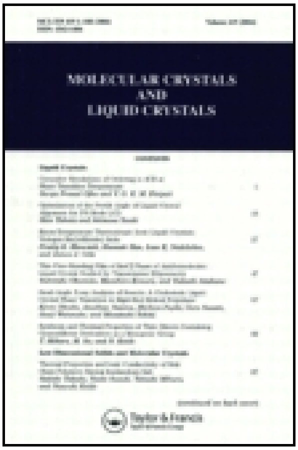

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Surface Morphology and Photoluminescence of Alq_3 Films Grown by Hot-Wall Method

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Surface Morphology and Photoluminescence of Alq_3 Films Grown by Hot-Wall Method

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Tris-(8-hydroxyquinoline) aluminum (Alq_3) films were deposited on hydrogen-terminated Si(111) substrates changing the substrate temperature from 80 to 160°C by hot-wall method. The deposited films were characterized by surface morphology and photoluminescence (PL). With increasing substrate temperature, the emission intensity of the Alq_3 films increases and the wavelength of the emission peaks shifts to lower wavelength from 528 to 507 nm. In addition, the vibronic structure with distinct five peaks was observed in the PL spectra of the films deposited at substrate temperatures of 100 and 120°C.

Keywords: Alq_3; crystalline phase; hot-wall method; photoluminescence; surface morphology

1. INTRODUCTION

Tris-(8-hydroxyquinoline) aluminum (Alq_3) is frequently used for green emitting and/or electron transporting layer in organic light emitting diodes since Tang and VanSlyke have demonstrated efficient electroluminescent diodes [1]. The Alq_3 films reported previously have usually deposited using conventional thermal evaporation, and these films were of amorphous phase. Recently, the crystalline Alq_3 films have also been reported by several authors [2,3]. The thermal evaporation is a deposition method under a non-equilibrium condition. On the other hand, it is well known that the hot-wall method is a deposition technique under a quasi-thermal equilibrium condition. In addition, the hot-wall method has also been used for epitaxial growth

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of semiconductors with high vapor pressure such as II-VI semiconductors, ZnTe [4] or CdS [5].

In this study, we have applied the hot-wall method to deposit Alq_3 films on hydrogen-terminated Si(111) substrates. The films were deposited with substrate temperatures ranging from 60 to 160°C, as a growth parameter. The deposited films were characterized by surface morphology and photoluminescence (PL) measurements.

2. EXPERIMENTAL

The hot-wall growth system employed in our laboratory consists of four zones: substrate zone, wall zone to regulate the vapor transport of sublimated source material, source zone to sublimate material, and reservoir zone to dope another material in the film. In this study, the reservoir zone was not used. The temperature of each zone was independently controlled with an accuracy of 0.5°C. The base pressure of our hot-wall system is lower than 1×10^{-6} Torr. The Alq_3 powder with a purity of 99.995% from Aldrich was used for a starting material without any further purification. Si(111) substrate was cleaned with acetone and ethanol solution and subsequently dipped in a dilute HF(2%) solution for the so-called hydrogen termination of Si(111) surface. Two kinds of series of depositions were performed: one is the source and wall temperatures were kept at 220 and 200°C, and the other were 180 and 170°C, respectively. The substrate temperature was changed from 60 to 160°C. In this study, we focus on the results of the former deposited films.

Surface morphology was observed using digital microscope (Keyence, VH-7000). Photoluminescence spectra were measured at room temperature. The samples were excited by the 325-nm (less than 0.3 mW) line of a He-Cd laser (Kimmon IK3351R-G). The emission from the samples were dispersed with a 50-m single grating monochromator and detected with a photomultiplier (Hamamatsu R928). Microscopic emission spectra excited at 365 nm were measured using a fluorescence microscope (Nikon) attached with a fiber spectrometer (Ocean Optics USB4000).

3. RESULTS AND DISCUSSION

Figures 1(a–e) shows surface morphologies of Alq_3 film on Si(111) deposited at different substrate temperatures, where the source and wall temperatures were kept at 220 and 200°C. Figure 1(f) shows a fluorescence micrograph on the Alq_3 film deposited at 120°C. The films deposited at 80 and 100°C exhibits smooth surface, as shown in

