K-1-03

Extended Abstracts of the 2018 International Conference on Solid State Devices and Materials, Tokyo, 2018, pp621-622

Enhanced Electrical Properties and Air Stability in High-Density Amorphous Organic Films

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Abstract

To enhance the performance of organic electronic devices, further understanding of the relationship between amorphous structures and electrical properties of organic thin films has been demanded. In this study, we controlled substrate temperature during the vacuum deposition of a hole-transporting material α-NPD to change their density and molecular orientation. Hole current and air stability were clearly raised in highly densified films while molecular orientation was not effective. The improved electrical properties can be attributed to the enhanced carrier hopping between α-NPD molecules and suppressed penetration of oxygen and water.

1. Introduction

Organic thin films used in functional devices can be mainly categorized into polycrystalline and amorphous films. The presence of gaps at grain boundaries in polycrystalline films and gaps originating from inefficient molecular packing in amorphous films impede carrier hopping because they work as carrier traps and energy barriers, and reduce air stability by water and oxygen molecules migrating through the gaps.

Recently, we demonstrated that cold isostatic pressing increases the density and enhances the electrical properties of polycrystalline films by physically compressing the gaps between grain boundaries [1–3]. However, it was virtually impossible to compress amorphous organic films and improve their electrical properties using this method. On the other hand, Ediger's group has established that controlling substrate temperature during vacuum deposition (T_{sub}) can produce thermally stable amorphous films with high film density and molecular anisotropy [4–6]. This is because T_{sub} governs kinetic mobility of molecules migrating on a film surface during deposition, which strongly affects the film morphologies. Therefore, it is expected that if highly densified amorphous films can be obtained by controlling T_{sub}, these films should display enhanced electrical properties and air stability. In this study, we comprehensively investigate the influence of T_{sub} on the film density, molecular orientation, electrical properties, and air stability of amorphous films of a typical hole-transporting material, α-NPD [7].

2. Experimental

Film fabrication and characterization

For the measurements of density and molecular orientation, α-NPD films with a thickness of approximately 100 nm were vacuum-deposited on Si substrates kept at various T_{sub} ranging from 200 to 350 K. Variable angle spectroscopic ellipsometry (VASE) was performed on these films with an optical model considering anisotropy of molecules to evaluate their refractive index *n*, extinction coefficient *k*, orientational order parameter *S*, and film thickness *d*. The relative density (ρ_{rel}) of each film was estimated from the ratio of *d* values before and after annealing at a temperature higher than the glass transition temperature ($T_{g,bulk}$) of α-NPD [6].

Hole-only device fabrication and characterization

To investigate a T_{sub} effect on electrical properties, hole-only devices (HODs) were fabricated with the following structure: glass substrate/ITO anode (100 nm)/α-NPD (about 350 nm)/MoO_3 (30 nm)/Au cathode (50 nm). An α-NPD layer was vacuum-deposited on substrates kept at various T_{sub} ranging from 200 to 350 K. After T_{sub} was returned to room temperature, MoO_3 and Au layers were vacuum-deposited on top of the α-NPD layer to complete HODs. Current density (*J*) – voltage (*V*) properties of HODs were measured under nitrogen in the dark. For a better comparison, we used electric field *E* instead of *V* to calibrate a small variation of the α-NPD thicknesses among samples. *E* was calculated by simply dividing *V* by the α-NPD thickness measured from each HOD. After the *J*-*V* measurements, the air stability of HODs was evaluated from the temporal change of driving voltage under continuous current application at 0.1 mA/cm^2 in air (without encapsulation) under the dark condition.

3. Results and discussion

Film structure

Figure 1 shows *S* and ρ_{rel} of α-NPD films deposited at different T_{sub}. While the molecular orientation changed from horizontal (relative to a substrate) to random as T_{sub} was increased, ρ_{rel} exhibited a convex trend with a maximum value between 270 and 300 K (0.75−0.83 of $T_{g,bulk}$). These trends of *S* and ρ_{rel} can be explained by the change of kinetic mobility of molecules on a film surface during vacuum-deposition. If the kinetic mobility is too small in the low T_{sub} region or too large in the high T_{sub} region, the density becomes lower because molecules are less likely to reach or settle at an energetically stable position, respectively. However, when the kinetic mobility is suitable (0.75–0.83 of $T_{g,bulk}$), molecules can move a large distance on a film surface to find a stable position. For this reason, the films fabricated at 0.75–0.83 $T_{g,bulk}$ have higher density than those formed at other T_{sub}. When the kinetic mobility is small at low T_{sub}, molecules cannot move much and therefore keep their horizontal orientation. As the kinetic mobility of molecules increases at higher T_{sub}, molecules move intensely, which causes the orientational order to gradually become random.

