

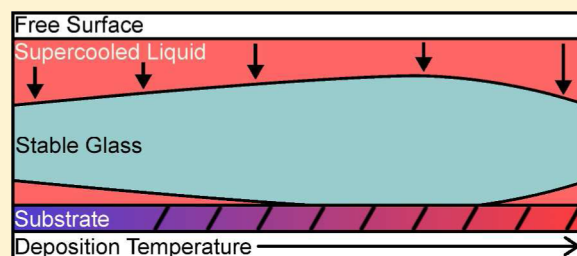
Influence of Substrate Temperature on the Transformation Front Velocities That Determine Thermal Stability of Vapor-Deposited Glasses

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S Supporting Information

ABSTRACT: Stable organic glasses prepared by physical vapor deposition transform into the supercooled liquid via propagating fronts of molecular mobility, a mechanism different from that exhibited by glasses prepared by cooling the liquid. Here we show that spectroscopic ellipsometry can directly observe this front-based mechanism in real time and explore how the velocity of the front depends upon the substrate temperature during deposition. For the model glass former indomethacin, we detect surface-initiated mobility fronts in glasses formed at substrate temperatures between $0.68T_g$ and $0.94T_g$. At each of two annealing temperatures, the substrate temperature during deposition can change the transformation front velocity by a factor of 6, and these changes are imperfectly correlated with the density of the glass. We also observe substrate-initiated fronts at some substrate temperatures. By connecting with theoretical work, we are able to infer the relative mobilities of stable glasses prepared at different substrate temperatures. An understanding of the transformation behavior of vapor-deposited glasses may be relevant for extending the lifetime of organic semiconducting devices.



INTRODUCTION

Glasses or amorphous solids are a class of materials that intersect with many areas of technical and scientific importance. They are used in applications such as optical fibers and organic light-emitting diodes, where their compositional flexibility, macroscopic homogeneity, and ease of processing make them the material of choice. Glasses are out of equilibrium, providing both challenges and opportunities for their use as materials. Glasses prepared by cooling a liquid are generally only marginally stable, and their properties can slowly evolve with time in a process called physical aging.^{1,2} This can cause problems in applications where tight performance tolerances must be maintained. On the other hand, the nonequilibrium nature of glasses means that many different glasses (with different properties) can be formed with the same chemical composition. If the process for producing a wide range of glasses can be adequately controlled, this provides a dimension for materials design that is absent for equilibrium materials.

Work in the last seven years has shown that very unusual glasses of low molecular weight organic molecules can be prepared by physical vapor deposition.³ When the substrate temperature is held somewhat below T_g (the glass transition temperature), “stable glasses” with unprecedented kinetic stability can be formed.^{4–12} In many respects, stable glasses have the properties expected for liquid-cooled glasses that have aged toward equilibrium for thousands of years,¹³ even reaching the density of the metastable equilibrium supercooled liquid state far below the conventional T_g .⁶ These materials also resist transformation when heated, with the onset of the glass

transition elevated by as much as 35 K over ordinary liquid-cooled glasses.¹⁴ Structural characterization has shown evidence of anisotropic molecular orientation and packing that depends upon the substrate temperature during deposition ($T_{\text{substrate}}$).^{5,6,15–18} Given the importance of vapor-deposited glasses in organic electronics,^{16,17,19,20} it is important to understand how substrate temperature influences kinetic stability. For example, one could ask if kinetic stability is controlled by the glass density. Such a connection would facilitate optimization of vapor-deposited glasses for applications.

When a stable organic glass is heated above T_g , it eventually transforms into the supercooled liquid by a mechanism that has not been observed for liquid-cooled glasses. A propagating front of mobility moves into the glass from the free surface at a constant velocity, leaving behind the equilibrium supercooled liquid; this process has also been described as a growth front or a propagating transformation front.^{11,21–29} Here we use “mobility front” to focus on the key difference between the stable glass and the supercooled liquid. For the system studied here, indomethacin ($T_g = 309$ K), this front can propagate up to $1 \mu\text{m}$ into the bulk of the material²⁴ at temperatures from T_g up to $T_g + 75$ K ($T_m - 50$ K),²⁸ in order to facilitate motion of molecules trapped in the glassy state.³⁰ This process is highly heterogeneous; while the transformation occurs, part of the

