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Vapor Deposition of a Smectic Liquid Crystal: Highly Anisotropic, Homogeneous Glasses with Tunable Molecular Orientation

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ABSTRACT

Physical vapor deposition (PVD) has been used to prepare glasses of itraconazole, a smectic A liquid crystal. Glasses were deposited onto subtrates at a range of temperatures ($T_{substrate}$) near the glass transition temperature (T_g), with $T_{substrate}/T_g$ ranging from 0.70 to 1.02. Infrared spectroscopy and spectroscopic ellipsometry were used to characterize the molecular orientation using the orientational order parameter, S_z, and the birefringence. We find that the molecules in glasses deposited at $T_{substrate} = T_g$ are nearly perpendicular to the substrate ($S_z = +0.66$) while at lower $T_{substrate}$ molecules are nearly parallel to the substrate ($S_z = -0.45$)**.** The molecular orientation depends on the temperature of the substrate during preparation, allowing layered samples with differing orientations to be readily prepared. In addition, these vapor-deposited glasses are macroscopically homogeneous and molecularly flat. We interpret the combination of properties obtained for vapor-deposited glasses of itraconazole to result from a process where molecular orientation is determined by the structure and dynamics at the free surface of the glass during deposition. Vapor deposition of liquid crystals is likely a general approach for the preparation of highly anisotropic glasses with tunable molecular orientation for use in organic electronics and optoelectronics.

KEYWORDS vapor deposition, liquid crystals, glasses, molecular orientation

INTRODUCTION

Control of molecular orientation and packing in the solid-state is a long-standing goal in chemistry, and a wide variety of approaches have been utilized to obtain both equilbrium and nonequilibrium structures. In crystal engineering, for example, molecular structure is manipulated to produce a desired equilibrium packing arrangement. For nonequilibrium solids such as glasses, there is a much richer range of possible structures. While the traditional view of glasses has been that packing is highly disordered and molecules are randomly oriented, recent work has challenged this paradigm.

Physical vapor deposition (PVD) is a relatively new approach for controlling molecular organization in solids, with the advantage that a functional solid can be prepared directly without subsequent thermal processing. Organic glasses prepared by PVD with the substrate temperature ($T_{substrate}$) near the glass transition temperature (T_g) can show remarkable properties. Due to enhanced mobility at the surface of the glass, high density[1–4], high kinetic stability[1–3,5–8], and low enthalpy[5,7–12] materials can be prepared. Yokoyama and others[1,13–16] showed that PVD glasses can be anisotropic with a preferred molecular orientation. Recently, Dalal et al. showed[4] that molecular orientation in PVD glasses of organic semiconductors can be systematically tuned by changing $T_{substrate}$ while maintaining high density and high kinetic stability. For deposition near 0.95 T_g, rod-like molecules show a slight tendency to orient normal to the substrate, while at lower substrate temperatures molecules show a strong tendency to lie parallel to the substrate.

Molecules with liquid crystalline (LC) phases have attracted special attention in efforts to control molecular orientation in the solid state. A principal reason for this attention is that for these systems there are well-developed methods to control molecular orientation in the fluid state. Molecular alignment achieved in the fluid can then be transferred into the solid state in two ways. In one approach, the LC phase organizes molecules over large areas and subsequent cooling prepares crystals that inherit orientation from the LC phase.[17] In a second method, the order of the LC phase is transferred into a solid by cooling into a nonequilibrium glassy state.[18] Both of these approaches have been utilized recently to show that molecules with LC phases can create optimal molecular orientation in the active layers in electronic and optoelectronic devices[18] such as organic photovoltaic cells (OPVs), organic field effect transistors (OFETs) and organic light emitting diodes (OLEDs).[17,19–21] Columnar phases are of particular interest due to high overlap of aromatic cores that can result in high charge mobility along the columns.[20,22,23] Solids prepared from smectic liquid crystals, which show strong layering with the long axes of the molecules nearly perpendicular to the layer boundaries, have also found utility.[17,21] For example, glassy films formed from a smectic B phase were shown[24] to have better charge carrier transport than a polycrystalline film formed from the same molecules. Effective molecular orientation in solids, glassy or crystalline, prepared from LC phases may require substrate treatments that align molecular tilt relative to the substrate in order to optimize molecular orientation, thus charge transport.

