A Method for Absolute Determination of the Surface Areal Density of Functional Groups in Organic Thin Films[†]

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To develop a methodology for absolute determination of the surface areal density of functional groups on organic and bio thin films, medium energy ion scattering (MEIS) spectroscopy was utilized to provide references for calibration of X-ray photoelectron spectroscopy (XPS) or Fourier transformation-infrared (FT-IR) intensities. By using the MEIS, XPS, and FT-IR techniques, we were able to analyze the organic thin film of a Ru dye compound ($C_{58}H_{86}O_8N_8S_2Ru$), which consists of one Ru atom and various stoichiometric functional groups. From the MEIS analysis, the absolute surface areal density of Ru atoms (or Ru dye molecules) was determined. The surface areal densities of stoichiometric functional groups in the Ru dye compound were used as references for the calibration of XPS and FT-IR intensities for each functional group. The complementary use of MEIS, XPS, and FT-IR to determine the absolute surface areal density of functional groups on organic and bio thin films will be useful for more reliable development of applications based on organic thin films in areas such as flexible displays, solar cells, organic sensors, biomaterials, and biochips.

Key Words : Organic thin films, Functional group quantification, MEIS, XPS, FT-IR

Introduction

Recently, applications of organic and bio thin films in areas such as flexible displays, solar cells, organic sensors, biomaterials, and biochips have been intensively studied. The performance of these films in terms of sensing and bio-compatibility are mainly determined by surface functional groups, and as such, to increase performance reliability and extend general knowledge in these areas, quantitative determination of the surface areal density of functional groups on organic and bio thin films is important. Although a number of surface analysis techniques with molecular chemical specificity have been applied to do this,[1-5] these efforts have been unsuccessful because of the difficulty of determining the relativity sensitivity factors (RSFs) of the functional groups. For example, most of the RSF values used for x-ray photoelectron spectroscopy (XPS) analysis are for elemental analysis so that XPS cannot quantitatively measure the surface areal density of functional groups on organic and bio thin films, despite the molecular chemical information on the surface functional groups that XPS provides. Other techniques, such as Fourier transformation infra-red (FT-IR) spectroscopy and secondary ion mass spectrometry (SIMS), that are widely used for molecular chemical analysis of organic and bio thin films are also inadequate for producing a quantitative analysis of surface functional groups.

In this study, we develop a methodology for the absolute determination of the surface areal density of functional groups on organic and bio thin films by using medium energy ion scattering (MEIS) spectroscopy to provide references for calibration of XPS or FT-IR intensities. MEIS is especially useful to determine the absolute surface areal density of atomic elements with high atomic numbers, since MEIS analysis is based on ion scattering cross sections accurately predicted by the coulomb interactions.[6] Using MEIS, XPS, and FT-IR, we analyzed an organic thin film of a Ru dye compound (Ru atom and various functional groups in a stoichiometric compound), from which the absolute surface areal density of Ru atoms (or Ru dye molecules) could be determined. The surface areal densities of stoichiometric functional groups in the Ru dye compound were used as references for the calibration of XPS and FT-IR intensities for each functional group.

For a more reliable development of biochips and surface modification of biomaterials, we propose here that the complementary use of MEIS, XPS, and FT-IR can be a new methodology to determine the absolute surface areal density of functional groups on organic and bio thin films.

Experimental

Fabrication of Organic Thin Layers. To fabricate an organic thin layer, a Ru dye complex that includes various functional groups was employed. In particular, Ru 535 bis-TBA (*cis*-bis(isothiocyanato)bis(2,2'-bipyridyl-4,4'-dicarboxylato)-ruthenium(II) bis-tetrabutylammonium) is a stable organic dye material widely used as a sensitizer in solar cell
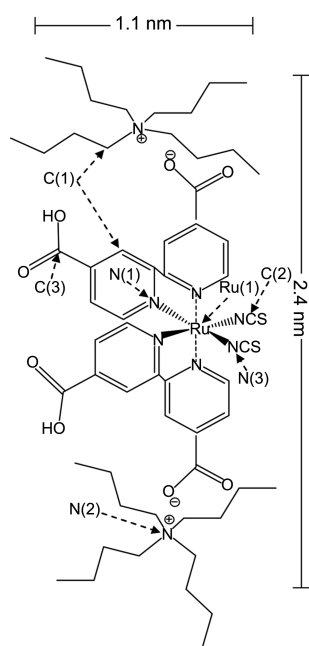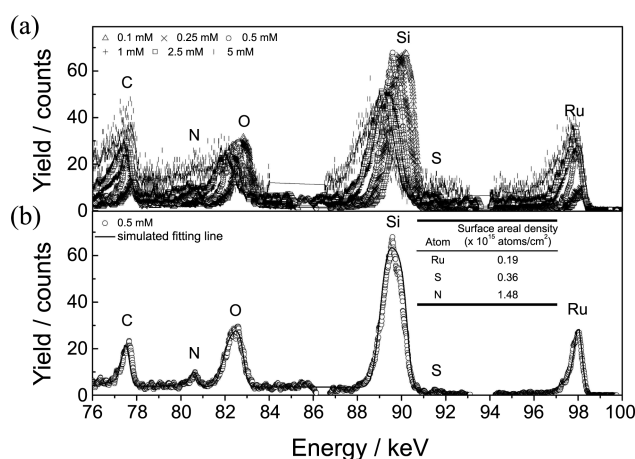

