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# Influence of substrate temperature on the stability of glasses prepared by vapor deposition

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Physical vapor deposition of indomethacin (IMC) was used to prepare glasses with unusual thermodynamic and kinetic stability. By varying the substrate temperature during the deposition from 190 K to the glass transition temperature ( $T_g=315$  K), it was determined that depositions near  $0.85T_g$  (265 K) resulted in the most stable IMC glasses regardless of substrate. Differential scanning calorimetry of samples deposited at 265 K indicated that the enthalpy was 8 J/g less than the ordinary glass prepared by cooling the liquid, corresponding to a 20 K reduction in the fictive temperature. Deposition at 265 K also resulted in the greatest kinetic stability, as indicated by the highest onset temperature. The most stable vapor-deposited IMC glasses had thermodynamic stabilities equivalent to ordinary glasses aged at 295 K for 7 months. We attribute the creation of stable IMC glasses *via* vapor deposition to enhanced surface mobility. At substrate temperatures near  $0.6T_g$ , this mobility is diminished or absent, resulting in low stability, vapor-deposited glasses. © 2007 American Institute of Physics. [DOI: 10.1063/1.2789438]

## INTRODUCTION

Physical vapor deposition is often used to create thin films of organic, inorganic, and metallic materials.<sup>1</sup> These thin coatings have applications in optics, electronics, and in emerging optoelectronic technologies.<sup>2,3</sup> During deposition, individual atoms or molecules are transferred from the vapor phase to a sufficiently cold substrate where they condense. Vapor deposition can be used to produce very thin films (down to 10 nm or less) which are also extremely flat (less than 1 nm roughness). Multilayer structures can be produced in this manner and these are used, for example, in some organic light emitting diodes to optimize charge recombination on luminescent species.<sup>2–5</sup> Often, vapor deposition is used to produce films that are amorphous rather than crystalline.<sup>6–10</sup> In some cases, this is done to eliminate the negative effects of crystalline grain boundaries. In other cases, vapor deposition can be utilized to create glasses of molecules that tend to crystallize when cooled as a liquid.<sup>7,8,10</sup>

The dominant view in the literature is that vapor-deposited glasses are *unstable* relative to a glass formed by cooling a bulk liquid at a typical rate used in the laboratory ( $\sim 1$  K/min).<sup>8,11–14</sup> For convenience, we refer to the latter throughout this paper as an “ordinary” glass. For example, vapor-deposited glasses of 1-pentene<sup>14</sup> and butyronitrile<sup>12</sup> have been studied with *in situ* calorimetry techniques. Upon deposition, these glasses had enthalpies that were 10–20 J/g greater than the corresponding ordinary glasses. These

vapor-deposited glasses were so unstable that any increase in temperature resulted in an irreversible decrease of the enthalpy even though the sample was far below the conventional glass transition temperature  $T_g$ . In another study, the densities of vapor-deposited toluene, ethylbenzene, and propylbenzene films were measured using light interference techniques.<sup>8</sup> The vapor-deposited glasses were 4%–10% less dense than the equilibrium supercooled liquid near  $T_g$ ; in comparison, an ordinary glass is more dense than the supercooled liquid near  $T_g$ .

Swallen *et al.* have recently shown that physical vapor deposition of small organic molecules can produce glasses that are substantially *more stable* than the glass formed by cooling the liquid.<sup>15</sup> They showed that slow deposition at temperatures close to  $T_g$  produced glasses of indomethacin (IMC) and 1,3,5-(tris)naphthylbenzene (TNB) with enthalpies as much as 10 J/g *lower* than the ordinary glass. The difference between the results of Ref. 15 and the prevailing literature view of vapor deposition is summarized schematically in Fig. 1. The solid curves indicate the enthalpy or molar volume of a typical liquid upon cooling through the glass transition region. As the temperature of the liquid is lowered, molecular motion slows dramatically and, at some point, the molecules no longer have time to equilibrate before further cooling. At this temperature (described by  $T_g$  or the fictive temperature  $T_f$ ), the enthalpy and volume deviate from the values expected in the liquid. Slower cooling rates allow the system to stay in equilibrium to lower temperatures but the dynamics are such a strong function of temperature that decreasing the cooling rate by a factor of 10 only lowers  $T_f$  by only a few kelvin. The two points in Fig. 1 qualitatively illustrate the different results for vapor-deposited glasses reported in Ref. 15 and in the previous literature.

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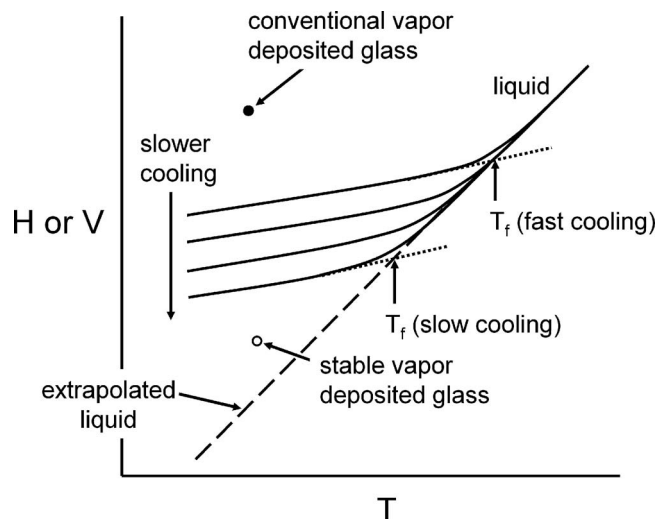


FIG. 1. Schematic representation of the effect of cooling rate on enthalpy and volume. Also shown are the results for conventional, unstable (filled circle), and stable (open circle) vapor-deposited glasses. The dashed and dotted lines represent the extrapolated liquid and glass behavior, respectively. The intersection of these lines defines the fictive temperature of a glass created by cooling a liquid.