Very recently PVD has been utilized as a third approach to prepare solids with controlled molecular orientation from LC molecules. In the past, PVD was mainly used[23,25] as a way to obtain crystalline thin films from LC precursor states. However, PVD of LC glass formers can provide a direct route to solids with useful internal organization. For example, it was recently demonstrated[26] that as-deposited films of a perylene-based columnar LC material had an electrical response similar to a thermally annealed sample and far superior to a spin-coated sample. The structure of the as-deposited sample is proposed to be similar to the columnar LC phase.

In this report, we demonstrate that PVD of LC molecules provides new opportunities for controlling molecular orientation in the solid state beyond what is achievable with non-LC molecules or with the thermal treatment of pre-aligned LC phases. We report that vapor deposition of a model smectic A glass former results in macroscopically homogeneous films with molecular orientations that can be tuned over a much wider range than achievable for non-LC molecules.[4] Glasses of itraconazole were vapor-deposited onto substrates held at temperatures near T_g and then characterized by IR spectroscopy and spectroscopic ellipsometry. For $T_{substrate}$ close to T_g, the itraconazole molecules are nearly vertically oriented while at lower $T_{substrate}$ they are nearly parallel to the substrate. Deposition of layered films shows that the molecular orientation of the top layer depends on the temperature of the substrate and not on the molecular orientation of the underlying layer. In addition, atomic force microscopy and polarized optical microscopy show that the as-deposited glasses are molecularly flat and macroscopically homogeneous. The deposition of this smectic LC system results in glasses with a much larger range of orientations than previously achieved for similar rod-like molecules without known LC states.

We interpret the combination of properties achieved by vapor deposition of itraconazole to result from a process where molecular orientation in the glass is determined by the structure and dynamics at the free surface during deposition of the glass. This suggests that PVD with control of the substrate temperature will generally be a useful strategy for producing tunable molecular solids from LC molecules. The ability of PVD to produce molecularly smooth glass films suggests that this method might be particularly useful for preparing multilayer structures with nanoscopic resolution, with each layer having distinct molecular orientation. Such multilayer structures would be difficult to prepare by other methods that involve the alignment of LC phases in the fluid state.

EXPERIMENTAL METHODS

Vapor deposition: Itraconazole was obtained from Sigma Aldrich (≥ 98 %) and Acros Organic (99 %) and used without further purification. Films were vapor deposited at pressures of 10^{-7} torr in a custom-built vacuum chamber. Silicon wafers with a native oxide layer (Virginia Semiconductor; cut to approximately 3.6 cm in length and 1 cm in width) were used as substrates and double-sided polished wafers were used for IR measurements. Substrates were cleaned with ethanol, acetone and deionized water prior to deposition. A custom-built temperature gradient stage was used as a sample holder. During deposition, the ends of the substrate were held at two different temperatures, resulting in a temperature gradient along the wafer such that glasses with different $T_{substrate}$ were deposited simultaneously; additional details are described in an earlier publication[2]. The samples were deposited at rates of 0.2 ± 0.03 nm/s; the deposition rate and thickness of the samples were monitored during deposition using a quartz crystal microbalance (Sycon).

Infrared measurements: Spectra were recorded in transmission at normal incidence with a Bruker EQUINOX55 and a KBR-5 Holographic Wire Grid polarizer, using an aperture size of 1.85 mm, 2 cm^{-1} resolution, and averaging 64 scans. The absorbance obtained was independent of polarization direction, indicating uniaxial anisotropy. A custom-built holder allowed the sample to be reproducibly translated to obtain absorbance data from glasses at different positions on the substrate, corresponding to different substrate temperatures during deposition.

