

Non-volatile phase change memory materials and their induced changes

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ABSTRACT

The problems of non-volatile phase change memories, are reviewed and discussed. Accent is given to materials, preparation of their thin films, and to their physico-chemical properties. Discussed are also changes of their properties induced by light and by electrical pulses.

INTRODUCTION

The problem of non-volatile optical and electrical memories based on phase changes from crystalline to amorphous state and vice versa is well known and has been in focus of interest of many laboratories, meetings and companies. It has been discussed many times (see, e.g. [1-18]). In this remark, some results published recently outside of this, as well as in this meeting (E*PCOS 05) [8] will be mentioned. Many problems of application and theory of phase change memory materials were solved. The process is already commercially applied; the progress in understanding is large. Many questions are still open and our knowledge is far from full understanding, many properties, and parameters of prepared components and processes in them still are not in optimum. We should mention, e.g., storage densities and speeds of recording and overwriting, long term performance and repeatability, durability etc.

The problems we would like to mention and discuss belong to two main categories, namely to

- active memory materials and their properties,
- preparation of active elements and their properties.

Technology of writing, reading, erasing and storage of information, its durability, compatibility, storage capacity as well as the economy questions are also very important and interesting. They would not be discussed in this paper.

MATERIALS FOR NON-VOLATILE PHASE-CHANGE MEMORIES

At first, the active non-volatile phase-change memory materials should be mentioned. The phase change storage of information is based on difference between electrical or optical properties of thin films of crystalline and amorphous material of the same composition (see, e.g. [2-8]). The optical reflectivity and electrical resistivity of amorphous and crystalline phase of many compounds and materials are different ($\Delta > 10\%$ of optical reflectivity and up to several orders of electrical conductivity).

The phase change between crystalline and amorphous state and vice versa (writing or erasing) can be produced by short electrical pulses (\sim ns or tens of ns) or short pulses (from fs to several tens of ns) of laser light that excite the atoms, electrons and holes and heat the material above the crystallization or melting temperatures. For writing process, the electrical or optical pulse produces local melting of active material and, possibly, also some amorphization below the melting

temperature. Quenching that should be quick to avoid crystallization, follows the melting and excitation. It preserves amorphous (disordered) state of material.

For erasing process, the amorphous material is crystallized (again by a short electrical or optical pulse). The speed of crystallization shall be again very high; it enables quick information overwriting. In classical glasses (oxides, halides, chalcogenides), the crystallization process is mostly slow, but in “poor” glasses or amorphous materials with a low glass-forming ability, e.g. in narrow-gap semiconductors, semimetals or metals, the crystallization of amorphous films is an easy and quick process. Many of “memory materials” cannot be prepared as a bulk glass at all (or it is extremely difficult), but their thin amorphous films can be prepared by quick cooling of vapors (ionic sputtering, vacuum thermal evaporation, pulsed laser ablation) or by quick cooling of melted very thin films. The evaluated rates for such cooling are high, up to the order of 10^{11} K/s (see, e.g. [17]).

Many materials were studied and proposed for phase change memories, e.g. $\text{Ge}_2\text{Sb}_2\text{Te}_5$, GeSb_2Te_4 , GeSb_4Te_7 , Ag-In-Sb-Te, Ge-Te, In-Te, Sb-Te, Ge-In-Sb-Te, In-Sb-Te, Ga-Sb, In-Sb, Sb-Se, Te, etc. (see, e.g. [1-9, 12, 19- 23]). It was found that many of these materials, e.g. crystalline $\text{Ge}_2\text{Sb}_2\text{Te}_5$, GeSb_4Te_7 , GeSb_2Te_4 , $\text{Sb}_2\text{Te}_{3\pm x}$ and the alloys based on the systems of Ge-Te, Ge-Sb-Te, Sb-Te, Bi-Te, Ge-Bi-Te, Ag-In-Sb-Te etc. are degenerated narrow gap semiconductors with high concentration of free carriers ($\sim 10^{20}$ - 10^{21} cm^{-3}) [24-29]. Their properties are close to metals [24-29], their melting points are relatively low (see, e.g. Fig. 1 [30]. The crystals of $\text{Ge}_2\text{Sb}_2\text{Te}_5$, GeTe, Sb_2Te_3 , GeSb_2Te_4 and GeSb_4Te_7 are of p-type conductivity, $\sigma_{\perp c} = 4.3 \times 10^3 \Omega^{-1} \text{cm}^{-1}$, $\sigma_{\parallel c} = 1.8 \times 10^3 \Omega^{-1} \text{cm}^{-1}$ (300 K, GeSb_2Te_4) and $\sigma_{\perp c} = 3.4 \times 10^3 \Omega^{-1} \text{cm}^{-1}$, $\sigma_{\parallel c} = 1.03 \times 10^3 \Omega^{-1} \text{cm}^{-1}$ (GeSb_4Te_7), relatively low hole mobility (~ 30 - $200 \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$), and low values of Seebeck and Ettingshausen coefficients. Their dielectric constants and refractive index are high ($\epsilon_r \sim 30$ - 50 , $n \sim 4$ - 7 , Tab.I). The values of electrical conductivities decrease with temperature (110 to 430K). The temperature dependence of Hall mobility $\mu_H \sim 1/T$ and corresponds to the scattering on acoustic phonons in ternary compounds. At temperatures below 300 K, the scattering on ionized impurities starts to play a role. The Seebeck coefficient, α , rises with temperature (Eq. 1).

