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We study the evaporation process by means of a single evaporation source putting in the mixture of two hole-transport materials (HTMs) for organic light-emitting diodes. In the case of the mixture of two HTMs with large difference, 120, of evaporation threshold temperature ($T_e$), when evaporation temperature rises at a constant rate with time, the HTM with higher $T_e$ vaporizes after the HTM with lower $T_e$ vaporized. In the case of the mixture of TPD:α-NPD =1:1 with the difference of 50K, only a single evaporation curve is observed in the temperature region between the evaporation curve of only TPD and that of only α-NPD. The fabricated thin films using the mixture of TPD:α-NPD =1:1 under a constant temperature consist of TPD:α-NPD = 10:1. This is because the $T_e$ of TPD increases and that of α-NPD decreases.

Keywords: organic alloy, evaporation process, mixture, single source

1. Introduction

Organic thin films are used in such most organic electronic devices as organic light-emitting diodes (LEDs), organic thin-film solar cells, organic thin-film transistors. Organic materials have many advantages as compared with inorganic materials: diversity of material, processability, flexibility, low input energy for manufacture etc. But organic material also have fatal instability and low mechanical endurance. Since the instability of organic materials is often caused by moisture and oxygen, the stability can be improved by an appropriate capsulation. On the other hand, although it is not easy for organic materials to enhance mechanical endurance at the inorganic material level, a mechanically and electrically stable layer structure could be produced if a thin single-crystalline layer were fabricated. However, it is extremely difficult to fabricate a single-crystalline layer on any organic or inorganic layer. In fact, most organic thin films which one can use usually are polycrystalline or amorphous. Organic polycrystalline layers are often used in organic FET and organic amorphous layers are generally used in organic LEDs and solar cells.

Because the amorphous structure is thermodynamically unstable, the constituent material tends to change to a more stable state: a crystalline structure[1]. The stability of film structure can often be achieved by the suppression of molecular motions. The increase in glass transition point ($T_g$) can suppress molecular motions around room temperature and is effective for prolonging the lifetime of devices[2-4]. We reported that the stability and mechanical property of film structure can be improved by an organic alloy method[5-9]. We define organic alloy (structure) as the mixture with two hetero organic materials under amorphous or nanocrystalline structure. We fabricate organic alloy films by means of a co-evaporation method. Of course, 2 evaporation sources or more are necessary for the co-evaporation method. The increase in evaporation source is not a good idea because it equals to the increase in apparatus cost and the complexity of fabrication process. Therefore, the idea that a co-evaporated layer is fabricated with only a single evaporation source has been proposed since 1990’s. As an extreme case, Wang et al. reported that a single layer is deposited by the mixture with
hole-transport, emitting, and electron-transport materials[10]. However, although the material contents (i.e. weight%) in evaporation sources are written clearly in the previous papers, the composition contents of evaporated layers are not checked.

In this paper, we set out to fabricate stable hole-transporting organic alloy films by evaporating the mixture of two hole-transport materials. And we clarify the evaporation phenomena of the mixture and the composition contents of the evaporated layer.

2. Experimental

Methoxy-substituted 1,3,5-tris[4-(diphenyl amino)phenyl]benzene (MeO-TDAPB), N,N'-di(1-naphthyl)-N,N'-diphenyl-1,1'-diphenyl-1.4'-diamine) α-NPD) and 4,4'-bis[N-(p-tolyl)-N-phenyl- amino] biphenyl (TPD) were used as a hole-transport material in Fig. 1.

Fig. 1 Chemical structures of organic materials.

Sublimated α-NPD is obtained from Nippon Steel Chemical Co. The preparation of mixture, molar ratio 1:1, was carried out by an automatic mortar (ALM-150, Nitto Kagaku Co.). Organic thin films were prepared on a glass substrate with an indium-tin-oxide (ITO) transparent electrode (anode). The organic thin films were prepared using the vacuum deposition at a pressure of 0.8 ~1x10⁻³ Pa at room temperature. We carried out a vacuum-deposition with EO-5 (EIKO Co.). All amounts in evaporation sources are 40 mg. Evaporation rate was estimated with a crystal oscillator (ULVAC Co.). The temperature of evaporation source was raised with time as shown in Fig. 2.

Absorption spectra were measured by spectrophotometer (U-3000, Hitachi Co.). Photoluminescence (PL) spectra were measured using a spectrophotometer (FP-777, JASCO Co.). We observed the NPD film prepared on an ITO substrate with a polarizing microscope, OPTIPHOTO-2 accompanied with a polarizing unit (Nikon Co.) and took photographs using Digital Sight (DS-L1, Nikon Co.).

