Large surface potential of $\mathrm{Alq_3}$ film and its decay

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The surface potential across Alq₃ [tris(8-quinolinolato)aluminum] evaporated films on a metal (Au, Al) electrode was measured by the Kelvin probe method and the results were discussed taking into account the orientational ordering of Alq₃ molecules, the presence of surface charges on Alq₃ films and the displacement of excess charge (electrons and holes) from the electrode into Alq₃ films. The very large surface potential established in as-deposited Alq₃ films was mainly due to the alignment of dipoles of Alq₃ molecules, whereas the small surface potential that remained in the films after photoirradiation was due to excess charge. In order to clarify the drastic decrease of surface potential by photoirradiation, the surface potential decay was examined. © *2005 American Institute of Physics*. [DOI: 10.1063/1.1835543]

I. INTRODUCTION

Recently, organic semiconductors have attracted much attention in electronics along with the successful preparation of films with high mobility and high electrical conductivity. Organic solar cells, organic electroluminescent devices, and organic field-effect transistors have been fabricated. In these devices, carrier injection, carrier separation at organic/metal interfaces, and carrier transport in the films are the key processes. Therefore, in the field of organic electronics, the understanding of nanointerfacial electrostatic phenomena is of great importance to improve device performance. Classically, electrostatic phenomena at organic/metal interfaces were discussed assuming the Fermi-level alignment between metal and organic materials. However, this assumption is not valid when an interfacial dipole layer is formed at organic/metal interfaces due to the alignment of polar molecules, image charge effects and chemical bond formation, *etc.*[1] For Alq₃ films, the permanent dipole moment is one of the main origins of the surface potential. Therefore, it is instructive to study the interfacial electrostatic phenomena at the metal/Alq₃ film interface. In our previous studies, using polyimide Langmuir-Blodgett (LB) films[2,3] and phthalocyanine films,[4,5] we investigated the electrostatic potential across these organic films on various electrodes (Au, Al, Cr, etc.) by the Kelvin probe method as a function of film thickness. From these studies, we concluded that electronic charges were displaced from metal to organic films within the range of several nanometers from the metal/organic film interfaces. Recently, Ito *et al.* reported that a very large surface potential, up to 28 V, was established in as-deposited tris(8-quinolinolato)aluminum (Alq₃) films with a thickness of 560 nm, though this potential decayed upon photoirradiation.[6] Such a large potential across Alq₃ films cannot be explained completely by the contribution of excess charge at the metal-film interface. In other words, it is very difficult to consider the establishment of the Fermi-level alignment at metal/Alq₃ interfaces in a manner as predicted by the well-known Mott–Schottky model.[7] In this article, we examine the surface potential built across Alq₃ films, and discuss the results taking into account the orientational ordering of the Alq₃ molecules, the displacement of excess charge from the metal electrodes into Alq₃ films, and the presence of surface charges on the deposited Alq₃ film surface. Furthermore, the potential decaying process was examined in order to clarify the origin of surface potential of as-deposited Alq₃ films.

II. EXPERIMENTS

A. Samples

The Alq₃ molecule, whose chemical structure is shown in Fig. 1, was purchased from Sigma-Aldrich Co. and was used without further purification. For Alq₃ molecules, two geometric isomers, meridional (*mer*) and facial (*fac*), are known, and *mer* isomer possesses permanent dipole moment as shown in Fig. 1(b).[8] Thus we may expect that the permanent dipole moment of Alq₃ makes a significant contribution to the surface potential when these dipoles align unidirectionally on the substrate. In our experiment, the Alq₃ film was prepared on Al and Au electrodes by vacuum evaporation at a process pressure of 9×10^{-7} torr. The deposition rate was monitored by a quartz crystal microbalance, and was controlled to about $0.4-0.6$ Å/s. The deposited Alq₃ film was amorphouslike and it was composed of *mer* isomers, in a manner as reported in Ref. 9.

