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Molecular Ordering of Vacuum-Deposited 4,4′,4″-tris(N-(1-naphthyl)-N-phenylamino) triphenylamine Thin Films

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Summary: A thin film of vacuum deposited 1-TNATA(4,4′,4″-tris(N-(1-naphthyl)-N-phenylamino)triphenylamine) is placed between indium tin oxide (ITO) electrode and a hole transporting layer (HTL) in OLEDs. The molecular ordering of 1-TNATA thin film is obtained by thermal annealing and electromagnetic field. As-deposited 1-TNATA thin films were not molecularly ordered according to Raman spectra results. Thermal annealing after deposition lead to closer stacking of 1-TNATA molecules and made the 1-TNATA film well-ordered. While thermal annealing at 110 °C, the average surface roughness decreased from 10.2 to 7.2 nm.

Keywords: electromagnetic field; molecular ordering; OLED; surface Raman spectra; 1-TNATA

Introduction

It is known that highly ordered organic thin films are of great importance for OLEDs, organic TFTs and organic solar cells because charge injection and mobility through the layers in the devices are improved, so that it is important to control the stacking and ordering of the organic molecules like metal phthalocyanines and 1-TNATA(4,4′,4″-tris(N-(1-naphthyl)-N-phenylamino)triphenylamine). Until now, few works have been done to control the molecular ordering of organic materials during vacuum deposition process. The molecular ordering of vacuum-deposited organic thin films can be achieved by means of thermal annealing and electromagnetic field induction since many macrocyclic organic materials like metal phthalocyanine possess magnetic behavior.[1–6] In the present study, vacuum-deposited 1-TNATA, widely used as a hole injection material in OLEDs, thin films were thermally treated under electromagnetic field to investigate the effect of thermal annealing on the molecular ordering of the films.[7,8] The film annealed in the electromagnetic field was compared to both the as-deposited sample and the same annealed at the same temperature but without the electromagnetic field.

Experimental Part

As an organic material, 4,4′,4″-tris (N-(1-naphthyl)-N-phenylamino)triphenylamine (1-TNATA) was sublimed to obtain thin films via vacuum process and the chemical structure of 1-TNATA (formula: $C_{66}H_{48}N_4$, molecular weight: 897.15, melting point: >245 °C, T_g: 112 °C, H. W. Sands Corp.) is shown in Figure 1.

1-TNATA thin films were deposited on the pre-patterned ITO-coated glass and the deposition rate was controlled to 30 nm/min to obtain 50 nm thickness of the 1-TNATA thin films. After deposition, thermal treatment of the deposited 1-TNATA films was performed in a cylindrical furnace in which the electromagnetic field (≈6 mT)

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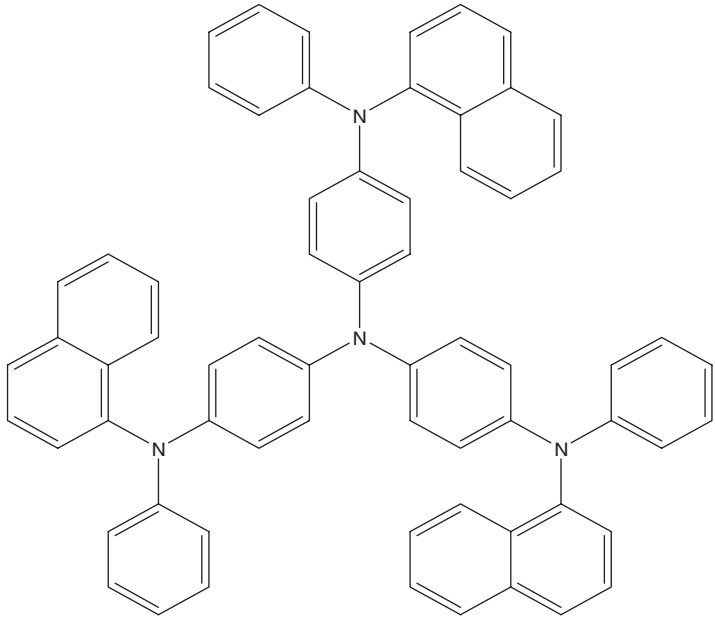

Figure 1.
Chemical structure of 4,4′,4″-tris(N-(1-naphthyl)-N-phenylamino)triphenyl amine (1-TNATA).

