Coexistence of Electron-Glass Phase and Persistent Photoconductivity in GeSbTe Compounds

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Abstract

It is demonstrated that persistent-photoconductivity (PPC), well-studied in lightly-doped semiconductors, is observable in GeSbTe compounds using infrared excitation at cryogenic temperatures. The low level of energy-flux necessary to induce an appreciable effect seems surprising given the high carrier-concentration n of these ternary alloys (n\approx10^{20}cm^{-3}). On the other hand, their high density of carriers makes GeSbTe films favorable candidates for exhibiting intrinsic electron-glass effects with long relaxation times. These are indeed observed in GeSbTe thin-films that are Anderson-localized. In particular, a memory-dip is observed in samples with sheet resistances larger than \approx10^{4} \Omega at T\approx4K with similar characteristics as in other systems that exhibit intrinsic electron-glass effects. Persistent-photoconductivity however is observable in GeSbTe films even for sheet resistances of the order of 10^{5} \Omega, well below the range of disorder required for observing electron-glass effects. These two non-equilibrium phenomena, PPC and electron-glass, are shown to be of different nature in terms of other aspects as well. In particular, their relaxation dynamics is qualitatively different; the excess conductance \Delta G associated with PPC decays with time as a stretched exponential whereas a logarithmic relaxation law characterizes \Delta G(t) of all electron-glasses studied to date. Surprisingly, the magnitude of the memory-dip is enhanced when the system is in the PPC state. This counter-intuitive result may be related to the compositional disorder in these materials extending over mesoscopic scales. Evidence in support of this scenario is presented and discussed.

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INTRODUCTION

Many phenomena in solid state systems exhibit monotonous conductance changes, suggestive of a non-equilibrium phenomenon. Annealing of defects during heat-treatment, irradiation by an external source, diffusion of injected particles, and illumination by light, are familiar examples of such phenomena.

There are two specific phenomena that exhibit sluggish conductance relaxation following excitation by a light-source: persistent-photoconductivity (PPC) that has been studied extensively as of 1968 \cite{1–13}, and the less familiar (but just as controversial) electron-glass \cite{14–23}. In addition to the similar way these effects are reflected in the sample conductance once triggered by light, both become more prominent at lower temperatures and both exhibit a non-exponential relaxation. This sometimes led to assuming a common mechanism to these phenomena \cite{24}.

In this work we describe some light-induced nonequilibrium transport properties in thin films of GeSb_{x}Te_{y}. The study was initiated as a test of the conjecture that intrinsic electron-glass effects, with long relaxation-times, are generic and should be observable in all Anderson insulating systems with sufficiently large carrier-concentrations \cite{25, 26}. The ternary compound GeSb_{x}Te_{y} reported by several groups to have carrier-concentration n in the range \approx10^{20}-10^{21}cm^{-3} \cite{27, 28} appeared to be a suitable candidate for this test. This expectation turned out to be correct; in their insulating state, GeSb_{x}Te_{y} films do exhibit electron-glass behavior. However, a surprisingly large photosensitivity was encountered in the very first experimental run. The sample was initially tested by a short exposure to infrared radiation using a power level that in other electron-glasses yielded a few percent increase in conductance G. In the GeSb_{x}Te_{y} sample this resulted in the conductance-reading promptly going off-scale. It soon became clear that this photo-response is a manifestation of persistent-photoconductivity rather than the anticipated electron-glass phenomenon. Persistent-photoconductivity is referred to in this work for processes that involve charge generation by exposure to light without change of stochiometry; this should not be confused with instances where self-doping is affected when e.g., oxygen is expelled from the sample by exposure to high-energy photons as happens in In_{2}O_{3-x} \cite{31} and ZnO \cite{31}. The latter processes may appear to be similar in that they show sluggish conductance relaxations, but they are of a different nature.

Persistent-photoconductivity typically occurs in systems with carrier-concentration smaller than \approx10^{19}cm^{-3} like lightly-doped semiconductors \cite{1–13}. Intrinsic electron-glass effects were never observed in these low-density systems \cite{26}.

