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Norifumi Kajimoto, Takaaki Manaka, and Mitsumasa Iwamoto[a)]
Department of Physical Electronics, Tokyo Institute of Technology, 2-12-1 O-okayama, Meguro-ku,
Tokyo 152-8552, Japan

In order to clarify the decaying process of a large surface potential of as-deposited Alq$_3$ films on a metal electrode by heating and photoexposure, Kelvin probe method and optical second harmonic generation (SHG) measurement were employed. The change of surface potential during heating was not in accordance with the change of SH intensity at a temperature lower than 100 °C. For heating at less than 100 °C and photoexposure, x-ray diffractions showed no change. We discussed these results from a viewpoint of the disordering of orientational polar structure of Alq$_3$ molecules and the injection of electrons from metal electrodes. Then the following model was suggested. The potential decay process of Alq$_3$ films on aluminum (Al) electrodes by heating was found to be due to electron injection from Al electrode into Alq$_3$ films, which does not accompany the structural change of Alq$_3$ films in the region of temperature lower than 100 °C, though the crystallization of Alq$_3$ evaporated film was suggested at a temperature higher than 100 °C. On the other hand, the disordering of polar structure of Alq$_3$ film that does not accompany the structural change was elucidated as the potential decay process by photoexposure. © *2006 American Institute of Physics*. [DOI: 10.1063/1.2338137]

I. INTRODUCTION

Much attention has been paid to organic materials along with the development of organic thin film devices. Tris(8-quinolinato)aluminum (III) (Alq$_3$) is one of the important organic materials and it is used as the electron transport layer material of organic electroluminescent (EL) devices. The carrier transport and electroluminescent properties of Alq$_3$ have thus been intensively investigated. Recently, it has been reported that a large potential is built in as-deposited Alq$_3$ film and it decays rapidly by exposure to light.[1,2] The establishment of such potential in as-deposited film is well known as an initial polarization phenomenon and has been found in many dielectric materials such as polymers through the observation of pyroelectric effect.[3] However, the large surface potential observed in as-deposited Alq$_3$ films is unique in that it reaches up to several tens of volts for films with several hundreds of nanometers in thickness. The initial polarization is considered to be due to the orientational alignment of dipoles, injected excess charges, impurity ions, etc., and its origin has been extensively investigated by exploring the decay process of the polarization by means of thermally stimulated current measurement, potential decay measurement, etc.[3] As to the potential decay process of the initial polarization of Alq$_3$ films, there are still controversial arguments. Among them are mechanisms based on the photoinduced randomization of the alignment of Alq$_3$ molecules,[1] the cancellation of the potential by either photoexcited carriers in bulk[4] or injected carrier from electrodes, etc. In our previous study, using surface potential measurement, we investigated the potential decay of Alq$_3$ films deposited on gold (Au) and aluminum (Al) electrodes, and showed that electron injection from Al electrode made a significant contribution to the potential decay of Alq$_3$ on Al electrode by

heating, whereas the dipole disordering of Alq$_3$ films on Al and Au electrodes was a main origin of the potential decay by photoexposure.[2] However, it was still not clear whether injected electrons trigger the randomization of polar structures or not, etc. In the present study, in order to further clarify the potential decay process of Alq$_3$ films on Al electrodes, surface potential measurement and optical second harmonic generation (SHG) measurement were employed.

