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Comments on the electronic transport mechanisms in the crystalline state of Ge—Sb—Te phase-change materials

K. Shimakawa✉[1], R. J. Freitas[2]

[1] Gifu University, 1–1 Yanagido, Gifu 501-1193, Japan
[2] National University of Timor Lorosa'e, 10 Rua Formosa, Dili, Timor-Leste

Authors

Koichi Shimakawa, e-mail: koichi@gifu-u.ac.jp

Ruben Jeronimo Freitas, ORCID: 0000-0001-7708-6947, e-mail: ruben.freitas@untl.edu.tl

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Abstract. It is known that phase-change materials, such as Ge–Sb—Te ternary system, are promising resistive non-volatile random-access memory applications with ultra-rapid reversible transformations between the crystalline and amorphous phases. This class of electronic transition is categorized to be the metal-insulator transition (MIT). The Anderson-type MIT has been discussed extensively in phase-change materials (PCMs) and isothermal annealing of amorphous PCMs (a-PCMs) which, above a certain temperature, leads to the metallic (crystalline) phase. In the insulator regime near the MI transition, Mott-type variable-range hopping (VRH) and/or Efros-Shkolvskii hopping (ESH) at low temperatures below 20 K (and down to 1 K) in $Ge_1Sb_2Te_4$ (GST124) have been discussed extensively, however, we criticize the above argument through a detailed discussion of physical parameters that support the VRH mechanism. It is not clear whether or not the density-of-states (DOS) near the Fermi level is localized (like the Fermi glass) in the crystalline phase. It is also suggested that grain boundaries are expected to interfere with the electronic transport in the crystalline state. We should take into account the grain boundary effects on the electronic transport in the crystalline phase of Ge—Sb—Te system.

Keywords: Ge—Sb—Te phase-change materials, crystalline phase, electronic transport, grain boundary, metal-insulator transition, degenerate semiconductor, dirty metal.

Introduction

In phase-change materials, such as Ge—Sb—Te system, rapid reversible transformations between highly electrically conducting crystalline and resistive amorphous phases are produced by the application of short voltage pulses, realizing random-access memory (called the phase-change random-access memory: PCRAM) (Raoux et al. 2014; Terao et al. 2009; Wuttig, Yamada 2007). The rapid transformations are known to be due to local Joule-heating. On the other hand, it is known that isothermal annealing produces the same type of phase change, which is called the metal-insulator transition (MIT) in GST (Kato, Tanaka 2005; Siegrist et al. 2011; Terao et al. 2009; Volker et al. 2015). One of the examples of the electronic conductivity covering the angular frequency range ω, d. c. – 10^{16} (rad/s), is shown in Fig. 1. Note that the electronic conductivity in the optical frequency range around 10^{15} (rad/s) is often called the *optical conductivity*. We can see a big difference in the electronic conductivity of crystalline (circle) and amorphous (triangle) phases through all frequencies.

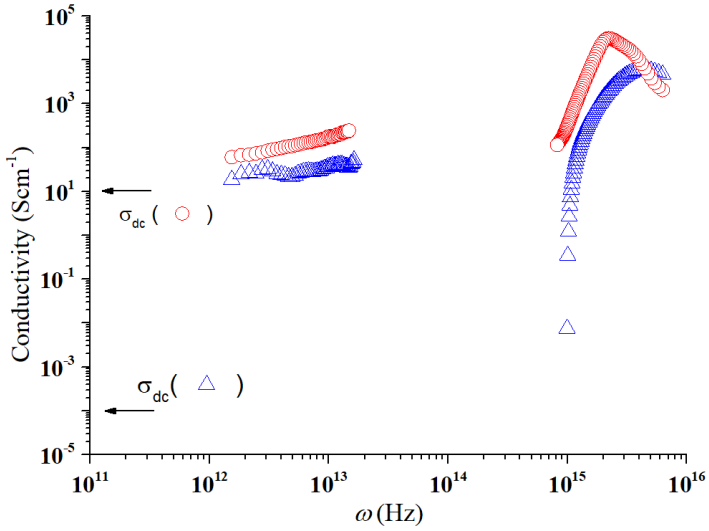

Fig. 1. Frequency dependent conductivity in GST225 films. Open circles and triangles, respectively, are the conductivity in the crystalline phase and the amorphous phase. The arrows indicate the DC conductivity

