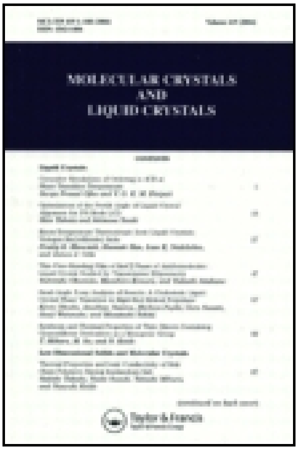

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Long-Term Relaxation of Molecular Orientation in Vacuum-Deposited ALQ$_3$ Thin Films

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Long-Term Relaxation of Molecular Orientation in Vacuum-Deposited ALQ$_3$ Thin Films

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Long-term measurement of noncentrosymmetric molecular orientation of vacuum-evaporated tris(8-hydroxyquinolinato) aluminum (III) (Alq$_3$) thin film was performed by means of first-order electroabsorption (EA) spectroscopy. This molecular orientation is responsible for the giant surface potential of Alq$_3$ film, and it might be utilized to nonlinear optical devices. Although the EA response presented reduction, the relaxation time constant was on the order of year. Possible mechanisms for the reduction are discussed.

Keywords: Alq$_3$; electroabsorption spectroscopy; giant surface potential; noncentrosymmetric molecular orientation; orientation relaxation; vacuum evaporation

1. INTRODUCTION

Tris(8-hydroxyquinolinato) aluminum (III) (Alq$_3$) is an organic semiconductor popularly used for the electron transport layer of organic light emitting diodes (OLEDs). Electronic and optical properties of this material have been widely investigated [1,2]. Giant surface potential (GSP) is a peculiar property among those reported so far: huge surface potential linearly proportional to the film thickness, up to 50 V/μm, appears when Alq$_3$ is vacuum-deposited in dark [3]. Noncentrosymmetric orientation of the molecule is considered as the origin of GSP [3–5], but mechanism for the noncentrosymmetry is

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not elucidated yet. Although the order parameter for the molecular orientation, obtained from the magnitude of GSP and the permanent dipole moment of Alq_3 molecule, is as small as 0.01, such spontaneous noncentrosymmetric molecular orientation can be interesting and useful for some nonlinear optical (NLO) device applications such as optical second harmonic generation (SHG) devices and optical modulator devices utilizing Pockels effect. More interestingly, GSP is reduced by irradiation of visible light. Two hypotheses have been proposed so far: photoinduced randomization of molecular orientation [6] and electrostatic screening by photogenerated carrier [7]. By means of first-order electroabsorption (EA) measurement, we have demonstrated that an Alq_3 thin film presents noncentrosymmetric molecular orientation even after GSP reduction by light irradiation, suggesting that photocarrier hypothesis is more plausible for the GSP reduction mechanism.

In this paper, we report a long-term EA measurement of an Alq_3 thin film to investigate molecular orientation relaxation property, and discuss from applicational and fundamental point of view, i.e., suitability to NLO devices and possibility of photoinduced orientation randomization, respectively.

2. EXPERIMENTAL

A thin film sample of Alq_3 (Fig. 1) was prepared by vacuum deposition of *as-purchased* Alq_3 powder (98.6% purity, Tokyo Kasei Kogyo Co., Ltd) on an ITO-coated glass substrate (100 Ωsq, Kinoene Kogaku, Co., Ltd.) in dark. The deposition rate was about 0.2 nm/s and the film

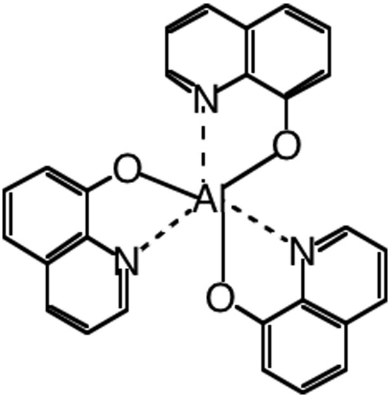

FIGURE 1 Molecular structure of Alq_3.

thickness was 401 nm. GSP was measured to be +18.5 V by Kelvin probe method (KP-6500, McAllister Co.). For EA measurement, sandwich structure was fabricated by vacuum deposition of semitransparent Al electrodes onto the Alq_3 thin film. After exposing the sample to the room light for a day to reduce GSP, EA measurement was performed using a home-made setup, applying an AC external electric field of 1.3×10^5 V/cm at 138 Hz. Wavelength was scanned from 360 nm to 600 nm. First-order EA response was obtained by detecting the component in the transmitted light intensity changing at the same frequency as the external AC electric field using a lock-in amplifier (SR830, Stanford Research, Inc.). EA measurement was performed mostly once per week, and was repeated for a half year. Except during measurements, the sample was exposed to room light.

