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Effective escape depth of photoelectrons for hydrocarbon films in total electron yield measurement at the C *K*-edge

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We performed X-ray Absorption Near Edge Structure (XANES) and Atomic Force Microscope (AFM) measurements for the system of multilayers, HTC (hexatriacontane, $n\text{-C}_{36}\text{H}_{74}$) / polyimide / Si, to determine an effective escape depth of photoelectrons, L_{eff} , in HTC films for total electron yield detection at C *K*-edge. Quantitative degrees of superposition of C *K*-edge spectra of a saturated hydrocarbon and a polyimide with aromatic rings were examined to obtain L_{eff} for HTC films. L_{eff} of *n*-alkane at the C *K*-edge has been determined to be 35 Å and spectroscopy agree closely.

Keywords: XANES, effective escape depth, total electron yield, hydrocarbon films, AFM

1. INTRODUCTION

When investigating molecular conformations and orientations in organic thin films by X-ray Absorption Near Edge Structure (XANES), also refer to as NEXAFS, we often need to pay attention to the escape depth L of materials, which depends on an electron-detection method. In the case of Auger electron yield mode for C *K*-edge, for example, C *KVV* Auger peak is observed at around 260 eV [Stöhr, 1992]. Since an electron energy dependence of the escape depth has been measured [Cartier et al., 1987] [Bain and Whitesides, 1989] [Laibinis, Bain and Whitesides, 1991], the escape depth of the Auger electron can be easily estimated as 20 Å. On the other hand, in total electron yield (TEY) mode of detection, which is also commonly used, photoelectrons suffer multiple scattering and exact escape depth is difficult to obtain due to the lack of information for secondary photoelectrons. The effective escape depth L_{eff} is assumed to be about 50 Å, it should strongly depends on the materials and their phases. Reliable information on L_{eff} for C *K*-edge TEY mode is still lacking.

In this study, we performed XANES and AFM measurements for multilayer systems to deduce the L_{eff} at C *K*-edge TEY mode. The sample used in our experiment was a HTC

(hexatriacontane, $n\text{-C}_{36}\text{H}_{74}$) / polyimide (biphenyl-3,3',4,4'-tetracarboxylic dianhydride type) / Si multilayer. A saturated hydrocarbon compound was chosen because it is one of the most fundamental organic materials, and can be used as a standard. Quantitative degrees of superposition of C *K*-edge spectra of HTC and polyimide with aromatic rings were evaluated to obtain L_{eff} .

2. EXPERIMENTAL

HTC was purchased from Tokyo Kasei Co, and purified by recrystallization from benzene solution. The multilayer-sample were prepared as follows: To begin with, polyimide / NMP (N-methyl-2-pyrrolidone) solution was spin-coated on a Si substrate. Then, HTC was evaporated on the polyimide. Three samples with different HTC thicknesses (#0: 0 Å, #1: 70 Å and #2: 94 Å) monitored by a quartz oscillator were prepared. C *K*-edge XANES spectra were taken at the BL-2B1 of UVSOR Facility at Institute for Molecular Science Okazaki with a Grasshopper monochromator (1800 lines/mm). Measurements were performed in TEY mode with normal incidence under a vacuum of 10^{-8} Pa range. AFM images of the sample were taken in dynamic force mode (DFM) not to damage the HTC layers. Ten AFM images ($10\mu\text{m} \times 10\mu\text{m}$) at different positions of each sample were taken and then averaged.

3. RESULTS AND DISCUSSION

In Fig. 1, we summarize C *K*-edge XANES spectra for various

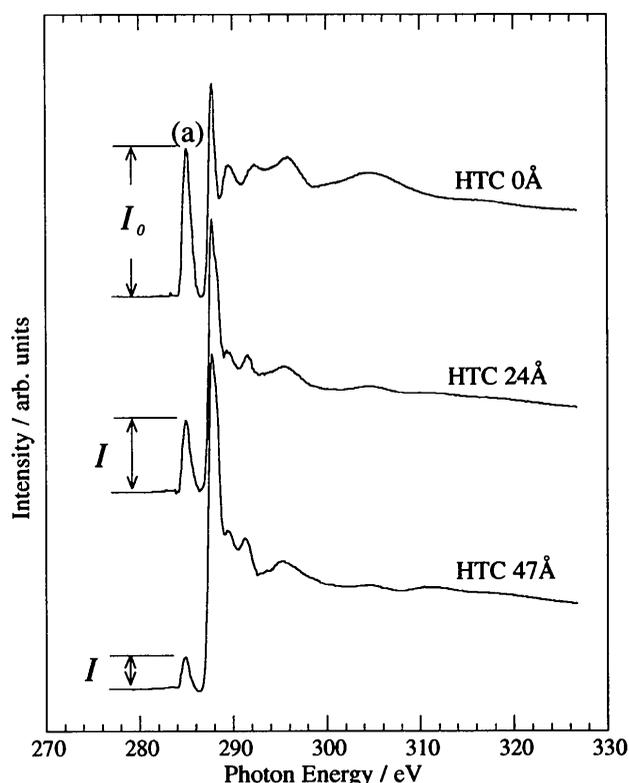


Fig.1
C *K*-edge XANES spectra for various HTC thicknesses. These thicknesses were monitored by quartz oscillator. I and I_0 are defined in this figure.

