

Analysis of the charge transfer from ultrathin films of organic molecules grown on nanolayer semiconductor surfaces

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1 Introduction

Interfaces between organic molecules and semiconductor surfaces are important to fabricate electronic devices based on organic semiconductors in nanoscale. In particular, molecular orientation and ordering at the interface are crucial for the quality of the devices. Among organic molecules, oligothiophene has been extensively studied because of their novel electronic and optical properties [1]. In the previous study, we demonstrated using surface reflectance spectroscopy that the molecular orientation of α -sexithiophene (α -6T) is controlled by the type of passivation of Si(001) surface [2].

In this study, α -6T ultrathin films on other type of passivated surfaces, that is a surface of layered semiconductors, have been investigated. Near edge X-ray absorption fine structures (NEXAFS) were measured during the film growth on GaSe and WSe₂ surfaces, and compared with those of the films on SiO₂/Si(001).

2 Experiment

GaSe and WSe₂ crystals were fixed on Si substrates and mechanically exfoliated just before installation to the sample holder. Native oxide layer was used as the surface of SiO₂/Si(001). α -6T molecules were deposited on these surfaces at room temperature to the nominal thickness of 4.5 nm at most. NEXAFS spectra of S-1s edge were measured with the facilities at BL-27A.

3 Results and Discussion

Figure 1(a) shows NEXAFS spectra at three incident angles of 3.5 nm film grown on GaSe. The spectrum at grazing incidence is dominated by the electronic transition to π^* states, while the spectrum at normal incidence is dominated by that to σ^* states. These spectral features do not change with the thickness. The transition moments for the transitions to π^* states and σ^* states are normal to the molecular plane and parallel to the long axis of the molecule, respectively. Angles between the transition moments and the surface can be quantitatively evaluated from the relationship between the peak intensities and the incident angles [3]. Thus obtained angles indicate that α -6T molecules are almost lying with the molecular plane inclining to the surface at 3.5 nm, and moreover the type of molecular orientation changes from the "flat lying" at initial stage to "edge on" above 2.5 nm.

Figure 1(b) shows NEXAFS spectra at three incident angles of 3.5 nm film grown on WSe₂. The spectrum is dominated by the transition to σ^* states at all incident angles. The peak intensity is the lowest at 55 degree

incidence. These spectral features do not change with the thickness. The result means that α -6T molecules are standing and aligned with the long axis of the molecule inclined for 35 degree from the surface normal.

From NEXAFS spectra of the film on SiO₂/Si(001), α -6T molecules are shown to be randomly standing on the surface. It is thus demonstrated that slightly different physical properties of layered semiconductor surfaces, such as lattice mismatch, surface roughness and so on, cause different molecular orientation and ordering.

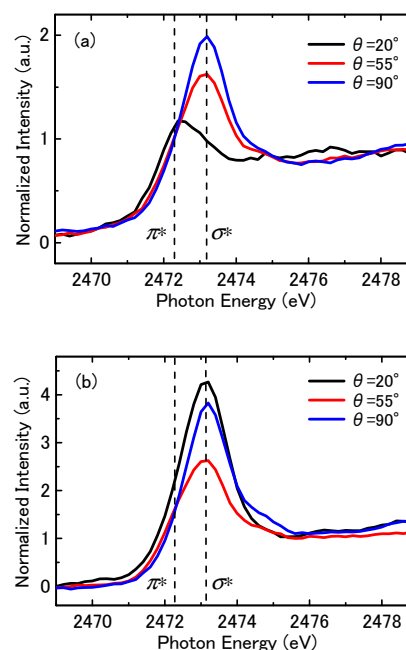


Fig. 1. NEXAFS spectra of 3.5 nm 6T films grown on (a) GaSe and (b) WSe₂.

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References

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