Organic field-effect transistors by a wet-transferring method

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Organic field-effect transistors (OFETs) were prepared from an epitaxially grown film fabricated by a wet-transferring process. 2,3,7,8,12,13,17,18-octaethyl-21H,23H-porphyrin platinum(II) was grown by thermal evaporation on the (001) surface of potassium bromide (KBr) single crystals. When the film was grown at room temperature, the planar molecules were aligned orthogonally on the crystal surfaces along the [110] direction with edge-on orientation to the surface normal direction. The epitaxy film was transferred to on SiO_2/Si surface immediately after removing the KBr on the water surface to product the OFETs. The calculated μ_{FET} of the OFET for the wet-transferred vertically aligned film were 1.3×10^{-4} and 2.2×10^{-4} $cm^2 V^{-1} s^{-1}$ at the linear and saturation regions, respectively, at $V_g = -50$ V at an I_{ON}/I_{OFF} (on/off ratios of source–drain current) of $10^4 \sim 10^5$. © *2003 American Institute of Physics.* [DOI: 10.1063/1.1600518]

Organic field-effect transistors (OFETs) have attracted a great deal of interest for use in applications such as thin-film transistors for active matrix liquid crystals or organic light-emitting displays, as well as low-end data storage.[1] Electron and hole mobility has been improved via the production of highly ordered organic film via thermal evaporation using an optimum substrate temperature,[2-5] Langmuir–Blodgett films,[6] or self-ordered films from solution casting with regular shaped organic polymers.[7-10] Films with edge-on oriented molecules show a practically high mobility, since the stacking direction of the π orbital is in-plane with the current direction of flow from the source-to-drain electrodes.[3,9] Organic epitaxy growth on a single-crystal substrate has also attracted attention because of the potential of electronic and optoelectronic applications through highly ordered films.[11-16] Organic light-emitting diodes or photovoltaic devices using epitaxially grown films have been reported.[15,16]

Herein, we report on the preparation of OFETs from 2,3,7,8,12,13,17,18-octaethyl-21H,23H-porphyrin platinum(II) [PtOEP, inset of Fig. 2(a)] with epitaxially grown films fabricated by a wet-transfer method. The morphology and crystal orientation of the films were investigated by means of atomic force microscope (AFM) and x-ray diffraction (XRD) analysis. When the film is grown at room temperature, planar molecules are aligned orthogonally on the crystal surfaces along the [110] direction with needle-like grains. The epitaxial growth of PtOEP was expected because the lattice parameter of (001) plane of PtOEP matches well with that of the (110) plane for KBr. OFETs were produced using a wet-transferring method containing an epitaxially grown film.

The calculated μ_{FET} for the OFET for the case of a wet-transferred film are 1.3×10^{-4} and 2.2×10^{-4} $cm^2 V^{-1} s^{-1}$ at the linear and saturation region, respectively at $V_g = -50$ V and an I_{ON}/I_{OFF} (on/off ratios of source–drain current) of $10^4 \sim 10^5$.

PtOEP (Porphyrin Products Inc.,) was grown from a synthetic quartz Knudsen-type cell at a pressure of 1×10^{-3} Pa after purifying the material by train sublimation.[17] The PtOEP crystal was grown onto the air-cleaved (001) surface of potassium bromide (KBr) at a deposition rate of 0.04 nm/s or less. After evaporation, the PtOEP films were transferred [described in the inset of Fig. 2(b)] to a silicon dioxide (300 nm) (SiO_2)/a heavily doped silicon wafer (Si) by a wet-transferring method. The deposited thin film on KBr single crystal put on the SiO_2/Si substrate in a precleaned glass petri dish with the deposited face toward the upside. Next, deionized water was filled in the petri dish up to the level of KBr surface. The PtOEP film was transported on SiO_2/Si after complete dissolving of the KBr single crystal. The film was kept in a vacuum oven with dynamic vacuum more than 6 h to remove residue water. The evaporation of gold through a shadow mask to form source and drain electrodes on the wet-transferred PtOEP thin films served to complete the OFET preparation. This device has a channel length and width of 20 μm and 5 mm, respectively. The FET characteristics were measured with KEITHLEY 6430 and 2400 source-measurement units in an air atmosphere.