B. Kelvin probe method

Figure 2(a) shows the experimental setup for the Kelvin probe measurement. The plate detector (top electrode) is placed parallel to the sample surface and is vibrated vertically toward the substrate at a frequency of 120 Hz during the measurement. The surface potential V_s is referenced from the metal electrode, and it is determined by adjusting the compensation voltage V_b such that the current flowing am-

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FIG. 3. The surface potential across Alq$_3$ films on Au (triangle mark) and Al (circle mark) electrodes. Solid lines for as-deposited films, and broken lines for photoirradiated films.
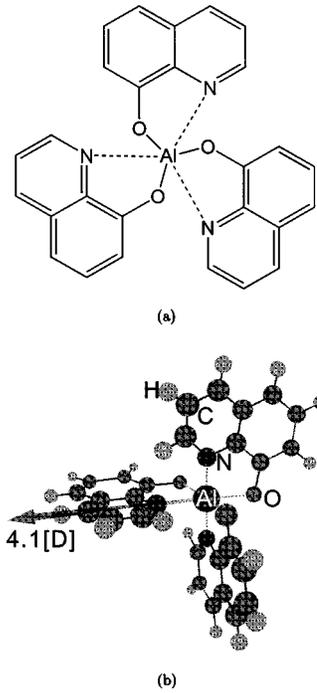
FIG. 1. (a) Chemical structure of Alq$_3$. (b) Three-dimensional figure of Alq$_3$ (*m*er). The dipole moment is indicated.

meter A becomes zero. In this study, the potential was measured in a vacuum of the order of 10^{-6} torr, using a surface potential meter (Trek, model 320B).

III. RESULTS AND DISCUSSION

A. Surface potential of Alq$_3$ evaporated film before and after irradiation

Figure 3 shows the surface potential of as-deposited Alq$_3$ films with various thicknesses on Al and Au electrodes. The inset of Fig. 3 shows the profile of the surface potential near the interface. As shown in the figure, the surface potentials of as-deposited Alq$_3$ films increase steeply and linearly with the film thickness (solid line). Surprisingly, the potential is quite large and reaches 15 V for films on Au electrodes
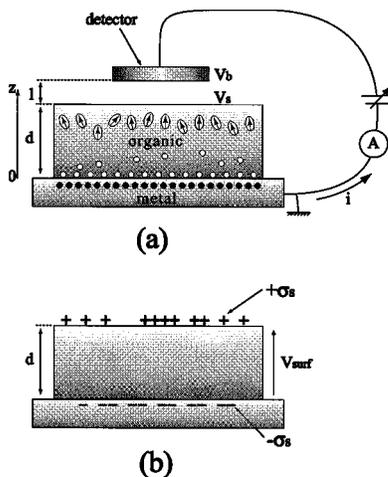
FIG. 2. (a) The experimental setup for the Kelvin probe measurement. (b) Schematic illustration of the surface charge on Alq$_3$ film.

and 8 V for films on Al electrodes when the film thickness is 200 nm. That is, the average induced electric field in the films is about 10^5 V/cm. These results were very similar to that reported by Ito *et al.*[6] The establishment of such a large voltage across Alq$_3$ films cannot be explained only by assuming the electron transfer at the Alq$_3$ film/metal interface, which leads to the Fermi-level alignment at the film-metal interface in a manner as predicted by the Mott–Schottky model.[7] We further need to consider the orientational ordering of Alq$_3$ molecules in as-deposited films, the presence of surface Fermi level at the metal/Alq$_3$ interface, and the presence of surface charges on the deposited Alq$_3$ films. The surface potential V_s across Alq$_3$ films is considered as the sum of the surface potential due to excess charges V_c and that due to alignment of dipolar molecules V_p [see Fig. 2(a)], if the contribution of surface charge σ_s is minor [see Fig. 2(b)].

V_s is given by

$$V_s = V_c + V_p, \tag{1}$$

where V_c is the surface potential due to excess charge, and it is expressed as[2]

$$V_c = \int_0^d \frac{z\rho(z)}{\varepsilon_s \varepsilon_0} dz. \tag{2}$$

Here, $\rho(z)$ is the space charge density at position z from the film/metal interface, ε_0 is the dielectric permittivity of a vacuum, ε_s is the dielectric constant of the organic film, and d is the film thickness.

