

Optical properties of phase change memory $\text{Ge}_1\text{Sb}_2\text{Te}_4$ glasses

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Phase change memory materials are promising for the next-generation of non-volatile flash memory that will serve in new mobile computing, entertainment and other handheld electronics. Among them are chalcogenide glasses Ge-Sb-Te (GST) which can exist in two separate structural states – amorphous and crystalline. Switching of the material from one to another state can be done by heating applying an electrical pulse or by exposure to intense laser beam. We report the changes of optical parameters of amorphous $\text{Ge}_1\text{Sb}_2\text{Te}_4$ films under heat treatment and light exposure.

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1. Introduction

The discovery of chalcogenide glasses in 1955 year as non-crystalline semiconductors and the first systematical investigation of this class of materials belong to Prof. N.A.Goriunova and B.T.Kololmiets [1,2]. The new class of non-crystalline semiconductors is the chalcogenide glasses containing elements of the VI group such as S, Se, Te. The typical representatives of chalcogenide glasses are the arsenic sulfide (As_2S_3) and arsenic selenide (As_2Se_3). The chalcogenide glasses exhibit excellent electrical properties and are suitable optical materials for IR region [3]. In 1968 S.R.Ovshinsky discovered the electrical switching and memory (OVONIC) effects in amorphous semiconductors [4]. These effects stays on the bases to use the amorphous materials as new phase change materials for optical storage media such as CD and DVD recordable and rewritable discs. The concept of phase change memories consists in the use of such semiconductor materials which can exist in two separate structural stable states (for example, amorphous and crystalline). Switching of the material from one to another state can be done by applying an electrical pulse or by exposure to intense laser beam. Using of semiconductor materials with the same composition in amorphous and crystalline phases provides long life, and as such materials were chosen the ternary alloys of the Ge-Sb-Te (GST with the ratio 2:2:5) system and other more complicated chalcogenide glass [5]. Now we briefly will listed the two modern electronic devices: random access memory (RAM) and read only memory (ROM), because they provide high-speed storage [6].

I. Random Access Memory (RAM). RAM is used in the computer systems for main memory or primary storage. RAM can be divided in volatile and non-volatile type of memories. Volatile memory (temporary memory), also known as volatile storage, is computer memory that

requires power to maintain the stored information. Most forms of modern RAM are volatile storage, including dynamic random access memory (DRAM) and static random access memory (SRAM).

II. Non-volatile memory (NVM) is computer memory that can retain the stored information even when not powered. Examples of non-volatile memory include read-only memory (ROM), flash memory, most types of magnetic computer storage devices (e.g. hard disks, floppy disks), and optical disks. ROM is memory that users cannot write to – traditionally it has been used to store BIOS code in computers.

III. Phase Change Random Access Memory (PRAM) is also a type of non-volatile computer memory which uses the unique behavior of chalcogenide glass - the "switching" between two states, crystalline and amorphous with the application of heat. PRAM is one of a number of new memory technologies that are attempting to compete in the non-volatile role with the almost universal Flash memory. PRAM is viewed as a next-generation version of non-volatile flash memory that will serve in new mobile computing, entertainment and other handheld electronics.

2.1 Some historical aspects of development of phase change memory technology: [7]

- **September 1966:** [Stanford Ovshinsky](#) files first patent on phase change technology;
- **January 1969:** Charles H. Sie published a dissertation at Iowa State University on chalcogenide phase change memory device;
- **June 1969:** US Patent 3,448,302 licensed to Ovshinsky claims first reliable operation of phase change memory;
- **September 1970:** [Gordon Moore](#) publishes research in [Electronics Magazine](#);

