Tunable molecular orientation and elevated thermal stability of vapor-deposited organic semiconductors

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Physical vapor deposition is commonly used to prepare organic glasses that serve as the active layers in light-emitting diodes, photovoltaics, and other devices. Recent work has shown that orienting the molecules in such organic semiconductors can significantly enhance device performance. We apply a high-throughput characterization scheme to investigate the effect of the substrate temperature (Tsubstrate) on glasses of three organic molecules used as semiconductors. The optical and material properties are evaluated with spectroscopic ellipsometry. We find that molecular orientation in these glasses is continuously tunable and controlled by Tsubstrate/Tg, where Tg is the glass transition temperature. All three molecules can produce highly anisotropic glasses; the dependence of molecular orientation upon substrate temperature is remarkably similar and nearly independent of molecular length. All three compounds form “stable glasses” with high density and thermal stability, and have properties similar to stable glasses prepared from model glass formers. Simulations reproduce the experimental trends and explain molecular orientation in the deposited glasses in terms of the surface properties of the equilibrium liquid. By showing that organic semiconductors form stable glasses, these results provide an avenue for systematic performance optimization of active layers in organic electronics.

Significance

Glasses are solids that lack the regular order of crystals. Organic glasses, when produced by deposition from the vapor, can exhibit high levels of molecular orientation that improve performance of devices such as organic light-emitting diodes. We show here that molecular orientation in such glasses is primarily controlled by the substrate temperature during deposition, suggesting that the performance of almost any device based upon amorphous organic materials might be systematically optimized by this route. We explain molecular orientation in the glass in terms of the orientation present near the surface of the corresponding liquid. The highly oriented glasses formed here also exhibit high density and improved thermal stability. These features will likely further enhance the performance of organic electronics devices.


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Equilibrium and becomes the ordinary, liquid-cooled glass. By transition temperature, $T_g$, after which the material falls out of controlled rate. The thickness decreases linearly until the glass after the entire sample has become the SCL, it is cooled at a (SCL). This results in an abrupt change in the film thickness. Here, the glass begins to transform into supercooled liquid compounds form stable glasses, and we show that the orientation of the vapor-deposited molecules is controlled by $T_{\text{substrate}}/T_g$ and is nearly independent of the molecular aspect ratio. Using simulations, we show that anisotropic molecular orientation in the glass can be understood in terms of molecular orientation and mobility near the free surface of the equilibrium liquid. By connecting two apparently disparate bodies of work, we develop avenues for research on organic devices and the physics of glasses, and further the development of "designer" anisotropic solids.

Results

Fig. 1 illustrates our experimental procedure. Molecules are vapor-deposited in a vacuum chamber with base pressure near $10^{-7}$ torr onto a substrate with a controlled gradient of temperatures using a previously described apparatus (21). On a single substrate, this produces many glasses with identical chemical composition but different physical properties (Materials and Methods). The different glasses are characterized using spectroscopic ellipsometry with a focused beam. (C) Example optical constants for TPD at $T_{\text{substrate}} = 215$ K. The optical constants for light polarized normal to (z) and in the plane of the substrate (xy) can be independently determined (49). (D) Using the optical constants, the orientation order parameter, $S_o$, can be computed at each $T_{\text{substrate}}$. $\theta$ is the angle of the long molecular axis relative to the substrate normal and $P_2$ is the second Legendre polynomial. (E) Structures and glass transition temperatures for the three compounds studied.

Fig. 2 illustrates the determination of key material properties of a vapor-deposited glass using spectroscopic ellipsometry. When the "as-deposited" glass is initially heated, it expands as a solid not maintaining its as-deposited molecular orientation. At $T_{\text{onset}}$, which is greater than $T_g$ for all of the materials reported here, the glass begins to transform into supercooled liquid (SCL). This results in an abrupt change in the film thickness. After the entire sample has become the SCL, it is cooled at a controlled rate. The thickness decreases linearly until the glass transition temperature, $T_g$, after which the material falls out of equilibrium and becomes the ordinary, liquid-cooled glass. By comparing the film thickness before and after temperature cycling, we are able to determine the density of the as-deposited glass relative to the ordinary glass ($\Delta \rho$). For temperature gradient samples, $T_{\text{onset}}$ is determined for many glasses during a single heating experiment, whereas $\Delta \rho$ is determined by mapping the sample thickness before and after heating (21).