V_p is the surface potential due to alignment of dipolar molecules, and it is expressed as

$$V_p = \int_0^d \frac{\mu n \cos\theta}{\varepsilon_s \varepsilon_0} dz \tag{3a}$$

$$= \frac{\mu n S_1}{\varepsilon_s \varepsilon_0} d, \tag{3b}$$

assuming the orientational order parameter S_1, defined as $S_1 = \langle\cos\theta\rangle$, is constant. Here, μ is the dipole moment of the molecules, n is the molecular density, θ is the orientational angle from the normal direction to the substrate, and $\langle\,\rangle$ represents the thermodynamic average of the molecules over all directions. Of course, there are many other origins, e.g., adsorbed molecules on the film surface and image charge effects, contributing to the surface potential.[1,9] If the surface

charge σ_s on the deposited Alq$_3$ film also makes a significant contribution as shown in Fig. 2(b), the potential V_{surf} $= \sigma_s d / \varepsilon_s \varepsilon_0$ is added to Eq. (1). If the observed surface potential shown in Fig. 3 is entirely attributed to the surface charge $+\sigma_s$, σ_s is estimated around 10^{12} surface charges per cm^2. This value is reasonable if the deposited Alq$_3$ film is a good electrical insulator.[10] On the other hand, if the orientational ordering of the molecule is the main contribution to the observed surface potential, S_1 is calculated as 0.07 and 0.04 for Alq$_3$ films on Au and Al electrodes, respectively, using Eq. (3b), where $\mu = 4.1$[D],[8] $n = 2.0 \times 10^{27}$[m^{-3}],[11] and $\varepsilon_s = 2.8$.[12] The values of S_1 are very small, but not zero. In other words, Alq$_3$ molecules are tilting and nearly facing to the substrate, but they contribute to the establishment of the spontaneous surface potential. As mentioned above, the large surface potential in as-deposited Alq$_3$ films can be tentatively explained by the presence of surface charges on Alq$_3$ films or the orientational ordering of Alq$_3$ molecules.

The situation of the established large potential changes when the deposited Alq$_3$ film is irradiated by a light with a wavelength of 400 nm (2.1 mW/cm^2 for 1 h) from a xenon lamp through an appropriate band pass filter. That is, the established large potential decays drastically as shown in Fig. 3. It is instructive here to note that the wavelength of 400 nm corresponds to the absorption maximum of Alq$_3$ films (see Ref. 5). In more detail, the potential decay is dependent on the wavelength of photoirradiation and not dependent on the metals (Au, Al). In other words, the inception of the surface potential decay happens when Alq$_3$ molecules absorb photons, i.e., the electron injection from metals into films is not dominant. Furthermore, it is more instructive to note that the surface potential decay is not observed when the Alq$_3$ film is irradiated by light with a wavelength longer than the absorption band, e.g., 700 nm.

As shown in Fig. 3, the surface potential decreased drastically and never recovered (broken lines). Only very small potentials of several hundred millivolts remained indicating that the spontaneous polarization due to the alignment of dipoles was almost destroyed or the surface charge σ_s was removed. In other words, the potential decay can be explained by assuming that either order parameters S_1 for Alq$_3$ films on Au and Al electrodes decreased to nearly zero after photoirradiation or the surface charge σ_s decreased to zero. In Sec. III C, we discuss that the injection of surface charge on the Alq$_3$ film σ_s depicted in Fig. 2(b) into Alq$_3$ film to combine with charge $-\sigma_s$ on metal electrode is not a main contributor on the basis of the temperature dependence of the surface potential.

