Dielectric relaxation in amorphous and crystalline Sb$_2$Te$_3$ thin films

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ABSTRACT

Sb$_2$Te$_3$ is an endpoint of the GeTe-Sb$_2$Te$_3$ quasi-binary tie-line that represents phase-change alloys widely used in optical and non-volatile phase-change memory devices. In the crystalline form it is also a prototypical topological insulator with a layered structure where covalently bonded quintuple layers are held together by weak van der Waals forces. One of the ways to fabricate a crystalline phase is solid-state crystallization of an amorphous film, whereby the three-dimensional (3D) structure relaxes to the two-dimensional (2D) crystalline phase. The mechanism of the 3D-2D transformation remains unclear. In this work, we performed a study of relaxation processes in thin Sb$_2$Te$_3$ films in both amorphous and crystalline phases. We found that both phases possess two kinds of relaxators (type I and type II), where the type I fragments are identical in the two phases, while the relaxation of type II fragments are shifted to lower temperature in the amorphous phases. The activation energies of the associated relaxation processes and the values of the Havriliak–Negami parameters were determined. The differences between the relaxation processes in the two phases are discussed. The obtained result will contribute to better understanding of the 3D-2D transformation during the crystallization of van der Waals solids.

1 Introduction

Antimony telluride, Sb$_2$Te$_3$, is at the same time a narrow-gap semiconductor and a topological insulator. Due to its properties Sb$_2$Te$_3$ has wide range of industrial applications in thermoelectric devices, such as thermal sensors [1] and micro-coolers [2] and in laser fabrication [3]. It is also an endpoint of the GeTe-Sb$_2$Te$_3$ quasi-binary alloys successfully used in optical and non-volatile electronic memory devices [4, 5]. Sb$_2$Te$_3$ belongs to the class of layered van der Waals solids, where covalently bonded quintuple layers with the Te-Sb-Te-Sb-Te stacking sequence are held together by weak van der Waals interactions.
Various methods have been used to fabricate antimony telluride thin films: thermal evaporation [6], electrochemical atomic layer epitaxy [7], sputtering [8], electrochemical method [9], flash evaporation [10], metalorganic chemical vapor deposition [11], and molecular-beam epitaxy [12].

While the structure and electronic properties of Sb$_2$Te$_3$ have been thoroughly investigated, studies of its dielectric properties have been rather limited. The dielectric properties of thermally evaporated Sb$_2$Te$_3$ thin films have been investigated in Refs. [6, 13] but to date there have been no reports on comparative studies of the amorphous and crystalline phases. Such a study would foster a significant interest because amorphous film possesses a three-dimensional (3D) structure, while the dimensionality is changed to 2D in the crystalline phase. Recently, 2D materials have become a topic of great interest and one potential fabrication technique is solid-state crystallization from the amorphous phase [14]. In the present work, Sb$_2$Te$_3$ films obtained by magnetron sputtering were studied, since this method allows growth of homogeneous films.

One of the methods that allow the study of the structural and electrophysical properties of materials is dielectric spectroscopy. The technique allows the monitoring of the polarization of a material over a wide range of frequencies and temperatures; the obtained data make it possible to calculate the activation energy of relaxation processes and the dipole relaxation time. The purpose of the present work was to carry out a comparative investigation of the dielectric properties of amorphous and crystalline Sb$_2$Te$_3$ films.

3 Results and discussion

The frequency dependence of the normalized dielectric constant for amorphous and crystalline Sb$_2$Te$_3$ films at room temperature is shown in Fig. 1. It can be observed that $\varepsilon'$ decreases with increasing frequency, while the curves change their slope several times. This result indicates the presence of several types of relaxators in the material, which are involved in the polarization process at different frequencies. At low frequencies ($f < 10^3$ Hz), the dielectric constant reaches its maximum and goes to a plateau – the polarization saturates.

Figures 2 and 3 present the temperature dependences of $\tan\delta$ obtained for amorphous and crystalline Sb$_2$Te$_3$ films, respectively.

