Polyamorphism of vapor-deposited amorphous selenium in response to light

Aixi Zhang, Yi Jin, Tianyi Liu, Richard B. Stephens, and Zahra Fakhraai

*Department of Chemistry, University of Pennsylvania, Philadelphia, PA, 19104; and †Department of Physics & Astronomy, University of Pennsylvania, Philadelphia, PA, 19104

Enhanced surface mobility is critical in producing stable glasses during physical vapor deposition. In amorphous selenium (a-Se) both the structure and dynamics of the surface can be altered when exposed to above-bandgap light. Here we investigate the effect of light on the properties of vapor-deposited a-Se glasses at a range of substrate temperatures and deposition rates. We demonstrate that deposition both under white light illumination and in the dark results in thermally and kinetically stable glasses. Compared to glasses deposited in the dark, stable a-Se glasses formed under white light have reduced thermal stability, as measured by lower density change, but show significantly improved kinetic stability, measured as higher onset temperature for transformation. While light induces enhanced mobility that penetrates deep into the surface, resulting in lower density during vapor deposition, it also acts to form more networked structures at the surface, which results in a state that is kinetically more stable with larger optical birefringence. We demonstrate that the structure formed during deposition with light is a state that is not accessible through liquid quenching, aging, or vapor deposition in the dark, indicating the formation of a unique amorphous solid state.

Physical vapor deposition (PVD) is broadly used to prepare amorphous thin films. Over the past decade, a variety of systems have been shown to produce stable glasses (SGs) during PVD, when the deposition temperature (T_{dep}) is held below their glass transition temperature (T_g) (1–8). SGs have improved thermal (1, 2, 6, 9) and kinetic stability (3, 4, 7, 8, 10) compared to liquid quenched (LO) glasses, resembling glasses aged for hundreds or millions of years. Most SGs are also shown to have anisotropic packing that depends on the deposition conditions and molecular structures (10–13).

It is understood that SG formation is due to enhanced surface mobility (5, 8, 12, 14–17). When T_{dep} < T_g, at slow deposition rates (~0.2 nm/s for most organic glasses), the surface region has sufficient mobility (18) to reach more energetically favored states before being buried into dynamically arrested states. The stability of a PVD glass thus strongly depends on T_{dep} (3, 4, 6, 7, 19) and the deposition rate (2, 8, 20). Surface-mediated equilibration (SME) also influences the structure and birefringence of PVD glasses, which are inherited from the equilibrium states at the glass surface (21, 22) and the layers directly below the free surface (12, 16).

Inorganic glasses can also produce stable and/or anisotropic glasses upon PVD (7, 8, 23). However, surface mobility in these systems is less pronounced (8, 14, 24); thus, lower deposition rates are required to achieve a similar extent of stability as organic SGs (8). In all SG systems, besides T_{dep} and deposition rate, few factors are available to control the degree of enhanced surface mobility and its penetration depth (5).

a-Se is an exception, where above-bandgap light can strongly affect its surface structure and dynamics. a-Se is of interest because it is important in applications such as digital X-ray detection (25) due to its outstanding X-ray cross section. Extensive studies on a-Se structure (26–28) show that a-Se is primarily made of disordered Se_n helical chains with some coordination defects and vast interchain nonbonding interactions. Viscoelasticity measurements indicate that the temperature dependence of creep compliance in a-Se close to its T_g is similar to polystyrene with M_w ~ 12,000 close to its respective T_g. Thus, the chain length of a-Se is estimated to be ~230 atoms per chain around T_g (29). There are also studies showing that a-Se has more threefold and fourfold coordination sites at its free surface (27) than in the bulk. With its low bandgap, ~2 eV (25), a-Se’s structure can be altered by white light (30, 31). Electrons excited by above-bandgap irradiation (31) increase the system’s coordination number (30, 32) and facilitate bond rearrangements (31) and valence alternations. As a result, a-Se chains exhibit extra fluidity under illumination. The penetration depth of these effects is estimated to be ~50 to 1,000 nm below the surface, depending on light conditions (SI Appendix, Fig. S9). The free drift time of light-generated electrons/holes is estimated to be ~10^{-6} to 10^{-4} s in the temperature range of interest in this study (33).