Determination of orientational order parameter (S_z) from IR: The absorbance of an IR transition dipole oriented along the long axis of the molecule can be used to calculate the orientational order parameter S_z. For a uniaxially anisotropic film, Equation 1 can be used to calculate S_z:

$$S_z = 1 - \frac{A}{A_0} \qquad (1)$$

The absorbance A was measured in the as-deposited glasses; the absorbance was independent of polarization direction, consistent with uniaxial anisotropy. A_o was obtained by heating the sample into the isotropic liquid (368 K) followed by fast quenching; the quenched samples were confirmed to be optically isotropic by ellipsometry. An equation analagous to equation 1 was recently utilized to determine molecular orientation from electronic transitions in the near UV. [27]

Spectroscopic ellipsometry measurements: Data was collected at room temperature with a J.A. Woollam M-2000U spectroscopic ellipsometer using seven incident angles and focusing optics (1.5 mm × 0.6 mm beam size). Data in the wavelength range from 500 to 1000 nm was modeled using a uniaxial anisotropic Cauchy model. The birefringence ($\Delta n = n_z - n_{xy}$) for samples quickly quenched from above the clearing temperature was 0.006, consistent with essentially isotropic molecular orientation.

Bilayer experiments: After depositing an initial layer, the deposition was paused by shielding the sample from the evaporating source while the substrate temperature was adjusted. The shield was removed and a second layer was deposited on top of the first layer. The samples were characterized by ellipsometry. The data was successfully modeled as two layers with independent optical constants, with each layer utilizing an anisotropic Cauchy model. (Additional details in the *Supporting Information*).

Polarized optical microscopy and AFM: An Olympus BX51 microscope was used in reflection with a Lumenera INFINITY 1-1c camera. Images were taken using crossed polarizers and a first order retardation plate; this is the source of the magenta tint in Figures 5c and 5d below. Images were processed in Image J freeware and adjusted for brightness and contrast. AFM measurements were done at room temperature using a Bruker BioScope Catalyst in Tapping Mode®. Images were flattened to a 3rd order plane.

RESULTS AND DISCUSSION

Glasses of itraconazole (Figure 1a) were prepared at many different substrate temperatures by PVD. As explained above, samples were deposited onto a silicon wafer attached to a sample holder which enforced a temperature gradient during deposition (Figure 1b). The substrate temperature was varied from 242 to 335 K. Bulk samples of itraconazole (Figure 1a) show two LC transitions[28] (isotropic to nematic at 363 K and nematic to smectic A at 346 K) and form a smectic A LC glass at temperatures below T_g = 330 K.[29]

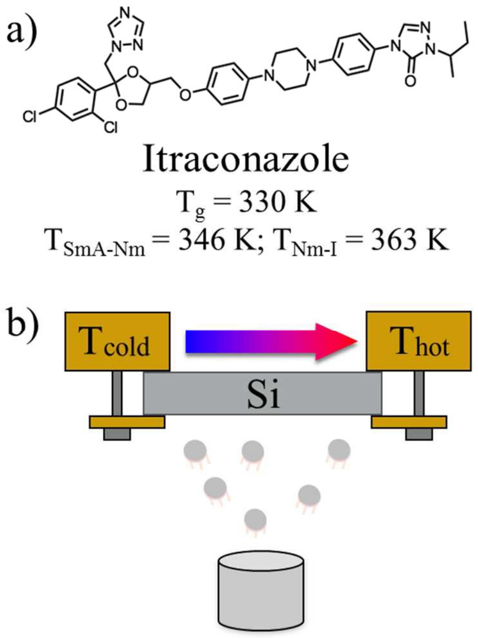

Figure 1. Vapor deposition of itraconazole: a) molecular structure, b) deposition scheme for simultaneous preparation of glasses across a range of substrate temperatures.

Molecular orientation in PVD glasses of itraconazole was characterized by IR spectroscopy and ellipsometry. Transmission IR measurements at normal incidence were performed at room temperature. Tarnacka and collaborators have reported[30] that the absorption at $\bar{\nu} = 1512$ cm^{-1} in itraconazole (Figure 2) can be attributed to the in-plane bending of the C-H bonds in the phenyl groups. These absorptions have transition dipoles nearly along the long axis of the molecule and can be used to probe the molecular orientation of the long axis. As seen in Figure 2 absorbance at $\bar{\nu} = 1512$ cm^{-1} decreases with increasing $T_{substrate}$; this is consistent with a greater tendency for the molecular long axis to lie in the plane of the substrate.

