Temperature and Thickness Dependence of Molecular Orientation of α-sexithienyl on Cu(111)

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Introduction
Thin films of π-conjugated organic materials have attracted wide attention not only for fundamental science but also for technological applications, such as field effect transistor (FET), electro luminescence (EL), etc. Among several candidate materials, oligothiophenes (α-nT) are attractive due to their fascinating electronic properties, such as high FET mobility. However, there has been little investigation of oligothiophenes on metal substrates. Furthermore, temperature or thickness dependence of molecular orientation was not fully investigated. It is necessary to know information of these dependences not only for understanding of metal-molecular interaction but also for control of molecular orientation in future organic devices. In the present study, we have, thus, studied the growth of 6T films on Cu(111) in detail by near edge X-ray absorption fine structure (NEXAFS).

Experiment
Mechanically and electrochemically polished Cu(111) was cleaned by repeated cycles of Ar⁺ sputtering and annealing. 6T was evaporated from a Knudsen cell. S K-edge NEXAFS and S-1s XPS measurements were carried out at the soft x-ray double-crystal monochromator station BL-11B of the Photon Factory in the Institute of Materials Structure Science.

Results and Discussion
Figure 1 shows the thickness and polarization dependence of S K-edge NEXAFS for 6T/Cu(111) at substrate temperatures at 120 K and 300 K. The spectra exhibited noticeable polarization dependence. The molecular orientation angle can be quantitatively evaluated from the polarization dependence of intensity of the peaks. In the Fig. 1, structural models of the 6T film was presented. When 6T molecules were deposited at substrate temperature lower than 300 K, they adsorbed with their molecular long axes parallel to the substrate, irrespective of film thickness. On the other hand, 6T molecules adsorbed with their molecular long axes parallel to the substrate at 360 K for the 4 Å thick film, while they adsorbed with their molecular long axes normal to the substrate for the film thicker than 20 Å. It has been proved that the molecular orientation of a promising organic semiconductor 6T on Cu(111) could be controlled by substrate temperature.

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