Effects associated with the electron-glass phase were duly observed in field-effect experiments on Anderson-localized GeSb_{x}Te_{y} samples. These revealed a memory-dip with the same characteristic features found in previously studied electron-glasses. GeSb_{x}Te_{y} is the first narrow-gap semiconductor that exhibits intrinsic electron-glass behavior. By “intrinsic” we mean that the glassy effects appear in a given substance independently of the way the sample was prepared to achieve the required parameters (resistance at the measuring tempera-
ture, carrier-concentration, and dimensionality). Most importantly, the system has to exhibit a memory-dip with a width that is commensurate with the carrier-concentration of the material \cite{26}.

That electron-glass phase and persistent-photoconductivity coexist in the GeSb$_x$Te$_y$ compounds gives us a unique tool to learn about both phenomena. The current study demonstrates that PPC and electron-glass effects are different phenomena. Using the empirically known behavior of the electron-glass and persistent-photoconductivity it is argued that some of the non-trivial transport effects observed when the two coexist may be a result of the inhomogeneous nature of the system.

**EXPERIMENTAL**

**Sample preparation and characterization**

Samples used for this study were prepared by e-gun depositing a GeSb$_x$Te$_y$ alloy unto room temperature substrates in a high-vacuum system (base pressure 0.8-1.0x10^{-7} mbar) with rates of 2-3Å/second. A constant thickness of 120Å was used for all films in this study. Two types of substrates were used; 1mm-thick microscope glass-slides, and 0.5µm SiO$_2$ layer thermally grown on <100> silicon wafers. The Si wafers were boron-doped with bulk resistivity $\rho \approx 2-10^{-3}$Ωcm, deep into the degenerate regime. These wafers were employed as the gate electrode in the field-effect measurements. The field-effect technique was used heavily in this study as an analytical tool. The microscope glass-slides were mostly 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. For the latter study, carbon-coated Cu grids were put close to the sample during its deposition. The TEM grids received the same post-treatment as the samples used for transport measurements.

The source material was 99.999% pure GeSb$_2$Te$_5$ (American Elements). Different preparation runs however, produced films that usually had different stoichiometry than the source material. In the samples used in this work the GeTe atomic ratio, for example, varied between 1:3.5 to 1:4.8. These films should therefore be referred to as GeSb$_x$Te$_y$. By itself, variations in film composition seem to make little difference to the transport properties; we were not able to identify a qualitative influence of the film global stoichiometry on the transport results reported below, the main effect on the latter turns out to be the film sheet-resistance $R_S$.

Transmission-electron-microscopy (TEM), using the Philips Tecnai F20 G2 were employed to characterize the films composition and microstructure. The Varian Cary-1 spectrophotometer was used for optical measurements.

Polycrystalline samples of GeSb$_x$Te$_y$ were obtained by subjecting the as-deposited (amorphous) films to heat-treatment at a temperature $T_H$ for 2-3 minutes during which the sample was crystallized. The difference in the optical properties in the visible due to the amorphous-crystalline transformation could be seen in films deposited on glass substrates as a mild change in the color tint. An example is shown in Fig.1.

![Figure 1](image1.png)

**FIG. 1:** The optical transmission in the visible (relative to the bare glass-slide) of the as-prepared amorphous and the crystallized film (at $T_H=455$K). The hatched area indicates the spectral range of the IR LED used in this work. The absorption of the GeSb$_x$Te$_y$ film at these wavelengths is smaller than 10%. The difference in the transmission between the two films is due to stronger reflection, absorption, and scattering of the crystalline material.

The heat-treatment temperature was held constant during the heat-treatment process to ±2K around a specific value $T_H$. This was limited to the range 430-490K for the samples used in this work. In agreement with reports by other groups \cite{26,32}, the resistivity of a given crystalline film was found to depend on the value of $T_H$. Using a heating-stage attachment in the TEM revealed that onset of crystallization could be as low as 400-410K, and that the grain size increases monotonically with $T_H$.

