Structural Dynamics in Thermal Treatment of Amorphous Indium Oxide Films

Zvi Ovadyahu

Thermal treatment of amorphous indium oxide (In$_x$O) films is used in various basic studies as a means of tuning the disorder perceived by the electronic system. In this process, the resistance of a given sample decreases, whereas its amorphous structure and chemical composition is preserved. The main effect of the process is an increase in the system density, which, in turn, leads to improved interatomic overlap manifested as improved conductivity. A similar effect has been observed in studies of other amorphous systems that were subjected to pressure. Herein, the Raman spectra of amorphous In$_x$O change in response to thermal treatment in a similar way as in pressure experiments performed on other disordered and amorphous systems. A study of how thermal treatment changes the system dynamics is presented by monitoring the resistance versus time of In$_x$O films following various stages of thermal treatment. The time dependence of the sample resistance fits the stretched exponential law with parameters that change systematically with repeated thermal treatment cycles. The implications of these results to slow dynamics phenomena that are governed by the Kohlrausch’s law are discussed.

1. Introduction

Understanding the properties of amorphous solids has been a great intellectual endeavor. The lack of long-range periodicity presents a challenge to theory, and the nonequilibrium nature of the systems adds another layer of complexity. In addition to a lack of long-range order, most amorphous solids exhibit mass density that is lower than their crystalline counterpart. This is presumably due to their being formed by a fast cooling from the liquid or gaseous phase. The latter preparation method, quench-cooling the material from the vapor phase onto a cold substrate, usually results in a spongy structure that has many microvoids, reducing the material bulk specific gravity. Consequently, an appreciable volume change may be affected in these structures upon application of pressure. Indeed, amorphous systems often show considerable volume change, $\Delta V$, under pressure; relative volume shrinkage, $\Delta V/V$, exceeding 15% was observed in a number of studies.$^{[1-13]}$

It was recently shown that similar densification may be affected by thermally treating amorphous indium oxide (In$_x$O) films.$^{[14]}$ The protocol used a cycle of heating–cooling on vapor-deposited films and demonstrated a volume change of up to ~20%. At the same time, a change of several orders of magnitude of the film resistance at room temperature was observed in this low-carrier concentration version of In$_x$O.$^{[15]}$

In addition to the similarity between the effects produced by pressure and thermal treatment, in terms of densification, both protocols seem to share a peculiar aftereffect; upon relief of pressure, as well as after cooling back to room temperature in the thermal treatment protocol, the system volume slowly crept back up toward its initial value. This “swelling” effect was observed in the time dependence of the optical gap of glasses following pressure relief.$^{[7,14]}$ In our previous study of In$_x$O films, the effect was observed in the time dependence of the optical gap and the system resistance studied in situ after the thermal treatment is terminated.$^{[14]}$

Previous thermal treatment experiments were performed using versions of In$_x$O with relatively small deviations from the In$_2$O$_3$ stoichiometry of the ionic compound.$^{[14]}$ Herein, we used indium-richer version of In$_x$O with larger carrier concentration $N$. This version is commonly used in superconductor–insulator transition studies.$^{[16]}$ It exhibits the main features of all In$_x$O versions in having the flexibility of being able to modify its volume by heat treatment and thus fine-tunes its resistance, whereas the relatively high $N$ ($\geq 5 \times 10^{20} \text{cm}^{-3}$) makes it possible to observe superconductivity at liquid-helium temperatures once the system disorder is made low enough. The In$_x$O system affords a wide range of carrier concentration (while keeping the Fermi energy in the conduction band) with $N$ as low as $8 \times 10^{18} \text{cm}^{-3}$ to $N \approx 10^{22} \text{cm}^{-3}$. The carrier concentration of In$_x$O is essentially determined by the In$_x$O ratio during material deposition.$^{[17]}$ Due to its high carrier concentration, the as-prepared film of the material naturally has much lower resistivity than In$_x$O films with $N < 10^{20} \text{cm}^{-3}$. The amount by which the room temperature resistivity of the sample could be reduced by thermal treatment is accordingly more modest; it is rarely more than a factor of $\approx 4$. On the contrary, the accompanying relative change in other physical properties, per change in resistivity, is actually larger.$^{[15]}$
Using Raman scattering, we also show results for the boson peak exhibited by the material before and after thermally treating it. The boson peak is a feature that appears in the Raman spectra of disordered systems as a peculiar broad peak at 10–100 cm\(^{-1}\).[18–22] The magnitude of the boson peak, characteristically observed in glasses, decreases with pressure.[22] As shown in the following paragraphs, the same occurs upon thermally treating In\(_2\)O samples, further supporting the similarity between applying pressure and thermal treatment of glasses noted earlier.[14]

The time-dependence of the Raman spectra while pressure is applied, or after its release, has not yet been reported in any glassy system, and it is likely a small effect. By contrast, monitoring the applied, or after its release, has not yet been reported in any glassy disordered systems as a peculiar broad peak at 10\(^{-1}\) cm. The boson peak is a feature that appears in the Raman spectra of glasses, decreases with pressure.[22] As shown in the following paragraphs, the same occurs upon thermally treating In\(_2\)O samples, further supporting the similarity between applying pressure and thermal treatment of glasses noted earlier.[14]

The time-dependence of the Raman spectra while pressure is applied, or after its release, has not yet been reported in any glassy system, and it is likely a small effect. By contrast, monitoring the resistance is an extremely sensitive measure of the structural change associated with the densification of In\(_2\)O, as demonstrated in refs. [14,15]. Resistance measurement is also a fast process that allows tracking these changes in real time.

