Japanese Journal of Applied Physics **49** (2010) 121602 **REGULAR PAPER**

Thermal Diffusivities of Tris(8-hydroxyquinoline)aluminum and *N*,*N*′-Di(1-naphthyl)-*N*,*N*′-diphenylbenzidine Thin Films with Sub-Hundred Nanometer Thicknesses

Nobuto Oka, Kazuki Kato, Takashi Yagi[1], Naoyuki Taketoshi[1],
Tetsuya Baba[1], Norihiro Ito[2], and Yuzo Shigesato*

Graduate School of Science and Engineering, Aoyama Gakuin University, 5-10-1 Fuchinobe, Chuo, Sagamihara 252-5258, Japan
[1]*National Metrology Institute of Japan, National Institute of Advanced Industrial Science and Technology (AIST), Tsukuba Central 3, 1-1-1 Umezono, Tsukuba, Ibaraki 305-8563, Japan*
[2]*Advanced Technologies Development Laboratory, Panasonic Electric Works, Ltd., 1048 Kadoma, Kadoma, Osaka 571-8686, Japan*

Received August 13, 2010; accepted August 28, 2010; published online December 20, 2010

The thermal diffusivities of tris(8-hydroxyquinoline)aluminum (Alq$_3$) and *N*,*N*′-di(1-naphthyl)-*N*,*N*′-diphenylbenzidine (α-NPD) films have been characterized quantitatively using a "rear heating/front detection-type" nanosecond thermoreflectance system. Alq$_3$ or α-NPD films sandwiched by Al films, Al/(Alq$_3$ or α-NPD)/Al three-layered films, were prepared by vacuum evaporation. Al acted as a reflective layer for pulse lasers in the thermoreflectance system. The nominal thicknesses of Alq$_3$ and α-NPD layers varied roughly from 30 to 100 nm. The thermal diffusivities of Alq$_3$ and α-NPD films were found to be (1.4–1.7) x 10^{-7} and 1.4 x 10^{-7} m^2 s^{-1}, respectively.

DOI: 10.1143/JJAP.49.121602

1. Introduction

Tris(8-hydroxyquinoline)aluminum (Alq$_3$) and *N*,*N*′-di(1-naphthyl)-*N*,*N*′-diphenylbenzidine (α-NPD) have been used as electron- and hole-transport layers, respectively, in organic light-emitting diodes (OLEDs). The thermal design for such devices has received considerable attention recently, because self-heating during operation could damage the device itself and decrease the intensity of electroluminescence.[1,2] For an effective thermal design, thermophysical properties, especially thermal diffusivity, are essential parameters. The thermal conductivities of die-pressed Alq$_3$ powder and a 200-nm-thick Alq$_3$ film have already been reported and correspond to the thermal diffusivities of 8.1×10^{-8} and 3.4×10^{-7} m^2 s^{-1}, respectively.[3,4] However, to date, detailed and systematic studies on Alq$_3$ and α-NPD thin films with structures similar to OLEDs and thicknesses close to the OLEDs' layer (tens of nanometers) have not been conducted. This is because it is difficult to observe heat propagation through a film thickness within a very short heat diffusion time.

In this study, Alq$_3$ or α-NPD films sandwiched between aluminum (Al) films [Al/(Alq$_3$ or α-NPD)/Al] were deposited by vacuum evaporation, commonly used during the manufacture of OLEDs. In order to quantitatively characterize the thermal diffusivity of the Alq$_3$ and α-NPD layers, a "rear heating/front detection-type" nanosecond thermoreflectance system developed by the National Metrology Institute of Japan (NMIJ)/AIST[5–9] was employed to directly observe heat propagation through a film thickness. Although Alq$_3$ and α-NPD films are transparent to the pulse lasers used in the thermoreflectance system, Al can act as a reflective layer for these lasers. Al films have also been used as electrodes in OLEDs. The thicknesses of Alq$_3$ and α-NPD varied roughly from 30 to 100 nm for a practical thermal design of OLEDs. Thus, heat propagation through the thickness of Al/(Alq$_3$ or α-NPD)/Al layered films was analyzed in detail.