A TEM micrograph and associated diffraction pattern of a typical film used in this study is given in Fig.2. This illustrates the polycrystalline nature of the film and a tight, space-filling packing of the crystallites with rare occasional cracks between adjacent crystallites. Grain-sizes as large as ≈10nm start appearing at $T_H=440$K, and grain-sizes as big ≈1 micron were observed for $T_H=540$K. Interestingly, at this grain-size, which is much larger than the film thickness ($d=120$Å), the film still maintains its mosaic, physically continuous structure.
The diffraction pattern taken from these films were consistent with the rhombohedral (R-3m) phase of GeTe in all our samples. No diffraction ring was found that could not be related to this basic structure. Note however that the presence of some amorphous component is always a possibility which is hard to rule out in these cases (especially when the film is supported on amorphous carbon). A small amount of texture (preferred orientation) was observed in these films (see diffraction pattern in Fig.2). There are quite a number of defects that are observed in the micrograph; grain boundaries and twinning being the most prevalent. These defects, as well as the compositional-disorder, discussed later, and surface scattering are presumably responsible for the low mobility of the films (a desirable feature in the context of this work).

Gold strips were deposited on the ion-bombarded glass substrates prior to the GeSb<sub>x</sub>Te<sub>y</sub> deposition. Lateral dimensions of the samples used here were 0.5-1mm long and 1mm wide. Samples had sheet resistance $R_{\Box}$ in the range 2kΩ-25MΩ at 4K. This range includes diffusive samples ($R_{\Box} < h/e^2$) as well as samples well into the hopping regime ($R_{\Box} \gg h/e^2$) at the measurement temperature. The room-temperature carrier-concentration of these films varied in the range of (4-9)$\times$10<sup>20</sup>cm<sup>-3</sup>, a range too narrow to show a definite correlation with the sample resistance.

**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 $T=4.1$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.

The ac voltage bias in conductivity measurements was small enough to ensure near-ohmic conditions (except for the current-voltage plots). Optical excitations in this work were accomplished by exposing the sample to an AlGaAs diode operating at $\approx 0.88\pm0.05$µm (see Fig.1), mounted on the sample-stage typically $\approx 10-15$mm from the sample. The diode was energized by a computer-controlled Keithley 220 current-source.

**RESULTS AND DISCUSSION**

**Non-equilibrium induced by optical-excitation in GeSb<sub>x</sub>Te<sub>y</sub>**

The experimental protocol used for optical excitation is illustrated in Fig.3 using a 120Å film of GeSb<sub>x</sub>Te<sub>y</sub>, deep in the insulating regime. 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, near-equilibrium conductance $G_0$. The IR source was 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 $\delta G_{IR}$ which decays slowly with time once the source is turned off (Fig.3).

This change in the sample conductance has a rather small effect on the conductance versus voltage characteristics as shown in Fig.4. The deviations from Ohm’s law at 4.1K start to become substantial at a field of $\approx 500$V/m, which is similar to what is observed in other disordered films of comparable resistance at these temperatures [26]. However, these deviations remain rather small at higher fields possibly suggesting a relatively small hopping length.

On first sight, the behavior of $G(t)$ depicted in Fig.3 appears to be similar to that of the "IR-protocol" applied to an electron-glass sample (see, for example, Fig.1 of [33]). A closer look reveals some differences. First, the effect is much larger than what is usually encountered with any of the previously studied electron-glass; note that a $\approx 3$mJ of infrared flux was sufficient to obtain $\delta G_{IR}/G_0 \approx 80\%$ (Fig.3). For comparison, an energy-flux of $\approx 80$mJ achieved only $\delta G_{IR}/G_0 \approx 15\%$ in the most IR-responsive electron-glass studied to date (see, Fig.6 of [33]).
Secondly, the initial fast drop of the excess conductance (once the IR source is off), common to all IR-excitations involving electron-glasses \[33\], is not observed here. More importantly, the temporal relaxation-law of \( G(t) \) is different: The inset to Fig.3 demonstrates that the slow component of the induced excess conductance relaxes with time as a stretched exponential, \( G(t) \approx \exp\left[-(t/\tau)\beta\right] \) with \( \beta=0.1 \) and \( \tau=4\times10^9\text{sec} \).

