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Structural and Electrical Properties of Fluorinated Copper Phthalocyanine for Organic Photovoltaics

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Abstract

We have investigated influence of substrate temperature and post annealing on morphology and current-voltage characteristics of organic films with copper phthalocyanine series, F_xCuPc (x = 0, 8, 16). The substrate heating at 120 ℃ improved rectifying properties for CuPc and F_{16}CuPc. In addition, the substrate heating from room temperature suppressed surface roughness. These results lead to improve current-voltage characteristics for F_8CuPc and F_{16}CuPc films.

1. Introduction

Organic photovoltaics (OPVs) have been drawing intense research interest because of its unique features such as being flexible, lightweight, and large area devices [1]. Phthalocyanine (Pc) series is promising materials for OPVs because of the high chemical and thermal stability [2]. Also, fluorination of Pc leads to decrease in energy levels in accordance with the number of fluorine atoms [3]. Thus, fluorinated Pc are useful to design high efficiency OPVs on basis of band engineering.

To investigate influence of substrate temperature and post annealing on properties of organic film is an important issue. This is because substrate heating considerably influences the structural and electrical characteristics of the organic film deposited on the substrate. However, there have been a few reports about properties of fluorinated CuPc films deposited on heated substrate and annealed [4].

In this study, we have investigated the influence of substrate temperature and post annealing on properites of fluorinated CuPc films to provide basic information for organic PVs.

2. Experiment

Molecular structures of CuPc, F_8CuPc and F_{16}CuPc are shown in Fig. 1 with the energy diagram determined by spectroscopic measurement. We prepared the single-layer devices with CuPc, F_8CuPc and F_{16}CuPc films deposited by thermal evaporation. An indium-tin-oxide (ITO) coated glass was used as a substrate. The substrate was exposed to O_2 plasma to increase the work function. Then, 120-nm-thick organic layers of CuPc, F_8CuPc, and F_{16}CuPc were deposited on the substrates at a rate of 0.02 nm/s, respectively. The substrate temperature during organic layer deposition was room temperature (RT) or 120℃. Some organic films deposited at 120 ℃ were consecutively annealed at 300℃ for 2 h on a hot plate in a nitrogen-filled glove box. A silver metal layer was deposited for organic single layer devices through a metal mask having 0.25 mm^2-area-size holes as an upper electrode. The current-voltage characteristic was measured in the glove box.

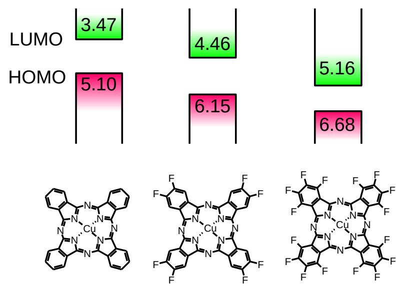

Fig. 1 Molecular structure and spectroscopically determined energy diagram of F_xCuPc (x= 0, 8, 16).

3. Results

Figure 2 shows the SEM images of CuPc and F_{16}CuPc films deposited on substrates prepared under different condition. The CuPc films deposited at RT and 120 ℃ have smooth surfaces. On the other hand, the CuPc film post-annealed at 300 ℃ has crystal-like domains. The F_{16}CuPc films have very rough surface as compared to the CuPc films. Needle-like structures are present in the films for all condition. The substrate heating and post-annealing enhance the surface roughness.

Figure 3 shows the X-ray diffraction pattern of CuPc and F_{16}CuPc thin films deposited at RT and 120℃. The peaks at 6.7˚ and 6.0˚ correspond to crystal of CuPc and F_{16}CuPc, respectively. The peak intensities increase with substrate temperature. This result indicates that the substrate heating improves crystallinity of CuPc and F_{16}CuPc thin film. Since substrate heating up to 120℃ does not change surface morphology of a CuPc film as seen in Fig. 2(a) and (b), the result of the XRD implies that we can improve the crystallinity of CuPc film without changing the surface morphology.

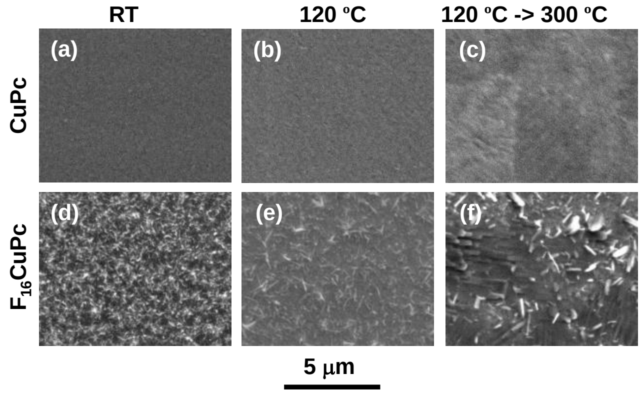

Fig. 2 SEM images of [(a)-(c)] CuPc and [(d)-(f)] F_{16}CuPc films deposited at [(a) and (d)] room temperature and [(b), (c), (e), (f)] 120℃. The sample for (c) and (f) were annealed at 300 ℃ after deposition.