Organic films were observed by AFM in the contact mode. The AFM system used in this study was a NanoScope III™ (Digital Instrument, Inc. Santa Barbara, CA) and the measurements were performed in air at room temperature. A Si_3N_4 cantilever with a spring constant of 0.12 N/m was used at a scanning rate of 2–3 Hz. XRD measurements of the evaporated films were performed by θ–2θ continuous scans

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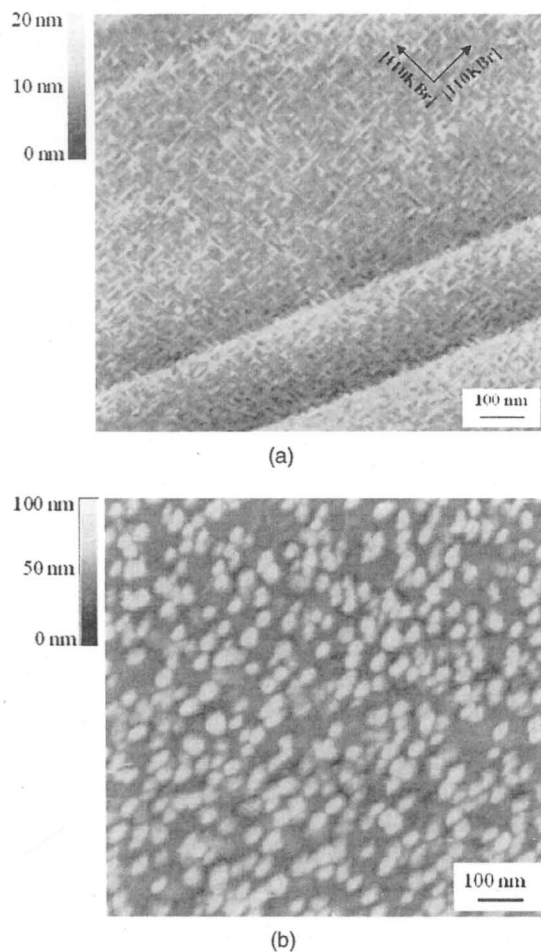[c]Electronic mail: k.yase@aist.go.jp

FIG. 1. AFM image of (a) 100-nm-thick PtOEP films evaporated on the (001) cleaved surface of a KBr substrate and (b) 50-nm-thick PtOEP films directly grown by thermal evaporation on SiO_2/Si maintained at room temperature.
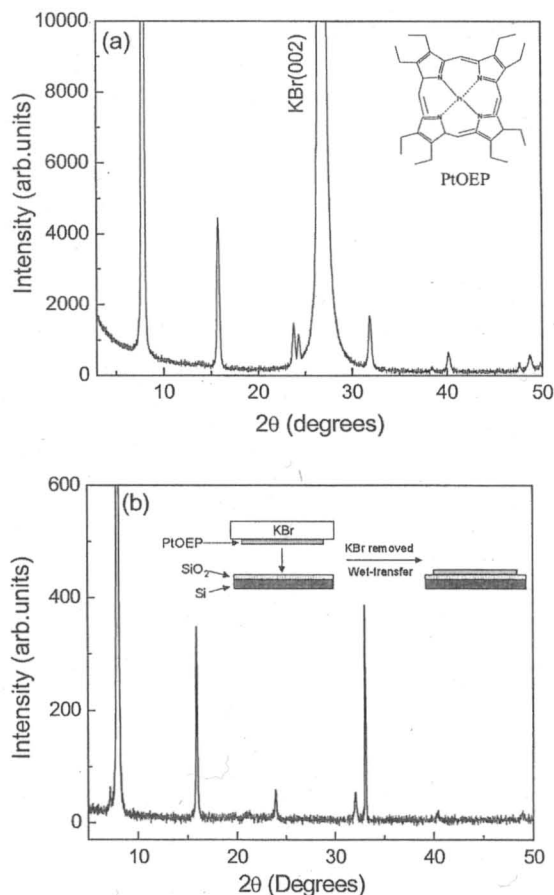

FIG. 2. XRD pattern of (a) 100-nm-thick films of PtOEP evaporated on the (001) cleaved surface of a KBr substrate (inset: molecular structure of PtOEP) and (b) 50-nm-thick PtOEP films directly grown on SiO_2/Si maintained at room temperature (inset: schematic illustration of wet-transfer method).

using a RU-300 powder diffractometer (Rigaku Co., Tokyo) with $Cu K_\alpha$ radiation.