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sample is stable glass and part is supercooled liquid.²⁷ In contrast, a homogeneous model reasonably describes the transformation of a liquid-cooled glass to the supercooled liquid; during the transformation, the entire sample has characteristics intermediate between the initial and final states.^{2,31}

In this paper, we use spectroscopic ellipsometry to perform the first real-time measurements of mobility front propagation in a glass. We establish quantitative agreement with previous measurements that used secondary-ion mass spectrometry (SIMS), the only other technique that has been shown to directly observe mobility fronts. We build upon a recently reported method that allows simultaneous characterization of glasses prepared at many substrate temperatures.⁶ We investigate how the velocity of the mobility front depends upon $T_{\text{substrate}}$, following the common thread of several recent experiments which show that $T_{\text{substrate}}$ affects the properties of stable glasses.^{4–6,11,32} We compare the mobility front velocity with the glass density to examine whether they are correlated, and our results are compared to recent theoretical work.²⁶

We find that glasses of indomethacin vapor-deposited at substrate temperatures between 210 and 290 K ($0.68T_g$ and $0.94T_g$) show propagating mobility fronts initiated at the free surface, and at some substrate temperatures, the front can propagate from the substrate as well. We find that the mobility front velocity depends significantly on the temperature of the substrate during the deposition but does not demonstrate a one-to-one correspondence with the glass density. As discussed below, the mobility front velocity can be interpreted as providing information about the molecular mobility of the stable glasses.

EXPERIMENTAL METHODS

Glasses of indomethacin (>99% purity, Sigma-Aldrich), $T_g = 309$ K, were prepared by physical vapor deposition at a deposition rate of 0.20 ± 0.02 nm/sec in an ultrahigh vacuum chamber. The silicon substrate was either held at a single temperature during deposition or at a range of temperatures using a temperature-gradient stage.⁶ The substrate temperature of temperature-gradient samples was verified by comparing to the known optical constants of vapor-deposited indomethacin and is consistent with previous results to ± 2 K. After deposition, the samples were annealed isothermally at either 320 or 325 K outside of the vacuum chamber; dry nitrogen was blown over the samples during annealing on our ex-situ temperature control stage to exclude water vapor. During annealing, the transformation of the as-deposited glass into the supercooled liquid was monitored using spectroscopic ellipsometry (M-2000 V, J.A. Woollam Company). Samples were measured at 3 incident angles; 50° , 60° , and 70° from the normal of the substrate. Isothermal samples were measured every 56 s while particular substrate temperatures on a temperature-gradient sample were measured every 600 s. The spot size of the ellipsometer (0.6 mm) is small compared to the temperature gradient sample (32 mm). The effective temperature gradient (~ 1.5 K) across the ellipsometer spot is negligible, and so we are able to independently measure different locations, and thus different glasses, on the same temperature-gradient sample. The temperature-gradient samples allow precise comparisons between glasses deposited at different temperatures since all the glasses are prepared and annealed under otherwise identical conditions. We note that

one of the $T_{\text{anneal}} = 325$ K samples is sample E from ref 6. The data has been refit to extract the mobility front velocity.

In order to determine the position of the mobility front with time, we interpret the ellipsometry data using an optical model (the “front model”) that explicitly includes an interface between the glass and the liquid. Figure 1 schematically shows the

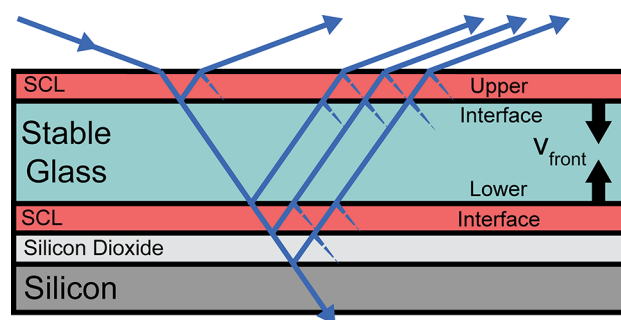


Figure 1. Schematic of the experimental system. When a stable glass is heated above T_g , the equilibrium supercooled liquid (SCL) propagates from the free surface at a constant velocity; for glasses deposited at some substrate temperatures, the supercooled liquid also propagates from the substrate. As time progresses, the positions of the interfaces evolve, but the optical properties of the supercooled liquid and stable glass remain unchanged. The rays show the reflection of a beam of light with the different layers in the sample. For simplicity, only the first reflection of light traveling into the sample is shown. The polarization of the reflected light is sensitive to the thicknesses of the layers.

