Nonequilibrium transport and Electron-Glass effects in thin Ge\textsubscript{x}Te films

Z. Ovadyahu

Racah Institute of Physics, The Hebrew University, Jerusalem 91904, Israel

Abstract

We report on results of nonequilibrium transport measurements made on thin films of germanium-telluride (Ge\textsubscript{x}Te) at cryogenic temperatures. Owing to a rather large deviation from stoichiometry (≈10% of Ge vacancies), these films exhibit p-type conductivity with carrier-concentration \(N \geq 10^{20}\) cm\(^{-3}\) and can be made either in the diffusive or strongly-localized regime by a judicious choice of preparation and post-treatment conditions. In both regimes the system shows persistent photoconductivity following excitation by a brief exposure to infrared radiation. Persistent photoconductivity is also observed in Ge\textsubscript{x}Te samples alloyed with Mn. However, in both Ge\textsubscript{x}Te and GeMn\textsubscript{y}Te\textsubscript{y} the effect is much weaker than that observable in GeSb\textsubscript{y}Te\textsubscript{x} alloys suggesting that antimony plays an important role in the phenomenon. Structural studies of these films reveal an unusual degree of texture that is rarely realized in strongly-disordered systems with high carrier-concentrations. Anderson-localized samples of Ge\textsubscript{x}Te exhibit non-ergodic transport which are characteristic of intrinsic electron-glasses, including a well developed memory-dip and slow relaxation of the excess conductance created in the excited state. These results support the conjecture that electron-glass effects with inherently long relaxation times is a generic property of all Anderson-localized systems with large carrier-concentration.

PACS numbers: 72.80.Ng 78.47.da 72.15.Rn 72.20.Jv

INTRODUCTION

The non-interacting Anderson-insulating phase has been called a Fermi-glass [1], presumably inspired by the spatial arrangement of the localized electronic wavefunctions resembling an amorphous structure. Further considerations, admitting for the long-range Coulomb interaction, inevitably present in a medium devoid of metallic screening, led several authors to suggest that a glassy phase, so called electron-glass (EG), should be observable in real systems [2 11].

Experimental observations consistent with the anticipated glassy behavior were reported in several Anderson-localized systems [12 13]. On the other hand, these effects were not seen in either Si or GaAs, systems that are readily made insulating and exhibit strong-localization transport properties. To some researchers, this shed doubts on the notion that the electron-glass is a generic phenomenon peculiar to the Anderson insulating regime.

It has been conjectured that the absence of electron-glass features in Si and GaAs is related to their relative low carrier-concentration \(N\) [14]. This was based on the observation that the dynamics in amorphous indium-oxide films [13] becomes much faster once \(N \leq 10^{20}\) cm\(^{-3}\). To date, a common feature in all Anderson-insulators that exhibit intrinsic EG effects, in addition to being strongly-localized, is their high carrier-concentrations, typically with \(N \geq 10^{20}\) cm\(^{-3}\). By “intrinsic” we mean that the non-ergodic effects appear in a given substance independently of the way the sample was prepared to achieve the required parameters (resistance at the measuring temperature, carrier-concentration, and dimensionality determined by the hopping-length to thickness ratio). Most importantly, the system has to exhibit a memory-dip with a width that is commensurate with the carrier-concentration of the material [14]. This distinction is important; slow conductance relaxation by itself is not necessarily a sign for EG, slow relaxation (and 1/f noise) may occur in lightly-doped semiconductors, presumably due to extrinsic effects [13].

The correlation between high carrier-concentration and sluggish relaxation rates may suggest the relevance of many-body effects. However, a case may also be made for the difference in disorder being the reason behind the correlation with carrier-concentration. Note that the requirement of strong localization means that a system with higher carrier-concentration has perforce more disorder (required to overcome the higher kinetic energy associated with higher carrier-concentration). One may then argue that the reason for the slow relaxation (and the various glassy features) exhibited by systems with higher Fermi energies is their considerably larger disorder rather than due to correlation effects. It may transpire that there is a peculiar type of disorder that exists in the high-n systems that lightly-doped semiconductors cannot sustain and it is this ”defect” which slows down the relaxation of the system from an out-of-equilibrium state. It is therefore of interest to experimentally test more systems with diversified structural properties.