The three semiconducting compounds investigated here (TPD, NPB, and DSA-Ph) all form stable glasses via vapor deposition. This is illustrated in Fig. 2B by the high onset temperatures and in Fig. 2C by the high densities. The elevated thermal stability of these materials may provide an avenue to increase device lifetime by imparting greater stability to the useful structures formed by the high densities. The elevated thermal stability of these materials may provide an avenue to increase device lifetime by imparting greater stability to the useful structures formed by the high densities.
vapor deposition (see Discussion). The results in Fig. 2 B and C are in good agreement with previously reported results for indomethacin (IMC) (21), the most extensively studied stable glass former, and can be interpreted as follows. At \( T_{\text{substrate}}/T_g \geq 1 \), surface and bulk mobility are high enough to allow total equilibration at the deposition temperature; when the sample is cooled to 293 K for measurement, it becomes the ordinary glass and has the expected values of \( T_{\text{onset}}/T_g \) and \( \Delta \rho \). At lower values of \( T_{\text{substrate}}/T_g \) there is a thermodynamic driving force to form the equilibrium SCL at that temperature resulting in higher stability, higher density materials. The mobility of the surface enables molecules to find these tight packing arrangements (20, 25, 27), even though this would require a prohibitively long time for a bulk material. \( T_{\text{onset}}/T_g \) and \( \Delta \rho \) are maximized when high surface mobility is paired with a large thermodynamic driving force. At the lowest \( T_{\text{substrate}}/T_g \) the surface is so immobile that only marginally stable glasses are formed despite the presence of the largest driving force for densification. Our results are in good agreement with a recent report that NPB forms a stable glass when deposited onto a room-temperature substrate (15).

Using spectroscopic ellipsometry, we find that vapor-deposited glasses of the three compounds are anisotropic, each with continuously tunable average molecular orientation that is well-correlated with \( T_{\text{substrate}}/T_g \). Fig. 3 shows the order parameter, \( S_z \), and the birefringence as a function of \( T_{\text{substrate}}/T_g \). Using films 70–150 nm thick, \( S_z \) is computed from the dichroism of the absorption associated with the long axis of each molecule (SI Text, Computing the Orientation Order Parameter). As shown in Fig. 1D, \( S_z \) is a measure of the average orientation of the long axis relative to the surface normal. At the lowest temperatures, \( S_z \) closely approaches the limit (\( S_z = -0.5 \)) where the long axes of all molecules lie in the plane of the substrate. Such horizontal alignment may be useful in increasing the light outcoupling efficiency of emitting molecules (2), or the absorption of light in the photoactive layer of a solar cell. Using films 70–900 nm thick, the birefringence, \( \Delta n = n_x - n_y \), is calculated at 632.8 nm; \( \Delta n \) results from molecular orientation and the anisotropic polarizability tensors of these molecules. By comparing different samples and models, we estimate that the \( S_z \) and \( \Delta n \) values reported in Fig. 3 are accurate to \( \pm 0.05 \) and \( \pm 0.01 \), respectively.

Our high-throughput methodology allows us to differentiate between the effect of molecular shape and \( T_{\text{substrate}}/T_g \) for the first time, to our knowledge. The influence of these two variables on molecular orientation has been studied by Yokoyama (3) and our results are broadly consistent with this previous work. Whereas Yokoyama concluded that molecules with more anisotropic shapes produce more anisotropic materials (30, 31), our extended data show in addition that even relatively short molecules like TPD and NPB can be significantly oriented, as long as \( T_{\text{substrate}}/T_g \) is correctly chosen. Given the similar trend observed for the three different compounds studied here, we propose that the parameter which primarily controls the orientation of linear molecules is \( T_{\text{substrate}}/T_g \) rather than molecular aspect ratio. This is a significant change in perspective, as it suggests that a wide range of molecular orientations might be achieved with almost any organic compound.