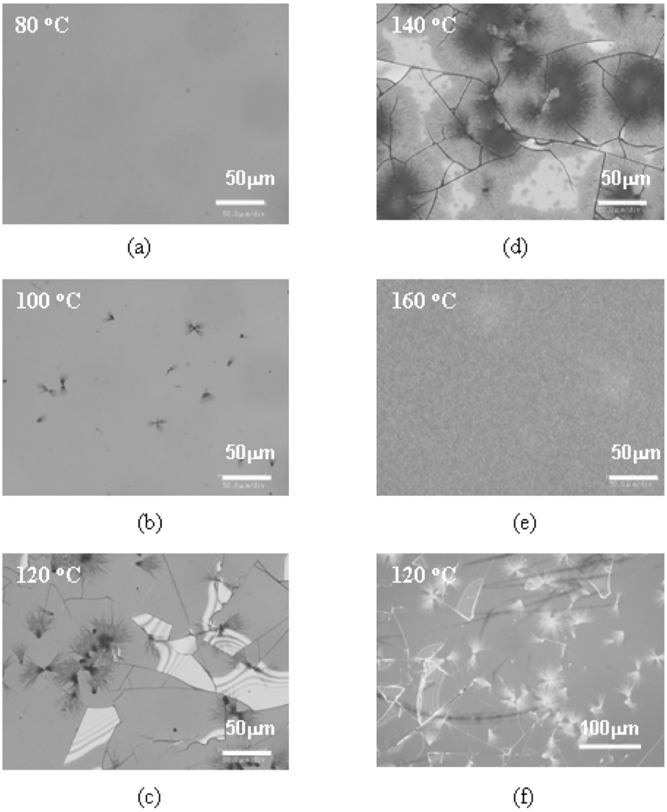

FIGURE 1 Surface morphologies of Alq_3 films deposited at different temperatures using a digital microscope (a)–(e), and (f) a fluorescence micrograph on Alq_3 film deposited at 120°C.

Figures 1(a) and 1(b). However, anomalous growth can be recognized as regions in the shape of feather on the surface of the film at 100°C, and their sizes enlarge at higher substrate temperature of 120 and 140°C. It should also be noted from Figure 1(f) that the fluorescence intensity from the anomalous growth region is brighter than that from the flat region surrounded. The spectroscopic difference between the two regions will be is discussed below. The Alq_3 film at 160°C is completely covered with rough surface. In addition, a number of cracks are randomly incorporated into the two films deposited at 120 and 140°C, and the films are separated into the small fragments. We also note that the interference fringes can be seen in the some of the fragments in Figures 1(c) and 1(d). These cracks are probably due to the difference of the thermal expansion coefficients between Si substrate and the deposited Alq_3 film. In other words, the cracks are incorporated into the film during the cooling from the deposition temperature to room temperature. We think therefore that the observed interference fringe is probably due to a warp in the fragment.

PL spectra and their integrated intensity of these films are shown in Figures 2 and 3. The integrated emission intensity increases by a factor of 15 as the substrate temperature increases. In addition, the vibronic structure is seen in the PL spectra of two films deposited at 100 and 120°C. The two PL spectra with vibronic progression are fitted well with at least five Gaussian peaks as shown in Figure 4. The locations of the individual Gaussian peaks are positioned at 474, 498, 530, 569 and 607 nm. Such vibronic progression in PL spectrum has been reported in crystalline Alq_3 films [3,6]. These two films are therefore in crystalline phase. However, no vibronic progression could be observed in the films deposited at 140 and 160°C. The reason why the absence of the vibronic structure is that the surfaces of those films are so rough (see Figs. 1(d) and 1(e)) that the coupling of vibrations of the individual ligands to the fluorescence transition (singlet-singlet transition) is probably very weak compared to the films with smooth surface deposited at 100 and 120°C. Therefore, we can regard the films

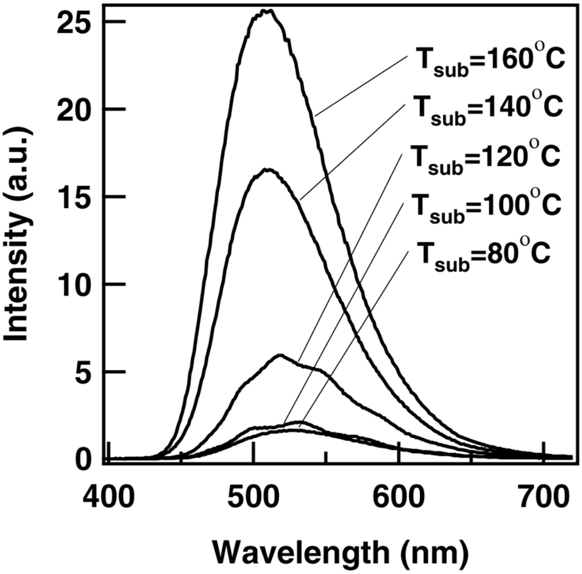

FIGURE 2 PL spectra of Alq_3 films deposited at different temperatures.

