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Characterization of light-erasable giant surface potential built up in evaporated Alq_3 thin films

K. Sugi[a,b], H. Ishii[a,b,*], Y. Kimura[a,b], M. Niwano[a,b], E. Ito[c], Y. Washizu[d], N. Hayashi[d], Y. Ouchi[d], K. Seki[e]

[a] *Research Institute of Electrical Communication, Tohoku University, 2-1-1 Katahira, Aobaku, Sendai 980-8577, Japan*
[b] *Core Research for Evolutional Science and Technology, Japan Science and Technology Agency, 2-1-1 Katahira, Aobaku, Sendai 980-8577, Japan*
[c] *Frontier Research System, RIKEN, 2-1 Hirosawa, Wako, Saitama 351-0198, Japan*
[d] *Department of Chemistry, Graduate School of Science, Nagoya University, Furo, Chikusaku, Nagoya 464-8602, Japan*
[e] *Research Center for Materials Science, Nagoya University, Furo, Chikusaku, Nagoya 464-8602, Japan*

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Abstract

Recently high and persistent spontaneous buildup of a surface potential (SP) upon vacuum deposition of tris (8-hydroxyquinolinato) aluminum (III) (Alq_3), which is widely used for organic light emitting devices, on a gold substrate under dark condition (28 V for 560-nm-thick Alq_3 film) has been reported. The removal of the giant surface potential by visible light irradiation has also been reported. These properties of Alq_3 film suggest potential applications to various organic devices such as memory. In this study, we investigated the retention time of the giant potential and the mechanism of the light-induced depolarization in order to discuss the feasibility of the device applications. The observed decay rate of the surface potential in vacuum condition was roughly 10% loss in 10 years, which is enough for memory devices. As to the decay rate by light-irradiation, the observed rate was successfully reproduced by a theoretical simulation based on the photo-induced randomization of oriented Alq_3 molecules.

Keywords: Alq_3 thin film; Light; Surface potential

1. Introduction

Tris (8-hydroxyquinolinato) aluminum (III) (Alq_3) is one of the most popular materials used for organic light emitting diodes (OLEDs). Very recently, high and persistent spontaneous buildup of the surface potential (SP) upon vacuum deposition of Alq_3 on Au substrate under dark condition (28 V for 560-nm-thick Alq_3 film) has been found by Ito et al. [1,2]. It is known that an Alq_3 molecule has a permanent dipole moment (4.1 D for meridional, 7.1 D for facial) [3]. Preferential orientation of such polar molecules during the deposition is proposed as a possible origin of the formation of the giant SP in dark condition. In most organic ferroelectric materials such as poly(vinylidene fluoride) (PVDF), spontaneous orientation of permanent dipole is achieved by applying external field, i.e. poling. In the case of Alq_3, it should be noted that the dipolar orientation of Alq_3 is achieved not by external field but by simple evaporation in dark without any external field. The SP was also found to vanish under the irradiation of light with larger energy than the absorption edge of Alq_3 [1,2]. These natures of Alq_3 films suggest the possible applications to various organic devices such as memory devices.

In this study, we have investigated two aspects about the giant SP of Alq_3 in relation to possible applications of this phenomenon to organic devices; (i) the retention time of the SP, and (ii) the mechanism of erasing the SP by light irradiation. The former is important to discuss the possibility of memory devices. The latter is indispensable for utilizing light-erasing process.

2. Experimental

Alq_3 was purchased from Aldrich (99.995% in nominal purity) and purified once by vacuum sublimation. An Au

* Corresponding author. Research Institute of Electrical Communication, Tohoku University, 2-1-1 Katahira, Aobaku, Sendai 980-8577, Japan. Tel.: +81-22-217-5502; fax: +81-22-217-5503.
E-mail address: ishii@riec.tohoku.ac.jp (H. Ishii).

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substrate was prepared by vacuum evaporation of Au on a silicon wafer. Alq_3 was deposited on it under dark condition in a vacuum chamber with base pressure of $<1\times10^{-6}$ Torr. The thickness of the Alq_3 film was monitored by a quartz microbalance. To suppress the effect due to ambient light, an ionization gauge in the vacuum chamber was turned off and all viewing ports were covered. SP was measured by Kelvin probe method with a commercial Kelvin probe head (McAllister KP-6500). A flashlight with red filter was used only during the sample handling in the chamber. Light irradiation was performed by visible light radiation from an incandescent lamp to the Alq_3 film through a viewing port. All experiments, except for the experiment in order to examine the retention time in air, were done in vacuum condition without exposing to air.

