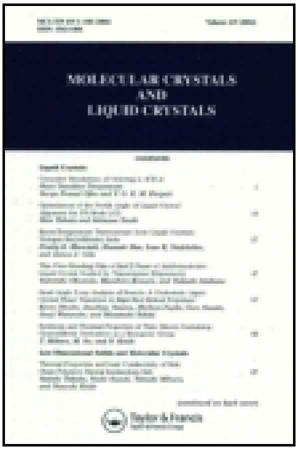

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Micro-Raman Spectroscopy on Pentacene Thin-Film Transistors

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Micro-Raman Spectroscopy on Pentacene Thin-Film Transistors

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Molecular orientation in pentacene films and thin-film transistors has been studied by micro-Raman spectroscopy. We have found that the relative intensity of the 1596-cm^{-1} band (B_{3g}) is sensitive to the molecular orientation. The standing orientation was observed for the films formed on the bare and hexamethyldisilazane (HMDS)-modified SiO_2 surfaces and the Au surfaces modified with self-assembled monolayers (SAMs), whereas the lying orientation for the films on the bare Au surface. We have explicitly demonstrated the differences of the molecular orientation in the films on SiO_2 dielectric layers and Au electrodes in the devices by mapping measurements.

Keywords: organic thin-film transistor; pentacene; Raman spectroscopy

INTRODUCTION

Organic thin-film transistors (OTFTs) have attracted much attention due to their great potential applications in low-cost fabrication and flexible electronics [1]. The performance of OTFTs depends on molecular orientation in organic semiconductor layers. Micro-Raman spectroscopy is useful in elucidating molecular orientation, because of high sensitivity, high space resolution, and *in situ* nondestructive analysis. Pentacene is one of the most promising materials for high performance p-channel OTFTs. In this study, we have investigated

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the molecular orientation in pentacene thin films with various thicknesses on a bare SiO_2 substrate, gold and modified Au substrates. We have measured two-dimensional distribution of the molecular orientation in bottom- and top-contact devices by micro-Raman spectroscopy.

EXPERIMENTAL

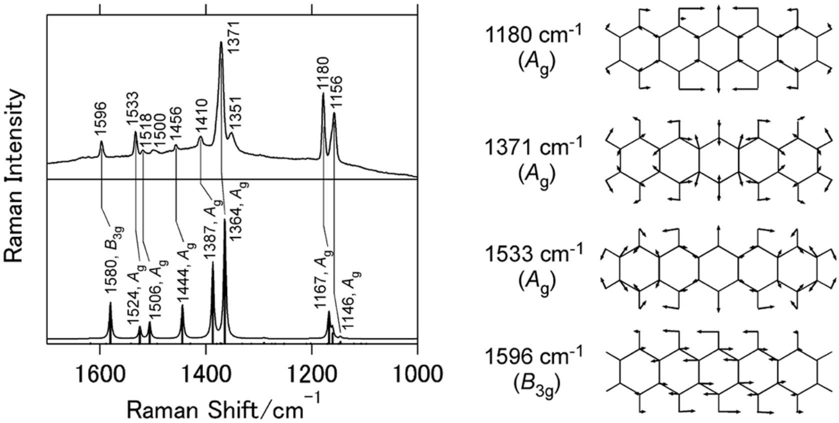
Pentacene was purchased from Aldrich and purified by vacuum sublimation. A pentacene film was prepared by vacuum vapor deposition on various substrates at room temperature. The deposition rates were 1.0–2.0 nm/min. An SiO_2 substrate was cut from an n^+-silicon wafer (0.02 Ωcm, <100> axis) covered with a thermally grown 500-nm thick SiO_2 layer (Sansho Shoji Co. Ltd). The SiO_2 surface was cleaned by sonication in acetone and 2-propanol for 5 min. An Au film was prepared by vacuum vapor deposition on the SiO_2 substrate. The substrate was dipped into 1 mM ethanol solutions of dodecanethiol or benzenethiol for 24 h. The Au surface was modified with the SAMs. Bottom-contact source and drain electrodes with chromium (5 nm) and gold (50 nm) were made on the SiO_2 substrate by the photolithographic method. The bottom-contact substrates were cleaned by the UV-ozone treatment. The SiO_2 surface was modified with HMDS by keeping it in a Teflon® container including neat HMDS for more than 12 h. Top-contact Au electrodes (50 nm) were prepared by vacuum vapor deposition through a shadow mask on the pentacene film formed on an HMDS-modified SiO_2 surface. Micro-Raman spectra were measured on a Raman microprobe (RENISHAW inVia) with excitation at 633 and 532 nm in the back scattering configuration. Density functional theory calculations of the structure and normal vibrations of a pentacene molecule were carried out with the Gaussian 98 program [2] at the B3LYP/6-311G** level with a scaling factor of 0.9669 [3].

