

Zinc Doped SnO₂ Electronic Structure Study by EELS

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Tin dioxide (SnO₂) is a wide bandgap semiconductor ($E_g=3.6$ eV at 300 K). SnO₂ has recently received a large interest because of its multiple technological applications, including gas sensors, solar cells, optoelectronic devices, flat panel displays, architectural windows and catalysts, owing to its good optical and electrical properties and excellent chemical and thermal stability [1]. It is well known that the enhanced dielectric behaviors can be observed in some metal oxide nanostructures, such as SnO₂ nanoparticles, Al₂O₃ nanobelts and MgO nanoflowers due to their great space charge polarization process [2]. The concentration of oxygen vacancies as native defects can influence the optical and electrical properties of the SnO₂ nanoflowers like morphology. Changes in the electronic structure and morphology of SnO₂ nanoflowers like as a function of dopants level were investigated in this work.

SnO₂ nanoflowers were successfully synthesized by hydrothermal route. In a typical procedure, SnCl₄ and NaOH were mixed in tri-distilled water, kept in constant agitation until reach a stable clear solution. The zinc acetate was diluted in ethanol, the it was added to the solution containing the tin tetrachloride and NaOH by dropwise until stabilized; the compound solution was transfer to a Teflon vial and stainless steel autoclave. It was maintained at 200°C for 48 hours.

Electron energy loss spectra were acquired using a Gatan Parallel Electron Energy Loss Spectrometer (PEELS model 766) attached to a transmission electron microscope (TEM). Spectras were acquired in diffraction mode with 0.1 eV/ch dispersion, using 3 mm entrance aperture and 2.7 mrad collection semi-angle. The spectra resolution was determined by measuring the full width at half-maximum (FWHM) of the zero loss peak and it was typically close to 1.5 eV, when the TEM was operated at 200 kV.

Fig. 1a shows pure SnO₂ flowers like morphology which end is square-based pyramidal. Fig. 1b image shows the morphology for Zn/Sn at % doped it can be notice a change in the morphology, the end now became in a conical sharpened tips. This change is due to the dopant precence.

Fig. 2 shows the energy loss function $\text{Im}(-1/\epsilon)$ of tin oxide doping for different atomic percentages in precursor solution (0, 5, 10, 15 & 20 at. %, respectively). For pure SnO₂ the dominant peaks at 15.53 eV correspond to the volume plasmon that represents the energy of collective excitation of the electronic charge density in the crystal. In the same figure we can observed a small displacement of plasmon position towards to high energy, it is due to the increase in volume electrons density which participate in the collective oscillations. The shape of the plasmon peak shows the interband transitions (labeled by A, B, C and D) which are associated.

Table 1 shows the plasmon values position (E_p) and other interband transitions peaks. A new interband transition was observed in 9.43 eV for SnO₂:Zn 10 at. % sample, which was not observed in samples with low doping contents, it can be a difference of great utility in the identification of the oxygen vacancies.

References:

- [1] Donglin Guo, Chenguo Hu, Applied Surface Science V 258 (2012), p. 6987–6992.
 [2] P.G. Li, X. Guo, X.F. Wang, W.H. Tang, J. of Alloys and Compounds V 479 (2009), p. 74–77.

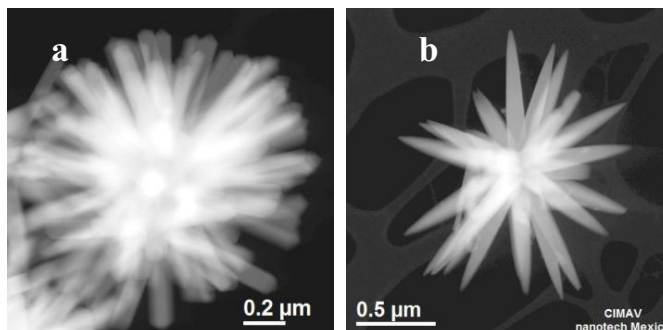


Figure 1. Typical image SnO₂ TEM (DF): a) SnO₂, b) SnO₂:Zn 5 % at

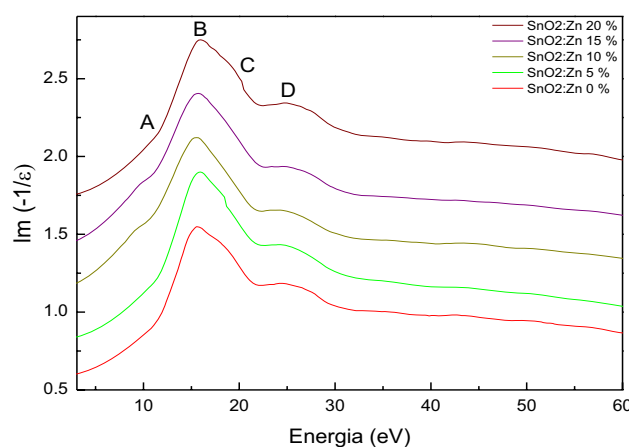


Figure 2. Energy loss function ($\text{Im}(-1/\epsilon)$) Spectra of SnO₂ peaks.

Table 1 Elemental composition in precursor solution and in the solid sample. There are the interband transition for different dopant levels SnO₂.

SAMPLE(Zn at % in precursor solution)	Zn/Sn at % by EDS	A	B(Ep)	C	D
SnO ₂ : Zn 0 %	0		15.53	18.90	25.43
SnO ₂ : Zn 5 %	2.3		15.97	18.45	25.20
SnO ₂ : Zn 10 %	2.8	9.45	15.52		25.20
SnO ₂ : Zn 15 %	3.7	9.83	15.75		25.21
SnO ₂ : Zn 20 %	5.1	9.90	15.97	20.25	26.55