Journal of the Physical Society of Japan
Vol. 56, No. 1, January, 1987, pp. 158-162

Structural Changes of Amorphous $GeTe_2$ Films by Annealing (Formation of Metastable Crystalline $GeTe_2$ Films)

Hirofumi FUKUMOTO, Keiji TSUNETOMO, Takeshi IMURA
and Yukio OSAKA

Department of Electrical Engineering,
Hiroshima University, Higashi-Hiroshima 724

(Received July 31, 1986)

Amorphous $GeTe_2$ films with the thickness $\sim 0.5\ \mu m$, prepared by sputtering technique, transform into the crystalline $GeTe_2$ films with the isomorphic structure to β-cristobalite, cubic SiO_2, at T_a(annealing temperature)$=200$°C. The cubic phase of $GeTe_2$ is metastable and decomposes into the mixed crystal of GeTe and Te at $T_a=250$°C.

§1. Introduction

The system $Ge_{1-x}Te_x$ is characterized by its ability to form glass when the chalcogen rich composition is quenched from the melt. Films deposited from the vapor are also amorphous over almost the entire compositional range when formed on substrates at room temperature. The memory-type electrical switching in the composition near $x=0.85$ (Te–GeTe eutectic composition) has aroused particular interest in this system.[1] Also the optical switching analogous to the electrical switching may be possible, as discussed in detail for the system $Ge_{15}Te_{81}Sb_2S_2$.[2]

The Te-rich amorphous alloys ($0.66 \leqq x < 1$) exhibit steadily increasing glass transition temperatures with increasing Ge content until the chemically ordered composition $GeTe_2$ is reached.[3-5] Unfortunately, the chemically ordered composition $GeTe_2$ was inaccessible by rapid quenching of the melt such as splat cooling technique.[4] The sputtered glass specimens extend the range of observation of T_g beyond the composition $GeTe_2$.[6] A T_g maximum (about 230°C) exists at the composition $GeTe_2$, which suggests that the composition can easily take stable amorphous phase. In addition, the composition $GeTe_2$ is associated with such a structure model as we find in vitreous SiO_2, that is, every pair of Te atoms has been cross-linked to another pair of Te atoms via a Ge atom.

Long before a new concept on the structures of inorganic covalent glasses[7] was developed, Zachariasen had suggested in his most famous paper on the structure of vitreous SiO_2 that the glass structure should be described as a chemically ordered (4–2 coordinated) continuous random network.[8] For more than four decades it became customary to describe diffraction data on network glasses in Zachariasen's language. In contrast, an alternative description has been proposed which regards glasses as consisting of at least two kinds of morphologically and stoichiometrically distinct large molecular clusters.[7] In this molecular cluster network model proposed by Phillips,[7] cluster interface play an integral role in determining the glass forming tendency. The existence of these heterogeneous clusters requires that the chemical order of the network is intrinsically broken.[9] However, irrespective of this new concept, Phillips' topological theory of network glass formation[7] has claimed that amorphous $GeTe_2$ is topologically isomorphic to amorphous SiO_2.[10] Another topological isomorphism that is similar to $GeTe_2$ has been also suggested by the compositional dependence of Mössbauer spectroscopy on anion ternary glasses $Ge(Te_xSe_{1-x})_2$.[11]

In bulk, the crystalline form for the system $Ge_{1-x}Te_x$ in the region $x \geqq 0.5$ is the mixture of crystalline GeTe and crystalline Te. The absence of crystalline $GeTe_2$ in bulk is attributed to the disproportionation reaction $GeTe_2 \rightarrow GeTe + Te$, which results also in the devitrification of the bulk glass for $x>0.6$.

In this paper, we report the structural change induced by annealing for amorphous films of GeTe$_2$ composition prepared by sputtering technique. From X-ray diffraction, electrical conductivity, optical absorption, and Raman scattering measurements, it is suggested that the amorphous GeTe$_2$ films with thickness 0.2~0.5 μm transform into a metastable phase of the crystalline GeTe$_2$ at T_a(annealing temperature)=200°C. The structure of crystalline GeTe$_2$ seems to be cubic and isomorphic to β-cristobalite SiO$_2$.