2. Experimental Procedure

Al/(Alq$_3$ or α-NPD)/Al layered films were prepared on alkali-free glass substrates (Corning 1737) by resistance heating vacuum evaporation at approximately 3.0 Å s^{-1} (Al layers) and 1.0 Å s^{-1} (Alq$_3$ or α-NPD layer) using Al wire (purity $\geq$ 99.999%, Furuuchi Chemical) and Alq$_3$ or α-NPD powder (purity $\geq$ 99%, e-Ray Optoelectronics Technology). The gas pressure was maintained below 10^{-4} Pa, and the temperature between the substrate and the substrate holder during deposition was maintained below 40 °C. The Al/(Alq$_3$ or α-NPD)/Al layered structure was fabricated without exposure to the atmosphere between each deposition. The nominal thicknesses were 30, 50, and 100 nm for Alq$_3$ layers and 40, 80, and 100 nm for α-NPD layers. For Al layers, the thicknesses were 100 nm for Alq$_3$ and 74 nm for α-NPD. In order to characterize their structural and mechanical properties, the Alq$_3$ and α-NPD monolayers were also deposited directly on alkali-free glass substrates under the same conditions as the layered films.

The thermoreflectance system operated as follows. A pulse from the pump laser of the thermoreflectance system was focused on the rear of the Al/(Alq$_3$ or α-NPD)/Al specimen, and a fraction of the pulse's energy was absorbed into skin depth of the bottom Al layer and converted into heat. Then, the heat diffused one-dimensionally toward the front side of the specimen. Next, a probe laser pulse detected the temperature change at the front side as a change in reflectivity. The normalized temperature rise, i.e., the thermoreflectance signal, was recorded as a function of the delay time relative to the pump laser pulse. To derive the thermal diffusivities of the Alq$_3$ and α-NPD films, the thermoreflectance signals were analyzed using an analytical solution of the one-dimensional heat flow across the three-layered film.[5)]

The nominal thickness for the films was estimated using a quartz crystal oscillator, which was calibrated using a surface profiler (Taylor Hobson Nanostep2). The density for the films was analyzed using an X-ray reflectivity technique (Rigaku SmartLab). X-ray diffraction (XRD) was performed

---

*E-mail address: yuzo@chem.aoyama.ac.jp

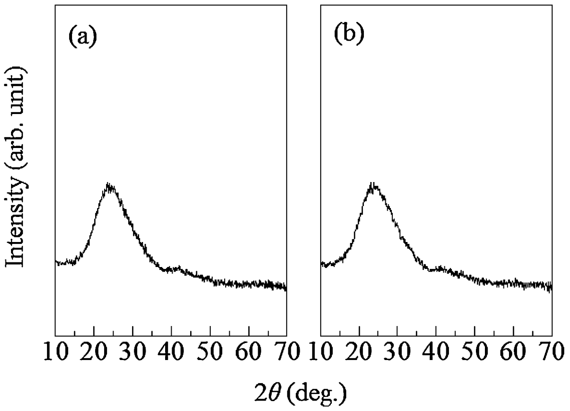

Fig. 1. XRD patterns of (a) Alq_3 and (b) α-NPD monolayers with a nominal thickness of 100 nm deposited on alkali-free glass substrate. The halo pattern observed around $2\theta = 20-25°$ was from the glass substrate.

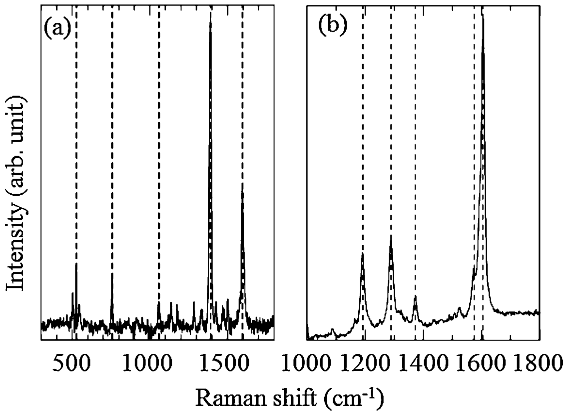

Fig. 2. Raman spectra of (a) Alq_3 and (b) α-NPD monolayers with a nominal thickness of 100 nm deposited on alkali-free glass substrate. Peaks marked with lines are assigned to the (a) Alq_3 molecule[10)] and (b) α-NPD molecule.[11)]