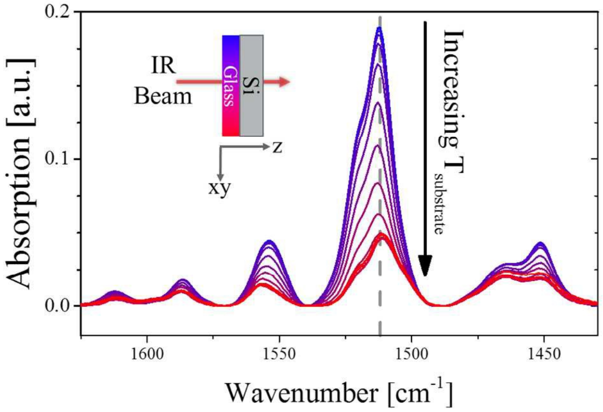

Figure 2: IR spectra of 650 nm thick glasses of itraconazole deposited at different substrate temperatures (279-353 K) taken at normal incidence (inset). The absorption at $\bar{\nu} = 1512$ cm^{-1} is strongest in films in which the molecular long axis is parallel to the substrate.

A high degree of control over molecular orientation in PVD glasses of itraconazole can be obtained by controlling the substrate temperature during deposition. Figure 3a shows the orientational order parameter S_z and the birefringence for the as-deposited glasses. Equation 1 was used to calculate the orientational order parameter (S_z) from transmission IR measurements.

Thickness and birefringence of all glasses were determined from spectroscopic ellipsometry. A value of $S_z = 1$ means that all the molecular long axes are perpendicular to the substrate while $S_z = -0.5$ indicates all molecules lie in the plane of the substrate. As shown in Figure 3a, at $T_{substrate}$ near T_g, the molecules are nearly vertically oriented relative to the substrate ($S_z = +0.66$). This is consistent with the order parameter previously observed[30] in the equilibrium smectic state for itraconazole on a substrate that promoted perpendicular orientation. In Figure 3a, S_z decreases systematically as the substrate temperature during deposition decreases and is as low as -0.45 for $T_{substrate} = 0.80\ T_g$, indicating molecules lying nearly parallel to the substrate; the uniaxial anisotropy observed by IR and ellipsometry indicates random orientations in the plane of the substrate on the millimeter scale. The S_z values obtained from IR are in excellent agreement with the birefringence data as expected when the transition dipole lies along the axis of greatest polarizability. For comparison in Figure 3a, we present previously reported[4] S_z data for PVD films of DSA-Ph (1–4-Di-[4-(N,*N*-diphenyl)amino]styryl-benzene); the range of S_z values shown (-0.4 to +0.2) is the largest reported for any organic molecule without LC states. Figure 3b illustrates schematically that the range of molecular orientation that can be obtained in glasses of a smectic liquid crystal former is much larger. In addition, Figure 3a illustrates that molecular orientation for vapor-deposited itraconazole films is independent of film thickness from 180-1800 nm.

