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# Effects of isomeric transformation on characteristics of Alq3 amorphous layers prepared by vacuum deposition at various substrate temperatures

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Organic tris(8-hydroxyquinoline)aluminum (Alq3) amorphous layers are prepared by vacuum deposition at various substrate temperatures  $T_{\text{sub}}$  from 30 to 180 °C. The surface morphology and electrical characteristics of these as-deposited layers are studied by atomic force microscopy and current-density versus electric-field ( $J$ - $E$ ) curves. The temperature dependence of the dark electrical conductivity  $\sigma(T)$  determined from  $J$ - $E$  curves is also examined. These experimental results reveal that the surface and electrical properties of Alq3 amorphous layers deposited at  $T_{\text{sub}}$  between 90 and 120 °C exhibit an anomalous  $T_{\text{sub}}$  dependence. However, this anomalous  $T_{\text{sub}}$  dependence is not observed from infrared absorption measurements, and therefore is not the result of chemical degradation. The observed behavior is explained in terms of the property that the vacuum deposition of Alq3 with  $T_{\text{sub}}$  between 90 and 120 °C involves a thermal interconversion between meridional and facial Alq3 isomers. © 2007 American Institute of Physics. [DOI: 10.1063/1.2749209]

## I. INTRODUCTION

The ease of processing organic materials has led to intense research into the preparation of organic light-emitting diodes, organic field-effect transistors, and organic solar cells over the last two decades.<sup>1-3</sup> The active layers in these devices are fabricated from small organic molecules, oligomers and/or polymers. These molecular materials have in common a conjugated  $\pi$ -electron system within which electrons can move via the overlap of  $\pi$ -electron clouds. The performance of these devices is then determined by the intramolecular and intermolecular charge transport mechanisms, which are strongly influenced by the packing of the molecules, and therefore by the growth process. Organic layers from small molecules or conjugated oligomers are generally prepared by vacuum deposition on a cold substrate; accordingly, these layers are not macroscopically homogeneous because of growth defects. The effects of substrate temperature  $T_{\text{sub}}$  and source temperature  $T_{\text{sou}}$  on the size, orientation, and crystallinity of the grains in molecular  $C_{60}$  polycrystalline films have been clearly observed.<sup>4,5</sup> Therefore, a systematic study of the effects of deposition conditions on the physical properties of as-deposited organic layers will be very useful in the design, development, and fabrication of future organic devices.

Among the aforementioned organic materials, tris(8-

hydroxyquinoline)aluminum (Alq3) is a stable metal chelate complex that can be sublimed to form thin films with excellent electron-transport and light-emitting properties.<sup>6,7</sup> Although Alq3 stands as one of the most successful organic materials used in organic light-emitting diodes and great attention has been paid to this organic semiconductor, many important questions about the morphology and electrical and optical properties of Alq3 films remain. One of the unresolved issues is the effects of Alq3 isomeric transformation on the characteristics of as-deposited Alq3 amorphous films.<sup>1,8</sup>

Alq3 has two geometrical isomers: meridional (*mer*,  $C1$  symmetry) and facial (*fac*,  $C3$  symmetry). Although such an isomeric transformation at about 115 °C was inferred from NMR measurements when dimethylsulfoxide was used as the solvent,<sup>8,9</sup> the possibility of isomeric transformation between *mer* and *fac* isomers is still unclear when Alq3 sublimes in a high vacuum.<sup>8</sup> A detailed density functional theory study of the isolated molecules indicated that the *mer* isomer is 0.17 eV lower in energy than the *fac* isomer, and the permanent dipole moments are estimated as 4.1 and 7.1 D for *mer* and *fac* isomers, respectively.<sup>10</sup> For crystalline phases,  $\alpha$ -Alq3 and  $\beta$ -Alq3 phases are identified as low-temperature phases, while  $\gamma$ -Alq3 and  $\delta$ -Alq3 phases are identified as high-temperature phases (above 395 °C).<sup>8</sup> The growth of low-temperature (low- $T$ ) *mer* isomer crystals to form ordered Alq3 films was noted by molecular beam deposition on cleaved KCl and KBr substrates at room temperature,<sup>11</sup> while

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the high-temperature  $\delta$ -Alq3 phase was identified as being composed of high-temperature (high- $T$ ) *fac* isomers.<sup>12,13</sup>