This sensitivity allows us to study the “aftereffect” mentioned earlier; after the heat treatment is ended, and the sample temperature returned to its pre-treatment value, the resistance of the sample first changes quickly upon cool-down and then slowly increases although the temperature is constant. The behavior of the resistance has a mechanical analogue; the volume of a “memory-foam” that has endured the squashing effect of a heavy object will show qualitatively similar time dependence as \(R(t)\) after the heat is turned off. In particular, it will swell back toward its original volume, partly as a rather fast change when the weight is lifted followed by a much slower process.

The time dependence of the swelling phenomenon, as reflected in the sample resistance, fits a stretched exponential law. A systematic study of how this law changes with consecutive annealing cycles reveals that, in addition to densification, the rate distribution that determines the slow structural dynamics becomes narrower. The implications of these results for data analysis of glass dynamics and transport studies are discussed.

2. Results and Discussion

2.1. Thermal Treatment Protocol

The protocol for thermal treatment of In\(_2\)O samples is composed of the following steps. The sample, deposited at \(T_p\) (typically \(\approx 298 \pm 2\) K), is anchored to a heat stage within the measuring cell, and electrical contacts are made to allow its resistance to be monitored. The cell is then evacuated by a rotary pump to a pressure of \(\leq 0.03\) mbar. Next, the heating stage is energized, and within a time interval \(\delta t\) (of the order of \(\approx 300\) s), the sample stage reaches an annealing temperature \(T_A\). The system is then kept at this temperature for a dwell-time \(t_d\) typically much longer than \(\delta t\). Finally, the heat supply is turned off and the sample is cooled back to ambient temperature within essentially the same \(\delta t\) as in the heat-up stage. The sample resistance and the stage temperature are continuously measured throughout the annealing cycle. A typical set of results for an annealing cycle is shown in Figure 1, including both \(R(T)\) and \(\Delta T(t)\), where \(T_A\) is the ambient temperature. A sharp response in resistance while the temperature increased upon heating and during cool-back to \(T_R\) is due to temperature dependence on sample

![Figure 1](image_url)

**Figure 1.** A typical protocol used in thermal treatment of In\(_2\)O films. a) Resistance data \(R(t)\) shown in open circles and refer to the left scale; sample temperature during the protocol is plotted vs. \(\Delta T(t)\) (open squares) refer to the right scale. The arrows mark the onset of the constant-temperature time intervals starting from which fits are shown (dashed lines) to the \(\Delta R(t)\) plots in part (b) and (c). The data in part (c) are for the annealing period (circles), and the data in part (b) (triangles) are for the “swelling” period. The fits (dashed lines) are based on Equation (2) and (3) with parameters \(\beta = 0.84, 0.60\) and \(\tau = 2 \times 10^6, 6 \times 10^5\) s, respectively.
resistivity (temperature coefficient of resistance was negative for all the samples studied). Note, however, the change in resistance even during the parts of the cycle where the temperature is essentially constant (Figure 1b,c). In particular, the resistance keeps going up long after the stage temperature stabilizes (Figure 1b). The time of $R$ is associated with an increase in the sample volume. This “swelling” effect has also been observed in pressure densification studies after the applied pressure has been relieved.$^{6,7}$

Both $\Delta R_{\text{swell}}(t)$ and $\Delta R_{\text{anneal}}(t)$ reflect changes in the system volume (rarefaction and densification, respectively). A change in volume during thermal treatment of In$_2$O films has been demonstrated in an interference experiment using grazing-angle X-ray technique.$^{[15]}$ The volume change was further correlated with in situ resistivity and optical spectroscopy measurements.$^{[15]}$

It was argued that the time-dependent processes that occur while the temperature was being kept constant can be qualitatively accounted for by assuming an effective two-body potential of the form depicted in Figure 2.$^{[14]}$ Moreover, the similarity of these effects with those produced by the application of pressure could be explained on the same footing as in thermal treatment of the system.$^{[14]}$ For completeness, a concise summary of these arguments is given in the subsequent sections.

