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Raman Spectra and Current-Voltage Characteristics of 4,4′,4″-Tris(2-naphthylphenylamino)triphenylamine Thin Films

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A thin film of vacuum-deposited 2-TNATA (4,4′,4″-Tris(2-naphthylphenylamino) triphenylamine), usually used as a hole injection layer (HIL) in OLEDs, was annealed after deposition and treated with electromagnetic field in order to get the film molecularly-ordered and analyzed by AFM, SEM and Raman spectroscopy. The treated film was placed between indium tin oxide (ITO) electrode and hole injection layer to investigate the current density-Voltage (J-V) and luminance-voltage (L-V) characteristics of the organic light-emitting diodes. According to the Raman spectra results, as-deposited 2-TNATA thin film was not molecularly ordered, and the films treated by the thermal annealing at near the glass transition temperature of 2-TNATA and electromagnetic field, were molecularly ordered and showed the significant increases of current density and luminance efficiency for devices at a given voltage compared to an as-deposited 2-TNATA film.

Keywords: 2-TNATA; electromagnetic field; molecular ordering; OLED; Raman spectra

INTRODUCTION

In recent years, much effort has been made to apply the macrocyclic organic materials to multi-layered organic light-emitting diodes (OLEDs)

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as a light-emitting layer, a hole injection layer, and a hole transport layer material. In OLEDs, much improvement has been achieved to get higher electroluminescent and power efficiencies as well as stability of the OLEDs [1–6]. Recently, it is known that highly ordered macrocyclic organic thin films have great importance for OLEDs, organic TFTs and organic solar cells because charge injection and mobility through the layers in the devices are improved [1,2]. In these fields, it is important to control at a molecular level. 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 [10,11]. Magnetic field-induced alignment of molecules in solution is a universal effect, originating from the fact that virtually any molecule features anisotropic magnetic susceptibility, and the macroscopic ordering of molecules can be achieved by means of high magnetic field typically in organic solutions. It is reported that substrate temperature and post-deposition annealing can affect on the performance of OLEDs [7,8]. Thermal annealing at near the glass transition temperature of the organic material improves the maximum luminance as well as the stability of OLEDs. Deposition at high temperature also significantly improves the electroluminescent efficiency and stability of the OLEDs. This thermal effect can be seen at much higher than the glass transition temperature of organic materials. Thermal annealing after deposition at much higher than glass transition temperature of organic materials may reduce current efficiency of the devices.

In this study, vacuum-deposited 2-TNATA (4,4′,4″-Tris(2-naphthylphenylamino)triphenylamine) widely used as a hole injection material in OLEDs, thin films were thermally treated at near the glass transition temperature of 2-TNATA under electromagnetic field to investigate the effect of thermal annealing on the molecular ordering and the current density-Voltage (J-V) and luminance-voltage (L-V) characteristics of 2-TNATA thin films.

EXPERIMENTAL

As an organic material, 4,4′,4″-Tris(2-naphthylphenylamino)triphenylamine(2-TNATA) was sublimed to obtain thin films via vacuum process and the chemical structure of 2-TNATA (formula: C66H48N4, molecular weight: 897.08, melting point: 245 ~ 247°C, T_g: 110°C, Tokyo Kasei Kogyo Co. Ltd.) is shown in Figure 1.

Vacuum deposition technique by thermal evaporation was used to obtain a homogeneous layer with well-controlled thickness. Before deposition, the ITO-coated glass was treated by acid solution followed

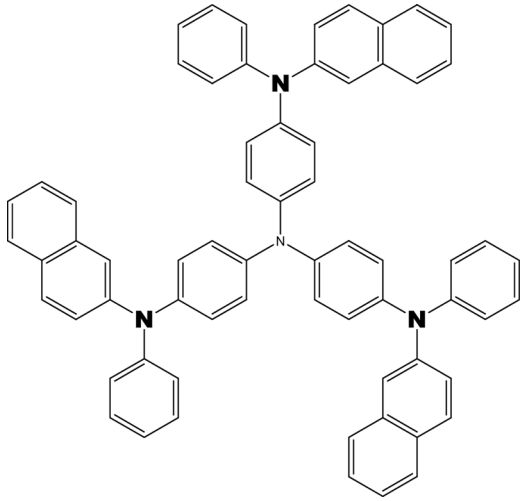

FIGURE 1 Chemical structure of 2-TNATA (4,4′,4″-Tris(2-naphthylphenylamino)triphenylamine).

by rinsing with de-ionized water, acetone and dried under nitrogen gas for cleaning the ITO-coated glass. 2-TNATA was deposited onto the pre-patterned ITO glass and the deposition rate was controlled to 0.5 nm/min to obtain 50 nm thickness of the 2-TNATA films. At this deposition rate the surface of the deposited films were found to be uniform throughout the deposition experiments in the present study. The deposition of the organic material was carried at a base pressure of 10^{-6} torr and the substrate was not intentionally heated during the device fabrication process. The cathode in all devices was composed of 100 nm of aluminum. The active area of the all devices was subject to the pre-patterned ITO glass.