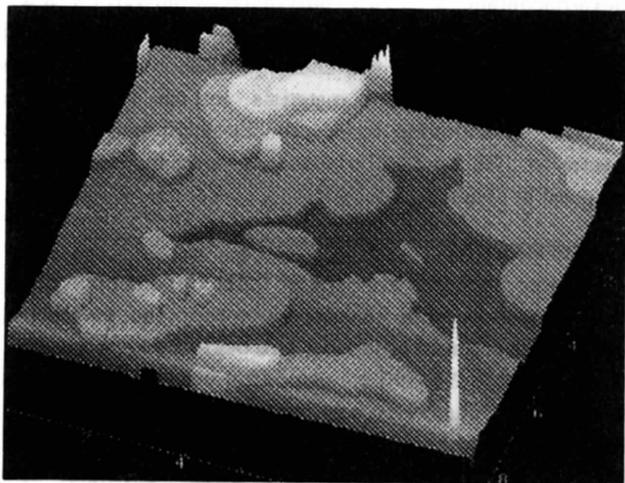


Fig.2
A typical example of AFM images of sample #1.

HTC thicknesses. Peak (a) has already been assigned as $C1s \rightarrow \pi^*(C=C)$ resonance [Schedel-Niedrig et al., 1991] [Jordan-Sweet et al., 1988], so this peak is originated from the polyimide layer. Figure.2 shows a typical example of AFM images of sample #1. Evaporated HTC molecules onto polyimide formed islands (or domains) with different thickness and the height of one step was nearly equal to 47 Å corresponding to a full length of HTC molecule. The values of L_{eff} were determined with use of a following formula ;

$$I/I_0 = \sum_{i=0} S_i \exp(-d \cdot i / L_{eff}) \quad (1)$$

where d is the thickness of one HTC layer (47 Å) and i is the number of the layers in the domain, respectively. S_i refers to the ratio of the domain size of corresponding thicknesses. Peak (a) intensity of samples #1 and #2 normalized by that of #0 (no HTC evaporated) gives I/I_0 . Values obtained are listed in Table 1. As a reference, we used the average thickness, d' and d'' , obtained from the quartz oscillator and the AFM image to deduce another L_{eff}' and L_{eff}'' with the following equation

$$I/I_0 = \exp(-d / L_{eff}). \quad (2)$$

As is shown in Table1, L_{eff} range from 30 Å to 39 Å. An experimental error of L_{eff} mainly comes from the inaccuracy in the evaluation of the domain size. These values are still quite reasonable when we consider XANES studies on the surface freezing effect of pentacontane (PC, $n-C_{50}H_{102}$) [Yamamoto et al., 1996], where a inclined PC monolayer is formed on top of the PC liquid phase for a couple of degrees. The tilt angle, $\sim 40^\circ$, of PC deduced from TEY measurement is greater than those, $\sim 30^\circ$ [Ocko et al., 1997], determined by X-ray diffraction. However, when account is taken of L_{eff} , the tilt angle from TEY measurement is about 35° and the agreement between the X-ray diffraction and TEY

Table.1
Obtained effective escape depths.

Sample	I/I_0	$L_{eff}/\text{Å}$	$d'/\text{Å}$	$L_{eff}'/\text{Å}$	$d''/\text{Å}$	$L_{eff}''/\text{Å}$
#1	0.107	39	70	31	101	45
#2	0.065	30	94	34	103	38

measurements improve considerably demonstrating the importance of determining escape length of photoelectrons which are used in detection method.

4. CONCLUSION

We determined the effective escape depth of photoelectrons, L_{eff} , in HTC films for total electron yield detection at C K-edge by XANES and AFM measurements for multilayers, HTC / polyimide / Si. We have found that the L_{eff} of n -alkane at C K-edge is approximately 35 Å. L_{eff} determined in this study is quite useful when we investigate organic thin films whose molecular orientation varies along its thickness direction, such as surface freezed layers of n -alkane. Tilt angles measured by X-ray diffraction and XANES are approximately same when L_{eff} is taken into account.

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