§2. Experimental

Films of a-Ge$_{1-x}$Te$_x$ alloy were prepared by rf sputtering of Ge target upon which small pieces of Te were placed in radial array. The Te content in the film was controlled by the area ratio of pieces of Te to the target. Typically, the pressure of Ar, the rf power and the substrate temperature were 0.67 Pa, 20 W and 20°C (water cooled), respectively.

Substrate materials used were: (1) crystalline silicon for Raman scattering, (2) fused silica for dc-conductivity, X-ray diffraction and optical measurements. The samples were annealed at fixed T_a in N$_2$ gas at an atmospheric pressure for 30 minutes.

After evaporation of Mo electrodes on the film ~0.2 μm thick, dc-conductivity measurements were carried out in vacuum (~10^{-1} Pa) as temperature increased. The crystal structure of films was examined by an X-ray diffractometer (JEOL JDX-10PA, CuK$_\alpha$). Optical transmittance and reflectance measurements were carried out with Shimadzu UV-365 spectrometer. Raman scattering measurements were carried out by Jasco R-500 Raman spectrometer with Ar$^+$ laser (5145 A). The chemical composition of films was determined by Rutherford backscattering spectrometry at 165° direction for 2.5 MeV He$^+$ ion beam (~10 nA) generated from a Van de Graaff accelerator installed at Faculty of Engineering, Hiroshima University.

§3. Results and Discussion

3.1 X-ray diffraction

Figure 1 shows X-ray diffraction patterns of Ge$_{0.32}$Te$_{0.68}$ (almost GeTe$_2$) film with the thickness $\lesssim$0.5 μm at T_a=200 (a) and 250°C (b). In the as-deposited film, the broad pattern observed shows that this film is amorphous. At T_a=200°C sharp diffraction lines appear at 2θ=13.3, 26.7, 40.6 and 55.2°. Full-widths at half maximum (FWHM's) of these lines are as narrow as the FWHM of the instrument. At T_a=250°C most of the sharp lines agree with those of crystalline GeTe and crystalline Te; slightly remaining lines as in Fig. 1(a) and small amount of GeTe$_4$ lines are included.

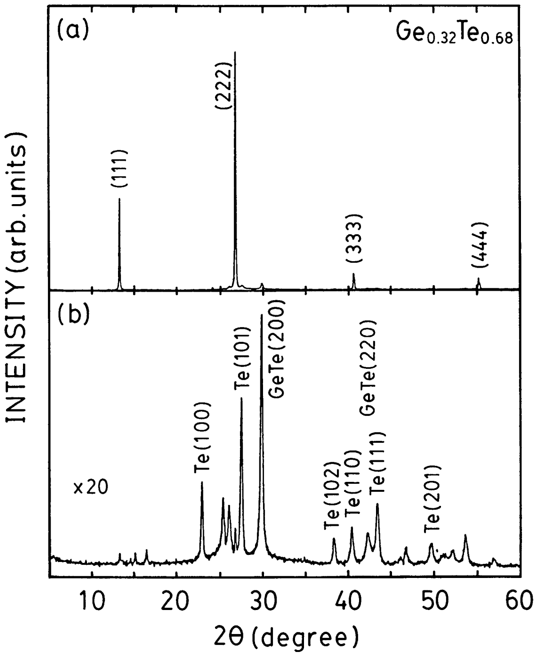

Fig. 1. X-ray diffraction patterns (CuK$_\alpha$) of GeTe$_2$ films: (a) T_a=200°C, and (b) T_a=250°C.