From external control and monitoring of  $T_{\text{sub}}$  and  $T_{\text{sou}}$ , our earlier experimental results demonstrated that, when  $T_{\text{sou}}$  is fixed at  $250 \pm 5$  °C,  $T_{\text{sub}}$  strongly affects the surface morphology, structural information, and electrical and optical properties of the as-deposited Alq3 amorphous layers.<sup>14,15</sup> An anomalous  $T_{\text{sub}}$  dependence of the surface and electrical properties was also observed for Alq3 amorphous layers deposited at  $T_{\text{sub}}$  between 90 and 120 °C.<sup>15</sup> In this paper, to explain these anomalous experimental results, we propose that the vacuum deposition of Alq3 with  $T_{\text{sub}}$  between 90 and 120 °C involves a thermal interconversion between *mer* and *fac* Alq3 isomers.

## II. EXPERIMENTAL DETAILS

The Alq3 layers adopted in this study are prepared in a thermal evaporation chamber with a base pressure of  $3 \times 10^{-5}$  Torr. Indium tin oxide (ITO) conducting glass with sheet resistance of  $13 \pm 2$   $\Omega/\square$  (for electrical measurements) or a sapphire plate with surface roughness of  $0.15 \pm 0.03$  nm (for surface morphology and x-ray diffraction measurements) is used as a substrate. The distance between source crucible and substrate is about 16 cm. The values of  $T_{\text{sub}}$  are varied from 30 to 180 °C when  $T_{\text{sou}}$  is fixed at  $250 \pm 5$  °C. Note that the glass-transition temperature  $T_g$  is around 175 °C for Alq3. The deposition rate is maintained at 2–3 Å/s. The thickness of the as-deposited Alq3 films is typically kept at 1500 Å, except for electrical characterization. Further details of the deposition processes have been presented elsewhere.<sup>14</sup>

For electrical characterization, a top Au-metal contact with an active area of approximately  $4 \times 4$  mm<sup>2</sup> is fabricated by ion sputtering. A current-voltage ( $I$ - $V$ ) measurement is applied to the sandwiched Au/organic-layer/ITO configuration. Usually, the sandwiched sample possesses low resistance. Thus, the thickness of the Alq3 films has to be sufficiently large; here, 4000 Å is adopted. In addition, to obtain the actual magnitude of electric  $E$  field across the organic film, a correction with respect to the internal resistance of the measuring circuit is carefully taken into account. In low  $E$  fields from 0 to 0.75 MV/m, the measured current-density versus  $E$  field ( $J$ - $E$ ) curves of all of the samples exhibit linear Ohmic behavior,<sup>14</sup> from which the dark electrical conductivity  $\sigma$  of the organic Alq3 layer is then estimated. To eliminate effects from water vapor and oxygen gas, all the measurements are made after the sample is put into a cryostat system in dynamic vacuum for at least 12 h. During that period, data are taken to test their stability and reliability at 300 K. Experimental results reveal that, after 12 h in a dynamic vacuum, the dark electrical conductivities  $\sigma(T=300$  K) of the amorphous samples reach an almost steady state.

## III. RESULTS AND DISCUSSION

Figure 1 presents the typical room-temperature atomic force microscopic (AFM) images of Alq3 amorphous layers deposited on a sapphire plate at various  $T_{\text{sub}}$ . Figure 2 plots

the calculated root-mean-square roughness ( $R_{\text{rms}}$ ). As  $T_{\text{sub}}$  is increased from 30 up to 60 °C, the as-deposited layers have a flatter surface morphology and a slightly smaller  $R_{\text{rms}}$ . However, at  $T_{\text{sub}}=90$  °C, the surface roughness of the amorphous layer reaches a local maximum. Surprisingly, on further increasing  $T_{\text{sub}}$  from 90 to 120 °C, the surface morphology of the as-deposited layers becomes flatter, and  $R_{\text{rms}}$  reaches a local minimum at  $T_{\text{sub}}=120$  °C. Finally,  $R_{\text{rms}}$  increases with increasing  $T_{\text{sub}}$  from 120 up to 180 °C.

