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Positive Giant Surface Potential of Tris(8-hydroxyquinolinolato) Aluminum (Alq₃) Film Evaporated onto Backside of Alq₃ Film Showing Negative Giant Surface Potential

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To examine the origin of spontaneous noncentrosymmetric molecular dipole orientation of an evaporated film of tris(8-hydroxyquinolinolato) aluminum (Alq₃), overlayer deposition of Alq₃ on the backside of a peeled Alq₃ film was investigated. Although the surface potential (SP) of the backside of the Alq₃ film was negative, the SP showed a positive shift by overlayer deposition of Alq₃. This means that the spontaneous dipole orientation of Alq₃ molecules in the overlayer is opposite to that in the underlayer. A molecular geometric effect due to a bulky molecular shape is proposed as the origin of the noncentrosymmetry. ⓒ 2012 The Japan Society of Applied Physics

Tris(8-hydroxyquinolinolato) aluminum (Alq₃, Fig. 1) is one of the promising materials for organic light-emitting diodes (OLEDs).[1] Among the many investigations on the film structures, electric properties, and optical properties of Alq₃, a peculiar phenomenon of giant surface potential (gSP) build-up, which reached $+50 \, V/\mu m$, was found in an Alq₃ film evaporated under dark condition.[2–6] Such huge polarization in an organic film is applicable to electronic devices and nonlinear optical devices, if we can control the polarity and magnutude. An Alq₃ molecule has a permanent dipole moment with 4.1 Debye[7] (for a meridional isomer that is more stable than a facial isomer[8,9]). The gSP build-up originates from the spontaneous noncentrosymmetric orientation of the molecular dipoles,[2,3] although an evaporated Alq₃ film has an amorphous form. The degree of anisotropy was estimated to be small (order parameter $\langle \cos \theta \rangle \sim 1 \cdot 10^{-2}$),[2,4,10] and the mechanism of such small anisotropy is not fully understood yet. It was reported that the gSP occurrence is not dependent on the substrate.[5] This suggests that the interfacial interaction between the 1st Alq₃ layer and the substrate is not the trigger for the macroscopic molecular orientational anisotropy and thus emergence of gSP. On the other hand, the fact that Alq₃ can take some crystal structures[8,9] suggests that the intermolecular interaction is sufficiently strong to determine the molecular orientation to each other. Following this consideration, even in an evaporated amorphous film, the newly deposited Alq₃ molecules might take the noncentrosymmetric molecular orientation succeeding the orientation of the underlayer. To examine whether this is the case is important for the elucidation of the mechanism of the noncentrosymmetric molecular orientation.

Recently, we have reported the fabrication of the backside of an Alq₃ film by the peeling-off method using a double-sided adhesive carbon tape (Fig. 2 inset).[11] The polarity of the SP of the backside was negative, which was opposite to that of the topside of the film. This shows that the opposite orientation of the Alq₃ molecules is realized in the peeled film, as shown in Fig. 2(b). In this work, we investigated the SP and thus the molecular orientation of the Alq₃ overlayer evaporated on the backside of a peeled Alq₃ film [Fig. 2(c)]. If the orientation of the Alq₃ molecules in the overlayer follows that in the substrate through the inter-
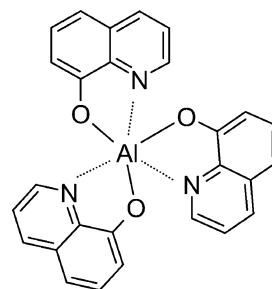

Fig. 1. Molecular structure of Alq₃.

molecular interaction, the SP should change negatively by the further deposition of Alq₃. On the other hand, if we observe a positive SP change by overlayer deposition, this is not the case.

