

XAFS studies on a molecular orientation of α -sexithienyl grown on Ag(111) surface

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Introduction

Oligothiophenes attract wide attention as one of the most promising π -conjugated polymers because of their captivating electric properties such as high mobility and have been applied to organic field-effect transistors (FET) and electronic devices. In particular, α -sexithienyl (6T) has been used for fabricating various devices since the carrier mobility of thiophene oligomers increase with the effective π -conjugation length to saturate at around six thiophene units. However, in order to obtain the film with better electrical characteristics, it is necessary to elucidate and control the orientation of molecules. It has been studied about the orientation of 6T molecules grown on various metal substrates. However, the definite orientation of 6T molecules grown on single crystalline Ag(111) surface, particularly in the initial stage of growth, have not been fully understood so far. In this study, we applied S K-edge EXAFS and NEXAFS to determine the orientation of 6T molecules grown on Ag(111) surface.

Experiment

Mechanically and chemically polished Ag(111) was cleaned by repeated cycles of Ar⁺ sputtering and annealing. 6T was evaporated from a Knudsen cell and the growth rate was on the order of 0.1 nm/min. S K-edge EXAFS and NEXAFS were both carried out at the station BL-11B of the Photon Factory in the Institute of Materials Structure Science.

Results and Discussion

Figure 1 shows the S K-edge EXAFS k^2 -weighted FT of 6T grown on Ag(111) surface at 300 K. Clear polarization dependence was observed, particularly on the main peak (1.4 Å) assigned to S-C bond, and it was enhanced at normal X-ray incidence (90°). Thus, it became apparent that 6T grew with its thiophen-rings aligned with Ag(111) surface parallel direction. Figure 2 shows the polarization and film thickness dependence of S-K edge NEXAFS for 6T grown on Ag(111) surface at 300 K. Two intense peaks were observed and they showed clear polarization dependence, that is, first peak was most enhanced at grazing X-ray incidence (15°), while second peak was enhanced at normal incidence (90°) irrespective of film thickness. Taking the result of EXAFS into consideration, the first peak (2472.4 eV) and the second peak (2473.3 eV) correspond to the transition from S 1s to π^* orbital (perpendicular to a thiophen-ring;

π^* -peak), and σ^* orbital (parallel to a thiophen-ring; σ^* -peak), respectively. Considering the molecular shape of 6T, σ^* orbital spreads out in 6T molecular long axis direction. Hence, it became clear that 6T grew with its molecular long axis and molecular plane (thiophen-rings plane) aligned with Ag(111) surface parallel direction irrespective of the film thickness.

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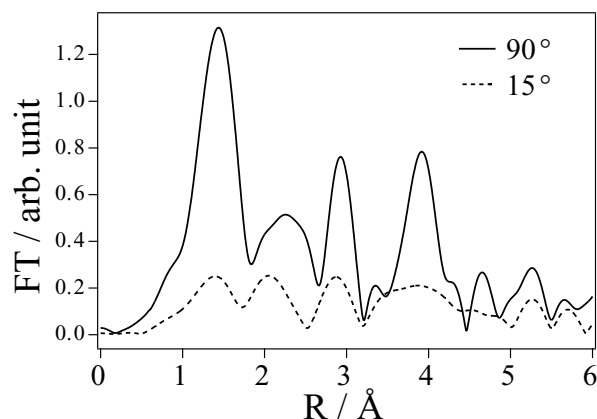


Fig. 1. k^2 -weighted FT of 6T on Ag(111) at 300 K.

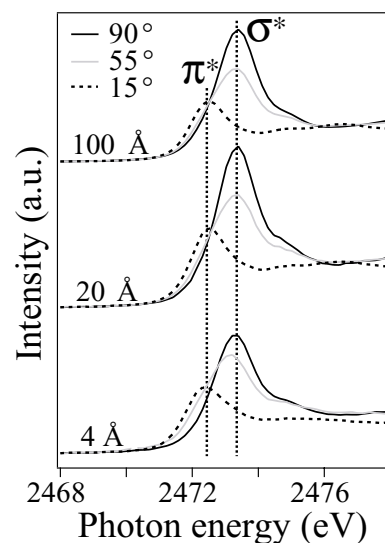


Fig. 2. S K-edge NEXAFS for 6T on Ag(111) at 300 K.