Characterization of PIII&D Deposited Multilayer Coatings by ERDA and EFTEM

G. Thorwarth [a], W. Assmann , M. Häberlen [a], F. Schwarz [a], J.K.N. Lindner [a], C. Hammerl [b], M. Kuhn [b], and B. Stritzker [a]

[a] Lehrstuhl für Experimentalphysik IV, Universität Augsburg

[b] AxynTeC Dünnschichttechnik GmbH, Augsburg

The development of multilayered and nanostructured coatings is fueled by the prospect of tribological improvements such as hardness and stress reduction as well as special applications like diffusion barriers and biocompatible coatings. While the deposition of such materials can be accomplished with relative ease using ion-assisted deposition methods like plasma immersion ion implantation and deposition (PIII&D), the quantitative analysis of stacked coatings exhibiting concentration gradients on a scale of a few nanometers is challenging. Energy filtered transmission electron microscopy (EFTEM) has been established as capable of such high spatial resolutions; however, possible compositional changes due to the TEM sample preparation process and uncertainties in the available models do not allow for a sufficiently accurate quantification of the EFTEM spectra.

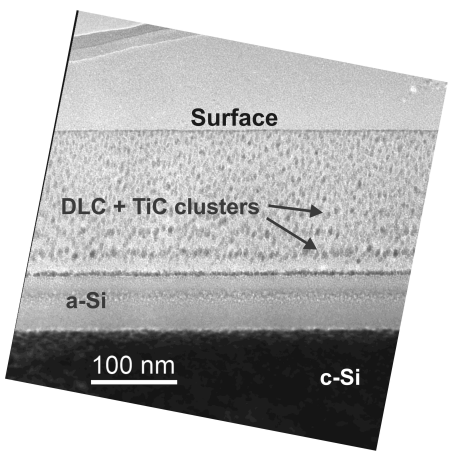

Fig. 1: TEM cross section image of an a–C:H layer incorporating self-organized layers of TiC nanoclusters.

In order to circumvent these shortcomings, the advantage of standard-less compositional analysis of the ERDA method was combined with EFTEM data to create enhanced elemental depth profiles of several multi-layered systems. One such system was found to be comprised of self-organized layers of TiC nanoclusters embedded in a diamond like carbon (a–C:H) matrix (Fig. 1). These layers were grown by PIII&D from a $TiCl_4$/hydrocarbon gas mixture using a nitrogen plasma and a pulsed acceleration voltage of -20 kV. The intended purpose of such layers is to facilitate stress relief and adhesion of biocompatible DLC-based wear protection coatings on medical implants. Fig. 2 shows EFTEM filtered segments of the cross section depicted in Fig. 1 divided by element. A further prerequisite for the normalization to the ERDA results is the accounting for the penetrated thickness of the TEM sample, which can be determined from the zero-loss to plasmon intensities in units of inelastic mean free path of the electrons (IMFP). As can be seen from both the titanium and thickness data, the TiC-rich cluster layers are spaced about 25 nm and also contain the majority of O and N species present in the film.

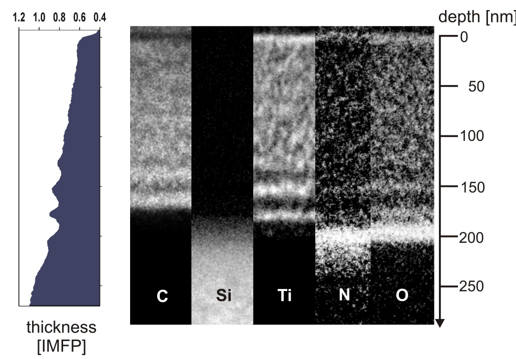

Fig. 2: EFTEM filtered segments and thickness profiles of the TiC/a–C:H sample.

Lateral integration of the EFTEM images and normalization to the integrated ERDA results yield the final elemental depth profiles as drawn in Fig. 3. The observed nanocluster bands, which are formed by titanium rich layers being buried and acting as diffusion sinks until leaving the ion range, are resolved clearly. Additional features are a nitrogen-rich pre-implanted substrate layer and a titanium-rich precipitate layer at the surface. The hydrogen content, estimated from the complement of the other elemental concentrations, shows maxima at the titanium rich ribbon structures, thus suggesting H-rich or H-terminated TiC clusters. The deviation of the H signal towards the interface (>170 nm) is caused by the Si substrate contribution, which was not evaluated here.

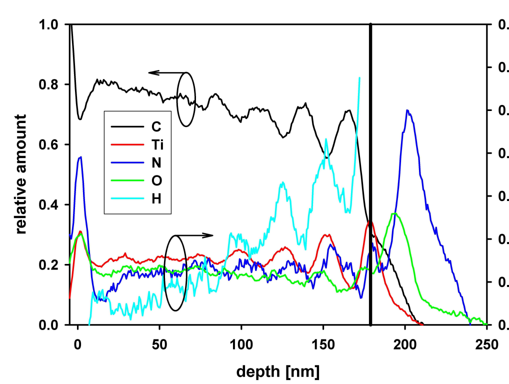

Fig. 3: Elemental depth profiles obtained by the ERDA/EFTEM method. All but the carbon profile refer to the right scale. The vertical line locates the transition to the Si substrate.