2.2. A Heuristic Picture of Densification-Rarefaction

The picture is based on the interparticle potential schematically shown in Figure 2. The figure depicts two local configurations of the interparticle potential; “S” and “D” are specific two-state systems featuring two local minima. The state labeled S (for “swell”) favors a larger interparticle separation, whereas D favors a denser structure. The system density at a given temperature and pressure is determined by the values of $\Phi$’s. Transitions of the type $S,D(1 \rightarrow 2)$, $S,D(2 \rightarrow 1)$, are assumed to be controlled by a Boltzmann factor, so the transition rate $\gamma$ is

$$\gamma = \omega \cdot \exp[-\delta/k_B T]$$

where $\delta$ is $\delta_{1,1}=\Phi(3) - \Phi(1)$ and $\delta_{1,2}=\Phi(3) - \Phi(2)$, respectively; $\omega \approx 10^{12}$ s$^{-1}$ is the attempt frequency and $T$ is the temperature.

Many of the local configurations in the as-prepared In$_2$O films are probably of the “swell type” because the samples were quench-condensed from the vapor phase onto room-temperature substrates and therefore are similar to rapidly chilled glasses.$^{[11]}$

Accordingly, the S configurations may initially be preponderant in the system. When $\Delta T > 0$ is applied, the balance of occupation in the $S(1)$ and $S(2)$ states changes and the density will increase toward the level dictated by Boltzmann statistics and controlled by the distribution of the $\delta_{1,2}$ barriers. If, while $\Delta T$ is on, there are no irreversible structural changes, then the density will eventually saturate at the “equilibrium” value set by the temperature. In this case, the density will acquire its pristine value when $\Delta T$ is reduced to zero. Irreversible changes that apparently occur when the asymptotic value of the resistance is lower than the starting value signify transformation of S-configurations into D-configurations.

2.3. Raman Spectra

Amorphous systems are, as a rule, disordered solids. One of the characteristic features of these systems is the boson peak. This peculiar feature may be detected in inelastic neutron scattering, where it shows up as an excess of vibration states over the parabolic Debye spectrum.$^{[18-22]}$ This boson peak is routinely observed in Raman scattering experiments where it exhibits a characteristic asymmetric shape with a peak value around 40–100 cm$^{-1}$. The effect of pressure on the boson peak has been studied in a number of disordered systems and showed a systematic reduction of the peak magnitude with increasing pressure.$^{[22]}$

Herein, we show Raman spectra before and after thermal treatment (Figure 3). The figure reveals the same trend as in other disordered systems; the magnitude of the boson peak is significantly smaller following densification. This gives further support to the observation that thermal treatment of In$_2$O has...
qualitatively the same effect as applying pressure on other structural glasses in agreement with the heuristic picture.\textsuperscript{[14]} A reduction of the boson peak magnitude was also observed after thermally treating the In\textsubscript{2}O\textsubscript{3} version used in a previous study.\textsuperscript{[14]}

The observed weakening of the boson peak is in line with the general correlation found in the simulation work of Shintani and Tanaka.\textsuperscript{[22]} However, the specific mechanism by which the reduced off-diagonal disorder associated with the annealing process\textsuperscript{[15]} affects the magnitude of the boson peak remains an open question. It should also be remarked that the present Raman setup, having a cutoff below $\approx 70$ cm$^{-3}$, is not low enough to determine the position where the boson peak reaches its maximum value, and therefore we are not able to tell whether it shifted due to the thermal treatment.

A further reduction in the boson peak magnitude is achieved upon crystallizing the In\textsubscript{2}O film. Crystallization proceeds rapidly by subjecting the In\textsubscript{2}O film to temperatures in excess of $\approx 370$ K. The Raman spectrum of the resulting In\textsubscript{2}O\textsubscript{3–x} polycrystalline film is compared with that of the as-deposited amorphous film and with the spectrum of the deposition source material In\textsubscript{2}O\textsubscript{3}. Obviously, the Raman spectra of the various structures of In\textsubscript{2}O samples are distinctly different. This makes Raman scattering a useful tool to identify them, and, in particular, to distinguish samples that are distinctly different. This makes Raman scattering a useful tool to identify them, and, in particular, to distinguish samples that are distinctly different. This makes Raman scattering a useful tool to identify them, and, in particular, to distinguish samples that are distinctly different. This makes Raman scattering a useful tool to identify them, and, in particular, to distinguish samples that are distinctly different.

The observed weakening of the boson peak is in line with the general correlation found in the simulation work of Shintani and Tanaka.\textsuperscript{[22]} However, the specific mechanism by which the reduced off-diagonal disorder associated with the annealing process\textsuperscript{[15]} affects the magnitude of the boson peak remains an open question. It should also be remarked that the present Raman setup, having a cutoff below $\approx 70$ cm$^{-3}$, is not low enough to determine the position where the boson peak reaches its maximum value, and therefore we are not able to tell whether it shifted due to the thermal treatment.

