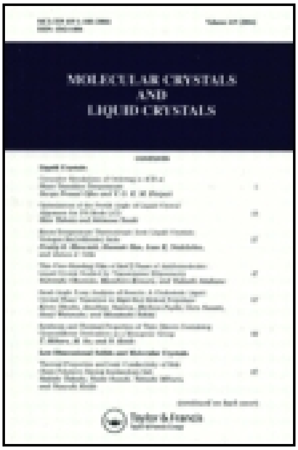

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Characteristics of Magnesium Phthalocyanine Field-Effect Transistors Due to Vapor Treatments

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Top-contact organic field-effect transistors (OFETs) were fabricated using vacuum evaporated magnesium phthalocyanine (MgPc) thin films with and without ethanol vapor treatments and OFET characteristics were investigated. The UV-vis absorption spectra, surface morphologies and x-ray diffraction patterns of the MgPc films were largely changed and the on/off ratio and field-effect mobilities of the OFETs were improved due to the vapor treatment. Hexamethyldisilazane (HMDS) vapor treatment of n-*Si substrate surface also induced improvements of the OFET performance.*

Keywords: ethanol; magnesium phthalocyanine; organic field-effect transistor; vapor treatment

1. INTRODUCTION

Organic field-effect transistors (OFETs) [1] are attracting much interest because of flexibility, simple fabrication processes and other

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advantages. Moreover, OFETs are very important for applications for various organic devices [2–4] such as organic light-emitting diode (OLED) displays. Many studies for improvement of OFET characteristics have been reported in recent studies [1,5–8]. Device performance depends on organic materials, structure of organic films, film interfaces and so on. Phthalocyanine is one of typical organic semiconductors and it has been investigated for photoconductors, OLEDs, photovoltaic devices and OFETs [1,9]. It is known that the polymorph state of some phthalocyanines, such as magnesium or chloroaluminum phthalocyanines, can be largely changed due to various organic vapor treatments [10,11]. Such polymorph change should be useful for improving OFET performance.

In this study, structures and FET properties have been investigated for magnesium phthalocyanine (MgPc) films with and without ethanol vapor treatment. MgPc is dissolved in ethanol, and large polymorph change of MgPc can be expected. Furthermore, silicon substrates with and without hexamethyldisilazane [12] (HMDS) treatment were used for OFET preparation and the device performances were compared.

2. EXPERIMENTAL DETAILS

MgPc was purchased from Sigma-Aldrich Co. MgPc thin films were fabricated by vacuum evaporation technique. Before the evaporation, MgPc powder was heated at 770 K for 90 min to remove impurities. For vapor treatment, MgPc film was set in a small cell with saturated solvent vapor in room temperature for desired time.

UV-vis absorption spectra and atomic force microscope (AFM) images were observed for the MgPc films before and after the ethanol vapor treatment. AFM images were observed using Nanoscope IIIa (Digital Instruments). Crystal structures were also observed using X-ray diffraction (XRD) pattern. Electrical properties were investigated in Au electrode top-contact FETs (channel-length $L = 15\,\mu m$, channel width $W = 1\,mm$) having the MgPc active layers. The ethanol vapor treatment was carried out before the deposition of the top electrodes. OFET characteristics were observed in dark vacuum vessel using Keithley 6517A electrometer. To observe UV-vis absorption and XRD patterns, MgPc films of 50 and 300 nm were deposited on glass substrates, respectively. To observe AFM image and OFET characteristics, MgPc films of 50 nm were deposited on heavily doped n-Si substrates with 100 nm SiO_2 film. n-Si substrates with and without HMDS vapor treatment (10 min) were used for the FET preparation. It has been reported that OFET performance can be improved by self-assembled monolayer formed on the substrate by HMDS treatment [12].

3. RESULTS AND DISCUSSION

Figure 1 shows UV-vis absorption spectra of MgPc films treated with ethanol vapor. MgPc molecules in the film before vapor treatment form αpolymorph [11]. Q-band of the spectra largely changed due to the treatments. Spectra changed pretty fast in several minutes and then changed slowly. New absorption peak was found at around 770 nm after the vapor treatment. It was reported that the MgPc treated by dichloromethane showed absorption peak at around 830 nm [10]. The polymorph state should depend on the used vapor. Copper phthalocyanine (CuPc), which is often used as active layer of OFETs, does not show large spectrum change due to the ethanol or dichloromethane vapor treatments.

