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A Core-Level Spectroscopic Study of Thiophene Film Deposited on Au(111): Structural Change at Initial Stage of Film Growth

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Introduction

Recently, heterocycle organic molecules adsorbed on metal substrates have attracted much attention because of its possibility of application for novel organic electronic devices. Particularly, the thin-film of thiophene (C_4H_4S) has been extensively studied since it is known as a precursor to form a conducting polymer by X-ray or electron beam irradiation. So far, it was found that thiophene molecules on Au(111) forms at least two different phases depending on the coverage, flat-lying monolayer and vertically aligned multilayer. It was unclear how the former phase transforms to the latter one. In this work, we have studied structural change of thiophene films on Au(111) in detail by C-*K* NEXAFS and XPS.

Experimental

Both C-*K* NEXAFS and XP spectra experiments were performed at BL-7A. Thiophene was adsorbed at substrate temperatures below 130 K by exposing the clean Au(111) surfaces to gaseous thiophene introduced with a gas doser. C *K*-edge NEXAFS measurements were carried out by the partial electron yield method with using a micro-channel plate. XP spectra were taken with hemispherical electron energy analyzer at a photon energy of 340 eV.

Results and Discussion

Figure 1 shows the tilt angle of thiophene ring estimated from the incident angle dependence of C-*K* NEXAFS plotted as a function of exposure. As we reported before, the molecules are adsorbed with flat configuration(~20 degrees) at low exposures(0.3~0.9L), and while at higher exposures(125L~) they form multilayers with vertically aligned configuration(~65 degrees). Between those two configurations, there are two transition regions; in the first transition(0.9~2.1L) the tilt angle is steeply increased, while in the second one(2.1L<), it shows gradual increase. Figure 2 shows the results of photoemission spectra of C1s(a) and S2p(b) exhibit no significant change in spectral shape and width except for a little peak shift when the exposure was increased from 0.9L to 1.2L. The absence of significant change of XP spectra indicates that the adsorbed layer keeps in the form of monolayer, though the coverage exceeds the completion of the flat-lying monolayer(0.9L). On the other hand, an obvious change of the shape and width is observed between 2.1L and 4.0L both for C1s and S2p XP spectra. This change is associated with the formation of the 2nd layer growth, which gives a higher binding-energy peak in XP spectra due to a lack of final state screening of by conducting electrons of the metal substrates. Thus, first transition region corresponds to the growth of "tilted" monolayer; however, we could not determine the completion exposure of this "tilted" monolayer. Fig. 1 suggests that the tilt angle at the completion of "tilted" monolayer is estimated to be 55 degrees. Beyond 2.1 L, where multilayer growth takes place, the tilt angle gradually increases with exposure and finally reaches 65 degrees at 123L. In conclusion, we confirmed that the flat-lying monolayer grows up the standing-up multilayer via tilted monolayer of which tilt angle is 55 degrees from the surface parallel.

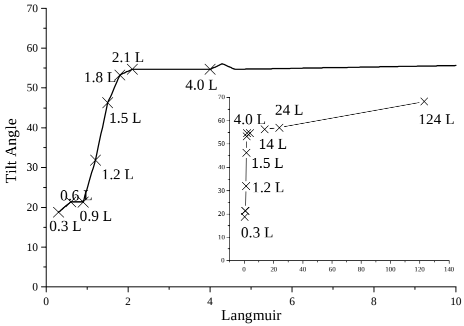

Figure 1 The change of tilt angle depending on the exposure of thiophene (From C *K*-edge NEXAFS)

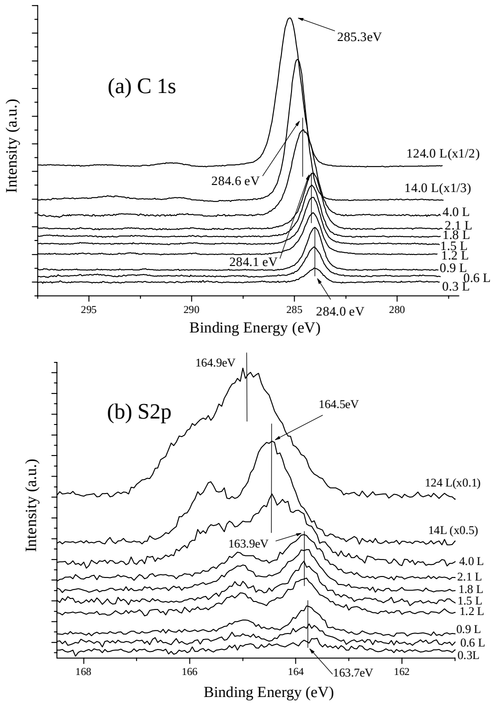

Fig. 2 C1s(a) and S2p(b) Photoemission Spectra
hv = 340eV Ep= 50eV

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