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# Molecular Oriented Thin Film of Biphenyl-4,4'-dithiol Fabricated by Molecular Beam Deposition Method

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Biphenyl-4,4'-dithiol was deposited as a stacked molecular layer onto several kinds of substrates by a molecular beam deposition method. It was found that both the gold thin film and the potassium bromide (KBr) single crystal were effective substrates for the control of the molecular orientation and also that the lattice constants of the substrate were responsible for the control of crystallinity of biphenyl-4,4'-dithiol thin films.

Assembly of functional organic molecules into highly oriented thin films is important in their applications to electronic and photonic devices. A molecular beam deposition (MBD) method is one of the most promising techniques for the fabrication of such organic thin films. Some reports on the fabrication of organic thin films by the MBD method have been presented.1-4) In these studies planar molecules such as perylene and phthalocyanine derivatives have been usually applied because of their interesting electrical and optical properties. The orientation of these molecules is generally controlled by *van der Waals* interaction between neighboring molecules rather than by the interaction between molecules and substrates. It is, therefore, rather difficult to deposit the molecules epitaxially only by such a weak interaction. The orientation of the first monolayer on the substrate is indispensable for the epitaxial growth of highly oriented thin films. It has been also pointed out that the matching of the lattice constants between the deposited materials and the substrate plays a significant role in the epitaxial growth of thin films.5)

We have studied on the thin film of biphenyl-4,4'-dithiol (BPDT) having thiol groups (-SH) at both the ends as a model molecule for the MBD method, because the thiol group is known to coordinate to metal atoms such as gold and silver6,7) and is also expected to be stably adsorbed at the lattice sites of ionic alkaline halide crystal with an electrostatic interaction. In this paper, we wish to report the fabrication of BPDT thin films by the MBD method and their characterization by FT-IR and X-ray diffraction methods.

The source material BPDT was evaporated onto several kinds of substrates under high vacuum of *ca.* $10^{-5}$ Pa. A Knudsen cell (K-cell) made of quartz was used for the heat-evaporation of BPDT. A cleaved KBr single crystal ((100) surface), a gold-deposited quartz plate, a polyimide-coated quartz plate, a bare quartz plate, and an optically polished $CaF_2$ single crystal were used as the substrates. They were rotated at the speed of *ca.* 10 r.p.m. and their temperature was kept at room temperature during the deposition. The film deposition rate was monitored by a quartz thickness sensor placed at the position just beside the substrate.

BPDT powder, whose melting point was determined to be 179 °C (lit. 179-181 °C)8) by differential scanning calorimetry, was evaporated at *ca.* 50 °C under high vacuum.9,10) The BPDT film (*ca.* 1000 Å) could be deposited on the gold and KBr substrates with the deposition rate of 1-5 nm/min regardless of its low evaporation temperature. On the other hand, the evaporated BPDT molecules were hardly deposited on the bare and polyimide-coated quartz substrates as well as on the $CaF_2$ substrate. The strong adsorption of the thiol end-group onto the KBr crystal is expected because of the electrostatic interaction between an ionic KBr single crystal surface and a polar thiol end-group. With regard to the gold substrate, Nuzzo's6) and Whitesides's7) groups have reported that alkanethiols and dialkyl disulfides are adsorbed to prepare monolayer films on the gold surface from their solution, whose long molecular axis are almost perpendicular to the substrate. It was suggested that such a unique adsorption was caused by the strong interaction of the thiol end-group with the gold thin film.6,7)

The FT-IR spectra of the BPDT thin films deposited by the MBD method are shown in Fig.1(a) and 2(a). The films on the KBr substrate and on the gold thin film were measured by a transmission mode and by IR-RAS

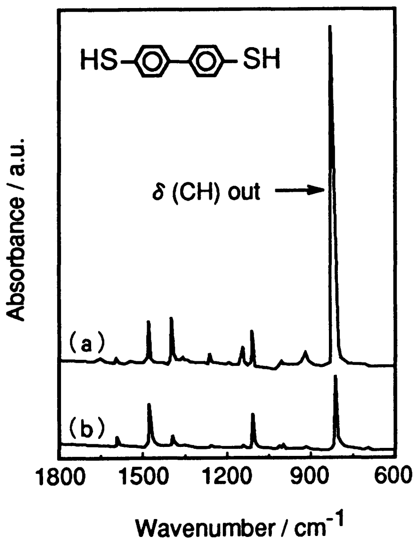

Fig. 1. FT-IR spectra of the BPDT
(a)on the KBr substrate and (b)in the KBr pellet.

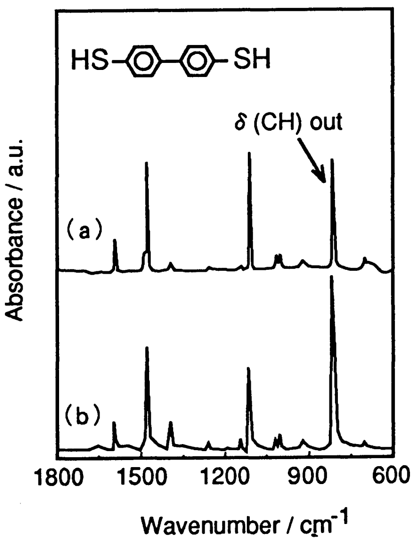

Fig. 2. FT-IR spectra of the BPDT
(a)on the Au film (IR-RAS) and (b)in the KBr pellet.

