Highly Ordered Molecular Orientation in a Phthalocyanine Film Deposited on a Well-Polished Indium-Tin Oxide Substrate

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Metal-free phthalocyanine (H$_2$Pc) was deposited on an indium-tin oxide (ITO) substrate with a pentacene buffer layer, and the effect of polishing of the ITO surface on the molecular orientation of H$_2$Pc was studied. By rubbing the ITO surface 10,000 times with a plastic eraser, the average surface roughness of ITO was decreased to 1.0 nm from its initial value of 2.0 nm, and the (313) X-ray diffraction peak of $\alpha$-form H$_2$Pc became significantly large. Rocking curves and optical absorption spectra indicated that, by polishing the ITO surface, the disorder in the orientation of the stacking axis ($b$ axis) of H$_2$Pc was reduced. A Schottky barrier cell of H$_2$Pc with a highly ordered molecular orientation showed a lower photovoltaic performance than that with a disordered orientation.

1. Introduction

The organic thin-film solar cell is one of the most actively studied organic semiconductor devices.$^{1,2}$ Enormous effort is being exerted to increase its energy conversion efficiency. One method is to control the molecular orientation in the thin films. The charge transport in many organic semiconductors is one-dimensional (1D), so that an orientation of the 1D axis standing on the electrode is expected to give a higher transport efficiency of photogenerated carriers. Furthermore, by reducing the disorder in the orientation, the carrier mobility may be increased.

In this paper, we report a method of obtaining a highly ordered molecular orientation in a phthalocyanine film deposited on an indium-tin oxide (ITO) substrate. Up to now, two methods have been reported to achieve the orientation of the 1D axis standing on an ITO or glass substrate: one uses a perlene-3,4,9,10-tetracarboxylic dianhydride (PTCDA) buffer layer between phthalocyanine and the substrate,$^{3-6}$ and the other uses pentacene instead of PTCDA.$^{7,8}$ Comparing the two methods, the latter is suitable for application in solar cells because pentacene is a hole-transporting material, while PTCDA is electron-transporting, so that the hole transport from phthalocyanine to ITO may not be disturbed by the insertion of the pentacene layer. However, Sakurai and co-workers reported that the performance of a solar cell with the pentacene buffer layer is lower than that of a solar cell without the buffer layer,

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Fig. 1. Illustration of how the ITO surface was rubbed in this study.

Fig. 2. (Color online) Scheme of the samples prepared in this study, and the molecular structures of H$_2$Pc and pentacene.

which is attributed to the generation of a hole injection barrier between phthalocyanine and pentacene.\textsuperscript{7,8} In the X-ray diffraction (XRD) data of Sakurai and co-workers,\textsuperscript{7,8} the intensity of the (313) peak of $\alpha$-form H$_2$Pc at $2\theta = 27.5^\circ$, which corresponds to the orientation of the 1D axis standing on the substrate, is markedly low. This suggests that the molecular orientation is largely disordered. In our present study, it will be shown that the (313) peak becomes significantly large by simply polishing the ITO surface. Sakurai et al. have already pointed out the importance of the smooth surface of the pentacene buffer layer in obtaining finite (313) intensity.\textsuperscript{8} However, an orientation order as high as that obtained in the present study has never been reported for the phthalocyanine film on the ITO substrate.

2. Experimental Procedure
Metal-free phthalocyanine (H$_2$Pc) and pentacene were purchased from Acros and Aldrich, respectively, and used after two or three sublimations in vacuum. The ITO substrate of organic EL grade with a 10 $\Omega$/sq. sheet resistance was purchased from Geomatec.

Polishing of the ITO substrate was performed by rubbing the ITO surface manually in one direction with a plastic eraser (PLUS Stationary Corp. AIR-IN) up to 10,000 times, as shown in Fig. 1. The force applied on the ITO surface by the eraser was roughly 2 N. Then, the substrate was washed with acetone and dichloromethane, and cleaned by illuminating it.
Fig. 3. (Color online) XRD patterns of (a) glass/H$_2$Pc (80 nm) and (b) glass/pentacene (10 nm)/H$_2$Pc (80 nm).

by UV light from a Hg lamp.