by 40 kV, 20 mA Cu Kα_1 radiation (Shimadzu XRD-6000). Raman spectroscopy was performed using 532 nm excitation (Renishaw inVia Reflex) in order to identify molecular species because the resistance heating for vacuum evaporation might damage the organic materials. A nanoindentation equipped with a Berkovich diamond indenter (Hysitron TS-70) was used to measure Young's modulus.

3. Results

3.1 Structure of Alq_3 and α-NPD films

Figure 1 shows the XRD patterns of Alq_3 and α-NPD films with a nominal thickness of 100 nm. Both films had an amorphous structure. Figure 2 shows the Raman spectra of Alq_3 and α-NPD films. These spectra confirmed that Alq_3 and α-NPD films were fabricated, as evidenced by the appearance of the Raman peaks.[10,11)]

3.2 Thermal diffusivity of Alq_3 and α-NPD films

Figures 3 and 4 show the thermoreflectance signals of Al/(Alq_3 or α-NPD)/Al three-layered films. The noise signal around a delay time of 150 ns was attributed to the electrical noise emitted by the equipment, which was confirmed not to affect the measurements. Areal heat diffusion time was defined as the area surrounded by the history curve, "thermoreflectance signal = 1" and "delay time = 0" (see Figs. 3 and 4), and also derived analytically from the following equation:[7)]

$$A = \frac{\left(C_{\mathrm{org}}d_{\mathrm{org}} + \frac{4}{3}C_{\mathrm{Al}}d_{\mathrm{Al}}\right)\frac{d_{\mathrm{Al}}^2}{\kappa_{\mathrm{Al}}} + \left(\frac{C_{\mathrm{Al}}^2 d_{\mathrm{Al}}^2}{C_{\mathrm{org}}d_{\mathrm{org}}} + \frac{1}{6}C_{\mathrm{org}}d_{\mathrm{org}} + C_{\mathrm{Al}}d_{\mathrm{Al}}\right)\frac{d_{\mathrm{org}}^2}{\kappa_{\mathrm{org}}}}{C_{\mathrm{org}}d_{\mathrm{org}} + 2C_{\mathrm{Al}}d_{\mathrm{Al}}} + \frac{2C_{\mathrm{Al}}d_{\mathrm{Al}}(C_{\mathrm{org}}d_{\mathrm{org}} + C_{\mathrm{Al}}d_{\mathrm{Al}})}{C_{\mathrm{org}}d_{\mathrm{org}} + 2C_{\mathrm{Al}}d_{\mathrm{Al}}}R_{\mathrm{bd}}, \qquad (1)$$

where A is the areal heat diffusion time (s); C is the heat capacity per unit volume ($\mathrm{J\,m^{-3}\,K^{-1}}$); d is the film thickness (nm); κ is the thermal diffusivity ($\mathrm{m^2\,s^{-1}}$), the subscript of which identifies an organic (Alq_3 or α-NPD) or Al layers; and R_{bd} is the thermal boundary resistance ($\mathrm{m^2\,K\,W^{-1}}$). C equals specific heat multiplied by density. Specific heat, the amount of heat energy required to raise the temperature for "a single gram" of some substance by one Kelvin, should be the same regardless of the morphology. For this analysis, a thermal diffusivity of $8.56 \times 10^{-5}\,\mathrm{m^2\,s^{-1}}$ for Al (κ_{Al}), a heat capacity per unit volume of $2.41 \times 10^6\,\mathrm{J\,m^{-3}\,K^{-1}}$ for Al (C_{Al}), derived from density[12)] and specific heat,[13)] and that of $1.26 \times 10^6\,\mathrm{J\,m^{-3}\,K^{-1}}$ for Alq_3 (C_{Alq3}), derived from a density of $1.23\,\mathrm{g\,cm^{-3}}$ and specific heat in ref. 3, were used. A heat capacity per unit volume of $1.52 \times 10^6\,\mathrm{J\,m^{-3}\,K^{-1}}$ for α-NPD ($C_{\alpha\text{-NPD}}$) was also used, which is derived from a density of $1.16\,\mathrm{g\,cm^{-3}}$ and specific heat measured by differential scanning calorimetry (Perkin-Elmer DSC-7). In addition, the thermal resistances at the interface between the layers were neglected in this study because a thermal boundary resistance should be much smaller than the total thermal resistance of the films.[7)]