Interestingly, the remained small surface potential is dependent on metal electrodes Au and Al. Alq$_3$ films on Al electrodes are more negatively charged than that on Au electrodes. Therefore, it is estimated that some excess charge is displaced from the metal to the Alq$_3$ film in a manner that has been seen for polyimide LB films[1] and phthalocyanine evaporated films,[5] where the surface potential of films on metals with small work functions is formed negatively in comparison with that of films on metals with large work
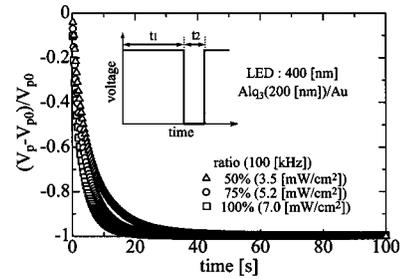
FIG. 4. Decay process of the surface potential across the Alq$_3$ evaporated films, thickness of 200 nm, on an Au electrode (duty ratio γ: 50%, 75%, 100%). Wavelength of light is 400 nm.

function. Hence, we may consider that the potential remaining after photoirradiation corresponds to V_c, due to the excess charge.

B. Surface potential decay process

As mentioned in Sec. III A, orientational ordering of molecules and the presence of surface charge are possible origins of the observed large potential. In order to further clarify the origins, the decay process of the surface potential of as-deposited films were further examined. We measured the surface potential decay, using light-emitting diode (LED), by controlling the incident light power, i.e., by changing the duty ratio of the incident light $\gamma = t_1/(t_1+t_2)$ (see the inset of Fig. 4) at 100 kHz.

As shown in Fig. 4, the surface potential decays more rapidly as γ increases. This means that the potential decaying process is dependent on the number of photons absorbed by the film, and not dependent on the dielectric relaxation process, such as the dipolar depolarization process described by the Debye rotational model,[13] i.e., randomization process of oriented dipoles. As shown in Fig. 4, the surface potential monotonously decays, and it is proportional to the irradiation time from the beginning of photoirradiation. Taking this into account, the surface potential decaying process is tentatively described at least in two ways. The first one is the disordering process and the second one is the extinction process of surface charges $+\sigma_s$ due to the combination with created electrons by photoirradiation. In the following, we discuss the potential decaying process separately on the basis of these two processes.

1. Disordering process

Assuming that the polar Alq$_3$ molecules disorder by the photoirradiation, the density of Alq$_3$ molecules $n_d(z,t)$ contributing to the surface potential decreases by photoirradiation so as to satisfy the following equation:

$$\frac{dn_d(z,t)}{dt} = -\eta \left\{ \frac{\alpha n_p(z)}{n} \right\} n_d(z,t) \tag{4}$$

with

$$n_p(z) = n_{p0} \exp\{-\alpha(d-z)\}. \tag{5}$$

Here, $n_p(z)$ is the density of incident photons per radiation area per second, α is the absorption coefficient of the Alq$_3$ evaporated film, η is a constant, d is the film thickness,

(a)

(b)
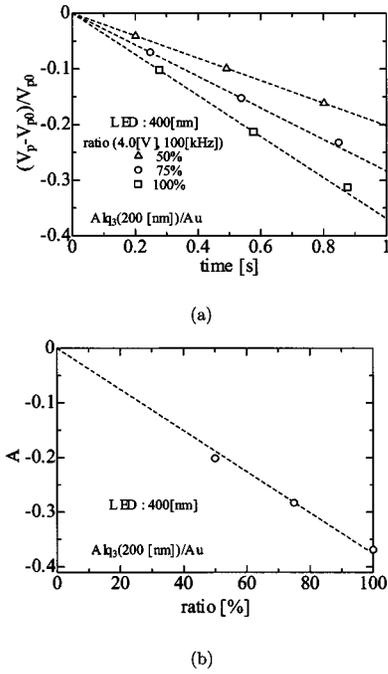
FIG. 5. (a) $(V_p - V_{p0})/V_{p0} - t$ plot, obtained from Fig. 4(a), just after photoirradiation with a wavelength of 400 nm. (b) Relationship between A and duty ratio γ.