Here we study how above-bandgap light affects the SME process and, in turn, the thermal and kinetic stability of a-Se SGs. This is a well-controlled study of the influence of light during PVD on the structure and stability of a-Se. We demonstrate that when lit, highly networked and kinetically stable SGs are produced that cannot be otherwise made through deposition in the dark or physical aging of any length of time, representing a region

Significance

Amorphous selenium (a-Se) has a complicated molecular structure with overcoordinated defects and dangling bonds. This light-sensitive structure can undergo significant changes including bond breakage, reconnection, and defect formation upon illumination with above-bandgap light. Light sensitivity makes a-Se a unique system to study the role of surface structure and dynamics on stable glass formation during physical vapor deposition. We show that illumination during deposition produces less dense, more anisotropic, and kinetically more stable glasses, due to better network formation at the surface. This is a demonstration that light can be used to manipulate surface properties to generate distinct polyamorphic solid states that are not accessible through liquid quenching or aging.

Author contributions: A.Z., R.B.S., and Z.F. designed research; A.Z., Y.J., and T.L. performed research; A.Z., R.B.S., and Z.F. analyzed data; and A.Z. and Z.F. wrote the paper.

The authors declare no competing interest.

This article is a PNAS Direct Submission.

Published under the PNAS license.

1To whom correspondence may be addressed. Email: fakhraai@sas.upenn.edu.

This article contains supporting information online at https://www.pnas.org/lookup/suppl/doi:10.1073/pnas.2009852117/-/DCSupplemental.

First published September 15, 2020.
in the energy landscape that was previously inaccessible. This is a unique demonstration of polyamorphism in an atomically simple structure, achieved through manipulation of the surface structure and dynamics using light.

Results and Discussion

The Structure and Stability of Vapor-Deposited \(a\)-Se Films. \(a\)-Se films are deposited in lit and dark conditions at a range of \(T_{\text{dep}}\) and deposition rates, as detailed in Materials and Methods and SI Appendix. The thermal and kinetic stability of as-deposited films are evaluated through measurements of film thickness and index of refraction, using spectroscopic ellipsometry (SE). As shown in Fig. 1A (more data in SI Appendix, Fig. S7), the relative density change (\(\Delta \rho\)) is defined as the difference between the density of as-deposited SG and LQ glasses at 273 K. The fictive temperature (\(T_f\)) is also measured as the temperature where the SG expansion line intersects the extrapolated supercooled liquid (SCL) line. Lower \(T_f\) values and positive \(\Delta \rho\) are indicative of higher thermal stability of as-deposited films. The kinetic stability is evaluated through measurements of the onset temperature of transformation (\(T_{\text{onset}}\)), as shown in Fig. 1A.

In the accessible range of \(T_{\text{dep}}\), all as-deposited films, both in dark and lit conditions, show positive \(\Delta \rho\), indicating that thermally SGs were formed (Fig. 2A for 0.2 nm/s deposition rate, \(T_f\) plots and data at 2 nm/s deposition rate are shown in SI Appendix, Figs. S5B and S6). Fig. 2A shows that as the \(T_{\text{dep}}\) is decreased, \(\Delta \rho\) is increased along the extrapolated SCL line (dashed line in Fig. 2A), reaching a maximum around \(T_{\text{dep}} \sim 0.86 T_g\). This maximum in \(\Delta \rho\) is a result of competition between the rate of SME, which decreases with decreasing temperature, and the depth of the equilibrium state, which increases with decreasing temperature. This behavior is consistent with SG formation in other organic (1, 6, 19) and inorganic glasses (7). It is an indirect indication that the surface mobility in both lit and dark conditions is enhanced compared to the bulk dynamics.