$$\alpha = \frac{2 \pi^{-2/3} k^2 m_d^{(k+1)}}{3^{5/3} e \hbar^2 N^{2/3}} T, \quad (1)$$

where m_d is effective mass of density of states, k is the Boltzmann constant and N is the concentration of free carriers.

Spectral dependence of the reflectivity of $\text{Sb}_2\text{Te}_3:\text{Ge}$, GeSb_2Te_4 and GeSb_4Te_7 exhibits minimums due to plasma oscillations (Figs. 2, 3 [24, 27]). For $\lambda \rightarrow 0$, the $\epsilon_r \sim 39$, the $n \sim 6.2$ (for GeSb_2Te_4), which indicates covalently-metallic character of chemical bonds in these compounds. Similar values were obtained for other studied tellurides (Tab.I). The reflectivity curves calculated using Drude theory (Eqs. 2, 3) fit very well with experimental data.

The curves can be simulated using classical Drude theory for free carriers

$$2nk = \frac{\epsilon_r}{\omega \langle \tau \rangle} \left\{ \frac{1}{(\omega / \omega_p)^2 + (1 / \omega_p \langle \tau \rangle)^2} \right\} \quad (2)$$

$$n^2 - k^2 = \varepsilon_r \left\{ 1 - \frac{1}{(\omega / \omega_p)^2 + (1 / \omega_p \langle \tau \rangle)^2} \right\}, \quad (3)$$

where ω_p is the angular frequency of the free carrier plasma and $\langle \tau \rangle$ is the mean relaxation time. The ε_r the relative permittivity, $\varepsilon_r = 39$, $\omega_p = 2.7 \cdot 10^{14} \text{ s}^{-1}$, (Tab. I).

Table I.
Physical parameters of some telluride crystals

Crystal	GeTe	GeSb ₂ Te ₄	GeSb ₄ Te ₇	Sb ₂ Te ₃
Space group	D ⁵ _{3d}	D ⁵ _{3d}	D ³ _{3d}	D ⁵ _{3d}
Conductivity type	p	p	p	p
Conductivity $\delta \cdot 10^{-3} (\Omega^{-1} \text{cm}^{-1})$	9.7	4.3	3.42	3.78
Hall mobility $u_H (\text{cm}^2/\text{V s})$	5.5	30	39	168
Free-carrier concentration $N_p \cdot 10^{-20} (\text{cm}^{-3})$	9.4	4.8	2.8	1.5
Energy gap $E_g (\text{eV})$	0.1			0.23
Fermi level $E_F (\text{eV})$	0.4	0.31	0.25	0.08
Mean relax. time $\langle \tau \rangle \cdot 10^{14} (\text{s})$	0.38	0.86	0.9	1.9
Dielectric constant ε_g	37.5	39	39	50
Refractive index n	6.1	6.2	6.2	7.1
Number of valeys		3	6	6
Conductivity effective mass m_c^*		0.55	0.46	0.21
Ref.	25, 31, 32	24	25	26

From optical reflectivity spectra in near- or mid-IR region, the free carries plasma frequency oscillations of ($\sim 10^{14} \text{ s}^{-1}$), their relaxation time ($\tau \sim 10^{-14} \text{ s}$) and the values of real and imaginary parts of dielectric constants were evaluated [25].

By analysis of transport properties, “three-valley” model of valence band top can be applied for GeSb₂Te₄ crystals. The IR reflectivity of GeSb₄Te₇ fits well with experimental values and 6-valley model is proper for description of the top of the valence band. In this behavior, the GeSb₄Te₇ is closer to Sb₂Te₃.