features of the model. The glass–liquid interfaces change the polarization of light reflected by the sample in a manner detectable by ellipsometry because the supercooled liquid and stable glass of a material, at the same temperature, have different indices of refraction. When fitting data using this model, the optical constants of the supercooled liquid (the top and bottom layer) were fixed to values obtained at the annealing temperature after the transformation was complete; a homogeneous model was used for this fit. The optical constants of the as-deposited glass (the central layer) were fixed by the first measurement at the annealing temperature. This model independently determines the positions of each interface at each time step. For glasses which showed only a single mobility front, the thickness of the stable glass layer gives the position of the upper glass–liquid interface. For glasses with two fronts, the thickness of the substrate-initiated supercooled liquid layer plus the thickness of the stable layer gives the upper interface position. Data from wavelengths of 500–1000 nm was fit using an anisotropic Cauchy model to represent each indomethacin layer.³³ (See the Supporting Information for an example of how the polarization of light at $\lambda = 1000$ nm changes with time during the transformation process.) For many samples, we also fit the data by allowing the optical constants of the stable glass to float; this changed the mobility front velocity by less than 1%. The front model allows for the detection of a substrate-initiated transformation front, but at many substrate temperatures only surface-initiated fronts were observed. Occasionally, the model detected a thin layer of supercooled liquid near the substrate. If this layer did not thicken with time it was presumed to be the result of overparameterization. In such cases, the thickness of this layer was set to zero for subsequent fits.

To test whether the transformation of a stable glass could be described as a spatially homogeneous process,³¹ we also fit samples with an optically homogeneous model. This model fits the entire organic film with a uniform index of refraction that is permitted to change during the annealing process. For films deposited at substrate temperatures between 210 and 290 K, the homogeneous model failed to accurately fit the data as measured by the root-mean-squared error (MSE),³⁴ except once the transformation was complete. The MSE is a goodness of fit parameter that computes the root-mean-square difference between the observed values of the ellipsometric observables N , C , and S at each wavelength and the values obtained from the best fit to the model; N , C , and S can be transformed into the more conventional Ψ and Δ . Small MSEs indicate that the model is better able to represent the behavior of the real sample. As a control experiment, we observed that liquid-cooled glasses aged for up to 3 months at 293 K were adequately characterized by the homogeneous model during isothermal transformation into the supercooled liquid.

RESULTS

Figure 2 compares the transformation of two vapor-deposited indomethacin glasses that were prepared at different substrate temperatures ($T_{\text{substrate}}$) but annealed at the same temperature. We performed spectroscopic ellipsometry measurements during annealing at 325 K ($T_g + 16$ K) and fit the data to two models as described in Experimental Methods. With the use of the front model that allows the existence of sharp interfaces, Figure 2a shows the position of the glass–liquid interface during the transformation. The interface position moves smoothly into the film from the free surface at a constant velocity; the constant velocity behavior is not imposed by the fitting as the data from each time is fitted independently. This behavior is expected on the basis of previous SIMS measurements on stable glasses of IMC.²¹ As discussed below, it is consistent with a kinetic facilitation mechanism. Figure 2c shows an analogous process but for a sample deposited at a lower substrate temperature. The lower $T_{\text{substrate}}$ results in two important differences in comparison to the glass shown in Figure 2a: (1) there is a mobility front which originates from the substrate interface in addition to the front initiated at the free surface and (2) both fronts propagate much more quickly than the front in Figure 2a. We tested an alternate interpretation of these two experiments by fitting the data with a homogeneous model. Figure 2 (panels b and d) compares the MSEs for these approaches and shows that the homogeneous description of the transformation process is less satisfactory. In combination with the good qualitative and quantitative agreement with the SIMS results (see below),^{22,23} we take this to be a strong confirmation that the mobility front model accurately describes the transformation process of these stable glasses.

