 383 K range at a heating rate of 0.1 K.sec⁻¹. Prior to each measurement, the samples were heated in dark up to 383 K in order to achieve charged carrier equilibrium and to desorb water molecules captured on the film surface. The applied temperatures are well below the glass transition temperatures we determined (> 500 K for all compositions studied) and the repetition of the described measuring cycle did not cause changes in the film conductivity and dark current activation energy.

The spectral dependence of the photocurrent was measured in air at 293 K in the wavelength range 500-1000 nm under illumination with monochromatic light (2 - 7×10¹⁵ photons.s⁻¹.cm⁻²) from a diffraction grating monochromator MDR 2 at a spectral bandpass per slit width of 2 nm.mm⁻¹. The films were illuminated with chopped light (2 Hz, ON/OFF ratio = 1) and thus only the contribution of photoexcited charge carriers in the total current through the films was detected. The as-measured photocurrent spectra were corrected for the spectral sensitivity of the system (to constant photon flux) and then normalized.

A preliminary test of the films sensitivity to various gases has been performed by measuring the dc dark current (I_d) at room temperature before (in a vacuum cryostat evacuated to ~ 10⁻² Torr) and after exposure to water vapour, ammonia, ethanol, acetone and isopropanol vapours in air as the carrier gas [15]. The vapour content in the air which entered the cryostat upon opening the entrance valve was not strictly controlled. The level of this content was determined by the vapour drawn into the cryostat from a soaked piece of cloth fixed to the valve entrance. The exposure procedure described was repeated several times on each sample for each analyte and a good reproducibility has been observed. Normally, the evacuation of the cryostat for 3 - 5 minutes was enough to completely return the samples in the initial state (i.e. to recover the initial I_d values) and sample heating was not necessary. Although these measurements are qualitative, they can be useful to distinguish compositions suitable for sensor applications.

3. Results and Discussion

3.1. Dark conductivity

Current-voltage characteristics measured at room temperature in air are depicted in figure 1. The linear fit performed shows that the characteristics are Ohmic-like (I_d ~ Vᵐ, m ≈ 1), which ensures correct determination of both film conductivity and its thermal activation energy. In order to eliminate the effect of water vapour and other molecules adsorbed on the film surface, the conductivity values were calculated using dark current values measured in vacuum of ~ 10⁻² Torr. It has been obtained that the room temperature dark conductivity varies within less than an order of magnitude (between 1 and 5×10⁻⁷ S.cm⁻¹). The weak conductivity variations observed upon increasing the Te content from 3 to 13 at % implies that the films are most likely amorphous. This implication is confirmed by the X-ray diffraction data given below (figure 2). Probably, Te atoms replace Se ones, but do not create high free carrier concentration. On the other hand, in amorphous chalcogenides a disorder increase results in an increase of the density of gap states trapping holes and thus diminishes the density of free holes in the valence band. Hence, the overall dark conductivity decrease observed with increasing Te content
(figure 1) may be connected with some increase of the level of network disorder. This suggestion is in agreement with the results of other authors [16].

Figure 2 shows an X-ray diffraction spectrum of a Ge32Se64Te4 film. A broad band is seen that is centred at $2\theta \approx 24^\circ$; no strong narrow bands are observed. Similar spectra have been obtained for the other three compositions. They show that films of all composition are amorphous, thus confirming the assumption made on the basis of the electrical measurements.

$$I_d \sim \exp(-E_d/kT)$$

which corresponds to a thermally activated process. In eq.(1) $E_d$ is the dark current activation energy, $k$ the Boltzmann constant and $T$ the measuring temperature. The obtained values for the activation energy are in the range (0.67-0.70) ± 0.03 eV i.e. the activation energy practically does not change with the composition. Activation energies of 0.8 - 1.1 eV [17,18] and ~ 0.35 eV [19] have been reported for amorphous GeSe2 and GeTe, respectively. The obtained values of 0.67 - 0.7 eV are smaller but close to the activation energy of amorphous GeSe2.

At high temperatures (normally $T > 300$ K), the electrical conductivity of most undoped chalcogenide glasses is due to transport of free carriers in the extended states of the valence bands and the activation energy $E_d$ represents the energy distance between the Fermi level $E_F$ and the valence band. Taking into account that the measuring temperatures in this study are $T \geq 293$ K one can relate the electrical conductivity of the Ge-Se-Te films to transport of holes via the extended state of the valence band.

3.2. Photoconductivity

Using the maximum current in the as-measured photocurrent spectral dependences, the relative film photoconductivity has been calculated. Comparison of the values obtained has shown that the film photoconductivity decreases approximately 100 times with increasing Te content. This decrease is most likely due to the above assumed network disorder increase which may cause a decrease of both lifetime and mobility of the photoexcited carriers.

