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Analytical TEM Investigation of Size Effects in SnO_2 Nanoparticles Produced by Microwave Plasma Synthesis

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Tin dioxide, a wide-band gap n-type semiconductor oxide, is a technologically interesting material with application potential in catalysis and as gas sensor. The semiconducting properties, such as band-gap, are particle-size dependent. The plasmon losses are influenced by size and shape of nanoparticles. Such influence is well known for many physical properties, especially for particles with sizes < 10 nm. Interestingly, only little literature is dealing with quantum-confinement effects in SnO_2. The minimum of the investigated particle size is 5 nm for $SnO_{1.5}$ to $SnO_{1.8}$ produced by gas condensation [1]. The Karlsruhe Microwave Plasma Process (KMPP) [2], a versatile gas-phase process, is able to produce nanoparticles with sizes below 5 nm, and narrow particle size distribution. Therefore, in this study SnO_2 nanoparticles are produced with particle sizes ranging from 2 to 5 nm, depending on the synthesis conditions. For comparison larger particle sizes of 10 nm are realized by annealing the powders at 1000°C, to study the influence of particle size on plasmon and core losses in a broader range. A Tecnai F20 ST, equipped with a GATAN Multiscan CCD and GIF is used, operated at 200 kV. Sample preparation is done by dipping lacey carbon films into the powder. The powders are studied by bright-field and dark-field imaging, by electron diffraction and by EELS. Electron diffraction images are scanned (Imacon Flextight Photo) with 600 dpi. Crystallite sizes are evaluated from line profiles of the digitized images, using Scherrer formula. EEL-Spectra are acquired in image mode. The spectrometer dispersion is set to 0.3 eV/channel. Special care is taken to analyze sample areas without carbon film. The relative sample thicknesses are determined by log-ratio method to be $t/\lambda < 1$ in all cases. Core loss spectra are deconvolved.

Syntheses of SnO_2 nanoparticles result for all experimental conditions in a white powder. Electron diffraction reveals crystalline cassiterite particles. The particle sizes show a clear dependence on the feeding rate (corresponding to precursor concentration) of the $SnCl_4$ precursor. The smallest particles have sizes around 2 nm and are produced with a precursor concentration of $3x10^{-6}$ mol/l. Although electron diffraction reveals more or less an amorphous like structure, crystalline nanoparticles are obvious in dark field imaging. At higher magnifications lattice fringes appear in bright field imaging. Figure 1 depicts the measured particle sizes as a function of the $SnCl_4$-precursor concentration (Fig. 1a) and electron diffraction of the powders produced with the lowest (Fig. 1b) and the highest concentration (Fig. 1c).

The general features of the low loss spectra are in good agreement with SnO_2 low loss spectra recorded by Powell [3]. Interband transitions are observed around 12.5 eV, the main bulk plasmon appears around 19 eV, and the Sn-$N_{4,5}$ peak around 32 eV. A broadening of the spectra and loss of features is observed with decreasing particle sizes. A well-defined peak at 27 eV, characteristic for SnO, does not appear clearly; however, a small shoulder can be observed in the case of 2 nm particles, potentially indicating some SnO at the surface. The low loss spectra for particle sizes below 5 nm are shown in figure 2a. For better visibility, the spectra are stacked. With decreasing particle size an increasing energy of the plasmon loss is observed. This is in good agreement to the results of

Nienhaus et al. [1] for $SnO_{1.5}$ to $SnO_{1.8}$. The plasmon loss for 10 nm SnO_2 particles realized by annealing does not fit in this image. The value of 20 eV corresponds to bulk values found in literature (e.g. [3]). This is a strong indication that nanoparticles produced by microwave plasma synthesis are in non-equilibrium, although electron diffraction reveals cassiterite. Figure 2b shows the dependence of plasmon loss from particle size for nanoparticles made by gas phase processes. It can be seen that the plasmon energies shift to higher values with increasing particle size. Core loss spectra are similar to the core loss spectra of Moreno et al. for SnO_2 [4]. The spectra are shown normalized and stacked in figure 2c.This is, together with electron diffraction, a strong indication for the absence of SnO on synthesized SnO_2 nanoparticle surfaces.

References

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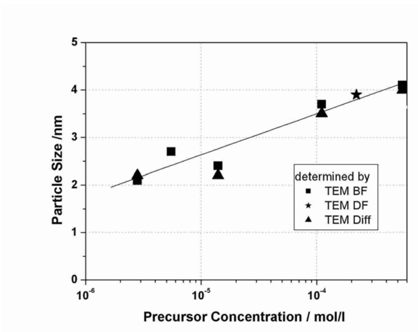

Figure 1a: Particle size as a function of precursor concentration, determined by different methods.

Figure 1b: Electron diffraction of powder synthesized with low precursor concentration ($3x10^{-6}$ mol/l).

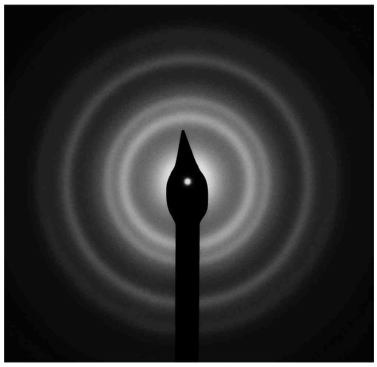

Figure 1c: Electron diffraction of powder synthesized with high precursor concentration ($5.5x10^{-4}$ mol/l).

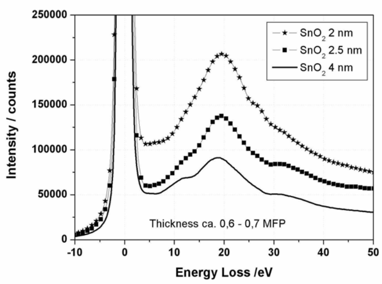

Figure 2a: Low loss spectra for nanoparticles made by microwave plasma process with different particle sizes.

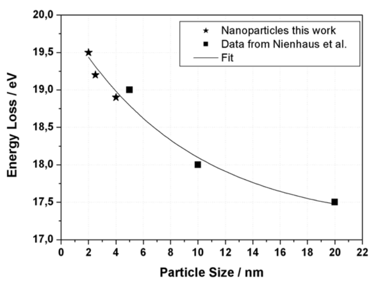

Figure 2b: Plasmon losses as function of particle size for nanoparticles around 20 nm and smaller. An increase of the plasmon energy with decreasing particle size is observed.

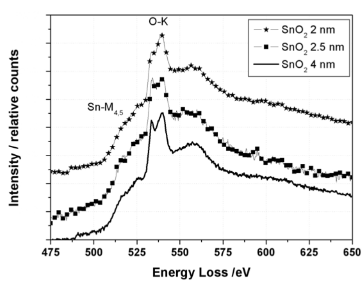

Figure 2c: Core loss spectra for O-K and $Sn-M_{4,5}$ edges.