To examine the role of substrate temperature on the mobility front velocity, in Figure 3 we show the motion of the upper glass–liquid interface for glasses prepared at many substrate temperatures. Because all of the materials we study here show mobility fronts that originate from the free surface, this provides a fair way to compare the stability of materials with different preparations. For the least stable glass, prepared at $T_{\text{substrate}} = 213$ K, the interface propagates through the entire film in 1300 s, so that only 2 measurements can be made before the transformation is complete. In comparison, it takes nearly 10000 s for the interface in the glass deposited at $T_{\text{substrate}} = 272$

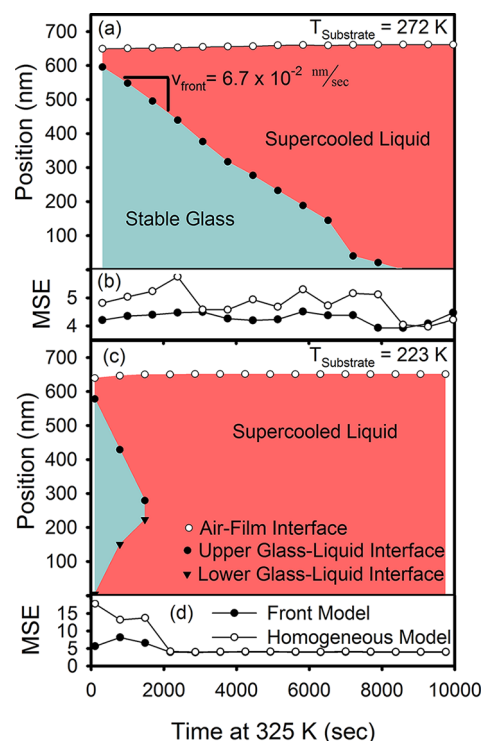


Figure 2. Time evolution of two stable glasses isothermally annealed at 325 K. (a) A glass of indomethacin vapor deposited at 272 K. The position of the glass–liquid interface moves into the film at a constant velocity. Symbols show the results of ellipsometric measurements. Filled sections of the plot show the cross section of the sample with time; in this case, the supercooled liquid originates only from the free surface. (b) The MSE for two types of models for the data in panel a. Until the transformation is complete, the front model is systematically better than the homogeneous model. (c) A glass of indomethacin deposited at 223 K. A front of supercooled liquid is observed, propagating from both the free surface and the substrate interfaces. (d) The MSE for two types of models employed to fit the data in (c). Until the transformation is complete, the front model describes the data significantly better than the homogeneous model.

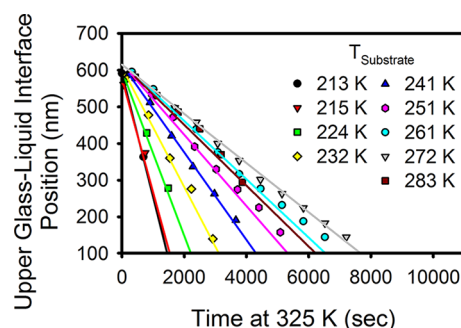


Figure 3. Evolution of the position of the upper glass–liquid interface during annealing at 325 K, for nine stable glasses from one temperature-gradient sample. Glasses deposited near 272 K transform into the supercooled liquid more slowly and thus exhibit higher thermal stability.

K to travel a similar distance. Figure 3 strongly resembles previous work which described the progress toward transformation using reversible heat capacity measurements.³⁵ Here, we have the advantage of being able to directly observe the glass–liquid interface instead of inferring its existence. We note that all the glasses shown in Figure 3 are extremely stable with

respect to a liquid-cooled glass, which would require on the order of $\tau_\alpha = 1$ s to transform into the supercooled liquid at this annealing temperature.³⁶

Figure 4 shows that the mobility front velocity of a stable glass does not depend on sample thickness. Two films were

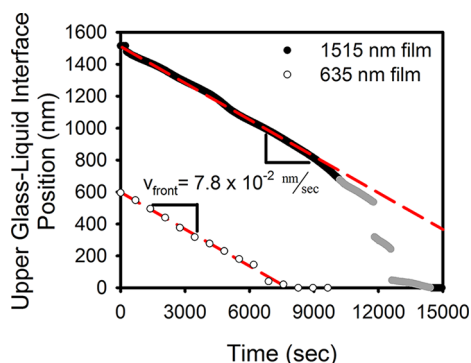


Figure 4. Evolution of the position of the upper glass–liquid interface during annealing at 325 K for 1515 and 635 nm indomethacin glasses. Both samples were deposited at $T_{\text{substrate}} = 265$ K. The two films show mobility fronts with the same velocity. The thicker film’s glassy fraction goes to zero quickly near 12000 s because of a competing bulk process.²⁴ The dashed red lines show the interface position as a function of time for the two films and is only vertically shifted between the two data sets. Gray points have elevated MSEs and provide only a qualitative indication of the sample’s composition.