RESULTS AND DISCUSSION

Pentacene is a planar molecules having D_{2h} point group. It has the following vibrational representation,

$$\Gamma_{\mathrm{vib.}} = 18A_g + 9B_{1g} + 7B_{2g} + 17B_{3g} + 8A_u + 17B_{1u} + 17B_{2u} + 9B_{3u}.$$

The A_g, B_{1g}, B_{2g}, and B_{3g} modes are Raman active. Figure 1(a) shows the 633-nm excited Raman spectrum of randomly oriented crystal powders of pentacene and the calculated Raman spectrum of pentacene. The observed bands have been assigned to in-plane modes



(a) (b)

FIGURE 1 (a) 633-nm excited Raman spectrum of crystalline powders (upper) and calculated Raman spectrum of pentacene (lower). (b) Atomic displacements for four distinctive normal modes.

(A_g or B_{3g}) on the basis of the results of the calculation, as shown in Figure 1(a). Figure 1(b) shows calculated atomic displacements for four distinctive modes.

We focus on the B_{3g} mode at 1596 cm^{-1}, which is sensitive to molecular orientation. In the back scattering configuration, the Raman intensity of a B_{3g} band, $I_{B_{3g}}$, can be expressed by the following equation (4):

$$I_{B_{3g}} = K\frac{1}{2}\left(1 + 2\cos^2\theta\right)\sin^2\theta \tag{1}$$

where K is a coefficient and θ is an averaged tilt angle between the surface normal and the molecular long axis. If the molecular long axis is perpendicular to the substrate, i.e., $\theta = 0$, the intensity of the B_{3g} band is zero. Equation (1) shows that the intensity of the B_{3g} band is deeply dependent on the tilt angle.

The film growth of pentacene on the bare SiO_2 substrate is examined by the 1596-cm^{-1} band (B_{3g}). Figure 2(a) shows the 633-nm excited Raman spectra of the pentacene thin films on the bare SiO_2 surfaces at the thicknesses of 2 and 50 nm. The 1596-cm^{-1} band (B_{3g}) in these films has smaller intensity than that in the randomly oriented bulk crystals. These results indicate that the tilt angle is small for these films.

The relative intensity of the 1596-cm^{-1} band (B_{3g}) to the 1533-cm^{-1} band (A_g) is sensitive to the tilt angle. We have prepared two pentacene films characterized by X-ray diffraction: one consists of the

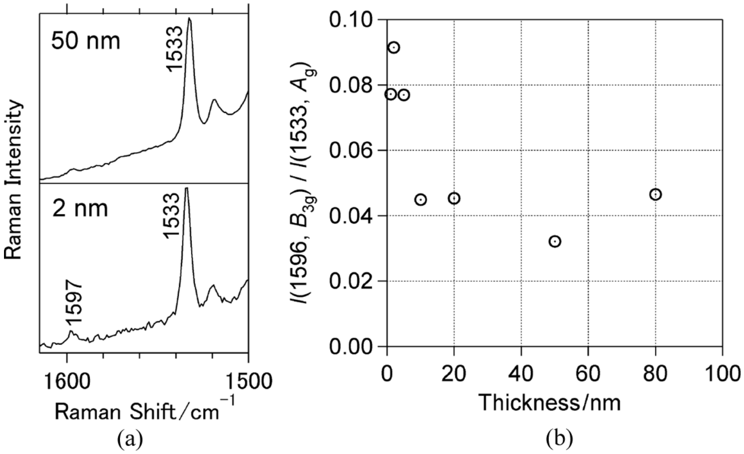


FIGURE 2 (a) 633-nm excited Raman spectra of a pentacene thin films on a bare SiO_2 surface at the thicknesses of 2 and 50 nm. (b) Evolution of the relative band intensity of the 1596-cm^{-1} band (B_{3g}) to the 1533-cm^{-1} band (A_g) as a function of film thickness.