A further reduction in the boson peak magnitude is achieved upon crystallizing the In\textsubscript{2}O film. Crystallization proceeds rapidly by subjecting the In\textsubscript{2}O film to temperatures in excess of $\approx 370$ K. The Raman spectrum of the resulting In\textsubscript{2}O\textsubscript{3–x} polycrystalline film is compared with that of the as-deposited amorphous film and with the spectrum of the deposition source material In\textsubscript{2}O\textsubscript{3}. Obviously, the Raman spectra of the various structures of In\textsubscript{2}O samples are distinctly different. This makes Raman scattering a useful tool to identify them, and, in particular, to distinguish samples that are distinctly different. This makes Raman scattering a useful tool to identify them, and, in particular, to distinguish samples that are distinctly different. This makes Raman scattering a useful tool to identify them, and, in particular, to distinguish samples that are distinctly different. This makes Raman scattering a useful tool to identify them, and, in particular, to distinguish samples that are distinctly different. This makes Raman scattering a useful tool to identify them, and, in particular, to distinguish samples that are distinctly different. This makes Raman scattering a useful tool to identify them, and, in particular, to distinguish samples that are distinctly different. This makes Raman scattering a useful tool to identify them, and, in particular, to distinguish samples that are distinctly different. This makes Raman scattering a useful tool to identify them, and, in particular, to distinguish samples that are distinctly different.

We turn now to discuss the main findings of this work—the slow processes that occur during the isothermal parts of the annealing cycle. The behavior shown in Figure 1 is typical, but the relative magnitude of changes that presumably take place, while the system temperature is constant, depends in an intricate way on $T_A$, time of thermal treatment, and on history. Two examples for protocols that are usually avoided are shown in Figure 5 and 6. Figure 5 shows an example of an unusually long heating process that is fed (dashed line) to Equation (3) with $\beta = 0.96$ and $r = 10^5$ s (dashed line). The arrow marks the chosen origin of time for $\Delta R_{\text{swell}}(t)$. Figure 6 shows an example of an unusually long heating process that is fed (dashed line) to Equation (3) with $\beta = 0.75$ and $r = 10^5$ s (dashed line). The arrow marks the chosen origin of time for $\Delta R_{\text{swell}}(t)$.
that is the way to get a substantial densification and lowering of the sample resistance when using moderate annealing temperatures \( T_A \). Figure 6, on the other hand, shows the unwanted result of actually ending up with a higher resistance than the value one started the protocol with. Such an outcome is not rare; it usually occurs when \( T_A \) is close to the temperature the sample was exposed to previously (e.g., during deposition), annealed for short period of time, or both. In essence, even though cooling back to room temperatures extends over hundreds of seconds, it is effectively tantamount to quench-cooling the sample because the cooling time is still much shorter than the relaxation time of the medium. In terms of the heuristic model, the most relevant configurations (see Figure 2) involved in the swelling effect are those having \( \Phi(1) - \Phi(2) \) just larger than \( k_B T_A \).

An intriguing question for which we have yet no answer is whether it is possible to completely eliminate “S-type” configurations from the amorphous system by careful annealing.

The temporal dependence of \( R \), while the system is under the annealing temperature \( T_A \), may be fitted to a stretched exponential law

\[
\Delta R_{\text{anneal}}(t) = \Delta R_s \cdot \exp\left[-\left(t/\tau^\beta\right)^\gamma\right]
\]

with the three parameters \( \beta \), \( \tau \), and \( \Delta R_s \).

A complementary behavior takes place during the asymptotic region of the annealing protocol, where the temperature has settled back at \( T_{RT} \). In this period, \( R(t) \) may also be described by a stretched exponential law (in general, with different parameters for \( \beta \) and \( \tau \))

\[
\Delta R_{\text{swell}}(t) = \Delta R_s \left[1 - \exp\left(-\left(t/\Delta \tau\right)^\delta\right)\right]
\]

Stretched exponential time dependence is often observed in the dynamics of disordered systems.\(^{[23,24]}\) There were several attempts to come up with a microscopic model that accounts for the origin of this so-called Kohlrausch law.\(^{[25]}\) However, for discussing the current results, a simple interpretation, suggesting that the stretched exponential is just a weighted sum of simple exponentials, may suffice.\(^{[26]}\) In this approach, the stretched exponential law is a convoluted effect of parallel events with relaxation rates \( \gamma \) distributed over a range with probability \( P(\gamma) \), the parameter \( \beta \) is a logarithmic measure of the distribution width, and \( \tau \) is a characteristic relaxation time.\(^{[26]}\) We shall argue, however, that, unless \( \beta \approx 1 \), associating \( \tau \) with a relaxation time may convey only part of the characteristics of the dynamics.

Fitting data of a rather plain form such as our \( \Delta R_{\text{anneal}}(t) \) or \( \Delta R_{\text{swell}}(t) \) plots to Equation (2) or Equation (3), involving three parameters, should be taken with some reservations. The main problem in trying to fit such data to Equation (2) or Equation (3) is the time the sample takes to stabilize upon heating-up to \( T_A \) and after cooling back to room temperature. This introduces uncertainty in the assignment of the origin of time. Nevertheless, fitting data to these stretched exponential expressions is still a reasonable tool to estimate (by extrapolation) the asymptotic value of the resistance, and to compare changes in dynamics on a relative basis. Our choice of the “starting time” for the isothermal process is marked by the arrows in Figure 1, 5, and 6.