separately prepared at the same substrate temperature and annealed at 325 K. The velocity of the glass–liquid interface is the same in both materials, but the thicker film takes longer to transform because the front has a greater distance to travel in order to complete the transformation process. This result is expected from previous work²⁴ and serves as an important check on the ellipsometric determination of the mobility front velocity. Figures 3 and 4 indicate that the mobility front velocity is useful for comparing glass stability across materials with different preparations and sample volumes.

Figure 5 shows the velocity of mobility fronts for indomethacin glasses prepared over a large range of substrate temperatures, observed during annealing at two different temperatures ($T_g + 11$ K and $T_g + 16$ K). At both annealing temperatures, the velocity of the surface-initiated fronts (solid points) is a minimum for glasses deposited at substrate temperatures near 275 K (about $0.88 T_g$). Below that substrate temperature, v_{front} monotonically increases, becoming a factor of 6 larger at $T_{\text{substrate}} = 210$ K. Larger values of v_{front} are also observed for substrate temperatures above 275 K. These measurements could not be extended to substrate temperatures nearer to T_g as the difference in the index of refraction between the supercooled liquid and the as-deposited glass³³ is not sufficient to be able to resolve the thicknesses of the individual layers. The data obtained here by ellipsometry is in good agreement with that previously reported based upon secondary-ion mass spectrometry measurements on isotopically labeled samples (red \star).^{22,23} The yellow \star shows data for the 1515 nm film in Figure 4. This sample was deposited onto a substrate with only a single temperature, and this result serves as a check that all the glasses on a temperature-gradient sample evolve independently. For samples deposited onto substrates outside the range 243–285 K, the ellipsometry measurements also detected mobility fronts initiated at the interface with the substrate (open points). While the presence of these substrate-

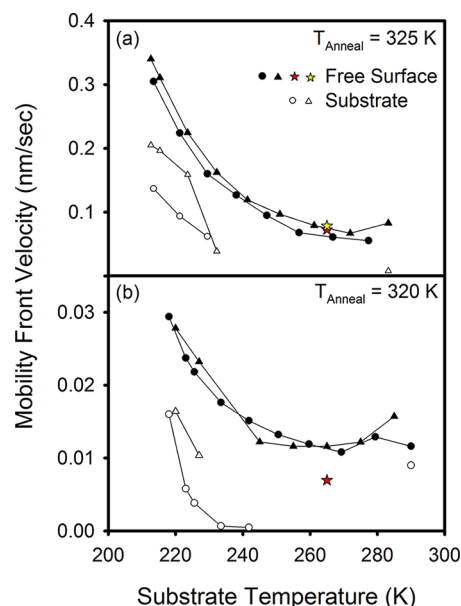


Figure 5. Velocity of mobility front propagation in stable indomethacin glasses for free surface (solid points) and substrate-initiated fronts (open points). Here we show data from two independently prepared temperature gradient samples at each of the two annealing temperatures. For $243 \text{ K} < T_{\text{substrate}} < 280 \text{ K}$, only fronts originating from the free surface were observed. Outside of this temperature range, fronts originating from both the substrate and the free surface were observed. Substrate-initiated fronts were slower, but velocities were not reproducible. Red stars are previously published results using secondary-ion mass spectrometry.^{22,23} The yellow star is a sample which had only a single substrate temperature.

induced fronts was reproducible, the associated front velocities were not, as indicated by the differences among samples. Modification of the substrate surface prior to deposition might improve this aspect of the experiment.