Normalized spectral dependences of the photocurrent are depicted in figure 4. Some difference is observed in the high energy part of the photocurrent spectra which is related to light absorption close to the film surface. This difference may be due to the effect of gas molecules absorbed on the films surface. It is also seen from figure 4 that the increase of Te from 3-4 at.% to 8-13 at.% causes a “red”
shift of the low-energy part of the spectrum and thus an extension of the range of film spectral sensitivity is obtained. This observation indicates that the optical band gap $E_g^o$ of the films decreases with increasing Te content. The “red” shift corresponds to formation of ternary Ge-Se-Te alloys whose band gap decreases with increasing Te content. Similarly, short wavelength absorption edge shift towards longer wavelength has been registered as a result of Te → Se substitution in the Ge$_{20}$Se$_{80-x}$Te$_x$ glass system [20]. A rough estimation of the optical band gap has been made based on the energy corresponding to the photocurrent value of $(I_p^{max}/2)$ at the low energy side of the curves. Reasonable values of ~ 1.9 eV and ~ 1.55 eV have been obtained for samples NNo 1, 2 and NNo 3, 4, respectively (the room temperature optical gap of GeSe $E_g^o = 2.1$ eV [21] and that of GeTe $E_g^o = 0.7$ eV [19]). The $E_g^o$ values we obtained from optical transmission measurements also show a gradual decrease with increasing Te content; values of 1.86, 1.58, 1.49 and 1.33 eV have been determined. The photoelectrically and optically determined $E_g^o$ values are in good agreement for the lowest Te content but not for the higher ones. The observed discrepancy may be understood assuming that the films are not completely homogeneous and the main contribution to the photocurrent comes from regions with lower Te content which displayed higher photoconductivity. The inhomogeneity assumed could also be the reason for the $E_g$ constancy with composition though the optical band gap decreases with increasing Te content.

3.3. Chemical sensitivity

The results from the test for the chemical sensitivity of the films are summarized in table 2. The films response time, i.e. the time for achieving the maximum dark current alteration, was quite short, between 5 and 40 sec. The films do not show any systematic change of their sensitivity to any vapour with changing Se/Te content. Additionally, films with very similar Te content of 3-4 at % show quite different behaviour. The most interesting result obtained in these experiments concerns the Ge$_{32}$Se$_{55}$Te$_{13}$ films which show high sensitivity to ammonia at room temperature and a response time of 20 sec. It is important that Ge$_{32}$Se$_{55}$Te$_{13}$ films are practically insensitive to water vapour.

In order to understand better the results of table 2, one should keep in mind that the sensitivity is mainly related to changes in the conductivity of the near surface region caused by the adsorbed vapour molecules. The observed dispersion of the results indicates that the initial surface state of the films is quite different, which implies different compositions or/and different structure. As mentioned in the introduction, tellurium plays an important role in the gas sensitivity of chalcogenide films. Because of the application of thermal evaporation for the film preparation, one could expect [22] that the near
Table 2. Chemical sensitivity of Ge-Se-Te thin films to five different vapours in carrying gas air. The ratio of the dark current under film exposure to the respective vapour, $I_{exp}$, to the equilibrium dark current in vacuum, $I_{eq}$, is taken as measure of the film sensitivity.

| Film composition | ammonia | ethanol | isopropanol | acetone | water |
|------------------|---------|---------|-------------|---------|-------|
| Ge$_{31}$Se$_{66}$Te$_3$ | 15      | 400     | 20          | 7.5     | 300   |
| Ge$_{32}$Se$_{64}$Te$_4$ | 28      | 22      | 28          | 42      | 40    |
| Ge$_{33}$Se$_{59}$Te$_8$ | 1.8     | 3.3     | 4.4         | 8.9     | 1.8   |
| Ge$_{32}$Se$_{55}$Te$_{13}$ | 750     | -       | -           | -       | 1.5   |

surface region will be slightly Te-enriched when compared with the interior of the film. The enrichment depends on the film deposition conditions and therefore it may vary from batch to batch thus causing variations in the film response. Precise control of the deposition conditions is required for obtaining reproducible results. From the SEM images the surface microstructure of all films was very similar and hence one could not expect that it will significantly affect the film sensitivity.

We have obtained structural (Raman) data for the near-surface (100-150 nm) layer of the films corresponding to the penetration depth of the 488 nm exciting line. Figure 5 shows the normalized spectra of two films, namely those with 4 and 13 at% Te. The spectra of the other two films with 3 and 8 at% Te are similar to that of the 4 at% film. Three main bands are observed, with two of them attributed [23] to symmetric vibrations in corner-sharing (CS, ~200 cm$^{-1}$) and edge-sharing (ES, ~215 cm$^{-1}$) Ge-Se$_4$ tetrahedra. The third band, at ~175 cm$^{-1}$, has also been observed in ternary Ge$_{20}$Se$_{80-x}$Te$_x$ glasses [24] showing a similar intensity increase for Te-rich samples. This, Te-content dependent, band has been related [24] to Te-Te short chains bridging Ge-Se$_4$ tetrahedra. Existence of Ge-Ge bonds may also have some contribution to this band. The spectrum of the 13 at% Te film shows a well expressed additional band at ~90 cm$^{-1}$ (figure 5) which may be attributed to bending vibrations in Ge-Te$_4$ tetrahedra [25]. The Raman scattering results confirm that the introduction of Te in the glassy network of Ge-Se$_4$ tetrahedra results in an increase of disorder and this is compatible with the photocurrent reduction observed upon increasing the Te-content. Hence, the structure of the near surface region of the 13 at% Te films is quite different from the structure of the other films and one can reasonably assume that this difference is responsible for the observed good room temperature sensitivity and selectivity of films with this composition.