As a result, the thermal diffusivities of Alq_3 and α-NPD layers were respectively $(1.4\text{–}1.7) \times 10^{-7}$ and $1.4 \times 10^{-7}\,\mathrm{m^2\,s^{-1}}$. The values for the Alq_3 film were approximately 2 times higher than those of Alq_3 powder, $8.1 \times 10^{-8}\,\mathrm{m^2\,s^{-1}}$, corresponding to the thermal conductivity measured by the laser flash technique[3)] (see Fig. 5). The phonon scattering in Alq_3 powder morphology should be more than that in the Alq_3 film. The phonons work as the main heat carriers in the insulating materials; hence, the thermal diffusivity of Alq_3 powder is relatively small. In contrast, our result is less than half of that already reported for Alq_3 films (200 nm in thickness) corresponding to the thermal conductivity measured by the 3ω technique[4)] (see Fig. 5). The technique needs a metallic wire on the measurement sample, which acts as both the heat source and temperature sensor. A possible explanation for this discrepancy is the difference in film quality. The metallic wire [gold (Au)] and an adhesion layer [titanium (Ti)] between Au and Alq_3 for the 3ω technique described in ref. 4 were deposited onto the Alq_3 films by the electron-beam evaporation method, whereas the top Al layer in this study was deposited onto the Alq_3 layer by the vacuum evaporation method, which is used as the manufacturing method of OLEDs.

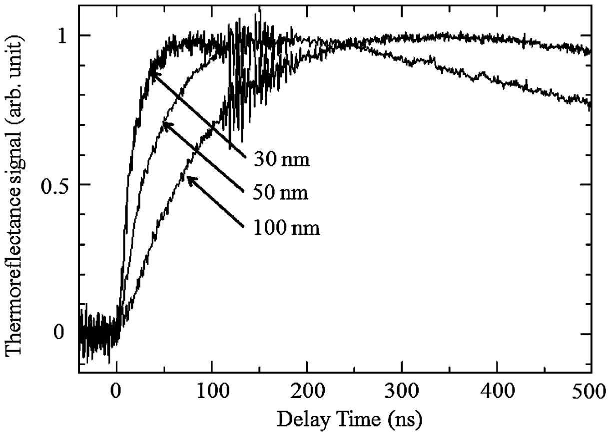

Fig. 3. Thermoreflectance signals of the Al/Alq3/Al three-layered thin films obtained by the nanosecond thermoreflectance measurement.

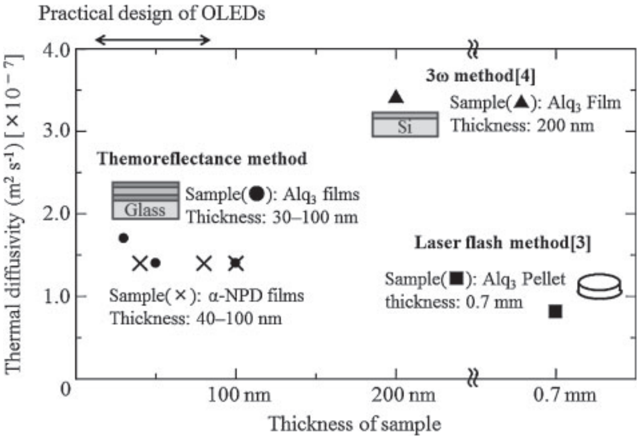

Fig. 5. Thermal diffusivities of Alq3 for the powder and the films, measured in this study and reported in refs. 3 and 4.