This should be contrasted with the logarithmic law for \( G(t) \) that is a characteristic feature of the intrinsic electron-glass \[26,34\]. The stretched exponential relaxation law has been consistently observed in more than twenty GeSb\(_x\)Te\(_y\) samples measured in this study. These included samples with sheet resistance \( R_{\square} \) covering the range 2.5k\(\Omega \) to 24M\(\Omega \) at \( T\approx4\text{K} \) all showing this relaxation law with the same \( \beta =0.1\pm0.005 \) as a best-fit parameter. Similar values for \( \beta \) are typically found at these temperatures in the relaxation law of the PPC in AlGa\(_x\)As\(_{1-x}\) compounds \[3\]. The other fit parameter in the stretched-exponential \( \tau \), turned out to be in the range of \( 10^8\text{sec} \) to \( 10^{10}\text{sec} \), and showed no systematic correlation with \( R_{\square} \). Apparently the disorder (assessed by the value of the sample \( R_{\square} \)) affects this phenomenon mainly through the relative magnitude of the excess conductance.

Whether the stretched exponential law is an inherent property of this phenomenon or is just a concise way to parametrize the data is open to debate (it may be possible to fit \( \delta G(t) \) by 2-3 exponential terms \[11\]). What is clear however is that the functional form of the relaxation deviates appreciably from the well-established logarithmic relaxation law of intrinsic electron-glasses \[26\]. This is obvious in the extended measurements that were taken here, but might be missed in runs that are shorter than two-decades in time (due to the rather small value of \( \beta \)).

It is noteworthy that this nonequilibrium effect persists throughout a wide range of disorder, including both the insulating and the diffusive regime. This is illustrated in Fig.5 for a series of GeSb\(_x\)Te\(_y\) films with different degrees of disorder but measured under identical IR-protocol conditions. This observation, by itself, is a strong evidence that the \( \delta G_{\text{IR}} \) is not an electron-glass effect; the latter is strictly a hopping-regime phenomenon and vanishes as the diffusive regime is approached \[26,35,36\].

Actually, the effects described in Fig.3 and Fig.5 are manifestations of a well-known phenomenon - persistent-photoconductivity (PPC). This phenomenon has been studied for more than four decades, mostly in lightly-doped semiconductors. In the majority of cases, the relaxation law was found to be stretched-exponential \[2,4–13\] as in this work. Different models were offered to account for PPC but they all share a common ingredient; a barrier that hinders the recombination of the photo-created electron-hole pairs. In essence, the excess conductance due to this mechanism is an enhanced carrier-concentration (in the hopping system \( \delta G_{\text{IR}} \) may depend exponentially on \( \delta n \)). The excess conductance in the electron-glass on the other hand is essentially due to enhanced mobility; the \( G(t) \) relaxation reflecting dressing of particles to form quasi-particles \[37\].

It is rather surprising to find PPC in degenerate semiconductors such as these GeSb\(_x\)Te\(_y\) compounds with their high carrier-concentration. To the best of our knowledge, this is the first occurrence of PPC in a
system with carrier-concentration \( n > 10^{20} \text{cm}^{-3} \). Typical values for \( n \) in systems exhibiting PPC range from \( 10^{15} \text{cm}^{-3} \) to \( 10^{19} \text{cm}^{-3} \) \[3, 7\]. These relatively low carrier-concentrations made it feasible to demonstrate, via Hall effect measurements, that the effect is associated with increase of carrier-concentration \[2, 7\]. High carrier-concentration, on the other hand, makes the GeSb\(_x\)Te\(_y\) a prime candidate to exhibit intrinsic electron-glass effects, which was the original reason for choosing this system for the study.

In the following we present further experimental results demonstrating that electron-glass effects and PPC are distinct phenomena. They may be separated by controlling the conditions required for the appearance of each in turn. They may also coexist, making it possible to learn something on the material from their interplay.