Pentacene and H$_2$Pc films were deposited on the ITO or glass substrate as shown in Fig. 2 by vacuum evaporation under a pressure of $1 \times 10^{-4}$ Pa. The speeds of evaporation were 0.05 nm/s for H$_2$Pc and 0.02 nm/s for pentacene, as monitored using a quartz oscillator (ULVAC CRTM-5000 or CRTM-6000). In the initial stage of the research, the substrate temperature during the evaporation was set at either 70 °C or room temperature. Since the room-temperature substrate gave a more ordered molecular orientation, all the results presented in this paper are those for the room temperature substrate.

XRD measurement was performed using a Rigaku RINT2100 diffractometer with Ni-filtered Cu-K$\alpha$ radiation. Optical absorption measurement and observation of surface morphology by atomic force microscopy (AFM) were performed using a Shimadzu UV-3100PC and a Digital Instruments NanoScope III, respectively.

3. Results and Discussion

3.1 Glass/pentacene/H$_2$Pc

Figure 3 shows the XRD patterns of glass/H$_2$Pc (80 nm) and glass/pentacene (10 nm)/H$_2$Pc (80 nm). For glass/H$_2$Pc, two peaks were observed at $2\theta = 6.8$ and $13.7^\circ$, which are respectively assigned to the (200) and (400) reflections of $\alpha$-form H$_2$Pc. For glass/pentacene/H$_2$Pc, on the other hand, a strong peak at $27.4^\circ$ was observed, which is assigned to the (313) reflection of $\alpha$-H$_2$Pc. Three other peaks at 5.7, 11.5, and 17.3° in Fig. 3(b) are respectively assigned to the (001), (002) and (003) reflections of pentacene in the thin-film phase.

These results indicate that the molecular orientation in the H$_2$Pc film is as shown in Fig. 4. Without a pentacene layer, the $a$-axis of $\alpha$-H$_2$Pc is perpendicular to the substrate plane. Since the crystal system of $\alpha$-H$_2$Pc is monoclinic with $\alpha = \gamma = 90^\circ$ and $\beta \neq 90^\circ$, the $b$-axis (the 1D axis) of phthalocyanine is oriented parallel to the substrate plane. With the pentacene buffer layer, on the other hand, the (313) plane of $\alpha$-H$_2$Pc becomes parallel to the
Fig. 4. (Color online) Molecular orientations of H$_2$Pc (a) without and (b) with a pentacene buffer layer.

Fig. 5. (Color online) Effect of the rubbing of the ITO surface on the XRD pattern of ITO/pentacene (10 nm)/H$_2$Pc (80 nm).

substrate. In this case, the $b$-axis is tilted by $32^\circ$ from the normal of the substrate plane, under reported unit-cell constants of $a = 26.1$ Å, $b = 3.8$ Å, $c = 23.9$ Å, and $\beta = 94.2^\circ$ for $\alpha$-H$_2$Pc. The molecular orientation of H$_2$Pc in glass/pentacene/H$_2$Pc is highly ordered because the intensity of the (313) peak in Fig. 3(b) is much stronger than that reported by Sakurai and co-workers for ITO/pentacene/H$_2$Pc.$^7,8$

3.2 ITO/pentacene/H$_2$Pc

Our objective is to obtain a strong (313) reflection, similar to that in Fig. 3(b), when ITO is used instead of glass. Comparing glass and ITO, the surface roughness is substantially larger for the latter. The average roughness ($R_a$) of the ITO surface was 2.0 nm before polishing, while that of glass was 0.7 nm.

We studied the effect of polishing the ITO surface on the (313) intensity of $\alpha$-H$_2$Pc.
The ITO surface was polished by rubbing it with a plastic eraser in one direction before the deposition of pentacene and H$_2$Pc. Figure 5 shows how the XRD pattern of ITO/pentacene (10 nm)/H$_2$Pc (80 nm) changed with repeated rubbing. Without rubbing, no clear peaks of H$_2$Pc or pentacene were observed. With repeated rubbing, the (31$\overline{3}$) peak of $\alpha$-H$_2$Pc and the (001), (002), and (003) peaks of pentacene became larger.