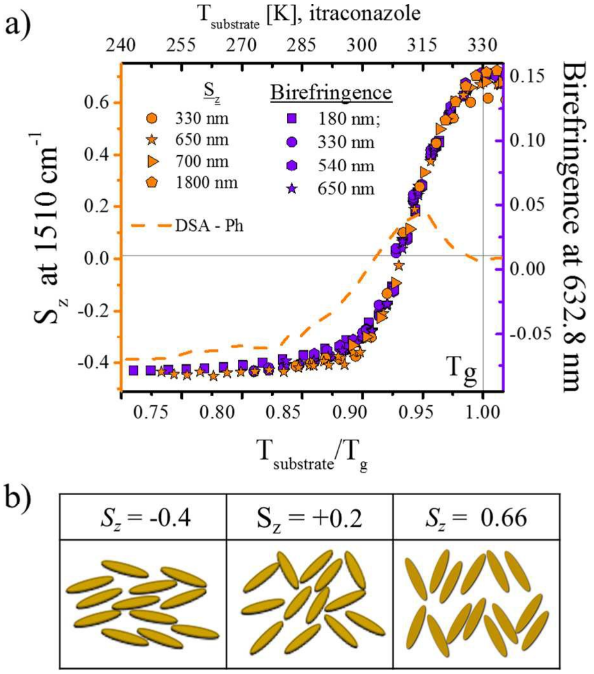

Figure 3. Molecular orientation in vapor-deposited glasses of itraconazole. a) The orientational order parameter S_z from FTIR (orange points) and the birefringence ($n_z - n_{xy}$; purple) from ellipsometry show that molecular orientation can be controlled by the temperature of the substrate during deposition. For comparison, the dashed line shows averaged S_z values for DSA-Ph, a molecule without LC phases, from ref. 4. b) Schematics of molecular orientation, illustrating the enhanced vertical orientation attained by itraconazole in comparison with DSA-Ph.

Analysis of two bilayer samples were consistent with the view that molecular orientation depends solely on the temperature of the substrate during deposition and not on the nature of the underlying layers. For these experiments, the substrate temperature was adjusted between the deposition of the first and second layers. Samples were measured using spectroscopic ellipsometry and the data was successfully modeled using two anisotropic Cauchy layers. As indicated by the schematics in Figure 4 and described in the *Supporting Information*, the birefringence (and thus the molecular orientation) of each layer is determined by the substrate temperature during deposition. For a given substrate temperature, the birefringence of a layer was the same within 0.003 if deposited directly onto silicon or on top of a glass with different orientation. Thus, in these experiments, molecular orientation depends solely on the temperature of the substrate during deposition independent of the molecular orientation of the underlying layer.

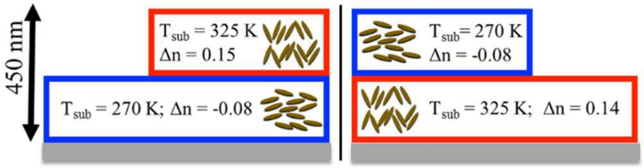

Figure 4. Schematic illustration of molecular orientation of itraconazole in two bilayer samples. In these experiments, the birefringence and molecular orientation of the upper layers depends only on the substrate temperature and not on the orientation of the underlying layer.

Atomic force microscopy (AFM) and polarized microscopy confirmed that the deposited films are homogeneous, molecularly flat glasses across the range of substrate temperatures. Figures 5a and 5b show AFM scans. Glasses deposited at low substrate temperatures show only 1 nm fluctuations in height (inset of Figure 5a). Films prepared by deposition at T_g (Figure 5b) show 3 nm fluctuations; this is comparable to the reported[30] length of itraconazole and is thus consistent with the molecular orientation of the molecules perpendicular to the substrate. Polarized microscopy images (Figures 5c and 5d) acquired with crossed polarizers and a full wave retardation plate show no birefringence in the plane of the substrate, consistent with the uniaxial anistropy observed with IR and ellipsometry. These films are homogeneous oriented solids without evidence of domain boundaries. Future work will investigate the extent of smectic layering in these films.

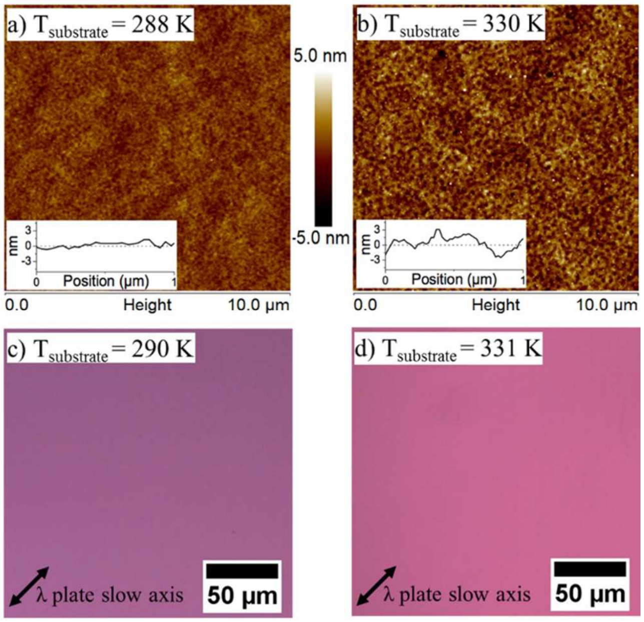

Figure 5. Vapor-deposited films of itraconazole are molecularly flat and optically homogeneous. a, b) AFM images from samples deposited at two substrate temperatures. Insets show that the samples are flat with 1 nm fluctuations at $T_{substrate}$ = 288 K and 3 nm fluctuations at $T_{substrate}$ = 330 K; the latter is consistent with vertical orientation of the molecules. c, d) Polarized optical microscopy images (20 X) for $T_{substrate}$ of 290 and 331 K indicate macroscopic homogeneity; results at other $T_{substrate}$ were similar.