**GeSb\(_x\)Te\(_y\) is an intrinsic Electron-Glass (when Anderson localized)**

It is straightforward to eliminate the PPC - just not turn it on! This should leave the scene to the electron-glass, which may be probed while in the "dark-state" by non-optical means. A dark-state of a pre-exposed sample may be restored by raising it above the helium bath and holding it for few minutes at \( T \approx 30 \text{K} \) while in the shielded Dewar. \( T \approx 30 \text{K} \) is presumably of the order of the energy-barrier associated with the PPC in this system. Thermal recycling (from 4K to 30-40K) was used to reinstate the sample in its dark-state if it was in the PPC state. This restored the original conductance and the field-effect characteristics the sample had prior to IR-exposure to a very high accuracy, which suggests that there are no irreversible material changes in the sample due to the IR illumination.

The acid test for intrinsic electron-glass is the existence of a memory-dip \[26\]. This involves a field-effect measurement; recording the conductance as function of a gate-voltage \( V_g \). Results of such measurements are shown below (Fig.6) for the same sample that was used in Fig.3.

Two traces are shown in Fig.6: the first was taken 20 hours after the sample was cooled down and allowed to equilibrate while \( V_g=0 \text{V} \) was held between the sample and the gate. The resulting field-effect trace \( G(V_g) \) is composed of two components; an antisymmetric component reflecting the underlying (thermodynamic) density-of-states (DOS), and a superimposed dip, centered around the \( V_g \) where the systems was allowed to relax (\( V_g=0 \text{V} \) in this particular case). The latter, the so called memory-dip, is the distinguishing feature of the intrinsic electron-glass \[26\]. The width of the memory-dip is comparable with that of the amorphous version of indium-oxide with a comparable carrier-concentration \[38\]. The second trace shown in Fig.6 was taken after the gate-voltage was moved to \( V_g=-10 \text{V} \) and left there overnight. A new \( G(V_g) \) trace was taken, 21 hours after letting the sample equilibrate under \( V_g=-10 \text{V} \), to produce the curve labeled by full circles. This field-effect shows the same thermodynamic component as the old one while the memory-dip is now centered around the newly imposed gate-voltage. This illustrates the “two-dip-experiment” another common feature of electron-glasses \[26\].
Note that $\partial G/\partial V_g$ of the thermodynamic component has the opposite sign to that observed in n-type semiconductors such as indium-oxide and thallium-oxide films [26]. This is consistent with the p-type nature of GeSb$_x$Te$_y$, where the Fermi energy lies at the valence-band [39].

A characteristic feature observed in all intrinsic electron-glasses is a monotonous dependence of the memory-dip (MD) magnitude on disorder (at fixed sweep-rate and temperature) and, in particular, that it vanishes at the diffusive regime [26, 32, 30]. The data in Fig.7 confirms that the same trend, and the same functional dependence for $\delta G_{MD}/G(0)$ vs. $R_\square$, is observed in GeSb$_x$Te$_y$ films.

In contrast with the electron-glass phase that categorically requires $R_\square>h/e^2$ for its existence, persistent-photoconductivity is observable in the entire disorder regime covered in this work which includes samples in the weakly-localized regime. The PPC relative magnitude $\delta G_{PPC}/G_0$ does depend on the film disorder as shown in Fig.5 above but it is clearly observed in samples with $R_\square<h/e^2$. In terms of the absolute value of the excess conductance it is actually larger in diffusive samples than in the strongly-localized regime. Once $R_\square$ becomes smaller than $\approx 10^5 \Omega$ the magnitude of the MD quickly approaches the limit of the experimental noise-level (Fig.7) while the excess-conductance associated with the PPC in these GeSb$_x$Te$_y$ films is not affected by the impeding diffusive phase; neither the magnitude nor the parameters of the relaxation law seem to show any qualitative change (Fig.5).

This observation can be illustrated by using a sample in this intermediate disorder regime. Such data are shown in Fig.8. The data in this figure demonstrate that an intermediate disorder regime may be reached in a sample that still exhibits prominent PPC but the signature for electron-glass is not to be seen above the noise level.