Figure 1. Molecular structure of a Ru 535 bis-TBA (N719, *cis*-bis(isothiocyanato)bis(2,2'-bipyridyl-4,4'-dicarboxylato)-ruthenium (II)bis-tetrabutylam-monium; $C_{58}H_{86}O_8N_8S_2$ Ru) dye complex. Ruthenium, carbon, and nitrogen atoms in major functional groups are marked with Ru(1), C(1)-C(3), and N(1)-N(3), respectively. The average size of Ru 535 bis-TBA was calculated to be by using molecular mechanics simulation.

Figure 2. (a) MEIS spectra for Ru thin layers produced by spin coating Ru dye solutions with different concentrations onto SiO_2/Si(100) substrates. (b) MEIS spectrum and simulated fitting line for 0.5 mM concentration.

based TiO_2 nanoparticles.[7,8] Figure 1 shows the molecular structure of a Ru 535 bis-TBA complex molecule. Reproducible organic layers were made on 2-3 nm thermal oxide layers grown on Si wafers by spin-coating, and the thickness of each layer was controlled by varying the concentration of the Ru dye compound dissolved in ethanol solvent. The Ru 535 bis-TBA was purchased from Solaronix. Si wafers were treated in a super-piranha solution (1:10:6) 61% HNO_3:30% H_2O_2:95% H_2SO_4 (v/v/v) as discussed elsewhere[9] for cleaning heavy organic contamination prior to the fabrication of the organic films. A 500 μL droplet each of Ru dye solution with varying concentrations of 5 mM, 2.5 mM, 1 mM, 0.5 mM, 0.25 mM, and 0.1 mM was dropped over silicon wafer (5×5 cm^2) specimens spun at 5000 rpm for 20 s.

MEIS Analysis for Absolute Determination of the Surface Areal Density of Atoms. MEIS analysis was performed by a MEIS system at KRISS, with a proton beam accelerated at 100 keV. The incident ions were along [111] in the (001) plane of a crystalline Si substrate and the scattering ions were along [00$\bar{1}$] with a scattering angle of 125° in double alignment in order to eliminate the backscattering signal from the crystalline Si substrate. The electronic energy loss of 100 keV protons was in the range of 300 eV/nm and could be measured precisely with a toroidal electrostatic analyzer with an energy resolution of 100 eV.[10,11] By using the ion scattering analysis program by Kido,[12-14] absolute surface areal densities of elements for an ultra-thin film could be determined from the MEIS spectrum. In order to determine the absolute areal densities of Ru, Ru peak was normalized
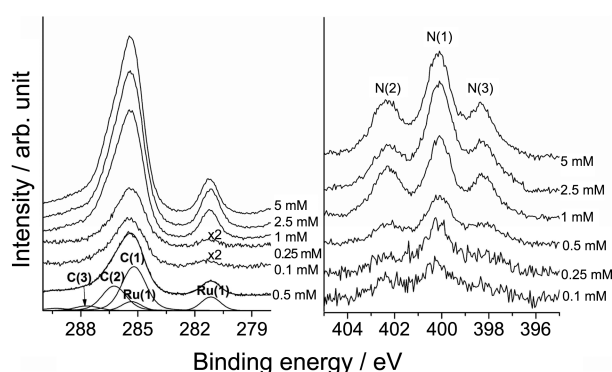
by Si peak originating from SiO_2 surface layer grown by thermal oxidation. Therefore, the stoichiometry of the thermal SiO_2 is the base of the MEIS calibration, which is commonly used in MEIS analysis.[15]