- **June 1999:** Ovonyx joint venture is formed to commercialize PRAM technology;
- **November 1999:** Lockheed Martin works with Ovonyx on PRAM for space applications;
- **February 2000:** Intel invests in Ovonyx, licenses technology;
- **December 2000:** ST Microelectronics licenses PRAM technology from Ovonyx;
- **March 2002:** Macronix files a patent application for transistor-less PRAM;
- **July 2003:** Samsung begins work on PRAM technology;
- **2003 through 2005:** PRAM-related patent applications filed by Toshiba, Hitachi, Macronix, Renesas, Elpida, Sony, Matsushita, Mitsubishi, Infineon and more;
- **August 2004:** Nanochip licenses PRAM technology from Ovonyx for use in MEMS probe storage;
- **August 2004:** Samsung announces successful 64 Mbit PRAM array;
- **February 2005:** Elpida licenses PRAM technology from Ovonyx;
- **September 2005:** Samsung announces successful 256 Mbit PRAM array, touts 400 μA programming current;
- **October 2005:** Intel increases investment in Ovonyx;
- **December 2005:** Hitachi and Renesas announce 1.5 V PRAM with 100 μA programming current;
- **December 2005:** Samsung licenses PRAM technology from Ovonyx;
- **July 2006:** BAE Systems begins selling the first commercial PRAM, [a Radiation Hardened C-RAM 512Kx8](#) chip;
- **September 2006:** Samsung announces 512 Mbit PRAM device;
- **October 2006:** Intel and STMicroelectronics show a 128 Mbit PRAM chip;
- **December 2006:** IBM Research Labs demonstrate a prototype 3 by 20 nanometers;
- **January 2007:** [Qimonda](#) licenses PRAM technology from Ovonyx;
- **April 2007:** Intel's chief technology officer Justin Rattner is set to give the first public demonstration of the company's PRAM (phase-change RAM) technology;
- **October 2007:** [Hynix](#) begins pursuing PRAM by [licensing Ovonyx technology](#);
- **February 2008:** Intel and STMicroelectronics announce four-state MLC PRAM and begin shipping samples to customers;
- **December 2008:** Numonyx announces mass production 128 Mbit PCM device to selected customer;
- **June 2009:** Samsung's phase change RAM will go into mass production starting in June;
- **September 2009:** Samsung announces mass production start of 512 Mbit PRAM device;
- **October 2009:** Intel and Numonyx announce they have found a way to stack phase change memory arrays on one die;

- **December 2009:** Numonyx announces 1 Gb 45 nm product;

- **April 2010:** Numonyx releases Omneo PCM Series (P8P and P5Q), both in 90 nm;

- **April 2010:** Samsung releases 512 Mbit PCM with 65 nm process, in Multi-Chip-Package.

During this period and at the present in many research centers in the world, the chalcogenide glasses with phase change properties are studied faceted. Special interests represent the phase change chalcogenides from the cut-of $\text{Sb}_2\text{Te}_3\text{-GeTe}$ (Fig.1a [8]). The investigated glass composition in the present work $\text{Ge}_1\text{Sb}_2\text{Te}_4$ is one of the most stable materials for switching and memory applications.

2. Experimental results and discussion

The chalcogenide $\text{Ge}_1\text{Sb}_2\text{Te}_4$ phase change material was synthesized from high purity initial components Ge, Sb, Te (99.999 %) by conventional melt quenching method. The mixture of high-purity precursors was melted in sealed evacuated quartz ampoules ($p=5\cdot 10^{-6}$ Torr) placed in a rocking furnace. The total weight of the synthesized sample was 10 grams. The temperature of the quartz ampoule was slowly increased to 550 $^\circ\text{C}$ at the rate of 50 $^\circ\text{C}/\text{hour}$ and kept at this temperature during 24 hours for homogenization. Than the temperature was increased up to 980 $^\circ\text{C}$ at the rate 50 $^\circ\text{C}/\text{hour}$ and homogenized at this temperature during 72 hours, and then quenched in the regime of the disconnected furnace. Fig.2 shows the fragment of the crystal structure of the $\text{Ge}_1\text{Sb}_2\text{Te}_4$ [9]. Thin film samples of thickness $d=1\div 2$ μm were prepared by flash thermal evaporation in vacuum of the synthesized initial glasses onto glass substrates.

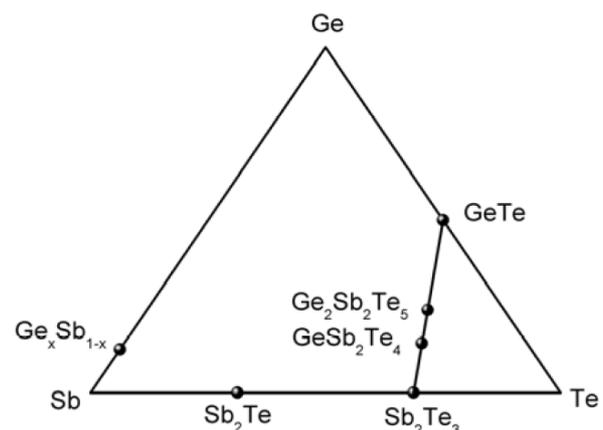


Fig.1. Ternary diagram of the Ge-Sb-Te with phase change materials [8].

For optical transmission spectra measurements a UV/VIS ($\lambda=300\div 800$ nm) and 61 NIR ($\lambda=800\div 3500$ nm) Specord's CARLZEISS Jena production were used. For calculation of the optical constants from the transmission

spectra, the computer program *PARAV-VI.0* (www.chalcogenide.eu.org) was used [10].