Obviously, strong-localization, a mandatory requirement for showing electron-glass effects, is not a condition for observing persistent-photoconductivity in GeSb$_x$Te$_y$. Empirically, these two phenomena tend to favor vastly different carrier-concentration for their observation: intrinsic electron-glass behavior, with relaxation times larger than seconds, has been observed only in systems with high carrier-concentrations [26]. Persistent-photoconductivity on the other hand, has been reported almost exclusively in lightly-doped semiconductors. Observation of the latter phenomenon requires in addition, the existence of a specific defect-type to form a barrier that hinders fast recombination [8, 13].

These different preferences however, are apparently not mutually exclusive. As shown next, the two phenomena may coexist.

Lighting-up the Memory-Dip

The existence of a memory-dip in GeSb$_x$Te$_y$ with $R_\square>10^6 \Omega$ was anticipated; these samples are Anderson-localized, and they have relatively high carrier-
concentration. These are the empirically established conditions for observing the electron-glass phenomenon over conveniently long time-scales [26]. At this time there is no known exception to this observation.

Exposing these samples to infrared radiation however, had an unexpected effect. Figure 9 compares the field-effect measured on the sample that was used in Fig.6 in the dark-state with a G(V\textsubscript{g}) taken with the same experimental protocol but after a brief IR exposure to set the system in its PPC state. The latter G(V\textsubscript{g}) reveals a more prominent MD than observed in the dark-state.

Note that the conductance in this case increased by 60% while the magnitude of the memory-dip increased by 150%, the absolute value of the MD component \(\delta G_{\text{MD}}\) increases by more than the average G. This photo-enhanced memory-dip has been observed in all our GeSb\textsubscript{7}Te\textsubscript{3} samples with \(R_{\text{IR}}>10^5\,\Omega\), and independent of the equilibrium value of V\textsubscript{g} in the dark-state within the range of -8V to +8V. It was never encountered in previously studied electron-glasses where, if anything, IR-exposure caused a diminishment of the MD magnitude [36, 40]. Actually in every instance where G increased, be it due to temperature, non-Ohmic field, or decrease of disorder \(\delta G_{\text{MD}}/G\) always went down.

Another deviation from the electron-glass norm is observed in the asymptotic dependence of the MD amplitude on time. In previously studied electron-glasses the MD amplitude was found to grow logarithmically with the time the system relaxes under a fixed V\textsubscript{g} [35]. In the PPC state however, the MD amplitude actually decreases at long times. The example shown in Fig.10 illustrates how, concomitant with the slow decay of the PPC, the MD magnitude diminishes with time.

These observations lead us to consider the following scenario to account for this seemingly paradoxical IR effect.

Let us assume that the sample is not uniform; some regions in it are not part of the electron-glass phase. These could be of two types; regions where the disorder is weak such that locally they are diffusive, and regions in the sample where the carrier-concentration is low. Neither type of a region would exhibit long-lasting electron-glass effects in field-effect experiments are only detectable in systems where both, high carrier-concentration \textit{and} strong disorder are present [26]. Therefore, regions that do not meet this requirement would exhibit just a linear G(V\textsubscript{g}), reflecting the material thermodynamic DOS dependence on energy, but no memory-dip. On the other hand, they are just as good as other regions to contribute to PPC. Actually, all other things being equal, regions with low carrier-concentration are more likely to be significantly affected by the optical excitation. Once primed by the IR, some of these regions will just exhibit smaller resistance. Some others, having sufficiently large resistance may have their carrier-concentration elevated enough to exhibit memory-dip thus adding weight to the global component. Either way, a larger magnitude of the MD should result in the PPC-state.
The inhomogeneity of these samples, being disordered, is tantamount to being inhomogeneous. The question is how the inhomogeneity manifests itself; what physical property varies in space and above what spatial scale can the system be considered homogeneous? In the present case it is of interest to assess the contribution of fluctuations in carrier-concentration to the quenched disorder.