Figure 3 plots the steady-state values of  $\sigma(T=300$  K) for the Alq3 amorphous layers deposited on ITO conducting glass at various  $T_{\text{sub}}$ . The value of  $\sigma(T=300$  K) increases with  $T_{\text{sub}}$  from 30 to 90 °C, anomalously falls to a local minimum at  $T_{\text{sub}}=120$  °C, and then increases again with  $T_{\text{sub}}$  from 120 to 180 °C.

The temperature dependence (with  $T$  in the range 40–300 K) of dark electrical conductivity,  $\sigma(T)$ , is used to test the thermal stability of physical properties of the as-deposited Alq3 amorphous layers. As presented in Fig. 4, a back-and-forth temperature scan ( $T$  scan) with a cooling and heating rate of about 2 K/min reveals many interesting features. After one complete  $T$  scan (300→40→300 K), the ratio of the second measured value of  $\sigma$  at  $T=300$  K to the first one, i.e.,  $R_\sigma = \sigma(T=300$  K, 2nd)/ $\sigma(T=300$  K, 1st), represents the thermal stability of the sample against  $T$  scan. As calculated from Fig. 4,  $R_\sigma$  equals 0.73 for  $T_{\text{sub}}=30$  °C, 0.90 for  $T_{\text{sub}}=60$  °C, and 0.94 for  $T_{\text{sub}}=90$  °C. The thermal stability of  $\sigma(T)$  for the Alq3 amorphous layers deposited at  $T_{\text{sub}}$  between 30 and 90 °C is observed to increase with  $T_{\text{sub}}$ . However, for Alq3 amorphous layers deposited at  $T_{\text{sub}}=120$  and 150 °C, during the first decreasing  $T$  scan,  $\sigma(T)$  falls rapidly at a specific  $T$  of around 150–200 K. Once the layer is in the lower- $\sigma$  state,  $\sigma$  becomes less sensitively dependent on  $T$ . After one complete  $T$  scan, the value of  $R_\sigma$  decreases sharply to 0.67 for  $T_{\text{sub}}=120$  °C, and to 0.31 for  $T_{\text{sub}}=150$  °C, respectively. For Alq3 amorphous layers deposited at  $T_{\text{sub}}=180$  °C above  $T_g$ , the variation of  $\sigma$  versus  $T$  is rather small, i.e.,  $R_\sigma=0.96$ , and these layers are thermally very stable.

As presented in Figs. 1–4, the experimental results on both ITO and sapphire plates clearly demonstrate that the surface and electrical properties of the as-deposited Alq3 amorphous layers not only sensitively depend on  $T_{\text{sub}}$  but also exhibit an anomalous  $T_{\text{sub}}$  dependence as  $T_{\text{sub}}$  is varied from 90 to 120 °C. Thus, this anomalous feature must come from  $T_{\text{sub}}$  and not from the nature of the substrate. However, this anomalous  $T_{\text{sub}}$  dependence is not observed from infrared (IR) absorption measurements. For the IR absorption spectra of Alq3 amorphous films deposited (on ITO plates with thickness of 4000 Å) at  $T_{\text{sub}}=90$  and 120 °C, as shown in Fig. 5, the aromatic stretching (C=C, 1450–1600 cm<sup>-1</sup>) and aromatic amine resonances (C-N-C, 1250–1370 cm<sup>-1</sup>) are clearly observed and are in good agreement with published data.<sup>16,17</sup> The similarity between these two spectra indicates that no chemical or photodegradation occurs in these two Alq3 amorphous films. Thus, the abovementioned anomalous  $T_{\text{sub}}$  dependence does not result from chemical degradation. It is interesting to mention here that, for polycrystalline Alq3 samples (i.e.,  $\alpha$ -Alq3 and  $\delta$ -Alq3 phases), a