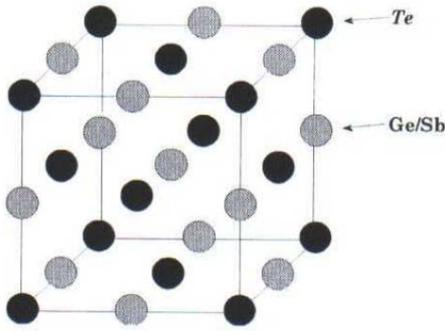


Fig. 2. Crystal structure of metastable Ge₁Sb₂Te₄ [9].

Fig. 3 shows the transmission spectra of as-deposited amorphous Ge₁Sb₂Te₄ thin films (1) and annealed at $T=150$ °C during 2 minutes. After annealing at high temperature $T=150$ °C, due to the crystallization process of the amorphous film the transmission decrease, and the Urbach tail is shifted in the long wave region of spectrum. The illumination with white during 1 hour does not change the transmission spectra of the as-deposited amorphous film. The spot of phase change transformation of the amorphous material was observed when the film was illuminated with UV laser pulses. According to [9], the samples Ge₁Sb₂Te₄ with small addition of oxygen the crystallization phase appear in the temperature range $T=130-145$ °C, and at higher temperature (around $T=275$ °C) this phase is transformed into the Ge₁Sb₂Te₄ hexagonal phase.

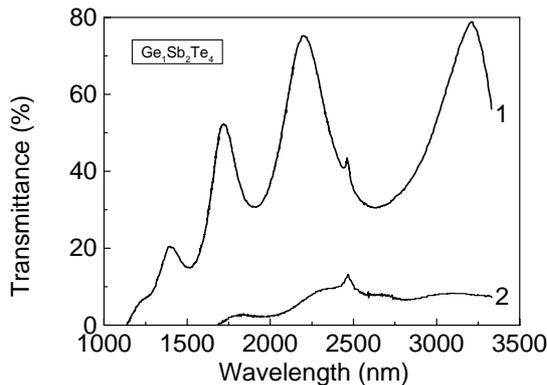


Fig. 3. The transmission spectra of as-deposited amorphous Ge₁Sb₂Te₄ thin films (1) and annealed at $T=150$ °C during 2 minutes (2). $d=1.57$ μm .

Fig. 4 shows the dependences of the absorption coefficient α versus photon energy $h\nu$ ($\alpha=f(h\nu)$) (curve 1) and $(\alpha \cdot h\nu)^{1/2}=f(h\nu)$ (curve 2) for as-deposited amorphous Ge₁Sb₂Te₄ thin films derives from the transmission spectra using the computer program *PARAV-VI.0* [8]. The optical transmission $T(\lambda)$ for thin semiconductor films is determined by the expression:

$$T = \frac{(1-R)^2 \exp(-\alpha d)}{1-R^2 \exp(-2\alpha d)}, \quad (1)$$

where R - is the optical reflection, α - the absorption coefficient, and d - the thickness of the amorphous film.

In the consideration that the member $R^2 e^{-2\alpha d} \ll 1$ from the equation (1) we can obtain the expression for calculation of the absorption coefficient

$$\alpha = \frac{1}{d} \ln \frac{(1-R)^2}{T} \quad (2)$$

The optical band gap E_g for as-deposited amorphous films was calculated from the relation:

$$(\alpha \cdot h\nu)^{1/2} = A(h\nu - E_g), \quad (3)$$

where A - is a constant. A plot $(\alpha \cdot h\nu)^{1/2} \sim h\nu$ (Tauc plot) yields a straight line and the extrapolation of the photon energy axis $(\alpha \cdot h\nu)^{1/2} \rightarrow 0$ give the values of the optical band gap E_g . The estimated value of the optical band gap of the as-deposited amorphous Ge₁Sb₂Te₄ film is $E_g=1.08$ eV. For Ge₁Sb₂Te₄ it was demonstrated that the measured indirect band gap energies are compared to those of the electronic band-structure calculations [12].

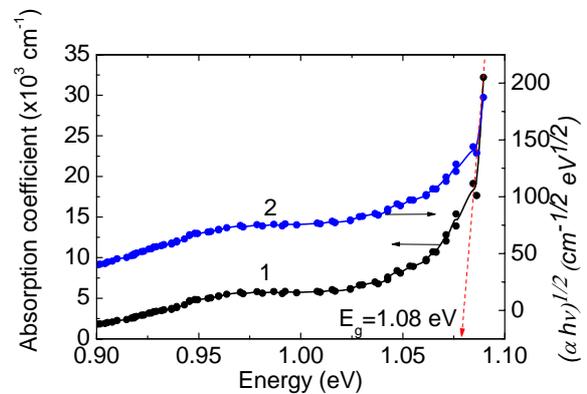


Fig. 4. The dependences of the absorption coefficient α versus photon energy $h\nu$ ($\alpha=f(h\nu)$) (1) and $(\alpha \cdot h\nu)^{1/2}=f(h\nu)$ (2) for as-deposited amorphous Ge₁Sb₂Te₄ thin films ($d=1.57$ μm).