Spatial variations of carrier-concentration is not uncommon in multi-component systems. It has been recognized for example, as the reason for magneto-transport anomalies in Hg$_{1-x}$Cd$_x$Te films [41] (also a chalcogenide compound). Palm et al referred to the nature of inhomogeneities in their Hg$_{1-x}$Cd$_x$Te samples by: "...different amounts of the insulator’s fixed charge in various regions..." stating that "...this is like having different devices within one sample..." [11].

This type of inhomogeneity appears also in amorphous compounds such as indium-oxide. As pointed out by Givan and Ovadyahu [42], the energy cost of forming charge-gradients in a conducting matter may be mitigated by variation in chemical composition. Inhomogeneous carrier-concentration is especially important when a many-body phenomenon like superconductivity is involved [42]. The sensitivity to carrier-concentration makes it also important for the electron-glass phenomenon.

GeTe-based compounds are as susceptible to this kind of disorder as any other multi-component system. Using heat-treatment, Bahl and Chopra were able to vary the carrier-concentration in their GeTe samples by more than an order of magnitude [43] while preserving the same crystalline symmetry of the material. Crystal chemistry constraints in these materials are therefore not very effective in suppressing stoichiometry fluctuations. This should be compared with the mere factor of 2 variation in carrier-concentration possible in (self-doped) crystalline indium-oxide In$_2$O$_{3-x}$ without doping by foreign elements [40]. Adding a third element (Sb) to the GeTe system apparently only allows for greater variability; reported values for n in GeSb$_x$Te$_y$ with various x and y range between $\approx 3 \times 10^{18}$ cm$^{-3}$ [32] to $\approx 10^{22}$ cm$^{-3}$ [29]. Also, the large dielectric constant of GeSb$_x$Te$_y$ [28] further reduces the energy-cost associated with carrier-concentrations gradients.

To examine the spatial extent of these inhomogeneities, we initiated a study of the variation in the local-stoichiometry in GeSb$_x$Te$_y$ films. Recall that these materials are conducting by virtue of vacancies [29] and therefore we expect that mapping stoichiometry may be indicative of local carrier-concentration. This was done by employing energy-dispersive-spectroscopy (EDS) in the STEM mode at 200kV beam. The methodology is based on building the distribution of the local stoichiometry by performing consecutive EDS reading over a square with lateral size L. The study revealed $\approx 20\%$ variations in both Ge:Te and Sb:Te atomic-ratios in a distribution based on stoichiometry readings of squares with
L=400nm taken across a given sample. A spatial scale of 400nm is much larger than typical values of the hopping-length in strongly-localized samples at \( \approx 4K \). This makes the inhomogeneous scenario plausible; the spatial scale associated with the compositional disorder is large enough to justify treating the sample as being composed of segments with different transport characteristics.

It is natural to ask why this IR-enhancement effect has not been observed, for example, in amorphous indium-oxide where compositional disorder similar to that of GeSb\(_x\)Te\(_y\), has been found. Actually, at least to some degree the effect might be expected to exist in any electron-glass: These systems are inherently inhomogeneous and the notion of regions in the current-carrying network being in series with bottleneck resistances is a natural part of percolation models that purport to describe their transport properties.

A likely reason for the absence of this effect in the previously studied electron-glasses is simple: they do not exhibit PPC. To show persistent-photoconductivity there are rather restrictive conditions to be met. The first is feasibility of charge-generation from the light-source. The optical gap of GeSb\(_x\)Te\(_y\) is 0.4-0.8 eV, allowing inter-band transitions which evidently involve generation of excess charge in the system (note however that effective PPC may be achieved sometimes even for smaller photon energies than necessary for inter-band transitions). Indium-oxide and other previously studied electron-glasses, tested with the same IR-protocol as in this work, do not meet this requirement. The photon energy of the IR source used in these experiments (\( \approx 1eV \)) is smaller than their optical gap. This allows only intra-band transitions, which may be effective in randomizing site-occupation, and thus diminish the MD. However, no extra charge is generated in the system under these conditions.