Figure 6 shows an important check on the accuracy of our fitting procedure with the front model. The symbols show the indices of refraction for the stable glass layer as determined by fitting with the front model during annealing at 325 K. These are compared to previously reported values for 293 K that were

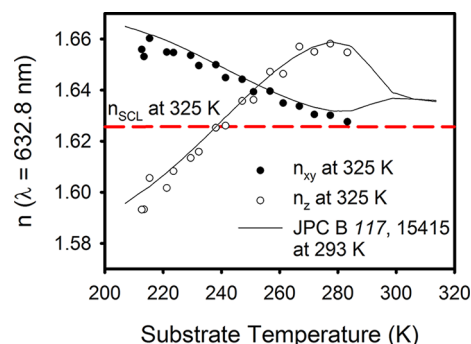


Figure 6. Indices of refraction for vapor-deposited glasses of indomethacin at 325 K, as determined by fitting to the front model during annealing (symbols). n_z and n_{xy} are the indices for light polarized out of the plane and in the plane of the substrate, respectively. The symbols are the indices of refraction determined during fitting. The black lines are literature values for n_{xy} and n_z of vapor-deposited indomethacin, reported at 293 K.⁶ The red line is the index of refraction of the supercooled liquid at 325 K.

obtained with a homogeneous model (black lines);⁶ at 293 K, the homogeneous model is adequate because the transformation process occurs very slowly. The good agreement between the more complex front model used here and the previously used homogeneous model is an indication that our characterization of these materials is robust.

One of the goals of these experiments was to connect the transformation behavior of stable glasses as closely as possible to that of ordinary glasses. In this effort, we tried to measure mobility propagation velocities at the highest possible substrate temperatures, since vapor-deposited glasses attain the properties of ordinary glasses as $T_{\text{substrate}}$ approaches T_g . Because ellipsometry relies on the reflection and refraction of light at interfaces, our ability to observe the mobility front depends on the optical contrast between the stable glass and the supercooled liquid. When $T_{\text{substrate}}$ is greater than 290 K, the index difference between the as-deposited glass and the supercooled liquid at the annealing temperature becomes too small to uniquely assign a front velocity.

DISCUSSION

Comparison to Other Experiments. The measurements reported here are the first real-time, direct measurements of the propagation of the mobility front in stable glasses. They also establish ellipsometry as the only technique other than SIMS capable of directly observing the interface between the as-deposited glass and the supercooled liquid. While SIMS has been used to measure mobility front velocities in previous experiments,^{21–23} it is not suitable for these experiments because of the time and expense associated with measuring a very large number of samples. Acquiring the results reported here with SIMS would have required approximately 600 measurements across 40 independently prepared, isotopically labeled samples. In contrast, only six independently prepared samples were measured by ellipsometry, and no isotopic labeling was required. In addition, because SIMS cannot make real-time measurements during the transformation, the experimental procedure is significantly more complicated. A strength of the SIMS approach which makes it an excellent basis for comparison is that the results require less modeling than the ellipsometry experiments. The high level of independence between the two experiments, and the agreement in the mobility front velocity between them, strengthens the validity of both measurements.

The previously reported SIMS measurements²³ also provide a point of comparison for the substrate-initiated fronts observed here at some substrate temperatures (see Figure 5). Neither the present experiments nor the SIMS experiments reported substrate-initiated fronts for $T_{\text{substrate}}$ equal to 265 K. However, in some SIMS experiments, propagation of a mobility front toward the top surface was observed to be initiated by an ordinary glass layer that was intentionally deposited in the film. Sepúlveda et al.²³ reported that the mobility front moving toward the free surface had a velocity about half the value of the front moving away from the free surface. Figure 5 illustrates a similar phenomenon in that fronts moving toward the free surface (in this case initiated at the substrate) have velocities considerably lower than fronts moving away from the free surface. The kinetic facilitation mechanism does not seem to provide an explanation for these observations.

Recent papers by Bhattacharya et al.¹¹ and by Rodríguez-Tinoco et al.²⁸ introduced a new and powerful method for understanding mobility front propagation into stable organic

glasses. Both groups used nanocalorimetry to confirm that thin films of stable glasses transform into the supercooled liquid via constant velocity propagation fronts, even at the very high heating rates (and correspondingly high temperatures) of their experiments. This method allows the mobility front velocities to be determined over a wide range of annealing temperatures. Rodríguez-Tinoco et al. did experiments on indomethacin deposited at 265 K and were able to deduce the annealing temperature dependence of the mobility front velocity up to $T_g + 75$ K. In addition, they showed that differential scanning calorimetry experiments could be used to extract mobility front velocities in reasonable agreement with those previously determined by SIMS (and determined here by ellipsometry). Rodríguez-Tinoco et al. concluded that the same mobility propagation velocity could be obtained from films over a range of thicknesses. We confirm these results in Figure 4 but are able to make this comparison more directly since the ellipsometry experiments can directly track the propagation of the mobility front through a thin film and determine whether a substrate-initiated front is present; in the calorimetry experiments, the number of propagating fronts must be assumed and this influences the calculated value of the mobility front velocity.

