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MS-1-O-2712 Spectral unmixing of electron energy-loss spectra of ~5 nm InP/ZnS nanocrystals

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We examine InP/ZnS nanocrystals (NCs), with possible core-shell or alloyed structures [1][2]. As InP and ZnS are both cubic and have very similar lattice constants, their compounds are difficult to distinguish using high-resolution transmission electron microscopy (TEM). This information is important, since the presence of a ZnS shell is essential in reducing surface recombination but also prevent oxidation of the InP [3].

Scanning TEM and electron energy-electron spectroscopy (EELS) were performed at 80 kV, in order to quantify the distribution of In- and Zn-containing compounds in individual NCs and their oxidation states after oxidation of the NCs in an oxygen/argon plasma to simulate aging process. Data analysis involved spectral unmixing using vertex component analysis (VCA) [4][5], in order to improve the signal-to-noise ratios of In and Zn elemental maps and to extract spectral signatures at the O K edge.

Figures 1a and b show conventional background-subtracted elemental maps measured for the In $M_{5,4}$ and Zn $L_{3,2}$ edges. VCA was applied over the energy range 850-1100 eV. A spectral component corresponding to the Zn $L_{3,2}$ edge can be identified. The corresponding map (Fig. 1e) is similar to Fig. 1b but less noisy. Surprisingly, an abondance map corresponding to In is also obtained over this energy range, where no In edge is present. This signal originates from the background of the In M_3 edge (678 eV) and is similar to Fig. 1a, which was extracted at the In $M_{5,4}$ edge.

Figure 2 shows results obtained using VCA over the energy range 450-600 eV. Of the three extracted components, component 1 corresponds to an In signal. The abundance map associated with this component is similar to the In maps as a result of the presence of the In $M_{5,4}$ edge in this energy range. More interestingly, the O K edge shows a shoulder at ~533eV. This shoulder is in a similar position but is less intense than the first peak in an In_2O_3 reference spectrum, suggesting that the NCs are partially oxidised. Although a clear signature of the oxidation of ZnS is not observed, oxidation of the In could be explained by the presence of either an incomplete ZnS shell or a ZnS layer that oxidized during the plasma treatment.

Our results show that a thin ZnS shell does not protect InP from oxidation sufficiently well for long-term applications. Our use of the VCA algorithm allows the oxidation of In in sub-5-nm InP/ZnS NCs to be identified with much greater confidence than using conventional background-subtraction methods.

