Anisotropy of electrical conductivity in a pentacene crystal grain on SiO₂ evaluated by atomic-force-microscope potentiometry and electrostatic simulation

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Conductivity anisotropy in a crystal grain of thin-film-phase pentacene has been estimated by a combination of atomic-force-microscope potentiometry (AFMP) and electrostatic simulation. The surface potential distribution and topography of a grain in a working pentacene thin-film transistor are simultaneously measured by AFMP. Then, the nonlinear potential profile due to the thickness variation is simulated by changing the anisotropic ratio of conductivity. The anisotropic ratio (corresponding to the anisotropy of carrier drift mobility) is estimated to be \( \alpha_x : \alpha_z = 45:1 \), where \( x \) is the horizontal (harmonic mean of those in \( a- \) and \( b- \) axes) direction and \( z \) is the vertical (\( c- \) axis) direction. © 2010 American Institute of Physics. [doi:10.1063/1.3430041]

Organic electronic devices with pentacene active layers are attracting considerable interest because of their applicability to flexible electronics. 1 The device performance varies with its structure, and therefore, optimization of the device geometry is important when designing an electronic circuit. Recent progress allows fabrication of very short channel organic TFTs, 2 which have advantages of quick response speed and low power consumptions. Since a pentacene crystal has a strongly anisotropic molecular structure, the anisotropy of electrical conductivity, which is derived from the carrier mobility anisotropy, is an important material parameter when designing and optimizing the short-channel device structure.

Several groups reported carrier mobility anisotropy in single-crystal pentacene for the \( a-, b-, \) and \( c- \) axes, 3 or within the \( a-b \) plane. 4 The anisotropy in pentacene thin films in their horizontal directions \( (a- \) and \( b- \) axis) was also reported. 5,6 However, the anisotropy in pentacene thin films between the horizontal and vertical \( (c- \) axis) directions has not been measured so far. Mobility of vertical direction is difficult to obtain by commonly used method (e.g., time-of-flight method), because film thickness is very thin. For low-cost and large-area fabrication, the use of thin films, whose crystallographic structure is different from that of single crystals, is preferred to that of single crystals. Therefore, evaluation of the anisotropy between the horizontal and vertical directions in the thin film is required. In this paper, the anisotropic ratio of the conductivity between the vertical and horizontal directions is estimated for a thin-film-phase pentacene grain on SiO₂ by a combination of atomic-force-microscope potentiometry (AFMP) and electrostatic simulation.

A specially designed quasi-one-dimensional pentacene thin-film transistor (TFT) [Fig. 1(a)] was fabricated as follows. A heavily doped n-type silicon wafer with a one-dimensional gratinglike structure (with a peak-to-valley height of 125 nm) was used as a gate substrate. The grating-like structure prevents electrical contact between the crystal grains grown on the higher and lower parts of the substrate surface. Thus, current conduction is confined to each strip of the pentacene film. A 250-nm-thick SiO₂ layer serving as a gate insulator was uniformly grown on the substrate by thermal oxidation. The substrate was cleaned by UV/O₂ treatment. No further treatments, such as chemical modification, were performed in this experiment. A 30-nm-thick pentacene film was then deposited by molecular-beam deposition in ultrahigh vacuum (\( \sim 10^{-7} \) Pa). 7 The deposition rate and growth temperature were 0.2 nm/min and 50 °C, respectively. Finally, 100-nm-thick source and drain gold ele-

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FIG. 1. (Color online) (a) Schematic structure of the pentacene TFT used in this work. (b) Topographic and (c) potential images of a single grain taken simultaneously by AFMP. The grating direction of the substrate is perpendicular to the source and drain electrodes. The top or higher part of the grating is shown in white in (b) to emphasize the topography in the lower parts of the grating.
trodes were deposited on the pentacene film [with a channel length (L) of 20 μm and a width (W) of 5 mm]. The field-effect mobility and threshold voltage calculated from the transfer characteristics of the device were 0.52 cm²/V s and 30 V, respectively. This relatively high mobility for a film on a bare SiO₂ surface indicates that a good-quality pentacene film was grown on the grating substrate.

The crystal phase of the grown film was determined using x-ray diffraction in θ-2θ mode (Cu K\(^\alpha1\)=0.154 nm). Figure 2 shows an x-ray diffraction pattern of the pentacene film. There are several diffraction peaks indexed as (00l). The d(001) value calculated from Fig. 2 is 1.53 nm, which corresponds to the thin-film phase of pentacene.\(^{8,9}\)

Topographic and potential images in the channel region of the TFT under operation were obtained simultaneously by AFMP. Details of the AFMP measurement are described elsewhere.\(^{10}\) All measurements were performed using a modified commercially available AFM (JEOL, JSPM-5200) in a nitrogen atmosphere. Silicon AFM levers (Olympus, AC240TS) with platinum-palladium conducting coatings were used in this work. The current-voltage characteristics between the conductive probe and pentacene were examined before the experiment, and we confirmed that they formed an Ohmic contact even at very low voltages. The good Ohmic contact is obtained because the probe tip was covered with pentacene molecules while scanning over another area of the sample.\(^{11}\) Also, the input resistance of AFMP (>10\(^14\) Ω) is much larger than the channel resistance (~10\(^8\) Ω for each strip). The potential distribution obtained in this work was, therefore, ensured to be that on the topmost surface of the film without any perturbation caused by the measurement. The spatial resolution of these images was about 20 nm, and the scanning time for an image was approximately 450 s. The gate-source voltage and drain-source voltage during the measurements were fixed at −30 V and −5 V, respectively. The channel of the TFT under this bias condition is well accumulated, and the TFT operates in the linear region.

