Non-destructive chemical depth-profiling of plasma polymers by variable excitation energy XPS

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Introduction

Thin layers made from organic precursors are very important in recent materials technology. Usually the surface of a certain substrate should have optimized properties for a selected purpose. The final goal is to "tailor" a functional surface on demand. To reach that goal analytical methods have to be found which are able to provide a real chemical depth profile of the outermost surface. Sputter based methods of depth profiling cannot be used in that case because the chemical state information will be destroyed by impinging energetic particles. Non-destructive depth profiling is possible by using photoelectron spectroscopy by exploitation of the variation of the information depth of the method from several monolayers down to the minimum of monolayer resolution. 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 of the exciting X-rays provides the possibility to adjust the kinetic energy of the photoelectrons and by doing this the EAL, too. The minimum of the EAL of C 1s photoelectrons should occur at roughly 350 eV X-ray photon energy.

The deposition of organic films with the help of a pulsed plasma process is a new topic earning more and more attention by the plasma science community. Pulsed plasma processing was found to provide chemically rather well defined polymer layers [1]. There is a need for a measurement of a chemical depth profile which must be, of course, undertaken without destruction of the surface chemistry. This knowledge is required to derive new technologies relying on pulsed plasma processing.

Experimental

100 – 200 nm thick pulse plasma deposited polymer films made from allyl alcohole, acrylic acid, allyl amine or ethylene/allyl alcohole mixtures were prepared at BAM.

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 μ m 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 at monochromatized Al K α excitation were done at BAM using a SSX 100 (Surface Science Instruments Inc.) spectrometer.

Results and Discussion

For all mentioned samples C 1s, O1s (when possible) and valence band spectra were acquired. We used excitation energies of 600, 450 and 350 eV giving estimated EALs of 1.8, 1.4 and 1.2 nm, respectively, for C 1s photoelectrons. As an example we present here the results obtained with a plasma polymer layer deposited on a silicon wafer using acrylic acid as the monomer (Fig.1). Fig. 1 clearely reveals a small but significant depletion of carboxyl groups at the outermost surface of the plasma polymer layer.

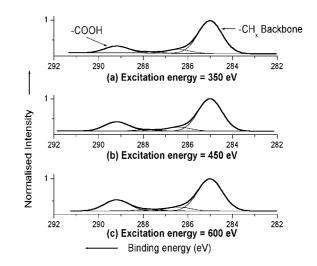


Fig.1 C 1s spectra of a plasma polymerized acrylic acid film obtained at different X-ray photon energies.

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References

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