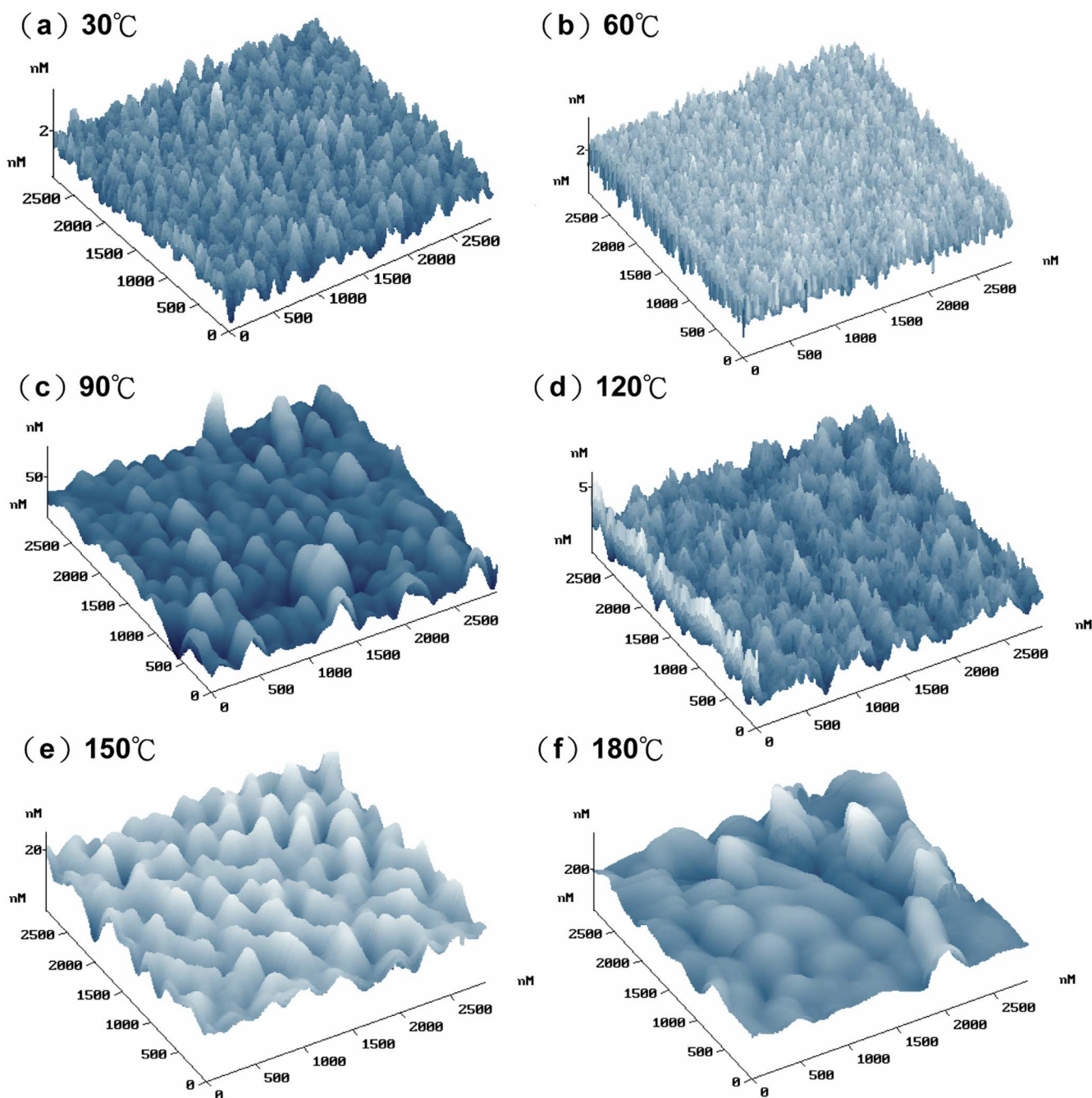


FIG. 1. AFM images of Alq3 amorphous layers deposited at various  $T_{\text{sub}}$ . Note the adjustment of the vertical scale.

splitting of the Al-N and Al-O stretching modes at 396 and 549  $\text{cm}^{-1}$  was observed due to the different molecular symmetry,<sup>13</sup> however, for amorphous Alq3 films deposited at  $T_{\text{sub}}=90$  and 120  $^{\circ}\text{C}$ , the IR signals are rather noisy in our data. This remains for further investigation.

