



Negative giant surface potential of peeled Alq₃ thin film

Youichi Okabayashi*, Eisuke Ito, Takashi Isoshima, Hiromi Ito, Masahiko Hara

Flucto-Order Functions Asian Collaboration Team, RIKEN Advanced Science Institute, 2-1 Hirosawa, Wako, Saitama 351-0198, Japan

Flucto-Order Functions Asian Collaboration Team, RIKEN Advanced Science Institute, Fusion Technology Center Building 5F, Hanyang University, Seongdong-gu, Seoul 133-791, Republic of Korea

ARTICLE INFO

Available online 14 July 2009

Keywords:

Surface potential
Alq₃
Vacuum deposition
Peeling off

ABSTRACT

In order to observe negative giant surface potential (gSP), vacuum-evaporated tris(8-hydroxyquinolinolato) aluminum (Alq₃) thin film on a polytetrafluoroethylene (PTFE) substrate was peeled off by an adhesive carbon tape in dark condition. Surface potential on the backside was negative, and the absolute values were about two-thirds of the surface potential values (positive values) of the films deposited on ITO with the same thickness. Our results indicate that the gSP does not originate in interfacial or bulk charge, but in anisotropic alignment of dipole moment of Alq₃ molecules in the film. With this simple procedure, we can realize Alq₃ film with opposite molecular alignment, which can be useful in device application.

© 2009 Elsevier B.V. All rights reserved.

1. Introduction

Tris(8-hydroxyquinolinolato) aluminum (Alq₃) is one of the key materials used in organic light emitting diodes (OLEDs), which is currently used as amorphous form. Recently giant surface potential (gSP) built-up, which reached +50 V/μm, was found on Alq₃ thin films when vacuum-evaporated in dark condition [1–5]. It is thought that origin of the gSP is spontaneous dipole alignment of Alq₃ molecule [2], but the mechanism of the dipole alignment is still unclear. One possibility is interaction between the deposited molecules and the substrate [6]. However, several groups have been reported that the gSP was observed independent of the substrates. In addition, another possible reason for gSP, charging of the film, is not directly negated yet.

Here, in order to examine the effect of the interface between the substrate and the Alq₃ film on the giant surface potential, we investigated the surface potential values measured on the backside of an Alq₃ film by peeling the film off the substrate, in order to examine these factors. If gSP were to originate in film charging, surface potential of the backside of the film would be also positive. But if gSP originates in anisotropic dipole alignment, negative surface potential would be observed on the backside of the film. By selecting the polytetrafluoroethylene (PTFE) as the substrate, we successfully peeled off, and obtained the negative surface potential on the backside of Alq₃ film. From the applicational point of view, this simple method is useful to realize negative gSP using the same material, which will benefit to the device application utilizing noncentrosymmetric molecular alignment.

2. Experimental

The procedure of the peeling was carried out as shown in Fig. 1: an Alq₃ thin film was vacuum-evaporated onto a PTFE substrate in dark condition; the Alq₃ thin film was peeled off the PTFE substrate by a double-sided adhesive carbon tape on an indium tin oxide (ITO)-coated substrate. As substrates, we used ITO and PTFE for measurements on the topside and the backside, respectively. At first, we tried peel off procedure using an Alq₃ film on an ITO substrate, however, it was unsuccessful because of the strong interaction between ITO and Alq₃: Alq₃ residuals remained on the ITO surface, and the Alq₃ film could not be completely transferred to the carbon tape. Instead, we found that PTFE was suitable for peeling Alq₃ layers off, as discussed later.

Alq₃ was purchased from Tokyo Kasei, and used without further purification. PTFE substrates purchased from Niloco were washed by ethanol before use. Alq₃ film was deposited by vacuum thermal evaporation in a high-vacuum evaporator (SVC-700TM, Sanyu Electron, Co.). The deposition rate was about 1 nm/s. The thickness was monitored by a quartz microbalance (XTC/2, Inficon, Inc.), and calibrated by a spectroscopic ellipsometer (M-2000UI, J. A. Woollam, Co. Inc). Surface potential was measured in air by a commercial Kelvin probe set-up (KP-6500, McAllister Technical Service, Inc.). Since the work function of the Alq₃ film and the substrates was not determined, contact potential difference (CPD) was adopted as a measure of gSP. CPD is the surface potential difference between the sample and the reference electrode (a stainless steel plate), thus might contain potential shift due to the substrate. To estimate this shift, CPD was measured for various substrates without Alq₃ layer, and obtained value was −0.35 V for ITO substrate, −0.20 V for carbon tape on ITO substrate, and −0.04 V for perfluorotetracosane on ITO substrate. These potential shifts are considerably small compared with the gSP values obtained in our experiment. In addition, quantitative comparison in this work was made only among the samples

* Corresponding author. Room-G, Laser science building, RIKEN, 2-1 Hirosawa, Wako, Saitama 351-0198, Japan. Tel.: +81 48 467 9600; fax: +81 48 462 4695.