The Anderson-type MIT (Mott 1993) has been discussed extensively in PCMs (Shimakawa et al. 2013; Siegrist et al. 2011; Volker et al. 2015). Isothermal annealing of amorphous PCMs (a-PCMs) above a certain temperature leads to the metallic (crystalline) phase (Kato, Tanaka 2005; Siegrist et al. 2011; Volker et al. 2015). In the insulator regime near the MIT, Mott-type variable-range hopping (Mott-VRH) (Mott 1993) and/or Efros-Shkolvskii hopping (ESH) (Shklovskii, Efros 1984), at low temperatures below 20 K (and down to 1 K) in $Ge_1Sb_2Te_4$ (GST124), have been discussed in extended (band) states in the crystalline phase (Siegrist et al. 2011; Volker et al. 2015). The disorder-induced localization in the crystalline can be the origin of VRH or ESH near the Fermi level.

In the present report, we criticize the above argument through a detailed discussion of physical parameters that support the VRH or ESH mechanism. It is not clear if the electronic states near the Fermi level are localized in the crystalline phase, such as the Fermi glass. Note also that the effect of grain boundaries is expected to play a significant role in the present system, since the crystalline phase of Ge–Sb—Te nucleated from the amorphous phase has a typical size of 5–20 nm (Siegrist et al. 2011; Wagner et al. 2009).

Metal-insulator transition

The crystalline phase of GST225, for a typical example in Ge—Sb—Te system, is known to have a NaCl type structure with ~20 % of vacancies (Wuttig, Yamada 2007). The deviation from the complete stoichiometry produces degenerate p-type behavior in the crystalline phase (Kim et al. 2007). Annealing of GST225 at 200 °C results in a p-type degenerate crystalline semiconductor with $p \sim 1.5 \times 10^{20}$ cm^{-3}, estimated from the Hall measurement (Siegrist et al. 2011; Volker et al. 2015) and the THz spectroscopy (Shimakawa et al. 2013; Shimakawa et al. 2020) which should show a metallic DC transport behavior; however, note that the conductivity increases with temperature. This is often called the negative temperature coefficient of resistivity (NTCR) and is reported in the so-called "dirty metals" (Mott 1993; Shimakawa et al. 2013). The Fermi level, $E_F = \hbar^2(3\pi p/M)^{2/3}/2m^*$, where M is the valley degeneracy (= 4 for GeSbTe) (Siegrist et al. 2011) and m^* the effective mass which is taken to be $0.3m_e$ (Shimkawa et al. 2013), is deduced to be 0.13 eV. The DOS at the Fermi level in three dimensions (parabolic band), $N(E_F) = 3p/2E_F$, is hence calculated to be 1.7×10^{21} cm^{-3}eV^{-1}.

It is clear that the annealing at above 200 °C produces metallic transport in GST225 and 124 (Shimkawa et al. 2013; Volker et al. 2015). A similar p-value (= 9×10^{19} cm^{-3}) is extracted from the Hall measurement by authors (Volker et al. 2015) (sample "f" in reference), which produces $E_F = 0.10$ eV and $N(E_F) = 1.4 \times 10^{21}$ cm^{-3}eV^{-1} in the crystalline states (after annealing at 175 °C) of GST124. The arguments above strongly suggest that the transport is dominated by free carriers.

The localization may be induced by a structural disorder existing in the crystalline state of the GST system, in particular, near the border of the metal-insulator transition at the annealing temperature

around 150–175 °C. When carriers are strongly localized, the conductivity is expected to be zero (insulator) at low temperatures even if E_F lies in the valence band (Siegrist et al. 2011; Volker et al. 2015). The occurrence of Mott-VRH is therefore suggested at low temperature down to around 1 K (Volker et al. 2015). Note that Mott-VRH is a single-phonon process and the most important factor for Mott-VRH to occur is that the Bohr radius a of localized carriers should be smaller than roughly a half of the optimum hopping distance R_{opt} (Mott, Davis 1979; Mott 1993). If not ($a > R_{opt}/2$), overlapping of localized wave functions occurs and hence the concept of Mott-VRH itself becomes meaningless. Additionally, when $a > a_o$, where a_o is a lattice constant, the localized carriers cannot interact with higher phonon energies leading to a low probability of single-phonon hopping (Mott, Davis 1979; Shimakawa, Miyake 1988).