The sharp lines at T_a=200°C are fitted very well to the (111) aligned pattern of such cubic GeTe$_2$ that the structure is isomorphic to that of β-cristobalite SiO$_2$. The lattice constant is determined to be 11.5 A from the lines at 13.3° (111), 26.7° (222), 40.6° (333) and 55.2° (444), which leads to the nearest neighbor distance between Ge and Te, 2.50 A. The electron diffraction of amorphous films of GeTe$_2$ composition prepared by a flash evaporation shows that the nearest neighbor distance is 2.55 A.[12] Using Paulings' value for the covalent radii,[13] the calculated Ge-Te distance is 2.54 A. These values suggest that the assumption of cubic GeTe$_2$ for the film at T_a=200°C is reasonable, although the present

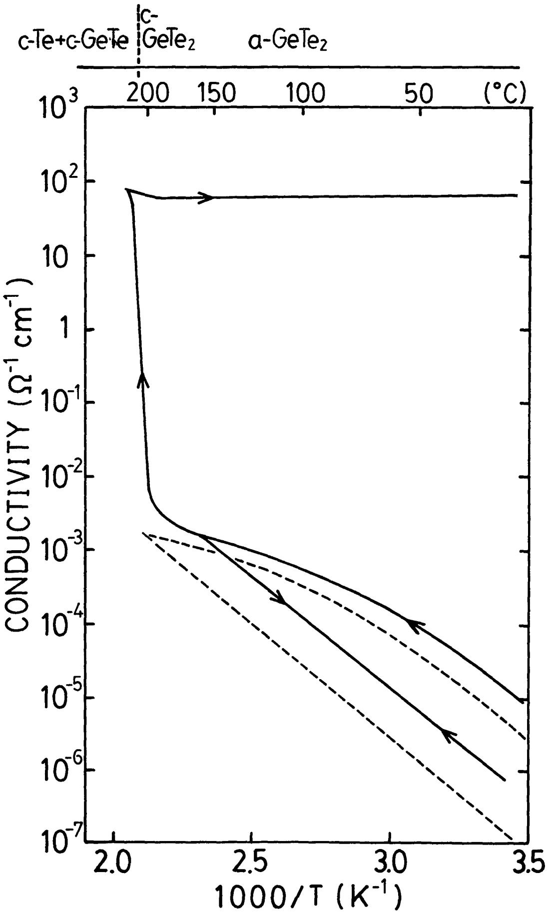

Fig. 2. Electrical conductivity of GeTe$_2$ films (0.2 μm) versus reciprocal temperature. Dashed lines show the results of sputtered GeTe$_2$ (0.59 μm) of ref. 6.

value is only about 2% smaller probably due to slight ionicity og Ge–Te bond.

3.2 *Electrical conductivity and optical absorption*

Figure 2 shows the temperature dependence of the electrical conductivity of the film with thickness of 0.2 μm. The conductivity shows pronounced annealing effects below $T_a = 170$°C. As the comparison, the result on amorphous GeTe$_2$ (thickness 0.59 μm, prepared by rf sputtering technique) obtained by deNeufville[6] is also shown with dashed lines. The activation energy of the conductivity before and after anneal at $T_a = 170$°C was 0.52 eV and 0.61 eV, respectively. Our value of the activation energy after anneal agrees very well with that of deNeufville.[6] deNeufville pointed out that the uniqueness of the GeTe$_2$ composition is verified by the activation energy for the conductivity after anneal (0.61 ± 0.02 eV), which is higher than the values reported for amorphous films of Te[14] and GeTe,[15] and that it is consistent with a structural model for this composition involving only Ge–Te bonds.

The vanishing of annealing effects above $T_a = 170$°C seems to correspond to the appearance of cubic GeTe$_2$. The rapid increase of the conductivity between $T_a = 200$°C and $T_a = 220$°C corresponds to the irreversible transformation from cubic GeTe$_2$ into the mixture of crystalline GeTe and crystalline Te, both semimetallic materials.

The transmittance and reflectance of films deposited on fused silica were analysed by a standard method[16] to obtain the absorption coefficient. Figure 3 shows the absorption coefficient spectra. The absorption coefficient for crystalline GeTe is also shown by a dashed curve.[17] At $T_a = 200$°C, the absorption coefficient decreases slightly in comparison