AFM images of the MgPc films on Si-wafers with HMDS treatment are shown in Figures 2(a)–(c). MgPc grains were formed after the vapor treatments. After 24 hours, micron-size grains were formed in the films. Such changes were also observed for the films on Si-wafer without HMDS treatment, and clear difference of the morphology

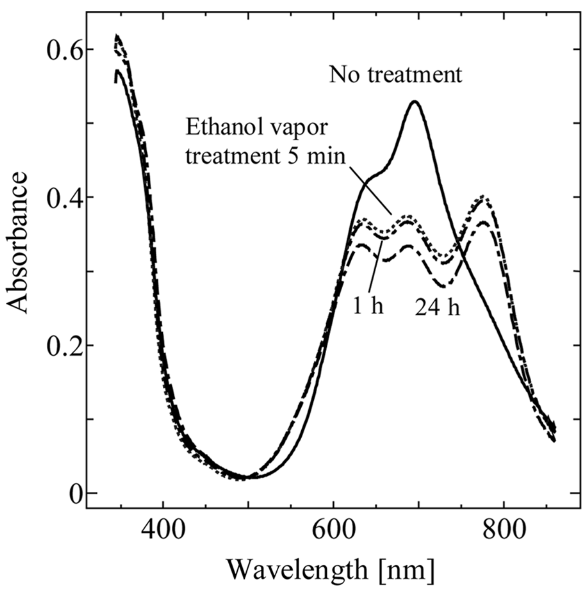

FIGURE 1 UV-vis absorption spectra change due to ethanol vapor treatment.

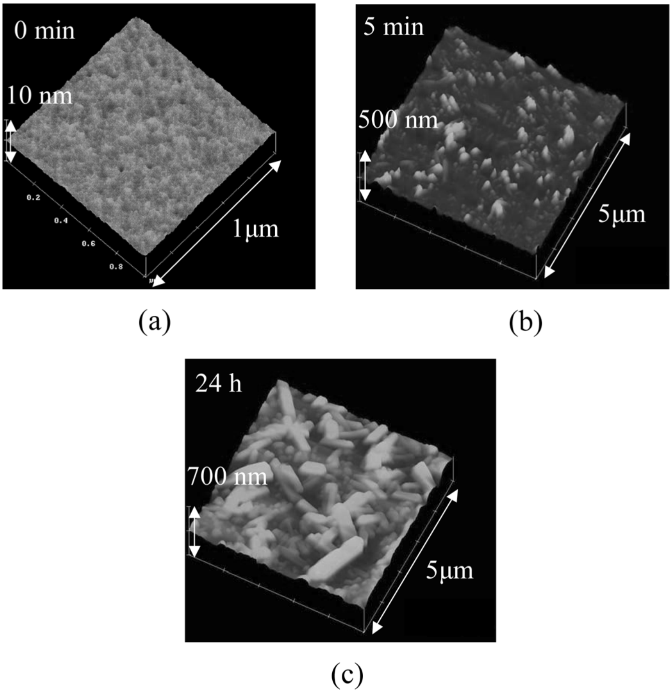

FIGURE 2 AFM images of MgPc film: (a) before the ethanol vapor treatment, (b) after 5 min treatment, (c) after 24 hour treatment.

change was not observed. Figure 3 shows the XRD patterns for the MgPc film treated before and after the ethanol vapor treatment. Diffraction peak at 6.5° before vapor treatment indicates MgPc molecules before vapor treatment formed α polymorph, and it supported the result of Figure 1. Diffraction peak shifted to higher angle with the vapor treatments. The peak angle was close to reported one of β polymorph [10]. However, reported optical absorption peak of β polymorph is 820–830 nm and is different from the result of Figure 1. The polymorph structure has not been clarified and further investigation is needed.

MgPc FETs were fabricated with various conditions and the results are shown in Figures 4(a)–(c). All the MgPc film thickness was 50 nm. Figure 4(a) shows V_D-I_D characteristic for MgPc FET without ethanol vapor treatment and without HMDS treatment for n-Si wafer. Off-current was large and I_D saturation due to V_D was not clearly observed. The result for MgPc FET with ethanol treatment and without HMDS treatment is shown in Figure 4(b). The vapor treatment

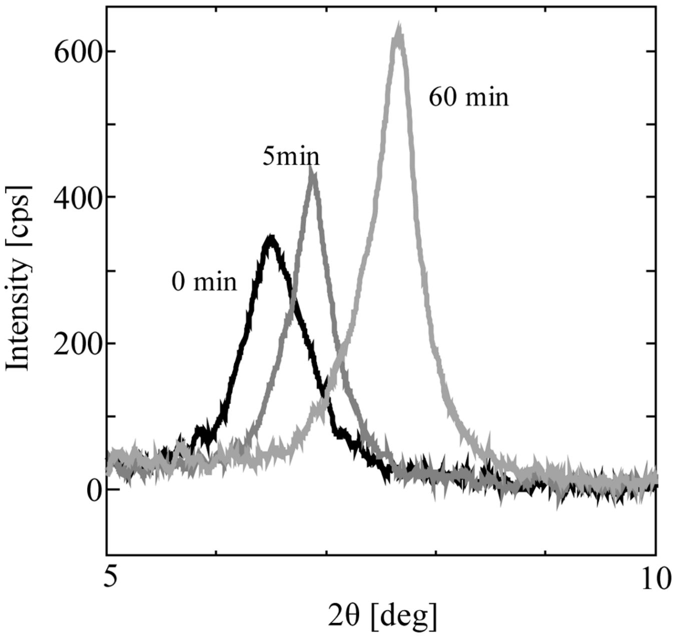

FIGURE 3 XRD patterns of MgPc films: (a) before the ethanol vapor treatment, (b) after 5 min treatment, (c) after 24 hour treatment.

was carried out for 5 min before the deposition of Au drain and source electrodes. Vapor treatments after the electrodes deposition were also carried out, but the devices did not work well. It was considered to be due to degradation of interface between electrode and MgPc film. The off-current decreased and on-current largely increased with the vapor treatment. V_D-I_D characteristic for FET with ethanol (5 min) and HMDS treatments is shown in Figure 4(c). The drain currents are over ten times larger than those of FET in Figure 4(a). Detailed mechanism has not been clarified yet, but changes of polymorph structure and/or interface between MgPc and SiO_2 should contribute to the improvement.