To understand the origin of molecular orientation in vapor-deposited glasses, we simulated the vapor deposition of a coarse-grained representation of TPD composed of six Lennard-Jones spheres connected by harmonic springs (Fig. 4, Inset). We used a previously described algorithm that mimics the essential features of the deposition process (Materials and Methods) (32). A small number of molecules is introduced to the simulation box in the gas phase and allowed to condense at the free surface of a growing film. The just-deposited molecules are maintained at an elevated temperature to mimic the effect of enhanced surface mobility; these molecules are then gradually cooled to the substrate temperature. After an energy minimization step, the next
group of molecules is introduced. The process is continued until a vapor-deposited film with a thickness of roughly 15 molecular diameters is obtained. These simulations were performed over a range of substrate temperatures. Fig. 4 shows that the molecular orientation in these simulated vapor-deposited films has the same dependence upon substrate temperature as observed in the experiments shown in Fig. 3A. In particular, near $T_g$, the simulated glasses display a weak tendency to orient molecules normal to the substrate, and at lower temperatures a stronger tendency to orient molecules in the plane of the substrate. The simulated glasses exhibit high density and high onset temperatures, in analogy to Fig. 2 (SI Text, Simulations). Note that this model was designed to explore the generic features of the experiments and has not been parameterized against atomistic simulations, ab initio calculations, or the experimental results.

Molecular orientation in vapor-deposited glasses can be understood to be a remnant of the molecular orientation present near the surface of the equilibrium liquid. We performed additional simulations, using conventional molecular dynamics, to investigate the order parameter and density for thin films of the equilibrium liquid above $T_g$. These results are shown in Fig. 5A and B. Molecules nearest the free surface ($0 < z < 1.5$, in bead diameter units) have a propensity to lie in the plane of the surface. Further from the surface as the liquid reaches the bulk density ($1.5 < z < 3.5$), molecules have a tendency to orient vertically, and this tendency becomes stronger at lower temperatures. Beyond $z = 3.5$, orientation in the liquid is isotropic, as expected for a bulk liquid. At a given deposition rate, there will be some substrate temperature at which surface mobility is just sufficient to equilibrate the surface to a depth of $z = 2.5$ but no further. Molecules at this depth show a tendency toward vertical orientation and will become locked into this orientation when further deposition takes place.

Within the context of the simulations of the deposition process, we can test this hypothesis for the origin of molecular orientation in the glass. We quantify the depth at which molecular orientation becomes fixed during deposition by calculating $P_2(\mu_{\text{final}})$, where $\mu_{\text{final}}$ is the orientation of the long axis of the molecule after the deposition is complete. This function, shown in Fig. 5C, approaches unity as each molecule attains its final orientation in the glass and we use the 1/e point of this approach to define the thickness of the equilibrated layer at the free surface during deposition. We observe that equilibration to $z \sim 2.5$ occurs near $T_{\text{sub}}/T_g = 0.99$, and Fig. 4 shows that this indeed is the vapor-deposited glass with the maximum value of $S$. At $T_{\text{sub}}/T_g = 0.86$, the surface will only be equilibrated to a depth of $z \sim 1$. At this depth, molecules tend to be orientated parallel to the surface, and this orientation becomes locked into the glass. When $T_{\text{sub}}/T_g$ is above 1.02, mobility extends far enough into the film to ensure that an isotropic set of orientations are trapped in the vapor-deposited glass. We note that this explanation accounts for the qualitatively different dependences of $S$ and $\Delta \rho$ upon the substrate temperature, as shown in Figs. 2 and 3.

The simulations suggest that orientation in vapor-deposited organic glasses is explained by two factors: (i) molecular orientation near the free surface of the equilibrium liquid at $T_{\text{sub}}$, and (ii) mobility near the surface of the glass. The first factor might be investigated in greater detail with atomistic simulations and surface sensitive spectroscopy (33), whereas a number of new experimental methods are available to probe dynamics at the surface of glasses (25, 34). Structure at liquid surfaces is an active area of study (35, 36), and our results indicate that physical vapor deposition might be a useful tool in this endeavor.

**Discussion**

We anticipate that these results can influence work in organic electronics and related fields in several ways. Molecular orientation is already recognized as a key factor influencing device performance (1, 2, 4, 5, 10–15, 37, 38) and our results provide a predictive tool for choosing the deposition temperature needed to produce the desired orientation, effectively adding a dimension to device design. The ability to predictably tune refractive indices across a wide range is analogously useful in applications that rely on redirection of light, such as waveguides or antireflective coatings (39). Although the results shown in Fig. 3 are only known to apply to molecules of roughly linear shape, they suggest that a more general understanding of molecular orientation in vapor-deposited glasses may be attainable with high-throughput characterization and simulations. It is possible that liquid-crystal–forming molecules or systems with specific intermolecular interactions will exhibit orientation trends distinct from those found here, and this would be a further route toward control of molecular anisotropy in glassy solids. High-throughput experiments that directly measure charge mobility (16–18) would complement the results presented here.