2.5. How Disorder Is Reflected in the Swelling Dynamics

Next we wish to focus on how the dynamics observable through analyzing \( \Delta R_{\text{swell}}(t) \) data reflect on the degree of the disorder after a given thermal treatment cycle. In transport measurements, it is the sample resistivity \( \rho_{RT} \) that is often taken as the criterion for disorder. Thermal annealing modifies the sample resistance at the end of the heat cycle and therefore it changes the disorder. However, in addition to the value of the average resistivity, there are changes observable in the dynamics of the “aftereffect” that may give further information on the modified system disorder.

We have studied three series of samples that were progressively annealed by subjecting them to thermal treatment for successively longer times, higher \( T_A \) (or both). This resulted in a lower resistance at the end of each annealing cycle. The dynamics of the system was then tested at each cycle end by the very same protocol: The sample was exposed to \( T_A = 325 \pm 1 \text{ K} \) for \( \approx 60 \text{ min} \), then allowed to cool back to room temperature, and the ensuing \( \Delta R_{\text{swell}}(t) \) was monitored. A fit was then made for these data to Equation (3) using the same criteria for the choice of the origin of time for each heat treatment cycle. It turns out that the best-fit parameters \( \beta \) and \( \tau \) consistently increased as the annealing stages progressed and the sample resistance decreased. Three plots that illustrate this trend are shown in Figure 7. Note that the asymptotic value of \( \Delta R_{\text{swell}} \) gets progressively smaller with further thermal cycles, but it seems to reach a limit as further annealing gives little or no improvement of the conductance. In addition, the time dependence of \( \Delta R_{\text{swell}}(t) \) also changes: more annealing causes \( \Delta R_{\text{swell}}(t) \) to exhibit a smaller curvature. This is shown in Figure 7 comparing the plots for the first, second, and third thermal treatment cycles (the latter shown in a magnified view to facilitate comparison of change in curvature).

![Figure 7](image-url)
The $\Delta R_{\text{swell}}(t)$ plots in Figure 7 are the results of three consecutive annealing stages carried on the same sample. In each of these heat treatment cycles, the sample was held for 1 h under $T_A = 338 \pm 0.5$ K, then quickly cooled back to room temperature, and its resistance versus time was monitored to determine $\Delta R_{\text{swell}}(t)$. The latter was fitted to Equation (3), yielding best-fit values for $\beta$ and for relaxation times $\tau$. These parameters are shown in Table 1. These were purposefully chosen for display because their $\beta$'s are close to 1/2, 7/8, and 24/25 for thermal cycles 1, 2, and 3, respectively. Note that $P(\tau; \beta)$, where $\beta$ equals the ratio of integers, may be readily calculated by the prescription suggested by Johnston.[26]

It might seem natural to take the value of the fitted $\tau$ as a characteristic relaxation time for a given sample. In this case, one may conclude from Figure 8b that the dynamics of the swelling effect becomes slower with progressive annealing. However, when plotting against the peak value $(\gamma \tau)_p$ of $P(\gamma \tau)$ associated with the best-fitted $\beta$, one observes an intriguing correlation in our data; $\tau$ is linear with $(\gamma \tau)_p$ (Figure 8b). This, in turn, means that $(\gamma \tau)_p$, the most probable rate involved in the dynamics of $\Delta R_{\text{swell}}(t)$, actually remains constant as the annealing proceeds to further reduce the sample resistance (Figure 8c). It should be emphasized that a trend of $\beta$ getting larger with further annealing was observed in all our thermal treatment experiments, but without knowing the associated $P(\gamma \tau)_p$, we cannot ascertain that the $\tau \propto (\gamma \tau)_p$ relation holds in each interim annealing stage. What is clear is that larger $\beta$ means narrower and more symmetric rate distribution. Therefore, it is fair to conclude that, in addition to increasing the material density, thermal treatment of In$_2$O films improves their homogeneity. This agrees with independent data obtained using X-ray interferometry.[15] The lesson here is that the value of the best-fitted $\beta$ by itself conveys only part of the information relevant for the system dynamics (unless $\beta$ is close to unity). When $\beta$ is small, the relaxation time is an ill-defined quantity and its value may depend on the specific protocol one uses to estimate it.

Using Equation (1), the effective barrier that would give the most probable transition rate found above for In$_2$O films may be estimated by

$$\delta_p = k_B T \cdot \ln(\omega / \gamma_p) \quad (4)$$

With $k_B T \approx 25$ meV, $\omega \approx 10^{12}$ s$^{-1}$, and $\gamma_p \approx 10^{-5}$ s$^{-1}$ (from Figure 8c), one gets $\delta_p \approx 1.0 \pm 0.05$ eV. It should be noted that, within the experimental error, this $\delta_p$ is identical with the value estimated for the barrier of another version of this material with a lower carrier concentration.[16] The order of magnitude difference (in terms of carrier concentration) between these versions of In$_2$O has apparently little effect on the value of the barrier. This suggests that its origin has to do with local chemistry rather than the specific stoichiometry of the compound.