Figure 1(b) shows a topographic image of the pentacene grains on the lower part of the grating. We have chosen a grain that can be regarded as a single crystalline domain without significant barriers that inhibit carrier transport.\(^{12}\) The grain shape is categorized as pyramidal, and the grain width is expected to have been larger than the width of the grating if the growth had not been interrupted by the grating structure. Figure 1(c) shows a potential image at the same location as Fig. 1(b). The surface potential abruptly changes at the edge of the grating, which indicates that the pentacene strips are electrically disconnected from each other. We can, therefore, consider that the current flows quasi-one-dimensionally throughout the channel.

Since the surface potential distributions in the channel of the quasi-one-dimensional TFT under current flow were obtained and their gradient appeared to be dependent on the film thickness as shown in Fig. 1(c), we attempted to estimate the conductivity anisotropy in a thin-film-phase grain by simulating the experimental potential profile by performing an electrostatic simulation assuming a steady-state current.

The simulation was carried out using two-dimensional field simulation software (Tera Analysis, QUICK FIELD). The structural model used to simulate the grain in Fig. 1(b) is shown in Fig. 3(a). The cross section of the pyramidal grain was reproduced from the AFM image and the mean thickness of the film. A thin highly conductive region (2 nm in thickness) was placed at the bottom of the grain as the accumulation region of the TFT. Each grain boundary was defined as a Dirichlet voltage boundary.\(^{13-15}\) The potential difference between both boundaries was set to the experimentally obtained value. The gate dielectric was assumed to be a perfect insulator.

The simulation relies on the ratio of three values of conductivity: horizontal bulk conductivity \(\sigma_x\), vertical bulk conductivity \(\sigma_z\), and channel conductivity \(\sigma_{ch}\). \(\sigma_{ch}\) was set to

**FIG. 2.** (Color online) X-ray diffraction pattern of the pentacene film. The incident direction of the x-ray (Cu K\(^\alpha1\)) was set parallel to the grating direction to prevent the shadowing effect of the grating structure.
reproduce the current density of the TFT under the same bias condition as the AFMP measurement. The density of carriers in the accumulation region of the experimental sample was roughly estimated to be $3 \times 10^{19}$ cm$^{-3}$, which is more than 100 times larger than the acceptor density of naturally oxygen-doped pentacene films.\footnote{14,15} $\sigma_z$ was, therefore, assumed to be 1/100 of $\sigma_{ch}$. In fact, the simulated potential profile was almost independent of $\sigma_{ch}$, unless $\sigma_{ch}$ became less than 100 $\sigma_z$, $\sigma_z$ was then used as a fitting parameter and was set to be smaller than $\sigma_z$.

Figure 3(b) shows experimental and simulated profiles of the surface potential. Although the potential profile in the channel must be linear when we assume the gradual channel approximation, the experimental potential profile appears to be S-shaped. The simulated potential profile also exhibits the same tendency and varies with the anisotropic ratio of conductivity. These results indicate that the S-shaped profile is mainly caused by the conductivity anisotropy of the pentacene grain. In the experimental result, small fluctuations are superimposed on the S-shaped curve. These small irregular fluctuations are commonly observed in potential images and one possibly due to the random fluctuation of the highest-occupied-molecular-orbital (HOMO) band\footnote{16} or partly due to the measurement noise. In either case, such a random signal does not significantly affect the parameter fitting using statistical methods. In this work, most probable anisotropic ratio of the conductivity was estimated by the method of least-squares. The sum of the squares of the residuals S is given by

$$S = \sum_{i=1}^{n} (\phi_{S,i} - \phi_{C})^2,$$

where $\phi_{S}$ is the experimental potential and $\phi_{C}$ is the calculated potential. The fitting result for the profile in Fig. 3(b) is shown in Fig. 3(c). We examined several grains in the same manner and obtained an average anisotropic ratio of conductivity of $\sigma_z : \sigma_x = 45:1$.

Here, we discuss the carrier transport within a thin-film-phase grain. According to our recent study on the crystallographic structure of thin-film-phase pentacene on SiO$_2$,\footnote{17} a thin-film-phase grain is a mosaic crystal with a crystallite size of 30–50 nm. This indicates that the crystal grain studied in this work contains a large number of randomly oriented small crystallites. Therefore, the horizontal mobility is regarded as the harmonic mean of the mobility values for the $a$- and $b$-axes and, moreover, it is degraded by HOMO-band-edge fluctuation due to the crystallite boundaries.\footnote{16} As a result, horizontal mobility in the thin-film-phase grain\footnote{12} is much smaller than that in a single crystal.\footnote{5} Since the film thickness is smaller than the crystallite size, mobility in the vertical direction will not be affected by the mosaic structure. On the basis of these considerations, we can explain the difference in the anisotropic ratio between a thin film ($\sigma_z : \sigma_x = 45:1$) and a single crystal ($\sigma_z : \sigma_x = 450:1$).\footnote{5} The degradation of horizontal mobility in a thin film resulted in the smaller anisotropic ratio. Although the ratio estimated in this work is not the intrinsic value in an ideal thin-film-phase crystal, it is a practical value that can be used for device simulations and analyses because the deposition of a mosaic-free thin film is very difficult on most substrates.

In conclusion, we evaluated conductivity anisotropy in a thin-film-phase pentacene grain by a combination of AFMP and electrostatic simulation with a steady-state current. The simulated potential profile was in good agreement with the experimental profile, and the anisotropic ratio of conductivity was determined to be $\sigma_z : \sigma_x = 45:1$. This ratio is smaller than that in a single crystal because of the mosaic structure of the thin-film-phase grain and can be applied to most pentacene TFTs.

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