This work describes transport measurements on Ge\textsubscript{x}Te samples, yet another system with carrier-concentration \(N \geq 10^{20}\) cm\(^{-3}\), somewhat above the empirical limit for observing electron-glass effects (when the system is strongly-localized). Comparison with films made with the alloy GeSb\textsubscript{y}Te\textsubscript{x} reveals a much weaker persistent-photoconductivity (PPC) in the Ge\textsubscript{x}Te films. The relaxation law from the photo-excited state also differ from that observed in GeSb\textsubscript{y}Te\textsubscript{x}, presumably associated with another kind of a defect. The microstructure of the Ge\textsubscript{x}Te films prepared by the method of this work

Typeset by REVtEX
show some unique features such as preferred orientation (texture) over a extremely large spatial scale, a single-crystal-like attribute. Yet, Anderson-localized films of this material exhibit nonequilibrium transport effects including a memory-dip characteristic of the electron-glass phase just like found in all previously studied systems. The implications of these finding to the origin of slow relaxation of electron-glasses are discussed.

Sample preparation and characterization

Samples used in this work were prepared by e-gun depositing GeTe onto room temperature substrates in a high-vacuum system (base pressure 1·10⁻⁷mbar) using rates of 1-2Å/second. The source material was 99.999% pure GeTe (Equipment Support Company, USA). Film thickness was in the range of 30-75Å. Lateral dimensions of the samples used for the low temperature studies were 0.3-0.5mm long and 0.5mm wide. Two types of substrates were used; 1mm-thick microscope glass-slides, and 0.5µm SiO₂ layer thermally grown on ⟨100⟩ silicon wafers. These were boron-doped and had bulk resistivity ρ ≃ 2·10⁻³Ωcm, deep into the degenerate regime. This makes this substrate suitable to perform as a gate-electrode even at low temperatures. Samples deposited on these wafers were configured as three-terminal devices for field-effect measurements. These were designed to probe ∂n/∂µ(E), the thermodynamic density of states versus energy of the material as well as to test for electron-glass behavior. Samples prepared on microscope glass-slides were mainly used for optical characterization and for Hall-Effect measurements, both performed at room-temperatures.

Each deposition batch included samples for optical excitation measurements, samples for Hall-effect measurements, and samples for structural and chemical analysis using a transmission electron microscope (TEM). For the latter study, carbon-coated Cu grids were put close to the sample during its deposition and received the same post-treatment as the samples used for transport measurements.

The Philips Tecnai F20 G2) was used to characterize the films composition (using energy dispersive spectroscopy, EDS) and microstructure. The EDS typically showed Ge deficiency so, we refer to our deposited films as GeₓTe. The Cary-1 spectrophotometer was used for optical measurements.

Films deposited at room temperatures were amorphous. TEM and associated diffraction pattern of typical GeₓTe sample deposited an hour prior to being inserted to the TEM are shown in Fig.1. Crystalline samples of GeₓTe were obtained from the amorphous GeₓTe depositions by subjecting them to temperatures in the range of 470-490K for 2-3 minutes. The amorphous-crystalline transformation is reflected in the optical properties of the films as a mild change in color tint. In this regard the result is very similar to corresponding situation in the GeSbₓTe_y compound studied previously [12] as can be seen in the comparison shown in Fig.2.

In terms of other properties however, there are significant differences between our crystalline versions of GeₓTe and the GeSbₓTe_y. In particular, their microstructure is different; while both systems exhibit mosaic film structure with a tight, space-filling packing of the crystallites, the GeₓTe film shows a much more pronounced preferred orientation extending over large scales. This may be seen
in both transmission electron microscope (TEM) micrographs depicted in Fig.3 (same sample as shown in Fig.1 after crystallization at 485K) and Fig.4 (same sample after being 'aged' for a week). The diffraction patterns in these figures were taken in selected-area mode covering 0.8 micron circle diameter. Pronounced preferred orientation was still conspicuous using a selected-area of 4 microns, which is at least order of magnitude larger than the average size of the grains in the studied films. This extensive texture, extending over a scale much larger than a typical grain size, was uniformly observed across the 3 mm TEM grid by scanning it with a constant electron-beam.

