

Non-destructive chemical depth-profiling by variable excitation energy XPS: TFAA derivatized allyl alcohol - ethylene plasma polymer films

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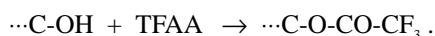
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Introduction

Sputter based methods of depth profiling cannot be used to obtain in-depth chemical state information because these will be usually destroyed by impinging energetic particles. Non-destructive depth profiling is possible by using photoelectron spectroscopy by a variation of the information depth of the method in the low nanometer range. This is possible because there is a correlation of the effective attenuation length (EAL) of electrons in a solid with their kinetic energy. A variation of the energy $h\nu$ of the exciting X-rays provides the possibility to adjust the kinetic energy of the photoelectrons and, by doing this, the EAL, too. For instance, the minimum of the EAL of C 1s photoelectrons in a polymer, ca. 1.2 nm, is obtained at around 350 eV X-ray photon energy.

The deposition of organic films from small organic molecules with the help of a pulsed plasma process is a technologically relevant topic earning more and more attention. Pulsed plasma processing was found to provide chemically rather well defined polymer layers [1]. There is a need for a chemical depth profiling of plasma polymers which must be, of course, undertaken without destruction of the surface chemistry. One question is whether there is a certain kind of –OH group depth profile for a plasma deposited (co-)polymer or a homogeneous distribution. In order to enhance the analytical sensitivity of XPS usually –OH groups are marked by a derivatization reaction with TFAA providing a CF₃ marker:



Selected plasma polymer films were exposed to TFAA and the CF₃ marker C 1s photoemission signal was used to measure a depth profile.

Experimental

XPS was done at a high resolution soft x-ray insertion device beamline (BL13C) of KEK-PF which may cover an energy range of 70 – 1500 eV [2] using a PHI 1600 C spectrometer. The resolution for the 750 l/mm grating and a 20 μm slit opening was 0.15 eV at 350 eV and 0.40 eV at 600 eV. The incident angle of X-ray was 54.7° and the photoelectron take-off angle was 0° relative to the surface normal. Additionally, laboratory XPS measurements with monochromatized Al K α excitation were done using a SSX 100 (Surface Science Instruments Inc.) spectrometer.

Thin (ca. 100 nm) films on silicon wafer were obtained from a pulsed (0.1 duty cycle) plasma deposition process

using allyl alcohol as well as allyl alcohol/ethylene mixtures.

Results and discussion

We used excitation energies of 600, 450 and 350 eV at BL13C providing estimated EALs of 1.8, 1.4 and 1.2 nm, respectively, for C1s photoelectrons.

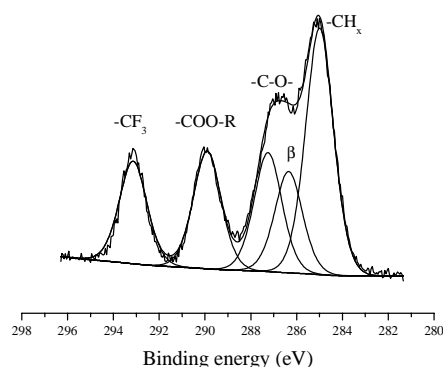


Figure 1: C1s XPS for a TFAA exposed allyl alcohol/ethylene plasma copolymer film at $h\nu = 450$ eV.

Table 1: C1s(CH₃)/C1s(CF₃) intensity ratios for a TFAA exposed allyl alcohol/ethylene plasma copolymer film at different excitation energies

350 eV	450 eV	600 eV	1486.6 eV
2.11	2.40	2.79	17.76

The interpretation of the data displayed in Tab.1 is that, relying on the marker technique, indeed a –OH group density depth profile, here an enrichment at the outermost surface, exists for the co-polymer film. Analysis of a plasma polymer film, prepared exclusively with allyl alcohol and analyzed by the same technique, revealed a constant –OH group related C1s(CF₃) signal for all applied excitation energies ruling out a –OH enrichment at the outermost film surface for this sample.

References

- [1] I. Retzko et al., JESRP 121, 111 (2001).
- [2] H. Shimada et al., Rev. Sci. Instrum. 66, 1780 (1995).

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