With a barrier of the order of 1 eV, the only dynamics expected below $\approx 100$ K on a time scale relevant for most experiments would be of quantum nature; at liquid nitrogen temperatures, the over-the-barrier transition rate would already be smaller than $10^{-14}$ s$^{-1}$.

Table 1. Fitting parameters for the data shown in Figure 7.

| Thermal treatment cycle | $\beta$ | $\tau$ ($\times 10^3$ s) |
|------------------------|--------|----------------------|
| 1                      | 0.51 ± 0.05 | 1.6 ± 0.08 |
| 2                      | 0.87 ± 0.02 | 6.4 ± 0.1  |
| 3                      | 0.96 ± 0.015 | 8.1 ± 0.2  |

Figure 8. a) The normalized probability distribution of the dimensionless parameter $\gamma \tau$ that gives the stretched exponential relaxation law[26] for three values of $\beta$, and $(\gamma \tau)_p$ is the value at the respective point where $\partial P(\gamma \tau) / \partial (\gamma \tau) = 0$. b) The best-fitted value of the parameter $\tau$ for the three annealing cycles shown in Figure 7. c) The transition rates of these samples at the peak of the respective $P(\gamma \tau)$ distribution.
The lack of observable increase with time of the average resistance for a sample immersed in liquid helium suggests that tunneling transition is also practically suppressed. The effective distance for tunneling may be of atomic dimension, but it probably involves many-body effects, making the mass of the tunneling object large. This effective freezing-out of the system disorder makes thermal treatment a useful tool for a variety of low-temperature electronic transport studies where one seeks a way to fine-tune the disorder. Not only does it allow to change the average disorder over a range large enough to affect the metal–insulator or superconductor–insulator transition, but, by letting the system retrieve some disorder through the swelling effect, it also allows a certain degree of reversibility. This is especially useful for study of the insulating phase where a small change in room-temperature resistance translates into an exponentially large change at low temperatures.13

3. Summary

We studied in this work several effects associated with thermally treating In2O films. Two effects that were studied previously are a reduction in the system volume and optical gap during heat treatment, as well as a partial recovery of these quantities after the sample is cooled back to room temperature.14 Here it is shown that thermal treatment also leads to a reduction of the boson peak magnitude. These three effects were observed in other disordered systems by applying pressure. The response of a system volume to application of pressure and the rarefaction that takes place once pressure is relieved appeals to one’s intuition based on everyday experience. That thermal treatment has similar effects may seem counter-intuitive, again, due to common experience; a rise in temperature usually (but not always) causes the system to expand.27 It is in these nonequilibrium solids such as amorphous systems, especially those quench-condensed from the vapor phase, that this peculiar behavior may turn out to be prevalent. There is no reason to believe that In2O films are unique in this regard.

Monitoring the system resistance allows real-time sensitive tracking of the dynamics and energetics associated with these phenomena during both densification and after heat treatment is terminated while the system relaxes toward a new (metastable) state. These processes are presumably activated and exhibit temporal dependencies that fit the Kohlrausch law often encountered in experiments involving slow dynamics of structural glasses. The parameters that fit the relaxation law β and r change systematically with the degree of annealing. An analysis of these changes suggests that, in addition to densification, there is a narrowing of the rate distribution induced by thermal treatment. This narrowing is a natural consequence of the heterogeneous relaxation scenario. Assuming that the observed stretched exponential relaxation law is indeed a parallel process involving different rates, each controlled by a barrier, then, while under Tc, transitions controlled by the lowest barriers will occur exponentially faster than activated events associated with larger barriers. Therefore, with continued annealing, the high-rate part of the distribution will be preferentially eliminated from the distribution. This will be reflected in the fit parameter β progressively approaching unity. It would be interesting to see how general are these findings by studying the effects of thermal treatment on other metallic glasses.

4. Experimental Section

Sample Preparation and Characterization: The In2O films used here were e-gun-evaporated onto room-temperature substrates using 99.999% pure In2O3 sputtering target. Undoped silicon wafers were used as substrates for both electrical and Raman spectroscopy measurements. Deposition was performed at the ambience of 3 ± 0.5 × 10−5 Torr oxygen pressure maintained by leaking 99.9% pure O2 through a needle valve into the vacuum chamber (base pressure ≃10−6 Torr). Rates of deposition were 1.4–2.5 Å s−1. With this range of rate-to-oxygen pressure, the In2O samples had carrier concentration N in the range (6–25) × 1017 cm−3 measured by Hall effect at room temperature. Note that the carrier concentration of the samples used in a previous study was considerably lower.14 The evaporation source to substrate distance in the deposition chamber was 45 cm. This yielded films with a thickness uniformity of ±2% across a 2 × 2 cm2 area. Lateral sizes of samples used for transport measurements were typically 1 × 2 mm2 (width × length respectively), and 1 × 1 cm2 for the Raman spectroscopy. The film thickness of the samples used for transport measurements was 510 ± 10 Å.