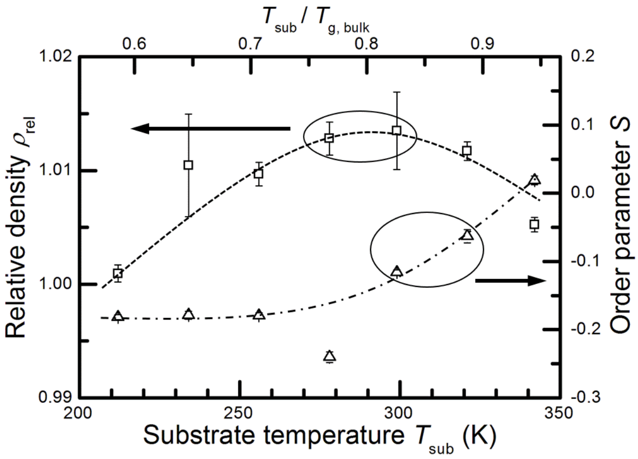

Fig. 1. Plots of orientational order parameter S (triangle symbol) and relative film density ρ_{rel} (square symbol) as a function of substrate temperature during deposition T_{sub}.

Electrical properties

J-E properties of HODs are strongly affected by T_{sub}. The J values at an E of 1.0×10^5 V/cm are plotted as a function of T_{sub} in Fig. 2. J changes in a similar manner to that of ρ_{rel} in Fig. 1. A higher ρ_{rel} indicates decreased intermolecular distance because the α-NPD molecules are packed more closely, which might be expected to enhance carrier transport in a film. Moreover, in films with higher density, the width of their density of states (DOS) might be expected to be narrower because of the location of molecules at more stable positions. This DOS narrowing can result in a lower barrier between neighboring states near the center of the DOS distribution. The significant increase of J is explained by the decrease in activation energy and enhanced rate of carrier hopping because of the closer molecular distance and narrower DOS in high-density film. In contrast, there was no clear relationship between J and S, even though it has been suggested that the horizontal orientation on a substrate leads to the enhanced carrier transport because of the better overlap of π orbitals between neighboring molecules in a substrate normal [8].

Air stability

The temporal changes of driving voltage V was also affected by T_{sub}. All HODs had a gradual increase of V with operation time; the slopes of V are displayed in Fig. 2. In this figure, a smaller slope means higher air stability. The air-stability data well-matched with the ρ_{rel} curve in Fig. 1. These results reveal that α-NPD films with higher ρ_{rel} have higher air stability, while S has no relation to not only the electrical properties but also the air stability of the films. Although the detailed mechanism is now under investigation, suppressed absorption of water and oxygen molecules and crystallization of α-NPD molecules are possible reasons of the enhanced air stability.

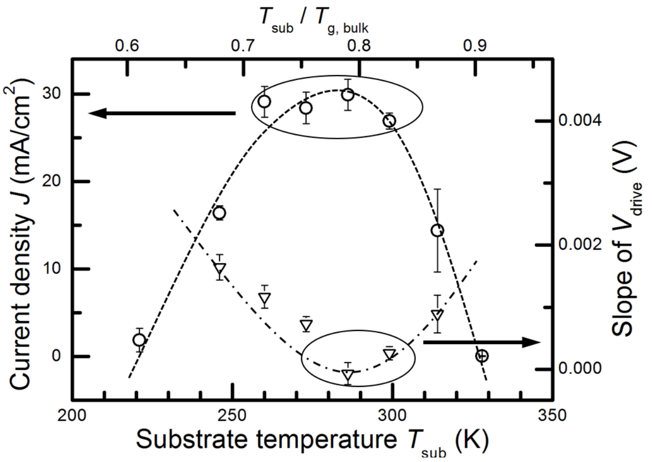

Fig. 2. Plots of current density J value at an electric field $E = 1.0 \times 10^5$ V/cm (circle symbol) and slopes of driving voltage V during continuous driving (triangle symbol) as a function of substrate temperature during deposition T_{sub}.

4. Conclusion

The relationship between molecular orientation, film density, electrical properties, and air stability were investigated. For α-NPD, the film density has more influence on carrier transport than the molecular orientation does. An increase in driving voltage during continuous driving was suppressed in higher-density film, implying enhanced air stability. Even though the ρ_{rel} variation observed here is very small, just 1%–2%, its effect on electrical properties and air stability is considerable.

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