The primary goal of this paper is to understand why vapor deposition yields extremely stable glasses under some conditions and quite unstable glasses under other conditions. To investigate this, we prepared vapor-deposited glasses of indomethacin on substrates ranging in temperature from 190 to 315 K ( $T_g$ ). The thermodynamic and kinetic stabilities of our glasses were determined by differential scanning calorimetry (DSC). Thermodynamic stability was observed as a low fictive temperature ( $T_f$ ) and kinetic stability was characterized by a high onset temperature ( $T_{\text{onset}}$ ). Several different types of substrates were used in order to determine if the substrate had any influence on the stability of the vapor-deposited glass.

We find that the substrate temperature  $T_{\text{substrate}}$  during deposition has a strong impact on the stability of the vapor-deposited glass. The most stable glasses, both in kinetic and thermodynamic terms, were prepared by depositions near  $0.85T_g$  (265 K). The enthalpy of these samples was 8 J/g less than the ordinary glass prepared by cooling the liquid, corresponding to a 20 K reduction in  $T_f$ . The most stable vapor-deposited IMC glasses had thermodynamic stabilities equivalent to that of ordinary glasses aged at 295 K for 7 months. The chemical and mechanical characteristics of the substrate had no influence on the stability of the vapor-deposited glasses.

These results allow us to understand the very different stabilities of vapor-deposited glasses reported by Ref. 15 and in the previous literature.<sup>8,12–14</sup> The conventional view of the vapor deposition process is accurate at low substrate temperatures. Under these conditions, molecules hit the surface and stick without significant rearrangement. Since the packing of neighboring molecules is not optimized in this process, the resulting glasses have high molar volumes and high enthalpies. On the other hand, if the substrate temperature is not too far below  $T_g$ , a mobile surface layer may allow configurational sampling after a molecule arrives from the vapor

phase. Under these conditions, the molar volume and enthalpy of the vapor-deposited material may be even lower than that of the ordinary glass, since equilibration occurs at a lower temperature. We show that the previous literature on vapor-deposited organic glasses can be understood qualitatively if  $T_{\text{substrate}}/T_g$  is used as the classifying variable.

## EXPERIMENTAL SECTION

### Materials

Indomethacin with purity greater than 99% was purchased from Sigma (St. Louis, MO) and was used as received. The IMC was completely crystalline as the  $\gamma$  polymorph. Melting temperature comparisons of the as-received material ( $T_m=432.8$  K) agreed with literature data for the  $\gamma$  polymorph to within 1 K.<sup>16,17</sup>

### Vapor deposition

The source for vapor deposition of indomethacin (IMC) was a heated quartz crucible containing the crystalline solid. The crucible was held 3 cm away from the substrate target in a vacuum chamber with a base pressure of  $10^{-8}$  torr. The substrate temperature was controlled using a Lakeshore 340 temperature controller with four-wire platinum resistance temperature detectors (Omega); during deposition the substrate temperature was held isothermally to within 1 K. DSC pans and other substrates were attached to the temperature stage using Apiezon N vacuum grease. The deposition rate was controlled by the temperature of the crucible and monitored with a quartz crystal microbalance (Sycon Instruments). The deposition rate was held constant at  $15 \pm 3$  nm/s during the deposition, except for a five minute period during which the deposition rate ramped up from zero. A typical deposition required 45–60 min to complete. During this period, 2–4 mg of IMC glass was deposited into each of three DSC pans. The thickness of the IMC glass in the DSC pans ranged from 30 to 60  $\mu\text{m}$ .

### Differential scanning calorimetry analysis

After deposition, the samples were prepared for DSC analysis. The vapor-deposited glass was brought to room temperature under vacuum and then the chamber was vented with dry nitrogen. Upon opening the chamber, the pans were immediately removed and hermetically sealed. After sealing, the samples were placed in dry ice to minimize the effect of any aging before DSC analysis. The typical amount of time needed to bring the samples up to room temperature, remove and seal the pans, and place the sample in dry ice was 45 min.

DSC analysis (TA Instruments Q1000) of each sample consisted of three scans, as shown in Fig. 2. The first scan heated the as-deposited IMC from 253 K up to 388 K at a rate of 10 K/min. The sample was then held isothermally at 388 K for 600 s to allow the vapor-deposited IMC to completely crystallize. The crystalline sample was then cooled at a rate of approximately 40 K/min to 253 K and heated again at 10 K/min to 443 K, 10 K above  $T_m$  for the highest melting polymorph. The liquid was then cooled again at approxi-

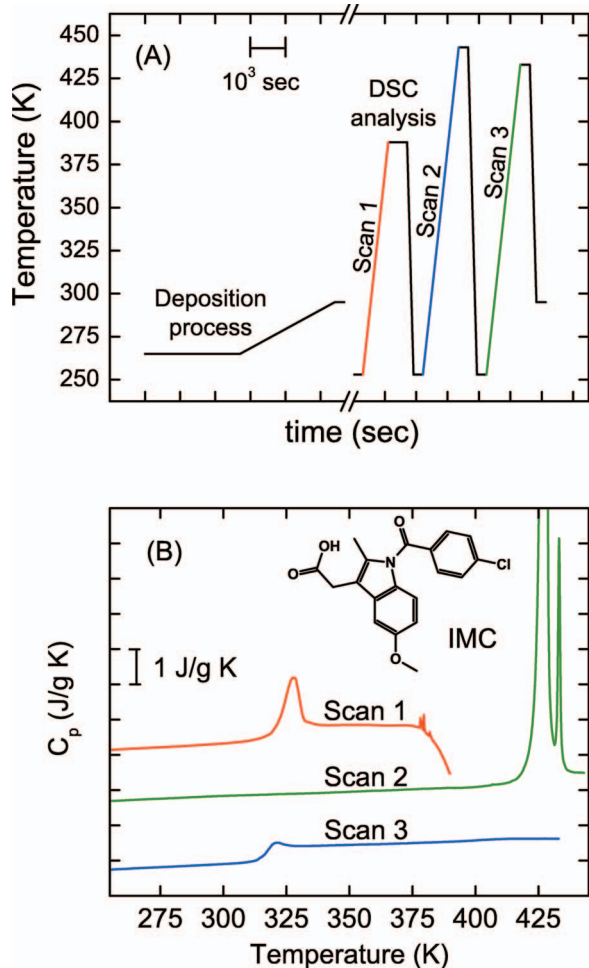


FIG. 2. (Color) (A) Thermal history of the deposition process and the thermal cycling used in the DSC analysis. The sample shown was deposited at a substrate temperature of 265 K. (B) Heat capacity  $C_p$  of individual scans. Scan 1 shows the results for the glass vapor deposited at 265 K with the enthalpy overshoot and eventual crystallization above 375 K. Scan 2 shows the  $C_p$  of the completely crystallized sample. Scan 3 shows the ordinary glass obtained by cooling the melt of the previous scan. Inset: Structure of IMC.

mately 40 K/min to 253 K. This created a glass cooled from the liquid for comparison, which we refer to below as the “ordinary” glass. The ordinary glass was heated at a rate of 10 K/min. Indium standards were used prior to analysis to calibrate the DSC instrument.