The field-effect mobility μ was calculated from the saturated region using following equation,

$$I_D = \frac{WC_i}{2L}\mu(V_G - V_T)^2$$

where C_i is capacitance of oxide film and V_T is threshold voltage. Table 1 shows the mobilities of the devices. OFET with HMDS

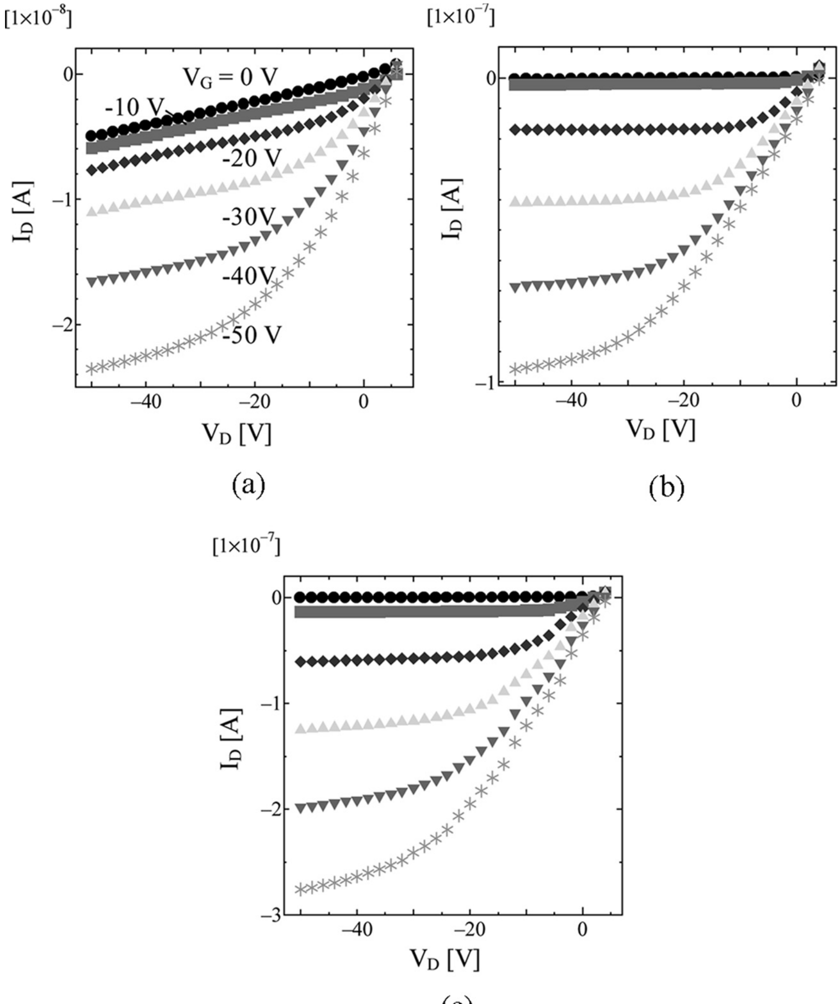

FIGURE 4 V_{DS}-I_D curves of MgPc FETs: (a) no treatment, (b) with ethanol vapor treatment and (c) with HMDS and ethanol treatments.

treatment and without ethanol treatment was also prepared and the mobility was shown. Although the obtained values in Table 1 are smaller than those of reported values of CuPc ($\sim 10^{-2}\,cm^2/Vs$) [9], we believe that optimization of sample preparation condition should improve the mobility of MgPc FET. The on/off ratios of the FETs are also shown in Table 1. The decrease of off current contributes to improvement of on/off ratio about 100 times after the treatments.

TABLE 1 Field-Effect Mobility and on/off Ratio of the Prepared OFETs

	μ (cm^2/Vs)	On/off ratio
No treatment	1.15×10^{-5}	4.71
HMDS treatment	5.10×10^{-5}	10.7
Ethanol vapor treatment	1.75×10^{-4}	160
HMDS and ethanol vapor treatments	2.33×10^{-4}	460

Vapor treatment is quite easy and reasonable way of improving OFET performance. Further experiments for optimizing device preparation are under way.

3. CONCLUSIONS

FETs were fabricated using MgPc thin films with and without ethanol vapor treatments and FET characteristics were investigated. The vapor treatment induced large change of the UV-vis absorption spectra, surface morphologies and X-ray diffraction patterns. Furthermore, the on/off ratio and field-effect mobilities of the MgPc FETs were improved due to the vapor treatment. HMDS treatment for n-Si substrate surface also contributed to the improvements of the OFET performance.

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