A long-lasting PPC state is not guaranteed even when using a source with a photon energy that exceeds the optical gap. To keep the photo-generated electron-hole pairs from recombining and preserve the excess conductance, a mechanism has to exist to create an effective barrier against fast recombination. In general it is hard to identify this mechanism in a given system. It has not yet been identified in GeSb\(_x\)Te\(_y\). It would be interesting to extend the study of infrared excitation to GeTe samples, eliminating the Sb, which may help in identifying the effect responsible for in the persistent-photoconductivity we observe in the GeSbTe compounds.

As already mentioned, PPC has been observed in many systems but, to our knowledge, not in a system with carrier-concentration as high as in these GeSb\(_x\)Te\(_y\) films. Enhancing the conductance of a system with a carrier-concentration of \( n=10^{20} - 10^{21}\) cm\(^{-3}\) by 10-100\% (Fig.6) seems to require a photoinduced \( \delta n \) of not smaller smaller than \( \approx 10^{19} - 10^{20}\) cm\(^{-3}\). This may be estimated by comparison to field-effect data; \( \delta G(V_g) \) associated with the thermodynamic component results from adding (removing) a charge of \( \delta n \) to (from) the sample. This charge is determined by \( \delta V_g \) and the sample-gate capacitance \( C \). For \( \delta V_g=20V \), and \( C=10nF\cdot cm^{-2} \), the extra charge \( \delta n \) typically associated with the range of our \( G(V_g) \) measurements is of order \( 10^{18} - 10^{19}\) cm\(^{-3}\) (depending on whether the charge is confined to a screening-layer or is spread evenly along the film thickness). The conductance change \( \delta G \) associated with this \( \delta n \) varies between 0.7\% to 9.5\% for samples with \( R_\|=2.5k\Omega \) and \( R_\perp=24M\Omega \) respectively. The conductance incremenent in the PPC state \( \delta G_{IR} \) is an order of magnitude larger (see Fig.6), which may suggest that the associated \( \delta n \) is also larger. Perhaps much larger.

To put things in perspective, it is interesting to compare our PPC results with those obtained for another chalcogenide that is well known to exhibit persistent-photoconductivity, Pb\(_{1-x}\)Sn\(_x\)Te. This compound has similar material characteristics as GeSb\(_x\)Te\(_y\) (chemistry, optical-gap, large dielectric-constant, p-type conductivity). Persistent-photoconductivity in Pb\(_{1-x}\)Sn\(_x\)Te compounds doped with In or Ga has been extensively studied [7]. Working with bulk crystals allowed the researchers an effective way to estimate the photoinduced excess charge \( \delta n \) by analyzing Shubnikov-de Haas oscillations data. Values for \( \delta n \), under energy-flux levels of similar magnitude as used in this work, reached only \( 10^{17} - 10^{18}\) cm\(^{-3}\) [7]. Such values appear to be too low to account for our PPC results. This may indicate that photogeneration of charge is more efficient in GeSb\(_x\)Te\(_y\) or that the two processes of inserting the same \( \delta n \) to the system affect its conductance differently, perhaps due to the inhomogeneity (an inherent property of the hopping systems). These issues must await a direct measurement of the photoinduced excess-charge in GeSb\(_x\)Te\(_y\) films.

In sum, we presented in this paper experimental results that demonstrate the existence of persistent-photoconductivity in the degenerate semiconductor GeSb\(_x\)Te\(_y\). This non-stoichiometric compound has rather high carrier-concentration and thus it also exhibits electron-glass effects when in the strongly localized regime. It is demonstrated that persistent-photoconductivity and electron-glass phase are different nonequilibrium phenomena. They manifestly may coexist in the strongly localized regime of GeSb\(_x\)Te\(_y\) although it is not entirely clear that they share the same spatial regions in the disordered system. The memory-dip, a distinguishing feature of the electron-glass, is appreciably enhanced in the PPC-state. There is also an intriguing interplay between these phenomena in terms of a dramatic slowdown of the electron-glass dynamics while in the PPC-state that will be treated in future work.

Further work is needed to study the detailed temperature dependence of the persistent-photoconductivity in these materials and to elucidate the nature of the defects that are associated with this effect.
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