What Controls the Velocity of the Propagating Mobility Front? In order to understand why the mobility front velocity depends on substrate temperature, we have attempted to correlate the front velocity with the density of the glass. The idea that glass and supercooled liquid properties are determined by density has been often utilized, for example in “free volume” theory.³⁷ For several polystyrene glasses, Simon and Bernazzani showed that the instantaneous segmental mobility of the polymer was highly correlated with the density³⁸ and so it is reasonable to ask if such a connection might exist between the mobility front velocity and the density for stable glasses. Figure 7 shows that the mobility front

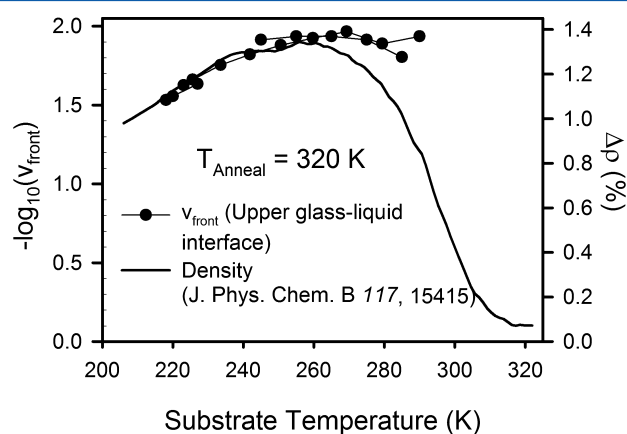


Figure 7. Comparison between the mobility front velocity (nm/s) and glass density. $\Delta\rho$ is the density difference between the glass in its as-deposited state and in the liquid-cooled ordinary glass.⁶ Between 220 and 260 K, the density and mobility front velocity are well-correlated. Above 260 K, that correlation is no longer valid.

velocity is imperfectly correlated with the sample density. Between 220 and 260 K, there appears to be good correlation, but that correlation is lost above $T_{\text{substrate}} = 260$ K. In this respect, vapor-deposited glasses may be more complex than liquid-cooled glasses.

Theoretical and simulation work explain the propagation of the mobility front into stable glasses using kinetic facilitation

(i.e., the concept that mobility is most easily created in regions directly adjacent to already mobile regions).³⁰ Because the surface has a significantly higher mobility than the bulk,^{39–41} a transformation front starts at the free surface. As the front propagates into the interior, molecules in the liquid facilitate the liberation of molecules from the glass. Because stable glasses have much lower mobility than liquid cooled glasses,²¹ the mobility present at the free surface is able to propagate far (up to 1 μm) into the depth of a film²⁴ before independent sources of mobility within the film become significant. At a microscopic level, one could view the front propagation as a “melting” phenomenon that occurs from the interface because the barriers for molecular rearrangement are much higher in the interior of the stable glass.

Using random first-order transition theory, Wisitsorasak and Wolynes have recently performed numerical calculations of the front propagation process for stable glasses.²⁶ Their calculations were performed for glasses of $\alpha\alpha\beta$ -trisnaphthylbenzene (a molecule that shows similar stable glass properties as indomethacin) and reproduced the experimental mobility front velocity within about a factor of 2. They also investigated the extent to which the initial fictive temperature of the glass influences the mobility front velocity. Over the 10 K range of fictive temperatures that they investigated, no systematic dependence was reported. Figure 5 shows that stable glasses of indomethacin do show a systematic variation of the mobility front velocity over the large range of substrate temperatures investigated here, amounting to a 6-fold variation for annealing at 325 K.