To explain these interesting behaviors, based on the fact that an isomeric transformation was indicated by NMR measurements at about 115  $^{\circ}\text{C}$  when dimethylsulfoxide was used as the solvent,<sup>8,9</sup> the following model is then proposed. When Alq3 molecules sublime in a high vacuum, thermal interconversion between low- $T$  *mer* Alq3 and high- $T$  *fac* Alq3 isomers may occur between 90 and 120  $^{\circ}\text{C}$  (as in the solution case). Since  $T_{\text{sub}}$  is fixed at  $250 \pm 5$   $^{\circ}\text{C}$ , high- $T$  *fac*

Alq3 isomers should be the dominant molecules from the source region. Near the growing interface,  $T_{\text{sub}}$  plays an important role not only in the surface diffusion and re-evaporation processes, but also in the possibility of thermal interconversion between *fac* and *mer* isomers. Accordingly, for  $T_{\text{sub}} \leq 90$   $^{\circ}\text{C}$ , the as-deposited Alq3 amorphous layers are assumed to be composed of low- $T$  *mer* isomers; while for  $T_{\text{sub}} \geq 120$   $^{\circ}\text{C}$ , the layers are mainly formed from high- $T$  *fac* isomers.

At  $T_{\text{sub}} \leq 90$   $^{\circ}\text{C}$ , the Alq3 molecules that adhere to these “colder” substrates may undergo an isomeric transformation from high- $T$  *fac* phase to low- $T$  *mer* phase, and the irregular stacking of the *mer* Alq3 molecules dominates the vacuum

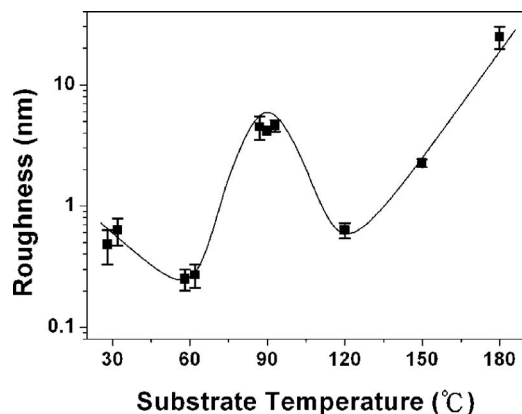


FIG. 2. Calculated values of  $R_{\text{rms}}$  for Alq3 amorphous layers deposited at various  $T_{\text{sub}}$ .

deposition. As  $T_{\text{sub}}$  is increased from 30 °C up to 60 °C, the adhering Alq3 molecules gain slightly more surface diffusion energy, and the surface morphology of the as-deposited layers becomes flatter, as presented in Figs. 1 and 2. However, at  $T_{\text{sub}}=90$  °C, the higher thermal energy may promote some preferential rearrangements of the short  $\pi$ - $\pi$  contacts between the ligands of neighboring Alq3 molecules, producing some prototype  $\alpha$ -Alq3 or  $\beta$ -Alq3 crystallites.<sup>8,11</sup> Therefore, the surface roughness of the amorphous layer reaches a local maximum. Accordingly, the closer  $\pi$ - $\pi$  links between the ligands in *mer* Alq3 molecules of the as-deposited amorphous layers correspond to the easier hopping of charge carriers. As displayed in Fig. 3,  $\sigma(T=300$  K) of the as-deposited Alq3 amorphous layers increases with  $T_{\text{sub}}$  between 30 and 90 °C. Additionally, the closer  $\pi$ - $\pi$  links also result in the higher thermal stability of  $\sigma(T)$  for the Alq3 amorphous layers as presented in Fig. 4.

At  $T_{\text{sub}} \geq 120$  °C, on “hotter” substrates, the irregular stacking of high- $T$  *fac* Alq3 molecules dominates the vacuum deposition. Since the high- $T$  *fac* isomer has a larger dipole moment than the low- $T$  *mer* isomer and a stronger dipole-dipole interaction can further stabilize the aggregate phase,<sup>10</sup> the amorphous layers deposited at  $T_{\text{sub}}=120$  °C then have flatter surfaces and smaller  $R_{\text{rms}}$  as comparing with those deposited at  $T_{\text{sub}}=90$  °C (which are dominated by the low- $T$  *mer* Alq3 molecules with a smaller dipole moment). Addi-

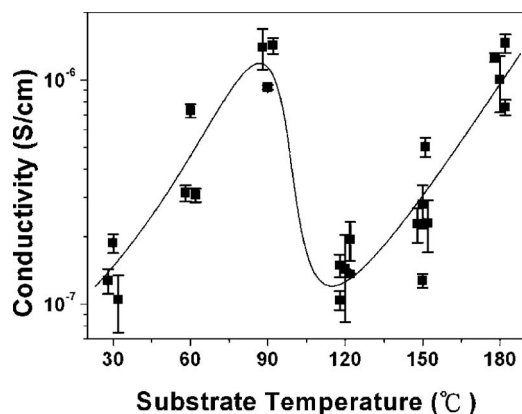


FIG. 3. Values of  $\sigma(T=300$  K) for Alq3 amorphous layers deposited at various  $T_{\text{sub}}$ .

