Understanding the complicated crystallization behaviors in Germanium-Tellurides

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Crystallization behaviors and configurations of germanium-tellurides (Ge\textsubscript{x}Te\textsubscript{100-x}) at a wide compositional range (12.5 ≤ x ≤ 85) have been investigated. It is found Ge\textsubscript{55}Te\textsubscript{45} films exhibit one- or two-step crystallization behavior with a complicated competition between GeTe and Te (or Ge) phases. The composition dependences of crystallization temperature and activation energy have been revealed. They exhibit four singularities at x = 20.4 (GeTe\textsubscript{4}), x = 33 (GeTe\textsubscript{2}), x = 49 (GeTe), and x = 22 (Ge\textsubscript{22}Te\textsubscript{78}). Based on the method of X-ray photoelectron spectroscopy, the structural sketches for the Ge\textsubscript{x}Te\textsubscript{100-x} glasses that is helpful to understand the evolution of crystallization behavior are built up. It is evident that, the presence of homopolar Te−Te and heteropolar Ge−Te bonds is the main reason for the structural and thermal stability of Ge-deficient films, and Ge−Ge bond in GeGe\textsubscript{4} tetrahedron appears when x > 50 and effectively enhances the stability of Ge-rich films.

\section{1. Introduction}

Chalcogenide bulk glasses and thin films have received considerable attention due to their excellent transmission in the infrared and the profound structural transformations upon external energy input like light, thermal and ion irradiation. These excellent properties have opened new technique applications in many areas [1]. For example, Te-based thin films, especially GeTe and GeTe\textsubscript{4}, have been frequently employed in the fields of information storage and optical waveguide in the infrared [2,3]. Ge−Te was first used as one of the phase-change materials in 1986 [4]. By measuring the optical transmission of the sample, the maximum and minimum crystallization temperature were detected at GeTe\textsubscript{2} and GeTe, respectively [4]. It was subsequently reported that, the GeTe\textsubscript{2} film shows the highest crystallization temperature and activation energy in Te-rich system [5]. In Ge-rich film, it was found that, the crystallization temperature increases from 180 °C to 360 °C with increasing Ge content from Ge\textsubscript{50}Te\textsubscript{50} to Ge\textsubscript{76}Te\textsubscript{24} [6], and phase separation of Ge and rhombohedral GeTe appears in crystalline Ge-rich films [7]. In the study of Ge-Te films with Ge content from 6 to 54 at%, two-stage crystallization or phase separation was reported in all the films except GeTe [5]. Other investigations also confirmed that the glasses containing 10 and 15 at% Ge show two-stage crystallization [8,9]. Nevertheless, it was also reported that, the Ge−Te films containing Ge content of 20 and 25 at% exhibit only one-step crystallization with simultaneous formation of GeTe and Te phases [8]. It was also shown that, Ge\textsubscript{50}Te\textsubscript{50} film crystallizes in a one-step process but Ge\textsubscript{60}Te\textsubscript{40} film crystallizes in two-step process [10]. These contradicted results are somehow confusing to understand crystallization behavior for Ge-Te system that thus need to be further clarified.

The complicated thermal and crystallization behaviors have aroused the interests in unravelling Ge−Te glass structure. A model including Ge−Te tetrahedra and Te−Te chain has been used to simulate the structural factors of Ge\textsubscript{50}Te\textsubscript{50} and Ge\textsubscript{60}Te\textsubscript{40} from high-energy synchrotron X-ray diffraction experiments [11]. Using the reverse Monte-Carlo simulations based on the electron diffraction data, it was shown that large amounts of Te atoms do not bond with Ge in non-stoichiometric Te-rich films [12]. It was also found that, GeTe or GeTe\textsubscript{2} structural units with a random bonding structure exist in amorphous Ge−Te network [13].

Obviously, these models cannot be used to describe the structures of...
GeTe and Ge-rich film due to the deficiency of Te. Other models, like the random cubic symmetry distribution [14], ring structure model [15], and ABAB square model [16], were proposed to explain the fast crystallization kinetics of GeTe. Apparently, the so-called “8-N” bonding rule was broken in these models. In terms of the mean coordination number (MCN) of Ge and Te, it was found that, they could be Ge(4)-Te (2) (the MCN is 4 and 2 for Ge and Te, respectively) or Ge(3)-Te(3) in Te-rich Ge-Te compounds [17]. Phillips predicated that, in the glass-forming region (Ge content in the range of 10–33 at%), Ge and Te has an MCN of 4 and 2, while for Ge content more than 33 at%, they become 6 and 3, respectively [18]. The MCN of Te and Ge was also reported to be slightly larger than 2 [19–21], and close to 4 in Te-rich film [22], respectively. Although the structural model and MCN of amorphous Ge–Te are discussed intensively in recent years, the evolution of the MCN with varied compositions in the Ge–Te films is unclear yet.