"thin-film" phase with the interlayer periodicity, $d(001)$ spacing, of 1.54 nm, and the other the "bulk" phase with $d(001)$ spacing of 1.44 nm. The tilt angles are 5.6 and 6.8° for the thin-film phase and 20.4 and 22.1° for the bulk phase, respectively [5,6]. The values of the relative intensity are 0.035 for the thin-film phase and 0.0825 for the bulk phase, respectively. The relative intensity increases with increasing tilt angle.

Figure 2(b) shows the relative intensity as a function of film thickness. The relative intensity in the thickness region below 10 nm is about 0.08, and then decreases quickly with increasing the thickness. It keeps the small value of about 0.04 in the region of 10 to 80 nm. There exist pentacene molecules with the large tilt angles in the region below 10 nm. Probably such inclined molecules are located at defect sites on the substrate. In the region of 10 to 80 nm, the averaged tilt angle is very small: most of the molecules are arranged with their molecular axes nearly perpendicular to the substrate. These films correspond to the thin-film phase.

Figure 3 shows the 633-nm excited Raman spectra of the 5-nm thick pentacene films on the bare, dodecanethiol-, and benzenethiol-modified Au substrates. The relative intensity of the 1597-cm^{-1} band (B_{3g}) to the 1533-cm^{-1} band (A_g) on the bare Au and the Au substrates modified by dodecanethiol and benzenethiol are 0.40, 0.12, and 0.11,

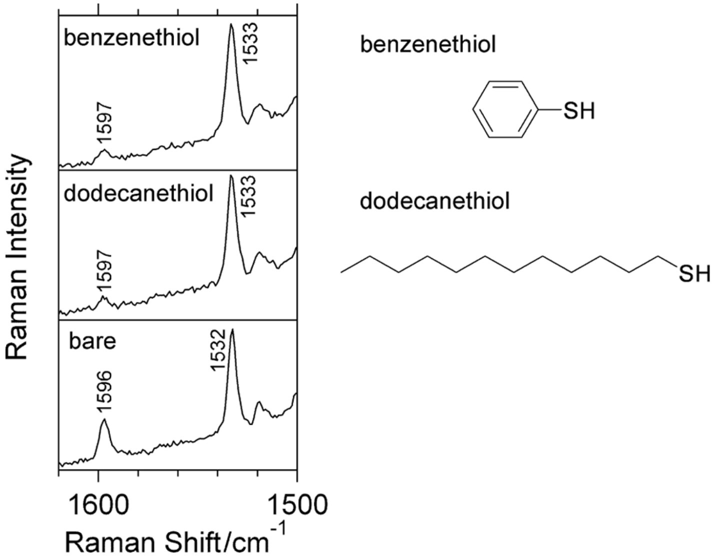


FIGURE 3 633-nm excited Raman spectra of the 5-nm thick pentacene films on the bare, dodecanethiol-, and benzenethiol-modified Au substrates. Right-hand schematic views show the chemical structures of dodecanethiol and benzenethiol.

respectively. The pentacene film on the bare Au surface exhibits the large value, indicating that the molecules are arranged with their axes nearly parallel to the substrate. The small values for the modified substrates indicate small tilt angles. Käfer *et al.* have reported [7] that the SAM-modification suppresses the flat-lying pentacene molecules and forms the orientation with the standing molecules.

Micro-Raman spectroscopy has space resolution with μm-order and can detect film structures of pentacene on the SiO_2 dielectric layer and the Au electrode of the device separately. Figure 4 shows the evolutions of the relative intensity of the 1596-cm^{-1} band (B_{3g}) in the 633-nm excited Raman spectra of the films on the HMDS-modified SiO_2 surface and the Au surface as a function of film thickness. The variation of the relative intensity on the HMDS-modified SiO_2 surface exhibits the same tendency as the pentacene films on the bare SiO_2 surface shown in Figure 2(b). The HMDS-modification does not affect the molecular orientation. The relative intensity on the Au surface is larger than that on the SiO_2 surface in the whole region. The pentacene molecules on the Au surface take the larger averaged tilt angles than those on the SiO_2 surface does. Furthermore, the relative