We found it hard to get films with appreciable sheet resistance even in quite thin specimen. The reason for that is presumably the reduced grain-boundary scattering and better mobility relative to that observed in the GeSb x Te y alloys (assuming that impurity-contents, and carrier-concentration are the same). Special measures had to be taken in fabricating films with high values for R□ (which were required for observing electron-glass properties). These included reducing the film thickness (down to 30Å relative to the constant 120Å used in the study of GeSb x Te y [12]), and aging the films in the lab atmosphere. A micrograph and associated diffraction of an aged film is shown in Fig.4.

The room-temperature resistance of our films span the range 600Ω-29kΩ which yielded 0.8kΩ-5.6MΩ at T≈4K. The upper limit of this range was obtained by reducing the film thickness to 30Å and exposing the sample to the lab atmosphere for several days. However, we were yet unable to produce films with R□>5.6MΩ at 4.1K. By comparison, using the GeSb x Te y alloy it was rather easy to obtain samples with R□ as high as 50MΩ even with films that were 3-4 thicker [12] than the Ge x Te used in this work.

The Hall effect that was monitored for some of the films showed a rather small change during the aging process; for a ≈100% increase of the film R□ the Hall resistance has increased by ≈6%. Based on these Hall
effect measurements the carrier-concentration n of the films was $N = (1.5 - 2) \times 10^{24} \text{cm}^{-3}$, somewhat smaller than the $N = (4 - 9) \times 10^{20} \text{cm}^{-3}$ found in the GeSb$_x$Te$_y$ compound [13]. In both cases the Hall effect had the sign of p-type carrier consistent with theoretical prediction for the material [15]. The latter, based on equilibrium concentration of Ge vacancies in the ideal crystal anticipated carrier-concentration of $\approx 10^{19} \text{cm}^{-3}$ holes. The carrier-concentration in our films, larger by roughly order of magnitude is probably a result of the abundant structural defects (readily observable in the TEM micrographs, Fig.3 and Fig.4) that apparently allows more Ge vacancies than the ordered crystal can sustain in equilibrium.

**Measurement techniques**

Conductivity of the samples was measured using a two terminal ac technique employing a 1211-ITHACO current preamplifier and a PAR-124A lock-in amplifier. All measurements were performed with the samples immersed in liquid helium at $T \approx 4.1 \text{K}$ held by a 100 liters storage-dewar. This allowed up to two months measurements on a given sample while keeping it cold (and in the dark) which was utilized to extend the time-duration of relaxation processes as well as many cycles of excitation-relaxation experiments. Fuller measurement techniques related to electron-glass properties are described elsewhere [19].

The ac voltage bias in conductivity measurements was small enough to ensure near-ohmic conditions (except for the current-voltage plots and the ‘stress protocol’ described in the Results section below). Optical excitations in this work were accomplished by exposing the sample to an AlGaAs diode operating at $\approx 0.88 \pm 0.05 \mu \text{m}$, mounted on the sample-stage typically $\approx 10 - 15 \text{mm}$ from the sample. The diode was energized by a computer-controlled current-source (Keithley 220).