MEIS spectra of organic thin films containing Ru and fabricated by spin-coating Ru dye solutions with concentrations of 5 mM, 2.5 mM, 1 mM, 0.5 mM, 0.25 mM, and 0.1 mM are shown in Figure 2(a). The Si peaks are from Si atoms in silicon oxide surface layers grown by thermal oxidation in a furnace. As the concentration of the Ru dye solutions increased, the Ru and C peaks became elevated. The increased background at the lower energy side of the Ru peak reflects the formation of flat multilayer thin films for Ru dye concentrations below 1 mM. A similar change at the lower side of the C peak can be seen for the 2.5 mM and 5 mM MEIS spectra. With the thickening of the Ru dye organic thin films, Si and O peaks are shifted into low energy due to the increased energy loss of the scattered proton ions in the Ru dye thin films. The broadened Si and O peaks are due to the increased straggling of the electronic energy loss. By using the Kido simulation for the MEIS spectrum, a simulated MEIS spectrum for 0.5 mM was obtained and compared with the measured one, as shown in Figure 2(b). The surface areal densities of Ru, S, and N, calculated from the simulation, are also given at the inner table in Figure 2(b). The ratios of S and N to Ru are 1.89 and 7.79, respectively. These values are consistent with the stoichiometric values (*i.e.*, 2 for S and 8 for N) of a Ru 535-bisTBA compound ($C_{58}H_{86}O_8N_8S_2Ru$) to within 5%. Furthermore, the areal density of Ru was determined to lie within an error of 5% by MEIS simulation based on a comparison of the two spectra, calculated and measured.[16] The simulation results for the Ru densities are exhibited in Table 1. It should be mentioned that the Kido simulation code cannot be used for a 3D island structure and the estimated error of 5% depends on the counting statistics. Therefore, the Ru densities for 2.5 mM and 5 mM are approximate value and the errors for the low concentration samples are higher than 5%.

Table 1. Measured Ru densities, the number of layers[a] and thicknesses[b] of Ru dye thin films

Concentration/ mM	Ru Density /× 10^15 cm^−2	Number of Layers	Tickness/ nm	
0.10	0.05	~1	~2.0	Monolayer
0.25	0.07	~2	~2.8	Multilayer
0.50	0.19	~5	~7.6	Multilayer
1.00	0.26	~7	~10.4	Multilayer
2.50	0.38	~10	~15.2	3D Island
5.00	0.56	~14	~22.4	3D Island

[a]The number of layers was calculated from dividing the measured Ru density by the areal density of Ru atoms (or Ru molecules) in a monolayer (0.04×10^{15} cm^{-2}). [b]The thickness was calculated by multiplying the number of layers by the average size (1.6 nm) of a Ru molecule.

Figure 4. Fitting plots of XPS intensities of (a) Ru(1), C(1)-C(3), and (b) N(1)-N(3) against Ru density by MEIS.
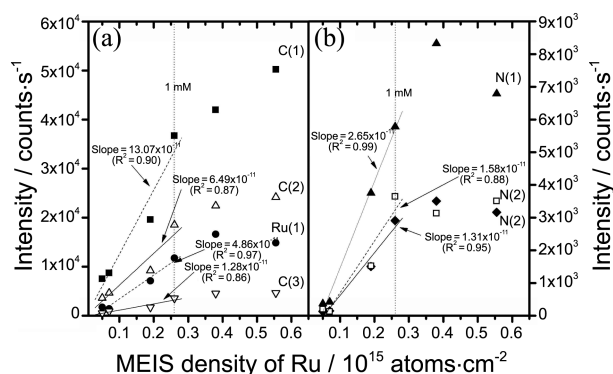

Figure 3. (a) C 1s, Ru 3d, and (b) N 1s XPS spectra for Ru thin layers produced with varying concentrations. The C 1s peak was deconvoluted into three C peaks originating from different functional groups such as C-C (C(1)), CN or NCS (C(2)), and COO (C(3)), and the branching peak Ru 3d3/2 of Ru 3d5/2 from N_6Ru (Ru(1)). Also, N 1s had three peaks corresponding to nitrogen in three different groups of C_2NRu (N(1)), C_4N^+ (N(2)), and NCS (N(3)).

The size of a Ru 535 bis-TBA molecule as shown in Figure 1 was estimated by a molecular mechanics simulation.[17] Based on the average size (1.6 nm) of the molecule, the areal density of Ru atoms (or Ru dye molecules) in a monolayer was calculated to be 0.04×10^{15} cm^{-2}.