However, the measured \(\Delta \rho\) of \(a\)-Se SGs, in both lit and dark conditions, is lower than typically observed in molecular SGs. In molecular SGs, within the \(T_{\text{dep}}\) range of \(0.9 T_g < T_{\text{dep}} < T_g\), near-equilibrium states are obtained with densities close to that

![Diagram](image-url)

Fig. 1. (A) Normalized thickness vs. temperature for an \(-2 \mu\text{m}-\text{thick} \(a\)-Se film deposited in the dark at \(T_{\text{dep}} = 262 \pm 1 \text{ K (0.86}(T_g)\) with \(0.1 \pm 0.02 \text{ nm/s deposition rate. The as-deposited film was heated from 253 to 323 K and held isothermally until film thickness reached a plateau, then cooled to 253 K, transforming into an LQ glass. The heating/cooling rates were 10 K/min. Black, red, blue, and purple dashed lines are linear fits to the SCL, LQ, SG, and transforming regions, respectively. \(T_g = 304 \pm 1 \text{ K, } T_f = 288 \pm 1 \text{ K, } T_{\text{onset}} = 319 \pm 2 \text{ K, and } \Delta \rho = 0.5 \text{%. (B) In-plane (}n_{xy}\text{; dark blue) and out-of-plane (}n_z\text{; light blue) refractive indices vs. temperature for the same film. Arrows show the directions of heating and cooling. Unfilled symbols represent the regime with transformation growth fronts, which results in large fitting error (details in SI Appendix).}

![Diagram](image-url)

Fig. 2. (A) Relative density, \(\Delta \rho\), of \(a\)-Se films deposited in dark (blue) and lit (red) conditions vs. \(T_{\text{dep}}\). The black dashed line is the extrapolated equilibrium values. (B) In-plane (\(n_{xy}\)) and out-of-plane (\(n_z\)) change in the index of refraction of lit (red) and dark (blue) SG films vs. \(T_{\text{dep}}\). Lines are guides for the eye. Error bars are based on multiple independent experiments.
of the extrapolated SCL \( \Delta_{\text{SCL}} \sim 1.2 \) to 1.8\% (3, 6). In a-Se, even when \( T_{\text{dep}} \) is only slightly below \( T_g \), density increase remains noticeably smaller (\( \Delta_{\text{SCL}} \sim 0.5\% \)) and \( T_g \) stays well above the corresponding SCL values (Fig. 24 and SI Appendix, Fig. S5B), indicating that other kinetic barriers hinder the system’s ability to achieve near-equilibrium states. To understand this apparent kinetic trapping, we note that the molecular weight of the incoming Se oligomers [predominately \( \text{Se}_5 \) to \( \text{Se}_{12} \) (34)] is similar to that of the organic molecules from which SGs can be made; thus, we may expect them to have similar mobility. However, after the oligomers have combined to make larger chains (equilibrium chain length \( \sim 200 \) atoms per chain) within \( 10^{-6} \) to \( 10^{-4} \) s (33), the barrier for relaxation is increased. The interaction between the oligomers can potentially slow the surface mobility and reduce the depth of the mobile region, limiting the packing efficiency during SME, analogous to what has been observed in molecular SGs with strong intramolecular interactions (5, 16, 35).

Indirect evidence for the polymeric nature of a-Se on its packing is the emergence of optical birefringence, despite a-Se’s atomic nature. All as-deposited films, both lit and in the dark, show negative optical birefringence (Fig. 2B) with larger values of the in-plane index of refraction \( (n_{xy}) \) compared to the out-of-plane index \( (n_z) \). The optical birefringence disappears upon heating above \( T_g \) and subsequent cooling to the \( \text{LQ} \) state. The negative birefringence \( (n_{xy} > n_z) \) is an indirect indication that chains are primarily aligned horizontally and the packing is more frustrated normal to the surface. It is notable that \( n_z \) for SG is smaller than \( n_z \) for \( \text{LO} \) glass, implying the average atomic distance normal to the film’s plane is even larger than the \( \text{LQ} \) state. These effects become stronger at lower \( T_{\text{dep}} \) and under lit conditions, explaining their lower density at low \( T_{\text{dep}} \). This is likely due to the fact that during lit deposition more networks are formed at the free surface, further prohibiting the SME process. We note that the signatures of this anisotropic packing are not resolvable in the Grazing Incidence Wide Angle X-ray Scattering (GIWAXS) measurements performed in house (Xenocs Xeuss 2.0; more details in SI Appendix). However, the measured ellipsometry values are systematically larger than the \( \text{SE} \) resolution limit (typically \( \Delta n \sim 0.005 \)). Optical birefringence is also observed in molecular glasses. The effect has been attributed to either molecular orientation (36, 37), which is analogous to the in-plane orientation of polymeric chains in a-Se, or layering, which typically results in a distinct layering peak in GIWAXS (22, 37), but this peak is not observed in our GIWAXS experiments (SI Appendix, Fig. S11).