and z is the distance from the surface. It is instructive to note that η is constant and it is proportional to the number of dipoles which lose their contribution to the surface potential per second by the absorption of one photon. From Eq. (4), $n_d(z,t)$ is written as

$$n_d(z,t) = n \exp\left[-\eta\left\{ \frac{\alpha n_p(z)}{n} \right\} t \right] \qquad (6)$$

with the initial condition of $n_d(z,0)=n$. With Eqs. (3a) and (6), the surface potential is approximately given as a function of irradiation time

$$\frac{V_p - V_{p0}}{V_{p0}} \simeq \frac{1 - \exp(-\xi)}{\xi}\left(-\frac{t}{\tau} \right) = At \qquad (7)$$

with $V_{p0}=\mu S_1 nd/\varepsilon_s\varepsilon_0$, $1/\tau=\eta\alpha n_{p0}/n$, and $\xi=\alpha d$. Here V_{p0} is the initial surface potential due to the alignment of dipoles in as-deposited films. From Eq. (7), it is expected that A changes proportionally to the duty ratio γ, namely, in proportion to the density of incident photons n_{p0}. Figure 5(a) shows the $(V_p - V_{p0})/V_{p0} - t$ plot, obtained from Fig. 4 just after the photoirradiation at a wavelength of 400 nm. As Fig. 5(b) shows, A changes in proportion to γ. Thus we may consider that the model mentioned here explains the potential decaying process phenomenologically. A similar tendency was also observed when the Alq$_3$ film was irradiated at a wavelength of 470 nm (not shown here).

From these results, η was estimated to be approximately 10 at a wavelength of both 400 and 470 nm, assuming the values of the absorption coefficient determined from the optical density of our Alq$_3$ films (1.2×10^7 m^{-1} at 400 nm and 4.1×10^5 m^{-1} at 470 nm). This means that the absorption of one photon from the surface of radiation per second leads to disordering of about 10 Alq$_3$ molecules per second. The

value of 10 seems large. We expect that the disordering of Alq$_3$ molecules surrounding the photon absorbed Alq$_3$ molecules is triggered as the result of the photon absorption. Of course, we need further investigation, but the disordering process is the possible mechanism.

2. Extinction process of surface charge σ_s

By photoirradiation, electron-hole pairs are created in the bulk of Alq$_3$ film. Then excited electrons and holes are conveyed in the opposite directions by the force of the local electric field generated by the large surface potential V_s, subsequently, they combine with surface change $\pm\sigma_s$ and extinguish them. Of course, for the detailed discussion, we need to consider the creation process of electron-hole pairs, transport process of created electrons and holes, and combination process of created electrons and holes with surface charge σ_s. However, we may tentatively describe the surface charge decay process, as follows:

$$\frac{d\sigma_s}{dt} = -\left[\frac{1}{d}\int_0^d \eta'\left(\frac{\alpha n_p}{n} \right)dx \right]\sigma_s. \qquad (8)$$

Here η' is constant and proportional to the number of electrons conveyed to the surface of Alq$_3$ film to combine surface changes σ_s. Substituting Eq. (5) into Eq. (8), we obtain Eq. (9) as

$$\frac{d\sigma_s}{dt} = -\eta'\alpha\left(\frac{n_{po}}{n} \right)\frac{1 - \exp(-\alpha d)}{\alpha d}\sigma_s$$

$$= -\frac{1}{\tau}\frac{1 - \exp(-\xi)}{\xi}\sigma_s. \qquad (9)$$

Here ξ and τ are the same parameters defined in Eq. (7). If the observed surface potential V_s is entirely attributed to the surface charge σ_s, V_s is proportional to σ_s, i.e., $V_s = \sigma_s d/\varepsilon_s\varepsilon_0$. Thus, from Eq. (9), we have the same relation given by Eq. (7), replacing V_p and V_{po} to V_s and V_{so}, respectively. This means that the potential decay process can be explained in a similar manner as we have done in Sec. III B 1.