(incident angle=85°), respectively. It should be noticed that the molecular vibrations whose transition dipole moment has a component parallel to the substrate are observed in the FT-IR spectra. On the other hand, the molecular vibrations whose transition dipole moment has a component perpendicular to the substrate are selectively observed in the IR-RAS spectra.[11,12] Figs.1(b) and 2(b) show the spectra of BPDT source powder in a KBr pellet for the sake of comparison where BPDT molecules are randomly oriented. Each peak in Fig.1 and 2 is normalized by the intensity of the peak at 1477 $cm^{-1}$ assigned to the C=C stretching vibration of benzene ring. Therefore, we can estimate the molecular orientation by comparing these (a) with (b) spectra.

The peaks at 808 $cm^{-1}$ are assigned to the CH out-of-plane vibration of benzene ring (δ(CH)out).[13] The peak δ(CH)out which has the transition moment perpendicular to the molecular long axis is much stronger than that for the BPDT powder in Fig.1. This result can be understood by considering that the molecular long axis is oriented almost perpendicular to the substrates. Moreover, it supports that the BPDT molecules are adsorbed on the KBr substrate with the thiol end-group. On the other hand, the peak δ(CH)out is weaker than that for the BPDT powder in Fig.2. This result suggests that the BPDT molecules also stand on the gold substrate.

The X-ray diffraction pattern of the BPDT film on the KBr substrate shows sharp six peaks, together with some intense peaks attributed to (n00) planes of the KBr substrate itself (Fig.3). The obtained d-space distance from these six peaks is *ca.* 1.50 nm. This value is almost comparable with the molecular length of BPDT obtained by the MNDO calculation. The X-ray diffraction peaks, therefore, exhibit that the BPDT film has a periodic layered structure parallel to the KBr substrate. This result indicates that the BPDT molecules stacked on the monolayer anchored on the substrate with the thiol end-group in the first monolayer.

Figure 4 shows the X-ray diffraction pattern of the BPDT thin film on the gold thin film. The diffraction pattern contains only two peaks except those of gold (111) and (200) planes. A broad reflection peak near the 22° is obviously derived from the amorphous quartz glass used as the substrate. The obtained d-space of the lattice from two peaks is *ca.* 1.43 nm. These results indicate that the BPDT molecules on the gold thin film also have a

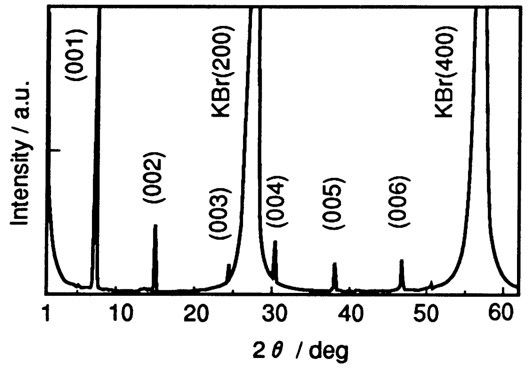

Fig. 3. X-ray diffraction pattern of the BPDT film deposited on the KBr substrate.

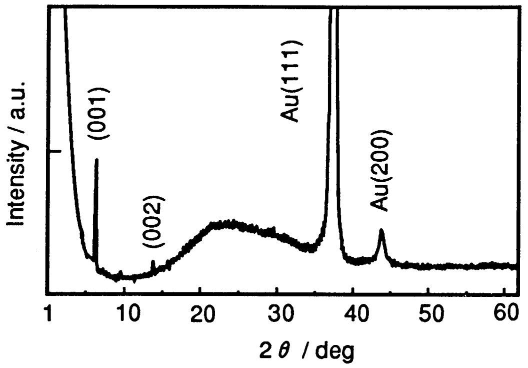

Fig. 4. X-ray diffraction pattern of the BPDT film deposited on the Au film.

layered structure and the BPDT molecules incline from the surface normal to some extent.

The X-ray diffraction pattern of the BPDT source powder gave the crystal lattice constants of a=5.99 Å, b=9.37 Å, c=11.8 Å, and β=97.9° by assuming its single crystal of monoclinic structure. The resulting b value is close to the value (9.33 Å) which is twice the distance between the closest potassium atoms at the KBr (100) surface. These results show that the lattice quasi-matching between BPDT and KBr is helpful for the improvement of crystallinity of the thin films.[14)]

In conclusion, the gold thin film and the KBr single crystal were selected as the suitable substrate for the preparation of BPDT thin film by the MBD method. They had a strong interaction with BPDT and showed a small difference in the orientation of BPDT molecules. In particular, the KBr substrate having the lattice quasi-matching with BPDT molecules gave a high crystallinity of BPDT thin film. On the basis of these results, further investigation on the preparation of functional thin films using dithiols is in progress.

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