Charge referencing of XPS spectra from fluorocarbon polymer films using fluorine as an internal standard

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A charge referencing method for the correction of differential charging effects using an internal standard has been studied. Correction based on the simple model is demonstrated to be practically useful for the quantitative analysis of distorted C 1s spectra from fluorocarbon polymer films. The validity of the present approximation is due to the relatively small influence of the vertical differential charging compared with the lateral one.

1. Introduction

Surface analysis of fluorocarbon films using XPS is increasingly used in the research of ULSI fabrication process such as oxide etching in fluorocarbon plasmas and deposition of low dielectric interlayer films as well as in the conventional field of chemical-resist coatings. Since fluorocarbon is an insulator, surface charging during measurements often causes serious broadening and distortion of spectra, and hence many researchers have given up interpreting XPS spectra from thick films. Spectrum deformation is actually due to the differential charging (DC) and is reported to be prominently observed especially when using a focused monochromated X-ray source or when the sample is so thin that significant leak current may flow to the conducting substrate [1-7]. In this paper, we have examined the charge referencing method for the correction of DC effects using an internal standard and discuss its usefulness.

2. Experimental

Fluorocarbon polymer films were deposited on 1 cm^2 platinum substrates from C_4F_8 by inductively coupled plasma enhanced chemical vapor deposition (ICP-CVD) at a pressure of 10 mTorr and 13.56 MHz RF power of 500 W. Film thickness was measured using a stylus profilometer or estimated from the intensity attenuation of photoelectrons from the substrate. Samples were analyzed ex-situ using ULVAC-PHI model 1600 with a monochromated Al K_α X-ray source after confirming that the surface potential of samples reached its steady state. Unless otherwise stated, the conditions — X-ray spot size 2 mm×3 mm (rugby ball shape), aperture size of the energy analyzer 0.8 mmϕ, CHA pass energy 11.75 eV, energy resolution < 0.1 eV and, a take-off angle of sampled photoelectrons 45°— were chosen for the data acquisition. Samples were fixed on the grounded metallic holder. Measured spectra were analyzed after subtracting Tougaard-type backgrounds.

3. Results and Discussions
3.1. Model of the samples with differential charging

We denote F 1s and C 1s spectra from the ultrathin film, that is, with no charging influence as $f_F(E)$ and $f_C(E)$, respectively. Since the C 1s spectrum from the fluorocarbon polymer is a sum of component peaks attributed to chemical bonds of C-C, C-CFx, CF, CF_2 and CF_3,

$$f_C(E) = X_{C-C}f_{C-C}(E) + X_{C-CFx}f_{C-CFx}(E)$$
$$+ X_{CF}f_{CF}(E) + X_{CF_2}f_{CF_2}(E) + X_{CF_3}f_{CF_3}(E)$$
$$= \sum_j [X_{C(j)}f_{C(j)}(E)],$$

where index j represent individual components of C-C, C-CFx, CF, CF_2 and CF_3, and $X_{C(j)}$ is the concentration of each component.

The distorted spectrum due to differential charging is modeled as a sum of peaks from the N blocks which differ by their potential as illustrated in Fig. 1. Then F 1s and C 1s spectra from charged samples can be described as follows.
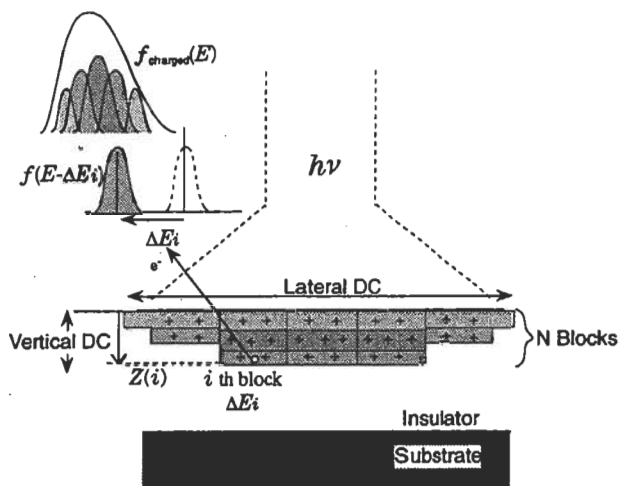
Fig. 1 The model for the explanation of the distorted spectrum due to differential charging. The model in ref [1] is modified with the concept of vertical differential charging.