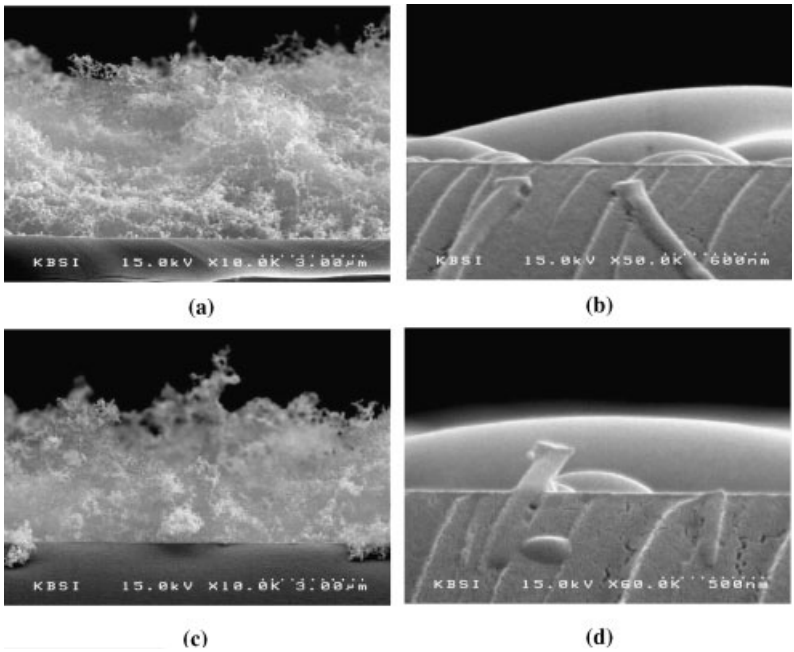

Figure 2.
SEM images of 1-TNATA films: (a) as-deposited film, (b) after thermal annealing at 110°C for 1 h, (c) film deposited under electromagnetic field. (≈6 mT), and (d) after thermal annealing at 110°C 1 h under electromagnetic field.

was selectively applied as well. Film thickness was measured with a profilometer model Alpha-step 100(KLA-Tencor Co. Ltd.) as well as SEM (HITACHL S-4200). The conductivity of organic films was estimated using four-point probe measurement technique using a source multi-meter (KEITHLEY 2004). Raman spectra analysis was carried out using a Bruker FRA 106/S Fourier Transform Raman Spectrometer. AFM (Nanoscope III-a, Digital Instruments Co. Ltd.) analysis was employed to investigate the topology of the 1-TNATA thin films.

Results and Discussion

The SEM images of 1-TNATA thin films deposited on the ITO-coated glass for 10 min are shown in Figure 2. According to the cross-sectional view images of the films, the apparent density of 1-TNATA thin film after thermal annealing seems to be much higher than that of the as-deposited film. But, the apparent density of 1-TNATA thin film after electromagnetic field treatment has been slightly changed with comparison to the as-deposited film. Clean surface was obtained by means of thermal annealing at near glass transition temperature.