We should therefore examine whether or not Mott-VRH occurs under the value of $N(E_F)$ stated above, since the $N(E_F)$ is very much higher than the values expected for Mott-VRH in semiconductors or insulators (Volker et al. 2015). In Figures 2 (a), (b) temperature-dependent logarithmic scale of resistivity ρ is plotted against $T^{-1/4}$ and $T^{-1/2}$, respectively, in the crystalline state of GST124. Data are re-plotted for the sample "f" in ref. (Volker et al. 2015). The straight lines in Fig. 2 (a) and (b) indicate the theoretical predictions from Mott-VRH and the ESH, respectively. Note again that Mott-VRH requires that the states near the Fermi level should be localized (uniform density-of-states (DOS) near E_F) and an open-up of the Coulomb gap at the E_F is required in ESH (Shklovskii, Efros 1984) (DOS at E_F is zero).

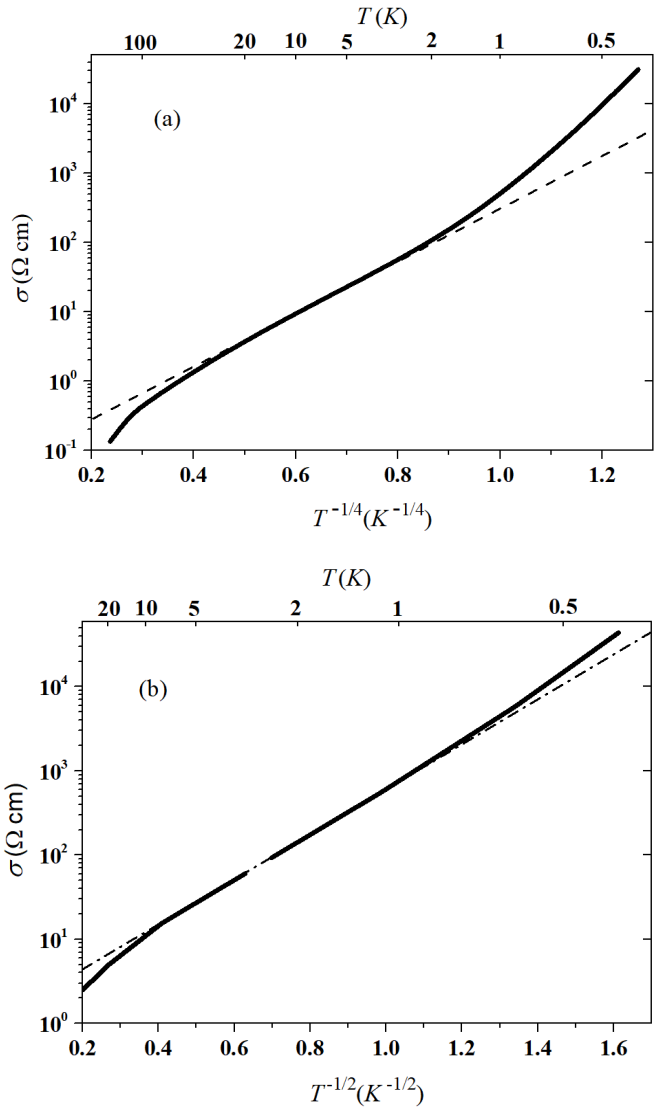

Fig. 2. Temperature dependence of the resistivity in GST124 films; (a) Fitting to the Mott-VRH, (b) Fitting to the Efros-Shklovskii model (Data from (Volker et al. 2015))