In this work, therefore, we studied the thermal behavior and structures of Ge xTe100-x film at a wide compositional range of 12.5 ≤ x ≤ 85. We investigated the crystallization behaviors of the films, and observed four singularities in activation energy and crystallization temperature for the first time. Based on X-ray photoelectron spectroscopy analysis, we proposed structural sketches of the amorphous Ge xTe100-x films to illustrate the complicated crystallization behaviors.

2. Experimental methods

A series of amorphous Ge xTe100-x (12.5 ≤ x ≤ 85) films were deposited on SiO2/Si(100) by the magnetron co-sputtering method using separated Ge and Te target. The base and working pressures were set to ~4 × 10−4 and 0.35 Pa, respectively, for each deposition. The thickness was in situ controlled by a thickness monitor equipped in the vacuum chamber and ex-situ checked by Veeco Dektak 150 surface profiler in air. The film thickness is in a range of 1.2–1.6 μm for Ge xTe100-x films. The thickness fluctuation is less than 2%. The compositions of the films are examined by the Energy Dispersive X-ray Spectroscopy (EDS) more than 5 times in the different position, and the results are listed in Table 1. The temperature dependent sheet resistance (R-T) of the as-deposited film was measured using a homemade system based on the four-probe method in a nitrogen atmosphere. The crystallization behaviors were detected by X-ray diffraction (XRD, Bruker D2) in the 20 range of 10–60° using Cu Kα radiation with a wavelength of 0.154 nm. The bonding structures were examined by X-ray photoelectron spectroscopy (XPS, Scienta ESCA-300 spectrometer) with monochromatic Al Kα X-rays of 1486.6 eV and energy step of 0.05 eV. The XPS data analysis was conducted with CasaXPS software package.

3. Results and discussion

Typical R-T curves of Ge xTe100-x at different heating rates were shown in the left panel of Fig. 1. The corresponding differential curves which were used to accurately determine the peak temperature for crystallization (T p) were shown in the middle panel of Fig. 1. The values of T p at a heating rate of 20 K min−1 for various Ge-Te compound were put forward in Table 1. The results can be summarized as follows. When 19.2 ≤ x ≤ 21.7, 23 ≤ x ≤ 33, x = 50 and 85, the films show one-step crystallization behavior with only one T p. In all other cases, they exhibit two-step crystallization behavior with two T p. Especially in 33 < x < 50, two T p are very close and this has been confirmed by the time-resolved XRD data from Raoux et al. [11]. In amorphous Ge xTe100-x, it was reported that the glass transition temperature (T g) increases as Ge content increased, and it is not detectable when Ge content is more than 31 at% [22]. We found a similar result in this work but the details are not shown here. However, there is a sharp drop of T g was revealed in Ge xTe80 film, i.e., the T g value is 450 and 410 K for Ge xTe78.3 and Ge xTe78, respectively. We believe the sharp drop of T g is due to the collapsed thermal stability in Ge xTe80 film.

The XRD method was used to detect the crystalline phases in Ge xTe films. As shown in the bottom of Fig. 2(a)–(g), the red lines represent the standard diffraction peaks that belong to crystalline GeTe phase (PDF No. 7-125), the blue lines correspond to the Ge xTe80 and Ge xTe78 as shown in Fig. 2(b) and (d), respectively. However, these two crystalline phases appear simultaneously with increasing annealing temperature in Ge xTe80 and Ge xTe78 which is shown in Fig. 2(e). Such crystallized Te phase is completely suppressed in Fig. 2(f) where only crystallized GeTe is precipitated. In Fig. 2(g) corresponding to Ge xTe50 film, both GeTe and Ge crystalline phases are found in the film annealed at 450 °C.

