2009

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Kanchibotla, B. R., Garre, K., & Aurongzeb, D. Correlated growth of organic material tris (8-hydroxyquinoline) aluminum (Alq3) and its relation to optical properties. Journal of Applied Physics, 106, 096101 (2009). Copyright © 2009 American Institute of Physics.

Correlated growth of organic material tris (8-hydroxyquinoline) aluminum (Alq3) and its relation to optical properties

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(Received 29 June 2009; accepted 17 September 2009; published online 3 November 2009)

We report slow correlated growth mode in energetic cluster vapor deposited organic light emissive material tris(8-hydroxyquinoline) aluminum from 5 to 100 nm. Phase modulated atomic force microscopy shows very slow grain growth with thickness, with very small phase differences within the film. Fractal dimension calculated from correlation function shows growth process above 10 nm consistent with diffusion-limited aggregation. For low thickness (5 nm), photoluminescence measurement shows the emission peak is shifted by ~0.4 eV toward lower wavelength.
[doi:10.1063/1.3247587]

Organic materials continue to attract scientific and technological interest due to their easy applicability to fabricate light-emitting diodes and large area flexible display with wide range of advantages such as fast response time, low power consumption, and structural simplicity.[1–4] With continued improvement in material and fabrication process (FD), the improvements are showing feasibility for panel lighting. However, a wide range of fundamental issues needs to be addressed in order to optimize any device structure. From a materials point of view, formation/transport of spin, singlet/triplet excited states, and effect of surface/interface morphology remains a strong focus.[5–7] The vapor deposition process itself poses a wide range of methods and in this context, identification of the relevant diffusion mechanisms and parameters is critical for optimal performance as devices become in the order of nanometers.

Recently, organic light-emitting diode (OLED) based on aluminum tris(8-hydroxyquinolinate) (Alq3), gained considerable interest due to its properties such as relative stability, easy synthesis, good electron transport, and emitting properties.[8–12] Systematic investigations of the structural and optical properties of Alq3 in the solid state, as well as of the influence of the preparation conditions and deposition rate on these properties were carried out.[13,14] Curioni *et al.*[15] showed using *ab initio* calculations the coexistence in the thin film of two geometrical isomers, meridianal Alq3 and facial Alq3. According to the above results, the facial isomer is less stable in energy than the meridianal.[16] Along with the well-known three crystalline phases of Alq3 (α,β,γ), the existence of δ phase showing blueshifted luminescence was reported.[17] While most of the studies are available on true device structure, few studies are available on surface properties of this material with thickness dependence,[18] especially with high-resolution phase contrast surface microscopy. Therefore, understanding surface evolution and its correlation to optical properties requires further studies.

In this paper, we report surface evolution and optical properties of Alq3 deposited by an energetic cluster mask[19] that is very similar to a previously reported system.[20] We identified typical surface growth mode of this organic material by calculating fractal dimension.[21–23] We show that using this method, very high quality film can be deposited with very uniform phase distribution. We also report very high blueshift and infrared transmission measurement for low thickness percolation type cluster showing wide tunability of this material with surface conditions.

Alq3 (Alfa Aesar, 99.9% purity) with varying thicknesses have been thermally evaporated on indium tin oxide (ITO) substrates. The rest of the impurities do not affect the results. ITO of about 1200-A-thick coated onto glass substrates with dimension of 1.1-mm-thick and 2×3 in.^{2} in area have been purchased from Delta Technologies Ltd. The resistance of the substrates is about $\sim 60\Omega/\square$. The substrates are then cut into smaller dimensions about 1×0.5 in.^{2} with the help of a diamond scribe. The substrates are scribed on the glass side to minimize contamination of the ITO surface from the glass particles. The cut substrates are then cleaned by ultrasonic agitation in a detergent solution, thoroughly rinsed in de-ionized water and UV radiated. The substrates are then heated on a hot plate to about 80 °C for 30 min to remove the moisture on the surface and loaded into the vacuum chamber. The deposition of Alq3 is carried out in high vacuum $\sim 2\times 10^{-6}$ Torr by heating the source. The deposition rate is maintained between 0.2 and 1.0 Å/s by accurately controlling the current passing through the evaporation source with the help of SQC122 deposition controller from Sigma Instruments, Colorado. The surface was characterized with atomic force microscopy (AFM)[24,25] in a phase imaging mode (Digital Instruments) and normal mode. In phase imaging, a variant of tapping mode AFM imaging, the phase lag of the cantilever (Si, 5 N/m stiffness, ~10 nm apex) oscillation relative to the signal sent to the cantilever's piezodriver is used as a basis for image generation. Phase images can be generated as a consequence of variations in material properties such as adhesion or friction thus shows superior contrast and a qualitative compositional variation in the surface. Photoluminescence data were taken *ex situ* in a matrix form using xenon lamp as an excitation source with autocorrection for reflection. A thermocouple near the

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0021-8979/2009/106(9)/096101/3/$25.00