In addition, 2-TNATA thin films were deposited under a magnetic field (∼6 mT) and without electromagnetic field to investigate the effect of electromagnetic field on the ordering of 2-TNATA molecules during deposition process. After deposition, thermal annealing of the deposited 2-TNATA thin films was performed in a cylindrical furnace in which the magnetic field (∼6 mT) was selectively applied as well. During thermal annealing, temperature was 110°C for 1hr. The film annealed in electromagnetic field was compared to both the as-deposited sample and the sample annealed at the same temperature without electromagnetic field.

The ITO/2-TNATA/Al devices were fabricated and the current density-Voltage (J-V) characteristics were measured. Film thickness

was measured with a profilometer model Alpha-step 100 (KLA-Tencor Co. Ltd.) and SEM (HITACHI S-4200). XRD (Rigaku Model D/Max 2400), Raman(Bruker IFS 66) and AFM (Nanoscope III-a, Digital Instruments Co. Ltd.) analysis were employed to characterize the molecular ordering and topology of the 2-TNATA thin films, respectively.

FABRICATION OF MULTI-LAYERED DIODES

The multi-layered ITO/2-TNATA/NPD/Alq_3/LiF/Al devices were fabricated as shown in Figure 2 and the luminance-voltage (L-V) characteristics were measured to investigate the effect of the molecular ordering of 2-TNATA on the enhancement of hole injection from ITO (Indium Tin Oxide) into HTL (Hole Transporting Layer) through a well-ordered 2-TNATA layer.

RESULTS AND DISCUSSION

Cross-sectional views of 2-TNATA films are shown in Figure 3. Many separated aggregates of molecules are found in an as-deposited film. However, there are no separated aggregates of molecules in the thermally-annealed film due to the enhanced interactions between molecules during the thermal annealing at near the glass transition

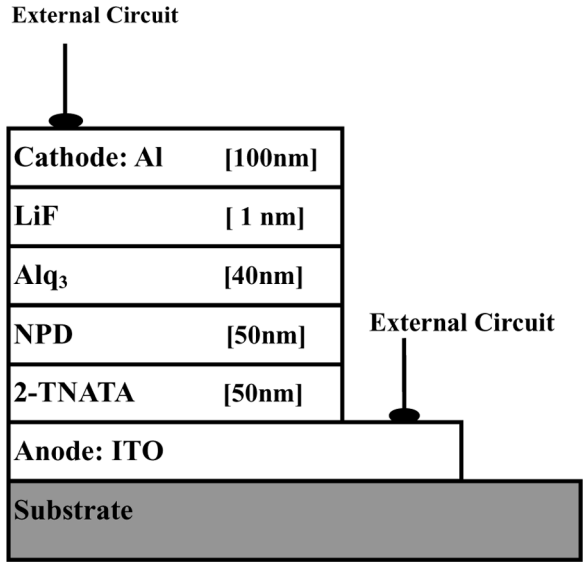

FIGURE 2 Configuration of multi-layered diodes.