3. Results and discussion

3.1. Decay rate of the SP in dark condition

Fig. 1 shows the variation of the SP of 100-nm-thick Alq_3 film deposited under dark condition as a function of time. The inset is the magnification of the data curves. The SP shows very slow decay from its initial value of 7.0 V; a few percents decay in several hundred hours. Although the precise plot function is not clear, we can roughly estimate the decay rate to be about 10% decay in 10 years. Considering 10 years guarantee of commercial nonvolatile memories, this result demonstrates that the SP has enough retention time for possible device applications. The mechanism of the observed decay of SP in dark is not clear at this present. However, the observed slow decay suggests that the polarized Alq_3 film is not in thermal equilibrium;

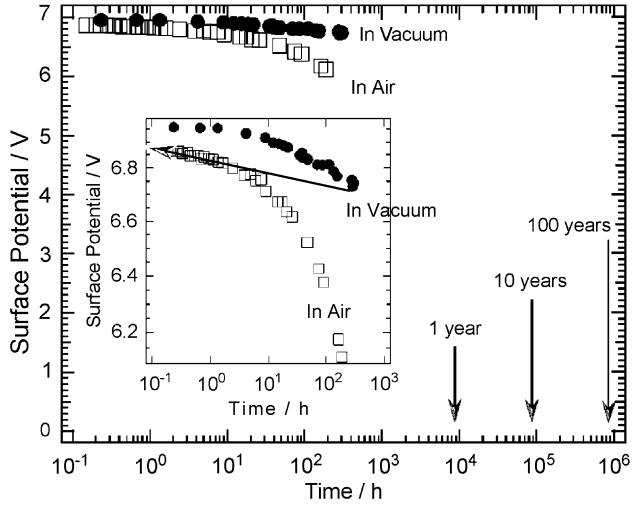

Fig. 1. Surface potential of Alq_3 thin film deposited under dark condition as a function of time. After the measurements in vacuum, the sample was exposed to air, and then the variation was measured again. The inset is the magnification of the data curves.

the Fermi level alignment between the Alq_3 film and the substrate is apparently not achieved due to the potential difference across the Alq_3 film.

After monitoring the SP in vacuum, the sample was exposed to air. The exposure induced the change of the SP by several tens mV. This change can be ascribed to the water adsorption on the film surface and/or the reference electrode of Kelvin probe. Actually this shift is reversible; the change with the same magnitude and reverse polarity occurred when the system is pumped again. The decay rate in air is larger than that in vacuum. This may be caused by the adsorption of counter ions from air. Such compensation of the polarization is often reported in ferroelectric materials. When Alq_3 is applied to layered devices in sandwich structure, the surface of Alq_3 film cannot be exposed to the atmosphere because of the protection by a top electrode on the film. Thus this effect does not affect the devices if the molecular orientation Alq_3 does not change upon the deposition of the overlayer.

3.2. Possible models for removal of the SP by light irradiation

3.2.1. Compensation by photo-induced charges (model I)

As a model for explaining the removal of SP by light irradiation, the compensation by photocurrent-induced charges is plausible. In this model, excitons are created by light absorption, and they are decomposed by the internal field in the film due to the giant SP, leading photocurrent generation. Electrons and holes thus created can move to the surface and the substrate interface of Alq_3 thin film, respectively. The initial polarization is expected to be compensated by the charges at both ends of the Alq_3 layer.

In order to examine this model, the following experiment was performed. Fig. 2 shows the change of the SP of Alq_3 film deposited under dark condition as a function of the film thickness. The SP linearly increased with increasing thickness. It reaches 27 V at the thickness of 575 nm. Here the polarization ρ is estimated to be 0.44 mC/m^2. The Alq_3 film was irradiated by light, and the SP reduced to almost zero. If model I holds, the densities of counter charges accumulated at the surface and the substrate interface of Alq_3 film equal $-\rho$ and $+\rho$, respectively. Thus the polarization is completely compensated by the counter charges. Next, additional Alq_3 layer was deposited on the film under dark condition, again. The counter charges accumulated at the surface of the depolarized film can migrate to the surface of the additionally deposited film to compensate the polarization of the additionally deposited film again. Thus we can expect no variation of the SP during the additional deposition if the additional layer has the same molecular orientation as the original Alq_3 film. However, the increase of SP is observed by the additional deposition, and SP is proportional to the thickness of the additional layer. The slope of SP is the same as the original film. This result clearly excludes the possibility of model I.