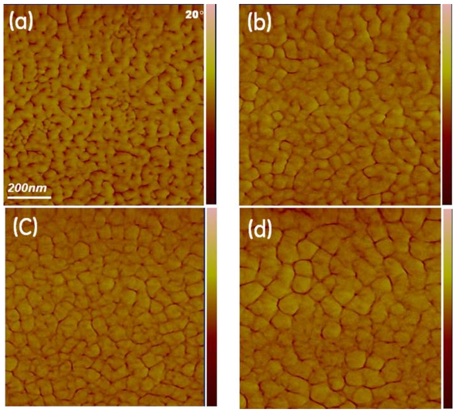

FIG. 1. (Color online) Phase modulated AFM image at various thicknesses. (a) 5, (b) 10, (c) 20, and (d) 100 nm.

sample showed consistent room temperature during measurement. Infrared transmission measurements were taken at room temperature using Bruker equipment. The thickness of 5, 10, 20, and 100 nm were chosen to obtain surface properties, which is widely studied[3,4,7,8,13,14,26] in a true OLED device format over two decades.

Figure 1 shows AFM image of 5, 10, 20, and 100-nm-thick films in phase contrast mode. At 5 nm the films are uniform with no grain formation but percolation boundaries with small pinholes/nanovoids are seen.[7] Influences of nanovoids on photoluminescence properties were previously reported but clear picture of density/size was not reported. At this thickness the nanovoids are uniformly distributed throughout the film. For all thicknesses the phase contrast is 20° indicating unchanged film physical properties over all thickness, compared to 90° with wide variation seen in other system.[27]

Figures 2(a) and 2(b) show the three-dimensional (3D) images of 5 and 100-nm-thick film. Consistent with phase imaging data from Fig. 1, at low thicknesses, we observe several grain size distributions. At higher thickness, a single size distribution is prominent. This is also seen in height-height correlation function (HHCF), shown in Fig. 2. HHCF is defined as $\mathrm{HHCF}(r,t)=\sqrt{\langle|h(r-r')-h(r')|^2\rangle}$,[20,22] where $h(r)$ is the surface height at position $r[=(x,y)]$ on the surface relative to the average surface height. For any arbitrary surface, the HHCF scales as $\mathrm{HCF}\sim r^{\alpha}$ and the fractal dimension is given by $D=d-\alpha$. Figure 2(c) shows fractal dimension of the surfaces for all thicknesses except for 5 nm. Figure 2(d) shows fractal dimension of the film at 5 nm. The bump at the lower window length is consistent with the image in Fig. 2(a), where wide distributions of grains are seen. For thicknesses > 10 nm, the fractal dimensions have wide distribution but consistent with diffusion-limited aggregation process.[23] This implies that the surface has very low sticking coefficient and molecules diffuse on the surface randomly and forms planer surface without forming mounds or pyramids[28] due to formation of potential barriers. At 5 nm the fractal dimension can imply a different growth mode where thickness-dependent transition is observed.[21] The correlation to FD to photoluminescence shift shows that the shift is very likely to be surface state and growth mode related and increases in maximum peak intensity is intrinsic, related to interface and orientation/phase as discussed in the last paragraph.

The classification in terms of fractal growth mode has mathematical correlation to the photoluminescence data. Figure 3(a) shows photoluminescence data in matrix form for 5-nm-thick film. The peak luminescence is shifted toward the lower wavelength compared to the other thicknesses, as seen in Fig. 3(b) (10 nm) and Fig. 3(d) (100 nm). The approximate shift is calculated to be 0.4 eV. It is possible to have similar effect at 5 nm due to distribution of grain formation, as seen in the image and HHCF of Figs. 3(a) and 3(d) In one of the previous studies, Braun *et al.*[17] shown that δ-Alq3 formation at the surface at high temperature can exhibit blueshift of ~0.2 eV, which is lower than what we have observed. Recently, Levichkova *et al.*[7] showed that for isolated molecules in solid state matrix, blueshift of up to 0.3 eV can be observed. A similar trend is also observed for simple thickness-dependent study.[8]

Figure 4 shows increase in peak intensity with thickness after 10 nm and shift in peak location after 5 nm. The shift in

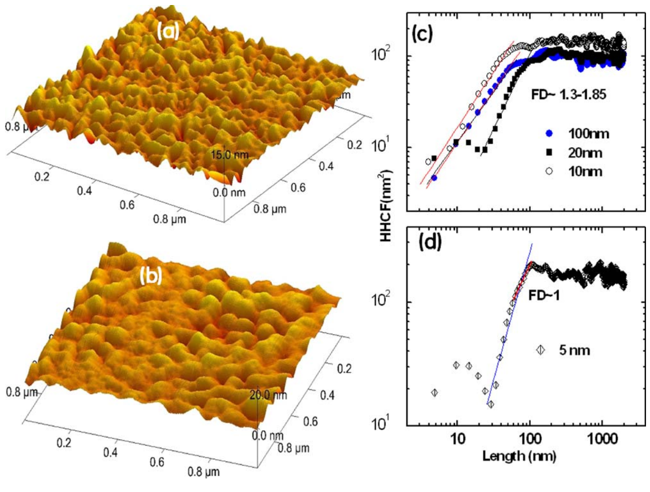

FIG. 2. (Color online) (a) 3D AFM image at 5 and (b) 100 nm to show surface evolution. (c) Correlation function for 10, 20, and 100 nm. (d) Correlation function for 5 nm. The bump at lower window length capturing small size grain distribution in the surface for 5 nm.

