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Influence of Organic Overlayer on Giant Surface Potential of Alq₃ Film

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We examined influence of an organic overlayer deposition on giant surface potential (GSP) of tris-(8-hydroxyquinolino)aluminum (III) (Alq₃) using Kelvin probe method. Before deposition of organic overlayer, surface potential (SP) of an Alq₃ film on a silicon wafer was $+13 \pm 2$ V under the dark condition. When we deposited copper phthalocyanine (CuPc) on the Alq₃ film, the SP value remained the same at first and then rapidly decreased with time. It is suggested that the charge transportation through the CuPc layers causes the reduction of SP value. On the other hand, the SP value did not change by deposition of n-hexatriacontane. These results indicate that the GSP possibly vanishes without the photoabsorption of the Alq₃ molecules by organic overlayer deposition, depending on the electronic/optoelectronic properties of the overlayer.

Keywords: Alq₃; copper phthalocyanine; giant surface potential; hexatriacontane; Kelvin probe method

INTRODUCTION

Recently, persistent and spontaneous build up of surface potential (SP) was found in the film of tris-(8-hydroxyquinolino)aluminum (III) (Alq₃) without light irradiation during vacuum deposition (dark condition) [1,2]. We obtained +28 V of the SP on an Alq₃ film with thickness

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of 560 nm, indicating that the film surface is positively charged. From the second harmonic generation measurements [1,3], it has been suggested that this giant surface potential (GSP) originates from noncentrosymmetric orientation of polar Alq₃ molecules. The GSP is very stable in the dark condition, while it reduces rapidly by irradiation of white light [2,4]. It has been suggested that the reduction of the SP is caused by photoabsorption of the Alq₃ molecule [1,2], and photocurrent flow and reorientation of the molecules through the photoexcitation have been suggested as possible origins. However, the mechanism of GSP and its reduction is not fully understood yet.

In this study, we examined the effect of depositing an organic overlayer on an Alq₃ film with the GSP. We used two organic compounds as the overlayer material. One is copper phthalocyanine (CuPc), which is well known as an organic semiconductor. The other is *n*-hexatriacontane (*n*-C₃₆H₇₄, HTC), which is an insulating material. We measured SP values by Kelvin probe (KP) method and investigated their temporal evolution.

EXPERIMENTAL

Alq₃, CuPc, and HTC were purchased from Tokyo Kasei, Japan, and further purification was not carried out. In each evaporation process, Alq₃ was deposited on two Si wafer plates under the 10⁻³ Pa with a deposition rate of 6–12 nm/min. The thickness of the Alq₃ was about 400 nm, monitored with a quartz oscillator in situ and confirmed later by spectroscopic ellipsometry in air. Note that the sample was electrically isolated during the deposition. After deposition of Alq₃, we measured SP of an Alq₃-only film using one of two deposited films as a reference. This reference was kept in the air under the dark condition, and the other sample was set to the evaporation chamber again for depositing an overlayer.

Fabrication of the overlayer (CuPc or HTC) was also carried out in the same condition as that of Alq₃. The thickness of CuPc and HTC layer was about 150 nm. After deposition, the sample was taken out from the deposition chamber and was put onto the sample holder for SP measurement. During the sample transfer to the KP system, we used a flashlight with red filter to cut the light at the wavelength shorter than about 600 nm, in order to avoid photoabsorption of the Alq₃ molecules leading to the reduction of the GSP. SP value was determined by KP method in air using KP-6500 (McAllister, U.S.A.).

RESULTS AND DISCUSSION

The SP of the Alq₃ film obtained in this study was $+13 \pm 2$ V, varying on each deposition procedure. This fluctuation of the SP value among

samples is probably due to the different thickness and/or rate of deposition. Further quantitative investigation will be necessary for precise control of the GSP value.

When we measured CuPc/Alq₃ film, we firstly obtained the same SP value as that of the Alq₃-only film. However, the reduction of the GSP was observed in the dark condition. Figure 1 shows the temporal evolution of SP of the CuPc/Alq₃ film kept in the dark condition. The y-axis is the SP value relative to the reference electrode (see the figure caption). For comparison, we measured SP of Alq₃-only film before and after the measurement of the CuPc/Alq₃ film, and it did not change with time. The SP value of a single CuPc-only film was -0.02 V presenting no GSP. These results indicate that the CuPc overlayer promoted reduction of the GSP value even without irradiation of white light.

It is well known that a CuPc film presents semiconducting behavior. The charge carriers can be more easily transported in the film than in the Alq₃ film, because the carrier mobility of a CuPc film ($10^{-3} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$) [5] is much higher than that of the Alq₃ film ($10^{-6} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$) [6]. This large mobility might be a possible reason