Results and Discussion

A Ru 535 bis-TBA molecule has various functional groups as shown in Figure 1. XPS spectra were obtained using a hemispherical electron analyzer (VG-Scienta SES100) and a photoelectron spectrometer equipped with a Mg Kα source producing a photon energy of 1253.6 eV. Each core level spectrum was collected with a pass energy of 50 eV and step energy of 0.05 eV. The dwell times were 3.99 s for carbon and ruthenium atoms, and 25.5 s for nitrogen atom. Using a relatively low-power x-ray source of 300 W, there was no detectable degradation effect for XPS analysis.

In Figure 3(a), a doublet with the constant spin-orbit splitting (with width of 4.17 eV[18]) was taken into consideration for the Ru 3d peak, and the branching peak Ru 3d3/2 was subtracted to calculate C 1s peak area with the Shirley

background correction method. The C 1s signal can be also deconvoluted into three C peaks originating from different functional groups such as C-C (C(1)), CN or CNS (C(2)), and COO (C(3)) at the binding energies of 285.0, 286.2, and 288.8 eV, respectively. Also, N 1s spectra had three peaks corresponding to nitrogen in three different groups of C_2NRu (N(1)), C_4N^+ (N(2)), and NCS (N(3)) at 400, 402.5, and 398 eV, respectively. Our assignment for the binding energies of carbon and nitrogen is consistent with a former study.[19]

The XPS intensities of Ru 3d (Ru(1)), C 1s (C(1)-C(3)), and N 1s (N(1)-N(3)) versus the surface areal densities of Ru atoms from MEIS analysis for the same samples are plotted in Figure 4. The XPS intensities are linear to the MEIS intensity until 1 mM and show curves thereafter. This behavior would be due to a limited attenuation length of the photoelectrons in XPS. The effective attenuation lengths of C 1s, N 1s, and Ru 3d photoelectrons in Ru 535 bis-TBA compounds are estimated to be around 3.0 nm,[20] which is almost the same order of molecular size. However, taking into account the loosely-packed molecules on the spincoated film surface, the real attenuation length could be longer than the calculated value. Above 10 nm at 1 mM, the XPS intensities can no longer be fitted by a linear plot. From each slope in the linear region, the calibration factors (CFs) of the Ru atoms and functional groups can be calculated according to the following equation,

$$CF_a = \frac{\text{XPS intensity}}{\text{Areal density of functional group}} = \frac{\text{slope}_a}{N_a}$$

where N_a is the number of a specified functional group in a molecule. These CFs are given in Table 2. The relative atomic percentage values of Ru, C, and N in each functional group obtained are consistent with the stoichiometric fractions of them as shown in Table 2. Taking into account the complexity of the Ru-535 molecule as well as the preparation procedure in liquid phase, each calibration factor was similar within uncertainty of about 10%.[21] The ratio CF(N):CF(C) is 1.8, which is in a reasonable range under the current XPS setup according to the literature.[22] In principle, relative sensitivity factor (RSF) databases which are reported in those literatures may be very effective for analyzing similar

Table 2. Calibration factors (CFs), calibrated atomic concentrations of 0.5 mM Ru films, and stoichiometric fractions in a Ru 535-bisTBA molecule

| XPS Atomic bands		Functionsl groups	Calibration factors (CFs) /× 10^{-11} counts cm^2·atoms^{-1}·s^{-1}	Concentration (%) calculated by CF	Stoichiometric fraction (%)
Ru 3d	Ru(1)	N6Ru	4.86	1.52	1.49
C 1s	C(1)	C-C	0.36	56.73	53.75
	C(2)	CN, NCS	0.36	26.53	26.87
	C(3)	COO	0.32	5.61	5.97
N 1s	N(1)	C2NRu	0.66	5.87	5.97
	N(2)	C4N+	0.79	1.99	2.99
	N(3)	NCS	0.65	2.39	2.99
Total				100	100

samples using the relevant instrument with the accuracy limited to ± 5-10%, based on the analysis of stoichiometric compounds.[23] Therefore, it can be proposed that the XPS intensities of each functional group in any similar organic thin films can be converted to the surface areal densities using CFs.

IR vibration spectra were measured with a FT-IR (Thermo electron, Nicolet 6700) equipped with a LN-cooled mercury-cadmium-telluride detector. The IR beam was focused on one end of the beveled wafer after which the transmitted beam was delivered to the detector using two gold mirrors. All spectra were averaged at 256 scan with 4 cm^{-1} resolution with a stream of N$_2$ gas. A P-type double-side polished Si(100) wafer (resistivity ~2 Ω·cm) was used as a substrate. The Si wafer was cut to 55 mm × 10 mm × 0.58 mm, and each end was beveled to be parallel at 45°, and polished using a 0.3 μm alumina lapping film (3 M) to achieve an internal reflection of > 100 times.