Figure 6 shows the rocking curves of the (31$\overline{3}$) reflection at $2\theta = 27.4^\circ$, i.e., the curves measured by scanning the angle $\theta$ with the detection angle fixed at 27.4$^\circ$. From the width of the rocking curve, the distribution width of the direction of the (31$\overline{3}$) plane is roughly estimated.

The half-widths at half maximum (HWHM) of the two rocking curves of ITO/pentacene/H$_2$Pc for the 1,000 and 10,000 times of rubbing were 3.1 and 2.1$^\circ$, respectively. This indicates that the disorder in the orientation of the (31$\overline{3}$) plane is reduced by repeated rubbing. However, the disorder for the 10,000 times of rubbing was larger than that for glass/pentacene/H$_2$Pc because HWHM for the latter was only 1.2$^\circ$.

In Fig. 5, another small peak is observed at $2\theta = 26.6^\circ$. A possible assignment of this peak is the (312) reflection of $\alpha$-H$_2$Pc whose detection angle should be lower than that of (31$\overline{3}$) by 0.8$^\circ$. To check this possibility, the calculation of the structure factors of the (312) and (31$\overline{3}$) reflections was performed using a program XRAY originally developed in our laboratory. In $\alpha$-H$_2$Pc, the monoclinic unit cell contains four H$_2$Pc rings at $(a, b, c) = (0, 0, 0), (1/2, 0, 1/2), (1/2, 1/2, 0)$ and $(0, 1/2, 1/2)$. The two rings at $(0, 0, 0)$ and $(1/2, 0, 1/2)$ have identical orientations. The same is true for the rings at $(1/2, 1/2, 0)$ and $(0, 1/2, 1/2)$. The calculation showed that, with no disorder in the crystal structure, the diffraction intensity of (312) is zero while the diffraction intensity of (31$\overline{3}$) is finite. However, if there is a disorder in the orientations and/or locations of the H$_2$Pc rings, the intensity of the (312) reflection becomes finite and that of (31$\overline{3}$) decreases. In Fig. 5, the relative intensity of the peak at 26.6$^\circ$ to that of (31$\overline{3}$) increased by reducing the number of rubbing times from 10,000 to 1,000. This trend is consistent with the results of the calculation because the crystal structure for the smaller
number of rubbing times should have a larger disorder. However, the absolute value of the peak intensity at 26.6° in Fig. 5 does not increase with a reduction in the number of rubbing times. This can be explained by a larger surface roughness of the ITO surface for the smaller number of rubbing times, resulting in a decrease in the fraction of the XRD-detectable phase in which the (312) plane is exactly parallel to the substrate plane.

Figure 7 shows AFM images of the ITO surfaces with no rubbing and 10,000 times of rubbing. The values of $R_a$ in the two cases were 2.0 and 1.0 nm, respectively. Thus, it was confirmed that the surface roughness was actually reduced by the rubbing. It is noted that the $R_a$ of the glass substrate was as low as 0.7 nm, which caused a very strong (31\overline{3}) reflection for glass/pentacene/H$_2$Pc in Fig. 3(b).

In Fig. 5, the (001) reflection of pentacene grows with increasing number of rubbing times for ITO, which indicates that the (001) plane of pentacene becomes parallel to the substrate plane with the rubbing. It is known in the case of the pentacene films on SiO$_2$ and Al$_2$O$_3$ substrates that the (001) orientation of pentacene becomes highly ordered by making the substrate surface hydrophobic.$^{15,16}$ However, the present ITO surface was hydrophilic both before and after the rubbing, with a water-contact angle of 7°. The increase in the orientation order of pentacene caused by the rubbing is attributed to a decrease in the surface roughness of ITO: Pentacene has a tendency to be (001)-oriented on ITO, but because of the large surface roughness of the unrubbed ITO, the molecular orientation of pentacene has a large disorder. By reducing the surface roughness of ITO by the rubbing, the orientation order of pentacene is increased.