Surface images of 1-TNATA thin films before and after thermal annealing were shown in Figure 3 and 4. Sharp spikes or sharp grains on the surface can lead to severe current shortage due to the concentrated current flow through a spike or sharp grain. In this reason the control of the surface topology is very important. After thermal annealing at 110 °C for 1 h, it was found that the surface roughness decreased from 10.2 to 7.2 nm and the lowered grains on the surface were observed. According to the top-view images in Figure 4, smaller size grains were observed for the film treated with both thermal annealing and

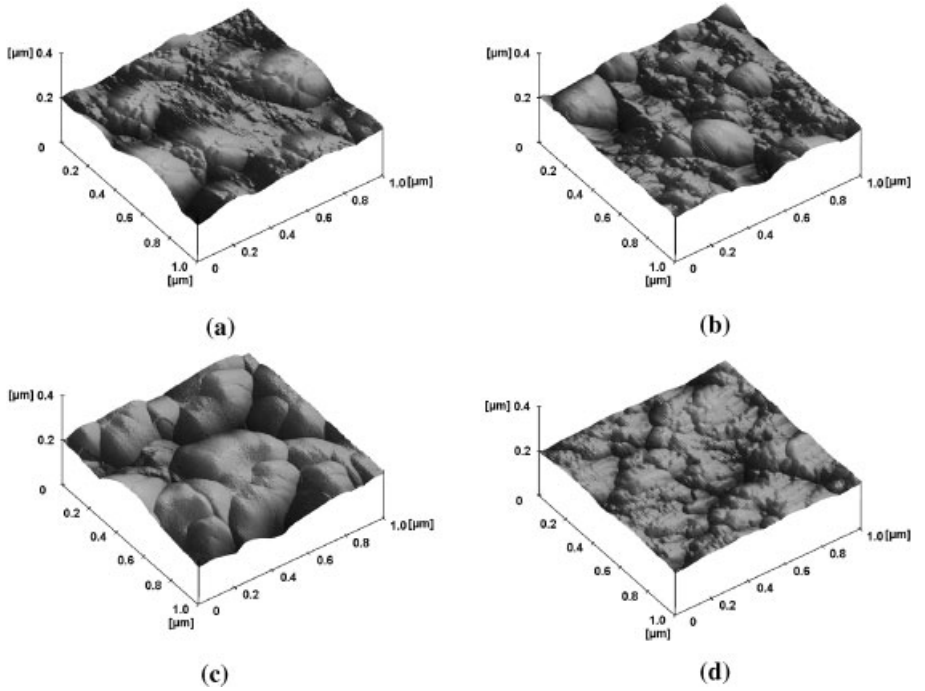

Figure 3.
AFM images (3D) of 1-TNATA film surfaces: (a) as-deposited film, (b) after thermal annealing at 110°C for 1 h, (c) film deposited under electromagnetic field. (≈6 mT), and (d) after thermal annealing at 110°C 1 h under electromagnetic field.

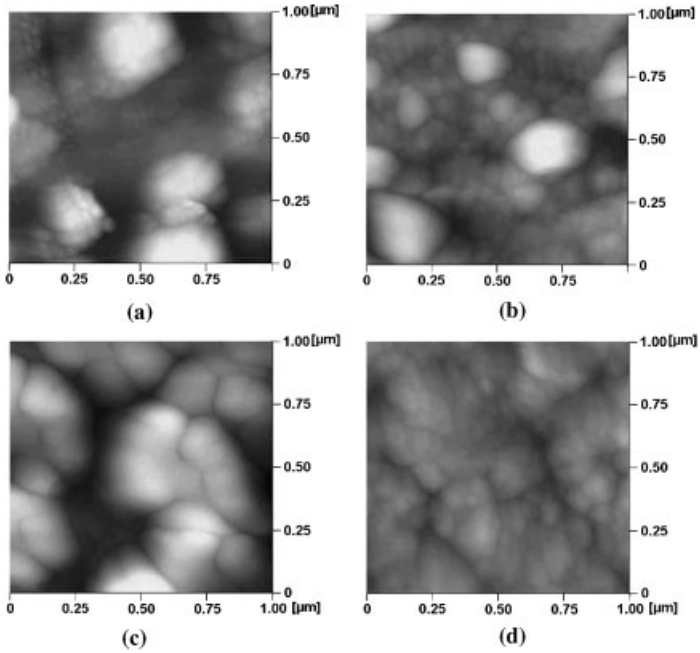

Figure 4.
AFM images (2D) of 1-TNATA film surfaces: (a) as-deposited film, (b) after thermal annealing at 110°C for 1 h, (c) film deposited under electromagnetic field. (≈6 mT), and (d) after thermal annealing at 110°C 1 h under electromagnetic field.