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Let us briefly review the Mott-VRH theory as follows. Mott-VRH conductivity is normally given as (Mott, Davis 1979; Mott 1993)

$$\sigma = \sigma_0 \exp\left[-\left(\frac{T_M}{T}\right)^{1/4}\right], \tag{1}$$

with

$$T_M = \frac{\beta}{k_B N(E_F) a^3}, \tag{2}$$

and

$$\sigma_0 = e^2 V_{ph}\left[\frac{N(E_F)a}{32\pi k_B T}\right]^{1/2}, \tag{3}$$

where β is a numerical value around 20, which depends on the details of the model, k_B the Boltzmann constant, a the Bohr radius, and ν_{ph} the phonon frequency which interacts with localized carriers. The hopping length R_{opt} optimizing the hopping rate is given as

$$R_{opt} = \left(\frac{9a}{8\pi N(E_F)kT}\right)^{1/4} = a\left(\frac{9}{8\pi\beta}\right)^{1/4}\left(\frac{T_0}{T}\right)^{1/4}. \tag{4}$$

Volker (Volker et al. 2015) have deduced, by taking β = 18, the following physical parameters in the crystalline state of GST124 (after annealing at 175 °C): T_0 = 5692 K and a = 2.4 nm, and $N(E_F) = 2.5 \times 10^{21}$ cm^{-3}eV^{-1}, from which R_{opt}, for example at 10 K, is estimated to be 1.83 nm. The present values, however, do not support the Mott-VRH, since the necessary condition, $a < R_{opt}/2$, is not satisfied.

From the conductivity prefactor σ_0 (= 19.1 S cm^{-1}) (Volker et al. 2015), using Eq. (3) and taking the same values for a and $N(E_F)$ obtained above, ν_{ph} is estimated to be 5.4×10^{23} s^{-1} which is an unreasonably large value, while Volker deduced a value around 5×10^{11} s^{-1} which looks reasonable but is not a correct value. In the paper by Volker et al. (2015), the presentation of the prefactor (Eq.(10)) is in serious error (their dimension does not give the *conductivity*). It should also be noted that there is the so-called *prefactor problem* in the Mott-VRH theory (Brodsky, Gambino 1972; Ortuno, Pollak 1983; Shimakawa, Miyake 1988), namely, when we use the proper values of a and $N(E_F)$ in Eq. (3), unreasonably large values of ν_{ph} are always produced, and if we use a proper value of ν_{ph}, unreasonably large values of $N(E_F)$ are produced. The estimated value of a (= 2.4 nm) is very much larger than the lattice constant a_0 and hence localized carriers do not interact with high-frequency phonons. It is therefore suggested that a single-phonon process such as Mott-VRH cannot occur under this condition (Mott, Davis 1979; Shimakawa, Miyake 1988).

Let us examine ESH as well in the present material. ESH conductivity is given as (Shklovskii, Efros 1984; Volker et al. 2015)

$$\sigma = \sigma_0' \exp\left[-\left(\frac{T_{ES}}{T}\right)^{1/2}\right], \tag{5}$$

with

$$T_{ES} = 2.8\frac{e^2}{4\pi\varepsilon_0\varepsilon k_B a}, \tag{6}$$

where ε is the static dielectric constant. A good fit to ESH shown in Fig. 2 (b) may indicate that a Coulomb gap at E_F dominates the hopping of localized carriers, and a is extracted to be 13.3 nm (Volker et al. 2015). The same difficulty, however, exists in the ESH theory when we apply ESH to the present material. The most serious problem is the extracted large a which violates the condition

for the single hopping to occur as stated above, while the functional form of ESH fits well to the experimental data. This type of difficulty in ESH has also been pointed out in doped crystalline semiconductors (Zhang et al. 1990).

Now, we should address whether or not the states near E_F (inside the valence band) are localized. A fact that high density of *free* holes ($p > 0.8 \times 10^{20}$ cm^{-3}) in the crystalline state estimated from the Hall effect measurements (at 300 K) indicates that the transport is dominated by free carriers. If, on the other hand, the states are localized, such a large p should not be obtained from the Hall measurements, i.e., hopping of localized carriers does not produce such a large p (Avdonin et al. 2016; Mott 1993; Mott, Davis 1979).