The present results indicate that H$_2$Pc takes the (31\overline{3}) orientation on the (001)-oriented pentacene layer. Under the (001) orientation, the long axes of the pentacene molecules make an angle of about 17° from the surface normal.$^{12}$ The H$_2$Pc rings in contact with the pentacene molecules, on the other hand, are nearly parallel to the substrate plane under the (31\overline{3}) orientation. Thus, pentacene and H$_2$Pc have a T-shaped configuration.$^7$ This indicates that the T-shaped configuration is more stable than the side-by-side configuration. Jorgensen and

![AFM images of ITO surfaces](image)

**Fig. 7.** (Color online) AFM images of ITO surfaces (a) with no rubbing and (b) with 10,000 times of rubbing. Average roughnesses $R_a = 2.0$ and $1.0$ nm, respectively, for (a) and (b).
Severance showed that, in a benzene-benzene or benzene-naphthalene dimer, the T-shaped configuration gives a lower free energy than the face-to-face configuration, while, in a benzene-anthracene dimer, the face-to-face configuration becomes stable. A situation similar to the former case may occur in the present pentacene-H$_2$Pc system. Besides the highly ordered $(001)$ orientation of pentacene, the surface roughness of the pentacene layer is another important parameter that determines the orientation order of H$_2$Pc, as shown in the next paragraph.

The dependence of the $(31\bar{3})$ intensity on the pentacene thickness was studied for ITO (with 10,000 times of rubbing)/pentacene $(x \text{ nm})$/H$_2$Pc $(80 \text{ nm})$ on the film thickness $x$ of pentacene.

![Figure 8](image_url)

**Fig. 8.** (Color online) Dependence of the XRD pattern of ITO (with 10,000 times of rubbing)/pentacene $(x \text{ nm})$/H$_2$Pc $(80 \text{ nm})$ on the film thickness $x$ of pentacene.

The values of $R_\alpha$ for $x = 5$ and 20 nm were 1.3 and 2.0 nm, respectively. Comparing the peak heights of the $(001)$ reflection of pentacene for $x = 10$ and 5 nm in Fig. 8, the former is 2.6 times larger, although the film thickness is twice as large, indicating that the orientation order of pentacene is higher for $x = 10$ nm, while the orientation order of H$_2$Pc is lower for $x = 10$ nm. Thus, the orientation order of pentacene is not the only parameter that determines the orientation order of H$_2$Pc; the surface roughness of the pentacene layer is another important parameter.

The orientation shown in Fig. 4(b) should give a stronger optical absorption than that in Fig. 4(a) when the light enters perpendicularly to the substrate.
optical absorption spectra of the present samples. As expected, ITO/pentacene/H$_2$Pc showed larger absorbance than ITO/H$_2$Pc and glass/H$_2$Pc. The peak height at $\sim$620 nm for ITO (with 10,000 times of rubbing)/pentacene/H$_2$Pc was 1.7 times larger than that for glass/H$_2$Pc.

By comparing the absorption spectra of ITO (with 10,000 times of rubbing)/pentacene/H$_2$Pc and ITO (with no rubbing)/pentacene/H$_2$Pc in Fig. 9, it was found that the peak height for the former was only 1.13 times larger than that for the latter, although the XRD (31$\bar{3}$) intensity of the former was more than 10 times larger. This indicates that the molecular orientations of the two samples are basically the one shown in Fig. 4(b), but the latter sample has a larger disorder in the orientation, resulting in an extremely low (31$\bar{3}$) intensity because XRD is detectable only when the (31$\bar{3}$) plane is exactly parallel to the substrate.