The heat flow recorded by the DSC instrument was used to obtain the apparent heat capacity  $C_p$ . Figure 2(B) shows typical  $C_p$  data for the three scans. The two peaks observed in scan 2 are associated with two different polymorphs of IMC,  $\alpha$  ( $T_m=426.6$  K) and  $\gamma$  ( $T_m=432.75$  K).  $T_m$  of these polymorphs agreed with literature values to within 1.5 K,<sup>16,17</sup> indicating that the vapor deposition process does not result in decomposition products co-condensing with IMC. Scan 3 shows the  $C_p$  associated with the ordinary glass. The glass transition temperature  $T_g$  as defined by the onset of the transition from the glass to the supercooled liquid in this scan is 315 K. This same  $T_g$  value is obtained from IMC that has been placed into the DSC pan as a crystal, then melted and analyzed according to the protocol for scan 3; this is further evidence that the vapor deposition process does not chemi-

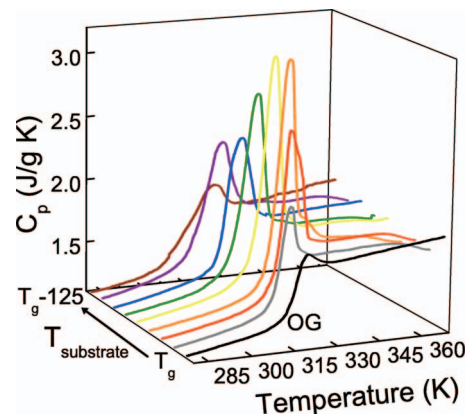


FIG. 3. (Color)  $C_p$  of indomethacin samples vapor-deposited at various  $T_{\text{substrate}}$ . OG designates the ordinary glass created by cooling the liquid. The vapor-deposited scans are presented sequentially from highest to lowest  $T_{\text{substrate}}$ . Gray:  $T_g=0$  (315 K), red:  $T_g=-20$  (295 K), orange:  $T_g=-40$  (275 K), yellow:  $T_g=-50$  (265 K), green:  $T_g=-60$  (255 K), blue:  $T_g=-75$  (240 K), purple:  $T_g=-100$  (215 K), and maroon:  $T_g=-125$  (190 K).

cally modify IMC. Throughout this paper, we use  $T_g=315$  K as a convenient reference temperature for the ordinary glass without specifying each time the particular cooling and heating rates that produce this value.

In order to accurately obtain enthalpy and  $T_f$  values, we need to accurately know the mass of the vapor-deposited glasses. We determined the IMC mass by weighing the DSC pans before and after deposition. There is some inaccuracy in this procedure because the total mass is small and because it is difficult to completely remove the grease used to attach the pan to the cold stage. Incomplete removal of the grease results in an overestimation of the actual IMC mass. To account for this, we multiplied the experimental  $C_p$  data for individual experiments by a factor from 1.00 to 0.93 in order to match the experimental  $\Delta C_p$  at  $T_g$  to the value of 0.40 J/g K reported by Shamblin *et al.*<sup>18</sup> The average correction factor was 0.96. The corrected  $C_p$  values were integrated to get the enthalpy and  $T_f$  values discussed below. The  $\Delta C_p$  correction increases the calculated  $T_f$  by at most 2 K. As a further check, for some samples we estimated the sample mass from the enthalpy of fusion in scan 2 (see Fig. 2). This estimate yielded essentially the same masses as the above procedure, with an average deviation of 3% and no deviation greater than 7%. The reported values of  $T_f$  and  $T_{\text{onset}}$  are based on three to nine replicate measurements.

## RESULTS

### Observed heat capacity

Figure 3 shows the heat capacity  $C_p$  of IMC films directly vapor-deposited into DSC pans held isothermally at various temperatures during the deposition. Shown for comparison is  $C_p$  for the ordinary glass prepared by cooling the liquid.  $C_p$  for the vapor-deposited samples changes systematically with the substrate temperature  $T_{\text{substrate}}$ . Samples deposited near 265 K ( $T_g=50$  K) show the largest enthalpy overshoots (i.e., the peaks in  $C_p$ ) with smaller overshoots observed at both higher and lower  $T_{\text{substrate}}$ . In the next two

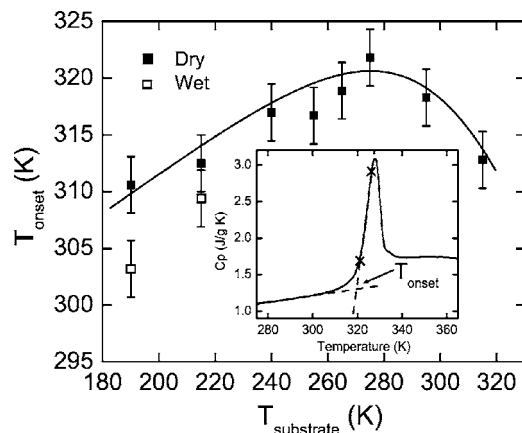


FIG. 4. Kinetic stability of vapor-deposited IMC glasses as indicated by onset temperature  $T_{\text{onset}}$  from DSC. Individual samples were held isothermally at the indicated  $T_{\text{substrate}}$  during deposition. The solid line is a guide to the eye for samples that either showed no evidence of water or were corrected for water (filled squares). Open squares are the uncorrected  $T_{\text{onset}}$  values (see text). Error bars indicate the standard deviations characterizing the range of  $T_{\text{onset}}$  values obtained from three to nine samples. Inset: Definition of  $T_{\text{onset}}$ .  $C_p$  vs  $T$  is plotted for a sample deposited at 265 K.

sections, we analyze these curves to quantitatively determine the kinetic and thermodynamic stability of the glass formed at each  $T_{\text{substrate}}$ .