The one- or two-step crystallization behaviors found in the XRD patterns are in agreement with those in Fig. 1 for Ge xTe100-x films (12.5 ≤ x ≤ 85). Interestingly, GeTe is crystallized after crystalline Te phase appears in Ge xTe80, while GeTe is crystallized first and then Te phase in Ge xTe100-x when 33 < x < 50, and GeTe is crystallized before Ge phase in Ge xTe100-x films when 50 < x < 85. Moreover, four singularities include two maxima and two minima in compositional dependent T p for the first crystallization process can be detected, i.e., Ge xTe79.6 (GeTe4), Ge xTe74 (GeTe2), Ge xTe51 (GeTe), and peculiar Ge xTe78. The maximum T p around Ge xTe4 and Ge xTe2 have been carried out by the previous researches [4,5]. The stoichiometric GeTeX is well known as phase-change material due to its fastest crystallization speed with a relative lower T p in Ge-Te system. Interestingly, the minimum T p in the peculiar component of Ge xTe32 which also exhibits phase separation behavior has never been revealed before. It should be emphasized that, the results of conventional differential scanning calorimetry from our previous work is in excellent agreement with the results shown in Fig. 1. Together with the results from XRD, we plotted phase diagram of crystallization for Ge xTe100-x films as shown in Fig. 3, to understand the complicated crystallization behaviors in binary Germanium-Telluride materials.

<table>
<thead>
<tr>
<th>Ge (at%)</th>
<th>T p1 (K)</th>
<th>T p2 (K)</th>
<th>Q (eV)</th>
<th>Ge (at%)</th>
<th>T p1 (K)</th>
<th>T p2 (K)</th>
<th>Q (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>12.5</td>
<td>443.5</td>
<td>504.2</td>
<td>1.62</td>
<td>921.6</td>
<td>–</td>
<td>3.50</td>
<td></td>
</tr>
<tr>
<td>14.5</td>
<td>446.5</td>
<td>504</td>
<td>1.84</td>
<td>305.2</td>
<td>3.75</td>
<td>–</td>
<td></td>
</tr>
<tr>
<td>16.0</td>
<td>448</td>
<td>500</td>
<td>1.87</td>
<td>336.9</td>
<td>4.51</td>
<td>–</td>
<td></td>
</tr>
<tr>
<td>17.0</td>
<td>456.3</td>
<td>502</td>
<td>2.04</td>
<td>524</td>
<td>4.44</td>
<td>–</td>
<td></td>
</tr>
<tr>
<td>19.2</td>
<td>517</td>
<td>–</td>
<td>2.20</td>
<td>520.8</td>
<td>4.28</td>
<td>–</td>
<td></td>
</tr>
<tr>
<td>19.8</td>
<td>518.2</td>
<td>–</td>
<td>2.98</td>
<td>503</td>
<td>3.93</td>
<td>–</td>
<td></td>
</tr>
<tr>
<td>20.4</td>
<td>519.5</td>
<td>–</td>
<td>3.11</td>
<td>470.4</td>
<td>3.67</td>
<td>–</td>
<td></td>
</tr>
<tr>
<td>21.7</td>
<td>519.6</td>
<td>–</td>
<td>2.96</td>
<td>555.7</td>
<td>515</td>
<td>3.74</td>
<td></td>
</tr>
<tr>
<td>22</td>
<td>464.8</td>
<td>505.5</td>
<td>2.09</td>
<td>625</td>
<td>628</td>
<td>3.39</td>
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</tr>
<tr>
<td>23</td>
<td>501.4</td>
<td>–</td>
<td>2.70</td>
<td>632</td>
<td>638</td>
<td>4.60</td>
<td></td>
</tr>
<tr>
<td>25</td>
<td>508.7</td>
<td>–</td>
<td>2.88</td>
<td>650</td>
<td>652.9</td>
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<td>26</td>
<td>512.8</td>
<td>–</td>
<td>3.13</td>
<td>656</td>
<td>5.44</td>
<td>–</td>
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</table>
The activation energy for crystallization ($Q$) was calculated by the Kissinger method [24]:

$$\ln\left(\frac{\phi}{T_p}\right) = -\frac{Q}{RT_p} + A$$

where $\phi$ is the heating rate, $T_p$ is the peak temperature for crystallization at a given heating rate, $R$ is the gas constant, and $A$ is a constant. The Kissinger plots of these films are shown in the right panel of Fig. 1. The calculated values of $Q$ for the first crystallization of Ge$_{20.4}$Te$_{79.6}$ were listed in Table 1, and the composition dependence of $Q$ was plotted and shown in Fig. 4. Two maxima and two minima of $Q$ can be found in Ge$_{20.4}$Te$_{79.6}$ (GeTe$_4$), Ge$_{33}$Te$_{67}$ (GeTe$_2$), Ge$_{49}$Te$_{51}$ (GeTe),