**RESULTS AND DISCUSSION**

**Persistent photo-conductivity in Ge$_x$Te**

A main difference between the transport properties of Ge$_x$Te and the GeSb$_x$Te$_y$ alloy is their different sensitivity to optical excitation. The experimental protocol used for observing photoconductivity is illustrated in Fig.5 using a diffusive Ge$_x$Te film with $R_{\Box} = 5 \text{k}\Omega$ and, for comparison, a GeSb$_x$Te$_y$ film with similar $R_{\Box}$ and thickness measured under the same conditions. The experiment begins $\approx 24$ hours after the sample is cooled-down to 4.1K by recording $G(t)$ for 1-2 minutes to establish a baseline conductance $G_0$. The IR source is then turned on for 3 seconds then turned off while $G(t)$ continues to be measured. The brief IR burst causes $G$ to promptly increase by $\delta G_{\text{IR}}$ which decays slowly with time once the source is turned off (Fig.5). Both samples exhibit excess conductance that persists for a long time after the optical excitation. In terms of magnitude, the persistent photoconductivity (PPC) signal is however much more conspicuous in the GeSb$_x$Te$_y$ film at all values of $R_{\Box}$. A detailed comparison of the PPC magnitude versus $R_{\Box}$ illustrating the difference between the two systems is given in Fig.6. This figure includes three GeMn$_x$Te$_y$ samples. These were prepared by co-depositing Mn with the Ge$_x$Te compound to test the effect of magnetic impurities. The Mn inclusion had only a small effect on the samples mobility, reducing it by 10-20% (for $\approx 20\% \text{ Mn}$) relative to the pure compound. As shown in Fig.6 it also had a negligible effect on the PPC performance of the compound.

Actually it appears that the PPC in pure Ge$_x$Te and GeMn$_x$Te$_y$ compound differs from that in the GeSb$_x$Te$_y$ system not just by magnitude. The relaxation law that fits the time dependence of the excess conductance $\delta G_{\text{IR}}$ in the GeSb$_2$Te$_7$ compounds showed a rather good fit to a stretched exponential law: $\delta G_{\text{IR}}(t) \propto \exp\left\{-\left(t/\tau\right)^\beta\right\}$ with $\beta=0.1$ for all samples with $R_{\Box}$ in the $10^3 - 10^7 \Omega$ range. A similar expression could be fitted to the PPC data of our most resistive Ge$_x$Te films ($\delta G_{\text{IR}}$ for the lower resistance samples was too small to allow a meaningful fit) but with $\beta=0.14 - 0.22$. An example of a fit is shown in Fig.7.

This, and the much smaller $\delta G_{\text{IR}}$ (all other things being equal) suggests that the presence of the Sb plays a similar role in enhancing the PPC performance in germanium-tellurides compounds as that of In impuri-
Strongly localized Ge$_x$Te is an intrinsic electron-glass

Like in previously studied materials, a pre-requisite for observing electron-glass features is that the system must be strongly-localized. This applies in particular to the appearance of a memory-dip (MD) in the field-effect measurement, which is the identifying signature of the intrinsic electron-glass. A memory-dip appeared in our films at T≈4K once their R□ ≫ ℏ/ε$^2$. A well-developed MD can be seen in Fig.8 for a Ge$_x$Te film with R□=195kΩ.

The sign of $\frac{\partial}{\partial V_g} G(V_g)$ (reflecting how thermodynamic density of states $\partial n/\partial \mu$ changes with energy) is consistent with hole conduction (Fig.2 and Fig.8) and the sign of Hall-effect measurements on these films. Both the slope of $G(V_g)$ and the relative magnitude of the MD increases with disorder as shown in Fig.9. The disappearance of the MD as the system approaches the diffusive regime is common to all intrinsic electron-glasses, and has been seen in both two-dimensional and three-dimensional systems [22]. This is a crucial attribute of the phenomenon and should be the starting point for any theoretical model.

As may be expected, Ge$_x$Te films that exhibit MD also show the other characteristic features of electron-glasses. Fig.10 shows the excitation and ensuing relaxation of the excess conductance due to a sudden change of the gate voltage.

Another way to take the system away from equilibrium is the ‘stress-protocol’ [23]. By applying sufficiently strong electric field across the sample (between the ‘source’ and ‘drain’), the system accumulates en-

---

**FIG. 6:** The relative magnitude of the infrared induced excess conductance in the PPC state for our Ge$_x$Te films as function of their R□. These data are compared with the respective data for the GeSb$_x$Te$_y$ studied previously [13] and measured under the same conditions. Also shown are results for three Mn-doped Ge$_x$Te samples. Dashed lines are guides to the eye.