### Kinetic stability

The kinetic stability of a glass can be defined by the onset temperature  $T_{\text{onset}}$ , as shown in the inset to Fig. 4.  $T_{\text{onset}}$  marks the temperature at which the apparent  $C_p$  begins to rise above the  $C_p$  value characteristic of the glass. Below  $T_{\text{onset}}$ , the molecules in the sample are so immobile that they cannot absorb the heat from their environment that is required to transform the sample into an equilibrium liquid. Thus,  $T_{\text{onset}}$  marks the temperature at which mobility first begins. Higher values of  $T_{\text{onset}}$  indicate greater kinetic stability.

The main panel of Fig. 4 shows  $T_{\text{onset}}$  for indomethacin glasses created by vapor depositing into DSC pans held isothermally at various  $T_{\text{substrate}}$ . When the substrate is held at 315 K ( $T_g$ ), the onset temperature is nearly that of the ordinary glass. As  $T_{\text{substrate}}$  is lowered, the onset temperatures become greater reaching a maximum for deposition near 275 K; glasses deposited at 40–50 K below the conventional  $T_g$  show the greatest kinetic stability. Lowering  $T_{\text{substrate}}$  further clearly decreases the kinetic stability of the glasses.

When the substrate was held at 215 K or lower, the resulting glasses were observed to contain a small amount of water. Since amorphous IMC is slightly hygroscopic, water can be absorbed during the transfer of the pans from the vacuum chamber until they are hermetically sealed. If this occurs, it is observed as a shift in  $T_m$  of the second DSC scan and a shift in  $T_g$  of the third DSC scan; in both cases, the shifts would be to lower temperatures. We quantify the shift of  $T_g$  in the third scan and use it to approximately correct the onset temperature of the as-deposited sample. For instance, if  $T_g$  in the third DSC scan is shifted to lower temperatures by 5 K, then  $T_{\text{onset}}$  for the as-deposited sample was shifted 5 K higher to account for the water content. These corrected  $T_{\text{onset}}$  values are referred to as the “dry” samples in Fig. 4.

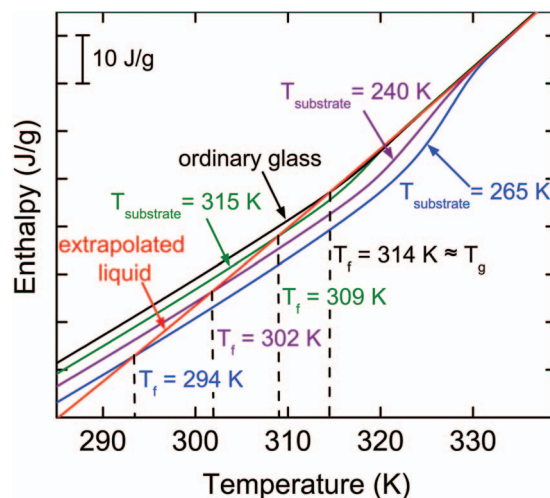


FIG. 5. (Color) Enthalpy for IMC samples created under various conditions. The fictive temperatures  $T_f$  are calculated from the intersection of the experimental enthalpy with the extrapolated liquid enthalpy (red) calculated from Shamblin *et al.* Four samples are shown: ordinary glass, black; deposited at 315 K, green; deposited at 265 K, blue; and deposited at 240 K, purple. Vertical dotted lines indicate the  $T_f$  values.

Although all the samples shown in Fig. 4 were handled in an equivalent manner, only the samples deposited at 215 K or below showed the presence of water. Thus, the glasses formed at these substrate temperatures inherently have a greater tendency to absorb water.

The inset of Fig. 4 shows how we defined  $T_{\text{onset}}$  quantitatively. The glassy region of the  $C_p$  curve is extrapolated to higher temperatures using a linear fit of the glass from 280–300 K. The sharp rise in the observed  $C_p$  data is also fit linearly. For samples deposited at 240 K or higher, the observed  $C_p$  was fit from 1.7 J/g K up to 95% of the overshoot peak height as indicated in the inset. For samples deposited at temperatures below 240 K or cooled from the melt, the  $C_p$  was fit from 1.5 J/g K up to 95% of the peak height. The intersection of the glass line and enthalpy overshoot line defines  $T_{\text{onset}}$  from the DSC data. As mentioned above, we use  $T_{\text{onset}}$  for the ordinary glass (315 K) as our reference temperature and denote it as  $T_g$ .

### Thermodynamic stability

We quantify the thermodynamic stability of the vapor-deposited glasses from the enthalpy. The  $C_p$  curves from Fig. 3 were integrated to yield enthalpy curves as shown in Fig. 5. The enthalpy curves are vertically shifted to coincide above the glass transition region since all the samples are in the same thermodynamic state in this temperature range. The three vapor-deposited samples shown in Fig. 5 all have lower enthalpies than the ordinary glass, indicating enhanced thermodynamic stability of up to 8 J/g.

It is convenient to compare the thermodynamic stabilities of different glasses using the fictive temperature  $T_f$  calculated from the enthalpy.  $T_f$  is defined graphically in Fig. 1 for samples prepared by cooling a liquid. For such samples,  $T_f$  indicates roughly the temperature at which the sample left equilibrium.<sup>19</sup> Far below  $T_f$ , the enthalpy of such a glass can be altered reversibly by changing the temperature. In this

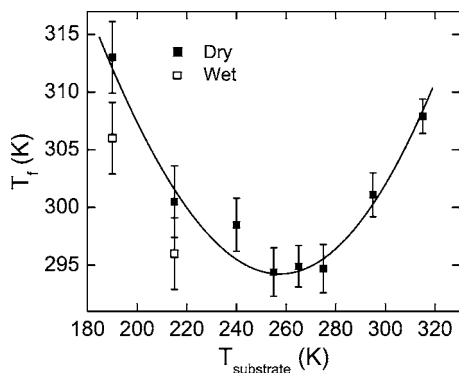


FIG. 6. Summary of fictive temperatures  $T_f$  for IMC glasses prepared at various  $T_{\text{substrate}}$ . Filled squares indicate samples without any water as-deposited or  $T_f$  values that were corrected for the presence of water. Open squares are the uncorrected  $T_f$  values where the presence of water was evident. Error bars indicate the standard deviations characterizing the range of  $T_f$  values obtained from three to nine samples. The solid line is a guide to the eye.

temperature range far below  $T_f$ , the “structure” of the glass is constant and  $T_f$  is a one-parameter measure of the enthalpy content of the glass. Lower  $T_f$  values indicate greater thermodynamic stability.