II. EXPERIMENT

A. Sample preparation

Alq$_3$ molecules were purchased from Tokyo Kasei Kogyo Co. Ltd. and was used as supplied without further purification. They were then evaporated onto Al electrodes with or without UV/ozone treatment at a deposition rate of 0.5–1.5 Å/s at a vacuum pressure of 2.0×10^{-6} torr in dark. The work functions of Al electrode with and without UV/ozone treatment were estimated as 3.9 and 3.4 eV, respectively, from the photoelectron yield spectroscopy in air (AC-1: Riken Keiki Co.). From elemental analysis of x ray, transmission electron microscopy (TEM), etc., and references cited in Refs. 5 and 6, we concluded that the evaporated Alq$_3$ films on Al electrodes were amorphouslike and they were composed of mer isomers of Alq$_3$ molecules with a dipole of 4.1 D. Here, in the x-ray diffraction measurements, RINT 2000 diffractometer (Rigaku) with Cu $K\alpha$ radiation was used, where x-ray generator was operated at 40 kV and 40 mA. For recording the x-ray diffraction pattern, θ-2θ scans in the range of 5.0°–9.5° with a step width of 0.02° were carried out in the Bragg-Brentano geometry.

B. Surface potential measurement

The Kelvin probe method was employed for the surface potential measurements.[2] The surface potential V_s was mea-

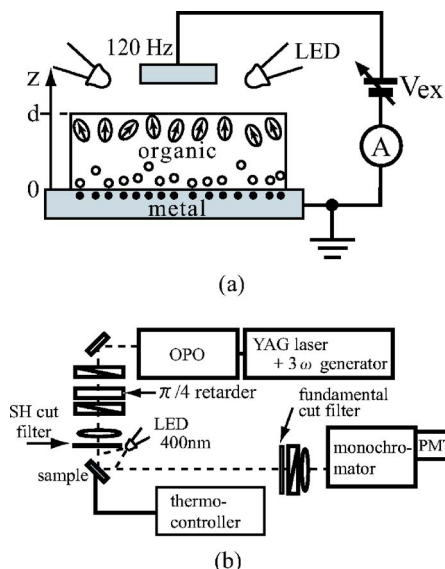a)Electronic mail: iwamoto@pe.titech.ac.jp

(a)

(b)

FIG. 1. The experimental setup (a) for Kelvin probe method and (b) for the SHG measurement.

sured in a dark condition at a vacuum of 10^{-5} torr, except that the surface potential was measured in nitrogen (N_2) atmosphere when Alq_3 film was kept at a temperature of 150 °C, to eliminate the evaporation of the deposited Alq_3 film. For the potential decay measurement by photoexposure, Alq_3 films were irradiated by a blue light with a wavelength of 400 nm using a light-emitting diode (LED) with a power of 2.0 mW/cm^2, in the same manner as we did in our previous study [see Fig. 1(a)].

C. Second harmonic generation

Figure 1(b) shows the experimental arrangement for the SHG measurements. The samples were irradiated by *p*-polarized fundamental light with an incident angle of 45° after passing through a SH cut filter, and generated SH signal was detected by a photomultiplier tube (Hamamatsu Photonics: R928) after passing through a fundamental cut filter and a monochromator (NIKON: G-250). Obtained signals were averaged by the boxcar integrator (Stanford Research: SR-250). To avoid the reduction of the SH intensity during SH measurement by fundamental light exposure, the wavelength of the fundamental light was chosen as 1200 nm.[7] The SHG experiments were carried out at room temperature and also during heating in the dark.

III. RESULTS

Figure 2 shows the surface potential of as-deposited Alq_3 films on Al electrodes with or without UV/ozone treatment. As the film thickness increases, the surface potential increases linearly, in a manner as previously reported,[2] where the surface potential of Alq_3 film deposited on Al electrode with UV/ozone treatment was greater than that of deposited films on Al electrode without UV/ozone treatment. To clarify the dependence of the work function of base Al electrodes on the potential decay process, we measured the temperature dependence of the surface potential of Alq_3 films on Al electrodes with and without UV/ozone treatment. Here, as we
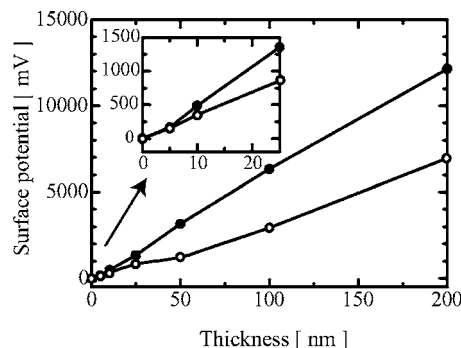