As mentioned above, we could argue the surface potential decay process in two ways on the basis of the experiment using the LED. Recently in order to distinguish two processes, we have carried out optical second harmonic generation (SHG) measurement, for Alq$_3$ films deposited on glass slide. It was found that SH intensity decreases to 1/5 of the initial intensity after irradiation of the sample with a wavelength of 400 nm, whereas it does not decrease with a wavelength of 600 nm. Since the SHG signal vanishes from the materials with inversion symmetry under the dipole approximation, the presence of the polar ordering in as-deposited Alq$_3$ films was confirmed by the SHG measurement.[14]

Thus the decrease of SH intensity of our experiment indicates the disordering of polar molecules. Based on this experimental result, we conclude that the disordering of Alq$_3$ molecules is the most probable process, though we need to continue experiments to clarify the details of SH process. Because, there is a possibility that the SH process was acti-
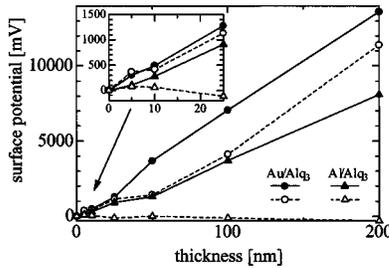
FIG. 6. Relationship between the potential and the thickness of Alq$_3$ films before heating (solid line) and after annealing (broken line). Temperature and period of annealing are 100 °C and 5 h, respectively.

vated by the internal field due to the surface potential.[15] Further investigation proceeds to clarify the details.

C. Temperature dependence of Alq$_3$ evaporated film

In order to further clarify the potential decaying process, we also measured the temperature dependence of the surface potential. Alq$_3$ films evaporated on metal (Au, Al) electrodes were heated from 30 to 100 °C at a heating rate of 1.0 °C/min, and the surface potential was measured every 10 min during heating. After annealing at 100 °C for 5 h, samples were cooled to 30 °C.

Figure 6 shows the relationship between the potential and the thickness of the films before and after annealing. The potential was measured at 30 °C. Surface potential across the Alq$_3$ film on Al electrode decreased more clearly than that on the Au electrode. The remarkable dependence of the surface potential change on the metal electrodes implies that the interfacial phenomena occurring at the metal/Alq$_3$ film interface is a main factor explaining the temperature dependence of surface potential. If the contribution of surface charge σ_s decay by the injection into Alq$_3$ film is dominant, the potential decay should not be dependent on the electrode materials (Au or Al). Because the deposited surface charge on Alq$_3$ film injects into the film and the charge decays on satisfying the relation $\sigma_s = \sigma_0 \exp[-(H'/kT)]$, where H' is the activation energy required to remove surface charge σ_s into the Alq$_3$ film. Therefore within the constraints of our experiment, we may discuss that the decay of σ_s through the injection into Alq$_3$ films to combine with the charges on metal electrode is not a main contribution of the potential decay [see Fig. 2(b)]. Therefore, to explain the potential decay process by heating, we need to consider the electron injection from metal electrodes into Alq$_3$ film.

Figure 7 shows the surface potential V_s for various films with different thicknesses as a function of time. The potential is plotted as V_s/V_0, where V_0 is the initial surface potential, i.e., the potential of as-deposited Alq$_3$ film. As the thickness increases (>50 nm thickness), the V_s/V_0-t characteristics gradually coincide. In other words, the heat-treatment effect appears in the region close to the metal-film interface. In order to explain the potential decay process related to the large surface potential by heating, we focus on the surface potential decay of the thick films (>50 nm thickness). The surface potential is approximately given as

(a)

(b)
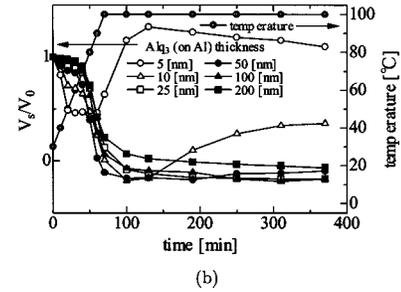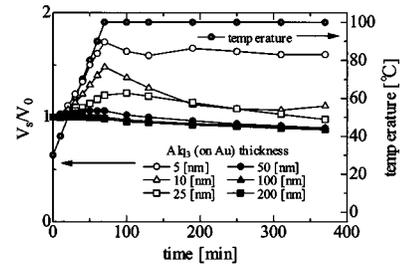
FIG. 7. Surface potential V_s for various films with different thicknesses as a function of time. (a) Alq$_3$ on Au, (b) Alq$_3$ on Al.