FT-IR spectra of five Ru films are presented in Figure 5(a). Each spectrum in the range of 1650-2250 cm^{-1} was deconvoluted by fitting with five Gaussian modes using the regularized method of deconvolution in Figure 5(b). The major peaks at 2100 cm^{-1} and 1716 cm^{-1} in this spectra were assigned to the stretching vibrations modes of –N=C=S and

C=O, respectively.[24] The corrected absorbance of –N=C=S and C=O peaks by deconvolution are plotted in Figure 5(c). The fitting lines show a good linearity (R^2 = 0.993 for –N=C=S and 0.996 for C=O, respectively) between absorbance and Ru densities measured by MEIS experiments, without a limitation of attenuation length. As shown by XPS analysis, FT-IR CFs for the two functional groups –N=C=S and C=O could also be calculated to be 3.49 × 10^{-15} OD·cm^2·atoms^{-1} and 0.87 × 10^{-15} OD·cm^2·atoms^{-1}, respectively, according to Eq. (1). With these CFs, the ratio of absorbance of –N=C=S and C=O for 1 mM Ru thin film were calibrated to be 0.49 and 0.84, and their ratio (0.58) was consistent with the stoichiometric ratio (0.5).

The proposed methodology for absolute determination of surface areal functional densities is demonstrated for organic layers made of a Ru dye compound. Presumable, it can be extended to other metal containing bio-organic compounds. Calibration factors for XPS or FT-IR can be determined from reference samples of known surface areal densities of functional groups determined with MEIS analysis of thin films grown with a metallo-organic compound with constituents of metallic elements and various stoichiometric functional groups with varying concentrations. Reference samples can be produced and disseminated by standards laboratory with MEIS capabilities. Calibration factors estimated from the slope of XPS and FT-IR intensities corresponding to each functional group versus absolute surface areal densities of metallic elements can be used to convert XPS and FT-IR intensities into surface areal densities of functional groups. The calibration factors determined from a metallo-organic compound can be used for other bio-organic thin films such as biochips and biomaterials. Limitations on the range of bio-organic thin films that the calibration factors determined by a metallo-organic compound can be applied would be given by matrix effects.[25] Matrix effects in different bio-organic thin films are presumably not severe, since most of the constituents are carbon, nitrogen, and oxygen in general. More detailed studies on the effect of matrix effects are required. However, the possibility that XPS intensities be converted into absolute areal densities of functional groups is clearly demonstrated in this report. The thickness of the organic film should be less than the effective electron attenu-
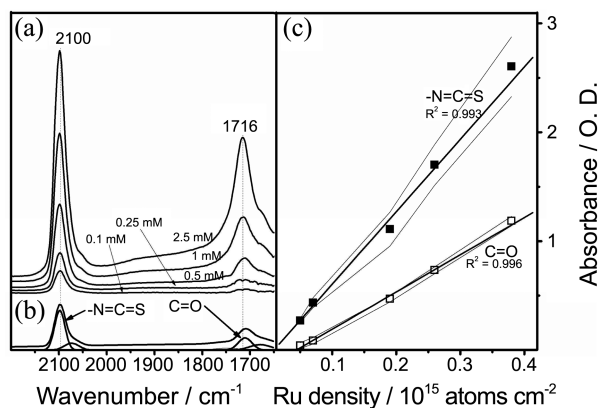
Figure 5. (a) FT-IR spectra of five Ru films in the range of 1650 cm^{-1} to 2250 cm^{-1} (b) deconvoluted spectrum, and (c) plots of IR absorbances of –N=C=S band and C=O band against Ru densities obtained from MEIS analysis.

ation length for XPS. The proposed methodology for XPS can be used for organic thin films thinner than the effective attenuation length and that for FT-IR can be used for thicker organic films (up to 0.5 μm).

Conclusion

We propose a methodology for absolute determination of the surface areal density of functional groups on organic and bio thin films based on the complementary use of MEIS, XPS, and FT-IR. From the analysis of an organic thin film of a Ru dye compound, it was demonstrated that the surface areal densities of functional groups in the Ru dye compound determined by MEIS can be used for the calibration of XPS and FT-IR intensities for each functional group. The proposed methodology to determine the absolute surface areal density of functional groups on organic and bio thin films will be useful for a more reliable development of biochips and surface modification of biomaterials.

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