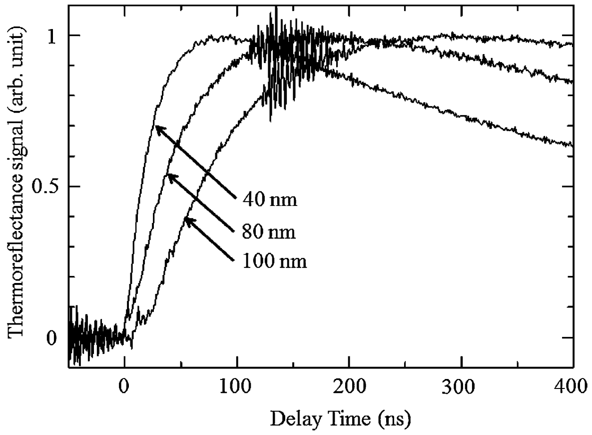

Fig. 4. Thermoreflectance signals of the Al/α-NPD/Al three-layered thin films obtained by the nanosecond thermoreflectance measurement.

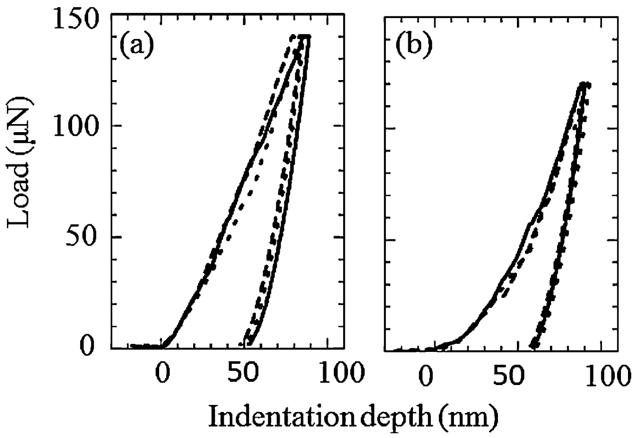

Fig. 6. Indentation depth–load hysteresis curve for (a) Alq3 and (b) α-NPD films with a thickness of 1000 nm obtained by the nanoindentation measurement. It was measured three times in this study.

4. Discussion

The mechanism of thermal transport in Alq$_3$ and α-NPD films must be discussed in terms of phonons' contribution in order to determine the heat propagation mechanisms. The thermal conductivities of the Alq$_3$ and α-NPD layers were respectively 0.18–0.22 and 0.21–0.22 W m^{-1} K^{-1}, which could be estimated from the measured thermal diffusivities. The main heat carriers should be the phonons. It is of intrinsic importance to estimate the nominal mean free path of phonons $l_{\rm ph}$ in terms of phonon scattering in Alq$_3$ and α-NPD. The thermal conductivity $\lambda_{\rm ph}$ is described by the following equation:14,15)

$$\lambda_{\rm ph} = \frac{1}{3} C v l_{\rm ph}, \tag{2}$$

$$v = \left(\frac{E}{\rho}\right)^{1/2}, \tag{3}$$

where v is the average phonon velocity. C was presupposed to be uniform in the film. Assuming in this study that v was the sound velocity, v was calculated from the Young's modulus E and density ρ. Figure 6 shows the indentation depth–load hysteresis curves for Alq$_3$ and α-NPD films with a thickness of 1000 nm measured by a nanoindentation technique. The indentation depth of approximately 90 nm was adopted by taking into account the influences of the surface and substrate. Assuming a value of 0.3 for Poisson's ratio of both these films, the values of Young's modulus for Alq$_3$ and α-NPD were obtained to be 11 and 9.6 GPa. Thus, $l_{\rm ph}$ can be calculated using eqs. (2) and (3). The $l_{\rm ph}$ values of the Alq$_3$ and α-NPD films were estimated to be approximately 0.15 nm. The $l_{\rm ph}$ values were almost the same as the single bond length, such as C–C of benzene (0.139 nm)16) and C–H of methane (0.110 nm).17) The mean free path of amorphous solids should be of the order of interatomic distance.18) We have already reported that the $l_{\rm ph}$ values of amorphous indium zinc oxide and amorphous aluminum trioxide were respectively 0.408) and 0.47 nm;9) hence, our results in this paper should be valid.