3. RESULTS AND DISCUSSIONS

Figure 2 shows a typical 1st-order EA spectrum obtained by the measurement. Significant response was observed. Since the first-order EA response is a second-order NLO response originating from the total noncentrosymmetry in the film, this suggests noncentrosymmetric molecular orientation of Alq_3 molecules in the film. The spectral profile is close to the first derivative of absorption spectrum, suggesting that this response is originating from Stark shift. At longer wavelength,

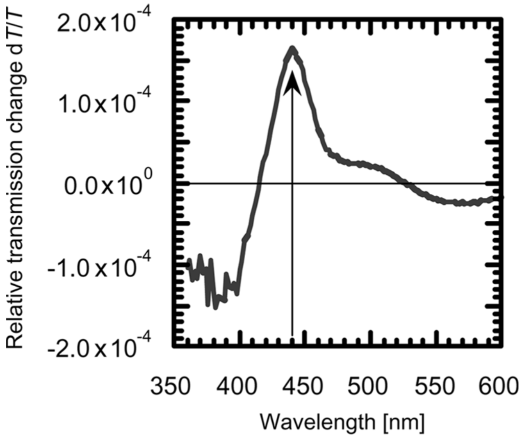

FIGURE 2 Electroabsorption spectrum of Alq_3. Vertical axis represents the relative change in optical transmission $\Delta T/T$ induced by the external electric field. The arrow shows the peak of $\Delta T/T$ at the wavelength of 440 nm, which is plotted in Figure 3.

there was some response originating from interference effect due to the optical reflection at the top electrode and the interface between Alq_3 and ITO layers. Figure 3 shows evolution of the peak EA-response value at 438–442 nm for about half a year. There was some fluctuation due to change in experimental condition, since the sample was set and removed time to time for measurement of other samples. Except for the fluctuation, the peak value presented slight reducing tendency by *ca.* 10% for 6 months. To determine the time constant for reduction, we performed fitting with a single exponential function. The time constant for reduction τ was 1.14×10^3 days (3.1 years). We also tried a single-exponential function with offset, $a\ \exp(-t/\tau) + b$, and obtained fitting parameters $a = 3.1 \times 10^{-5}$, $b = 1.4 \times 10^{-4}$ and $\tau = 1.1 \times 10^2$ days, which provided slightly better fitting result as shown with the dotted line in Figure 3. In the latter case, although the time constant is not so large, the reduction will be limited to 18% of the initial value.

This reduction of EA response is due to reduction of noncentrosymmetric molecular orientation. Possible mechanisms are a) photoinduced randomization of noncentrosymmetric molecular orientation [6] and b) thermal orientation randomization. In any case, this orientation randomization is not the origin of GSP reduction by light irradiation, because in this measurement GSP has been sufficiently reduced before the first EA measurement. In other words, the reduction of

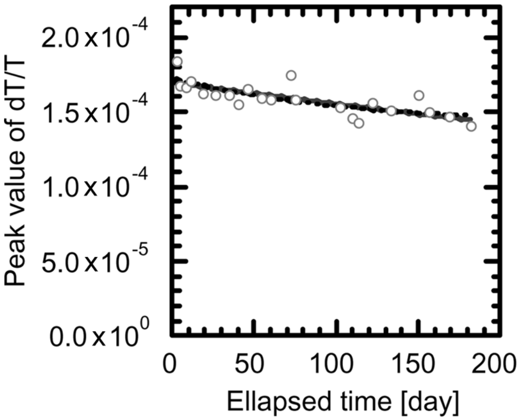

FIGURE 3 Long-term evolution of peak EA response of Alq_3. Open circles stand for experimental values. Full line represents the single-exponential function fitted to the experimental values with the decay time constant τ of 1.14×10^3 days. Dotted line represents the fitted single-exponential function with offset, $a\ \exp(-t/\tau) + b$, where $a = 3.1 \times 10^{-5}$, $b = 1.4 \times 10^{-4}$ and $\tau = 1.1 \times 10^2$ days.

noncentrosymmetric molecular orientation is very slow and thus almost negligible for elucidation of GSP reduction by light irradiation. There is another possible mechanism for reduction of EA response: slow crystallization of Alq_3 in the film [8,9]. If Alq_3 molecules are centrosymmetrically aligned in the microcrystals and/or the orientation of the microcrystals is centrosymmetric, they do not contribute to the first-order EA response and thus the EA response would reduce with the progressing crystallization.

From the viewpoint of application of vacuum-deposited Alq_3 thin films to NLO devices, the time constant of 3.2 years for orientation relaxation is, although not excellent, acceptable. If the reduction dynamics is not a simple single exponential but the single exponential with offset, even though the time constant of 100 days is too short, more than 80% of the response is predicted to remain for long time. This is also acceptable for NLO device applications. Furthermore, there are some possibility to suppress the reduction by device structure [8,9], such as addition of protection layer to prevent crystallization due to humidity.

4. CONCLUSIONS

Vacuum-deposited Alq_3 thin film, which presents giant surface potential, was characterized in terms of the long-time evolution of molecular orientation by first-order EA spectroscopy. EA response presented a slow decreasing tendency, and the time constant for reduction of the EA response was 3.2 years, acceptable value for application to NLO devices. Possible mechanism for reduction of molecular orientation was discussed, and possibility of suppression of reduction was suggested.

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