3. Results and Discussions

3.1. Evaporation of the mixture of α-NPD and MeO-TDAPB

First, we study on the evaporation using the mixture source of α-NPD and MeO-TDAPB, molar ratio 1:1. The evaporation of α-NPD and MeO-TDAPB start beyond 250°C and 370°C, respectively, as shown in Fig. 3.

Fig. 2 Typical rising curve of temperature with time.

Fig. 3 Evaporation rates of α-NPD, MeO-TDAPB and the mixture against temperature.

The evaporation curve of the mixture has two peaks below 450°C. The deposition rate peak in the low temperature region will be due to the evaporation of α-NPD and that in the high temperature region will be due to the evaporation of MeO-TDAPB. However, the evaporation of 1st peak starts from higher temperature of 270°C than the evaporation temperature of 250°C. The deposition rate of MeO-TDAPB for the mixture source does not
continue to increase till 450°C and has the maximum value. The existence of the peak suggests that it runs low on MeO-TDAPB in the mixture source. The molar amounts of MeO-TDAPB in 40 mg (MeO-TDAPB only) and (mixture 1:1, corresponding to 25 mg) are 4.0 x 10^{-5} and 2.5 x 10^{-5} mol, respectively. If the evaporation of MeO-TDAPB starts from 370°C, it is thought to continue to increase because of almost same material amount in both sources. Therefore, it is suggested that a part of MeO-TDAPB is evaporated with α-NPD.

3.2. Evaporation of the mixture of TPD and α-NPD

Fig. 4 shows the evaporation rate curves of TPD and α-NPD vs. source temperature. While TPD is gradually evaporated from 200°C, α-NPD is evaporated over 250°C. Therefore, we predicted a broken line in Fig. 4: after TPD will be evaporated in the low temperature region, α-NPD will be evaporated in the high temperature region. But the evaporation curve of mixture source lies between those of TPD and α-NPD as shown in Fig. 5.

Fig. 4 Evaporation rates of TPD and α-NPD, and the expected rate of the mixture (broken line) against temperature.

All initial amounts of evaporation source material are always 40 mg. Since the amounts of TPD and α-NPD exists enough in the initial stage, the vapor pressure of TPD in the crucible of the mixture is thought to be almost the same as that in the crucible of TPD only, nevertheless the evaporation rate curve of the mixture source is shifted to the higher temperature region. The existence of α-NPD is suggested to prevent TPD from vaporizing. On the other hand, since there is only an increase in the evaporation rate curve of the mixture of TPD: α-NPD=1:1, α-NPD may vaporize with TPD below 250°C. We discuss the content of evaporated thin films by means of PL spectra afterward.

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Fig. 5 Evaporation rates of TPD α-NPD, and the mixture (dotted line) against temperature.

Fig. 6 shows the evaporation rate under a constant temperature of evaporation source. In the case of the mixture source of 40 mg, a stable evaporation rate can be kept for about 40 min after attaining a constant rate.

Fig. 6 The evaporation rate of the mixture and rising curve of temperature with time.

Fig. 7 shows the PL spectra of TPD, α-NPD and co-evaporated TPD: α-NPD thin films. The peak wavelength of α-NPD is shifted about 40 nm to the longer wavelength region than that of TPD. Since 355 nm-light can excite both TPD and α-NPD, 355 nm-light is used as an excitation light. The absorption of TPD is almost overlapped with that of α-NPD. The configurations of PL spectra for co-evaporated thin films are similar to that for α-NPD thin film. The former is shifted to the shorter wavelength region than the latter. In addition, the co-evaporated thin film of TPD: α-NPD=10:1 has a shorter PL spectrum than the co-evaporated thin film of TPD: α-NPD=1:1. It is thought that the excitation energy of TPD is transferred to α-NPD since the emission of TPD is overlapped with the absorption of α-NPD as shown in Fig. 8.
Fig. 7 PL spectra of TPD, α-NPD, co-evaporated TPD: α-NPD thin films (d = 10 nm).

Fig. 8 PL spectrum of TPD and absorbance of α-NPD.

However, it should be thought that the PL from TPD is also superimposed with the PL spectra of co-evaporated thin films, especially the specimen with high TPD content. Therefore, the TPD content can be estimated from the blue-shift of PL spectrum against the PL spectrum of pure α-NPD.

Table 1 Summarized PL emission peaks of serially fabricated 10 nm-thick thin films by the mixture of TPD: α-NPD=1:1.