The as-deposited samples typically had a sheet resistance R of the order of (5–10) × 104 Ω at room temperatures, much smaller than for the films with lower carrier concentrations used before. This was usually the starting stage for thermal treatment cycles performed on each preparation batch (three different batches were used in the study). The annealing process will be described in the next section. Details of the changes in the material microstructure in the process of thermal treatment are described elsewhere.14,15

Measurement Methods: After removal from the deposition chamber, the sample was mounted onto a heat stage in a small vacuum cell wired to make contacts with the sample and a thermocouple thermometer attached to the sample stage for electrical measurements. The cell used for monitoring the sample resistance and temperature was made of 0.2-mm light-weight copper sheet equipped with a thermofoil heating strip on its back side. The characteristic time to reach 90% of the asymptotic temperature after applying power to the heating element was typically ≃300 s for the range of temperatures used in this work.

Copper wires were soldered to indium contacts pressed into the sample strip to facilitate resistance measurements. These were performed by a two-terminal technique using either the computer-controlled HP34410A multimeter or the Keithley K617.

Raman spectra were taken with a Renishaw inVia reflex spectrometer using a laser beam with either 514 or 785 nm wavelength and edge filter at ≃70 cm−1.

Acknowledgements

The assistance by Dr. Anna Radko with the Raman spectra work is gratefully acknowledged. This research was supported by the 1030/16 grant administered by the Israel Academy for Sciences and Humanities.

Conflict of Interest

The author declares no conflict of interest.

Keywords

amorphous systems, Kohlrausch’s law, thermal treatment
Received: June 1, 2019  
Revised: September 11, 2019  
Published online: October 7, 2019