Figures 1(a) and 1(b) show AFM images of PtOEP films deposited on KBr and SiO_2/Si substrates, respectively. The molecules were found to be self-aligned as needle-like crystals on single-crystal KBr, and were orthogonally oriented along the [110] directions of KBr. The width and height of one needle are ~90 and ~1.5 nm, respectively. The sizes of the needles decrease with increasing the film thickness as the result of strong interactions with neighbor crystals. On the other hand, polycrystalline domains several tens of nanometers in size were formed on the amorphous SiO_2/Si substrate, as shown in Fig. 1(b). The grain sizes enlarge with increasing substrate temperature up to a temperature of 150 °C. It was not possible PtOEP molecules to deposit on the SiO_2/Si substrate at temperature above 200 °C since the molecules can also be desorbed from the KBr substrates at these temperatures.

To determine the surface normal alignment, XRD measurements of the evaporated films on KBr and SiO_2/Si were performed. Figure 2(a) shows an XRD pattern of the PtOEP film grown on the KBr substrate. Two strong peaks were observed at 26.8° and 7.86°. The strongest peak, at 26.8°, corresponds to (002) of the KBr substrate. The other long period peak at 7.86° corresponds to the lattice spacing of the PtOEP crystals deposited on the KBr substrate. The sharp diffraction peak indicates that the deposited layer has a well-ordered crystal structure. The lattice constant, as calculated from the peaks, was 11.2 Å. This lattice constant is almost the same as the length of the long axis of this molecule calculated by the CACHE program. Therefore, this value indicates PtOEP molecules have an edge-on orientation to the surface normal direction since the long period peak and a series of higher-order diffraction peaks were observed clearly. In other words, the stacking direction of the $\pi-\pi$ orbital is parallel to the substrate. Milgrom et al. reported on the crystal structure of PtOEP.[18] However, the lattice spacings of PtOEP thin-film crystals on KBr are not consistent with the lattice spacings calculated from single crystals. The reason for this is assumed to be the difference between ordered thin-film structure and single-crystal structure.

Figure 2(b) shows an XRD pattern of the PtOEP film on the SiO_2/Si substrate. The location of the peaks is similar to the XRD data of the PtOEP films deposited on SiO_2/Si substrates. This indicates that PtOEP molecules were also grown with an edge-on orientation, even though the molecule was deposited on the amorphous substrate at room temperature. The intensity of this diffraction peak is smaller than that of PtOEP films on KBr. Therefore, we conclude that the ordering and crystallinity of the films on SiO_2/Si is decreased to some extent.

Before fabricating PtOEP OFETs from the epitaxy films, it is necessary to verify that the molecular alignment is conserved after the wet-transferring process, which could lead to deformation of the film. Figure 3(a) shows an XRD pattern
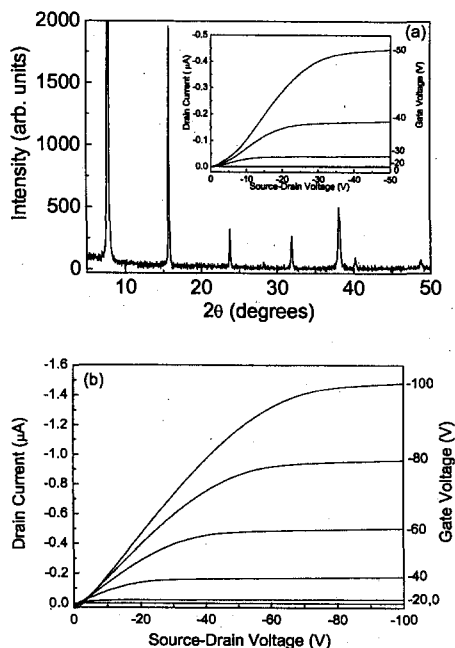
Appl. Phys. Lett., Vol. 83, No. 6, 11 August 2003