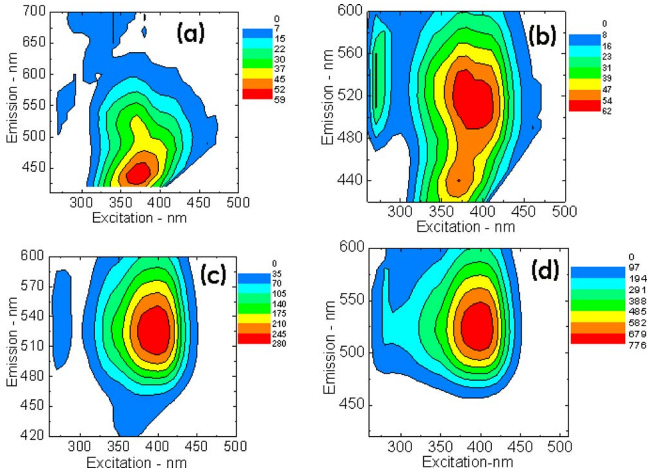

FIG. 3. (Color online) 2D photoluminescence emission-excitation map of the samples at various thicknesses at room temperature. (a) 5, (b) 10, (c) 20, and (d) 100 nm. The true intensity is scaled down by 10 000 for all cases.

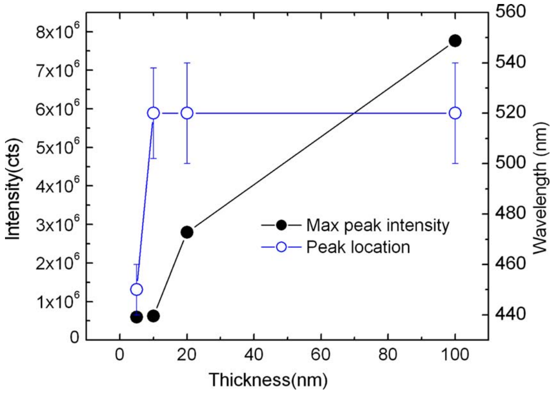

FIG. 4. (Color online) A summary of all journal observations at various thicknesses capturing intensity and shift.

peak location corresponds to fractal dimension calculation. Therefore it is likely that some surface effect is mainly responsible for peak shift. The increase in intensity with thickness is observed and reported before for other organic molecular system.[18] The trend in the peak intensity and increase in peak intensity are similar to our observation, however, the thickness range they have studied ranges from 55 to 210 nm. The dipole method simulation based on transfer matrix formalism predicts their observation. One point we should mention is that temperature and postenvironmental conditions can change the optical and electronic properties[6] of Alq3. Our samples were secured *ex situ* and measured inside a clean room. AFM scan showed no surface roughness change before and after measurement. Therefore, observed trend is morphology formed due to growth conditions. Since we observe consistent phase at the surface, one possibility is excitons confinement effect.[5] Change in porosity and nanoscale surface roughness can account for observed shift.

To further verify any consistent trend based on thickness and find out any unusual absorption peaks, we performed infrared transmission measurement of all the thicknesses as seen in Fig. 5. Interestingly, 5 nm is less transmissive than the other thicknesses. The vibrational feature at 3000 cm^{-1} is not consistent in terms of thickness since it reappears for 100 nm. From phase contrast image, it is clear the surface has more voids and separated grain boundaries. Disorder can induce dipole moment in the cavities causing more absorption in the film.[29]

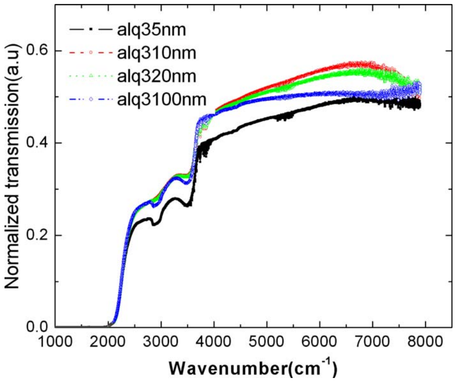

FIG. 5. (Color online) FTIR transmission measurements at various thicknesses.

In conclusion, we observe thickness-dependent luminescence shift in a widely used organic material. We show a good correlation between the blueshift and intrinsic scaling property by calculating fractal dimension of the surface. Using phase contract AFM we have shown clear formation of nanovoids and grain growth. The results add to the fact that growth conditions and surface structure can be tuned to fabricate highly stable OLED device. Further study in terms of interface and transient electroluminescence can help explain some of the observations.

ACKNOWLEDGMENTS

The work was partly supported by National Science Foundation Grant No. CTS-0210141.

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