$$f_{\mathrm{F,charged}}(E) = \sum_{i}^{N} k_i f_{\mathrm{F}}(E - \Delta E_i) \exp(-z(i)/\lambda_{\mathrm{F}}(E)\cos\theta)$$

$$f_{\mathrm{C,charged}}(E) = \sum_{i}^{N}\sum_{j} k_i [X_{\mathrm{C}(j)} f_{\mathrm{C}(j)}(E - \Delta E_i)$$

$$\times \exp(-z(i)/\lambda_{\mathrm{C}}(E)\cos\theta)]$$

As a first approximation, we neglect the vertical DC. Then the terms concerning to the attenuation can be omitted, and hence

$$f_{\mathrm{F,charged}}(E) = \sum_{i}^{N} A_i f_{\mathrm{F}}(E - \Delta E_i)$$

$$f_{\mathrm{C,charged}}(E) = \sum_{i}^{N}\sum_{j} A_i [X_{\mathrm{C}(j)} f_{\mathrm{C}(j)}(E - \Delta E_i)]$$

Since A_i depends on the volume of the ith block at the potential of ΔE_i and represents the spatial distribution of charging, we would call A_i as DC contribution factor in this paper.

In the practical analysis procedure, it is convenient to express distorted spectra as a sum of the spectra from the blocks at the different charging potentials ΔE as follows.

$$f_{\mathrm{F,charged}}(E) = \sum_{\Delta E} B(\Delta E) f_{\mathrm{F}}(E - \Delta E)$$

$$f_{\mathrm{C,charged}}(E) = \sum_{\Delta E}\sum_{j} B(\Delta E)[X_{\mathrm{C}(j)} f_{\mathrm{C}(j)}(E - \Delta E)]$$

First the coefficient $B(\Delta E)$ is derived from the curve fitting of measured F1s spectra using the charging-free F1s spectrum shape. Then these $B(\Delta E)$ values are convoluted to the each standard component peaks of C1s. Finally the ratio of each component peaks in C1s, i.e., $X_{\mathrm{C}(j)}$ is evaluated by the fitting of measured C1s spectra with the charging convoluted component peaks. In other words, peaks in C1s spectra were separated with

the convolution of the DC contribution factor derived from internal standard of F 1s.

3.2. Deformation of measured spectra due to differential charging

a. Effects of fluorocarbon film thickness

Figure 2 shows raw F 1s and C 1s spectra from samples with various thickness. Neither charging shift nor peak broadening were observed for the spectra obtained from films deposited within 10 sec. F 1s and C 1s spectra from these very thin films were used as standard spectra for charging correction, and were well fitted by Gaussian-Lorentzian mixed functions. Then peak energy of F 1s was 688.4 eV, and C 1s spectra comprised of C-C, C-CFx, CF, CF$_2$ and CF$_3$ peaks at 285.2, 287, 289.3, 291.4 and 293.5 eV, respectively. The shift of F 1s peak position and polymer film thickness are plotted against deposition time in Fig. 3. Charging shift was observed for the samples thicker than 20 nm. With the increase of film thickness both C 1s and F 1s spectra linearly shifted towards the higher binding energy due to the positive charging caused by photoelectron emission. F 1s spectra showed the asymmetric peak with the
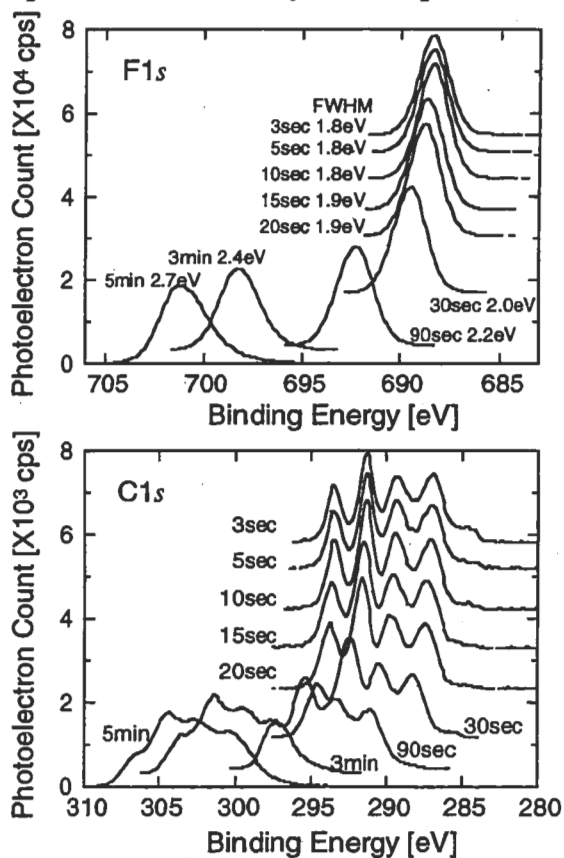