The transport and optical properties of obtained crystals can be changed by heavy doping or by change of composition. The small differences between chemical properties of forming (constituting) elements, e.g. of Ge, Sb and Te, makes easy formation of solid solutions. Non-stoichiometric compounds containing excess of Ge, Sb, Te, GeTe or Sb₂Te₃ can be thus formed. From this point of view, these compounds are similar to semi-metallic alloys.

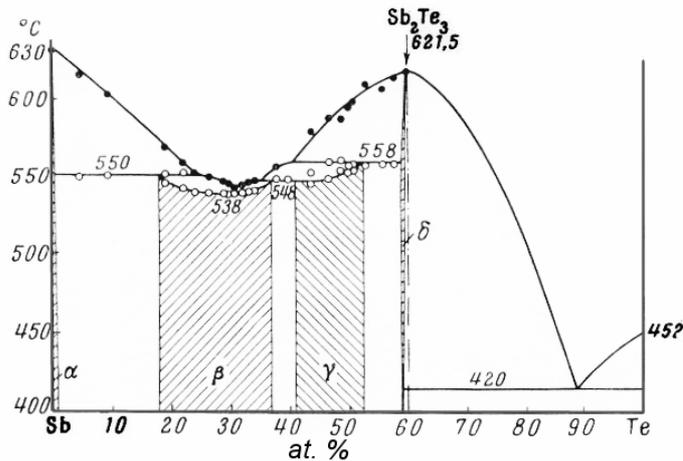


Fig. 1. T-x diagram of the system Sb-Te [30].
 α , β , γ and δ are homogeneous phases.

Typical property of binary, ternary, or multinary telluride systems and crystals (compounds) of above given type, is a possibility to form substitutional and antisite defects [30, 33, 34], e.g. defects of the type $\text{Ge}_{\text{Te}}(\text{I})$, $\text{Te}_{\text{Ge}}(\text{II})$, $\text{Ge}_{\text{Sb}}(\text{III})$, $\text{Sb}_{\text{Ge}}(\text{IV})$, $\text{Sb}_{\text{Te}}(\text{V})$, etc., where, e.g., the Ge atom is placed on the crystal position of tellurium (I), tellurium is in the position of Ge (II), Ge atom substitutes antimony (III), antimony substitutes germanium (IV) or Sb substitutes tellurium (V).

The ability to form solid solutions of substitutional type in broad compositional regions was observed in hexagonal crystals of GeSb_2Te_4 , GeSb_4Te_7 and $\text{Ge}_2\text{Sb}_2\text{Te}_5$ prepared

from melt by Bridgman method or by chemical transport reactions from the gas phase [29]. Such crystals can be considered as so called intermediate phases, e.g. the phases of the type β and γ in Fig. 1. By this behavior, these crystals are similar to metallic alloys where the intermediate phases are formed very frequently. Broad concentration ranges of existence of such phases allow changing their composition in a broad range without any phase separation and without change of structure. The composition of active materials for phase change memories prepared from them can be changed as well, which allows to tune their properties. Such materials can be amorphized and crystallized without larger movement (transport) of atoms by diffusion and thus by process that is usually slow. The possibility to form substitutional solutions is probably behind the fact that the structure of GeSb_2Te_4 and $\text{Ge}_2\text{Sb}_2\text{Te}_5$ is similar not only to each other but also to amorphous bulk GeTe (Tab.I). Without a possibility to form highly non-stoichiometric solids with high density of substitutional defects, the quick solidification (crystallization) without larger diffusion processes would be confined only to stoichiometric compounds that are solidified without any change of composition.

The glass forming ability of chalcogenides (and their resistance to crystallization) is generally decreasing from sulfides and selenides with low-coordination number of S and Se (C.N. ≈ 2), to tellurides with higher coordination numbers (C.N. ≤ 6). The glass-forming ability is generally low in metals, semimetals and narrow-gap semiconductors; the crystallization abilities, and very often also speeds of crystallization of such materials are very high. This factor is probably behind the increased speed of crystallization of some binary and ternary systems based on antimony that contain only small amount of Te or they do not contain any tellurium or other chalcogen at all. Such phases can be formed by e.g. intermetallic compounds or alloys like $\text{Ga}_{11}\text{Sb}_{89}$, $\text{Ge}_{17}\text{Sb}_{83}$, In-Sb or by antimony telluride with strong overstoichiometry of Sb, e.g. by $\text{Sb}_{89}\text{Te}_{11}$ [17]. To extend this idea, one would expect that the good phase-change memory materials would be formed by typical metals, e.g. by Ag, or Cu. Unfortunately, many metals can be amorphized with extreme difficulty and their crystallization could be spontaneous. Their melting points are often high, which is valid especially

for transition metals. The phases based on antimony (or its alloys) that is a semimetal with relatively low melting point could be probably a compromise and good solution – at least for present time.

