Electrical Characteristics of Pentacene Films on Cross-Linked Polymeric Insulators of Varying Thicknesses

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ABSTRACT: Pentacene films vacuum-sublimed on a cross-linked polymeric insulator (CPVP−C₆) prepared using poly(4-vinylphenol) (PVP) and 1,6-bis(trichlorosilyl)hexane (C₆H₄Cl₂Si) were studied with a special concern on possible influences of the CPVP−C₆ thickness on the electrical characteristics of the pentacene films. It was found that the conductivities of the pentacene films on a thin CPVP−C₆ film (10 nm) were approximately 2 orders of magnitude higher than those on a glass substrate and increased slightly with the increase in the thickness of the underlying CPVP−C₆ film. In addition, the X-ray diffraction measurements showed that the stacking structure of pentacene molecules was remarkably enhanced by increasing the thickness of the CPVP−C₆ film, suggesting that the increase in conductivity is due, at least in part, to the improvement in carrier mobilities caused by the growth of large pentacene grains. An attempt to directly evaluate carrier mobilities using pentacene/CPVP−C₆ field-effect transistors was made, and a seeming increase in the carrier mobilities observed with the increase in the CPVP−C₆ thickness was ascribed to a hygroscopic nature of the CPVP−C₆ film, which was evidenced by the capacitance and quartz crystal microbalance measurements. Possible reasons are discussed to explain the enhanced conductivities of the pentacene films on the increased thicknesses of CPVP−C₆.

INTRODUCTION

Organic semiconductors have attracted an increasing interest as active components in electronic and optoelectronic devices such as organic field-effect transistors (OFETs), organic light-emitting diodes, and organic solar cells because of their low-cost, easy fabrication, light-weight, and possible integrations. Among their applications to (opto)electronic devices, a recent progress of the OFETs has been remarkable.¹⁻¹¹ Hole mobilities of OFETs developed so far are already comparable to or exceed those of amorphous Si transistors used commonly in liquid crystal displays, showing that they are eligible for coming into the market as long as the switching rate is concerned. Before practical applications, however, there are still several points to overcome. One of these is a low-bias operation for a facile interfacing with conventional electronic devices such as large capacitance, low leakage currents, and smooth morphology. Hydroxyl (−OH) groups in PVP react with the trichlorosilane of C₆H₄Cl₂Si to give the cross-linked structure through the formation of C−O−Si bonds. The CPVP−C₆ film can be prepared using the spin-coating technique and is found to give low-voltage-operated OFETs.