Since vapor-deposited samples cannot be characterized by cooling the liquid, we use the enthalpy obtained upon heating to determine  $T_f$ . The intersection point between the enthalpy of the vapor-deposited samples and the enthalpy of the supercooled liquid (obtained by extrapolation) defines  $T_f$ .<sup>20,21</sup> This generalization of the procedure described in the previous paragraph maintains the quantitative relationship between  $T_f$  and the enthalpy content of the glass. The enthalpy of the supercooled liquid at low temperatures must be obtained by extrapolating higher temperature data. We fit IMC  $C_p$  data reported by Shamblin *et al.*<sup>18</sup> for supercooled IMC with the following equation:

$$C_p(\text{J/g K}) = 3.10 \times 10^{-3} T/K + 6.8 \times 10^{-1}. \quad (1)$$

After integration the enthalpy becomes a second order polynomial,

$$H(\text{J/g}) = 1.55 \times 10^{-3} (T/K)^2 + 6.8 \times 10^{-1} T/K + C. \quad (2)$$

Figure 5 shows enthalpy curves for four different IMC samples with a range of thermodynamic stabilities. For the ordinary glass,  $T_f$  equals  $T_g$  within experimental error as expected. Vapor-deposited samples with  $T_{\text{substrate}}$  equal to 315, 265, and 240 K are also shown. Of the three substrate temperatures, the sample deposited at 265 K shows the lowest  $T_f$  and, therefore, the greatest thermodynamic stability.

A summary of fictive temperatures as a function of substrate temperature for vapor-deposited IMC glasses is shown in Fig. 6. The greatest thermodynamic stability is observed for  $T_{\text{substrate}}$  near  $0.85T_g$  (265 K); this is the same substrate temperature that maximized kinetic stability. As noted above, depositions at low temperature create samples that absorb water during transfer from the deposition chamber. Once again the data is shifted to account for this effect. Our analysis can only measure the enthalpy content of the vapor-deposited glasses at the beginning of the DSC scan. Since samples vapor-deposited at low temperature were exposed to

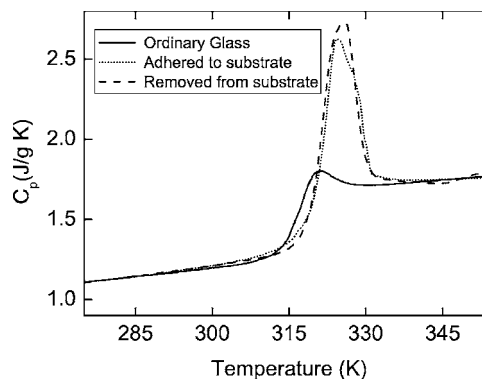


FIG. 7. Effect of substrate on the measured  $C_p$ . The dotted line is a sample deposited directly onto the DSC pan. The dashed line represents a sample deposited onto and removed from aluminum foil, and then placed into a DSC pan for analysis.  $T_{\text{substrate}}$  for both conditions was 295 K.  $C_p$  for the ordinary glass is given for reference.

room temperature prior to analysis, it is likely that some enthalpy relaxation occurred in this process. We expect that this effect is the largest for samples deposited at 240 K and below since these materials are less stable kinetically and thermodynamically. If this effect could be avoided, it is likely that the data at lower  $T_{\text{substrate}}$  would show even higher  $T_f$  values. We would anticipate that these low energy samples would show undershoots in the observed  $C_p$  similar to what has been seen in stressed and hyperquenched samples.<sup>22</sup> This would give rise to much higher  $T_f$  values. *In situ* measurements of  $C_p$  for these samples would allow for direct observation of any undershoots. We are currently working to obtain such *in situ* measurements.

Finally, we would like to comment upon our use of the term “thermodynamic stability.” Rigorously, differences in thermodynamic stability at constant temperature and pressure are defined by comparisons of the Gibbs free energy, which we have not calculated. We use the enthalpy of the system to compare thermodynamic stabilities since it is directly available from our measurements and closely related to the position of the system on the potential energy landscape.

### Substrate effects

We investigated the influence of the substrate on the properties of the vapor-deposited glasses and found that the substrate did not alter the properties of the glass. In addition to depositions directly into aluminum DSC pans, we also deposited glasses onto aluminum foil, copper foil, and thin polycarbonate film. For these latter experiments, the vapor-deposited glass was removed from the foil or film and packed loosely into a DSC pan prior to analysis. Figure 7 compares data for IMC deposited directly onto an aluminum DSC pan with data for IMC deposited onto and removed from aluminum foil; in both cases, the substrate temperature during deposition was 295 K. The observed  $C_p$  curves are essentially identical and the calculated  $T_f$  values agree to within 1 K. When IMC was deposited at 265 K onto copper foil and polycarbonate film and then removed from the substrate before analysis, highly stable glasses were formed. In these cases, we observed qualitative but not quantitative agreement with the  $C_p$  curves for glasses directly deposited