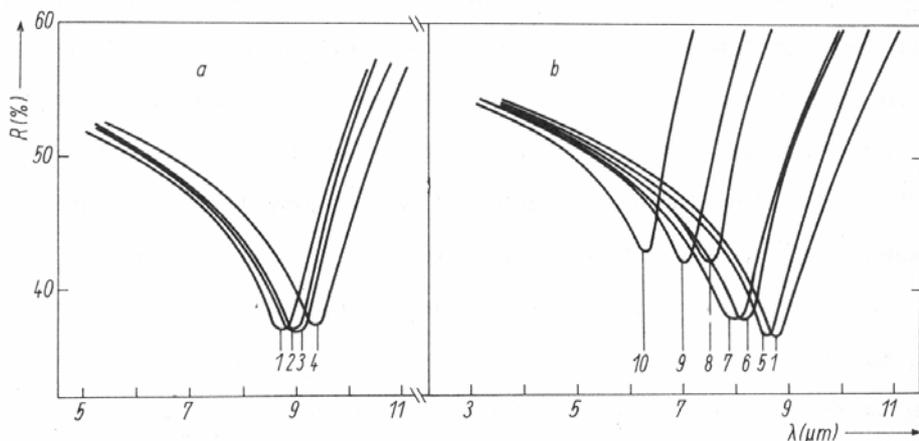


Fig. 2. Optical reflectivity of Sb_2Te_3Ge in plasma oscillations region [26]. 1 Sb_2Te_3 ; 2-10 Sb_2Te_3 with increasing content of Ge (0.01-2.2 at%).

The process of crystallization of thin films of phase change materials surrounded by isolation or protective layers e.g. of $ZnS-SiO_2$ [10], nitrides or ZrO_2 [35] and in contact with crystallized part of the material is highly non-equilibrium. At first, the relative surface (S/V , S is for surface, V for volume) of the active thin film material is very large and the isolation layers can play a role of

crystallization centers. The crystallization can be then partly or fully growth-controlled process. To avoid it, in cases when it is necessary, the anti-crystallization layer below and upon the active layer can be placed in phase-change write-once discs [36].

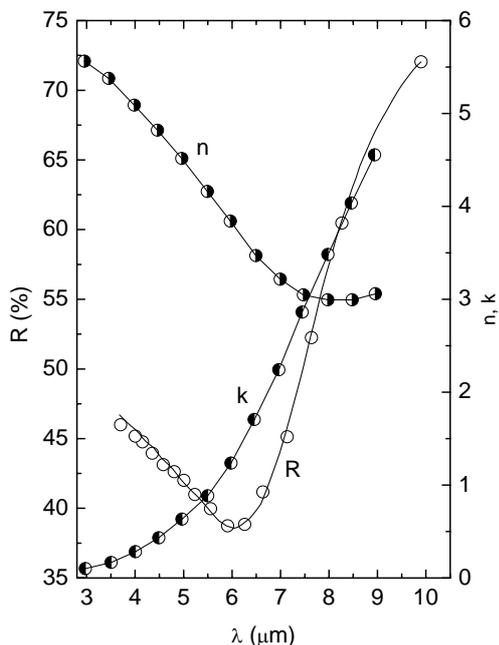


Fig. 3. Reflectivity R , index of refraction n and extinction coefficient k of hexagonal crystals of $GeSb_2Te_4$ [24], E.L.C.

The sputtering of the active material can proceed not only in an inert but also in a reactive atmosphere, e.g. in oxygen or nitrogen [10, 11, 13, 17, 37]. It is known, that Ge reacts with nitrogen, forming a compound Ge_3N_4 [9] that is analogous to well known Si_3N_4 . Such compound have probably a low solubility in tellurium containing phase change materials or in other active materials. It can form crystallization centers and initiate heterogeneous crystallization that could be quicker [11], because the crystallization centers are present in material before its crystallization, they should not be formed after its heating to crystallization temperature. The crystallization centers could be numerous (the content of N in the film can be up to 1.3% [14] and not far from each other. The crystallization centers could be formed not only by Ge_3N_4 but also by TeN or Te_3N_4 that can be created by interaction of the film with nitrogen during sputtering or heating of the material [38].