We interpret the combination of properties obtained for vapor-deposited glasses of itraconazole to result from a process where molecular orientation is determined by the structure and dynamics at the free surface of the glass during deposition. Our speculative interpretation makes an analogy with the recently[4] proposed mechanism for molecular orientation of PVD glasses of non-LC materials. For that case, computer simulations[4,31] have shown that, during deposition, the surface of the glass tends to equilibrate toward the interfacial structure of the equilibrium liquid at the deposition temperature; the value of $T_{substrate}$ determines the surface mobility and thus controls the extent to which the equilibrium structure can be attained. The key point is that the equilibrium structure near the free surface is not isotropic. During deposition, molecules near the surface orient in response to the surface and then subsequent deposition locks these oriented molecules into place. As described in ref. 4, this mechanism can explain the qualitative features of the DSA-Ph data shown in Figure 2b. We propose that this interpretation also is applicable to vapor-deposited glasses of itraconazole, with the understanding that the structure of the equilibrium surface will be quite different. For itraconazole near T_g, we assume that the long axes of the molecules at the free surface will have a preference to orient nearly perpendicular to the surface, as expected[32] for a smectic A phase at the air interface. Near T_g, there is enough mobility for this structure to be attained during deposition and this explains the high values of S_z displayed in Figure 2b. Our results show that at substrate temperatures below 0.8 T_g, itraconazole molecules lie parallel to the substrate. In this regime, mobility at the surface is insufficient to organize smectic layers and the incoming molecules lie parallel to the free surface in order to minimize the energy; orientation in this regime is similar to that observed for molecules that do not have LC phases (e.g., DSA-Ph in Figure 2b). This proposed surface-assembly mechanism is qualitatively consistent with all our results, especially the observation that molecular orientation apparently does not depend upon the nature of the substrate. We anticipate that recent computer algorithms that mimic the deposition process[4,31] can provide a test of the proposed surface-assembly mechanism.

Glasses of itraconazole prepared by vapor deposition have a combination of properties that, to our knowledge, have not been reported elsewhere. While crystalline films prepared from smectic LC precursors can be highly ordered[25], we have prepared solids in which molecular orientation is nearly vertical, nearly horizontal, or somewhere in between by controlling the temperature of the substrate during deposition. While it is possible to control molecular orientation in vapor-deposited glasses without utilizing LC materials[1,4,13–16], we have prepared far more ordered materials with itraconazole without sacrificing macroscopic homogeneity. The orientational order parameter range for itraconazole (-0.46 to +0.66) is near the extremes of what is theoretically possible for linear molecules. While previous work has obtained high orientational order in LC materials by thermal processing[17,23,25,33,34], we prepared highly ordered materials directly in the as-deposited film. Because of this, we can prepare layered structures that could never be attained in an equilibrium material and which would be very difficult to obtain if each layer independently required thermal processing.

CONCLUSION

Here we report that vapor deposition of itraconazole, a model liquid crystalline glass former, results in glasses with high molecular orientation at substrate temperatures near the glass transition temperature. Molecular orientation can be controlled over a wide range through a 50 K change in the temperature of the substrate during deposition. The as-deposited films are molecularly flat and optically homogeneous. Layered structures of different molecular orientations can be readily prepared by this route in contrast to approaches that require thermal processing to attain order. We explain these results in terms of a mechanism in which the free surface organizes molecular orientation during deposition. Our proposed mechanism suggests that PVD may also prepare interesting ordered structures of other LC phases, and that the substrate temperature might allow significant control of the structure. Very recent work by Eccher et al.[26], involving vapor deposition of a columnar LC system at a single substrate temperature, is consistent with this view.

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