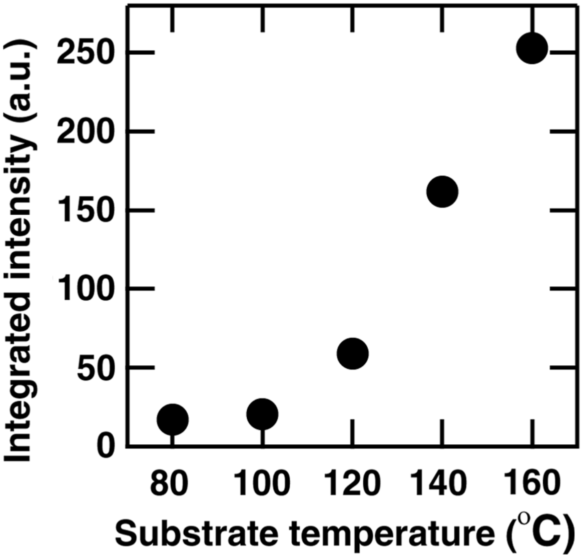

FIGURE 3 Integrated intensity of PL spectra in Figure 2 as a function of substrate temperature.

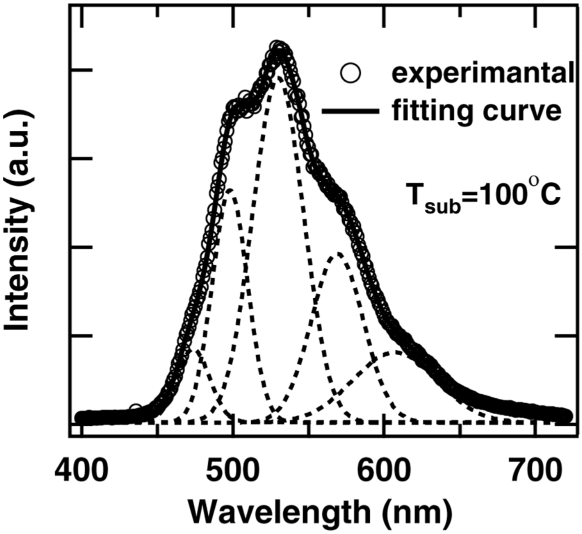

FIGURE 4 PL spectrum with a vibronic progression of the film deposited at 100°C. The spectrum is fitted to using at least five Gauss functions.

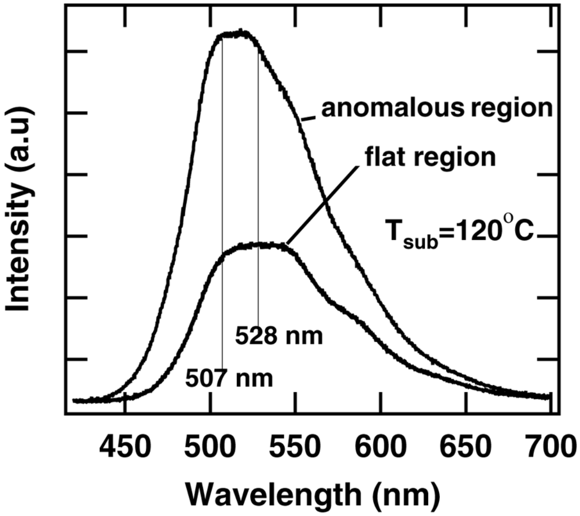

FIGURE 5 Micro-PL spectra from the anomalous growth and flat regions on the surface of the film at 120°C.

deposited at higher temperature than 100°C as crystalline α-phase or mixed (crystalline and amorphous) phase.

As shown in Figure 2, the emission peak shifts to the high energy side of ~20 nm from 528 to 507 nm as the substrate temperature increases. It has been reported that the emission peaks in crystalline (α-Alq_3) and amorphous phase were located at ~505 nm [6,7] and 520–540 nm [3,6,8], respectively. The observed blue shift of ~20 nm in our films agrees with the peak difference between the crystalline and amorphous phase reported. We therefore conclude that the crystalline phase in our films begin to emerge from the temperature range of 80 to 100°C. To examine further associated with the blue shift, we measured the microscopic emission spectra using a fluorescence microscope. Figure 5 shows micro-PL spectra from typical two surface regions (~35 μm in diameter) of the film deposited at 120°C: one is flat region and another is anomalous growth region. The emission intensity from the anomalous region, under which the flat region underlies, is stronger than that from the flat region. The emission peak from the anomalous region is located at higher energy than that from the flat region. From the above results, the observed blue shift in Figure 2 is due to an increase in anomalous growth region, i.e., an increase in crystalline phase (α-Alq_3) occupying on the surface. Similar trends on surface morphologies and PL spectra (the integrated intensity and emission peak) were observed in another series of films deposited at the source and wall temperatures of 180 and 170°C.

In summary, we have deposited the Alq_3 films on hydrogen-terminated Si(111) using hot-wall method. The PL emission intensity increased and their peak energy shifted to high energy side as the substrate temperature increased from 80 to 160°C. These results could be explained by an increase in the crystalline phase α-Alq_3 covered on the surfaces.

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