**Extraordinary Kinetic Stability of Films Deposited under Light.** Despite their thermal stability measured as lower \( \Delta \rho \) (Fig. 2A), lit samples show extraordinary kinetic stability compared to dark samples. For example, a film deposited at 0.8678 cm\(^{-5}\) and 0.2 nm/s and heated at 10 K/min has an onset of transformation temperature of \( T_{\text{onset}} = 328 \pm 2 \) K under lit conditions (SI Appendix, Fig. S7), which is 9 K higher than the \( T_{\text{onset}} = 319 \pm 2 \) K for dark deposition (Fig. 1A) and 24 K higher than \( T_g \). This same film has a density increase of \( \Delta \rho = 0.34 \pm 0.08 \)% deposited lit as opposed to \( \Delta \rho = 0.55 \pm 0.08 \)% when deposited in the dark, indicating lower thermal stability. This observation is in contrast with most organic SGs whose thermal and kinetic stabilities are generally positively correlated (3, 9). To understand the origin of this phenomenon, we focus on the unique surface structure of a-Se and how it is affected by light.

Similar to other chalcogenides, a-Se exhibits photoinduced structural rearrangement. Upon illumination with above-bandgap light, a-Se undergoes a volume increase (38, 39) and anisotropic crystallization (40). An increase in the coordination number is also observed with the emergence of more threefold and fourfold coordinated pairs (30, 41). Simulations show more bond breaking with excited electrons and structural topological changes (32). Given a-Se’s high absorption coefficient (\( \sim 10^3 \text{cm}^{-1} \)) above bandgap, these effects penetrate somewhere between 50 and 1,000 nm into the film’s surface (42) (details in SI Appendix, Fig. S9) and are thus not pronounced in bulk a-Se glasses. However, the increase in volume and coordination number, as well as increased surface mobility can significantly affect the properties of the PVD glass through SME. We note that we do not observe any evidence of surface crystallization in our GIWAXS and atomic force microscopy (AFM) measurements (SI Appendix, Figs. S10 and S11).

The effects of light on the surface mobility and structure are indeed indirectly observed in our study. Lower \( \Delta \rho \) and \( n_z \) of lit SGs (Fig. 2) indicate larger volume at the surface region, which templates the SG structure as the atoms are dynamically arrested upon further deposition. A higher fraction of highly coordinated networked structure can also explain the improved kinetic stability of lit samples. Breaking the covalently bonded networked likely requires heating to a higher temperature than transforming a molecular SG with van der Waals interactions.

We note that states obtained during lit deposition cannot be obtained by physical aging process of \( \text{LO} \) glass, either in dark or lit conditions. While aging can potentially increase the network density (43), this process is reasonably similar to the degree of network formed during PVD in dark condition. The density of networks in lit condition is typically only affected at the surface region. As such, the propagation of this higher network density throughout the film is only possible by PVD while lit. This templating of the structure through the free surface is analogous to the birefringence in molecular glasses that are templated by the orientation of molecules at the surface, except...
that here this is achieved by actively altering the free surface state using light.

The Dependence of the Stability on Deposition Rate. The complicated structure of a-Se SGs also affects the dependence of their thermal and kinetic stability on the deposition rate in nontrivial ways. Fig. 3 shows Δρ and T_onset measurements of films deposited both in lit and dark conditions vs. deposition rate. Focusing first on samples deposited in the dark, in the accessible deposition rate range (0.02 to 4 nm/s), Δρ slightly increases (Fig. 3A), and T_onset decreases (SI Appendix, Fig. S13) with decreasing deposition rate. This trend is expected given the kinetic nature of the SME process. However, decreasing the deposition rate by 2 orders of magnitude from 2 to 0.02 nm/s only elevates Δρ by ~0.3% and lowers T_onset by ~8 K. More surprisingly, T_onset is more or less unaffected by the deposition rate in this range. This is in contrast with molecular SGs where the deposition rate has a more significant impact on both the thermal and kinetic stability (2) of SGs. Similarly, limited existing data shows significant increase of T_onset in metallic SGs when the deposition rate is decreased (8).