Experimentally, the backside surface of Alq₃ was prepared as reported previously.[11] Firstly, Alq₃ (Tokyo Chemical Industry Co., Ltd., used as purchased) was evaporated with a conventional vacuum evaporator (Sanyu Electron SVC-700TM) onto a polytetrafluoroethylene (PTFE) substrate (Nilaco), at an evaporation rate of *ca.* 1 nm/s monitored using a quartz thickness monitor (Inficon XTC/2) [Fig. 2(a)]. The film thickness was calibrated by spectroscopic ellipsometry (J. A. Woollam M-2000UI). The obtained Alq₃ film was peeled off the PTFE substrate with a double-sided adhesive carbon tape on an indium tin oxide (ITO)-coated glass substrate (Fig. 2 inset). The amount of residual PTFE on the peeled Alq₃ surface is negligibly small, as confirmed by X-ray photoemission spectroscopy (Thermo Fisher Scientific Theta Probe).[11] After measurements of the SP in air, further deposition of Alq₃ was performed on the backside surface of the peeled Alq₃ film [Fig. 2(c)]. SP values of the samples were measured in air with a commercial Kelvin probe (KP) system (McAllister Technical Service KP-6500). Strictly speaking, the KP measurement provides contact potential difference (CPD), i.e., the SP difference between the sample and the reference electrode (a stainless steel plate). In this letter, we adopted this CPD to represent the SP change. All the processes including first deposition, peeling-off, and further deposition were performed under dark condition.

Figure 3 shows the CPD values of the Alq₃ films as a function of "total" Alq₃ thickness, including the peeled-off Alq₃ underlayer and the further deposited overlayer. The
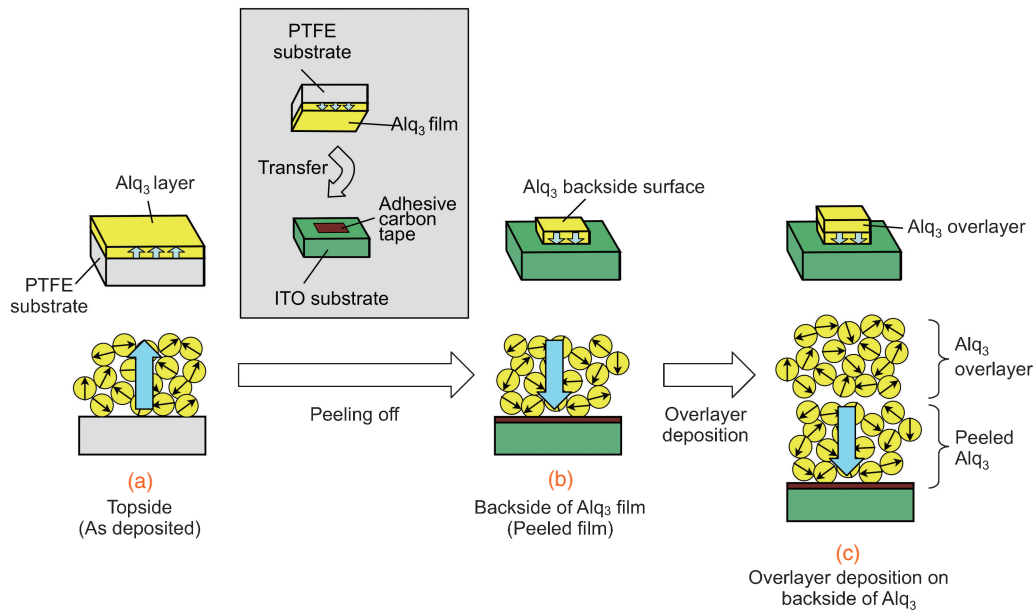
*E-mail address: isoshima@riken.jp

Fig. 2. Schematic illustration of preparation procedure of Alq$_3$ backside surface and formation of Alq$_3$ overlayers. Direction of polarization in the film is shown below each process. (a) (topside) Alq$_3$ thin film was vacuum-deposited on a PTFE substrate. SP value of the topside surface was positive. (b) (backside) Peeled-off film by an adhesive tape on an ITO-coated glass substrate. The inset shows the schematic procedure of peeling off. SP values of backside surface are negative. (c) (overlayer) Further deposition of Alq$_3$ on backside surface.
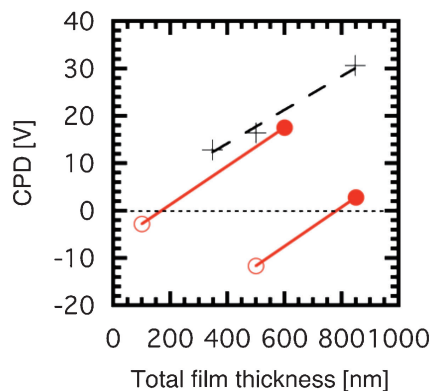

