Exploring the Formation and Growth of Organic Semiconductors with mm-Scale Grains

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Abstract

While record mobilities have been reported for organic semiconductors in their single crystal form, the bulk nature of such crystals prohibit their practical application in devices. Here, we discuss our efforts to realize pinhole free films of organic semiconductors with grains of up to 1 mm in extent. One such material is rubrene, but we will also show our efforts on other materials applicable to organic light emitting diodes, such as the electron transport layer 2,2',2"-(1,3,5-benzinetriyl)-tris(1-phenyl-1-H-benzimidazole) (TPBi). For rubrene, we will show our efforts to understand crystal formation, epitaxy, and transistors. Homoepitaxial studies uncover evidence of point and line defect formation in these films, indicating that homoepitaxy is not at equilibrium or strain-free. Point defects that are resolved as screw dislocations can be eliminated under closer-to-equilibrium conditions, whereas we are not able to eliminate the formation of line defects. We are, however, able to eliminate these line defects by growing on a bulk single crystal of rubrene, indicating that the line defects are a result strain built into the thin film template, indicating that, in general, organic crystalline thin films may not adopt the exact lattice of a bulk crystal. Transistors made out of these large-grained films of rubrene display charge carrier mobility of up to 3.5 cm^2 V^{-1} s^{-1}, very close to single crystal values, highlighting their potential for practical application.

Author Keywords

organic semiconductor; crystals

1. Introduction

A key metric for efficient light emitting devices (LEDs) for either display or lighting applications is to minimize the driving voltage needed to achieve a particular level of light output. In this way, the power efficiency of LEDs can, at least in principle, be maximized. The most effective strategy to-date to reduce the driving voltage of organic LEDs (OLEDs) is through the use of molecular dopants, either n-type or p-type, that reduce or oxidize neighboring host molecules to increase the conductivity of the layer. The use of these dopants in transport layers have proven very effective to increase conductivity by orders of magnitude [1].

Another effective means to increase conductivity is to increase the long-range order of materials. For example, the mobility (directly proportional to the conductivity) of the organic semiconductor rubrene is orders of magnitude higher in a single crystal (up to 20 cm^2/Vs) compared to an amorphous film [2]. However, the means to prepare single-crystal-like films on a conductive substrate that is amenable to the fabrication of vertical devices such as OLEDs and solar cells is a considerable challenge.

Recently, a strategy to fabricate organic semiconductor films with grains with lateral dimensions of 100s of microns, and even up to mm-scale, has been realized from the archetypal organic semiconductor rubrene [3-7]. Here, we show that two other organic semiconductors that are important for OLEDs as electron and hole transport layers, respectively, 2,2',2"-(1,3,5-benzinetriyl)-tris(1-phenyl-1-H-benzimidazole) (TPBi) and N,N′-di(1-naphthyl)-N,N′-diphenyl-(1,1′-biphenyl)-4,4′-diamine (NPD), can also be made to crystallize into long-range-ordered and pinhole free films.

2. Results and Discussion

In Figure 1 is displayed a polarized optical micrograph of a rubrene thin film that has been annealed to convert the as-fabricated amorphous thin film to a long-range-ordered film with single crystal grains of 100s of microns in extent. The film crystallizes into the orthorhombic polymorph with the a-axis out-of-plane, with thickness of approximately 20 nm and is very smooth, as reported in our recent work [5, 6].

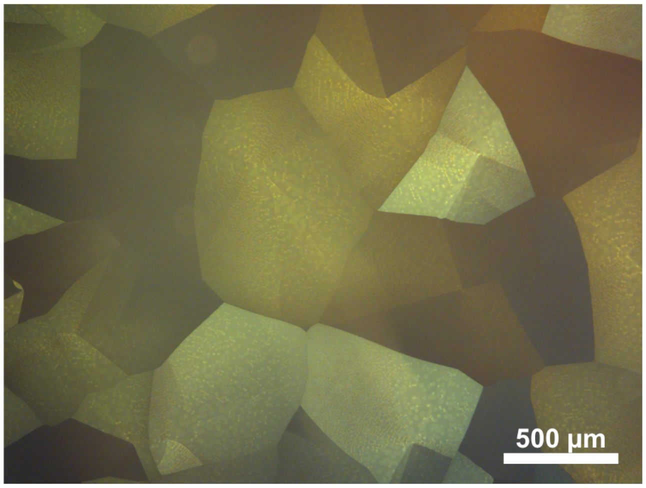

Figure 1. Polarized optical micrograph of a rubrene thin film that has been converted from an amorphous, as-deposited state, to a crystalline state.

