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Amorphous materials for optical storage I. Phase-change materials

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Amorphous thin films are generally used as the starting state of optical storage materials, because they are relatively easy to deposit homogeneously on large areas by means of vacuum evaporation or sputtering and more recently even by the sol-gel process.

There are mainly two leading contenders of erasible optical storage materials, magneto-optical and phase-change. Amorphous chalcogenide semiconductor compounds are used as phase-change materials for optical storage, for example In-Se, Ge-Te or Ge-Sb-Te thin films. The competition between these two contenders is still going on. Hence, attempts to improve the performance of the existing materials, search for new materials and exploit new deposition methods of amorphous thin films have never ceased.

An ideal phase-change material should possess high crystallization speed (short crystallization time) at its crystallization temperatures and high stability at room temperature. To meet the above requirements considerations can be taken based on the Johnson-Mehl-Avrami (J-M-A) equation.

$$X = 1 - \exp[-(vt)^n] \qquad (1)$$

Where X is the crystallized volume fraction, t is time, n is time exponent depending upon the mechanisms of the crystal growth and v is the crystallization speed.

Fig.1 shows two log v_0 vs. E_a curves, deduced from the J-M-A equation. The dashed area between the two curves is the required value range of E_a of the materials, which meets the requirements for both high crystallization speed and good stability.

It can be seen clearly from table 1. that the introduction of Pb, Cu and Co leads to increases in T_C and E_a and decrease in t_c. Based on the existing thermodynamic data of these elements we found that all these elements have low T_g/T_m ratio (about 0.2) and high critical cooling rate, R_c (10^9 - 10^{10} K/s).

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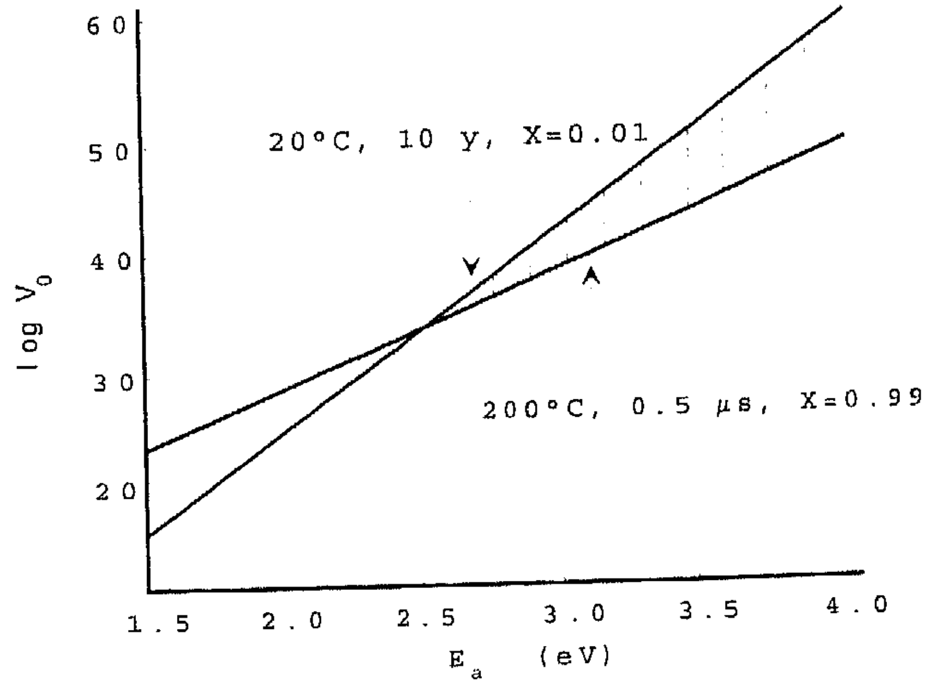

Fig.1. Log v_0 vs. E_a curves at the crystallization temperature (e.g. 200 °C) and room temperature (20 °C)

Table 1. Crystallization temperature (T_C), activation energy for crystallization (E_a) and laser erasing time (t_e) of some In-Se thin films

Composition	$In_{58}Se_{42}$	$In_{58}Se_{29}Pb_{13}$	$In_{58}Se_{23}Pb_{11}Cu_8$	$In_{58}Se_{23}Pb_{11}Co_8$
T_C (°C)	140	150	260	300
E_a (eV)	1.20	1.61	2.90	3.64
t_e (μs)	> 2	0.3	0.4	0.4

For practical applications, an acceptable signal-to-noise ratio, say >45 dB, must be achieved. This can be translated into a reasonably high reflectivity contrast between the two states of the thin films, (C>25%), $C=2|R_c-R_a|/(R_c+R_a)$.

The reflectivity, R, of a thin film to a light beam in normal incidence can be expressed as:

$$R = [(n-1)^2+k^2] / [(n+1)^2+k^2] \qquad (2)$$

where n and k are the refractive index and extinction coefficient respectively.