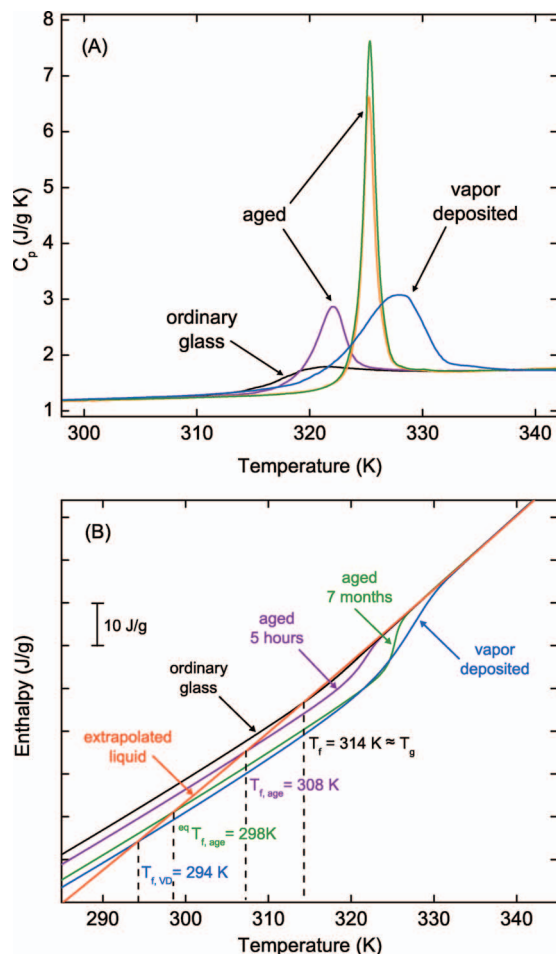


FIG. 8. (Color) Comparison of vapor-deposited IMC glasses and aged ordinary glasses. (A) Observed  $C_p$  for aged and vapor-deposited samples. Ordinary glasses were aged for 5 h (purple), 5 months (orange), and 7 months (green). The vapor-deposited sample (blue) was prepared with a substrate temperature of 265 K. (B) Enthalpies from integrated  $C_p$  curves shown in (A). The extrapolated liquid line is the same as in Fig. 5. Dotted vertical lines indicates  $T_f$  for the various samples. The sample aged for 7 months at 295 K has nearly reached equilibrium:  $T_{\text{age}} \approx T_f$ .

into DSC pans. The glass that was removed from the substrate absorbed more water from the atmosphere than did the material directly deposited into the DSC pans, resulting in a shift of  $T_f$  by a few kelvin.

### Aging ordinary glasses

The traditional way to make a more stable glass is to anneal an ordinary glass for long periods of time below  $T_g$ .<sup>23,24</sup> Since glasses are thermodynamically unstable, their free energy drops continuously with time and experiments typically observe a decrease in enthalpy and molar volume during this aging process. We performed a few DSC experiments on aged glasses formed by cooling the liquid for comparison with our vapor-deposited IMC glasses.

Figure 8(A) shows the  $C_p$  curves of ordinary glasses of IMC that were isothermally aged for up to 7 months at 295 K. Shown for comparison is the  $C_p$  curve for a sample vapor deposited at 265 K in about 1 h. Figure 8(B) shows the enthalpies and fictive temperatures for these samples. As ordinary IMC glasses are aged for longer periods of time, the

kinetic and thermodynamic stability increased as expected. As shown in Fig. 8(B), even after 7 months at 295 K, the isothermally aged ordinary glass had a higher enthalpy than the vapor-deposited sample which was created in approximately 1 h. It is not obvious how to compare the kinetic stability of these two samples since the shapes of the  $C_p$  curves are dissimilar.

## DISCUSSION

By controlling the substrate temperature during the vapor deposition of indomethacin, we have been able to create glasses of varying kinetic and thermodynamic stabilities. Depositions onto substrates near 265 K show the greatest kinetic and thermodynamic stability. When compared to glasses prepared by cooling the liquid, glasses created in 1 h by vapor deposition have thermodynamic stabilities that exceed ordinary glasses aged for up to 7 months.

In this section, we will focus on three topics. First, we rationalize the results presented here by a mechanism based upon enhanced surface mobility at the glass/vacuum interface during vapor deposition. Second, we discuss the influence of the substrate material on the glasses that are formed and use this information to argue against two alternative mechanisms for the formation of stable glasses. Finally, we compare our data with previous data on vapor deposition from the literature to understand why different deposition protocols yield glasses of differing stabilities.

### Surface mobility

As described in the Introduction, Swallen *et al.*<sup>15</sup> recently demonstrated that extremely stable organic glasses could be prepared by vapor deposition if the substrate temperature is held somewhat below the conventional  $T_g$  of the material. They explained this result in terms of enhanced mobility at the surface of the glass. They argued that mobility in the top few nanometers of the glass during deposition would allow time for configurational sampling before the surface layer is buried by additional molecules arriving from the vapor phase. Thus, in a layer-by-layer fashion, a very stable glass with a low molar volume and a low enthalpy could be constructed.

In order for this mechanism of stable glass formation to be efficient, the surface mobility must be many orders of magnitude faster than the bulk mobility. Swallen *et al.*<sup>15</sup> presented evidence that this is the case for trisnaphthylbenzene. Using neutron reflectivity, they observed interfacial broadening during deposition that was ascribed to surface mobility. At 50 K below  $T_g$  ( $0.85T_g$ ), they estimated the surface structural relaxation time as a few seconds. For comparison, the bulk structural relaxation time of TNB at this temperature likely exceeds 100 years.<sup>25,26</sup> Dramatically enhanced surface mobility has also been reported for other (primarily polymeric) glasses.<sup>6,27–30</sup>

The results in this paper can be interpreted in terms of the surface mobility mechanism and provide additional evidence that it is the correct explanation of stable glass formation. Figures 4 and 6 show that, at a fixed deposition rate of 15 nm/s, stable glass formation is optimized for substrate

temperatures near 265 K. Depositions onto substrates at temperatures above and below 265 K gave rise to IMC glasses with less stability. This trend is expected given the surface mobility explanation. When substrates are held at temperatures near  $T_g$ , surface equilibration should be very rapid and nearly complete. We expect to form glasses in this regime whose properties are essentially those of an equilibrium supercooled liquid at the substrate temperature. Indeed, the observed fictive temperatures in this regime are very close to the substrate temperatures. Thus, materials deposited near  $T_g$  are as stable as they can be (without crystallizing). As the substrate temperature is lowered, surface mobility slows to the point that equilibration during vapor deposition is far from complete. At the lowest substrate temperatures, the substrate is so cold that the surface is no longer mobile. Molecules now hit the surface and stick without any rearrangement creating high energy, low stability films. Deposition between these two extremes maximizes the effects of the enhanced surface mobility and creates the most stable glasses.

