Spectroscopy in STEM/TEM

IM.4.P097
Plasmon to carbon ratio imaging (PCR): *In situ* determination and imaging of physical properties of organic materials by TEM.

N. Matsko[1], F. Schmidt[2], I. Letofsky-Papst[2], M. Albu[1], A. Rudenko[3], V. Mittal[4]

[1]Graz Centre for Electron Microscopy, Graz, Austria
[2]Institute for Electron Microscopy and Nanoanalysis, Graz University of Technology, Graz, Austria
[3]J. R. Macdonald Laboratory, Department of Physics, Kansas State University, Manhattan, United States
[4]Chemical Engineering Department, the Petroleum Institute, Abu Dhabi, United Arab Emirates

nadejda.matsko@felmi-zfe.at
Keywords: EFTEM, PCR, VEELS.

Measuring material properties such as elasticity, hardness, valence electron density and cohesive energy at the nanoscale is critical to understanding the behavior of nanostructured materials [1]. A novel PCR imaging approach [2] described here represents a powerful asset towards a substantiated structural characterization of multifaceted organic and organic-inorganic materials having complex mechanical properties (interconnected domain organization, local elastic variation etc.), and large range of thickness variations (from 10 to 300 nm). The technique is based on the fact that the bulk plasmon peak (e.g. enrgy-filtered TEM (EFTEM) image from the corresponding energy region) is a sensitive function of the physical properties and thickness of the sample. Although plasmons were initially introduced for simple metals as a consequence of collective inter-electronic Coulomb interaction, they occur in all materials due to the excitation of bonding electrons into the conduction band, where they undergo collective oscillation [3]. Furthermore, Oleshko and Howe [1] have demonstrated that strong scaling correlations exist between the valence electron density, cohesive energy, mechanical properties of materials and volume plasmon energy, Ep. In accordance with the universal binding energy relationship (UBER), the Ep-material property scaling relationships are universal in their applicability to materials with metallic, covalent and partially ionic bonding, and this covers a vast majority of materials. The thickness-related effects, which substantially mask a material contrast in the EFTEM plasmon image, for the carbon-based samples can be adequately removed by normalizing the bulk plasmon image on the carbon elemental map. Normalization by the specimen thickness (t/λ map) which is used in absolute quantification algorithm, in this particular case cannot eliminate thickness (t) variation effects properly because the relative thickness map, in addition to sample thickness variation, also reflects variation in Z (atomic number), and depends on the accuracy of inelastic mean free path (λ) determination [3]. The carbon map reflects mainly the intensity distribution of the signal obtained from the inner shells of carbon atoms within the sample volume, and for thin organic samples can be considered as a more accurate representative of the sample thickness. The resulting PCR image contains enhanced signal from metal atoms which replicates the sample surface and consequently change it hardness/valence electron density (for the metal shadowed/negatively stained organic materials), and from mechanical properties of the sample (for the non modified carbon based systems) [2]. These structural characteristics are in good agreement with the topographical and phase variation obtained by AFM (Figure 1). The ultimate resolution of the PCR method depends on the sample thickness as well as on the energy window position and width (see Figure 2) for the bulk plasmon image, and might be optimized for each particular sample composition. The possibility to obtain both, volume projected and surface-related information in TEM provides a comprehensive description of the sample ultrastructure in terms of bulk morphology and surface characteristics.

1. J. Howe and V. Oleshko V. J. Electron. Microsc. (2004), 53(4), p.339.
2. N. Matsko, I. Letofsky-Papst, M. Albu, V. Mittal. Micros. Microanal. (2013), (doi:10.1017/S1431927613000366)
3. R. Egerton. Electron Energy-loss Spectroscopy in the Electron Microscope, (Springer, New York) (2011).
4. We are very grateful to Ferdinand Hofer for fruitful discussions.