The mechanism of incorporation of nitrogen into phase-change memory materials based on tellurides is probably more complex; nitrogen can be also incorporated into material, at least into $Ge_2Sb_2Te_5$, not

only as a new phase but also as a part of amorphous matrix. It was found [14, 17, 37] that the nitrogen doping of GST increases its crystallization temperature, activation energy of crystallization and also electrical resistivity. It also increases the transformation temperature for fcc to hexagonal modification and decreases the writing current for electrical memories. A part of nitrogen can be chemically bound to Ge or Te in amorphous matrix without phase separation and to form solid solution with higher covalence and higher melting and crystallization temperatures. Analogous could be the influence of oxygen [13], which easily forms oxides with Ge, Sb and also Te (GeO_2 , Sb_2O_3 , TeO_2 , ...) and can form solid solutions with telluride matrix again without any phase separation. Such solid solutions can be found even in phase-change materials with lower content of tellurium or even in materials without any Te, e.g. as solid solution of GeO_2 , Sb_2O_3 , etc.

Materials from the system Ge-Sb-Te (GST) and Ag-In-Sb-Te (AIST) are mostly used commercially as active parts of non-volatile phase change memories. Beside them, many other compounds or alloys were studied, described and proposed (see, e.g. [1-18] and papers cited); the group of possible materials is very large. Their discussion could be broad and is outside of this paper. It should be stressed again that the writing and erasing processes are far from equilibrium and oversaturated phases (frozen liquids and crystals) can be formed. The physics and chemistry of such fast processes and corresponding phases is in fact far from good understanding.

The phase-change transformation in many materials can be produced also by electrical pulses as we have mentioned. There is a very large amount of papers describing so called switching effects pioneered by discovery of S. R. Ovshinsky and his colleagues and collaborators (see, e.g. [1, 2, 5-8, 19-23]). The threshold switching can be produced not only in tellurides but also in selenides and sulfides and other compounds and even in many crystals [39]. The memory effect is connected with crystallization of a part of amorphous material induced by electrical pulses. The crystallized part has lower resistivity than the amorphous phase. The crystallization is partly a thermal effect and there were long discussions on its origin. The excitation of electrons to the conduction band (which is formed from anti-bonding levels of atoms present) and formation of electron plasma in a material lower the order of chemical bonds in the material and make the reorientation of atoms and their bonds, and consequently, their ordering and crystallization easier. The amorphous phase can be crystallized only partly (not fully), which opens the way for multilevel recording and to fully new concept of computing [2, 40]. The new ideas of cognitive computing given by S. Ovshinsky and his collaborators are revolutionary and we hope that they will become so mature to be applied and to be able to replace today's technologies. There still remains a question of long-time stability of multilevel phase change memories if they have several (many) levels of resistivity and if the number of cycles is much higher than 10^{12} , which is probably necessary for computers working many days, months and years. I hope that some combination of present silicon based technologies and phase-change materials can and will be found soon, which will combine advantages of both systems.

PREPARATION OF ACTIVE ELEMENTS AND THEIR PROPERTIES

Preparation of active elements for optical recording includes preparation of substrate, preparation of several interlayers that serve as thermal isolation, as reflective and protective films. These films are prepared mostly by classical thermal evaporation or magnetron or ionic sputtering in vacuum or sometimes in reactive atmosphere (O_2 , N_2 , [10, 13, 14, 17]). The active part of the film is mostly prepared by magnetron sputtering again in an inert or a reactive atmosphere. While

the reactive atmosphere (e.g. O₂) can keep the stoichiometry of interlayers in necessary range, in the case of active phase change layers small (nano?) crystals of e.g. nitrides (Ge₃N₄, TeN, Te₃N₄ [38]) can be formed that are not soluble or only partly soluble in active material and play a role of crystallization centers and speed up the crystallization rate. We have discussed it earlier.

The thin films of active material, at least for research purposes, can be prepared also by pulsed laser deposition method, when the material is evaporated by intensive short laser pulses, very often from UV light region (excimer lasers). While magnetron sputtering needs for every composition a relatively large and expensive target, the laser ablation can use only a small piece of material and the search for its optimal composition could be quicker and easier [41]. The properties of active layers were partly mentioned above; they should be chosen by a compromise and approved experimentally.

The scaling problem of memory elements arrays is a very important one; there is continuing demand for increase of capacity of all types of memories. In optical memories are several ways to increase the density of data: i) to use blue, or possibly UV light laser, ii) to use several active layers, iii) to use near – field techniques, all have been discussed in the meeting [9] and they are developing very quickly. The problem of scaling seems to be easier in electrical phase change memories. Even in this case it depends on possibilities of lithography and of etching capabilities.

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