Fig. 5 represents the dispersion curve of the refractive index $n=f(\lambda)$ for as-deposited amorphous Ge₁Sb₂Te₄ thin films. The points are the experimental data, and the continuum line is the computer fitting curve. The plot $(n^2-1)^{-1}$ vs. $(h\nu)^2$ (Fig.6) allow to determine the oscillator parameters by fitting a straight line to the experimental points. By extrapolating the fitting line towards $h\nu=0$, one can obtain the static refractive index $n_0=3.0$ and the static dielectric constant $\epsilon_s = n^2(0) = 9.0$.

The dispersion of the refractive index is related to the electronic absorption spectrum through the Wemple

equation based on the single electronic oscillator model [13]

$$(n^2 - 1) = \frac{E_d E_0}{E_0} - (h\nu)^2 \quad (4)$$

where E_0 is the average electronic energy gap, and E_d is the dielectric oscillator strength.

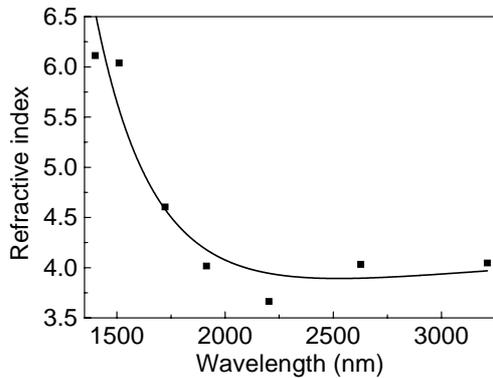


Fig.3a. The dispersion curve of the refractive index $n=f(\lambda)$ for as-deposited amorphous $\text{Ge}_1\text{Sb}_2\text{Te}_4$ thin films ($d=1.57 \mu\text{m}$).

Large values of the refractive index n are obtained for smaller E_0 and for large E_d and leads to a large dispersion throughout the chalcogenide glass material. From equation (4) we obtain

$$(n^2 - 1)^{-1} = \frac{E_0}{E_d} - \left(\frac{1}{E_0 E_d}\right)(h\nu)^2 \quad (5)$$

Using the plot from Fig. 3 b, the E_0 and E_d were calculated with the values $E_0=0.931 \text{ eV}$ and $E_d=7.448 \text{ eV}$, respectively. The value of E_0 is smaller than optical band gap $E_g=1.08 \text{ eV}$ obtained from the Tauc plot (Fig. 4).

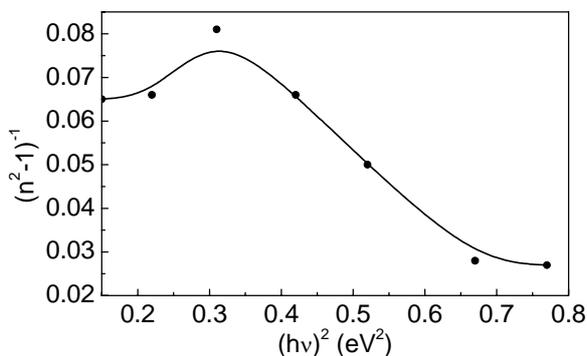


Fig. 6. The dependence $(n^2-1)^{-1} = f(h\nu)^2$ for as-deposited amorphous $\text{Ge}_1\text{Sb}_2\text{Te}_4$ thin films ($d=1.57 \mu\text{m}$).

4. Conclusions

The X-ray diffraction patterns and optical properties of phase change materials $\text{Ge}_1\text{Sb}_2\text{Te}_4$ were studied. It was established that after annealing of the amorphous films a high temperature ($T=150 \text{ }^\circ\text{C}$) take place the crystallization and the Urbach tail is affected. From the transmission spectra the optical constants absorption coefficient α , optical band gap E_g , and the refractive index n) of the amorphous $\text{Ge}_1\text{Sb}_2\text{Te}_4$ were determined.

The static refractive index $n_0=3.0$, static dielectric constant $\epsilon_s = n^2(0) = 9.0$, average electronic energy gap $E_0=0.931 \text{ eV}$, and the dielectric oscillator strength $E_d=7.448 \text{ eV}$ were estimated from the optical measurements.

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