With films of rubrene like those in Figure 1, we have been able to demonstrate field effect mobility of 3-4 cm^2/Vs in a top source, drain, and gate geometry thin film transistor [6]. Additionally, and owing to the fact that films are pinhole free, we have shown that solar cells made from a crystalline rubrene/C$_{60}$ donor/acceptor interface reveal lower energy losses compared to disordered rubrene/C$_{60}$ interfaces [8]. These lower losses were attributed to a highly delocalized charge transfer state that emerges at the donor/acceptor interface and which features a strong and highly oriented dipole moment.

In order to generalize this process to realize benefits to organic electronic devices more broadly, it is important to identify other archetypal molecules where similar long-range-ordered films can be prepared. In this way, the qualities of molecular thin films that allow for this structural transformation to occur can be revealed.

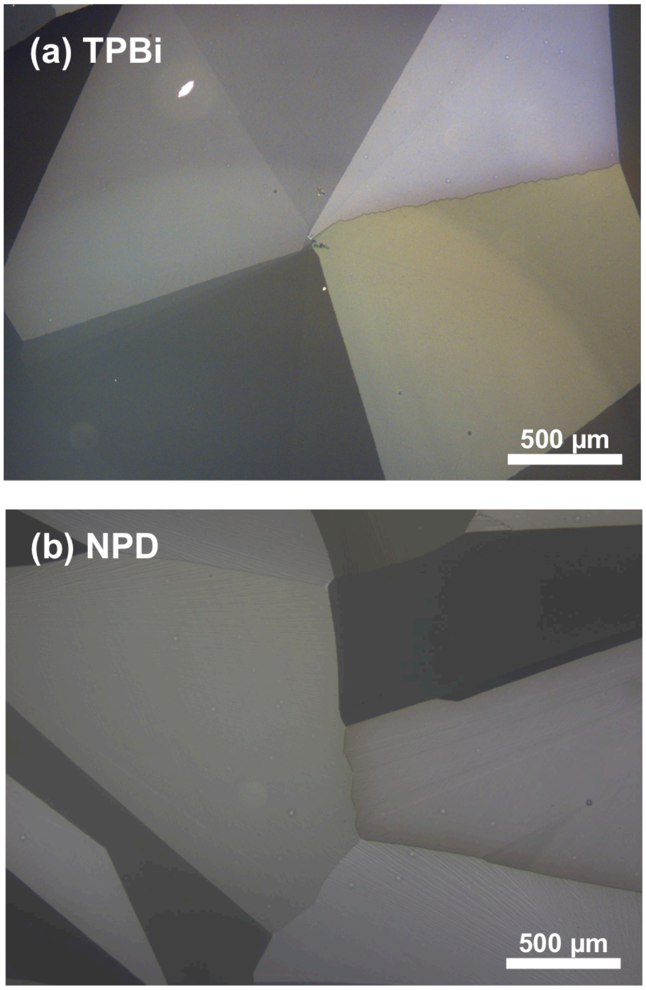

Figure 2. Polarized optical micrographs of crystalline (a) TPBi and (b) NPD thin films.

To that end, we have found that NPD and TPBi, each common transport materials for OLEDs, are capable of being transformed from their original amorphous state to a platelet-like crystalline state through an annealing process. Images of example films are shown in Figure 2, in (a) shown for TPBi and in (b) for NPD. In both cases, crystal domains possess lateral dimensions on the mm-scale, notably larger than the average lateral grain size for rubrene, as can be seen by comparison with Figure 1. We suspect that the reason for the larger grain size in TPBi and NPD compared to rubrene is that, while all films start out as being amorphous, the as-deposited films of TPBi and NPD have less aggregation compared to rubrene, and thus fewer crystal seeds. As a consequence, grains that grow from a central seed have further distance to travel laterally before colliding with a neighboring grain, terminating the crystal growth front.

3. Conclusion

In conclusion, we have shown that, in addition to rubrene, it is possible to prepare long-range-ordered films of NPD and TPBi, two canonical hole and electron transport layers commonly used in OLEDs. Because it can be expected that the crystalline morphology possesses orders of magnitude higher conductivity as compared to the amorphous film, we expect that the integration of these highly crystalline films within organic electronic devices can realize improved performance and stability.

4. Acknowledgements

This work was supported by the National Science Foundation Award No. ECCS-1709222.

5. References

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