Because the three systems investigated here show the density and onset temperatures expected for stable glasses, we anticipate that organic semiconductors will generally have other stable glass properties that should provide control over some known failure modes (40–42). For example, high glass density reduces uptake of atmospheric gases which can cause chemical degradation (43). Also, it is likely that stable semiconductor glasses will transform via a surface-initiated mobility front (26, 44, 45), allowing the
possibility of further enhancing thermal stability by engineering device interfaces.

These results also open avenues for increasing our fundamental understanding of glasses. At present, it is hard to discern what features of local packing provide the structural basis for high stability glasses. The anisotropic packing of these organic semiconductors provides additional experimental observables related to local structure [e.g., molecular orientation and anisotropic charge mobility (7)], thus providing the opportunity for a comprehensive understanding of structural stability in amorphous packing. One could ask whether it is possible to prepare stable glasses that do not have substantial anisotropy. Such systems would be ideal for understanding how the Kauzmann entropy crisis is resolved for very deeply supercooled liquids (46). Finally, anisotropy can be viewed as a type of ordering that drives a glass toward crystalline or liquid crystalline states. The existence of highly anisotropic glasses raises the question whether there is a level of anisotropy that cannot be surpassed while maintaining the macroscopic homogeneity associated with amorphous packing.

Materials and Methods

Experimental Methods. Our procedure for preparation and measurement of samples has previously been discussed (21). Physical vapor deposition of samples takes place inside a vacuum chamber with base pressure near 10⁻⁷ torr. After evacuating the chamber with a turbomolecular pump (occasionally in concert with cryopumping to lower the partial pressure of water) a copper cold cup is cooled via liquid-nitrogen–cooled gas. This copper cup is mechanically coupled to two fingers supporting a single substrate that are mechanically coupled to two fingers supporting a single compound, the two fingers are set to different temperatures, Tg, for TPD and NPB is determined by heating and cooling at 2.4°C/min. Substrate temperatures are confirmed by comparison of temperature gradients samples to single-temperature substrates. The glass transition temperature, Tg, for TPD and NPB is determined by heating and cooling at 2.4°C/min. Once the deposition is complete, the entire sample is brought to 293 K. The simulation box size is 20nm × 20nm in the plane of the substrate (x–y), and at least 10nm larger than the deposited film thickness normal to the substrate (z). Periodic boundary conditions are applied in the x–y plane. The substrate is generated from 1,000 randomly placed smaller Li particles. The LJ potential parameters for the substrate are chosen in such a way to minimize their effect on deposited molecules and prevent undesirable ordering (47). The parameters for the interaction with other substrate atoms are s = 0.6, c = 0.1, and with beads representing benzene rings s = 1.0 and c = 1.0, with a cutoff distance of 2.5nm, where σ_{e,b} ∈ s,b. All substrate atoms are fixed to their random initial position with harmonic springs.

The simulated vapor deposition process is analogous to that reported earlier (9, 32). Iterative cycles are repeated until a film with thickness of ~33nm is grown. Each cycle consists of (i) introduction of four randomly oriented molecules in proximity of the film surface, (ii) equilibration of newly introduced molecules at high temperature (T = 1.0), (iii) linear cooling of these molecules to the substrate temperature in 7 × 10⁵ time steps, and (iv) energy minimization of the entire system. The previously deposited molecules and the substrate particles are maintained at a constant temperature throughout the process using a separate thermostat. For the results shown in Fig. 4, the order parameter is calculated from the middle layer of the films to represent stable glasses that do not have substantial anisotropy. The equilibrium liquid profiles in Fig. 5 A and B were obtained by conventional molecular dynamics simulations and represent time averages over simulation runs comprising 10⁸ time steps. All simulations were performed using the Large-Scale Atomic/Molecular Massively Parallel Simulator package (48) in the canonical ensemble with simulation time step of 0.001.

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