Fig. 2 Evolution of F 1s and C 1s photoelectron spectra from fluorocarbon polymer films with deposition time.
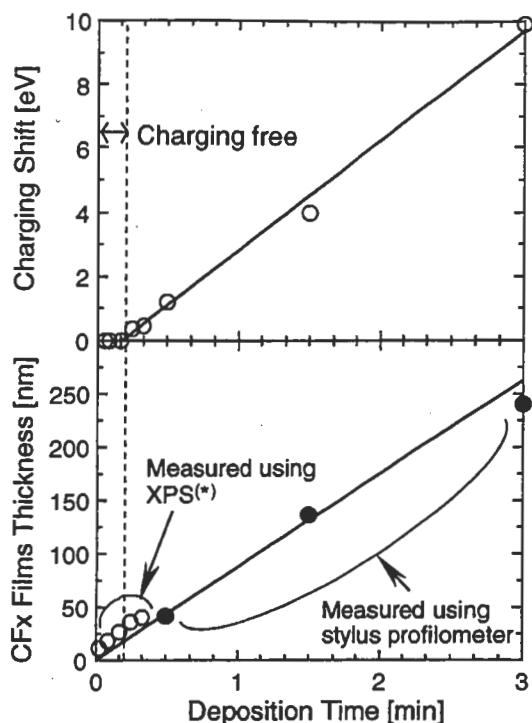
Fig. 3 Charging shift and polymer film thickness plotted against the deposition time. As for very thin films, thickness was evaluated assuming the attenuation length of $\lambda = 6$nm.
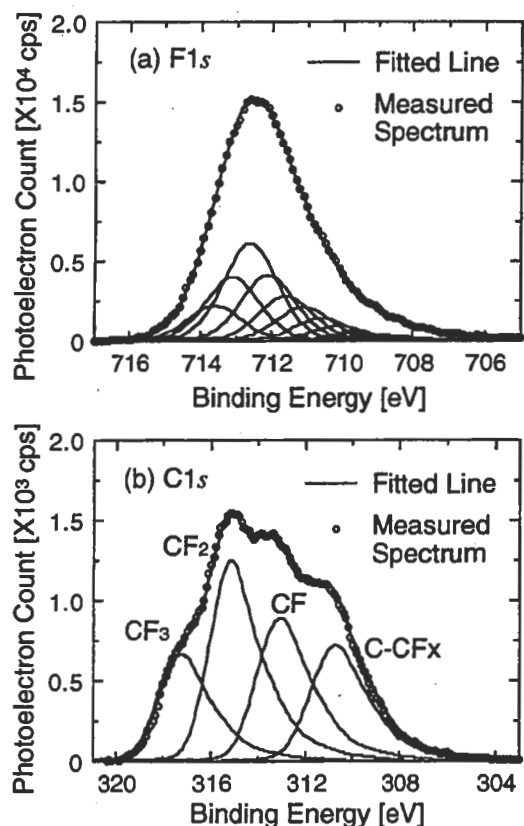

Fig. 4 (a) Derivation of DC factor from the F 1s spectrum.