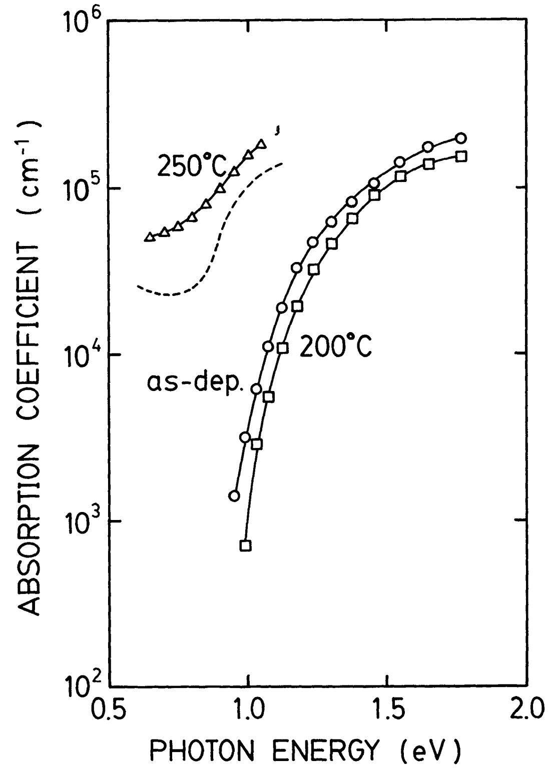

Fig. 3. Absorption coefficient spectra. The dashed curve shows the absorption coefficient of crystalline GeTe films (after ref. 17).

with the amorphous film (as-deposited film), which seems to be due to the appearance of cubic $GeTe_2$. These two spectrum, however, are similar on the whole, which suggests that the structure in the as-deposited amorphous film is a disordered phase of β-cristobalite substituted by Ge and Te. At $T_a=250°C$, the absorption coefficient below 1.0 eV increases remarkably. This corresponds to the formation of the mixed crystal of GeTe and Te. The difference between the absorption coefficient at $T_a=250°C$ and that of crystalline GeTe may be due to coexistence of crystalline Te.

3.3 Raman scattering

Figure 4 shows the variation of Raman spectra by annealing. The spectrum in as-deposited film is similar to that of amorphous $GeTe_2$ prepared by rf sputtering or evaporation.[18] The spectrum shows the two broad bands around 125 and 155 cm^{-1}. At $T_a=180°C$, the width of these bands becomes slightly narrow. The irradiation of Ar^+ laser (50 mW) for 9 hours at $T_a=180°C$ changes the spectrum remarkably. The broad band around 125 cm^{-1} became very sharp. This seems to be the appearance of cubic $GeTe_2$ by the laser irradiation, because the broad band around 125 cm^{-1} in the amorphous Ge_xTe_{1-x} system is assigned to be A_1 mode of $GeTe_4$ tetrahedral unit.[18] At $T_a=250°C$, the sharp band around 125 cm^{-1} disappears, and the sharp bands around 120 cm^{-1} and 140 cm^{-1} appear. These bands are assigned to be A_1 and E mode in crystalline Te, respectively.[19]

§4. Conclusions

From X-ray diffraction, electrical conductivity, optical absorption, and Raman scattering measurements, the following conclusions were derived;

1) the amorphous $GeTe_2$ film with the thickness ~0.5 μm transforms to the crystalline $GeTe_2$ at $T_a \simeq 200°C$,

2) the crystal structure of $GeTe_2$ films is cubic and isomorphic to β-cristobalite SiO_2,

3) the cubic $GeTe_2$ decomposes into GeTe and Te at $T_a \simeq 250°C$.

As mentioned in §1, the crystalline $GeTe_2$ was inaccessible in the bulk Ge_xTe_{1-x} system, which is attributed to the disproportionation reaction $GeTe_2 \rightarrow GeTe + Te$ for the region $x \geq 0.6$. In this sense, the cubic $GeTe_2$ growing near $T_a=200°C$ seems to be a metastable material that can exist only in the thin film. The stability of the metastable films may be supported by the thin-film character or the existence of the substrate. The preliminary results show that the films of which the thickness larger than 5 μm do not reveal at all the cubic $GeTe_2$ phase by annealing. The instability of cubic $GeTe_2$ phase will be discussed elsewhere in relation to the film thickness and the existence of the substrate.