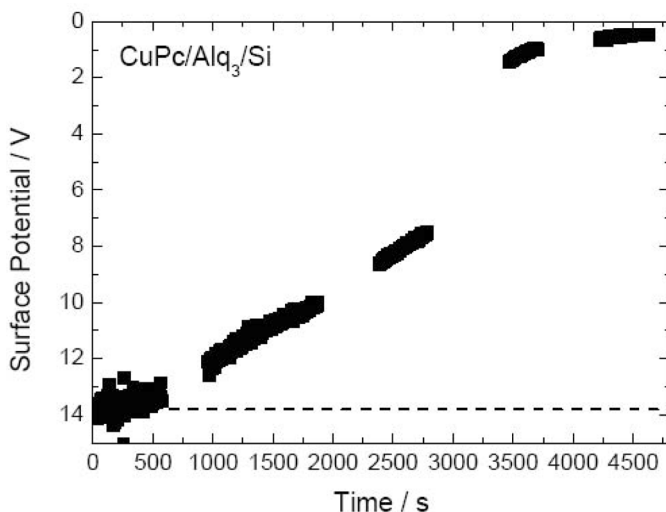


FIGURE 1 Temporal evolution of SP value of CuPc/Alq₃ film. The SP value of Alq₃ film before depositing CuPc is shown as a dashed line. Note that the direction of the y-axis (SP value) is opposite from the usual way as in the previous paper [1]. This direction corresponds to the work function change or vacuum level shift, and thus easier to compare with the energy diagram of the thin films. The upward shift in the graph means decrease of the SP (i.e., increase of the work function).

for spontaneous reduction of the GSP. However, the large SP value was initially observed (even after rather long sample cooling time for up to 1 hour after overlayer deposition in vacuum under dark condition) and then gradually decreased with time. This means that the GSP was maintained under the high-vacuum condition. After exposing the sample to the air, the charge carriers seemed to start transportation in the CuPc layers to reduce the GSP. The decay of the GSP in the CuPc/Alq₃ film lasted for about 1 hour until the GSP almost vanished. The reduction rate was not reproducible in this double-layered structure. Also, there seems to be a discontinuous change of the SP value between the times of 2900 sec and 3400 sec in Figure 1. These facts prevented us from theoretical modeling of the temporal change of the SP, but at least it is suggested that these time dependences of the SP value cannot be fully explained only by the electric conduction of the CuPc overlayers. There are other factors to be considered for clarifying the effect of the deposition of the CuPc layers.

One possibility is photocurrent generated by irradiation of the color-filtered light in the CuPc layer. When we moved the samples from the vacuum chamber to the KP system, the light at the wavelength longer than 600 nm was irradiated. The absorption wavelength of the CuPc layer is located around 600 nm [7], and therefore the CuPc layer absorbs the light and possibly generates photocarriers. However, we

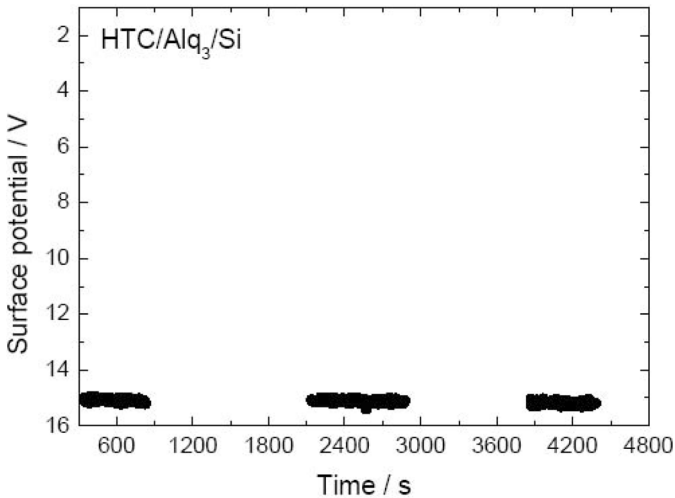


FIGURE 2 Temporal change of SP value of HTC/Alq₃ film. The direction of the y-axis is same as the Figure 1.

turned off the red light during the KP measurements during which the SP value gradually decreased. This suggests that the photogeneration of charge carriers in the CuPc layer is not a plausible explanation for the decay of the SP value. Another possibility is exposure of the sample surface to the air. In some organic semiconductors, the electric conductivity increases by exposing the oxygen or water in the air [8]. However, the detail of this spontaneous decay of the GSP is not clear at the present, and we need to carry out the further quantitative study on the effect of the light and electric conduction on the reduction of the GSP.

On the other hand, after deposition of HTC on the Alq₃ film, the SP value under the dark condition did not change at least for 1 hour as shown in Figure 2. For comparison, an HTC film directly deposited on a Si wafer presented the SP value of -0.01 V. The SP value of the HTC/Alq₃ was as large as the GSP of the Alq₃-only film, indicating that the HTC overlayer does not affect to the GSP of the Alq₃ film. As in the case of an Alq₃-only film, the SP value of this HTC/Alq₃ sample was significantly reduced by irradiation of the white light for 1 hour. Since HTC is an organic insulator, the charge carriers cannot be easily generated or transported in the film. Thus, the charge carriers flowing in the HTC layer do not cause the reduction of GSP.

SUMMARY

We investigated the influence of organic overlayer deposition on an Alq₃ film in terms of GSP. When we deposited CuPc on the Alq₃ film, we observed reduction of the GSP value with time under the dark condition. It was suggested that this reduction was caused by transport of the charge carriers in the CuPc film. On the contrary, GSP was not influenced by deposition of HTC because of no electric conduction in the insulating HTC film. Our results demonstrated that the electric conductivity of the overlayer significantly affects the GSP value, and that photoabsorption of the Alq₃ molecule is not essential to reduction of the GSP.

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