FIG. 2. The large surface potential across Alq_3 films on Al electrode with UV/ozone treatment (filled circle) or without UV/ozone treatment (open circle).

described in Sec. II A, the work functions of Al electrode with and without UV/ozone treatment were 3.9 and 3.4 eV, respectively. The films were heated from 30 to 150 °C at a heating rate of 1.0 °C/min, and the surface potential was measured every 10 min during heating. Figure 3 shows the result of the surface potential of Alq_3 films with a thickness of 100 nm. The surface potential of the film on the Al electrodes without UV/ozone treatment decayed at a temperature around 60 °C, whereas the surface potential of films on Al electrode with UV/ozone treatment decayed at a temperature around 100 °C. This clear difference of the surface potential decay was due to the difference in the work functions of Al electrodes with or without UV/ozone treatment, and could be argued that the electron injection triggers the potential decay of Alq_3 films on Al electrode.

In order to further confirm the potential decay process of Alq_3 film on Al electrode by heating, we measured the SHG during heating at a rate of 1.0 °C/min. The result is also shown in Fig. 3. The SH intensity of Alq_3 film on both Al electrodes with or without UV/ozone treatment was constant up to a temperature of 100 °C, but gradually decreased above 100 °C in the same way. This result indicates that the electrostatic dc field across the Alq_3 film does not make a contribution to the generation of SH.

IV. DISCUSSION

The surface potential V_s across Alq_3 films is considered as the sum of the surface potential due to the excess charges V_c, the alignment of dipolar molecules V_p, and the surface charge V_{surf}, that is, V_s is given as[2]
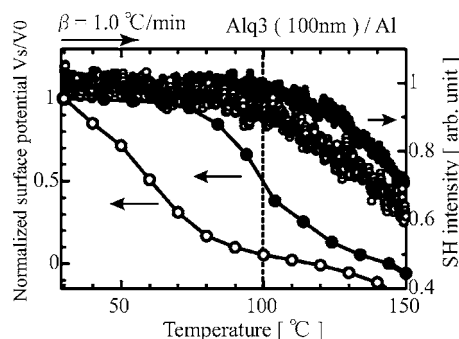

FIG. 3. The decay of surface potential and SH intensity of Alq_3 film deposited on Al electrode with UV/ozone treatment (filled circle) or without UV/ozone treatment (open circle) at a heating rate of 1.0 °C/min.

$$V_s = V_c + V_p + V_{\text{surf}}. \tag{1}$$

There are of course other origins, such as image charge effects, chemical bond formation, etc.,[8] which contribute to the generation of surface potential V_s. However, the above three terms are sufficient to discuss our results.[2] The potential V_c is expressed as

$$V_c = \int_0^d \frac{z\rho(z)}{\epsilon_s \epsilon_0} dz, \tag{2}$$

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

$$V_p \simeq \frac{\bar{\mu} n}{\epsilon_s \epsilon_0} d, \tag{3}$$

where $\bar{\mu}$ is the average dipole moment of a constituent molecule and n is the molecular density. The potential V_{surf} is given by

$$V_{\text{surf}} = \frac{\sigma_s}{\epsilon_s \epsilon_0} d, \tag{4}$$

where σ_s is the surface charge density on Alq$_3$ film due to deposited unexpected molecules, etc. In the following, we discuss the potential decay of Alq$_3$ film in terms of the above three potentials, but the third term is not a main contribution within the constraints of our experiment, as we clarified in our previous study.[2]