![Figure 5.](image)

Nowadays, the sensors using metal oxides hold a leading position in the group of chemical gas sensors [26]. However they have some drawbacks such as low selectivity, a relatively long response and recovery times, and a strong effect of the water vapour on their response. Besides, they operate at high temperatures (423 K – 623 K) and this requires power consumption of ~ 1 W. Therefore, the
observed high selectivity, good sensitivity and fast response make the Ge\textsubscript{32}Se\textsubscript{55}Te\textsubscript{13} films good candidates for the preparation of ammonia sensor operating at room temperature in standard conditions (in humid air).

4. Conclusions
It has been shown that the investigated Ge\textsubscript{x}Se\textsubscript{y}Te\textsubscript{z} thin films are amorphous. No considerable changes of both the room temperature conductivity (varying between 1×10\textsuperscript{-7} and 5×10\textsuperscript{-7} S.cm\textsuperscript{-1}) and the dark current activation energy (0.67 - 0.7 eV) have been observed with increasing Te content from 3 - 4 to 13 at % which has been related to the amorphous structure of the films. However, a strong photoconductivity decrease has been observed with increasing Te content which has been assigned to a disorder increase of the amorphous network. A “red” shift of the low-energy side of the photocurrent spectra has been seen with increasing Te content. It indicates that the optical band gap decreases as a result of Te → Se substitution in the films. It has been found that the Ge\textsubscript{32}Se\textsubscript{55}Te\textsubscript{13} films are sensitive to ammonia vapours, but not to air humidity. The observed sensitivity and selectivity have been connected with the specific network structure of the region nearest to the film surface. These properties, together with their short response time, make the Ge\textsubscript{32}Se\textsubscript{55}Te\textsubscript{13} films interesting for the preparation of ammonia sensors operating at room temperature in standard conditions (in humid air).

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References
[1] Zakery A and Elliott S R 2003 J. Non-Cryst. Solids 330 1
[2] Mehta N 2006 J Scientific and Industrial Research 65 777
[3] Yamada N, Nagata K, Nishiuchi K and Furukawa Sh 1998 EP patent 0899725 A1
[4] Liu J 2009 US patent 7638357 B2
[5] Lung H-L 2011 US patent 7932101 B2
[6] Schubert J et al 1999 Appl. Phys. A 69 [Suppl.] S803
[7] Kloock J P, Mourzina Y G, Ermolenko Y, Doll Th, Schubert J and Schöning M J 2004 Sensors 4 156
[8] Vassilev V S and Boycheva S V 2005 Talanta 67 20
[9] Marian S, Tsuilyanu D, Marian T and Liess H-D 2001 Pure Appl. Chem. 73 2001
[10] Tsuilyanu D, Stratan I, Tsuilyanu A, Liess H-D and Eisele I 2007 Sensors and Actuators B 121 406
[11] Tsuilyanu D, Marian S and Liess H D 2002 Sensors and Actuators B 85 232
[12] Sen S, Muthe K P, Joshi N, Gadkari S C, Gupta S K, M Roy Jagannath, Deshpande S K and Yakhami J V 2004 Sensors and Actuators B 98 154
[13] Wüsten J and Potje-Kamloth K 2010 Sensors and Actuators B 145 216
[14] Aljihmani L, Petkov K and Vassilev V 2012 J. Non-Cryst. Solids 358 364
[15] Nesheva D, Aneva Z, Reynolds S, Main C and Fitzgerald A G 2006 J. Optoeel. Adv. Mat. 8 2120
[16] Kalužný J, Ležal D, Mariani E and Zavadil J 2004 Chalcogenide Letters 1 41
[17] Bakr N A, Aziz M S and Hammam M. 2000 Egypt. J. Sol. 23 45
[18] Qamhieh M and Adriaenssens G J 2001 J. Non-Cryst. Solids 292 80
[19] Tsu R, Howard W E and Esaki L 1970 J. Non-Cryst. Solids 4 322
[20] Lezal D, Pedlikova J and Zavadil J 2004 J. Optoeel. Adv. Mat. 6 133
[21] Sleeckx E, Tich L, Nagels P and Callaerts R 1996 J. Non-Cryst. Solids 198-200 723
[22] Kasap S O, 1991 Handbook of Imaging Materials, (New York: Marcel Dekker Inc) p 329
[23] Sugai S 1987 Phys. Rev. B 35 1345
[24] Moharram A H, Hefni M A and Abdel-Baset 2010 *J Appl Phys* **108** 073505
[25] Andrikopoulos K S, Yannopoulos S N, Kolobov A V, Fons P and Tominaga J 2007 *J. Phys. Chem Solids* **68** 1074
[26] Baltes H, Göpel W and Hesse J (eds.) 1996 *Sensors Update* (Weinheim: Wiley VCH) vol 2