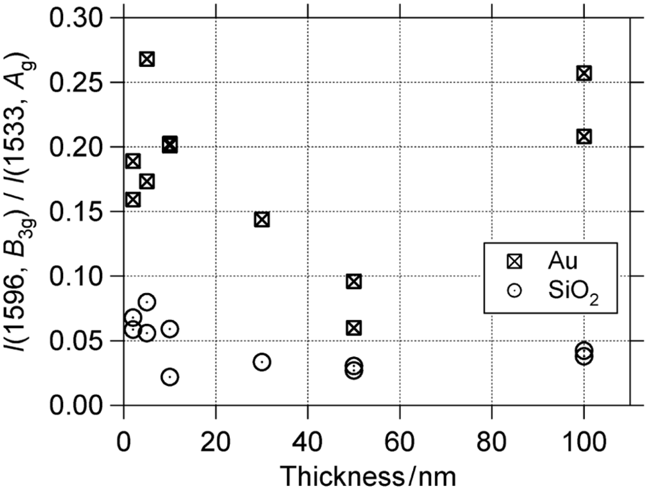
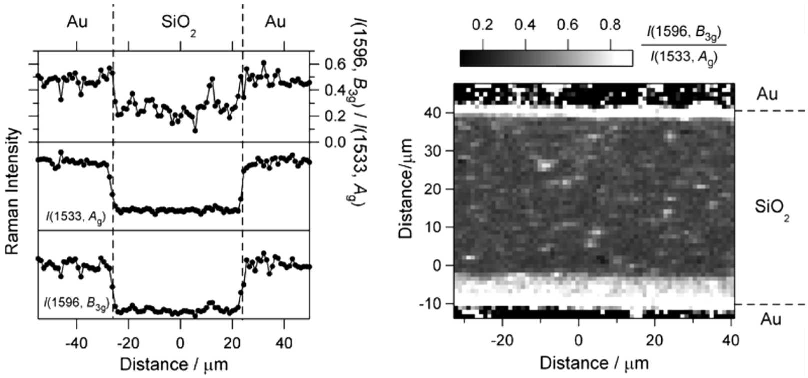


FIGURE 4 Evolution of the relative intensity of the 1596-cm^{-1} band (B_{3g}) to the 1533-cm^{-1} band (A_g) as a function of film thickness for the films formed on the HMDS-modified SiO_2 surfaces and Au surfaces in the bottom-contact devices. The excitation wavelength was 633 nm.

intensity on the Au surface changes frequently as a function of film thickness. In the thickness region below 10 nm the molecules tend to incline, and then show the relatively small tilt angle in the region of 10 to 50 nm. Käfer *et al.* have reported [7] that the film growth of pentacene on polycrystalline Au substrate exhibits the first-monolayer with flat-lying molecules and the multilayer with standing molecules. The further deposition leads to the increase of the inclined molecules.

The mapping measurements of the Raman spectra clearly exhibit the difference of the orientation at each position in the bottom- and top-contact devices. Figure 5(a) shows the line scan on the bottom-contact device. The relative intensity of the 1596-cm^{-1} band (B_{3g}) is strong on the Au electrode and weak on the SiO_2 layer. These results are in agreement with those in Figure 4. A two-dimensional image of the relative intensity of the 1596-cm^{-1} band (B_{3g}) in the top-contact device is shown in Figure 5(b). The boundary between the top electrodes and the channel region has the large relative intensity. This indicates that the Au particles during the deposition diffuse into the boundary and induce the degradation of the orientation. Nakamura *et al.* have reported [8] that the potential in the operating top-contact device drops at the boundaries. We have deduced that this drop is deeply related with the degradation of the orientation.



(a) (b)

FIGURE 5 (a) Line scan of the 532-nm excited Raman spectra of the bottom-contact device with the 50-nm thick pentacene film. The bottom line shows the intensity of the 1596-cm^{-1} band (B_{3g}), the middle line that of the 1533-cm^{-1} band (A_g), and the top line the relative intensity of the B_{3g} to A_g bands. (b) Two-dimensional image of the relative intensity in the top-contact device with the 50-nm thick pentacene film in the 532-nm excited Raman spectra.

SUMMARY

We have found that the 1596-cm^{-1} Raman band (B_{3g}) is useful in evaluating the molecular orientation in pentacene films. From the micro-Raman measurements, we have concluded that pentacene molecules take the standing orientation for the films formed on bare and HMDS-modified SiO_2 surfaces and the SAM-modified Au surfaces, but the lying orientation for the film on a bare Au surface. The mapping measurements clearly demonstrate the difference of the orientation at each position in the OTFTs.

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