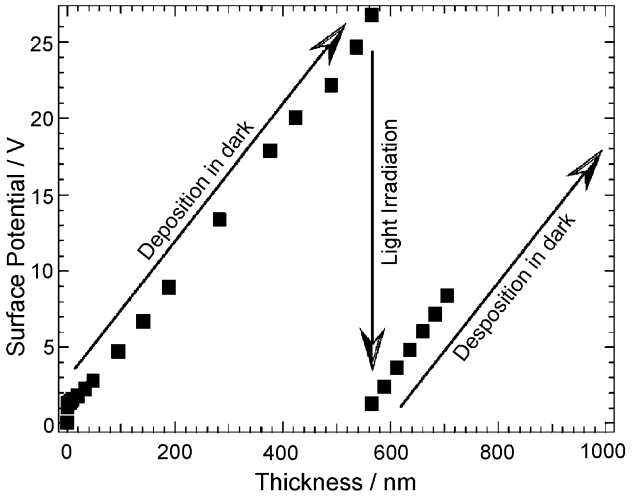

Fig. 2. The change of surface potential of Alq_3 thin film upon additional deposition. The large surface potential formed by deposition under dark condition was once removed by light irradiation. Additional deposition of Alq_3 on the film induced the increase of the surface potential again.

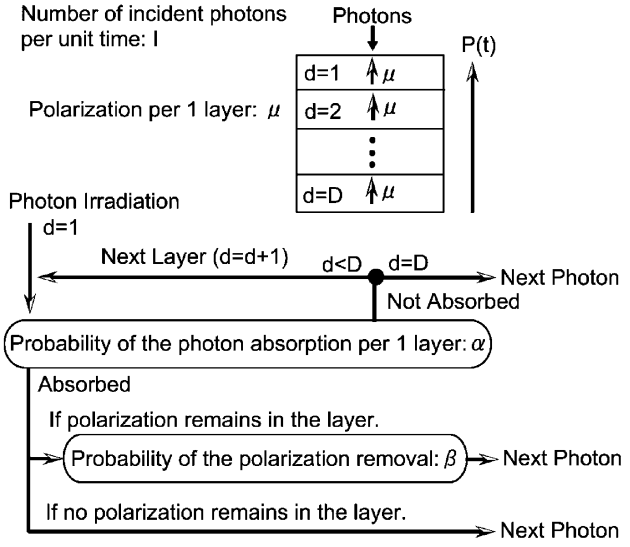

Fig. 3. The procedure of our theoretical simulation of removal of the surface potential by light irradiation.

3.2.2. Randomization of oriented molecules by light absorption (model II)

The other possible model is the randomization of oriented Alq_3 molecules triggered by light absorption. The detailed mechanism of such randomization is not clear, but possible rotation of the molecule is suggested [1]: part of Alq_3 molecules are oriented in the film, and the local field perpendicular to the film surface is formed in the film. The molecular orientation of the film in dark condition is energetically stable to the local field formed by other oriented Alq_3 molecules. Once an Alq_3 molecule absorbs a photon, the direction of the dipole moment can rotate by about 90° during the excitation. Actually, theoretical calculation predicts the dipole moment of the lowest excited state by light absorption is almost orthogonal to that of the ground state [4]. At this situation, the direction of the dipole moment in the excited state is no longer energetically stable to the local field. Thus the molecular rotation may be induced, which may trigger the randomization of the molecular orientation. As another possibility, the formation of dimer of Alq_3 molecules in which each dipole moment faces each other to cancel the dipole moments may be induced by light absorption.

Irrespective of the detailed mechanism of the randomization, here we assume that one event of photo-absorption of an Alq_3 molecule can induce the randomization of the constant amount of the oriented Alq_3 molecules. To examine this model, the decay rate of the SP by light irradiation was simulated and compared with the observed decay rate.

The outline of the simulation is as follows (Fig. 3): we assume an Alq_3 film of D layers. Each layer can have 0 or μ dipole moment depending on the orientation. In the initial state, each layer is assumed to have a dipole of μ. Thus the initial polarization of the film before the light irradiation is μD in total. I particles of photons impinge on the film in a second. The probability of the photon absorption per one layer is α. The probability that a polarized layer with dipole μ becomes randomized upon one photon absorption is assumed to be β. Thus the survival probability of the polarization of the dth layer for each incident photon, $S(d)$, can be shown as

$$S(d) = 1 - \alpha\beta(1-\alpha)^{d-1} \quad (1)$$

where $\alpha(1-\alpha)^{d-1}$ equals to the probability that a photon is absorbed just at dth layer. Thus the expected value of the remaining polarization of dth layer after the radiation of It photons becomes $\mu\{1-\alpha\beta(1-\alpha)^{d-1}\}^{It}$. Finally the polarization of the film at time t, $P(t)$, which corresponds to