A. Origin of SHG

Before going to the details, we focus on the origin of SHG obtained in our experiment on Alq$_3$ film. There are many origins leading to the generation of SH. For the generation of SH from Alq$_3$ film, besides the SHG under dipolar approximation (electric-dipole approximation), we need to consider the possibility of the dc-SHG, because the internal field E^{dc} established in as-deposited Alq$_3$ films is of the order of 10^5 V/cm (see Fig. 2).[9] The nonlinear polarization P_i^D is expressed under the electric-dipole approximation as

$$P_i^D = \chi_{ijk}^D E_j(\omega) E_k(\omega), \tag{5}$$

where χ_{ijk}^D is the second-order nonlinear susceptibility due to the electric-dipole mechanism and E_j and E_k are the electric fields of the fundamental light with an angular frequency ω. For the centrosymmetric system, the generation of SH is not allowed under the electric-dipole approximation because of $\chi_{ijk}^{(2)} = 0$. Therefore to explain the generation of SH from Alq$_3$ film on the basis of the electric-dipole approximation, we need to consider that mer-form Alq$_3$ molecules deposited on Al electrodes align so that $\chi_{ijk}^{(2)} \neq 0$, possibly due to the orientational ordering of deposited Alq$_3$ molecules.

On the other hand, the electric-field-induced nonlinear polarization P_i^{dc} is expressed as

$$P_i^{\text{dc}} = \chi_{ijkl}^{\text{dc}} E_j^{\text{dc}}(0) E_k(\omega) E_l(\omega), \tag{6}$$

where χ_{ijkl}^{dc} is the third-order nonlinear susceptibility due to the dc-induced mechanism and $E_j^{\text{dc}}(0)$ is the internal electric field of Alq$_3$ films. It should be noted that dc-SHG is the third-order nonlinear process, but the double frequency of fundamental light is generated because one of the concerned fields is a static electric field $E_j^{\text{dc}}(0)$. Since the electric-field-induced nonlinear polarization P_i^{dc} is proportional to the internal electric field $E^{\text{dc}}(0)$, SH signal should be generated in proportion to the square of the surface potential when dc-SHG is a main contribution.[9] Taking into account these, we discuss the experimental result of Fig. 3, where the SH intensity is nearly constant up to a temperature of 100 °C, whereas the surface potential decays at a temperature lower than 100 °C. This result indicates that dc-SHG signal generated from the Alq$_3$ films is not a main origin, and the orientational order structure of Alq$_3$ molecules does not change in the temperature region lower than 100 °C. Therefore we consider that the origin of SHG is ascribed to the electric-dipole mechanism due to the orientational ordering of Alq$_3$ molecules. In other words, we may consider that the V_p given by Eq. (3) is a main contribution to the generation of the surface potential.

B. Potential decay process by electron injection

As mentioned in Sec. III, the surface potential was strongly dependent on the work function of Al electrodes. This result indicates that the injection of electron from electrodes into Alq$_3$ film makes a significant contribution to the potential decay by heating. As a result, the potential V_s changes as

$$V_s(t) - V_s(0) = \int_0^d \frac{z\rho_{\text{inj}}(z,t)}{\epsilon_s \epsilon_0} dz = \frac{\bar{z}}{\epsilon_s \epsilon_0} \int_0^d \rho_{\text{inj}}(z,t) dz, \tag{7}$$

where ρ_{inj} is the injected charge density and $\bar{z}$ is the location of the centroid of the injected charge. When the electron injection occurs, electrons jump into the films over the barrier height H. Therefore, the total injected electrons in Alq$_3$ film is approximately given as

$$\int_0^d \rho_{\text{inj}}(z,t) dz \simeq -J_0 \exp\left(-\frac{H}{k_B T}\right) t \tag{8}$$

at the initial stage of the injection. Here J_0 is a constant and k_B is the Boltzmann constant. Substituting Eq. (8) into Eq. (7), we obtain

$$V_s(t) - V_s(0) \simeq -\frac{\bar{z}}{\epsilon_s \epsilon_0} \left[J_0 \exp\left(-\frac{H}{k_B T} t\right) \right]. \tag{9}$$

