MICROSTRUCTURES AND OPTICAL PROPERTIES OF $Te_{81}Ge_{15}Sb_4$ THIN FILMS USED FOR PHASE CHANGE RECORDING MATERIALS①

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ABSTRACT Amorphous $Te_{81}Ge_{15}Sb_4$ thin films have been prepared by meltquenching then vacuum evaporation technique. The differences of microstructures and optical properties of $Te_{81}Ge_{15}Sb_4$ films between the amorphous and the crystalline states have been studied. The results show that this material is a hopeful storage medium for short-wave laser, and can improve recording density.

Key words $Te_{81}Ge_{15}Sb_4$ storage medium optical properties

1 INTRODUCTION

Chalcogenide semiconductor materials have been extensively studied since Ovshinsky[1] found switching and memory effect in chalcogenide amorphous semiconductor in 1968. Especially, the foundation of optical storage effect[2] has pushed the study to climax. A number of promising media including Te-base materials, non Te-base materials and compound materials have been successively found. Afonso *et al*[3] have recently reported that ultrafast reversible phase change recording GeSb materials can realize the transition between amorphous and crystalline with ultrashort laser pulses. As a phase-change recording material, it first must crystallize and noncrystallize easily, and there is larger reflectivity difference between amorphous and crystalline. Second, the material should be stable after adequate write/erase cycles. This paper reported the microstructures and optical properties of $Te_{81}Ge_5Sb_4$ film with change produced by thermal-phase-change.

2 EXPERIMENTAL

The differences of vapor pressure among Te, Ge and Sb elements are very large, the film with homogeneous composition couldn't be prepared directly from their element powders without the device of multi-original simultaneous evaporation. So amorphous $Te_{81}Ge_{15}Sb_4$ films were prepared by two steps. First, high purity(99.9999%) Te, Ge, Sb elements were weighed according to normal composition and mixed homogeneously, and sealed in a 12 mm outer diameter and 10 mm inner diameter quartz ampoule under 0.1 Pa vacuum condition, melted 15 h(to obtain homogenous melting turned ampoule once per 5 min) and then quenched in ice-water to avoid any segregation. The prepared bulk glass was ground, and then the thin films were deposited using a resistively Mo-boat special-made in the evaporation device. The vacuum maintains at 4×10^{-3} Pa during evaporation. The cleaned glass slides were used as the substrates. "Fast evaporation" method was employed to avoid

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selective evaporation.

The vacuum heat anneal treatment was carried out in the evaporation room. When the vacuum reached 5×10^{-3} Pa, the temperature of the samples was fast heated to 500K within 20 min, then kept it for 1 h. The reflective spectra of the samples were measured using Lambda 9 spectrophotometer where the light is perpendicular to the film faces. The sample structures were analyzed using X-ray diffractometer.

3 RESULTS AND DISCUSSION

3.1 *X-ray Diffraction Analysis*

Fig. 1 shows the diffraction spectra of the as-deposited and the annealed $Te_{81}Ge_{15}Sb_4$ film samples. It can be seen that the state of as-deposited film is amorphous, because the spectrum does not exist sharp diffraction peak, but the state of annealed film is crystalline, its spectrum exists obvious sharp peak.

The phases of the crystalline sample determined are Te, GeTe and (Sb, Te)γ through comparing "d/n-I/I_1" data with standard diffraction card data. So $Te_{81}Ge_{15}Sb_4$ material produced phase separation during crystallization. This phenomenon will affect the service life of the material to some extent.