E-mail address: okabayashi@riken.jp (Y. Okabayashi).

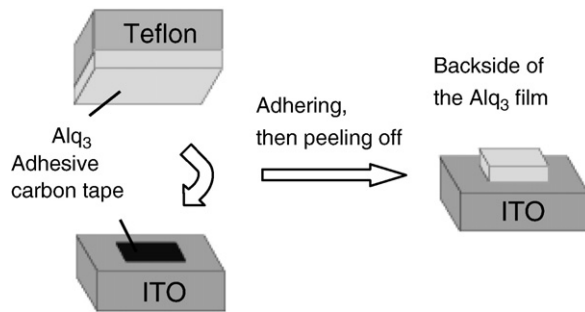


Fig. 1. Fabrication process of the backside of Alq₃ thin film. Vacuum-evaporated Alq₃ thin film on a PTFE substrate was peeled off by an adhesion tape on an ITO substrate.

with the same substrate. Therefore difference in the substrate does not affect conclusions of our work.

3. Results and discussion

In order to confirm that there was no PTFE on the Alq₃ backside by peeling off, the elemental analysis of the backside surface was performed by X-ray photoelectron spectroscopy (Theta Probe, Thermo Fisher Scientific K.K.). Although there was small F1s peak due to the PTFE residuals, the amount was estimated to be 0.1 nm in thickness, which is negligible. Therefore, we confirmed that PTFE is a suitable substrate for peeling Alq₃ film off, due to weak interfacial interaction between PTFE and Alq₃.

Next we examined whether gSP is formed on a PTFE substrate, by measuring an Alq₃ film deposited on a perfluorotetracosane (C₂₄F₅₀, Aldrich) thin layer on an ITO substrate. Since PTFE cannot be vacuum-evaporated, perfluorotetracosane was selected because of similarity of molecular structure with PTFE and ease of vacuum evaporation. The thickness of the perfluorotetracosane layer was 20 nm, which fully covers on the ITO substrate. By deposition of Alq₃ with a thickness of 533 nm, we obtained a large positive CPD value of +18.8 V, corresponding to 35 V/μm, which was slightly smaller than that of an Alq₃ film fabricated on an ITO substrate. This suggests that gSP and thus anisotropic molecular alignment of Alq₃ is also formed on a PTFE substrate, although CPD value may depend on the substrate.

Next we examined the possibility of surface charge-up during peeling off process (i.e. contact electrification), which might affect the surface potential. A 500-nm-thick Alq₃ film on PTFE substrate was firstly irradiated by light to eliminate gSP, and then peeled off in dark condition. If surface charge-up is induced by peeling off, large CPD would be observed. However, the obtained CPD value of the peeled film was +0.95 V. The peeled film was then irradiated by light, resulting into CPD change to +0.15 V. Thus effect of contact electrification is roughly estimated to be +0.8 V.

On the peeled Alq₃ film in dark condition, we apparently obtained negative gSP value, as described later. It should be noted that gSP of the peeled Alq₃ thin film decayed rather quickly, even when the sample was kept in dark condition. As shown in Fig. 2, the CPD value changed from −15 V to −6 V for 4 h. In order to avoid the influence of the gSP decay, the data used in the experiment were taken within a few minutes after peeling off. In this condition, potential drop after peeling off was estimated to be less than 0.5 V (see the inset of Fig. 2).

Interestingly, decay of surface potential of an as-deposited Alq₃ film is much slower [3] than that of the backside. The origin of much faster decay in our peeled film is an open question, and here we propose two speculative hypotheses. The first possibility is mechanical stress induced by peeling off: separated charge due to piezoelectric effect might remain in the film, and it might cause delayed drop of the negative gSP by migration through the film. Although piezoelectric effect of Alq₃ has not been examined, materials with macroscopic noncentrosymmetry generally present piezoelectricity. The second possibility is chemical components in

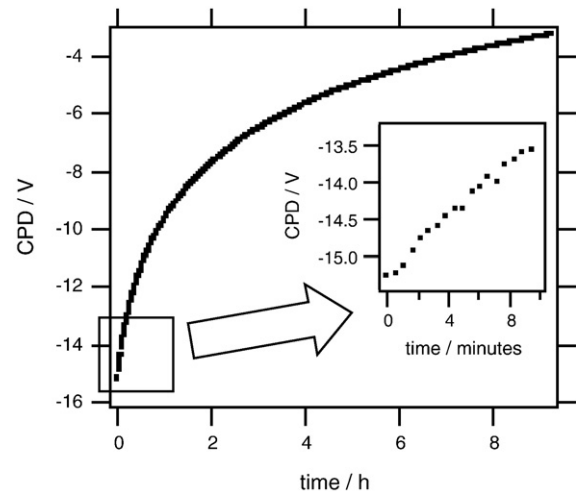


Fig. 2. Decay of giant surface potential of Alq₃ backside surface. The inset is the decay in the first 10 min.

adhesive tape: chemical components transferred from the carbon adhesive tape might diffuse in the film and thus cancel the negative gSP gradually. However, any evidence of such chemical diffusion was not found in our study yet, and further investigation using various component analysis methods is necessary.

