DOE final report: Physical vapor deposition of organic glasses (DE-SC0002161)

Abstract: As of 2009, when this project began, it had been established that physical vapor deposition (PVD) could produce high density and high stability ("ultrastable") glasses of two organic molecules. With this project, we established that ultrastability was a quite general result for PVD glasses of organic molecules and, in particular, for the organic semiconductors used to produce organic light emitting diodes (OLEDs). We established that ultrastable glasses have enhanced photochemical and chemical stability, and increased resistance to crystallization. We developed a temperature-gradient deposition stage to more efficiently screen the properties of PVD glasses. We established that PVD glasses are usually anisotropic and that this anisotropy can be controlled. We characterized the unusual transformation mechanism of PVD glasses, which superficially is more similar to crystals than liquid-cooled glasses. In the most recent grant cycle, we extended these results to co-deposition of two organic semiconductors, showing that mixed PVD glasses of these systems usually showed ultrastability and high density; in two cases, co-deposition results in component segregation, and deposition conditions can be adjusted to control domain size. In our work since 2009, we established that the surface equilibration mechanism can successfully explain almost all of the properties of PVD glasses, and that this mechanism can provide useful predictions regarding stability and anisotropy.

Publications and Patent: This project was funded by DOE from 2009 until 2024. It resulted in 41 publications. For the convenience of the reader, these 38 publications are ordered by publication year: (2011)[1,2,3]; (2012)[4, 5,6,5,7,8]; (2013)[9,10]; (2015)[11,12,13,14,15]; (2016)[16,17]; (2017)[18,19,20,21,22,23]; (2018) [24,25,26,27]; (2019)[28,29,30,31]; (2020)[32,33,34]; (2021)[35,36]; (2022) [37]; (2023)[38]; (2024)[39,40,41]. These publications have been influential, as indicated by an average of nearly 60 citations per publication (Web of Science). In addition, this project funded (or partially funded) the Ph.D. research of 8 students, and resulted in one patent.[42]

Introduction: Glasses combine the disordered structure of a liquid with the mechanical properties of a solid.[6] For crystals, long-range structural regularity is the basis for understanding a wide range of physical properties including thermodynamics, molecular transport, and mechanical properties. The long-range disorder of glasses has meant that it is much more challenging to understand these same physical properties at a fundamental level. Amorphous materials play an important role in modern technology, including polymers, inorganic and metallic glasses, amorphous semiconductors, and amorphous pharmaceuticals. In spite of their utility, glasses are *unstable* in two different respects. All glasses are continuously undergoing physical aging as they attempt to equilibrate into the supercooled liquid. Glasses are also unstable with respect to crystallization, which will occur once crystal nuclei are formed.

Increasing the stability of glasses has major implications, and prior to the start of this project, we had established the surprising result that "ultrastable" glasses could be formed using PVD, using two organic molecules that were model glassformers. We had shown for these two molecules that, relative to the liquid-cooled glass of the same compound, ultrastable PVD glasses had higher density (by about 1.3%), higher thermal stability (by about 7%), and higher moduli (by about 15%). In principle, higher density, stability, and moduli can all be attained by cooling a liquid into the glassy state more slowly, because this allows for greater equilibration. However, we estimated that it would take thousands of years or more to match the properties of ultrastable PVD glasses by liquid-cooling, because extremely slow cooling rates would be required. Thus PVD produces unique glasses that might have been considered "impossible materials". In our pre-DOE work, we showed that ultrastable glass do not undergo appreciable physical aging, because as-prepared they are equivalent to already aged glasses. At the start of this project, it was not known whether ultrastable glasses are more stable with respect to crystallization; they are, at least in some cases, as we discovered with DOE support and discuss below. All the work described below was performed as a result of DOE support.

High throughput preparation and characterization of PVD glasses: Early work showed that the substrate temperature during deposition had a strong impact on the properties of PVD glasses. In particular, for the two compounds initially studied, deposition near 0.85 Tg produced the most stable glasses (here Tg is the glass transition temperature of a liquid-cooled glass cooled at a standard rate of 1 K/min). The surface equilibration mechanism[19] provides a qualitative explanation: The surface of organic glasses are highly mobile,[4] even below Tg, and this allows just-deposited molecules to equilibrate to a considerable extent, even at 0.85 Tg. Below 0.85 Tg, surface mobility is not sufficient for substantial equilibration. Above 0.85 Tg, mobility is available but the gain in properties associated with equilibration is small.