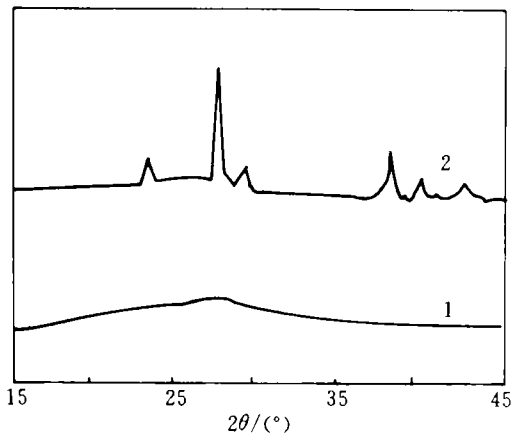

Fig. 1 X-ray diffraction spectra
1—as-deposited; 2—annealed

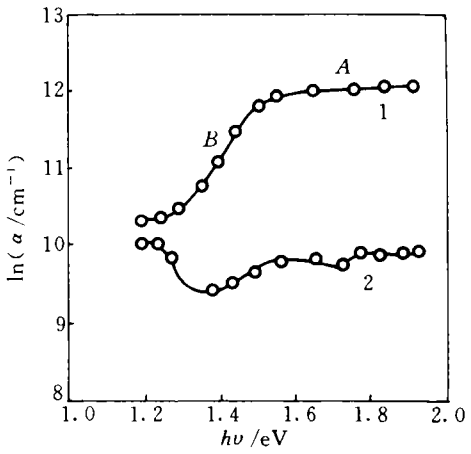

Fig. 2 α versus $h\nu$
1—amorphous; 2—crystalline

In the $Te_{81}Ge_{15}Sb_4$ material, the electronegativities of the component elements Te, Ge and Sb are 2.10, 2.01 and 2.05, respectively, their energies of the homonuclear bonds are 138.1, 157.3 and 126.4kJ/mol, respectively. According to Pauling formula[4]:

$$D(A-B)=[D(A-A)D(B-B)]^{1/2}+30(X_A-X_B)^2 \quad (1)$$

where $D(A-B)$ is the energies of the heteronuclear bonds, $D(A-A)$ and $D(B-B)$ are the energies of the homonuclear bonds, and X_A and X_B are the electronegativities of the elements. The energies of the heteronuclear bonds of the material obtained by calculation are: D(Ge—Te)=148.4kJ/mol, D(Sb—Te)=132.4kJ/mol, D(Ge—Sb)=141.2kJ/mol, respectively. Since the Ge—Te bonds are stronger than the Ge—Sb bonds and the Te atoms are very abundant, the valences of Ge are completely saturated by the Ge—Te bonds, so there don't exist the Ge—Sb bonds, and there only exist the Ge—Te, Sb—Te and Te—Te bonds. The results of theory calculation accord with those of X-ray diffraction.

2.2 *Optical Absorption Coefficient α and Optical Band Gap E_{opt}*

When the light with some energies irradiates perpendicularly its surface, the amor-

phous film could produce the optical phenomena of reflection, absorption and transmission. Supposed the reflection and the absorption coefficient of the samples with various thickness are the same, it can be derived out[5]:

$$\alpha = (\ln I_1 - \ln I_2)/(X_2 - X_1) \quad (2)$$

where I_1 and I_2 are the transmission light currents passing through the samples with thickness of X_1 and X_2, respectively. As long as the thickness of the sample and the transmission light current are measured, the optical absorption coefficient α can be calculated out. Fig. 2 shows optical absorption coefficient α versus photon energy $h\nu$. It can be seen that α is greater than 10^4 cm^{-1} in the amorphous and there exist obvious high absorption realm(A) and exponent absorption realm (B). The high absorption realm relates to electron jump from valence-band extended state to conduction-band extended state, but the exponent absorption realm relates to electron jump from valence-band extended state to conduction-band tail localized state or from valence-band tail localized state to conduction-band extended state. The α values of the crystalline are smaller than those of the amporphous and there exists minimum, this relates to existing some crystalline phases and every phase with different α in the sample after crystallization.

Most of the amorphous semiconductors abide by the following expression[5]:

$$\alpha h\nu = B(h\nu - E_{opt})^2 \quad (3)$$

where B is a constant. Thus($\alpha h\nu$)$^{1/2}$ versus $h\nu$ is a straight line. Extrapolation of the straight line to ($\alpha h\nu$)$^{1/2} = 0$ gives E_{opt} value. Fig. 3 shows ($\alpha h\nu$)$^{1/2}$ versus $h\nu$. It can be obtained that E_{opt} value of amorphous $Te_{81}Ge_{15}Sb_4$ film is 1.12 eV.

3.2 *Reflectivity R*

Fig. 4 shows the reflective spectra of the sample measured with spectrophotometer in the crystalline and the amorphous state. The peak at 860 nm is a false peak. It can be known from thin optics theory[6] that, to the single layer medium film, when the refractive index n of the film is larger than that of the substrate and n times the film thickness d satisfy the following equation: $nd = (2k + 1)\lambda/4$ (k is natural numbers), the reflectivity R of the film reaches the maximum, that is to say, the reflectivity R on this condition is related to film thickness. The thickness of the films prepared at experiment is about 1 500 nm. Therefore, the reflectivity peak at 860 nm belongs to this type. The higher crystalline reflectivities are the values measured by the film surface faces to incident light, and the lower crystalline reflectivities are the values measured by the glass surface faces to incident light. When recording and reading as well as erasing the information, the laser is projected from the glass surface, at calculating reflectivity difference, the crystalline reflectivity should employ the values measured by the glass surface faces to incident light. Thus the light waves are between 450 nm and 650 nm, the reflectivity differences between the crystalline and the amorphous are larger than 10%. So the material $Te_{81}Ge_{15}Sb_4$ can act as storage medium using short wave laser as light resource.