The limits in density gain upon reducing the deposition rate implies that there are significant kinetic barriers for a-Se toward further equilibration during PVD, presumably because of packing frustrations and network formation. The limitation on approaching equilibration is also consistent with nearly constant T_onset (Fig. 3B). Indeed we expect a larger drop of T_onset upon further increase of deposition rate, which appears to decrease slightly at 4 nm/s deposition. Our current setup does not allow faster depositions to probe this hypothesis.

At low deposition rates, Δρ is significantly lower for lit samples than films deposited in the dark with a surprisingly sharp improvement at a deposition rate between 0.4 and 1 nm/s, above which lit and dark depositions yield films with similar Δρ (Fig. 3A). Interestingly, the kinetic stability remains enhanced in lit conditions even at these rates, indicating that the light-induced network structure can still be created at higher deposition rates. Given the network formation only requires a very short time compared to the timescale of our accessible deposition rate and the insensitivity of T_onset to the deposition rate, we do not expect the effective molecular weight of lit samples to be very different at various deposition rates, except perhaps at the highest rate here where T_onset starts decreasing for both dark and lit samples, indicating lower kinetic stability. As such, it is not clear how the increased density is achieved despite the kinetic barriers introduced by network formation.

One possible explanation for this trend is that during deposition, light induces mobility in the bulk of the SG film, resulting in partial transformation. Previous studies have demonstrated photoinduced bond extension and volume expansion of LQ a-Se under irradiation (38, 39). It has also been previously demonstrated in molecular SGs that light-induced change in the molecular conformation can lead to SG transformation (44). Depositions at rates slower than 0.4 nm/s take several hours for a 2-µm-thick film, while depositions faster than 1 nm/s are completed within ~30 min. During longer depositions, a-Se films can potentially transform partially, resulting in increased thickness, which is measured as an effectively lower Δρ. Fig. 4A shows that indeed when a sample deposited in the dark is exposed to light, it partially transforms. However, this transformation is limited. A 0.3% volume increase is observed after 3 h of illumination, indicating that the top ~1,100±200 nm of the film has been transformed. This is consistent with the estimated penetration depth of light into the film’s surface (50 to 1,000 nm; SI Appendix, Fig. S9) (42). However, as detailed below, this explanation is not consistent with other aspects of this phenomenon.

When the kinetic stability of a lit film is compared with a sample deposited in the dark and held under white light for the same duration of 3 h, the two samples have similar densities but starkly different kinetic stability. The film illuminated after deposition is kinetically less stable than the lit sample and even the film deposited in the dark (Fig. 3B). Illumination after deposition reduces the kinetic stability of the film. However, illumination during deposition generates a uniquely networked structure with higher kinetic stability. Despite its larger specific volume, the structure is locked in a network that can only be transformed upon heating well above T_g. To further demonstrate this distinct structure, films were deposited and were illuminated during either the first half of the deposition or the second half of the deposition (SI Appendix, Fig. S12). Both films show two distinct onset temperatures, one at the same T_onset as the lit sample and one close to or below the T_onset of the dark film. The dark half which is deposited prior to the lit half indeed shows a lower T_onset, but in both films the portion of the film deposited lit has the same T_onset within error, regardless of whether it is deposited as the first layer or the second.

Polyamorphism of a-Se. Given the data shown in Fig. 3B and SI Appendix, Fig. S12, we can frame the process of lit deposition
The modification of the near-surface region of a-Se, which results in simultaneous changes in the network structure and the density of the PVD glass. The distinct structure obtained under light is inaccessible through liquid-quenching and can only be transformed into the low-networked state upon heating above $T_g$, indicating significant barrier between these two states. Illumination after deposition does not enable access to this part of the energy landscape and results in further transformation (Fig. 4B). It is worth noting that a-Se shares some common features of other polyamorphic systems, such as distinct structural change and directional bonding (50, 51), which typically signify polyamorphism.