The temperature–frequency dependences of the dielectric loss tangent make it possible to detect the presence of relaxation processes in a material and allow one to estimate the parameters of the process and the degree of its symmetry/asymmetry relative with a wide-band dielectric spectrometer “Concept-81” (Novocontrol Technologies). Gold-plated electrodes manufactured by Novocontrol Technologies GmbH were used to contact the sample. In this study, the dielectric properties were investigated over the frequency range $f = 1$ Hz – 1 MHz at $t = 60$ – 100 °C. The frequency dependences of the dielectric constant $\varepsilon'$, the dielectric loss factor $\varepsilon''$, and the dielectric loss tangent $\tan\delta$ were obtained for both amorphous and crystalline Sb$_2$Te$_3$ films.

2 Experimental

Amorphous Sb$_2$Te$_3$ thin films of 80 nm in thickness were obtained by RF magnetron sputtering on a silicon substrate at room temperature. The crystalline Sb$_2$Te$_3$ films were prepared by the two-step growth method, where a 3-nm-thick amorphous layer is grown first and subsequently the sample was heated to 230 °C in the sputtering chamber. The remainder of the film was grown at high temperature to ensure the crystallization of the film. The structures of both films were confirmed by X-ray diffraction method. The details on the sample fabrication are available elsewhere [15]. The dielectric spectra were measured...
to the maximum of the process. In the current case, Figs. 2 and 3 show two tanδ_{max} peaks, and, therefore, two polarization processes, which are indicated in the figures by the numbers I and II. Figures 4 and 5 show how the “humps” of the relaxation processes move to the high-frequency region with increasing temperature. This behavior is inherent to many semiconductors and is due to the increase in the mobility of kinetic units with increasing temperature.

Figures 4 and 5 show that for amorphous and crystalline samples the curves corresponding to processes I are in the same frequency and temperature range.

The analysis of the dielectric spectra was performed by describing complex permittivity ε* with the empirical Havriliak–Negami (HN) equation [16]:

\[
e^*(\omega) - \varepsilon_\infty = \sum_{k=1}^{n} \operatorname{Im} \left[ \frac{\Delta \varepsilon_k}{\left(1 + i\omega \tau_{\text{HN}}\right)^{\alpha_k}} \right]
\]

(1)

Here, ε* = ε'(ω) - i ε''(ω); ω = 2πf; Δε = ε_0 - ε_∞ is the increment of dielectric permittivity (ε_0 = ε' at ω→0, ε_∞ = ε' at ω→∞); τ_{HN} is the characteristic time of the HN equation; α and β are calculated parameters corresponding to the widening and asymmetry of the relaxation time distribution, respectively.

The separation of the observed processes and the calculation of the corresponding parameters were carried out with the program WinFit by “Novocontrol Technologies.” Examples of deconvolution of the dielectric spectrum according to Eq. (1) into two components (processes I and II) are shown in Fig. 6. It can be observed that the values of the dielectric loss factor ε''_{max} for the amorphous sample are larger than the corresponding crystalline values. One might have expected the opposite result based on the available literature data on phase change [17], however, we note that the frequencies used in our experiments are many orders of magnitude lower than optical frequencies. We further note that even in the optical range there are regions where the values n and k for the amorphous phase are higher than those for the crystalline phase. We believe that the observed higher values of ε'' are due to an increase in the degree of disorder, which increases the response to
an external electric field and, consequently, to an increase in dielectric losses.

The most probable relaxation time \( t_{\text{max}} \) corresponding to the position of \( \varepsilon''_{\text{max}} \) on the frequency dependence \( \varepsilon'' = \phi(f) \) has been calculated as \([18]\):

\[
\tau_{\text{max}} = \tau_{\text{HN}} \left[ \frac{\sin \left( \frac{\pi \beta}{2(\beta+1)} \right)}{\sin \left( \frac{\pi \alpha}{2(\beta+1)} \right)} \right] ^{1/\alpha}
\]

The temperature dependences of relaxation time are shown in Arrhenius coordinates in Fig. 7.

Figure 7 shows that processes I for amorphous and crystalline samples are similar – the dependences of the relaxation time are the nearly identical.