Noh et al.   1245

FIG. 3. (a) XRD patterns of 100-nm-thick PtOEP films on SiO_2 after a wet-transferring process from KBr substrates maintained at room temperature. Inset of (a) and (b) show drain current versus drain voltage (I_{DS}–V_{DS}) characteristics at different gate voltages for the FETs from wet-transferred and directly grown PtOEP films, respectively.

of the PtOEP film after wet-transferring from KBr to the SiO_2/Si substrate. The XRD data show peaks that are almost similar to those of a film grown on KBr, as shown in Fig. 2(a). This result indicates that the alignment of films was not altered, even after wet-transferring. OFETs were fabricated on SiO_2/Si from highly oriented PtOEP films originally deposited on KBr by wet-transferring. The inset of Fig. 3(a) shows a plot of source–drain current (I_{sd}) versus the source–drain voltage (V_{sd}) of the wet-transferred PtOEP film for a p-channel device as various gate voltages (V_g). The field-effect mobility (μ_{FET}) of the OFETs can be calculated from plotting Eqs. (1) and (2) for linear and saturation regions, respectively:[19]

$$I_d = (W/L)\mu_{FET}C_i(V_g - V_t)V_d,$$ (1)

$$I_d^{sat} = (W/2L)\mu_{FET}C_i(V_g - V_t)^2,$$ (2)

where L is the channel length, W the channel width, C_i the capacitance per unit area of the gate dielectric layer (C_i = 10 nF/cm^2 for 300-nm-thick SiO_2), and V_t the threshold voltage. The calculated μ_{FET} for the OFET for the wet-transferred vertically aligned film are 1.3×10^{-4} and 2.2×10^{-4} $cm^2 V^{-1} s^{-1}$ at the linear and saturation regions, respectively, at $V_g = -50$ V and an I_{ON}/I_{OFF} (on/off ratios of source–drain current) of $10^4 \sim 10^5$.

As a comparison, we also fabricated PtOEP OFETs by direct thermal evaporation on SiO_2/Si in high-vacuum conditions. Figure 3(b) shows a plot of I_{sd} versus V_{sd} for PtOEP FET deposited on SiO_2/Si for a p-channel device for various values of V_g. The threshold voltage of the device fabricated with the wet-transferring method shifted a little when compared with that of the direct device. We conjecture that this shift is due to a charging effect, which would be brought on by poor contacts between the gold electrodes and the films that were transferred. At present, we are conducting experi-

ments to confirm this. The calculated μ_{FET} for the OFET are 1.4×10^{-4} and 3.6×10^{-4} $cm^2 V^{-1} s^{-1}$ at the linear and saturation regions, respectively, at $V_g = -100$ V and the I_{ON}/I_{OFF} (on/off ratios of source–drain current) was $10^4 \sim 10^5$. Device performance is very similar to that for OFETs fabricated by a wet transferring. This indicates that the μ_{FET} value from the wet-transferred film might not be sufficient to utilize as an OFET compared with other materials. However, this may not be the result of the fabrication process, but may be because of PtOEP itself. PtOEP molecules show a slightly larger intermolecular gap with 4.3 Å to π–π stacking direction than other molecules (not shown). Therefore, we expect that OFETs with higher mobility can be fabricated from materials that have superior packing properties such as pentacene.

In conclusion, we fabricated OFETs from epitaxy-grown films on a single-crystal substrate by wet-transferring. The mobility of hole and I_{ON}/I_{OFF} for this device show values that are similar to those for OFETs from deposited films on SiO_2/Si. Even though some unconfirmed problem might be expected, such as a bad contact, we are certain that this fabrication method represents a potential candidate for use in further studies of the mobility of highly ordered organic films.

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