In the present study, electrical conductivities of the pentacene (Figure 1) films evaporated on the CPVP−C₆ films as well as those of the CPVP−C₆ films alone are investigated by paying special attention to possible influences on the film thickness of CPVP−C₆. Conductivities of the pentacene films on the CPVP−C₆ films are found to increase with the increase in the thickness of the underlying CPVP−C₆ film. The conductivity increase is likely to be ascribed to the increase in carrier mobilities as suggested by the enhanced...
As a matter of fact, conductivities of the CPVP shown in Figure 2d interest, however, it increased to $10^{-7}$ of the thickness of the CPVP nm. The conductivity of a pentacene plotted in Figure 3 against the thickness of the CPVP ambient atmosphere by using the four-probe method are thickness of CPVP images are also shown for the CPVP films with thicknesses of (a') 10 and (d') 200 nm. 3D laser microscope images are also shown for the CPVP - C6 films obtained using the laser microscopy. No obvious structure is seen in the phase-contrast images of the CPVP - C6 films ranging from 10 to 200 nm, along with 3D images of the CPVP - C6 films measured in an ambient atmosphere by using the laser microscope. No obvious structure is seen in the phase-contrast image shown in Figure 2a for the 10 nm film of CPVP - C6. However, as the thickness is increased from 25 to 200 nm (Figure 2b-d), a knobby structure starts to appear and the average size of the humps increases from 10 to 50 nm. The 3D image of Figure 2a' for the CPVP - C6 film (10 nm) shows that the surface is relatively smooth with an arithmetic mean roughness ($R_s$) of 9 nm. On the other hand, the 200 nm insulating film has a pitted uneven surface ($R_s = 82$ nm) as shown in Figure 2d'. Such a pitted structure of the CPVP - C6 films is likely to be caused by a shrinking of the polymer due to a cross-linking reaction between PVP and C6 as illustrated in Figure 2 of ref 21. Conductivities of the CPVP - C6 films measured in an ambient atmosphere by using the four-probe method are plotted in Figure 3 against the thickness of the CPVP - C6 film. As a matter of fact, conductivities of the CPVP - C6 films are almost constant (approximately $5 \times 10^{-8}$ S cm$^{-1}$), independent of the thickness of the CPVP - C6 film ranging from 10 to 200 nm. The conductivity of a pentacene film (60 nm) evaporated on a slide glass was similarly low ($6 \times 10^{-7}$ S cm$^{-1}$). Interestingly, however, it increased to $10^{-4}$ S cm$^{-1}$ when the pentacene film was placed on a 10 nm thick CPVP - C6 film. As the CPVP - C6 film thickness was increased further, the conductivity of the pentacene film increased gradually and reached $10^{-3}$ S cm$^{-1}$ at the CPVP - C6 thickness of 200 nm. The change in the conductivity of the 60 nm pentacene film with the thickness of the polymer film is anomalous. In general, the conductivity is proportional to a product of the mobility of charge carriers and their density in the film, implying that the change observed in the conductivity is ascribable to the increase in mobility and/or carrier density. The enhancement of a molecular stacking may facilitate hopping of charge carriers (holes) between adjacent pentacene molecules and thus can lead to the increase in mobility. From this viewpoint, XRD measurements were taken for the pentacene films (60 nm) evaporated on the spun films of CPVP - C6 as a function of the film thickness of CPVP - C6. stack the structure of the pentacene film observed with the X-ray diffraction (XRD) measurements. In addition, actually, mobilities evaluated with the FETs based on pentacene/CPVP - C6 were increased greatly with the increase in the thickness of CPVP - C6 film. However, the anomalous increase in mobilities was ascribable to a hygroscopic nature of the CPVP - C6 film, whose mechanism was not well-clear. Plausible reasons are discussed to account for the conductivity changes in the pentacene films evaporated on the polymeric insulator, together with detailed examinations of the hygroscopic nature of the CPVP - C6 film based on the capacitance and quartz crystal microbalance measurements.

## RESULTS AND DISCUSSION

Figure 2 illustrates phase-contrast images of the CPVP - C6 films ranging in thickness from 10 to 200 nm, along with 3D laser microscope images shown in Figure 2a for the 10 nm film of CPVP - C6. However, as the thickness is increased from 25 to 200 nm (Figure 2b-d), a knobby structure starts to appear and the average size of the humps increases from 10 to 50 nm. The 3D image of Figure 2a' shows the surface is relatively smooth with an arithmetic mean roughness ($R_s$) of 9 nm. On the other hand, the 200 nm insulating film has a pitted uneven surface ($R_s = 82$ nm) as shown in Figure 2d'. Such a pitted structure of the CPVP - C6 films is likely to be caused by a shrinking of the polymer due to a cross-linking reaction between PVP and C6 as illustrated in Figure 2 of ref 21. Conductivities of the CPVP - C6 films measured in an ambient atmosphere by using the four-probe method are plotted in Figure 3 against the thickness of the CPVP - C6 film. As a matter of fact, conductivities of the CPVP - C6 films are almost constant (approximately $5 \times 10^{-8}$ S cm$^{-1}$), independent of the thickness of the CPVP - C6 film ranging from 10 to 200 nm. The conductivity of a pentacene film (60 nm) evaporated on a slide glass was similarly low ($6 \times 10^{-7}$ S cm$^{-1}$). Interestingly, however, it increased to $10^{-4}$ S cm$^{-1}$ when the pentacene film was placed on a 10 nm thick CPVP - C6 film. As the CPVP - C6 film thickness was increased further, the conductivity of the pentacene film increased gradually and reached $10^{-3}$ S cm$^{-1}$ at the CPVP - C6 thickness of 200 nm. The change in the conductivity of the 60 nm pentacene film with the thickness of the polymer film is anomalous. In general, the conductivity is proportional to a product of the mobility of charge carriers and their density in the film, implying that the change observed in the conductivity is ascribable to the increase in mobility and/or carrier density. The enhancement of a molecular stacking may facilitate hopping of charge carriers (holes) between adjacent pentacene molecules and thus can lead to the increase in mobility. From this viewpoint, XRD measurements were taken for the pentacene films (60 nm) evaporated on the spun films of CPVP - C6 as a function of the film thickness of CPVP - C6.
that the crystallization of a pentacene film is affected greatly by the surface energy of the substrate material deduced from the measurement of a water contact angle and the hydrophobic surface leads to a well-crystallized pentacene film. When the water contact angles of the CPVP–C₆ films were measured, they were 58°, 63°, 68°, and 74° for the CPVP–C₆ film thicknesses of 25, 80, 200, and 650 nm, respectively, consistent with the results of the XRD experiments. The results of the contact angle measurements are given in Figures S1 and S2.