On the other hand, phenomenologically, the potential decay process is written as

$$\frac{dV_s}{dt} = -\frac{V_s}{\tau}, \tag{10}$$

with τ the relaxation time. From Eq. (10), we obtain

$$V_s(t) - V_s(0) = -V_s(0)\left[1 - \exp\left(-\frac{t}{\tau}\right)\right] \simeq -V_s(0)\frac{t}{\tau}. \tag{11}$$

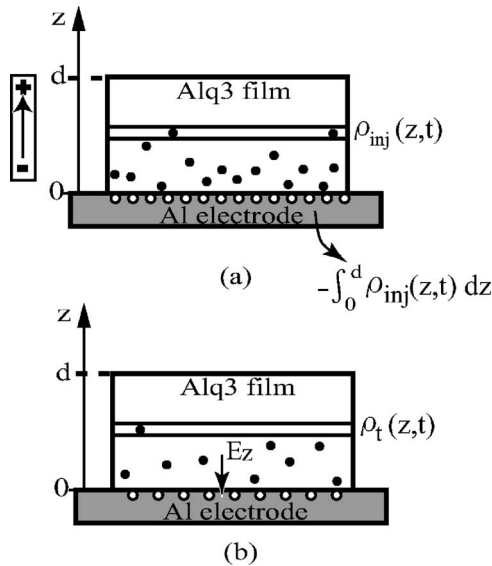Using Eqs. (9) and (11), we have the relation

FIG. 4. Model of injected charge distribution in Alq_3 film. (a) After the completion of the injection, charge ρ_{inj} is trapped in Alq_3 film ($<100\,°C$) and the charge corresponding to the injected charge, $\int_0^d \rho_{inj} dz$, remains on the electrode. (b) The trapped electrons in Alq_3 film during heating process are thermally excited by heating and smoothly return to the electrode to combine with the charge on the electrode, along with the disordering of the polar structure of Alq_3 films, possibly due to the electrostatic attractive force working between injected excess charge and the opposite charge that remained on the surface of the electrode.

$$\tau = \frac{V_s(0)\epsilon_s\epsilon_0}{J_0\bar{z}}\exp\left(\frac{H}{k_BT}\right) = \tau_0 \exp\left(\frac{H}{k_BT}\right). \tag{12}$$

From Eq. (12), we find that the potential decay process is dependent on the injection barrier height. In this experiment, temperature is controlled to satisfy

$$T = T_0 + \beta t, \tag{13}$$

$0 \leqslant t \leqslant 120$ min. Here T_0 is the initial temperature, and β is the constant heating rate. Using Eqs. (10), (11), and (13), we have the relation

$$\ln\left[-\frac{1}{V_s(0)}\frac{dV_s(t)}{dT}\right] = \ln\left(\frac{1}{\beta\tau_0}\right) - \frac{H}{k_BT}. \tag{14}$$

Using Eq. (14), the barrier heights H of the Alq_3 film on Al electrodes with and without UV/ozone treatment were estimated from Fig. 3 as 1.3 and 0.4 eV, respectively. These values are reasonable as the value of the barrier height of Al electrode for electron injection into Alq_3 films.[10] As mentioned above, in the region of temperature lower than $100\,°C$, the electron injection makes a main contribution to the potential decay by heating, but the randomization of polar molecules is not expected because of the constant generation of SH signal. After the completion of the injection, charge ρ_{inj} is trapped in Alq_3 film and the charge corresponding to the injected charge, $-\int_0^d \rho_{inj} dz$, remains on the electrode as shown in Fig. 4(a).