**Concluding Remarks**

In this study, we have prepared a-Se SGs through PVD both in dark and under white light illumination (lit) conditions. We demonstrated that when above-bandgap light is applied during vapor deposition, the kinetic stability of a-Se SGs is significantly improved despite their larger relative specific volume (lower thermal stability) compared to the corresponding SGs deposited in the dark. However, when films deposited in the dark are exposed to light after deposition, they show both lower density and reduced kinetic stability. We attribute these results to the changes in structure and dynamics of a-Se surface when illuminated by above-bandgap light. With light, more networked structures are produced on the constantly revitalizing surface. The resulting high-molecular-weight structure on one hand frustrates the packing and on the other hand, requires higher temperature to break. We show there is evidence the packing produced under these conditions is an amorphous state that is not accessible through aging or vapor deposition in the dark and, as such, is a distinct polyamorphic solid state. The corresponding state of these structures can likely be identified and studied in a-Se thin films.

A key aspect that enables access to these unique states is the increased thickness of the surface region (estimated to be 50 to 1,000 nm) while illuminated, as well as the distinct surface structure due to production of free electrons. This is an application of light to manipulate the SME process, to produce distinct SG structures. In addition to $T_{dep}$ and deposition rate, for light-sensitive materials, illumination can affect the surface dynamics, length scale, and the gradients of mobility, as well as the structure at the free surface, producing distinct packings. In a-Se, based on the light penetration depth, the first 50 nm of a-Se films during lit deposition likely have much faster dynamics than the other 1,000-nm region of the surface. Future work should focus on controlling the light intensity and wavelength (which can control the absorption depth and mobility gradients), as well as film thickness, to understand exactly the role of light. Designing corresponding organic molecules with light-sensitive functional groups will be beneficial as well in terms of expanding these studies to other systems and exploring the detailed structure of as-deposited SGs. We expect the implementation of other experimental techniques such as Raman and IR spectrum to be helpful to resolve these fine structures.

**Materials and Methods**

Selenium lumps (purity 99.999%) were purchased from Goodfellow Co. and used directly. a-Se films of approximately 2,000 ± 100 nm thickness (or 3,000 ± 100 nm thickness for the deposition rate of 4 mm/s) were deposited on Si substrates with a native oxide layer (Virginia Semiconductor Inc.) in high-vacuum chamber with a base pressure of ~1 × 10⁻⁷ torr. SE (Woollam M-2000 V) was used to measure film thickness, index of refraction, and optical birefringence (6, 11). Ellipsometry was also used to monitor the in situ changes in film thickness during temperature ramps to determine the degree of thermal and kinetic stability. Transformation experiments from 253 to 323 K (or 333 K when measuring $T_{mel}$) were performed in a custom-made environment-control stage with two 780-nm long-pass filters in the light path. Heating and cooling rates were maintained to be 10 K/min. Deposition was performed on a range of deposition temperatures ($T_{dep}$ ranging from 262 K (0.86$T_g$) to 291 K (0.96$T_g$); SI Appendix, Fig. S1).
and deposition rates between 0.02 and 4 nm/s. In the process of deposition, a white LED light illumination (emission energy 1.9 to 2.9 eV) was used to study the effect of light during deposition. Light intensity at the substrate position was determined to be 1.0 ± 0.5 mW/cm². More detailed description of sample preparation, ellipsometer fitting, and transformation process can be found in SI Appendix.

Data Availability. Experimental data are available on Open Science Framework (https://doi.org/10.17605/OSF.IO/AQEM3).

ACKNOWLEDGMENTS. This work was funded by NSF-Materials Research Science and Engineering Centers (MRSEC) DMR-1720530. The authors acknowledge the use of the Dual Source and Environmental X-ray Scattering facility operated by the Laboratory for Research on the Structure of Matter at the University of Pennsylvania (NSF-MRSEC DMR-1720530) and help from its director. Prof. Paul Heiney. The equipment purchase was made possible by an NSF Major Research Instrumentation Program (MRI) grant (17-25969), an Army Research Office (ARO) Defense University Research Instrumentation Program (DURIP) grant (W911NF-17-1-0282), and the University of Pennsylvania.