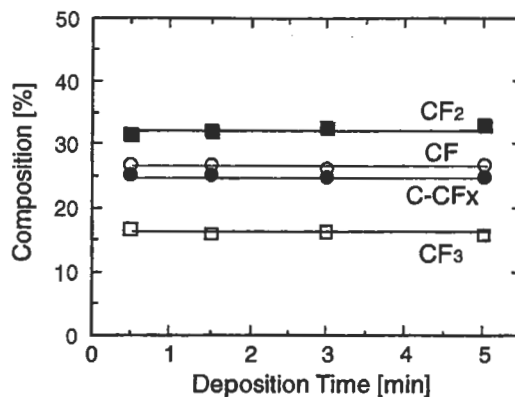(b) Peak separation of the C 1s spectrum by considering differential charging effect.

Fig. 5 Estimated composition of each component of C 1s spectra revealed no chemical structure change of the films with deposition time.

tail towards low binding energy, while shapes of C 1s spectra gradually varied as if the chemical structures changed with the film thickness.

Figure 4 shows an instance of the derivation of DC factor from the F 1s spectrum and the peak separation of the C 1s spectrum with the convolution of DC factor, as explained in the section 3.1. Here the energy resolution for the charging calibration was 0.5eV, namely, ΔE was incremented by every 0.5eV. The result of quantitative analysis of C 1s spectra after charging correction is shown in Fig. 5. As is expected, the estimated ratios of individual components of C 1s spectra revealed that the chemical structures in the polymer films does not change with the film thickness, i.e. C-CF$_x$: CF: CF$_2$: CF$_3$ = 24: 26: 33:17.

b. Effects of photoelectron sampling area

Figure 6 shows the change of measured spectra with the aperture size of electron energy analyzer, i.e. circular shape with the diameter of 0.4 mmϕ or 0.8 mmϕ or a rectangular shape with the dimension of 0.8 mm × 2 mm. The photoelectron sampling area is almost 1.5 times as wide as the aperture area. For the case of small aperture size, photoelectrons emitted from the central area of the X-ray irradiated spot are sampled [3], therefore, peak shift is relatively larger due to the high-flux density of X-ray and the consequent heavy charging, while deformation of spectra is suppressed due to the reduced potential distribution in the sampling area. On the contrary, in the case of large aperture size, photoelectrons emitted from the peripheral region, where X-ray flux density is lower and, therefore, charging is relatively small, are also sampled, resulting in wide broadening of spectra. Figure 7 demonstrates again the effectiveness of
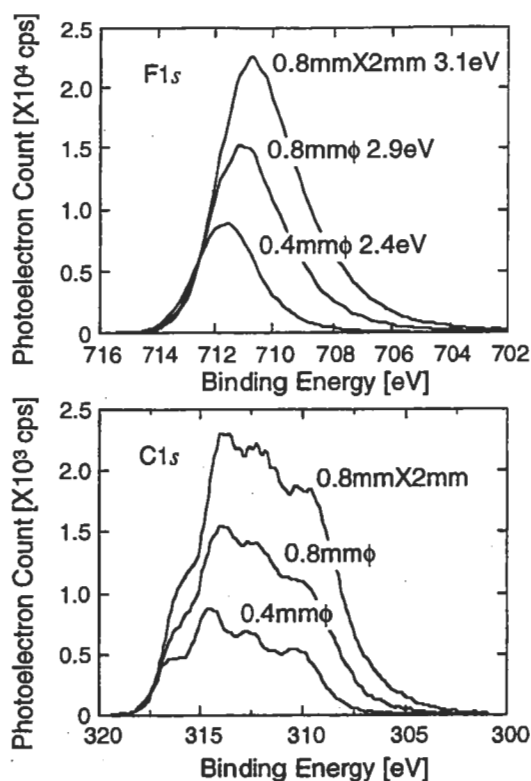
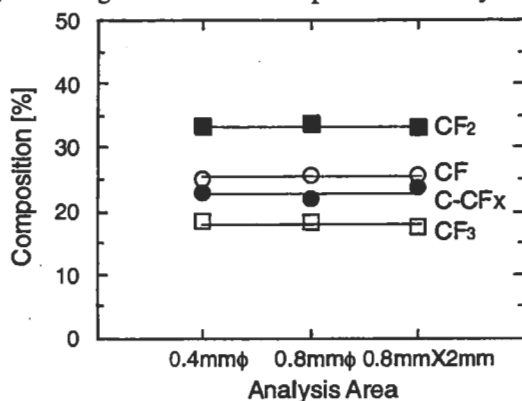Fig. 6 Change of F 1s and C 1s spectra with analysis area.