Fig. 3 shows the CPD values of the top surface (cross) and the backside (circle) of the Alq₃ films. Each data point of the backside surface was measured on independently peeled off sample, thus eight peelings were performed. The surface potential of the backside was negative and the magnitude was increased proportional to the thickness. As reported previously [1,2], the CPD values of the Alq₃ films on ITO substrates linearly change with the thickness, and the slope was 45 V/μm in our set-up. On the other hand, surface potential of the backside showed negative shift, and its slope was −30 V/μm. The inversion of sign of surface potential on the backside demonstrates that the gSP originates not in charging of the film but in anisotropic molecular dipole alignment. It also indicates that the preferential orientation of molecular dipole was kept during the peeling off process. Therefore we can realize an Alq₃ thin film with opposite molecular alignment by this simple peeling-off method, which can be useful to device application.

The slope of the surface potential of the backside surface, −30 V/μm, is two third of that of surface potential of the Alq₃ film on ITO substrate. One possible reason is the difference in the substrate material [5]. Hayashi et al. reported that the slope of the surface potential change with the

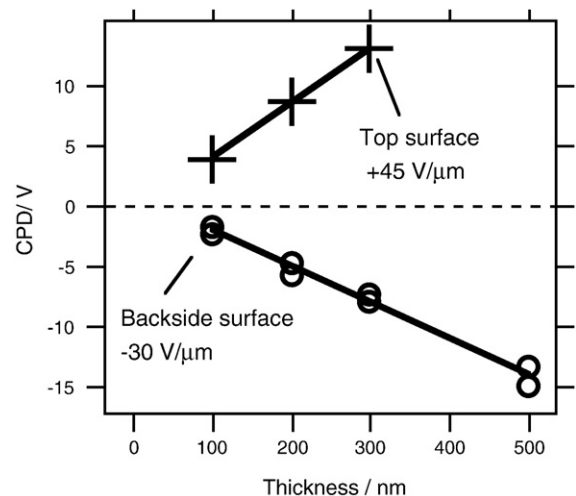


Fig. 3. Surface potential of backside (circle) and top surface (cross) of Alq₃ thin film.

thickness was dependent on the substrate. On the PTFE substrate, the magnitude of the gSP might be smaller than that of the ITO substrate. This is consistent with the result that the gSP on the Alq₃ film deposited on the perfluorotetracosane/ITO substrate was also smaller (35 V/μm) as described above. Such substrate dependence may come from difference in roughness, conductivity, and/or interfacial interaction with the Alq₃ molecules. Further investigation is necessary for examining the substrate dependence.

4. Conclusion

We successfully observed surface potential value of the backside of an Alq₃ film by peeling off the film deposited on a PTFE substrate. The sign of the obtained gSP was negative, which was opposite from the gSP value of the top surface of an ordinary evaporated film, supporting that gSP originates not in film charging but in anisotropic molecular dipole moment. We demonstrated that this method is simple and useful to fabricate a thin film with negative gSP and thus opposite alignment of molecular dipole.

Acknowledgement

This work was partly supported by Nanoscience Research Program in RIKEN.

References

- [1] E. Ito, Y. Washizu, N. Hayashi, H. Ishii, N. Matsuie, K. Tsuboi, Y. Ouchi, Y. Harima, K. Yamashita, K. Seki, *J. Appl. Phys.* 92 (2002) 7306.
- [2] E. Ito, Y. Washizu, N. Hayashi, H. Ishii, N. Matsuie, K. Tsuboi, Y. Ouchi, Y. Harima, K. Yamashita, K. Seki, *Synth. Metals* 137 (2003) 911.
- [3] K. Sugi, H. Ishii, Y. Kimura, M. Niwano, E. Ito, Y. Washizu, N. Hayashi, Y. Ouchi, K. Seki, *Thin Solid Films* 464/465 (2004) 412.
- [4] E. Ito, T. Isoshima, K. Ozasa, M. Hara, *Mol. Cryst. Liq. Cryst.* 462 (2007) 111.
- [5] N. Hayashi, K. Imai, T. Suzuki, K. Kanai, Y. Ouchi, K. Seki, *Proceedings of the International Symposium on Super-Functionality Organic Devices, Japan, October 25–28, 2004, IPAP Conference Series* 6 (2005) 69.
- [6] T. Ikame, K. Kanai, Y. Ouchi, E. Ito, A. Fujimori, K. Seki, *Chem. Phys. Lett.* 413 (2005) 373.