![Fig. 1. The $R-T$ curves at different heating rates (left panel), i.e., 10, 20, 40, and 70 K min$^{-1}$, for Ge$_{17}$Te$_{83}$, Ge$_{21.7}$Te$_{78.3}$, Ge$_{22}$Te$_{78}$, and Ge$_{23}$Te$_{77}$, respectively. The corresponding differential curves and Kissinger plots are shown in middle and right panel, respectively.](image-url)
Fig. 2. XRD curves for different temperature annealed Ge₅₀Te₅₀ film in composition of (a) Ge₁₇Te₈₃, (b) Ge₂₀Te₈₀, (c) Ge₂₂Te₇₈, (d) Ge₂₅Te₇₅, (e) Ge₃₈Te₆₂, (f) Ge₅₀Te₅₀, and (g) Ge₈₅Te¹₅. The annealing temperatures are 200, 250, 300, and 350 °C for Te-rich Ge₅₀Te₅₀ film, but they are 400, 450, and 500 °C for Ge₈₅Te¹₅ film. Three XRD curves represent crystalline Te (blue), GeTe (red) and Ge (yellow) from standard PDF cards are listed in the patterns to figure out the crystalline compounds in these films. Red dots and yellow squares indicate the crystalline GeTe and Ge phase in the films. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)
simple binary Ge-Te system was examined by XPS method. Ge and Te 3d spectra of typical Ge-Te films were recorded. The compositions of these Ge-Te films were calculated by integrating the XPS spectra. It results a negligible difference in Ge content (< 0.5 at\%) compared to those from EDS tests, and confirms the reliability of the compositions in this work. The adsorbed hydrocarbon was used as the internal reference and the binding energies of C 1s line was referenced at 284.5 eV. We decomposed the Te 3d spectrum into doublets by removing the Shirley baseline. The doublet separation was fixed and then the spectra were fitted with good fitting quality, the results were shown in Fig. 5(a). According to such Te 3d spectra, the content of Ge–Te and Te–Te bond can be extrapolated. Fig. 5(b) is the composition dependent normalized content of Ge–Te and Te–Te bond. An abrupt change can be found when the Ge content close to 22 at\%, indicating an obvious change of the structure in Ge–Te films.

Previous investigations showed that, unlike chalcogen elements S and Se that always has an almost fixed mean coordination number of 2, the MCN of Ge could change from 4 to 3 and that of Te could change from 5 to 3 in Ge\textsubscript{1-x}Te\textsubscript{x} with increasing Ge content. Following this and XPS results, we constructed a compositional dependent structural sketch for amorphous Ge–Te system as shown in Fig. 6(a). Compositional dependent ratios of the different bonds in those structural sketches were exhibited in Fig. 6(b). It is evidenced that, the ratio of Te–Te bond exhibits a minimum at Ge\textsubscript{33}Te\textsubscript{67} (Ge\textsubscript{3}Te\textsubscript{12}), respectively, and an abrupt increase at Ge\textsubscript{40}Te\textsubscript{60} (Ge\textsubscript{4}Te\textsubscript{14}). On the contrary, the ratio of Ge–Te bond shows a maximum at Ge\textsubscript{20}Te\textsubscript{80} and Ge\textsubscript{33}Te\textsubscript{67}, respectively, and a sharp decrease in Ge\textsubscript{40}Te\textsubscript{60}. All these is in good agreement with the results from XPS analyses (see Fig. 5(b)), and thus it presents a plausible explanation of the observed results based on such –sketches. In addition, Ge-Ge bond occurs and increases obviously when Ge content is more than 33 and 50 at\%, respectively.