In most cases, both n and k of a chalcogenide material in crystalline state are higher than those of the corresponding amorphous state. This leads to a difference in R between the two states. The greater the difference, the greater the contrast.

Table 2. Complex refractive indices of some chalcogenide compounds in amorphous and crystalline states

Compound	Amorphous state	Crystalline state	Refs.
GeTe	5.0 + 1.3 i	7.0 + 2.6 i	/1/
Sb_2Te_3	5.0 + 2.7 i	5.3 + 5.8 i	/2/
Sb_2Se_3	3.8 + 0.1 i	4.7 + 0.8 i	/2/
Bi_2Te_3	2.8 + 4.8 i	2.6 + 3.0 i	/2/

Table 2 shows the differences of n and k of some chalcogenide compounds between the two states.

In order to obtain high data transfer rates, direct overwritable phase-change materials have been developed. A direct overwritable material must be a high speed material with a crystallization time less than , say, 100 ns. For such a short crystallization time the crystal growth must not be diffusion-controlled, therefore the materials should have the same chemical composition in both the amorphous and crystalline states. Only stoichiometric compounds can satisfy this requirement, for example, GeTe and GeTe-Sb_2Te_3.

The writing and erasing characteristics of three kinds of stoichiometric compounds thin films were investigated using a focused and modulated He-Ne laser beam for writing and erasing. The results are given in table 3. It is shown that the erase (crystzallization) times of all the tested thin films are not longer than 100 ns. The GeTe-Sb_2Te_3 film possesses the highest reflectivity contrast. It has been finally selected as an overwritable phase-change optical storage material.

In order to improve the write/erase cycling performance, 2-4 wt.% Ag were introduced into the $GeSb_2Te_4$ films. The reversible phase change takes place only between the amorphous state and the metastable fcc crystalline state and thereby guarantee the high speed of the phase change process and the write/erase stability. The write/erase cycling number of the prototype optical disc (5.25") using the $GeSb_2Te_4$:Ag films as recording media is as high as 3x10^5 without degradation of reflectivity contrast and carrier-to-noise ratio (CNR), as shown in Fig.2.

Table 3. Writing and erasing characteristics of Sb_2Se_3, GeTe-Sb_2Se_3 and GeTe-Sb_2Te_3 thin films

Compositon	Writing (mW / ns)	R_a (%)	Erasing (mW / ns)	R_c (%)	C(%)
Sb_2Se_3	12.3 / 100	43.0	10.9 / 100	58.9	31.2
GeTe-Sb_2Se_3	8.5 / 100	31.0	5.6 / 100	37.5	19.0
GeTe-Sb_2Te_3	9.6 / 100	25.4	6.4 / 100	36.5	35.9

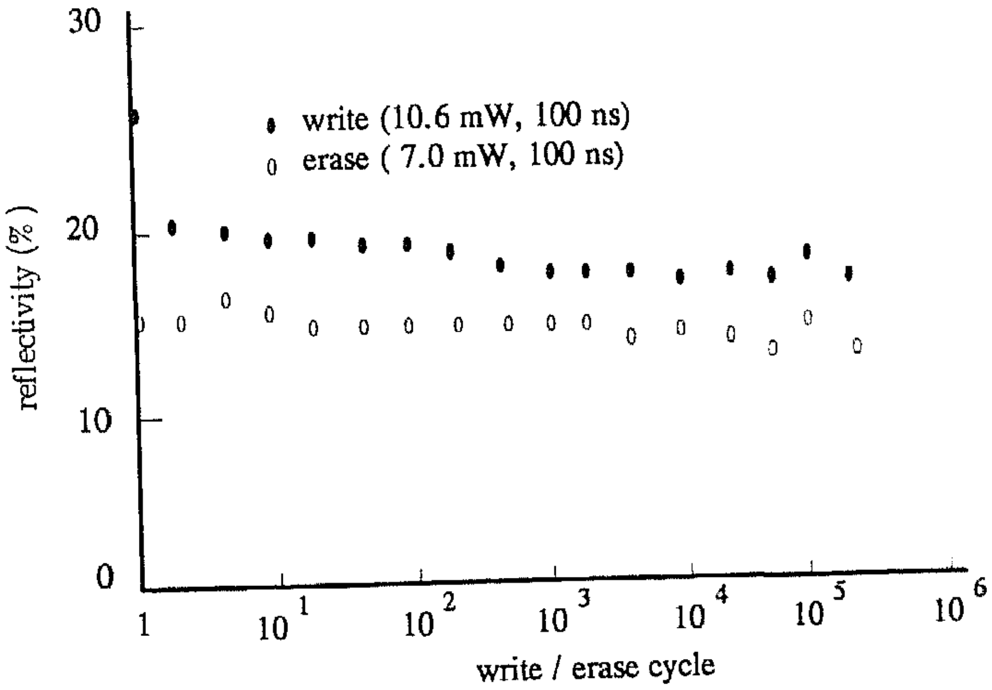

Fig.2 Reflectivity vs. write/erase cycling number of $GeSb_2Te_4$:Ag films

References

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