The temperature dependences of the relaxation time, \( -\ln \tau_{\text{max}} = \phi(1/T) \), are linear and can be described by the Arrhenius equation:

\[
\tau(T)_{\text{max}} = \tau_0 \exp \left( \frac{E_a}{RT} \right),
\]

where \( E_a \) is the activation energy.

The shape of the curves on the dependence \( -\ln \tau_{\text{max}} = \phi(1/T) \) allows determination of the type of polarization observed in the material. There are four polarization mechanisms that contribute to the relative permittivity of a material: electronic polarization, ionic polarization, dipolar polarization, and interfacial polarization. Dipolar polarization and interfacial polarization are dielectric relaxation processes, while ionic and electronic polarizations show resonances or oscillatory behavior \([19]\). The detected relaxation processes (Fig. 6) observed in the intermediate frequency range \( (f = 10^9 \text{ Hz} \rightarrow 10^4 \text{ Hz}) \) have linear dependences on the relaxation times (Fig. 7), and the maxima of the loss factor in Figs. 2 and 3 shifts towards high frequencies with increasing temperature—all these facts indicate that the processes under study are dipole relaxation processes. This conclusion is consistent with the results of Ref. \([13]\), who also discovered the existence of dipole-relaxation polarization in the same frequency range.

The activation energies for processes I and II were calculated according to Eq. (3) and are presented in Table 1.

### Fig. 6
The deconvolution of the dielectric spectrum at \( t = 0 \) °C by the HN equation into two components (processes I and II). Amorphous Sb\(_2\)Te\(_3\) – (a), crystalline Sb\(_2\)Te\(_3\) – (b)
The values of the relaxation parameters of the HN equation for the Sb$_2$Te$_3$ samples at different temperatures are presented in Table 2.

The parameters $a$ and $b$ for process $I_{cr}$ are equal to 1. Such parameter values satisfy the Debye dielectric dispersion equation for a symmetric distribution of relaxation times [20]:

$$\varepsilon^* = \frac{D(t)}{\varepsilon_0 E(t)} = \varepsilon_\infty + \frac{\varepsilon_0 - \varepsilon_\infty}{1 + i\omega\tau}. \quad (4)$$

Processes of this type are usually caused by the relaxation of a single type of dipoles in an alternating electric field. The above equation is not suitable for describing processes with wide distribution of interactions. Such a complex behavior is characteristic of the non-Debye process $I_{am}$ for which $a \neq 1$ and $b \neq 1$. This process is described by the Cole–Davidson model [21]:

$$\varepsilon^* = \varepsilon_\infty + \frac{\varepsilon_0 - \varepsilon_\infty}{(1 + i\omega\tau)^b}. \quad (5)$$

Thus, the process $I_{cr}$ is a typical relaxation process, which is caused by the relaxation of a single type of relaxators explained by the periodicity of the crystal structure. An amorphous material retains only short-range order. Consequently, the accumulating disorder leads to a distribution of bond lengths and angles in the local structural fragments, which, when superimposed on each other, lead to an asymmetric distribution of relaxation times. However, as observed from Fig. 7 and Table 2, these structural modifications do not lead to any significant changes in activation energy of the process $I$.

For the process $II$ of amorphous and crystalline Sb$_2$Te$_3$, the values of parameters are calculated to be $a = 1$ and $b = 1$ (Table 2). Such processes are described by the Havriliak–Negami equation (Eq. 1). These processes are observed at higher frequencies ($f = 10^2$ Hz – $10^3$ Hz), which suggests that they are caused by the movement of smaller relaxators than in the case of process $I$, whose concentration increases in the amorphous phase, causing to lower temperatures compared to process in the crystalline phase $II_{cr}$ (Fig. 7).

We also note that while the stable structure of the crystalline phase is 2D layered, a metastable cubic phase with a large concentration of vacancies has also been reported [22] and it is natural to assume that the 3D cubic phase is closer to the 3D amorphous phase.