With DOE support, we developed a temperature-gradient stage for use in the deposition chamber,[2,10] to allow the efficient preparation of many glasses that differ only in the substrate temperature. With this arrangement, we could cover a 150 K range in substrate temperatures in a single deposition. Because spectroscopic ellipsometry uses a tightly focused beam, this entire range of glasses could be efficiently characterized. This development was utilized in several later publications,[14,15,17,22,16,12] and has been subsequently adopted by other research groups. In this early work, we expanded the number of compounds that make stable glasses to five.[1]

***Preparation of ultrastable glasses of organic semiconductors*:** Glasses of organic semiconductors are important in organic electronics. For example, the active layers in

OLEDs are vapor-deposited organic semiconductors. With DOE support, were the first to show that PVD glasses of organic semiconductors are typically ultrastable.[14] We initially studied three organic semiconductors and showed that, for each molecule, PVD at substrate temperatures near 0.85 Tg produced high density glasses with very high thermal stability. Subsequent work revealed other examples of organic semiconductors that form ultrastable glasses.[22,32] We expect that this result holds for all organic semiconductors which do not utilize hydrogen-bonding.[18,23]

Chemical and photochemical stability of ultrastable glasses. We hypothesized that the efficient packing of ultrastable glasses would give rise to increased stability with respect to chemical and photochemical reactions, and that this stability would enhance the lifetime of OLED devices when deposition conditions produce ultrastable glasses. Using a model glassformer containing the azobenzene moiety, we tested the photochemical stability of ultrastable glasses in comparison to liquid-cooled glasses.[17] Remarkably, the highest density glass produced by PVD (1.3% more dense than the liquid-cooled glass), exhibited a 50-fold increase in photochemical stability. At a qualitative level, we confirmed the generality of this effect with two other systems.[25],[26] To test chemical stability, we challenged an ultrastable glass of an organic acid with a vapor containing ammonia. The resulting acid-base reaction was 8 times slower for the ultrastable glass as compared to the liquid-cooled glass.[31]

A group in Barcelona connected our work directly to OLED function, showing that OLEDs prepared using ultrastable glasses showed increases in device lifetime by a factor of 5. A group at Kyushu furthered the connection with OLED function, showing that the densest PVD glasses show up to a 20-fold increase in charge mobility relative to less dense glasses.

Anisotropy of PVD glasses. The idea of anisotropic glasses is sometimes regarded as an oxymoron, but there is no reason that amorphous materials must be isotropic. Liquid-cooled glasses typically are isotropic, but this is because they are formed by trapping the structure of the (isotropic) liquid. PVD glasses, because equilibration takes place during deposition at the free surface (an anisotropic environment), are often anisotropic. In our early DOE-supported work, we used the birefringence obtained from spectroscopic ellipsometry as our primary method to characterize macroscopic anisotropy.[2,7,8] The birefringence of PVD glasses can be quite large and is comparable in size to that of a typical organic crystal.[30] In this sense, PVD glasses can be regarded as hybrid organic solids that combine the anisotropy of crystals with the macroscopic homogeneity of glasses.[30] The birefringence systematically depends upon the deposition conditions such that even the sign can change. This indicates substantial changes in the average molecular orientation in the glass for different deposition conditions,[20] and demonstrates a level of control over molecular orientation that cannot be achieved in crystalline systems.

Wide angle X-ray scattering was also utilized in these early studies.[3,5] Consistent with ellipsometry, anisotropic scattering features were observed for PVD glasses. All of the scattering features for as-deposited materials had broad lines, consistent with the lack of long-range order expected for glassy materials.

Anisotropy of PVD glasses of organic semiconductors**.** With DOE support, we were the first to show that the anisotropy of PVD glasses of organic semiconductors could be systematically tuned with the substrate temperature.[14] Our initial paper showed a generic pattern for molecular orientation for rod-shaped molecules. Low temperature deposition results in glasses where the molecules have their long axes preferentially in the plane of the substrate, while high deposition temperature can cause the molecules to orient along the surface normal. A similar generic pattern exists for disk-shaped molecules.[22,28] Using molecular dynamics computer simulations, we were able to reproduce these trends with coarse-grained molecular representations and show that the result is consistent with the surface equilibration mechanism.[11] This means that the molecular shape determines the anisotropic packing, in combination with the available surface mobility.

Molecular orientation is important for OLED function. In particular, device efficiency is higher if the emitter molecules have their transition dipoles in the plane of the device. (Vertical orientation results in emission which does not leave the device.) Our work provided a systematic approach to optimize emitter orientation, and groups in Germany and Japan have made use of this.