C. Potential decay accompanying the randomization of Alq_3 films

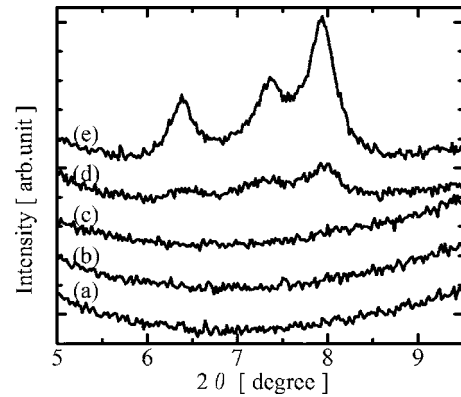In this section we discuss the potential decay by heating in the region of temperature higher than $100\,°C$. As shown

FIG. 5. X-ray diffraction obtained peak generated from Alq_3 films with a thickness of 520 nm. (a) As-deposited Alq_3 film ($30\,°C$), (b) after complete removal of surface potential of Alq_3 film by photoexposure with wavelength of 400 nm ($30\,°C$), (c) after being heated up to a temperature of $100\,°C$, and (d) after being heated at a temperature of $150\,°C$ for 40 min and (e) for 660 min. The surface potential of Alq_3 film decayed by (c) 25%, (d) 76%, and (e) 0% with respect to the initial potential, respectively.

in Fig. 3, the SH intensity of Alq_3 film on Al electrodes gradually decreased by heating. Interestingly, the potential also decreases in accordance with the decay of SHG. It is expected that the decay of the potential in this temperature region accompanies the randomization of polar structure in Alq_3 films together with the injection of electrons from electrodes. There are two types of randomization process of polar structure in Alq_3 films. One is the process accompanying the change of the orientational order structure of Alq_3 film composed of polar molecules. In this process, we may expect that the structure of Alq_3 film also changes in a manner like phase transition. Therefore, x-ray analysis, etc., will be helpful for the detection of such transition. On the other hand, there is a process that does not accompany the structural change but the randomization of polar structure is induced in a manner modeled like a two-site model by Debye.[11] Here the two-site model by Debye was proposed to explain the dielectric polarization process in solid condensed materials. In this process, x-ray diffraction, etc., may not change by heating. Figure 5 shows the x-ray diffraction measured from Alq_3 films deposited on Al electrode with a thickness of 520 nm. Our elemental analysis of x ray showed that the structural change in Alq_3 film was induced after being heated up to a temperature of $150\,°C$ [curves (d) and (e)], but the structural change was not induced after exposure to light at room temperature [curve (b)]. Taking into account this experimental evidence, we may consider that the polar structure is randomized during heating at a temperature higher than $100\,°C$ and noncentrosymmetry of Alq_3 film is broken along with the recrystallization of Alq_3 film.[12] In our previous studies, we concluded that the as-deposited Alq_3 film has a very small value of orientational order parameter S_1 and the films were amorphouslike from the elementary analysis, etc. In this case, it is not expected that x-ray diffraction will be very sensitive to the structural change of the film. However, to confirm our above conclusion by the x-ray diffraction, we also carried out the photoluminescence (PL) measurement. The slight blueshift in the emission peak was observed after being heated up to a temperature of $150\,°C$, whereas the

peak that appeared around 550 nm never shifted after the potential decay by photoexposure (not shown). These results supported our conclusion from the x-ray diffraction measurement. Therefore we argue that the disordering of polar structure of Alq$_3$ film composed of polar mer molecules is a main process of potential decay. That is, $\bar{\mu}$ of Eq. (3) changes due to the disordering of polar molecules. It should be noted here that the surface potential change due to V_c should be considered. The potential change given by Eq. (7) should remain after randomization of dipoles if the injected electrons are trapped in Alq$_3$ film during heating process. However, within the constraints of our experiment, the surface potential V_c decays and approaches nearly zero. In more detail, the potential $V_s < 0$ was never generated even when the film was heated from room temperature to a certain temperature below 100 °C and subsequently photoirradiated. This means that electrons injected from electrodes and subsequently trapped in Alq$_3$ film must extinguish during the randomization process of dipoles. In other words, trapped electrons in Alq$_3$ film during heating process are thermally excited by heating and smoothly return to the electrode to combine with the opposite polarity charge on the electrode, along with the disordering of the polar structure of Alq$_3$ films that accompany the recrystallization, possibly due to the electrostatic attractive force working between injected excess charge and the opposite charge that remained on the surface of the electrode (see Fig. 4). That is, injected electrons return to the electrode by the force of electric field $E_z = (1/\epsilon_s \epsilon_0) \int_0^z \rho_t(z,t) dz$, where $\rho_t(z,t)$ is the charge that remained in the sample.