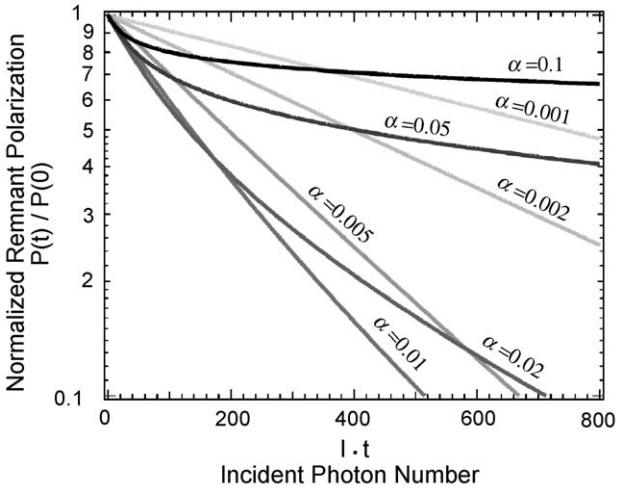

Fig. 4. The variation of the decay of SP calculated by the theoretical simulation for various α.

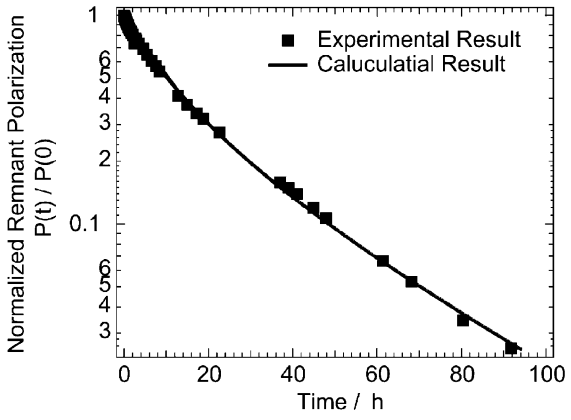

Fig. 5. The comparison between the experimental and theoretical results for the removal of the surface potential by light irradiation as a function of photon irradiation time.

the total sum of the expected values of all the layers can be expressed as

$$P(t) = \mu \sum_{d=1}^{D} \left\{ 1 - \alpha\beta(1-\alpha)^{d-1} \right\}^{It} \quad (2)$$

Fig. 4 shows the result of the simulation where the remnant polarization is plotted as a function of incident photon number. The polarization is normalized to the initial value before the light irradiation. The number of layers for 100-nm-thick Alq_3 film was roughly estimated to be 140 by considering the molecular size. $\beta = 1$ is assumed in order to simplify the model. The line shape of the curve is dependent on the value of α. For small α, the film is relatively transparent, and the probability of the randomization is nearly independent of the depth. Thus the polarization shows exponential decay. In contrast, for large α, most photons are absorbed at surface region, and the film cannot be depolarized completely.

By adjusting the parameters, the observed change of SP was successfully reproduced as shown in Fig. 5. The experimental data are for 100-nm-thick Alq_3 film deposited under dark condition. The intensity of the light was reduced to adjust the decay rate. $D = 140$ and $\beta = 1$ were used again. The simulated curve with $\alpha = 0.0164$ and $I = 0.00388$ well corresponds to the observed one. These results suggest the validity of the assumption that one event of photo-absorption of Alq_3 molecule can induce the randomization of the constant amount of oriented Alq_3 molecules.

4. Conclusion

In relation to possible applications of the giant SP of Alq_3 film to organic electronic devices, the retention time of the SP was investigated. The observed decay rate was roughly estimated to be 10% loss in 10 years. This result demonstrates that the SP has enough retention time for possible device applications. We also investigated the mechanism of light erasing of the SP. By comparison between the simulation and the observed data, we conclude that one event of photo-absorption of Alq_3 molecule can induce the randomization of the constant amount of oriented Alq_3 molecules. In order to clarify the mechanism of the light-erasing of SP, further study of temperature dependence of the built up of SP in dark and its light erasing is highly desired since thermodynamic factor is one of the important aspects to the observed phenomena. From the point of view of applying the polarization properties of Alq_3 film to electronic devices, a question, "Can the high SP state be recovered after the light irradiation?", becomes critical. The examinations of ferroelectricity of Alq_3 film as well as its temperature effect are now underway.

Acknowledgements

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