We further investigated the anisotropy of PVD glasses of organic semiconductors using grazing incidence wide angle X-ray scattering (GIWAXS) at SSRL. The molecular orientation indicated by the ellipsometry is clearly shown in the GIWAXS and quantified through a Hermans orientation parameter.[13] (All the GIWAXS patterns for as-deposited materials showed broad lines as expected for glasses.) Surprisingly, we also found anisotropic scattering features associated with molecular layers in some PVD glasses,[21] including Alq3; this feature can also be explained by the surface equilibration mechanism.[29] This last result is notable as there had been no previous reports of anisotropy in Alq3 (the organic semiconductor used in the very first OLED paper, published in 1987).

We found that the underlying substrate has little impact on the structure of a PVD glass, consistent with the (free) surface equilibration mechanism.[33,36, 37,34] This means that our results on thicker films are directly relevant for OLEDs where very thin films (~15 nm) are utilized.

Control of crystallization*.* A primary failure mode for glassy materials is crystallization. We hypothesized that the high density glasses produced by PVD would crystallize more slowly than less dense glasses. We verified this prediction using the prototypical organic semiconductor Alq3. We showed that an ultrastable glass of Alq3 crystallized about 10 times more slowly than glasses prepared away from the optimal substrate temperature.[35] Crystallization is an important failure mode for OLEDs, so we expect that OLED lifetimes will be generically increased by choosing the optimal deposition temperature.

Many organic semiconductors have multiple crystal polymorphs, and we showed that for at least one system, we can control polymorph selection. We studied CBP, which is a poor glassformer, in contrast to most organic semiconductors used in OLED research. Glasses of CBP typically begin to crystallize upon heating even below Tg. We hypothesized that different anisotropic glassy packings (produced by different substrate temperatures) might nucleate different crystal polymorphs. We found vapor-deposited glasses of CBP crystallized into either the alpha or gamma polymorph, depending on the glass structure.[27] To the best of our knowledge, this is the first demonstration that two glasses of the same organic compound, subjected to the same annealing conditions, grow crystals of different polymorphs.

Transformation mechanism for thin films of ultrastable glasses*.* When a liquid-cooled glass is heated even a little above Tg, the entire sample transforms into a liquid at the same time, to a good approximation. With DOE support, we used ellipsometry to show that thin glassy films of ultrastable glasses have a strikingly different transformation mechanism.[15,12] Material in the middle of film is so well packed that it cannot easily transform into the liquid, even well above Tg. Instead, transformation starts at the free surface where there is mobility. The transformation propagates through the film at constant velocity, in a manner superficially similar to crystal melting. With ellipsometry, we were able to directly resolve the front position in the thin film and track it in real time. Understanding this mechanism is important for OLEDs, because interfaces on each side of a PVD glassy layer can be controlled to avoid initiation of a front. This can dramatically extend the lifetime of the glassy material (and likely extend the device lifetime).

Co-deposition of organic semiconductors. Most of the results discussed above were obtained for single component systems. With DOE support, we recently extended our efforts to co-deposited systems. The PVD glasses used in OLEDs are often co-deposited and understanding whether co-deposited glasses are ultrastable and well-mixed is of practical interest.

We recently studied 7 different co-deposited pairs of organic semiconductors, and found that all of them form ultrastable glasses.[41],[40],[38] These studies utilized ellipsometry and differential scanning calorimetry. In all respects, PVD glasses of the co-deposited systems are very similar to PVD glasses of the neat materials, even though the Tg values of the neat components differ by up to 100 K. For these 7 systems, we also reported birefringence measurements for the mixed glasses. We showed that a model based upon the surface equilibration mechanism can successfully predict the birefringence of the co-deposited glasses from data on the pure components. We interpret the results to indicate that these 7 co-deposited systems are well-mixed.

Component segregation is one possible outcome of co-deposition and we found two binary systems that show this behavior. For one system (TPD/DO37), the two components are immiscible in the liquid state, and so component segregation is thermodynamically favorable. We utilized resonant soft X-ray scattering and PiFM (AFM with IR detection) to determine the size of the domains, and found large domains (> 100 nm) for high deposition temperature and small domains (~20 nm) for low deposition temperature.[39] A second system (TPD/TCTA) is even more interesting as the two components are completely miscible in the liquid state. Nevertheless, domains as large as 250 nm are formed during vapor deposition. Component segregation might be useful in certain applications and it is encouraging that domain size can be controlled by deposition conditions.

Impact on glass science. Our work on highly stable PVD glasses of organic molecules has stimulated a considerable amount of work with other types of materials. Many papers describe attempts to prepare ultrastable glasses of metallic alloys, and some of these appear to be highly successful. Ultrastable glasses have also been prepared from chalcogenide and low molecular weight polymer glasses. In addition, many computer simulation groups have implemented schemes that aim to prepare ultrastable glasses.[9]

Publications and Patents Supported by DOE (DE-SC0002161)

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