In Fig. 9, ITO (with 10,000 times of rubbing)/H$_2$Pc has a 1.28 times larger absorbance than glass/H$_2$Pc although both have the same molecular orientation shown in Fig. 4(a). This suggests that the former has a large disorder in the orientation of H$_2$Pc rings possibly containing an impurity phase with an orientation intermediate between the ones in Figs. 4(a) and 4(b).
3.3 Effect of molecular orientation on solar cell performance

The two simple Schottky barrier cells ITO/pentacene/H$_2$Pc/In/Al shown in Fig. 10 were prepared using two ITO substrates with no rubbing and 10,000 times of rubbing. The thickness of the H$_2$Pc film was chosen to be 120 nm, instead of 80 nm in Fig. 2, to prevent short circuit. An XRD measurement of the cells showed that the H$_2$Pc film of 120 nm thickness in the cell had a similar molecular orientation to that of 80 nm thickness. Among several types of organic thin film solar cells, a Schottky barrier cell was chosen because the effect of the H$_2$Pc orientation was expected to be more clearly observed than that in the case of the more complex cells such as heterojunctions or bulk heterojunctions. Figure 11 shows the current density ($J$) vs, bias voltage ($V_{bias}$) curves under white-light illumination and in the dark. Under the illumination, the $J$-$V$ characteristics were nearly identical between the two cells. In the dark, on the other hand, the cell with the rubbed ITO had a smaller forward current density, indicating that the resistance of the device became larger with the use of the rubbed ITO.

Generally, there are three possible explanations for the increase in the cell resistance, i.e., increases in the bulk resistances of 1) the H$_2$Pc layer, 2) the pentacene layer, and 3) an increase in the interface resistance. However, the bulk resistance of H$_2$Pc should be decreased by the rubbing for the following reason. In α-form phthalocyanine, the easy direction for charge transport is parallel to the stacking axis of the phthalocyanine rings, i.e., the $b$-axis, as demonstrated by a hole-mobility measurement of uniaxially aligned Cu-phthalocyanine thin-film transistors. The present XRD and optical absorption studies showed, on the other hand, that the (313) orientation of H$_2$Pc becomes highly ordered by the rubbing. The (313) orientation is suitable for the charge transport in solar cells because the $b$-axis stands on the substrate. Thus, the highly ordered (313) orientation obtained by the rubbing should give a smaller bulk resistance of the H$_2$Pc layer. Pentacene, on the other hand, develops a highly
ordered (001) orientation with the rubbing, as shown by the present XRD study. With the (001) orientation, the out-of-plane conductivity of the pentacene layer is smaller than the in-plane conductivity,\textsuperscript{21} so that the highly ordered (001) orientation obtained by the rubbing may give a larger bulk resistance of the pentacene layer. However, the bulk resistance of pentacene may be negligible compared with the cell resistance, because the film thickness of pentacene is only 1/24 that of H\textsubscript{2}Pc, and the hole mobility of pentacene is usually higher than that of phthalocyanine.\textsuperscript{20,22} Thus, the increase in the cell resistance caused by the rubbing may be attributed to an increase in the interface resistance. The detailed mechanism of the interface resistance, however, is unknown at present. Sakurai and co-workers showed that the performance of the cell with the pentacene buffer layer is lower than that of the cell without the buffer,\textsuperscript{7,8} and ascribed their results to the generation of a hole-injection barrier between H\textsubscript{2}Pc and pentacene. Our results showed that, even when two cells with pentacene layers of the same thickness are compared, the cell with the smaller disorder in the molecular orientation shows a lower performance.

4. Conclusions

The (31\textsubscript{1}3) XRD intensity of H\textsubscript{2}Pc deposited on ITO with a pentacene buffer layer became significantly high by polishing the ITO surface before the vacuum deposition of pentacene and H\textsubscript{2}Pc. The rocking curves and optical absorption spectra indicated that the increase in the (31\textsubscript{1}3) intensity was caused by a reduction in the disorder in the orientation of the (31\textsubscript{1}3) plane. However, the highly ordered molecular orientation achieved in this study did not result in any improvement of solar cell performance due probably to an increase in interface resistance.

Acknowledgment

This work was supported by a Grant-in-Aid for Scientific Research (21560018) from the Japanese Ministry of Education, Culture, Sports, Science and Technology.
References