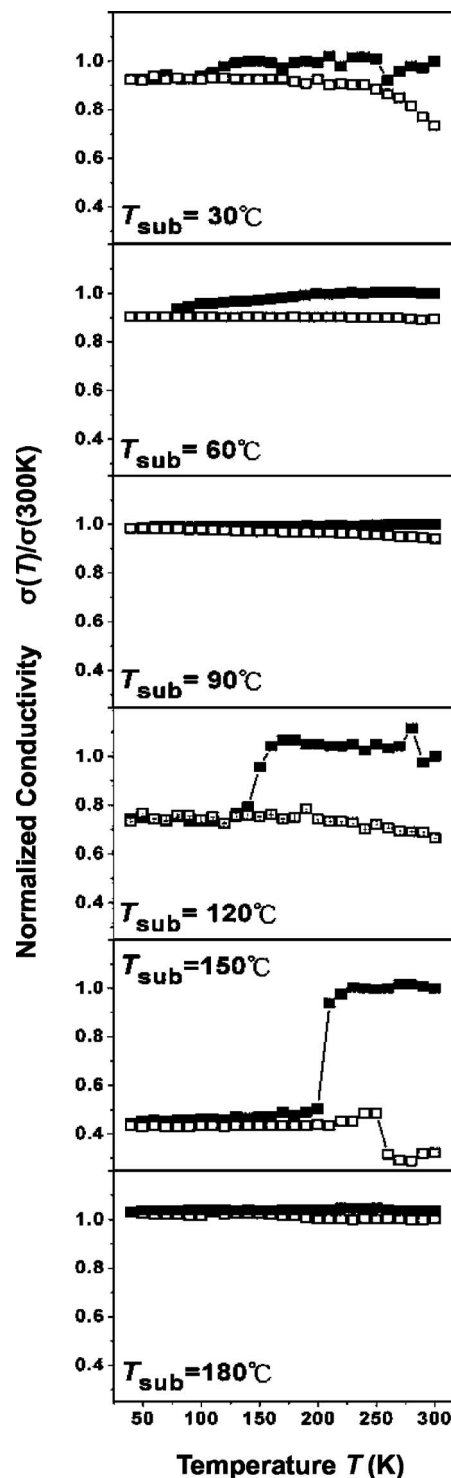


FIG. 4. Temperature dependence of normalized  $\sigma(T)/\sigma(T=300$  K) for Alq3 amorphous layers deposited at various  $T_{\text{sub}}$ . Solid symbols refer to the decreasing  $T$  scan and open symbols refer to the increasing  $T$  scan.

tionally, the *fac* isomer is reported to act as a trapping state in electron transport,<sup>10</sup> thus, the layers deposited at  $T_{\text{sub}}=120$  and 150 °C have much smaller values of  $\sigma(T=300$  K) as displayed in Fig. 3. These high- $T$  *fac* isomers in amorphous layers are not stable below room temperature. This fact is supported by both theoretical calculation and experimental results.<sup>10-12</sup> Hence, as plotted in Fig. 4, during the first cooling, these *fac* isomers are unstable in their “as-deposited”

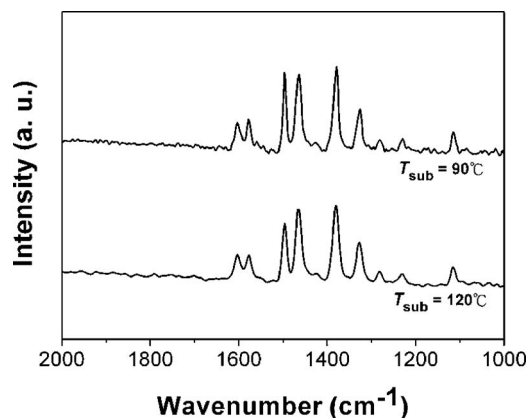


FIG. 5. IR absorption spectra of Alq3 amorphous films deposited at  $T_{\text{sub}} = 90$  and  $120$  °C.

amorphous states, and the conformational instability causes an abrupt discontinuity in  $\sigma(T)$ . This conformational instability is irreversible. Accordingly, the values of  $R_{\sigma}$  drop greatly to 0.67 ( $T_{\text{sub}} = 120$  °C) and 0.31 (150 °C).