<table>
<thead>
<tr>
<th>specimen</th>
<th>1st [min]</th>
<th>2nd [min]</th>
<th>3rd [min]</th>
<th>4th [min]</th>
</tr>
</thead>
<tbody>
<tr>
<td>depo. time</td>
<td>29-35.5</td>
<td>63-65</td>
<td>88-89</td>
<td>121-126</td>
</tr>
<tr>
<td>PL [nm]</td>
<td>423</td>
<td>425</td>
<td>425.5</td>
<td>428.5</td>
</tr>
</tbody>
</table>

We guess a composition analysis of evaporated thin films fabricated using the mixture by PL spectra. Figs. 9 a)-d) show the PL spectra of 10 nm-thick thin films which are fabricated in different deposition windows under a constant evaporation temperature. As shown in table 1, four start times from heating are 29, 63, 88, and 121 min.

Figs. 9 a)-d) The PL spectra of 10 nm-thick thin films: a)1st, deposition time 29-35.5 min; b)2nd, 63-65 min; c)3rd, 88-89 min; d)4th, 121-126 min; heavy line, TPD; dotted line, co-evaporated film.
The 1st deposition term is the initial stage of evaporation with low deposition rate of < 0.05 nm/s. The 2nd term is the steady stage of evaporation with a constant deposition rate ~ 0.1 nm/s and the 3rd term is the end of the steady stage. The 4th term is the declining stage. Since the PL spectrum of 1st specimen is roughly overlapped with that from TPD, the thin film fabricated in the 1st stage consists of TPD. On the other hand, the PL spectra of 2nd and 3rd specimens are shifted to the shorter wavelength region than that of co-evaporated thin film of TPD:α-NPD=10:1. The thin films fabricated in the 2nd and 3rd stages consist of the co-evaporated thin film of TPD:α-NPD=10:1.

3.3. Effect of initial input in evaporation process and thin films

Next we check the effect of initial input of evaporation source on the evaporation process and the composition contents of deposited thin films. Fig. 10 shows the evaporation rate curves of 40 mg and 200 mg for the mixture of TPD:α-NPD=1:1 with time. The temperature of evaporation source is always 240°C after 27 min from the beginning. Both the deposition rates of 40 mg and 200 mg are almost 0.2 nm/s under the constant temperature of 240°C. However, the steady rate of 40 mg cannot maintain above 40 min, but that of 200 mg can do during ~200 min.

Fig. 10 The evaporation rate curves of the mixture of 40 and 200 mg under a constant temperature of 240°C: two arrows show the timing of deposition start.

3.3. Polycrystallization of hole-transport layer

Fig. 13 shows the polarizing microscopic images of various hole-transport thin films. Dark areas are amorphous and white areas are crystal. The polycrystallization in organic alloy films of TPD:α-NPD=1:1 can be suppressed as compared with α-NPD thin films. However, the polycrystallization in organic alloy films of TPD:α-NPD=10:1 cannot be suppressed. Since TPD is more easily polycrystallized than...
α-NPD[6], the increase in TPD content enhances the polycrystallization of organic alloy films of TPD: α-NPD=10:1. Surprisingly, although the TPD content in the TPD: α-NPD thin film fabricated by the mixture source is larger than that in the co-evaporation film of TPD: α-NPD=10:1, the nuclei density of the former, 0.01 mm⁻² is much smaller than the latter, 0.22 mm⁻² and equal to that of organic alloy film of TPD: α-NPD=1:1, 0.01 mm⁻². But the growing rate of the former cannot be suppressed and is equal to that in the co-evaporation film of TPD: α-NPD=10:1. This suggests that the intermolecular interaction in the TPD: α-NPD thin film fabricated by the mixture source may be different from that in the co-evaporation film of TPD: α-NPD.

4. Conclusions
We fabricated organic thin films by means of a single evaporation source putting in the mixture of two hole-transport materials (HTMs). The evaporation curve of a single source of the mixture of TPD: α-NPD=1:1 lies between those of TPD and α-NPD. Organic thin films fabricated by a single source of the mixture of TPD: α-NPD=1:1 is TPD-rich films of TPD: α-NPD= >10:1. The composition content in the thin film fabricated by a single source of the mixture is thought to depend on the ratio of both vaporizing pressures in evaporation crucible. It is possible to evaporate a steady composition ratio above 180 min in the mixture of 200 mg. Evaporation of a single source of the mixture is effective for the improvement of stability of hole-transport layer and the fabrication of organic alloy films.

References