This surface mobility mechanism implies that very low substrate temperatures should produce glasses that are less stable than the ordinary glass. The experiments on IMC reported here do not show this result. It is possible that we do not observe this because of the short time that the sample spends at 295 K when transferring the sample out of the deposition chamber. If the samples that we prepared are extremely unstable, then it is reasonable to assume that substantial relaxation would occur quickly at 295 K. As we discuss below, previous *in situ* analysis of vapor deposition experiments on other molecules have observed the formation of unstable glasses at very low substrate temperatures.<sup>8,12-14</sup>

If the surface mobility mechanism is correct, giving the molecules more time at the surface to equilibrate would result in more stable glasses given an appropriately controlled substrate temperature. In data to be presented elsewhere,<sup>31</sup> we have explored this for both IMC and TNB. Lowering the deposition rate by nearly two orders of magnitude results in glasses with much greater thermodynamic and kinetic stability than those presented in this publication. This gives further evidence for the enhanced surface mobility mechanism.

The relaxation that takes place on the surface during deposition may also explain the crystallization seen in scan 1 of Fig. 2(B). As the molecules relax they are able to explore more of the potential energy surface of the system. During this process some groups of molecules may nucleate the crystalline phase. When the sample is subsequently heated into the supercooled liquid state, these nuclei can quickly grow and a substantial portion of the sample can crystallize. There is a second possible explanation for the presence of these crystal nuclei. IMC has a negligible vapor pressure at room temperature and crystals that grow on the chamber walls during a series of vapor depositions may be able to dislodge as the chamber is evacuated. If some of these crystals find the substrate surface, they will supply a nucleation site for growth. At present, we cannot distinguish between these two possibilities.

## Potential influences of the substrate

We tested two hypotheses about how the substrate might influence the properties or analysis of vapor-deposited IMC glasses. We conclude that the substrate has no influence on the results reported here.

It is conceivable that the substrate might somehow template the organization of the IMC molecules. Given the results presented above, this is extremely unlikely. Deposition onto a number of substrates (aluminum, copper, and polycarbonate) produced essentially identical stable glasses of IMC.

We also imagined that the thermomechanical properties of the substrate might be important in the analysis of our samples. It is known that glasses that are constrained by walls or containers can show very different relaxation properties than in the absence of these constraints.<sup>32-37</sup> Since our vapor-deposited glasses adhere well to the DSC pans, and since aluminum has a much smaller thermal expansion coefficient than IMC, the vapor-deposited IMC glasses are under compression as they are heated through the glass transition region. As shown in Fig. 7, we verified that any effect of this compression on the observed  $C_p$  curves is negligible. Samples that were removed from the substrate and loosely packed into a DSC pan gave essentially identical results as samples directly deposited into DSC pans.

One further test was performed to eliminate any possible influence of the substrate on our results. Compressive stresses like those discussed in the previous paragraph occur prior to removal of the vapor-deposited glass from the surface and could conceivably alter the properties of the glass. To eliminate any influence of this stress, we deposited IMC onto polycarbonate. The thermal expansion coefficient of glassy IMC is not known, but for organic glasses,  $\alpha$  is typically  $2 \times 10^{-4} \text{ K}^{-1}$ . Since  $\alpha$  for polycarbonate is  $1.9 \times 10^{-4} \text{ K}^{-1}$ , we expect much less compressive stress on polycarbonate than for glasses prepared on metal substrates. Glasses were removed from the polycarbonate and loosely packed in the DSC pans for analysis. Samples deposited onto and removed from polycarbonate still show the large enthalpy overshoots observed in Fig. 2 in agreement with samples deposited directly into DSC pans. We thus conclude that the substrate has no influence on the glasses that we create or on their subsequent analysis.

## Comparisons to previous literature

As described in the Introduction, the primary goal of this paper is to understand the range of stabilities of glasses formed by vapor deposition. While Ref. 15 and this work report the formation of glasses that are more stable than those produced by cooling the liquid, the previous literature emphasizes that vapor deposition produces quite unstable glasses. Two examples from this previous literature can be directly compared to our results. In the cases of 1-pentene ( $T_g=70 \text{ K}$ ) and butyronitrile ( $T_g=97 \text{ K}$ ),  $C_p$  measurements were performed on vapor-deposited glasses with a calorimeter placed in the deposition chamber.<sup>12,14</sup> For both materials, the authors deposited onto substrates held 20–30 K below  $T_g$ . The fictive temperatures of the vapor-deposited samples were calculated and compared to the liquid cooled sample. In



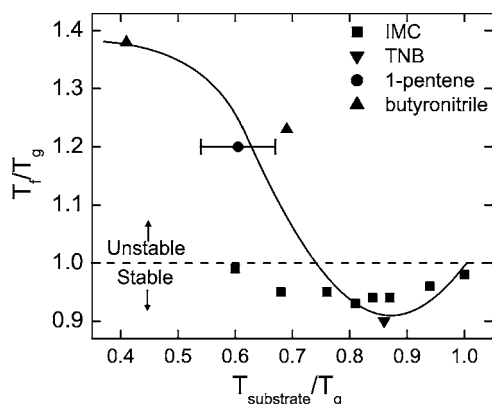


FIG. 9. Thermodynamic stability of IMC glasses in comparison with previous literature. The dotted line indicates the boundary between stable and unstable samples. A  $T_f/T_g$  value equal to unity indicates stability equal to the ordinary glass formed by cooling the liquid. The solid line is a guide to the eye.

both cases, the vapor-deposited glass had a  $T_f$  value much greater than that of the liquid cooled sample. For example, when 1-pentene was vapor-deposited onto a substrate held at 23 K below  $T_g$ ,  $T_f$  was found to be 85 K; note that this is 15 K above  $T_g$ . In contrast, we observed that depositing IMC 20–30 K below  $T_g$  resulted in samples with  $T_f$  values that are 15 K below  $T_g$ .