$$\frac{dV_p}{dt} = -\frac{V_p}{\tau} \qquad (10)$$

with

$$\tau = \tau_0 \exp\left(\frac{H}{kT}\right).$$

Here, T is the temperature, τ is the relaxation time, τ_0 is the pre-exponential factor, H is the activation energy, and k is the Boltzmann constant. In this experiment, temperature is controlled to satisfy

$$T = T_0 + \beta t, \qquad (11)$$

in the region $0 \leqslant t \leqslant 70$ min. Here T_0 is the initial temperature, and β is the heating rate. As mentioned earlier, in the region of film thickness greater than 50 nm, the main contribution of V_s is V_p. Thus, taking into consideration these with Eqs. (10) and (11), Eq. (10) is rewritten as

$$\frac{d}{dT}\left(\frac{V_s}{V_0}\right) = -\frac{1}{\beta\tau_0}\exp\left(-\frac{H}{kT}\right)$$
$$\times \exp\left\{-\frac{1}{\beta\tau_0}\int_{T_0}^{T}\exp\left(-\frac{H}{kT}\right)dT\right\}, \qquad (12a)$$

and is approximately given as

$$\ln\left\{-\frac{d}{dT}\left(\frac{V_s}{V_0}\right)\right\} = \ln\left(\frac{1}{\beta\tau_0}\right) - \frac{H}{kT}, \qquad (12b)$$

at the initial stage of heating. Using the relationship given by Eq. (12b), the activation energy H of the Alq$_3$ film on the Al electrode was estimated as 1.3 eV (see Fig. 8). On the other hand, the activation energy for the Alq$_3$ films on Au electrode is estimated higher than 1.3 eV, as the potential does not change so drastically by heating (see Fig. 6). As mentioned earlier, the potential decay process should be explained mainly due to the interfacial phenomena occurring at

FIG. 8. $\ln\{-d(V_s/V_0)/dT\}-1/T$ plot.

FIG. 9. Energy diagram of the interface between the metal and the Alq$_3$ film, where the energy level estimated from the surface potential measurement is plotted by dashed lines.

the interface between the metal and the Alq$_3$ film. Interestingly, the value of the calculated activation energy H is in good agreement with the estimated barrier height by other researchers.[16,17]

Thereby in the following, we discuss the surface potential decay process assuming the electron injection from metals. When electrons are gradually injected from metal to film, surface potential V_s changes as

$$V_s \simeq V_p = V_{p0} + \int_0^d \frac{z\rho_{in}(z,t)}{\varepsilon_s\varepsilon_0}dz, \tag{13}$$

where $\rho_{in}(z,t)$ is the injected charge density at a position z from the interface.

The total charge injected into the Alq$_3$ film is roughly given as

$$\int_0^d \rho_{in}(z,t)dz = \left\{-J_0\exp\left(-\frac{\Phi}{kT}\right)\right\}t = \frac{1}{\bar{z}}\int_0^d z\rho_{in}(z,t)dz, \tag{14}$$

where Φ is the barrier height for electron injection and J_0 is constant. Here we need the following relation $\bar{z}$, the average location of injected electrons.

$$\bar{z} = \frac{\int_0^d z\rho_{in}(z,t)dz}{\int_0^d \rho_{in}(z,t)dz}. \tag{15}$$

With Eq. (14), Eq. (13) is written as

$$V_p = V_{p0}\left(1 - \frac{t}{\tau}\right) \simeq V_{p0}\exp\left(-\frac{t}{\tau}\right) \tag{16}$$

with

$$\tau = \frac{\varepsilon_s\varepsilon_0 V_{p0}}{\bar{z}J_0}\exp\left(\frac{\Phi}{kT}\right) = \tau_0\exp\left(\frac{\Phi}{kT}\right)$$

It is found that V_p, given by Eq. (16), satisfies the differential equation of Eq. (10). In other words, the activation energy H estimated from Eq. (12b) corresponds well to the barrier height Φ.