[1] H. Borchert et al. Nano Lett. 2 (2002) 151; [2] K. Huang et al. ACSNano 4 (2010) 4799; [3] J. Jasinski et al. Solid State Commun. 141 (2007) 624; [4] M. Duchamp et al. Appl. Phys. Lett. 102 (2013) 133902; [5] C. Boothroyd et al. Ultramicroscopy, in press (2014)
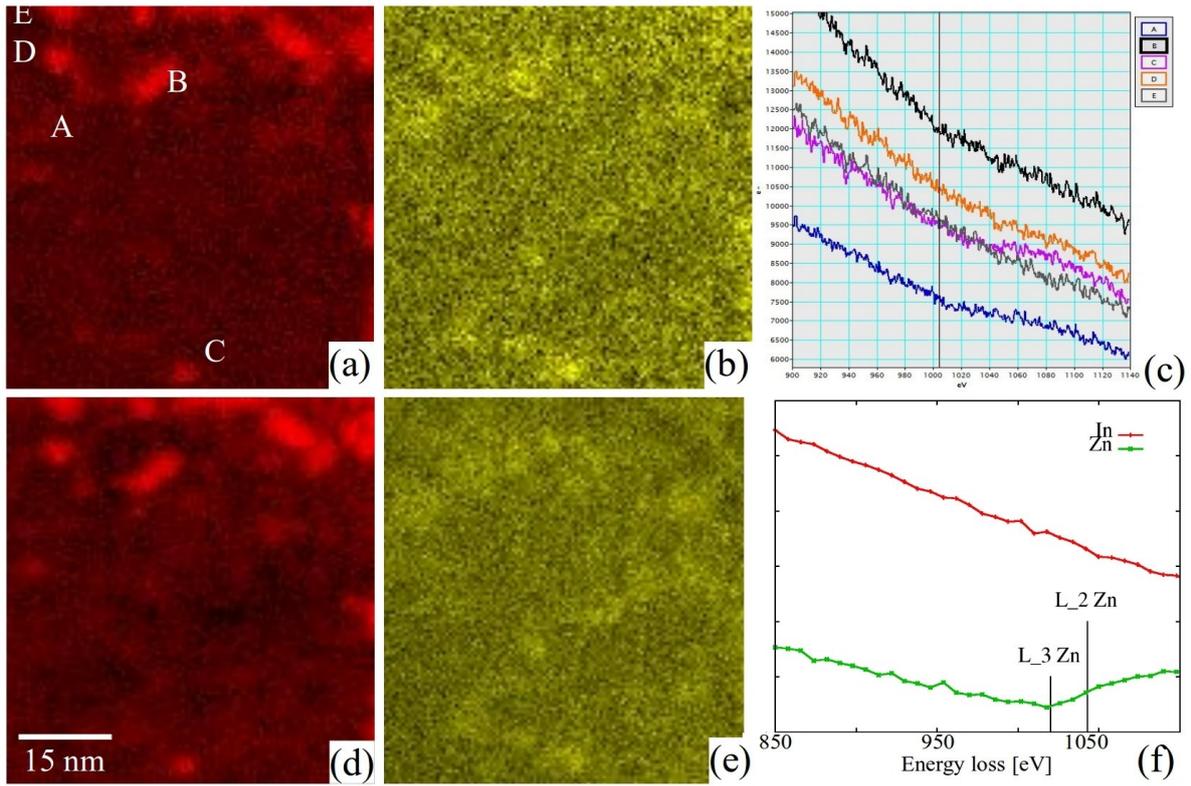
Fig. 1: (a, b) Background-subtracted elemental maps corresponding to the In $M_{5,4}$ and Zn $L_{3,2}$ edges; (d, e) Corresponding maps obtained by applying VCA over the energy range 850-1100 eV. (c) Spectra extracted from the spectrum image at the positions marked in (a); (f) Spectral components associated with the maps shown in (d, e)
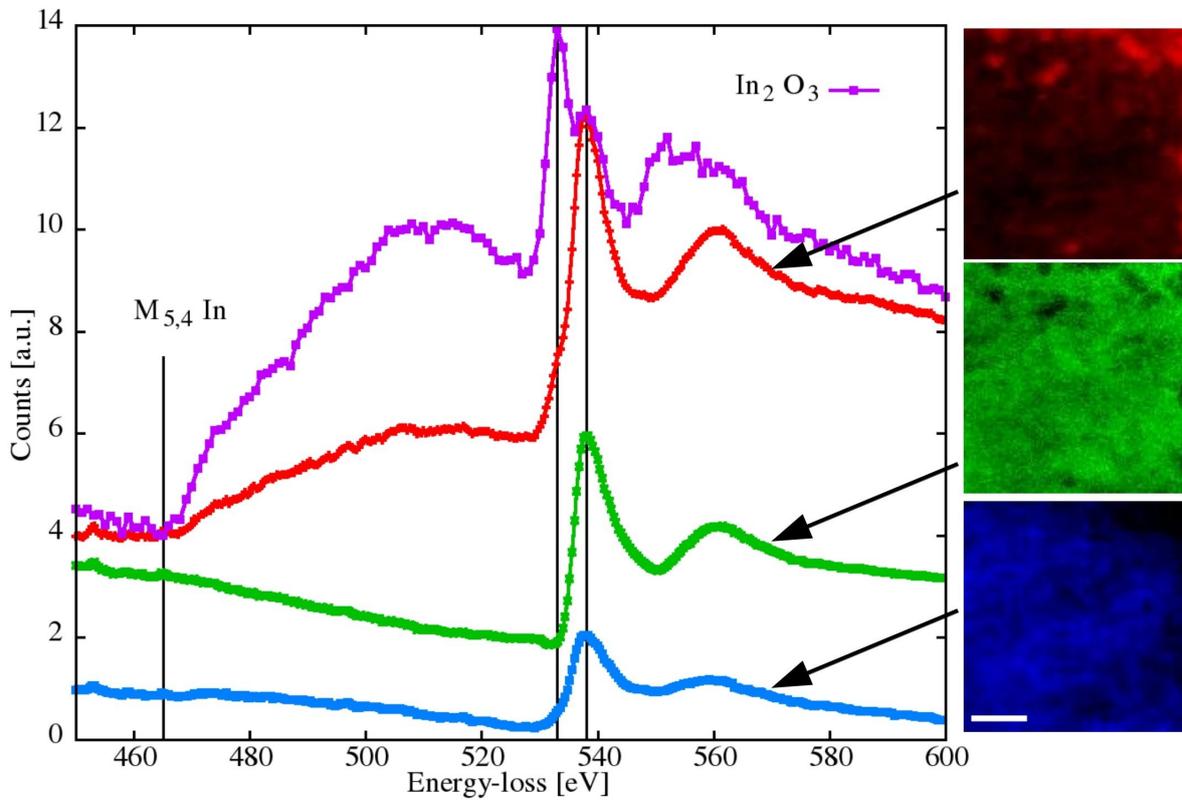

Fig. 2: Spectral components extracted over the energy range 450-600 eV, which includes the In $M_{5,4}$ and O K edges. The corresponding abundance maps are shown on the right. A reference In_2O_3 spectrum is also shown. The scale bar is 15 nm.