Fig. 7 Estimated composition of each component of C 1s spectra for different analyzer aperture sizes.
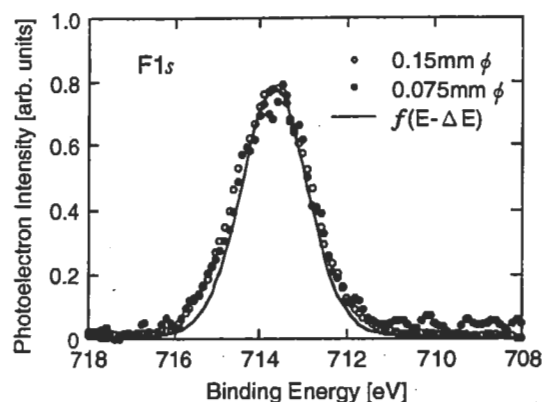
Fig. 8 When aperture size is small enough, the peak shape is no more affected by the aperture size. Slight peak broadening observed for the cases of such narrow sampling area is ascribed to the vertical differential charging effect.

Relatively small contribution of vertical DC on the distortion of XPS spectra than that of lateral one is the reason why the present rough approximation of neglecting vertical DC is practically effective with good accuracy.

the present charging correction method; individual components of C 1s spectra can be estimated from these spectra with the small dispersion within a few percent.

Figure 8 shows the F 1s peaks obtained with further smaller aperture size. Though such narrow sampling area is not preferable for the practical measurement of the C 1s spectrum whose ionization cross-section is relatively small, shapes of F 1s spectra are almost the same between the cases for 0.15 mmϕ and 0.075 mmϕ. This is because lateral potential distribution in such small sampling area is negligibly small. However, comparing with the imposed spectrum obtained from charging-free sample, slight peak broadening can be still recognized and is considered to be originated from the vertical DC.

4. Conclusion

Charge referencing of XPS spectra from fluorocarbon polymer films using fluorine as an internal standard has been applied to the samples with differential charging, and is demonstrated to be practically useful for the quantitative analysis of C 1s spectra, which gives significant informations of film structures. This approach is limited to the case where the influence of vertical differential charging is negligible compared with the lateral one, but is considered to be generally available for any multi-elemental insulators if containing at least one element with a defined binding energy.

References

[1] C. E. Bryson, III, Surf. Sci., 189/190, 50 (1987).

[2] T. L. Barr, J. Vac. Sci. Technol. A7(3), 1677 (1989).

[3] G. Beamson, D. Briggs, S. F. Davies, I. W. Fletcher, D. T. Clark, J. Howard, U. Gelius, B. Wannberg and P. Balzer, Surf. Interface Anal., 15, 541 (1990).

[4] G. Beamson, A. Bunn and D. Briggs, Surf. Interface Anal. 17, 105 (1991).

[5] A. Cros, J. Electron Spectrosc. Relat. Phenom., 59, 1 (1992).

[6] M. P. Seah, Practical Surface Analysis, Vol.1, Auger and X-ray photoelectron spectroscopy, 2nd Edn. (D. Briggs and M. P. Seah eds.), App.2, John Wiley & Sons (1990).

[7] X-r. Yu and H. Hantsche, Surf. Interface Anal. 20, 555 (1993).