In Fig. 6(a), Ge\textsubscript{33}Te\textsubscript{67} represents the typical structure in a compositional range of 12.5 ≤ x ≤ 19.2 where Te–Te chain is highlighted as red cycle. In such structure, Te phase crystallizes firstly at relatively low temperature due to the flexible Te–Te chain, and subsequently GeTe phase is separated out at high temperature. Ge\textsubscript{20}Te\textsubscript{80} represents the structure in the compositional range of 19.2 ≤ x ≤ 21.7, where Te–Te bond is highlighted as blue cycle. Such Te–Te bond is not easy to be precipitated from the network since it is connected to Ge atoms forming stronger Ge–Te bond. It results in a delay of Te phase separation, and therefore, crystalline Te phase would be separated out simultaneously with the formation of GeTe crystalline phase after breaking of Ge–Te bonds, which certainly enhances the thermal stability of the Ge\textsubscript{33}Te\textsubscript{67} films. However, an isostatic structure in Ge\textsubscript{33}Te\textsubscript{67} is collapsed with a slight increase of Ge in the glass network. It causes the Te–Te chain that is highlighted as red cycle presents in Fig. 6(a) again. Thus, the thermal stability is destroyed and it leads to a two-step crystallization behavior where Te phase crystallizes first and GeTe is separated out subsequently.

With further increase of Ge content, the pure Te–Te chain is absent again, and then the structure becomes stable and Te phase is separated out simultaneously with GeTe phase. As illustrated in Fig. 6(a), such configuration and crystallization behavior are presented in Ge\textsubscript{40}Te\textsubscript{60} (Ge\textsubscript{4}Te\textsubscript{14}), Ge\textsubscript{33}Te\textsubscript{67} (Ge\textsubscript{3}Te\textsubscript{12}), and Ge\textsubscript{20}Te\textsubscript{80} (Ge\textsubscript{3}Te\textsubscript{12}). When x = 33, Ge\textsubscript{33}Te\textsubscript{67} tetrahedron is dominated throughout the whole structure. It results in the second maximum in thermal stability for Ge–Te system. At x > 33, such as Ge\textsubscript{40}Te\textsubscript{60} as shown in Fig. 6(a), the structural stability is destroyed by the relative excess Ge. Ge–Te bond is distributed throughout the structure, so the GeTe phase can be easily precipitated.
The atomic configurations of Ge$_{12}$Te$_{12}$ (GeTe) and Ge$_{15}$Te$_{12}$ (Ge$_{55}$Te$_{45}$) are also presented in Fig. 6(a). A number of four-atomic rings that are highlighted by black quadrilaterals exist in amorphous GeTe structure, which is the basic configuration in crystalline GeTe, and they can accelerate the crystallization speed. This has been reported in the ring statistics analogy [15] and ABAB square model [16]. The number of Ge-Ge bond increases apparently when $x > 50$, which is in line with other reports [6,25]. As we can see, for Ge-rich Ge–Te (Ge$_{55}$Te$_{45}$) film, the thermal stability is enhanced by the presence of GeGe$_4$ tetrahedron that is marked as green dashed square in Fig. 6(a). It exhibits two-stage crystallization process with the formation of GeTe phase first and then Ge phase.

4. Conclusions

In this work, the crystallization behaviors and thermal properties of the as-deposited Ge$_x$Te$_{100-x}$ (12.5 $\leq x \leq$ 85) film were systematically studied. Based on the methods of R-T, XRD, it was found that, Ge$_x$Te$_{100-x}$ exhibits two-step crystallization behavior with the formation of Te phase ahead of GeTe phase at $x < 19.2$, one-step crystallization behavior with simultaneous formation of Te and GeTe phases at 19.2 $\leq x \leq$ 33 (except $x = 22$), and two-step crystallization behavior with the formation of GeTe phase ahead of Te phase (or Ge phase) at $x > 33$. Only GeTe crystalline phase is precipitated in the stoichiometric GeTe. Moreover, the two-step crystallization behavior with the formation of Te ahead of GeTe phase is also detected in Ge$_{22}$Te$_{78}$. Two maxima and two minima of compositional dependent crystallization temperature and activation energy for the first crystallization have been obtained, which is located at $x = 20.4$ (GeTe$_4$), $x = 33$ (GeTe$_3$), $x = 49$ (GeTe), and $x = 22$ (Ge$_{22}$Te$_{78}$), respectively. The peculiar crystallization behavior of Ge$_{22}$Te$_{78}$ results in a collapse in the thermal stability. Moreover, from the results of XPS spectra and the previous studies about the coordination number of Ge and Te, a plausible sketch of structural evolution has been proposed in this work for better understanding the compositional dependence of thermal behavior and crystallization behavior.

CRediT authorship contribution statement


Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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