Finally it is instructive to depict the energy diagram at the metal-film interface. Figure 9 shows an energy diagram at the interface between the metal and the Alq$_3$ film, where the energy level estimated from the surface potential measurement is plotted by dashed lines. The barrier heights for the electron injections from both the Au and Al electrodes to the Alq$_3$ film, Φ_{Au} and Φ_{Al}, respectively, are given by

$$\Phi_{Au} = W_{Au} - \Phi_{LUMO} - eV_{Au}, \tag{17a}$$

$$\Phi_{Al} = W_{Al} - \Phi_{LUMO} + eV_{Al}, \tag{17b}$$

where eV_{Au} ($\simeq 350$ meV) and eV_{Al} ($\simeq 100$ meV) are the energy level shifts estimated by the surface potential across the Alq$_3$ films on both the Au and Al electrodes after photoirradiation, respectively. W_{Au} ($=4.75$ eV) and W_{Al} ($=4.02$ eV) are the work functions of the Au and Al electrodes, respectively, and Φ_{LUMO} is the lowest unoccupied molecular orbital (LUMO) level of the Alq$_3$.

From Eq. (17b), Φ_{LUMO} is calculated to be 2.8 eV under the assumption that $\Phi_{Al}=H$ ($=1.3$ eV). The interfacial space charge layer is very thin, less than several nanometers thereby electrons will be injected into the film by electron tunneling. In this case, the minimum barrier height for an electron from the Au electrode to the Alq$_3$ film Φ'_{Au} is expected to be 1.6 eV, if electron tunneling injection happens at the interface, whereas it is expected to be 1.75 eV when electrons inject into film over the interface barrier. Figure 10 shows the calculated surface potential decay with respect to time for various energy heights at 373 K. The potential decays smoothly for 1.3 eV, whereas it does not decay for 2.0 eV. These results well support our experimental results (see Fig. 6). As mentioned above, the results obtained by heating are explained assuming the electron injection process from metals into Alq$_3$ films.

Further it is more instructive to note that the SH intensity from Alq$_3$ film on glass substrate does not decrease by heating up to a temperature of around 100 °C, though the potential decay on Al electrode happens at a temperature around 70 °C [see Fig. 7(b)]. Thus we may discuss that electron
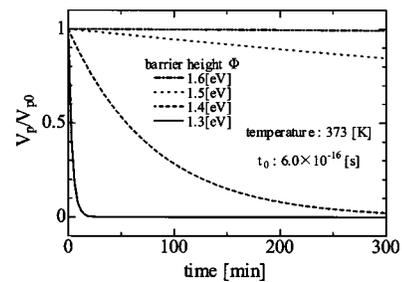
FIG. 10. Calculated surface potential as a function of time with various energy heights at 373 K.

injection from Al is the trigger of the large potential decay. The details of our SHG experiment will be reported in near future.

IV. CONCLUSION

The surface potential across the Alq_3 [tris(8-quinolinolato)aluminum] evaporated films on metal electrode was measured by the Kelvin probe method and discussed based on the alignment of dipoles and the presence of excess charge. It was found that a very large surface potential was established by the alignment of the dipoles in as-deposited films. However, this large surface potential decreased drastically when the Alq_3 film was photoirradiated. After the photoirradiation, excess charge displaced from the electrode to Alq_3 film remained and a very small surface potential appeared. The potential decay by photoirradiation is explained by assuming mainly the disordering of dipoles by the absorption of photons. On the other hand, the potential decay by heating can be tentatively explained by the injection of electrons from metal to Alq_3 film.

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