In both cases, there are extended …Te-Sb-Te-Sb… fragments with multicenter hyperbonds (Fig. 8a, b). Such bonds are usually asymmetric, i.e., possess dipole moments [23]. It is also remarkable that the shorter and longer bond lengths in such fragments are very similar in the amorphous and crystalline phases as can be observed from Fig. 8c [24]. We attribute the manifestation of process $I$ to the presence of such, relatively heavy, fragments. We further notice that the local motifs in the 2D layered phase and in the 3D cubic phase are different, namely, in the 2D phase octahedral fragments with central Sb atoms are surrounded by six Te atoms, while in the 3D phase there are defective octahedral sites with a

### Table 1

| $T$, K | $E_a(I_{am})$, eV | $E_a(I_{cr})$, eV | $E_a(II_{am})$, eV | $E_a(II_{cr})$, eV |
|---|---|---|---|---|
| 263 | 0.43 ± 0.01 | 0.44 ± 0.01 | 0.68 ± 0.02 | 0.70 ± 0.02 |

### Table 2

The value of the HN parameters of the Sb$_2$Te$_3$ samples. The error of the calculated values does not exceed 5%

| $T$, K | $a$ | $b$ | $a$ | $b$ | $a$ | $b$ |
|---|---|---|---|---|---|---|
| 263 | 1 | 1 | 0.73 | 0.93 | 0.76 | 0.84 |
| 283 | 0.98 | 0.99 | 1 | 0.84 | 1 | 0.54 |
| 303 | 0.99 | 1 | 0.82 | 0.78 | 0.79 | 0.26 |
| 323 | 0.98 | 1 | 0.78 | 0.89 | 0.28 | – |

Fig. 7 Dependences of $-\ln \tau_{max}$ on inverse temperature over the range of processes $I$ and $II$. Points are calculations of $\tau_{max}$ according to the HN Eq. (1). $II_{am}$ and $I_{am}$ – dependences for amorphous Sb$_2$Te$_3$, $I_{cr}$ and $II_{cr}$ – for crystalline Sb$_2$Te$_3$.
The larger number of the surrounding Te atoms may be the origin of heavier structural units and correspondingly higher temperatures in the crystalline phase.

4 Conclusion

We detected the existence of two relaxation processes in amorphous and crystalline Sb$_2$Te$_3$ films which is associated with the manifestation of dipole-relaxation polarization. In both cases there are two distinct relaxation processes. One of the processes is very similar in two phases, while the other one shifts to lower temperatures in the amorphous phase. The observed processes are associated with similarities and differences in the local bonding in the amorphous and crystalline phases. The process I is likely to be due to the presence of extended ...Te-Sb-Te-Sb... fragments with multi-center bonds, while differences in the process II may be caused by the different number of Te neighbors in the Sb-centered octahedral fragments.

Fig. 8 Fragments of crystalline (a) and amorphous (b) Sb$_2$Te$_3$ structures. In both cases, linear fragments with alternating short and long Sb–Te bonds are clearly visible. The shorter and longer Sb–Te interatomic distances are also very similar in the two cases (panel c). Panels (b) and (c) are reproduced from [24] with permission from John Wiley and Sons the Japan Society for the Promotion of Science (project number JPJSBP120204815).

Data availability

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Declarations

Conflict of interest The authors declare that they have no conflicts of interest.

References

1. K. Rajasekar, L. Kungumadevi, A. Subbarayan, R. Sathyamooorthy, Ionics 14, 69 (2008). https://doi.org/10.1007/s11581-007-0146-3
2. L.M. Goncalves, C. Couto, P. Alpuim, D.M. Rowe, J.H. Correia, Sens. Actuators 130–131, 346 (2006). https://doi.org/10.1016/j.sna.2005.10.014
3. J. Boguslawski, J. Sotor, G. Sobon, J. Tarka, J. Jagiello, W. Macherzynski, L. Lipinska, K.M. Abramski, Laser Phys. 24, 105111 (2014). https://doi.org/10.1088/1054-660X/24/10/105111
4. T. Ohta, J. Optoelectron. Adv. Mater. 3, 609 (2001)
5. J. Choe, Intel 3D XPoint memory die removed from Intel Optane™ PCM (phase change memory). (TechInsights Inc., 2017), https://www.techinsights.com/blog/intel-3d-xpoint-memory-die-removed-intel-optanetm-pcm-phase-change-memory.