The mobility front velocity can be viewed as a sensitive indicator of the mobility of the as-deposited glass. Wolynes has argued that the front velocity might generally be a function of the liquid mobility and glass mobility.⁴² For the experiments shown in Figures 3 and 5, the liquid mobility is constant for all samples transformed at a given annealing temperature. If we accept the Wolynes proposition then the observed variation in front velocities is a direct measure of the mobility of the glasses. This is an important idea as the structural relaxation time in stable glasses is so long at the deposition temperature that it likely cannot be measured directly.¹³ In this view, the mobility front velocities measured here are the first determination of the relative mobility of stable glasses and show that mobility is imperfectly correlated with the density.

Transformation Mechanism for Thicker Films and Films Without Free Surfaces. For stable glasses of indomethacin greater than $\sim 1 \mu\text{m}$ thick, the total time required for the sample to transform into the supercooled liquid state becomes independent of film thickness.²⁴ This means that a second transformation mechanism must be operative, in addition to mobility fronts propagating from the surface/interface. One aspect of this second process is seen for the thicker film in Figure 4. The front model accurately describes the data until the front has propagated about 800 nm from the free surface. Beyond this point, the transformation finishes more rapidly than expected, indicating the operation of a second parallel transformation mechanism. Dielectric relaxation experiments indicate that thick films of stable glasses transform by a heterogeneous mechanism;²⁷ at any time during the transformation, only the as-deposited glass and the supercooled liquid are present. From these observations, it has been inferred that a “bulk process” can create sources of mobility in thick stable glasses²⁴ that grow into coexisting pockets of supercooled liquid and glass.^{5,7,27,28,30,42,43} Many questions about the

bulk process remain unanswered, including the density and nature of the sites that initiate mobility and the rate at which fronts propagate away from these sites. Given this uncertainty, the mobility front velocity (as observed here for thin films) is a better candidate for characterizing the mobility of a stable glass than the bulk transformation time. This is analogous to using the melting velocity of a crystal to characterize its stability rather than the total time to remove crystallinity from a macroscopic sample.

Glass films with no free surfaces, such as the active layers in organic light-emitting diodes (OLEDs), are often prepared by vapor-deposition.^{16,17,20} At appropriate substrate temperatures, many of these materials will likely form stable glasses⁴⁴ and there are open questions about the transformation mechanism in this geometry. The active layers in OLEDs are thin (30–50 nm) and are in contact on both sides with other solid films. Any mobility front that is efficiently initiated at an interface will likely propagate through the entire film before the bulk process has a chance to become important. In this regime, the mobility front velocity will completely determine the structural stability of a glass; larger mobility front velocities may lead to faster device failure. On the other hand, Sepulveda et al. have shown that in transformation fronts do not necessarily originate at the interface of a stable glass and an adjoining layer.²³ If mobility at the interfaces could be completely suppressed then the films would exhibit enhanced thermal stability since only the slower bulk mechanism would be active.

SUMMARY

We have established that the transformation process by which mobility propagates into thin films of stable glasses can be efficiently characterized with ellipsometry. For vapor-deposited indomethacin, there is a wide range of substrate temperatures for which a propagating mobility front is observable and the front velocity depends significantly upon the substrate temperature. There is a good correlation between mobility front velocity and glass density over part of the range of substrate temperatures, but this correlation fails at the highest substrate temperatures. We corroborate previous observations that fronts propagating toward the free surface do not travel at the same velocity as the free-surface initiated front.²³ The mobility front velocity may provide an avenue to quantify the molecular mobility of stable glass samples and provides a convenient metric of glass stability for comparing different glasses. Future experiments in this area might examine the mobility front velocity at higher substrate temperatures, in an effort to connect the transformation routes for stable glasses with those observed for aged liquid-cooled glasses. An intriguing possibility is that a surface-initiated mobility front might be observed in a highly aged liquid-cooled glass.⁴⁵

There are notable gaps in our understanding of stable glasses that require significant experimental and theoretical work. An important advance would be an experiment that is able to measure the molecular mobility of a stable glass directly, without the inferences required here. Such an experiment would represent a significant advance toward being able to directly connect the molecular-level properties of stable glasses to ordinary glasses. Also of value would be experimental and theoretical methods that are able to more fully describe the bulk transformation process of stable glasses. Thus far, every observation of the bulk process has been indirect, and so even the most basic questions about the number of sites from which

mobility propagates and the nature of these sites remain unanswered.

■ ASSOCIATED CONTENT

■ Supporting Information

Sample ellipsometry data showing the change of the optical properties of a sample as it transforms via a mobility front. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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