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Attenuation Lengths of Photoelectrons in BDN-SA Langmuir-Blodgett Films

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Based on the X-ray photoelectron spectroscopy(XPS) of monolayer and multilayer dithiolene(BDN) stearyl alcohol(SA) complex Langmuir-Blodgett films on silicon and gold substrate, respectively, we measured the attenuation lengths(ALs) of photoelectrons in BDN-SA LB films. Combined with the Atomic Force Microscopy(AFM) investigations, the results are discussed.

Keywords: Langmuir-Blodgett film; attenuation length; XPS; AFM

INTRODUCTION

X-ray photoelectron spectroscopy (XPS) has been extensively used to study Langmuir-Blodgett (LB) films and self-assembled monolayers(SAMs). One of the most important aspects of this procedure is knowledge of attenuation lengths(ALs) of electrons from a sample as a function of kinetic energy, which is one of the most important and practically useful parameters for experimental analysis of XPS data. There are three methods reported to deduce ALs for organic compounds: the overlayer method, the absolute intensity method and the electron take-off angle method.^[1-4]

In this paper, using the overlayer method and the electron take-off angle(ETOA) method, we present data for the attenuation of Au 4f_{7/2}, Au 4f_{5/2}, Au 4p_{3/2}, Au 4s and Si 2p photoelectrons (with kinetic energies of 1402, 1398, 1151, 940 and 1383eV respectively) from gold and silicon substrates on which BDN-SA LB films were deposited.

EXPERIMENTAL

Monolayer and multilayer LB films were deposited onto two substrates: silicon with a little surface oxide and gold. The gold substrate was prepared by magnetron sputtering of ~ 150 nm of gold onto silicon (100) wafers. The fabrication of LB film was described elsewhere.^[5] The LB films over a $\sim \text{mm}^2$ area was checked by UV-Vis-NIR analysis and small-angle X-ray diffraction. The results showed that the LB films have a well-defined layered structure.

The XPS spectra were collected on a V.G ESCALab.220i-XL photoelectron spectrometer with Al K α (1486.4eV) X-ray source with a 50eV pass energy and 1 mm² spot. The pressure of the sample chamber was less than 2×10^{-10} torr.

RESULTS AND DISCUSSIONS

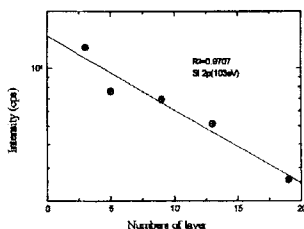


FIGURE 1 Si 2p(oxide) peak intensity vs. the number of layer for BDN-SA LB films (solid line is fitted result)

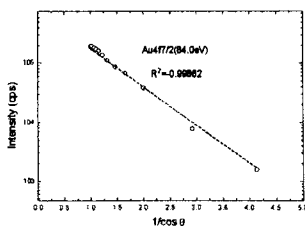


FIGURE 2 Au 4f peaks intensities as a function of the angle for a 11-layer BDN-SA LB films (dash line is fitted result)

To analyze the intensities of the substrate photoelectron peaks, we assume the equation:

$$I_s = I_s^0 \exp\left(-\frac{nd}{\lambda \cos \theta}\right) \quad \text{or} \quad \ln I_s = \ln I_s^0 - \frac{nd}{\lambda \cos \theta} \quad (1)$$

where I_s is the intensity of the substrate photoelectrons attenuated by n -layers, I_s^0 is the intensity of a clean substrate, n is the number of layers, d is the thickness of a

BDN-SA monolayer, λ is the electron ALs and θ is the angle between the surface normal and the analyzer axis. A graph of $\ln(I_0)$ against n (or $1/\cos\theta$) should yield a straight line with slope of $d/(\lambda\cos\theta)$ (or nd/λ), from which λ can be determined.

Figure 1 showed the Si 2p (oxide) intensity against n . Figure 2 showed the Au 4f_{7/2} peak intensity varies with $1/\cos\theta$. It appears that both Si 2p vs. n and Au 4f peak intensity vs. $1/\cos\theta$ agree with the equation (1). We also investigated the relation between Si 2p(oxide) intensity with $1/\cos\theta$ (ETOA method). Since the ETOA method is only applicable for substrates of essentially infinite thickness, no reasonable result was obtained from a very thin silicon oxide film on which Si 2p photoelectron line was analyzed. The ALs derived from the two plots are larger than the values calculated using Seah formula.^[6] We may attribute this enlargement of ALs to the existence of microcrystalline domains and pinholes on the LB films, which was confirmed by our AFM study^[7] (see Fig.3). In calculation here, we employed the d value obtained from XRD. However, as shown in Fig.3, a great difference in thickness of the LB films exists on nanoscale. Systematic experiments on the effects of defects are needed in order to clarify all the AL-influencing factors.

The linear correlation of the ALs of photoelectron in BDN-SA LB films with the kinetic energy was also obtained (figure omitted), which is in agreement with results of Bain.^[3]

The value of AL 32.5nm derived from the data for Si substrate is smaller than AL value 40.2nm estimated from the data for gold substrate. This result is not in good agreement with the Seah equation^[6] since the difference between the kinetic energy (E) of Si 2p (1383eV) and Au 4f_{7/2} (1396eV) is quite little. It is known that the surface roughness of substrate will cause an overestimation of AL at low take-off angles^[6]. Our AFM results revealed that surface roughness of Si is less than 5nm, while that of gold substrate is about 60nm ($1 \times 1\mu\text{m}^2$). And a large surface roughness will induce a relatively large surface area, consequently reduce the surface coverage. That means the area fraction of holes in LB films on Au is larger than that on Si. According to the model proposed by Suzuki^[2], a large area fraction of holes will lead to a large AL.

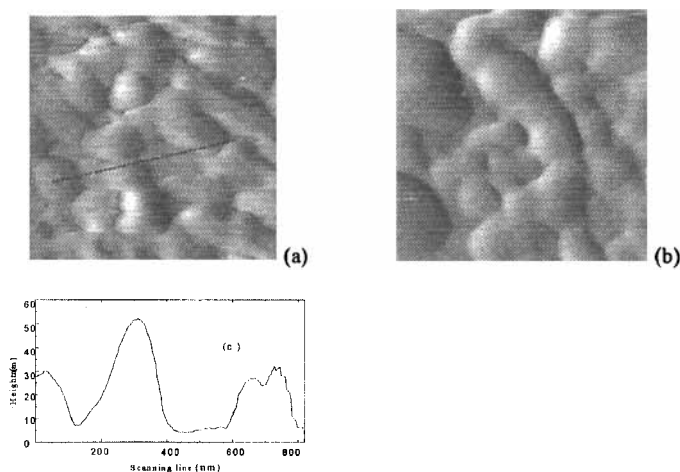


FIGURE 3 AFM images ($1 \times 1 \mu\text{m}^2$) of (a) 3-layer BDN LB films on Silicon, (b) 5 layer LB films gold, and (c) height profiles along a line marked as solid line showed in image (a).

CONCLUSIONS

We estimated the attenuation lengths of photoelectrons of monolayer and multilayer of BDN-SA LB films using the overlayer method and ETOA method. It is found that the ALs of photoelectron in BDN-SA LB films depends on the substrates. We suggested that the varied attenuation lengths might result from the existence of the pinhole defects in the LB films and surface roughness of substrate, based on AFM images analysis.

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