**FIG. 7:** The persistent photoconductivity of a Ge$_x$Te film with R□=750kΩ. The inset depicts a fit (dashed line) to a stretched-exponent for the associated excess conductance as function of time.

**FIG. 8:** The field-effect for a Ge$_x$Te sample with R□=195kΩ showing a a memory-dip with a relative magnitude of $\approx$0.75% magnitude (defined as by $\delta G_{MD}/Geq$ where Geq is the equilibrium value of the conductance at the bath temperature). The dashed line is the thermodynamic part of the field-effect measurement (as in the weakly-disordered sample in Fig.5).

---

ties in lead-telluride alloys [19]. It would be of interest to find what other elements are effective in enhancing PPC in these systems. That is important for understanding the basics of the PPC phenomenon but also as a tool for elucidating the physics of the electron-glass; the PPC, when prominent enough, may be an effective way to increase the carrier-concentration in a system which is an important parameter in controlling the dynamics of the electron-glass [21].
energy in excess of its thermal energy. This translates into excess conductance $\Delta G$ building up over the time the field is on. Once the strong field is removed, and the conductance is monitored under Ohmic conditions, $\Delta G$ decays with time and $G$ approaches its equilibrium value. Both the buildup and decay of $\Delta G$ involve a protracted process. Unlike the sudden increase of $G$ when $V_\text{g}$ is switched (Fig.10), $\Delta G$ grows continuously throughout the stress period without saturating. This is the analogue of the ‘time-dependent heat-capacity’ typical of glasses \[24\] which is due to the wide temporal spectrum of the system degrees of freedom. The stress protocol is illustrated in Fig.11a and Fig.11b for the conductance evolution $G(t)$ during the relaxation and during the stress respectively. The conductance dependence on the applied voltage of this sample is shown in Fig.12 with the voltage values used during the stress and relaxation periods are marked on the $G(V)$ curve.

The results of the stress-protocol (Fig.11) are essentially the same in all previously studied systems that exhibit electron-glass attributes \[25\]. Qualitatively different behavior has been observed in granular systems \[26\]. Granular systems differ from Anderson insulators in other aspects as well although they share some glassy features like a memory-dip \[27\].

It is also worth commenting on the mechanism by which the applied non-ohmic field takes the system out of equilibrium. The enhanced conductance that appears immediately after applying the field is associated with adiabatic modification of the hopping probabilities \[28\]. This is the dominant effect when the resistance is large but Joule-heating is to some degree also responsible to the increase of $G$ when a large voltage is applied (except when the applied field frequency exceeds the electron-phonon inelastic-rate \[29\]). Joule-heating is the reason for the slow buildup of excess conductance observed under large voltages. Qualitatively similar behavior is achieved by raising the bath temperature. However, comparing the behavior of $G(t)$ under field $F$ versus that of raising the bath temperature by $\Delta T$ (to achieve the same initial $\Delta G$), demonstrated that under $\Delta T$ the ensuing excess conductance increased with time at a faster rate \[30\]. This is just a manifestation of the fact alluded to above; heating is only part of the reason for non-ohmicity in the hopping regime. The advantage of using voltage-sweeps over raising-lowering the bath-temperature is the higher speed and controllability of the procedure. The price is the uncertainty in assigning a value of “effective-temperature” to the stress protocol; the value of $G$ under
non-ohmic fields is, in general, not a reliable thermometer; non-ohmic measurements of \( G(V) \) are not simply related to the \textit{equilibrium} values of \( G(T) \). 

As mentioned above, the visibility of the memory-dip, over the antisymmetric \( G(V_g) \) (controlled by the energy dependence of the thermodynamic DOS), increases with \( R_C \). The memory-dip for one of the most resistive samples we were able to manufacture in this study is shown in Fig.13 where it is compared with the MD of a GeSb\(_x\)Te\(_y\) film with the same \( R_C \) and measured under the same conditions (temperature, sweep-rate, and gate-voltage range).