To understand the Alq3 molecular aggregation state, x-ray diffraction (XRD) is applied. Figure 6 depicts the XRD patterns of Alq3 films deposited at various  $T_{\text{sub}}$ . For  $T_{\text{sub}} \leq 150$  °C, similar XRD curves are obtained with a broad diffuse peak representing an average nearest-neighbor distance. These results reveal that the films deposited with  $T_{\text{sub}} \leq 150$  °C possess almost identical amorphous character. It is also interesting to note that the anomalous  $T_{\text{sub}}$  dependence observed from surface and electrical properties in between 90 and 120 °C is not observed in XRD analysis. Although there is a different molecular symmetry between *fac* and *mer* Alq3 isomers, in the amorphous solid state of randomly distributed Alq3 molecules, this difference is averaged and is not strong enough to be exhibited in the XRD patterns. At  $T_{\text{sub}}$  above  $T_g$ , the as-deposited Alq3 films may be more orderly; some crystalline characteristics are expected. However, for  $T_{\text{sub}} = 180$  °C above  $T_g$ , amorphous character is still observed, but with a small shift in the diffuse peak as shown in Fig. 6. This shift represents a shorter average nearest-neighbor distance, which can be explained by the stronger interactions among Alq3 molecules because of the high  $T_{\text{sub}}$ .

The effects of  $T_{\text{sub}}$  on the physical properties of as-deposited small-molecule organic amorphous layers are

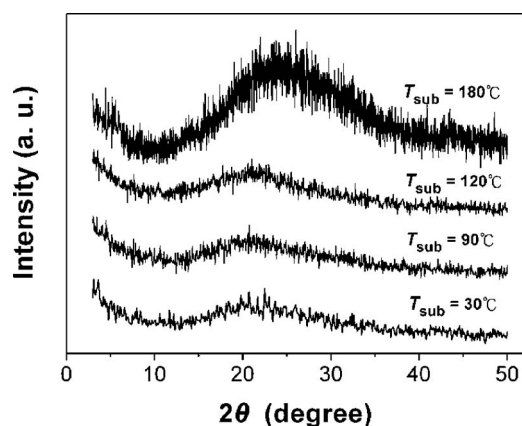


FIG. 6. XRD patterns of Alq3 films deposited at various  $T_{\text{sub}}$ .

much more complex and interesting than those of inorganic covalent compounds. The intrinsic characteristics of isomeric transformation, complex interactions between ligands of these small organic molecules, and the molecular dynamics of both bulk diffusion and interface diffusion are significantly involved in the fabrication of organic thin films from vacuum deposition. Therefore, a detailed study of the effects of deposition conditions on the physical properties of these as-deposited organic layers is of great value in the design, development, and fabrication of future organic light-emitting diodes, organic field-effect transistors, and organic solar cells.

#### IV. SUMMARY

In this study, organic Alq3 amorphous layers are prepared by vacuum deposition at various  $T_{\text{sub}}$  from 30 to 180 °C. The effects of  $T_{\text{sub}}$  on the physical properties of the as-deposited Alq3 amorphous layers are examined. The surface and electrical properties of the as-deposited Alq3 amorphous layers not only sensitively depend on  $T_{\text{sub}}$  but also exhibit an anomalous  $T_{\text{sub}}$  dependence as  $T_{\text{sub}}$  is varied from 90 to 120 °C. The observed behavior is explained in terms of the property that the vacuum deposition of Alq3 films with  $T_{\text{sub}}$  between 90 and 120 °C involves a thermal interconversion between *mer* and *fac* Alq3 isomers. For  $T_{\text{sub}} \leq 90$  °C, the as-deposited Alq3 amorphous layers are assumed to be composed of low- $T$  *mer* isomers; while for  $T_{\text{sub}} \geq 120$  °C, these layers are composed of high- $T$  *fac* isomers. Thus, this anomalous  $T_{\text{sub}}$  dependence of the surface and electrical properties of the as-deposited Alq3 amorphous layers is governed by the isomeric transformation

#### ACKNOWLEDGMENTS

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