D. Potential decay by photoexposure

As we described in Ref. 2, the remarkable wavelength dependence of the potential decay by photoexposure was observed. That is, the surface potential decays rapidly by exposure of light with a wavelength of 400 nm corresponding to the absorption maximum of Alq$_3$ film. On the other hand, the potential does not decay by photoexposure with a wavelength longer than that corresponding to the absorption band, e.g., 600 nm. Thus, the inception of the surface potential decay happens when Alq$_3$ absorb photons, that is, the electron injection from metal electrodes to Alq$_3$ film is not the dominant process of the potential decay by photoexposure.[2] Further we should note that the x-ray diffraction of Alq$_3$ film does not change after the potential decay by photoexposure [see Fig. 5 curve (b)]. Therefore the polar disordering process which does not accompany the structural change is the most probable potential decay process of Alq$_3$ films by photoexposure. The potential decay by photoexposure does not accompany the electron injection, that is, the potential decay is described as the disordering process of $\bar{\mu}$ that does not accompany the structural change. In other words, the potential decay process by photoexposure can be described in a manner as we described in our previous paper.[2] Finally it is instructive to compare the decrease of SH intensity by photoexposure and by thermally heating. Figure 6(a) shows the result by photoexposure with a wavelength of 400 nm, where the SH intensity of Alq$_3$ film on Al electrode with and without UV/ozone treatment decreases abruptly. Figure 6(b)
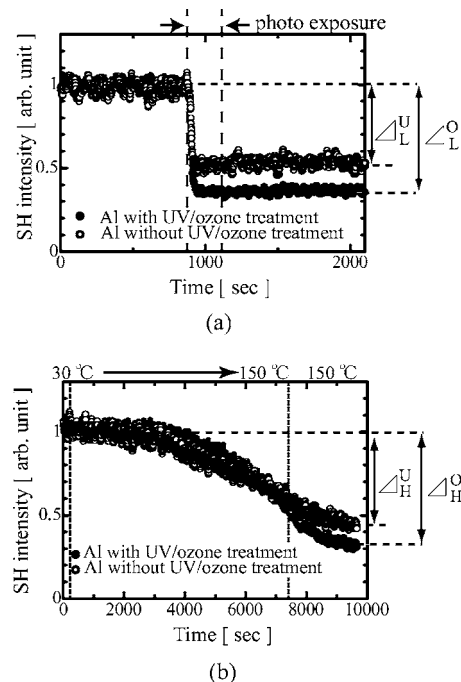

FIG. 6. The change Δ of SH intensity during (a) photoexposure and (b) heating.

shows the result by heating up to a temperature of 150 °C, where the SHG gradually decreases as the temperature increases. Interestingly, the change of SH intensity by light $\Delta_L(\Delta_L^U, \Delta_L^O)$ [Fig. 6(a)] is nearly the same as that by heating $\Delta_H(\Delta_H^U, \Delta_H^O)$ [Fig. 6(b)]. These results suggest that the polar structure of Alq$_3$ film is destroyed completely by either heating or photoexposure, though the film structures after heating and photoexposure would be quite different.

V. CONCLUSION

We examined the large potential decay process of as-deposited Alq$_3$ films on Al electrode by heating and photoexposure with Kelvin probe method and SHG measurement. It was found that the injection of electrons from Al electrode is a main contribution of the potential decay by heating, but the injection does not break the polar structure of the as-deposited Alq$_3$ film. The potential due to injected electrons extinguished after heating up to a temperature of 100 °C, possibly due to the recombination of charges on electrodes, during the disordering process of polar structure of Alq$_3$ film. The potential decay by photoexposure does not accompany the structural change.

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