The main difference between the two \( G(V_g) \) curves in Fig.13 is the steeper antisymmetric contribution of the GeSb\(_x\)Te\(_y\) sample. Closer examination reveals that the typical width of the MD is also somewhat wider for the Sb-doped alloy. The narrower width of the MD in Ge\(_x\)Te may be a result of the smaller carrier-concentration in this material which is in line with the general trend observed in previously studied electron-glasses. To date however, the only material where it was possible to change the carrier-concentration over a considerable range is amorphous indium-oxide [13]. The carrier-concentration in Ge\(_x\)Te is associated with Ge vacancies [17], and as demonstrated by Bahl and Chopra, the carrier-concentration in this system can be varied over a decade by heat-treatment during crystallization [16]. Ge\(_x\)Te may then be another system that allows testing the relation between the carrier-concentration, glass-dynamics, and the MD-width, by either controlling the sample stoichiometry during deposition, alloying with foreign elements, and thermal annealing. Future work will also focus on modifying the transport parameters of this system by various dopants.

With the addition of the currently studied Ge\(_x\)Te, there are now seven different Anderson-localized systems that exhibit intrinsic electron-glass effects. The previously studied systems and their properties were discussed elsewhere [21]. The only feature common to all these systems is having relatively large carrier-concentration; \( N \geq 5 \times 10^{19} \text{cm}^{-3} \). These systems have quite different structural properties making it hard to conceive of a common defect that might be responsible for the long relaxation times observed in their nonequilibrium transport properties. Grain-boundaries for example, are not likely to be relevant as their contribution to transport must be very weak in Ge\(_x\)Te relative to other electron-glasses while the electron-glass effects exhibited by all these systems are very similar; they all show slow relaxation and a memory-dip. It is therefore more likely that it is the \textit{magnitude} of the disorder rather than its specific nature that is the important factor. This, in turn, suggests that quantifying the disorder in the Anderson-insulating phase may be a vital step in the quest to unravel the mechanism responsible for the electron-glass dynamics.

This research has been supported by a grant administered by the 1126/12 grant administered by the Israel Academy for Sciences and Humanities.

[1] N. F. Mott, Phil. Mag., 26, 1015 (1972).
[2] J. H. Davies, P. A. Lee, and T. M. Rice, Phys. Rev. Letters, 49, 758 (1982); M. Grünewald, B. Pohlman, L. Schweitzer, and D. Würtz, J. Phys. C, 15, 1153 (1982); J. H. Davies, P. A. Lee, and T. M. Rice, Phys. Rev. B 29, 4260 (1984).
[3] M. Pollak and M. Ortuño, Sol. Energy Mater., 8, 81 (1982); M. Pollak, Phil. Mag. B 50, 265 (1984).
[4] G. Vignale, Phys. Rev. B 36, 8192 (1987).
[5] C. C. Yu, Phys. Rev. Lett., 82, 4074 (1999).
[6] M. Müller and L. B. Ioffe, Phys. Rev. Lett. 93, 256403 (2004).
[7] Vikas Malik and Deepak Kumar, Phys. Rev. B 69, 153103 (2004).
[8] R. Grempel, Europhys. Lett., 66, 854 (2004).
[9] Eran Lebanon, and Markus Müller, Phys. Rev. B 72, 174202 (2005); M. Müller and E. Lebanon, J. Phys. IV France, 131, 167 (2005).
[10] Ariel Amir, Yuval Oreg, and Yoseph Imry, Phys. Rev. B 77, 165207 (2008); Ariel Amir, Yuval Oreg, and Yoseph Imry, Annu. Rev. Condens. Matter Phys. 2, 235 (2011); Y. Meroz, Y. Oreg and Y. Imry, EPL, 105, 37010 (2014).
[11] Z. Ovadyahu, Phys. Rev. B 91, 094204 (2015).