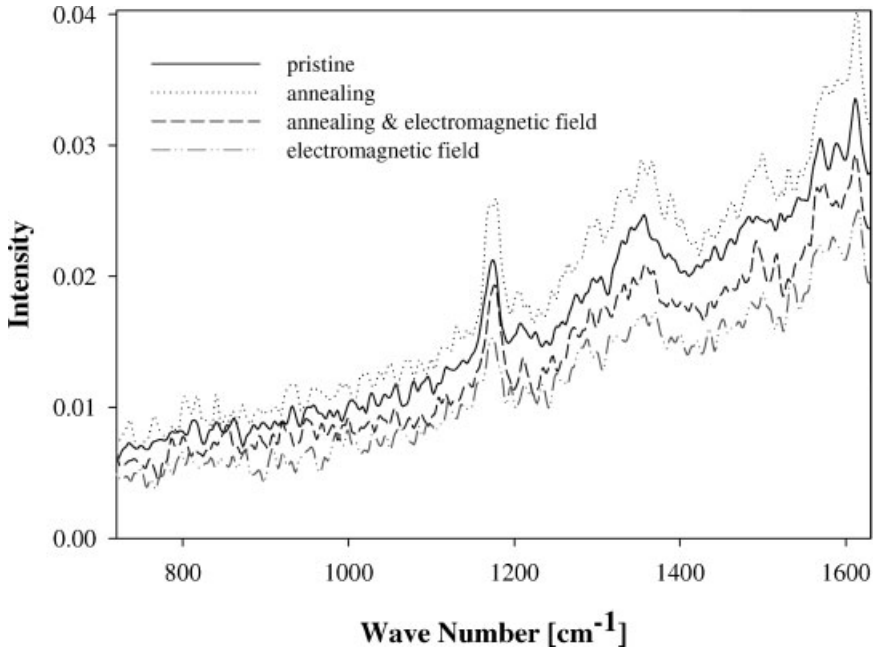

Figure 5.
Raman spectra of the 1-TNATA thin film at various treatments.

electromagnetic field. The Raman spectra are shown in Figure 5. For the aromatic ring containing organic materials, typical Raman bands are observed at 1609, 1594, 1574, 1530, 1374, 1288, 1222, and 1198 cm^{-1}.[9] The 1609-cm^{-1} band is attributed to a ring stretch and the 1288-cm^{-1} band to the inter-ring CC stretch. The 1198-cm^{-1} band is assignable to the CH bend. The width of each band in the amorphous state is broader than that in the crystalline state. These Raman bands can be used for in situ detection of the crystallization of organic materials, which is believed to be one of factors limiting the stability of organic light-emitting diodes.[9] No additional peaks were observed for all samples while thermal annealing with/without electromagnetic field and intensities at 1609 cm^{-1} in Figure 5 become higher and sharper with increasing temperature during thermal annealing. These higher intensities at 1609-cm^{-1} indicate that the 1-TNATA molecules come closer since thermal annealing participates to increase the interaction of the 1-TNATA molecules, which leads molecular ordering of the 1-TNATA thin films.[9,10]

Conclusions

Vacuum-deposited 1-TNATA thin films were formed and thermal annealing under electromagnetic field at 110°C for 1 h was carried out to obtain the molecularly ordered thin films. AFM results showed that the average surface roughness decreased from 10.2 to 7.2 nm after thermal annealing. The results of Raman spectra show that the 1-TNATA films are molecularly ordered with increasing temperature during the thermal treatment. The increase of peak intensities in Raman spectra indicates that the 1-TNATA molecules come closer and eventually are molecularly ordered in the films. A preferentially-ordered 1-TNATA thin layer will have an important role in improving the current flow through the layer as well as the stability of organic light-emitting diodes.

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