Are the states near E_F actually localized? To answer this question, we will try to give an alternative argument and replot the same resistivity data on the log scale, as shown in Fig. 3. The resistivity appears to decrease linearly with T in the medium temperature range (5–150 K). The behavior is very much similar to the behavior of other well-annealed (> 175 °C) crystalline GST (Shimakawa et al. 2013; Volker et al. 2015) and amorphous metals (Mott 1993), where the temperature-dependent conductivity is dominated by free carriers and empirically given as (Shimakawa et al. 2013)

$$\sigma = \alpha + \beta T^{1/2} + \gamma T, \tag{7}$$

where α, β, and γ are constants (Shimakawa et al. 2013). It is therefore suggested that the valence band is not localized.

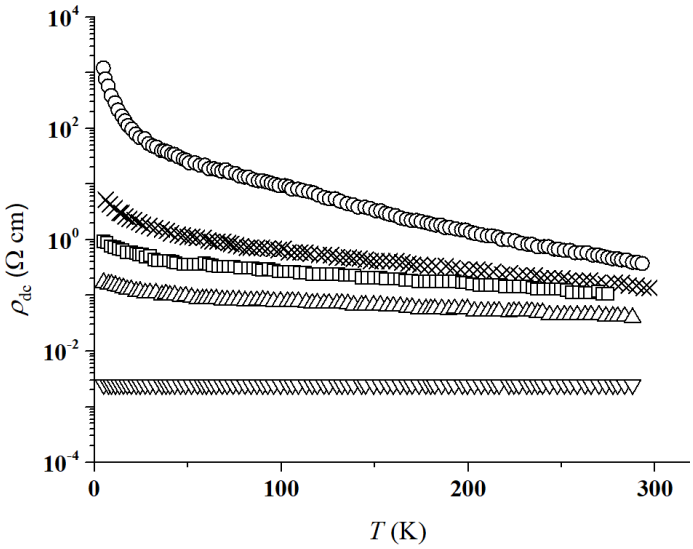

Fig. 3. Temperature dependence of the resistivity ρdc in GST124 films, annealed at 150 °C (◯), 175 °C (×), 200 °C (□), 225 °C (△), 275 °C (▽) (Shimakawa et al. 2013)

The Hall measurements and the THz spectroscopy should be performed at low temperatures to obtain a clear understanding of the low-temperature behavior and of the MIT in GSTs. Unfortunately, there is no report on this issue at low temperatures, and this is something we will discuss in a future paper.

Finally, we briefly discuss the effects of grain boundaries in GST. As we stated earlier, the crystalline phase of Ge—Sb—Te has a typical size of 5–20 nm (Kumar et al. 2013; Siegrist et al. 2011; Wagner et al. 2009), although its size depends on the preparation technique. As shown by open circles at $\omega \approx 10^{13}$ rad/s in Fig. 1, the conductivity does not follow the Drude law ($\propto \omega^{-2}$), which may be attributed to grain boundaries (Shimakawa et al. 2013). High density of localized states may exist at grain boundaries and hence hopping (or tunnelling) transport through the localized state should dominate the electronic transport in low temperatures. This suggests that grain boundaries interfere with the free carrier transport (Shimakawa et al. 2013; 2020). If the grain boundaries dominate the carrier transport in crystalline phase of GST, the above arguments of MIT should be modified to some extent.

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Conclusions

In the phase-change Ge—Sb—Te ternary system, the electronic transition is categorized to be thermally induced MIT. The Anderson-type MIT has been discussed extensively in this class of PCMs and isothermal annealing of a-PCMs above at a certain temperature leads to the metallic (crystalline) phase. In the insulator regime near the MIT, Mott-VRH and/or ESH at low temperatures below 20 K (and down to 1 K) in GST124 have been discussed extensively, however, we criticized the above argument through a detailed discussion of physical parameters that support the Mott-VRH mechanism. It is not clear whether or not the DOS near the Fermi level is localized (like the Fermi glass) in the crystalline phase. It was also suggested that in some GSTs grain boundaries were expected to interfere with the free carrier transport in the crystalline phase.

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