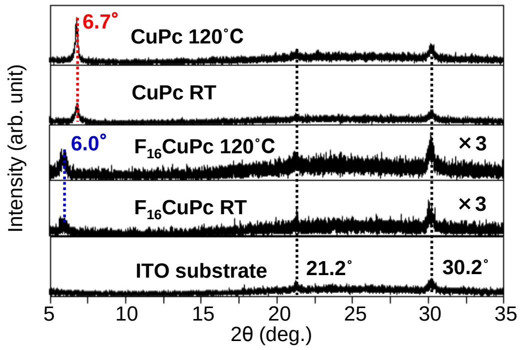

Fig. 3 XRD patterns for CuPc and F_{16}CuPc films deposited on ITO substrates at RT and 120℃. An XRD pattern for an ITO substrate is also shown as a reference.

Figure 4 shows the current-voltage characteristics of CuPc and F_{16}CuPc. The device structure is inset in the Fig.4 (a). The p- and n-type rectification property is confirmed in CuPc and F_{16}CuPc device, respectively. Furthermore, both devices heated at 120 ℃ have more clear rectifying characteristics than without heating. This is presumably due to improved layer crystallinity. On the other hand, for F_{16}CuPc devices heated at 120 ℃, the voltage over ±0.5 V lead to breakdown. This is presumably because rough thin film surface lead to electrically weak thinner area with 120 ℃ heating sample (Fig. 2 (e)).

We fabricated the F_{16}CuPc single layer devices with gradual heating. That is, the substrate temperature during organic layer deposition is gradually increased from RT to 120 ℃. As a result, the breakdown is not observed up to ±1.0V (Fig. 5 (a)). This is presumably due to suppression of the surface roughness compared to constant 120 ℃ heating sample. Additionally, the device represents clear rectifying characteristics.

We also fabricated F_8CuPc single layer device with gradual heating process. As shown in Fig. 5 (b), n-type rectifying characteristic is confirmed, while F_8CuPc device with constant 120 ℃ heating has no rectifying property because of very large leakage current probably due to existence of pinhole.

These results indicate the gradual heating process is useful to suppress the breakdown or pinhole for F_8CuPc and F_{16}CuPc devices. On the other hand, although the current at negative bias is larger than that at positive bias, the current at positive bias linearly increases with the bias. This implies the presence of the leakage current.

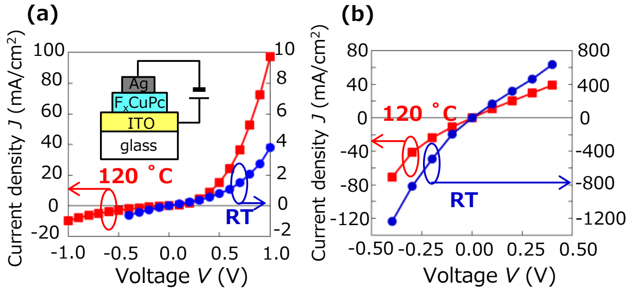

Fig. 4 Current-voltage characteristics of (a) CuPc and (b) F_{16}CuPc.

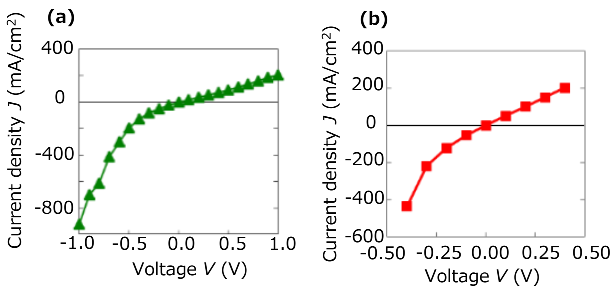

Fig. 5 Current-voltage characteristics of (a) F_{16}CuPc and (b) F_8CuPc single layer devices. The organic layers were fabricated with gradually substrate temperature increasing process from RT to 120℃ during deposition.

4. Conclusions

We investigated influence of substrate temperature and post-annealing on structural and electrical properites of F_xCuPc (x= 0, 8, 16) films. Single layer devices with CuPc and F_{16}CuPc film deposited at 120 ℃ exhibited superior rectifying properties to those with films deposited at RT. Substrate heating from RT during deposition suppresses surface roughness and improves the rectifying properties. Fluorinated CuPc films prepared under optimized substrate heading and post annealing will be useful for organic photovoltaics containing phthalocyanine series.

Acknowledgements

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