In microoptics[7], when d is defined as the diameter of the light spot where the light intensity decreases to a half of its original intensity after it passed through objective lens, there exists the following equation : $d =$

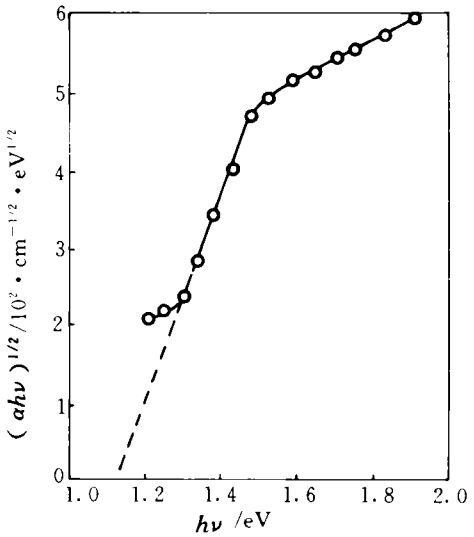

Fig. 3 $(\alpha h\nu)^{1/2}$ **versus** $h\nu$

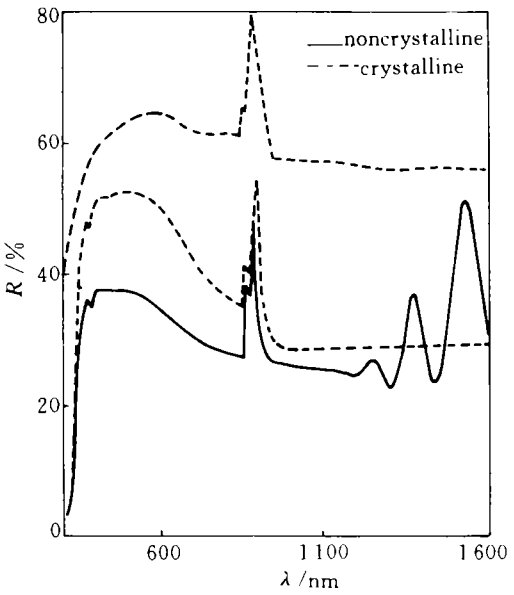

Fig. 4 Reflection spectra of the amorphous and the crystalline

$\lambda/(2NA)$, where λ is the laser wave, NA is the numberic aperture. With increasing NA, the allowance error of optical disk working decreases dramatically, so NA is generally between 0.4 and 0.5. It can be known from the above equation that the shorter the laser waves are, the smaller the diameters of the light spots are, and the larger the information recording densities are. Therefore, using the $Te_{81}Ge_{15}Sb_4$ material acting as storage medium can improve information recording density.

When the material is in the amorphous state, its arrangements of composition particles in the space are long-range disorder but short-range order. Thus the reflective optical path difference is not integer times of the light wave at the light beam incident upon the sample surface, the reflective intensity will be weakened after interference and superposition, and the reflectivity is slower. When the material is in the crystalline, its arrangements of composition particles in the space have ideal periodicity and translation symmetry, and form crystal face with definite interval. The reflective optical path difference is integer times of the light wave at the light incident upon the sample surface, the reflective intensity will be strengthened after interference and superposition each other, and the reflectivity is higher. As the glass is noncrystal, when the light beam is projected from the glass surface, the reflectivity will be weakened. That is identical to the reflective spectra measured.

4 CONCLUSIONS

(1) The amorphous $Te_{81}Ge_{15}Sb_4$ thin films can be prepared by melt-quenching then vacuum evaporating. The films crystallized exist three kinds of crystal phases. Thus they produce the phase separation during crystallization.

(2) Within the scope of visible light, the optical absorption coefficient of the amorphous $Te_{81}Ge_{15}Sb_4$ film is larger than $10^4 cm^{-1}$, but that of the crystalline film is smaller. The amorphous optical band gap E_{opt} is 1.12 eV.

(3) The reflectivity of the $Te_{81}Ge_{15}Sb_4$ film in the amorphous and the crystalline exists larger difference, $R > 10\%$ when the light waves at 450 to 650 nm. Therefore, it is suitable for acting as phase change optical storage medium using short wave laser as light resource.

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