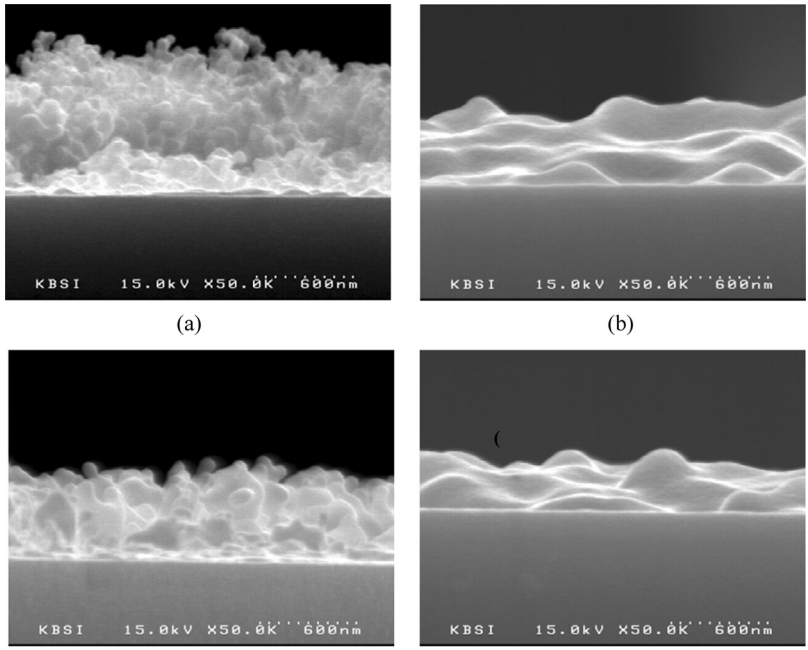

FIGURE 3 SEM images (cross-sectional view) of 2-TNATA films: (a) as-deposited film, (b) thermal annealing at 110°C for 1 hr, (c) electromagnetic field (~6 mT) during deposition, and (d) thermal annealing at 110°C for 1 hr with electromagnetic field.

temperature of 2-TNATA. Eventually, the film matrix becomes continuous and dense. The bigger size of separated aggregates of molecules was found in the film deposited under electromagnetic field compared to an as-deposited film. In this study, thermal annealing was carried out at near the glass transition temperature of 2-TNATA since it is reported that a significant improvement in materials when the organic film is annealed at near the glass transition temperature [7,8].

Surface images of 2-TNATA thin films are shown in Figure 4 and many grains are found on the surfaces of the films. By thermal annealing treatment, the grain size becomes bigger and the surface roughness decreases. By the treatment of electromagnetic field, the grain size becomes smaller but the surface roughness decreases. XRD images are shown in Figure 5 and there are no differences in peak patterns between samples. In this case, Raman spectra can be used to investigate the molecular stacking behavior since Raman spectra

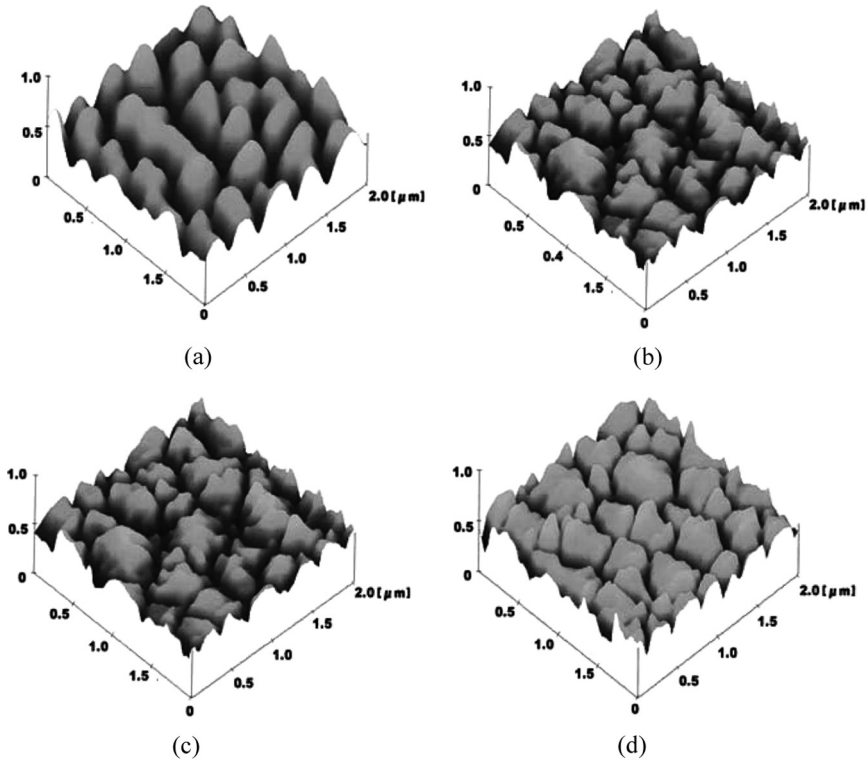

FIGURE 4 AFM images (3D) of 2-TNATA film surfaces: (a) as-deposited film, (b) thermal annealing at 110°C for 1 hr, (c) electromagnetic field (~6 mT) during deposition, and (d) thermal annealing at 110°C for 1 hr with electromagnetic field.

can reflect the overlapping of a ring stretch of neighboring molecules. The Raman spectra of the films are shown in Figure 6. For the aromatic ring containing organic materials, typical Raman bands are observed at 1609, 1594, 1574, 1530, 1374, 1288, 1222, and 1198 cm^{-1} [8,9]. 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 band. The width of each band in the amorphous state is broader than that in the crystalline state. In some reports, it was found that the position and width of Raman bands had been changed after thermal annealing of the films [8,9]. The observed intensity of each band arising from an organic layer mainly depends on the thickness of the organic layer and the cross-section of the Raman band(resonance Raman effect). In addition, the overlapping