Work by Turnbull<sup>10</sup> provides the key insight needed to understand the apparently contradictory results for vapor deposition of 1-pentene and IMC. Turnbull considered the problem of producing an amorphous binary metallic glass *via* vapor deposition. Such metallic glasses tend to crystallize much more easily than organic molecules and avoiding crystallization during vapor deposition is the central issue.<sup>7,38</sup> Turnbull argued that the substrate temperature must be low enough so that surface diffusion does not allow nucleation during the deposition process. Treating surface diffusion as an activated process, he argued that the substrate temperature should be less than  $0.25T_g$  in order to avoid crystallization. These low temperatures allow for the atoms at the surface to be configurationally frozen and disallow any rearrangement to minimize the free energy.

While Turnbull did not discuss the formation of stable glasses via vapor-deposition, the above analysis can be adapted to this issue. Low temperature depositions do not allow time for surface equilibration and thus unstable glasses should be expected. Higher temperature depositions will allow surface equilibration that can lead to the formation of very stable glasses. In order to compare materials with a wide range of  $T_g$  values, the ratio  $T_{\text{substrate}}/T_g$  should, to a first approximation, be a reasonable method of estimating where stable glass formation will occur.

Figure 9 compares  $T_f$  as a function of  $T_{\text{substrate}}$  for a number of different systems, in a format suggested by Turnbull's analysis. In broad terms, this figure successfully explains why vapor deposition can yield either highly stable or highly unstable glasses. The data on IMC from this paper, and the results on 1,3,5-(tris)naphthylbenzene from Ref. 15, come from depositions that are quite close to  $T_g$ ; this allows surface mobility to stabilize these glasses. In contrast, depo-

sitions of 1-pentene and butyronitrile occurred at sufficiently low temperature that surface mobility is negligible and unstable glasses were formed. A more fundamental choice for the abscissa in Fig. 9 would involve the product of the surface relaxation time and the deposition rate since this product determines the extent to which equilibration is possible during deposition. Until experiments are available to characterize the surface relaxation of these glasses, the ratio  $T_{\text{substrate}}/T_g$  will likely prove useful.

An important feature of the studies on 1-pentene and butyronitrile is that the thermal characterization was performed *in situ*. As discussed above, it is possible that some enthalpy relaxation occurred prior to DSC analysis for IMC samples with  $T_{\text{substrate}}$  below  $0.7T_g$ , since the sample temperature was raised to room temperature prior to analysis. We speculate that *in situ* analysis of IMC glasses with  $T_{\text{substrate}}/T_g \leq 0.7$  would reveal that the as-deposited glasses are less stable than the ordinary glass and that such experiments would yield data closer to the solid curve shown in Fig. 9. Finally, we note that the substrate temperatures in the study of 1-pentene were quoted to be between 38 and 47 K. A single  $T_f$  value is given for this range of  $T_{\text{substrate}}$  as indicated by the error bar in Fig. 9.

There are additional reports from the literature that may be relevant to the picture presented in Fig. 9. Djuricic *et al.* reported vapor deposition experiments on tris(8-hydroxyquinoline) aluminum,<sup>39</sup> Alq<sub>3</sub>, a material used as an electron transport layer in organic light emitting diodes. They performed photoluminescence studies of Alq<sub>3</sub> films vapor-deposited at room temperature ( $T_{\text{substrate}}/T_g=0.66$ ) and at 373 K ( $T_{\text{substrate}}/T_g=0.84$ ). The samples deposited at  $0.84T_g$  showed greater photoluminescence stability with time than did those deposited at  $0.66T_g$  or those deposited at  $0.66T_g$  and subsequently annealed at  $0.84T_g$ . To our knowledge, thermodynamic characterization of Alq<sub>3</sub> films has not been performed, but the results presented in Ref. 39 are consistent with the expectation that vapor deposition near  $0.85T_g$  creates stable glasses.

Ishii *et al.* recently used Raman scattering to characterize vapor-deposited glasses of 1,2-dichloroethane;<sup>40</sup> these results broadly support the picture presented in Fig. 9. All vapor-deposited glasses of 1,2-dichloroethane crystallized prior to reaching the glass transition temperature and the  $T_g$  value does not appear to be accurately determined for this system (but may be near 110 K). Reference<sup>40</sup> reports that for glasses deposited below 69 K, trans-gauche conformational changes occur as the temperature of the glass is increased. In contrast, glasses deposited at 82 K showed no conformation changes upon heating until crystallization occurred. These results indicate that the lower temperature depositions created materials that are less stable than deposition closer to  $T_g$ .

## CONCLUSIONS

Physical vapor deposition of indomethacin has been studied for substrate temperatures from 190 to 315 K in order to understand the influence of this variable on the thermodynamic and kinetic stability of vapor-deposited glasses.

The chemical and thermomechanical properties of the substrate did not have an influence on the stability of the vapor-deposited IMC glasses. Samples created with substrate temperatures near  $0.85T_g$  showed the greatest stability both thermodynamically and kinetically with samples deposited further below  $T_g$  being less stable. The most stable glasses produced in this study are comparable to those produced by aging an ordinary glass for 7 months. We will show in an upcoming publication that the rate of vapor deposition can be controlled to yield glasses of even greater stability.<sup>31</sup>

We attribute the ability to prepare stable vapor-deposited IMC glasses to enhanced surface dynamics where the top few nanometers of the glass is much more mobile than the bulk. Substrate temperatures used in previous thermodynamic studies of vapor-deposited glasses were well below  $0.85T_g$ , in a regime where the surface dynamics are no longer relevant. This explains why the dominant view in the literature has been that vapor deposition produces unstable glasses.

The ability to create stable glasses quickly with vapor deposition could have important technological consequences in a variety of fields. In pharmaceutical science, there is interest in utilizing amorphous drugs because of their enhanced solubility and bioavailability.<sup>41</sup> Controlling crystallization is a key challenge in this application. The availability of vapor-deposited glasses that are unusually stable may be useful in controlling crystallization. In the field of organic electronics, there is interest in tailoring the properties of individual amorphous layers including stability, density, and index of refraction.<sup>5,39,42-44</sup> A better understanding of the deposition conditions that control these properties for vapor-deposited glasses is likely to result in more useful and reliable devices. The ability to make low energy glasses could also have implications for understanding fundamental aspects of glass formation including the Kauzmann paradox and its potential resolutions.

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