[1] P. W. Bridgman, I. Simon, J. Appl. Phys. 1953, 405, 24.
[2] S. Sakka, J. D. Mackenzie, J. Non-Cryst. Solids 1969, 1, 107.
[3] J. D. Mackenzie, J. Am. Ceram. Soc. 1963, 46, 461.
[4] J. D. Mackenzie, J. Am. Ceram. Soc. 1963, 46, 470.
[5] C. T. Wu, H. L. Luo, J. Non-Cryst. Solids 1975, 18, 21.
[6] N. Sakai, H. Fritzsche, Phys. Rev. B 1977, 15, 973.
[7] S. Onari, T. Inokuma, H. Kataura, T. Ara, Phys. Rev. B 1987, 35, 4373.
[8] A. Polian, M. Grimsditch, Phys. Rev. B 1990, 41, 6086.
[9] S. Susman, K. J. Volin, D. L. Price, M. Grimsditch, J. P. Rino, R. K. Kalia, P. Vashishta, G. Gwannesia, Y. Wang, R. C. Liebermann, Phys. Rev. B 1991, 43, 1194.
[10] N. Ookubo, Y. Matsuda, N. Kuroda, Appl. Phys. Lett. 1993, 63, 346.
[11] D. J. Lacks, Phys. Rev. Lett. 1998, 30, 5385.
[12] K. Miyachi, J. Qiu, M. Shojoji, Y. Kawamoto, N. Kitamura, J. Non-Cryst. Solids 2001, 279, 186.
[13] V. V. Brazhkin, E. Bychkov, O. B. Tsiok, Phys. Rev. B 2017, 95, 054205.
[14] Z. Ovadyahu, Phys. Rev. B 2017, 95, 214207.
[15] Z. Ovadyahu, Phys. Rev. B, 2017, 95, 134203.
[16] a) D. Shahar, Z. Ovadyahu, Phys. Rev. B 1992, 46, 10917; b) D. Kowal, Z. Ovadyahu, Solid State Commun. 1994, 90, 783; c) V. Gantmakher, Int. J. Mod. Phys. B 1998, 12, 29; d) G. Sambandamurthy, L. W. Engel, A. Johansson, D. Shahar, Phys. Rev. Lett. 2004, 92, 107005; e) M. A. Steiner, G. Boebinger, A. Kapitulnik, Phys. Rev. Lett. 2005, 94, 107008; f) M. Steiner, A. Kapitulnik, Physica C 2005, 422, 16; g) M. A. Steiner, N. P. Breznay, A. Kapitulnik, Phys. Rev. B 2008, 77, 212501; h) N. P. Breznay, M. A. Steiner, S. A. Kivelson, A. Kapitulnik, Proc. Natl. Acad. Sci. USA 2015, 112, 215; i) P. Breznay, A. Kapitulnik, Sci. Adv. 2017, 3, e1700612; j) T. I. Baturina, A. Bilušić, A. Mironov, V. M. Vinokur, M. R. Baklanov, C. Strunk, Physica C 2008, 468, 316; k) S. Poran, E. Shimshoni, A. Kapitulnik, Phys. Rev. B 2011, 84, 014529; l) D. Sherman, G. Kopnov, D. Shahar, A. Frydman, Phys. Rev. Lett. 2012, 108, 177006; m) Y. Lee, A. Frydman, T. Chen, B. Skinner, A. M. Goldman, Phys. Rev. B 2013, 88, 024509; n) B. Sacépé, T. Dubouchet, C. Chapelier, M. Sanguer, M. Ovadia, D. Shahar, M. Feigel’man, L. Ioffe, Nat. Phys. 2011, 7, 239; o) D. Sherman, U. S. Pracht, B. Corshunov, S. Poran, J. Jesudasan, M. Chand, P. Raychaudhuri, M. Swanson, N. Trivedi, A. Auerbach, M. Scheffler, A. Frydman, M. Dressel, Nat. Phys. 2015, 11, 1882; p) I. M. Percher, I. Volotsenko, A. Frydman, B. I. Shklovskii, A. M. Goldman, Phys. Rev. B 2017, 96, 224511.
[17] U. Givan, Z. Ovadyahu, Phys. Rev. B 2012, 86, 165101.
[18] U. Strom, P. C. Taylor, Phys. Rev. B 1977, 16, 5512.
[19] U. Buchenau, M. Prager, N. Nücker N. Nücker, A. J. Dianoux, N. Ahmad, W. A. Phillips, Phys. Rev. B 1986, 34, 5665.
[20] V. K. Malinkovskiy, V. N. Novikov, P. P. Parshin, A. P. Sokolov, M. G. Zemlyanov, Europhys. Lett. 1990, 11, 43.
[21] W. Schirmacher, G. Diezemann, C. Ganter, Phys. Rev. Lett. 1998, 87, 136.
[22] a) K. Niss, B. Begen, B. Frick, J. Ollivier, A. Beraud, A. Sokolov, V. N. Novikov, C. Alba-Simionesco, Phys. Rev. Lett. 2007, 99, 055502; b) L. Hong, B. Begen, A. Kislius, C. Alba-Simionesco, V. N. Novikov, A. P. Sokolov, Phys. Rev. B 2008, 78, 134201; c) V. L. Gurevich, D. A. Parshin, H. R. Schober, Phys. Rev. B 2005, 71, 014209; d) S. Sugai, A. Onodera, Phys. Rev. Lett. 1996, 77, 4210; e) A. Monaco, A. I. Chumakov, G. Monaco, W. A. Crichton, J. Meyer, L. Gomez, D. Fioretto, J. Korecki, R. Rüffer, Phys. Rev. Lett. 2006, 97, 135501; f) L. Hong, B. Begen, A. Kislius, S. Pawlus, M. Paluch, A. P. Sokolov, Phys. Rev. Lett. 2009, 102, 145502; g) H. R. Schober, U. Buchenau, V. L. Gurevich, Phys. Rev. B 2014, 89, 014204; h) H. Shintani, H. Tanaka, Nat. Mater. 2008, 7, 870.
[23] C. A. Angell, K. L. Ngai, G. B. McKenna, P. F. McMillan, S. W. Martin, J. Appl. Phys. 2000, 88, 3113.
[24] B. Cui, R. Milks, A. Zacccone, Phys. Rev. E 2017, 95, 022603.
[25] a) E. W. Montroll, J. T. Bendler, J. Stat. Phys. 1984, 34, 129; b) R. G. Palmer, D. L. Stein, E. Abrahams, P. W. Anderson, Phys. Rev. Lett. 1984, 53, 958; c) J. S. Langer, S. Mukhopadhyay, Phys. Rev. E 2008, 77, 061505; d) J. C. Phillips, Rep. Prog. Phys. 1996, 59, 1133; e) I. M. Lifshitz, Usp. Fiz. Nauk 1964, 83, 617; f) R. Friedberg, J. M. Luttinger, Phys. Rev. B 1975, 12, 4460; g) P. Grassberger, I. Procaccia, J. Chem. Phys. 1982, 77, 6281.
[26] D. C. Johnston, Phys. Rev. B 2006, 74, 184430.
[27] a) T. A. Mary, J. S. O. Evans, T. Vogt, A. W. Sleight, Science 1996, 272, 90; b) A. K. A. Prydedag, K. D. Hammond, M. T. Dove, V. Heine, J. D. Gale, M. C. Warren, J. Phys.: Condens. Matter 1996, 8, 10973; c) J. S. O. Evans, J. Chem. Soc. Dalton Trans. 1999, 19, 3317; d) A. L. Goodwin, M. Calleja, M. J. Conterio, M. T. Dove, J. S. O. Evans, D. A. Keen, L. Peters, M. G. Tucker, Science 2008, 319, 794.