5. Conclusions

We have investigated the thermophysical properties of the Alq$_3$ and α-NPD layers using the nanosecond thermoreflectance method. The thermal diffusivities of the Alq$_3$ and α-NPD films, the nominal thicknesses of which varied roughly from 30 to 100 nm, were $(1.4–1.7) \times 10^{-7}$ and 1.4×10^{-7} m^2 s^{-1}, respectively.

Acknowledgments

The author would like to thank Dr. Ryo Endoh of Toray Research Center, Inc. for the specific heat measurement of α-NPD, Dr. Katsuhiko Inaba and Mr. Takayuki Konya of Rigaku Corporation for film density analysis, and Mr. Toshiro Okawa of Omicron NanoTechnology Japan, Inc. and Mr. Takashi Kihara and Mr. Kiyoaki Araki of Shimadzu Corp. for Young's modulus measurement. This work was supported by the New Energy and Industrial Technology Development Organization (NEDO) as a project of "Development of High-Efficiency Lighting Based on the Organic Light-Emitting Mechanism".

---

1) T. Sugiyama and Y. Furukawa: Jpn. J. Appl. Phys. **47** (2008) 3537.
2) G. Vamvounis, H. Aziz, N.-X. Hu, and Z. D. Popovic: Synth. Met. **143** (2004) 69.
3) M. W. Shin, H. C. Lee, K. S. Kim, S.-H. Lee, and J.-C. Kim: Thin Solid Films **363** (2000) 244.
4) N. Kim, B. Domercq, S. Yoo, A. Christensen, B. Kippelen, and S. Graham: Appl. Phys. Lett. **87** (2005) 241908.
5) T. Baba: Jpn. J. Appl. Phys. **48** (2009) 05EB04.
6) N. Taketoshi, T. Baba, and A. Ono: Rev. Sci. Instrum. **76** (2005) 094903.
7) T. Yagi, K. Tamano, Y. Sato, N. Taketoshi, T. Baba, and Y. Shigesato: J. Vac. Sci. Technol. A **23** (2005) 1180.
8) T. Ashida, A. Miyamura, N. Oka, Y. Sato, T. Yagi, N. Taketoshi, T. Baba, and Y. Shigesato: J. Appl. Phys. **105** (2009) 073709.
9) N. Oka, R. Arisawa, A. Miyamura, Y. Sato, T. Yagi, N. Taketoshi, T. Baba, and Y. Shigesato: Thin Solid Films **518** (2010) 3119.
10) Y. Sakurai, G. Salvan, Y. Hosoi, H. Ishii, Y. Ouchi, K. Seki, T. U. Kampen, and D. R. T. Zahn: Appl. Surf. Sci. **190** (2002) 382.
11) T. Sugiyama, Y. Furukawa, and H. Fujimura: Chem. Phys. Lett. **405** (2005) 330.
12) *Handbook of Physical Quantities*, ed. I. S. Grigoriev and E. Z. Meilikhov (CRC Press, Boca Raton, FL, 1997) p. 115.
13) *NIST–JANAF Thermochemical Tables Part I*, ed. M. W. Chase, Jr. (American Institute of Physics, New York, 1998) 4th ed., p. 59.
14) C. Kittel: *Introduction to Solid State Physics* (Wiley, New York, 1996) 7th ed., p. 132.
15) C. Kittel: *Introduction to Solid State Physics* (Wiley, New York, 1996) 7th ed., p. 88.
16) J. Mcmurry: *Organic Chemistry* (Brooks/Cole, Pacific Grove, CA, 2004) 6th ed., p. 503.
17) J. Mcmurry: *Organic Chemistry* (Brooks/Cole, Pacific Grove, CA, 2004) 6th ed., p. 12.
18) J. Michalski: Phys. Rev. B **45** (1992) 7054.