It is of interest to directly measure the mobilities of charge carriers (holes) in the pentacene films. Figure 5a depicts the output characteristics of a pentacene–FET with a 20 nm-thick CPVP–C₆ film as an insulator. The curves of drain current (I_D) versus drain voltage (V_D) show that the pentacene–FET can be operated by the gate voltages below 2 V, as has been reported by Marks et al. The capacitance for the 20 nm-thick CPVP–C₆ film measured at 1 to 10⁴ Hz was around 240 nF cm⁻², which is much lower than those of general OFETs (10⁻⁴ to 10⁻⁵宋cm⁻²) as shown in Figure 3.

Osterbacka et al. have reported OFETs composed of regioregular poly(3-hexylthiophene) as organic semiconductors and PVP as insulators. Their OFETs were characterized by a low-voltage operation and apparently high mobilities and were named “hygroscopic insulator field-effect transistors” (HIFETs) because the inclusion of water in the insulating PVP layer was essential for the FET operation. A simple diagnosis of the HIFET is to compare the FET operations in moist air and in vacuum. Indeed, the pentacene–FET with CPVP–C₆ as the insulator was sensitive to atmosphere, and the FET characteristics almost disappeared a couple of minutes after evacuation of the device. Also, ON and OFF currents of the pentacene–FET with CPVP–C₆ were in the ranges of 10⁻¹⁰ to 10⁻⁸ and 10⁻⁶ to 10⁻⁴ A, respectively, and the ON/OFF ratio was around 10⁴ to 10⁶, which is much lower than those of general OFETs (10⁵ to 10⁸). These results demonstrate the HIFET nature of our pentacene–FETs. The operating principle of HIFETs has been discussed and explained in terms of the formation of hydronium ions because of the interaction between the –OH group of PVP and a water molecule and the migration of the ion species in the insulator PVP film, leading to a high capacitance of the polymer due to the ionic polarization. In the relatively thick CPVP–C₆ films used in this study, the –OH groups of PVP may not react completely with

Figure 3. XRD spectra of pentacene films (60 nm) evaporated on CPVP–C₆ films ranging in thickness from 10 to 200 nm. Each spectrum is shifted upward for clarity.

Figure 5. (a) Output characteristics of pentacene–FET with CPVP–C₆ films (20 nm) as an insulator and (b) the corresponding transfer characteristics.
the chlorosilanes of C₆ and the remaining –OH groups may interact with water.

To further clarify the hygroscopic nature of the CPVP–C₆ films, capacitances of the CPVP–C₆ films were measured in air and under vacuum with oscillation frequency as a parameter. The results are shown in Figure 7. The capacitances of the 10 nm-thick CPVP–C₆ film in air are almost constant at 400 nF cm⁻² over a frequency range beyond 1 Hz, whereas it increases as the frequency is decreased below 1 Hz. No appreciable change in the capacitance was observed by evacuation for the thin CPVP–C₆ film. For the 200 nm-thick CPVP–C₆ film, on the other hand, the capacitance measured in air changed greatly from 35 nF cm⁻² at 10³ Hz to 2 × 10⁴ nF cm⁻² at 0.1 Hz (a 3 orders-of-magnitude increase). In contrast to the case of the 10 nm-thick CPVP–C₆ film, evacuation of the OFET device led to the decrease in capacitance, especially at low frequencies. The observed frequency dependence of capacitances is reasonably explained by the slow migration of hydronium ions in the CPVP–C₆ films. Furthermore, the capacitances of thick CPVP–C₆ films in the low-frequency region are decreased markedly by removing water from the insulators by evacuation. This is also consistent with the hygroscopic property of the CPVP–C₆ films. The change in the amount of water in the CPVP–C₆ film before and after evacuation was measured using a quartz-crystal microbalance technique. The change in frequency with time during evacuation was extremely slow; therefore, precise evaluation of the water content absorbed in the CPVP–C₆ films was difficult. In Figure 8, the amount of water evaluated from the frequency change measured 1 h after the start of evacuation is plotted against the thickness of the CPVP–C₆ film. The plot shows that the water content increases with the increase in the thickness of the CPVP–C₆ film, suggesting that water was absorbed not only on the insulator surface but also in the polymer bulk.