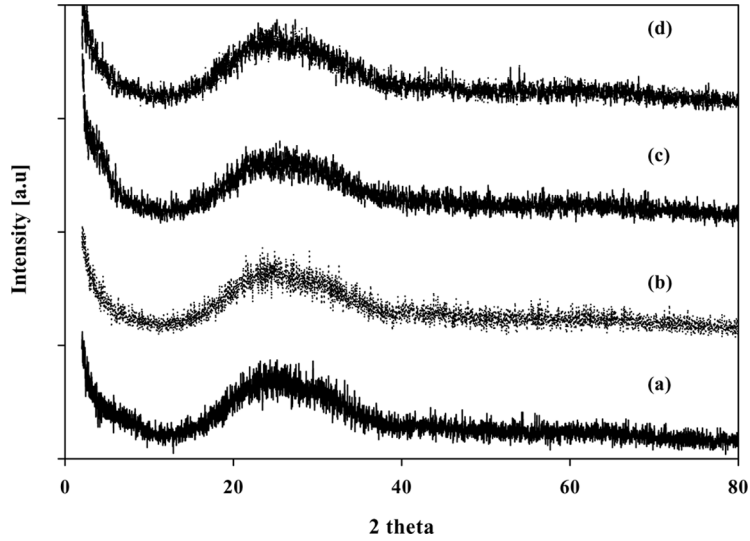

FIGURE 5 XRD images of 2-TNATA films: (a) as-deposited film, (b) thermal annealing at 110°C for 1 hr, (c) electromagnetic field (∼6 mT) during deposition, and (d) thermal annealing at 110°C for 1 hr with electromagnetic field.

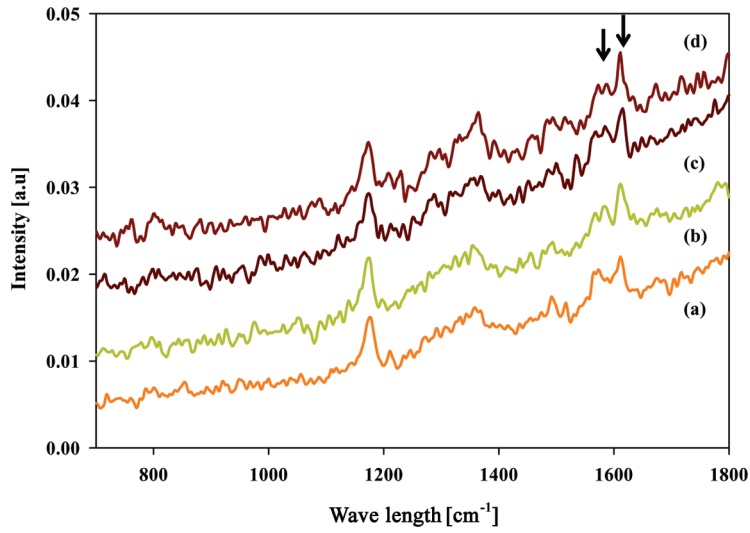

FIGURE 6 Raman Spectra of 2-TNATA with various treatments: (a) as-deposited film, (b) thermal annealing at 110°C for 1 hr, (c) electromagnetic field (∼6 mT) during deposition, and (d) thermal annealing at 110°C for 1 hr with electromagnetic field.

of π-bond of macrocyclic organic materials leads to the enhanced absorption intensity in Raman spectra [12]. The overlapping of π-bond of macrocyclic organic materials can be arisen from the closer packing of the organic materials. The peak intensities at near 1574 and 1609 cm^{-1} in Figure 6 become relatively higher and sharper with thermal annealing treatment and corresponding peaks are marked in Figure 6. Relatively higher intensities at near 1574 and 1609 cm^{-1} indicate that the aromatic rings of 2-TNATA molecules may be overlapped as the molecules come closer due to the stronger interactions between 2-TNATA molecules and eventually they are ordered in the thin films. In addition, electromagnetic fields can also affect on the interaction of 2-TNATA molecules since most of macrocyclic organic materials posses polar and/or a magnetic behavior, which can be attributed to the molecular ordering of 2-TNATA thin films [10,11]. In all samples treated with thermal annealing and electromagnetic field, molecular ordering of 2-TNATA films was observed in this study. There were no additional peaks which were observed for all films after treatments, which indicate that there should be no reaction during the treatments.