Fig. 3. Change of contact potential difference (CPD, representing surface potential change) with the total film thickness. Each set of marks connected with a line represents one series of experiment, composed of first-layer fabrication and additional overlayer deposition(s). Red open circles represent CPD of the backside of Alq$_3$ films, and red filled circles represent CPD of the overlayers deposited on the backsides. Black crosses and the broken line represent CPD of the topside of the Alq$_3$ first layer and that of the surface of the first and second overlayers. The slope of the lines represents normalized SP change by overlayer deposition.

black broken line with crossed data points corresponds to the CPD values of a pristine evaporated film on an ITO-coated glass substrate. These values were taken by repetitions of Alq$_3$ deposition and CPD measurement on the same sample. The CPD values of the topside were positive and proportional to the film thickness, as reported previously.[2,3,11] Red full lines show the results of the experiments of overlayer deposition on backsides. In Fig. 3, two individual series of experiments with different film thicknesses are plotted. Red open circles represent the CPD of the backsides of the peeled Alq$_3$ films, while red filled circles represent the CPD values of the surface of the Alq$_3$ overlayers deposited on the

backside. Although the SP values of the backside were negative as reported previously,[11] the SP values of the overlayers on the backsides were positive: the 500-nm-thick Alq$_3$ overlayer presented an SP shift of $+20.3$ V (from -2.8 to $+17.5$ V), and the 350-nm-thick Alq$_3$ overlayer presented an SP shift of $+14.5$ V (from -11.7 to $+2.8$ V). The slopes of the red lines (normalized SP change) were about 41 V/μm, consistent with that of the black line.

These results show that spontaneous molecular dipole orientation in an evaporated Alq$_3$ film is independent of the substrate, even though using the backside surface of an Alq$_3$ film. Considering this and the fact that, generally, the gSP of evaporated Alq$_3$ does not depend on the substrate, we conclude that the interfacial interaction between the newly deposited molecules and the underlayer or the substrate surface does not play an important role to determine the sense of the molecular dipole orientation in the Alq$_3$ film. Instead, we consider the molecular geometric effect: the shape of the molecule and the posture of a molecule on a surface may play dominant roles to determine the distribution of molecular orientation. A very simple illustration of this concept is that an asymmetric dice rolled on the table presents an uneven distribution of the postures. Intuitively considering the propeller-like molecular structure of Alq$_3$, most favorable postures on a flat surface are that in which each one position in three ligands attaches to the surface. There are two such postures, but those two attachment planes are not parallel to each other. Indeed, average of molecular dipole moment projected to the surface normal over those two postures is $+0.72$ Debye, consistent with the polarity of surface potential (positive value corresponds to positive surface potential). Although this illustration may be too oversimplified, the molecular geometric effect is a plausible factor to elucidate the experimental results qualitatively. Following this consideration, we can predict

that a peripheral substitution at the ligands of Alq_3 may significantly affect the molecular orientation, and thus, the gSP. If this is the case, we can control the molecular orientation and gSP of Alq_3 derivatives, so that we can design the molecule to tune the electronic and nonlinear optical properties for various device applications. Investigation of some derivatives of Alq_3 is in progress.

In summary, to discuss the origin of spontaneous non-centrosymmetric molecular dipole orientation of an evaporated Alq_3 film, SP of the Alq_3 overlayer deposited on the backside of Alq_3 film was measured. In spite of the negative SP value of the backside surface, SP of the Alq_3 overlayer showed a positive value, the same as a pristine Alq_3 film. Our results showed that the sense of spontaneous dipole orientation of Alq_3 molecules does not depend on the substrate even when the substrate is the backside of the Alq_3 film, which has an opposite orientation of Alq_3 molecules. To understand these results, we propose that the molecular geometric effect originating from the molecular shape of Alq_3 is the origin of the noncentrosymmetric molecular orientation. This consideration leads to a prediction that modification of the ligand of the Alq_3 molecule may enable us to control the molecular orientation and gSP value. This phenomenon is unusual and expected to result in the discovery of a new type of growth model, which will lead to a useful molecular design guideline for various electronic and optical devices.

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