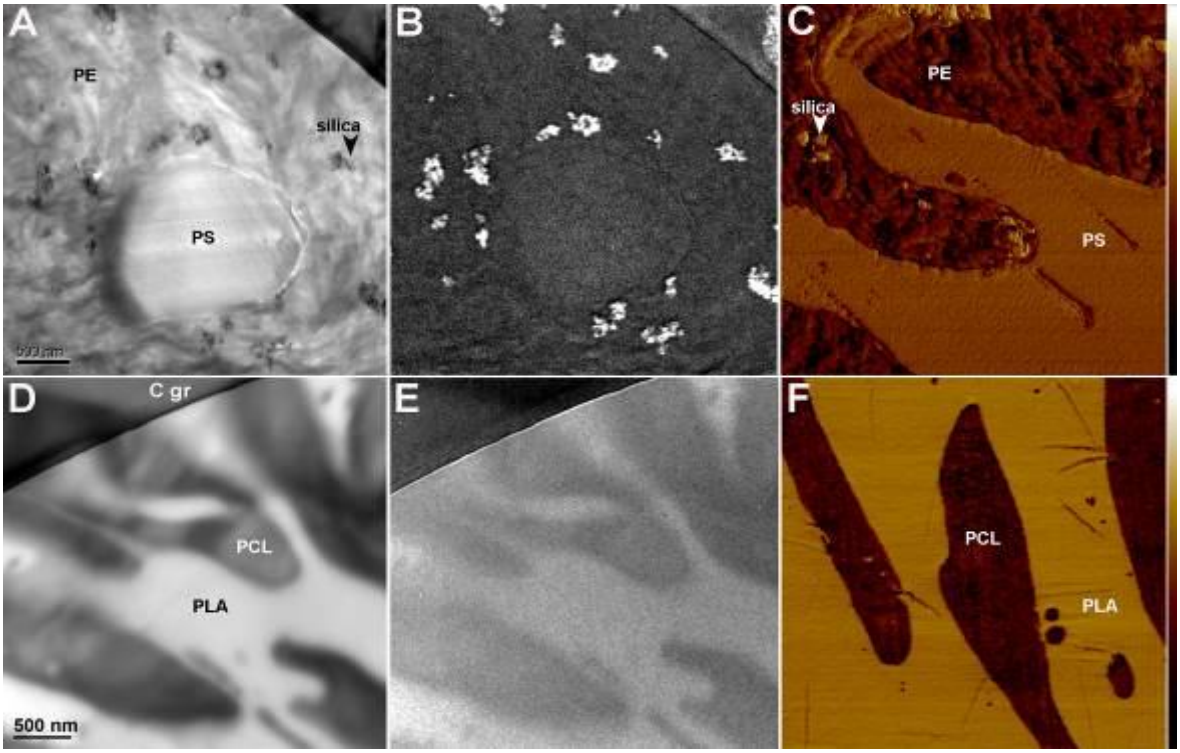

Figure 1. TEM, EFTEM and AFM images of organic(-inorganic) samples. (A, D) elastic filtered TEM images; (B, E) PCR images; (C, F) AFM phase images of the block face of the same samples

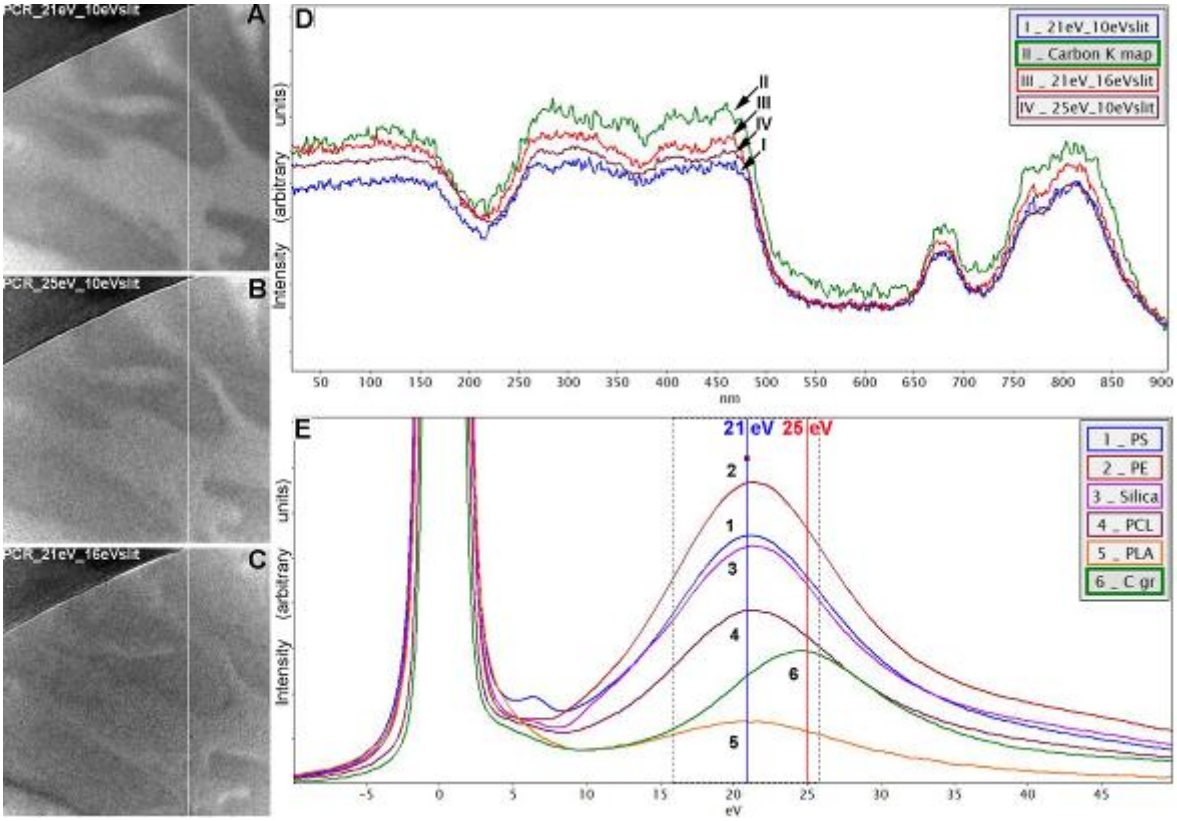

Figure 2. PCR images (A,B,C) which were calculated using different energy window position and width for the bulk plasmon images. (D) Intensity line profiles of corresponding carbon map (II) and bulk plasmon images (I, II, IV), which were used for PCR calculations. The profiles were taken with a 5-pixel integration window across the white lines from the same sample area. (E) EELS spectra of bulk plasmon energy region obtained from the each component of presented organic-inorganic samples. PE - polyethylene, PS - polystyrene, PCL - Poly[oxy(1-oxohexane-1,6-diyl), PLA - Polylactid, C gr - holey carbon grid.