**EXPERIMENTAL SECTION**

Pentacene, PVP (Mₙ = 20 000), and 1,6-bis(trichlorosilyl)hexane (C₆) were purchased from Aldrich and used without further purification. Pentacene–FETs were fabricated as described below. An Al film (10 nm in thickness) was evaporated onto a precleaned slide glass. CPVP–C₆ was prepared on the Al-coated slide glass by the spin-coating of a tetrahydrofuran solution containing the same concentrations of PVP and C₆ at 3000 rpm and was annealed in vacuum at 110 °C for 50 min. The film thicknesses of CPVP–C₆ were controlled by changing the concentration of PVP and C₆. Optical and 3D microscopy images of the polymer films were obtained by using a phase-contrast microscope (Olympus BX51) and a 3D color laser microscope (Keyence VK-9700/9710 Generation II), respectively. Pentacene films of thickness 60 nm were evaporated on the polymer films, and subsequently, an Au layer of 20 nm was deposited on the pentacene films. The channel length and total channel width were 50 µm and 3 mm, respectively. The Iₑₒ versus Vₒ characteristics of the pentacene–FETs were measured using Keithley 2400 source meters. Mobilities were evaluated from the following equation

\[ I_{DS} = \frac{W}{2L} \mu C(V_G - V_T)^2 \]

where \( I_{DS} \) is the drain current in the saturation regime, \( W \) and \( L \) are the channel width and channel length, respectively, \( \mu \) is the mobility, \( C \) is the capacitance of the insulator, \( V_G \) is the gate voltage, and \( V_T \) denotes the threshold voltage at which the transistor turns on. Capacitance measurements of the CPVP–C₆ films with varying thicknesses were performed using an LCR meter (HIOKI 3522-50). Conductivities of the CPVP–C₆ films and the pentacene films evaporated on the CPVP–C₆ films were determined using the four-probe method using a resistivity meter (Loresta-GP MCP-T610, Mitsubishi Chemical Corp.). Configurations of devices used for the measurements of FET and conductivities are shown in detail in Figure S3. The film thicknesses of CPVP–C₆ were evaluated from the capacitance values with a dielectric constant of 6.1, and they were confirmed using 3D color laser microscopy. A change in the weight of the CPVP–C₆ film upon evacuation was measured using a quartz-crystal monitor (ULVAC). XRD measurements were performed using a D8 Advance diffractometer (Bruker AXS) using Cu Kα radiation. All measurements were taken in an ambient atmosphere, unless otherwise stated.

**CONCLUSIONS**

CPVP–C₆ and the pentacene films on CPVP–C₆ were characterized through electrical, XRD, microscopic, water contact angle, and quartz-crystal microbalance measurements. One of the key findings in the present study is the conductivities of the pentacene films on the CPVP–C₆ films that increased with the increase in the thickness of CPVP–C₆. The increase in conductivity can be ascribed to the increase in either or both of the carrier mobility and the density of charge carriers because mobility is a product of the carrier mobility and the density of charge carriers in the single charge carrier model. To discuss the possible reasons for the increase in the
conductivity, the mobilities of charge carriers using the FET configuration of pentacene/CPVP–C₆ were measured. The FET mobilities obtained using the polymeric insulator CPVP–C₆ seemingly increased with the increase in the thickness of CPVP–C₆, but the increased mobilities on thicker CPVP–C₆ films were ascribed to a hygroscopic nature of the CPVP–C₆ film. Nevertheless, we presume that the conductivity increase in the pentacene films is ascribable to the increase in the mobilities of holes in the pentacene film as supported by the XRD measurements, which shows that the stacking structure of pentacene molecules is enhanced by increasing the thickness of the CPVP–C₆ film. The mobility increase due to the enhanced crystallinity may be insufficient for explaining the increase in conductivity as shown in Figure 3; therefore, we assume an increase in the density of charge carriers as well. Charge carriers (holes) may be generated in the pentacene film is ascribable to the increase in the density of charge carriers as well. Charge carriers (holes) may be generated in the pentacene film upon contact with the CPVP–C₆ film, if the work function of the latter film is larger than that of the former to build an accumulated region in the p-type pentacene films.

ASSOCIATED CONTENT

1 Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.6b00292.

Schematics of water droplets on CPVP–C₆ film, relationship between its thickness and contact angles, and device configurations for FET and conductivity measurements (PDF)

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Notes

The authors declare no competing financial interest.

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