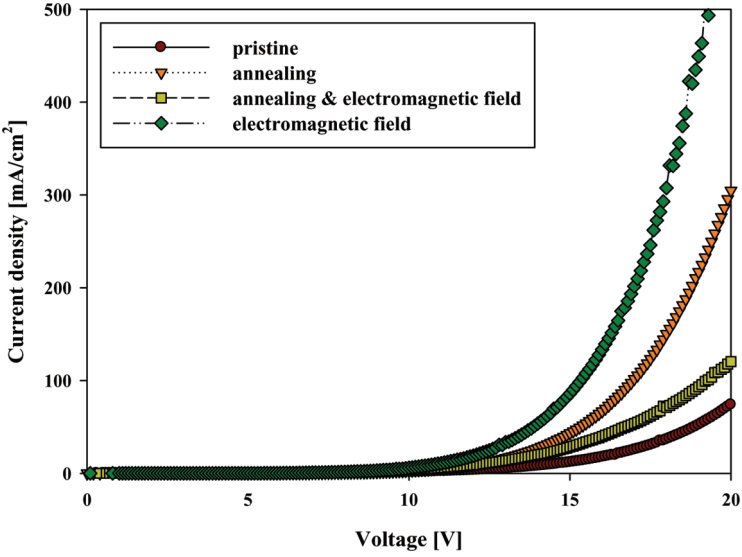

FIGURE 7 J-V characteristics of ITO/2-TNATA/Al devices fabricated under various conditions: (●) as-deposited film, (▼) thermal annealing at 110°C for 1 hr, (■) electromagnetic field (~6 mT) during deposition, and (◆) thermal annealing at 110°C 1 hr with electromagnetic field.

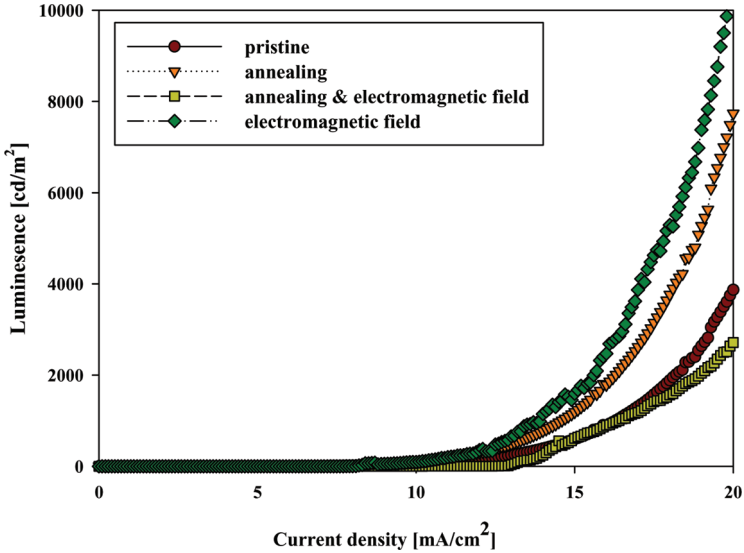

FIGURE 8 L-V characteristics of ITO/2-TNATA/NPD/Alq3/LiF/Al devices fabricated under various conditions: (●) as-deposited film, (▼) thermal annealing at 110°C for 1 hr, (■) electromagnetic field (∼6 mT) during deposition, and (◆) thermal annealing at 110°C 1 hr with electromagnetic field.

The J-V and L-V characteristics of the multi-layered devices, in which 2-TNATA film was used as a hole injection layer, are shown in Figures 7 and 8. The multi-layered device using thermally treated 2-TNATA film under electromagnetic field showed much enhanced current density and luminance at a given voltage compared to the multi-layered device using an as-deposited 2-TNATA film. It can be concluded that the molecular ordering can dramatically increase the charge mobility, which results in the improvement of the current density and flow through the film. Consequently, enhanced luminance performance of the organic light-emitting diodes can be obtained by using molecularly-ordered organic film as a hole injection layer.

CONCLUSIONS

The results of Raman spectra show that the 2-TNATA films are molecularly ordered after thermal annealing at the temperature of to 110°C, which is near the glass transition temperature of 2-TNATA, as well as electromagnetic field. In the Raman spectra, relatively

higher intensity at 1609 cm^{-1} indicate that the aromatic rings of 2-TNATA molecules may be overlapped and eventually ordered in the thin films due to the stronger interactions between the neighboring 2-TNATA molecules. By using molecularly-ordered 2-TNATA film, as a hole injection layer and prepared by thermal annealing and electromagnetic field treatment, the improved current density and luminance of the organic light-emitting diodes were obtained by using a molecularly-ordered hole injection layer in this study.

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