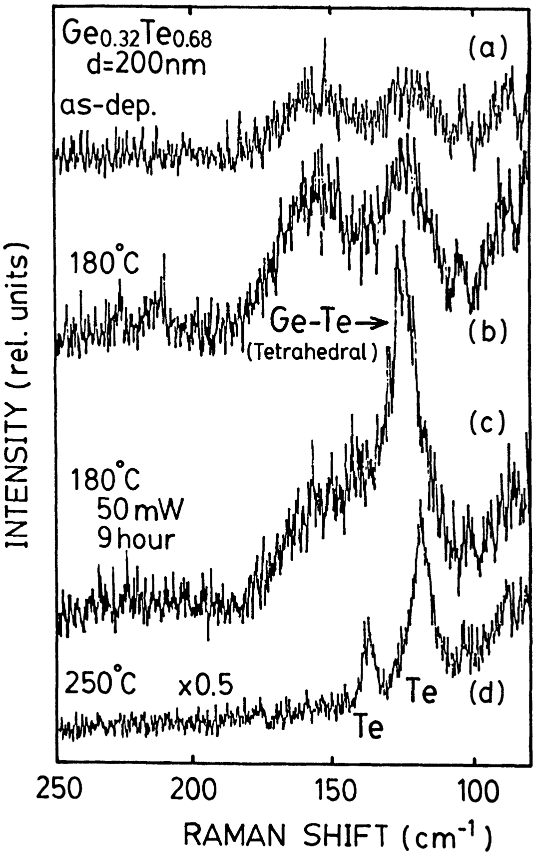

Fig. 4. Raman spectrum of $GeTe_2$ films (0.2 μm): (a) as-deposition, (b) $T_a=180°C$, (c) Ar^+ laser irradiation for 9 hours at $T_a=180°C$, and (d) $T_a=250°C$.

References

1) S. R. Ovshinsky: Phys. Rev. Lett. **21** (1968) 1450.
2) J. Feinleib, J. P. de Neufville, S. C. Moss and S. R. Ovshinsky: Appl. Phys. Lett. **18** (1971) 254.
3) C. Wood, L. R. Gilbert, R. Maeller and C. M. Garner: J. Vac. Sci. Technol. **10** (1973) 739.
4) T. Takamori, R. Roy and G. J. McCarthy: Mater.

Res. Bull. **5** (1970) 529.

5) N. K. Abrikosov, V. F. Bankina, L. V. Poretskaya, L. E. Schlimova and E. V. Skudnova: *Semiconducting II-VI, IV-VI, and V-VI compounds, Monographs in Semiconductor Physics* (Plenum Press, New York, 1969).

6) J. P. deNeufville: J. Non-Cryst. Solids **8 & 10** (1972) 85.

7) J. C. Phillips: J. Non-Cryst. Solids **34** (1979) 153; **43** (1981) 37.

8) W. H. Zachariasen: J. Am. Chem. Soc. **54** (1932) 3841.

9) P. Boolchand, J. Grothaus and J. C. Phillips: Solid State Commun. **45** (1983) 183.

10) J. C. Phillips: Solid State Commun. **47** (1983) 203.

11) M. Stevens, J. Gorthaus and P. Boolchand: Solid State Commun. **47** (1983) 199.

12) D. B. Dove, J. Chang and B. Molnar: J. Non-Cryst. Solids **8** & **10** (1972) 376.

13) L. A. Pauling: *The Nature of the Chemical Bond* (Cornell Univ. Press, New York, 1960) 3rd ed.

14) H. Keller and J. Stuke: Phys. Status Solidi **8** (1965) 831.

15) S. K. Bahl and K. L. Chopra: J. Appl. Phys. **41** (1970) 2196.

16) T. Nakashita, M. Hirose and Y. Osaka: Jpn. J. Appl. Phys. **17** (1978) 985.

17) S. K. Bahl and K. L. Chopra: J. Appl. Phys. **40** (1969) 4940.

18) G. B. Fisher and J. Tauc: *Proc. 5th. Int. Conf. Amor. Liq. Semicon* (Garmisch, 1973) p. 1259.

19) B. H. Torrie: Solid State Commun. **8** (1970) 1899.