Structure of obliquely vacuum-deposited organic compounds

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Introduction
Vacuum-deposition is widely used for producing organic and inorganic thin layers on a variety of base materials. In most cases, vaporized materials are deposited from the direction normal to the base materials. The structure of the deposition film changes sensitively depending on the conditions for vacuum deposition, and extensive studies have been carried out on this issue.

For example, the temperature of the base material is an important factor to determine the deposited layer structure. It has been clarified that the direction of the vapor deposition is another important factor. In some cases, the oblique deposition adds a characteristic property to the deposited film; the obliquely deposited layer is able to control the structure of the above layers. Interestingly, this property is unrelated to whether the obliquely deposited film is crystalline or amorphous, which suggests that this structural control is due to the mechanism other than epitaxial growth. In 2007 we have confirmed that a unique mesoscopic structure is formed in the obliquely deposited films of fullerene.

According to the previous studies, the influence of the deposition layer on the above layers varies depending deposition direction as well as vaporized material. It is assumed that the changes in the mesoscopic structure induce the changes in the above layers. In this study, we have studied the influence of these two factors on the mesoscopic structure.

Experimental
Fullerene, isotactic polystyrene (IPS), atactic polystyrene (aPS) and syndiotactic polystyrene (sPS) were obliquely deposited on glass plates at room temperature. The vacuum deposition was carried out at an angle in the range of 30 to 75° from the normal. Small angle scattering (SAXS) experiments were performed at BL9C using X-ray radiation of 0.10 nm, which impinged on a sample surface at a grazing angle < 1°. The scattering was recorded with imaging plates (Fuji BAS-IP MS 2025). The sample-to-detector length was around 1000 mm. The exposure time was 30-60 s.

Results and Discussion
Figure 1 shows a SAXS image of an IPS-deposited film, where the plane of X-ray incidence was set perpendicular to the plane of vapor deposition. A streak inclining opposite to the direction of vapor deposition was observed. The direction of inclination was inverted when the sample was rotated by 180° around its normal, which is an indication that the inclined streak is due to the structure of the deposited layers. These SAXS features correspond to those observed in the fullerene where elongated cylindrical columns are covered the substrate surface. On the other hand, there is no conspicuous feature in the WAXS pattern of the IPS substrate; only an amorphous hallow was observed, which means that the mesoscopic structure consists of amorphous IPS.

The results of SAXS experiments show that there is a systematic difference between IPS and fullerene in the direction of the columnar structure as shown in Table 1, which summarizes the relationship between the deposition direction and the column direction. For fullerene deposited films, the column inclination (CIA) angle varies from 30° to 50° by changing the deposition angle (DA) from 45° to 75°. In particular, CIA remains around 50° for DAs ≥ 60°. For IPS, CIA is already close to 50° even for DA = 45°.

Table 1. Inclination Angle of the columnar structure; the values are the angles from the normal of the substrate.

<table>
<thead>
<tr>
<th>Deposition Angle (degree)</th>
<th>BMF(C60)</th>
<th>IPS</th>
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</thead>
<tbody>
<tr>
<td>45.0</td>
<td>52.5</td>
<td>60.0</td>
</tr>
<tr>
<td>67.5</td>
<td>75.0</td>
<td>45.0</td>
</tr>
<tr>
<td>Inclination Angle (degree)</td>
<td>30</td>
<td>34</td>
</tr>
<tr>
<td>48</td>
<td>50</td>
<td>50</td>
</tr>
<tr>
<td>49</td>
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