

**Experiment title:**

Spatially resolved study of ZnO nanowires by X-ray fluorescence and X-ray diffraction techniques

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HS3592

Beamline:

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Highly ordered nanostructures based on ZnO were grown within Nanoporous of Anodic Alumina Membranes (NAAM) with different Cu contents. First, nanopore arrays were patterned with a self-ordered configuration on a high-purity Al substrate by a two-step anodization process.¹ The arrangement and shape of the alumina pores were determined by the applied voltage (40V), anodization temperature (0–2°C) and concentration of the electrolyte (H₂C₂O₄, 0.3M). Figure 1 displays a plane-view micrograph of the as-prepared porous alumina template taken by high-resolution scanning electron microscopy (Jeol HRSEM model JM6400). The template exhibits a perfect two-dimensional array with a well-aligned channel matrix in the nanometer scale. A high-periodicity and uniform close-packed nanoporosity characterizes the anodic alumina substrate. The pore diameter and interpore distance are about 35 and 105 nm, respectively. The average nanopore density is about 10¹⁰ cm⁻² with a nanopore length of 5 μm. Then, the electrochemical deposition of pure Zn metal in the resulting anodic alumina substrate took place, followed by an oxidation process of the embedded Zn nanowire arrays in air at 300°C up to obtain polycrystalline ZnO. The electrodeposition process was carried out applying 30 mA constant current. The aqueous bath contained 0.3 M ZnSO₄ · 7H₂O and 0.3 M H₃BO₃, and the pH was adjusted to 4.5 by addition of NaOH.

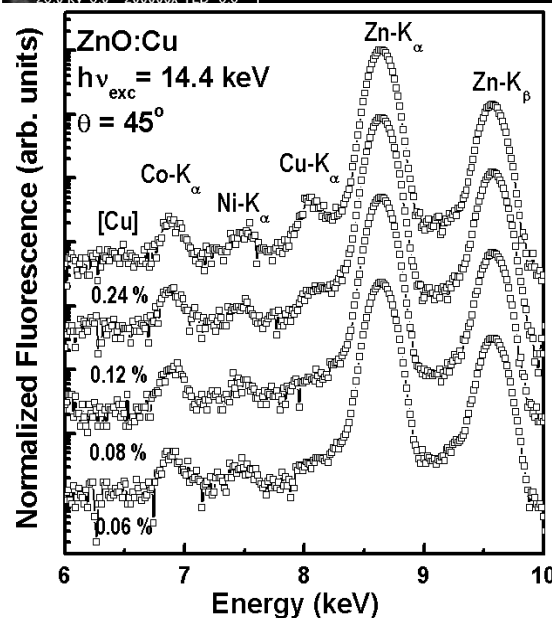
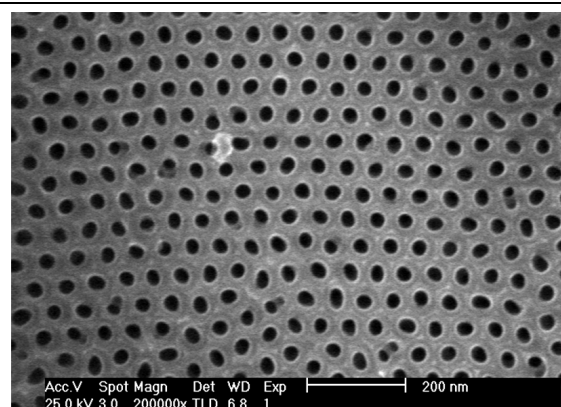


Fig. 1 Upper part: Plane-view SEM image of the as-prepared porous alumina template. Lower; 1 XRF spectra for ZnO nanowires with different Cu concentrations, shifted for clarity.

In order to study the incorporation of the chemical species during crystal growth, XRF analysis was carried out. The spectra are recorded at an incident angle of 45° with respect to the sample surface. Figure 2 shows the typical XRF signals of the Cu doped ZnO nanowires. The spectra consist of a well-defined background on which sharp characteristic lines and spectral artifacts are superimposed. The K_α and K_β fluorescence lines of Zn and Cu are shown. Taking only the peak-like structures statistically significant,

from the growth chamber (memory effects) or source materials as well as being introduced by growth processing procedures. Since almost no traces were identified from the XRF signal of the anodic alumina template, in principle the chemical pre-treatments of the Al sheet (99.997% pure) as well as its subsequent two-step anodization process could be ruled out. Thus, the control of background impurities might depend fundamentally on the Zn electrodeposition and further oxidation step. As a matter of fact, we believe that mostly the electrochemical system (electrolytic bath and metallic sources) plays the key role in the observed contamination. In general, the detected heavy transition elements could affect both the incorporation and agglomeration stages of microdefect formation, being crucial particularly in the magnetic properties. It has been shown that uncompensated spins in antiferromagnetic nanoparticles could produce additional sizeable spontaneous magnetization at high temperatures. However, by setting regions of interest around the dominant fluorescence lines, and taking advantage of the scanning capability the compositional homogeneity, filling factors and also segregation effects of all samples were also analyzed with micron spatial resolution and uniform patterns with no intensity changes were observed for all the samples, showing a homogeneous distributions at the length scale of the beam size.

From the peak intensities, assuming an incident monochromatic beam on a flat sample without secondary excitation, a rough quantitative analysis using PyMCA code yielded Cu concentrations ranging from 0.06 up to 0.24 %. In contrast to previous results obtained by EDX which pointed out that samples grown without an applied potential in the electrochemical deposition contained no measurable dopants,² our findings by XRF show nonnegligible improper handling and/or source contamination with a detectable overall elemental contribution into the fabrication processes.

We have also carried out XANES around the Zn K edge in every sample, probing the Zn fluorescence depth that covers the whole sample thickness of 0.5 μm . All XANES results, shifted for clarity, are shown in Fig. 2. Since the electronic transitions responsible for both XANES follow the dipole selection rules, the K edge reflects the p-partial density of states (PDOS). The spectra exhibit the typical data of fourfold Zn in ZnO.³ In general, the Zn K-edge XANES show a remarkable resemblance with the Zn K-edge XANES measured in wurtzite-type ZnO thin films collected under similar measurement conditions (Ref. 3), suggesting the preservation of the main hexagonal crystal structure and the high degree of axial order. Most of the spectral features present similar characteristics in both positions and shapes with slight differences as a function of the Cu content. However, there is no systematic damping effect revealing clearly a strong influence of the Cu dopant and/or residual impurities in any preferential crystallographic direction. Even for the case of the highest Cu doped ZnO, there is no indication of any other highly lattice symmetry other than the hexagonal on a tetrahedral site. Therefore, further XANES analyses around the Cu K edge are necessary in order to study in details the influence of such a doping on the local order.

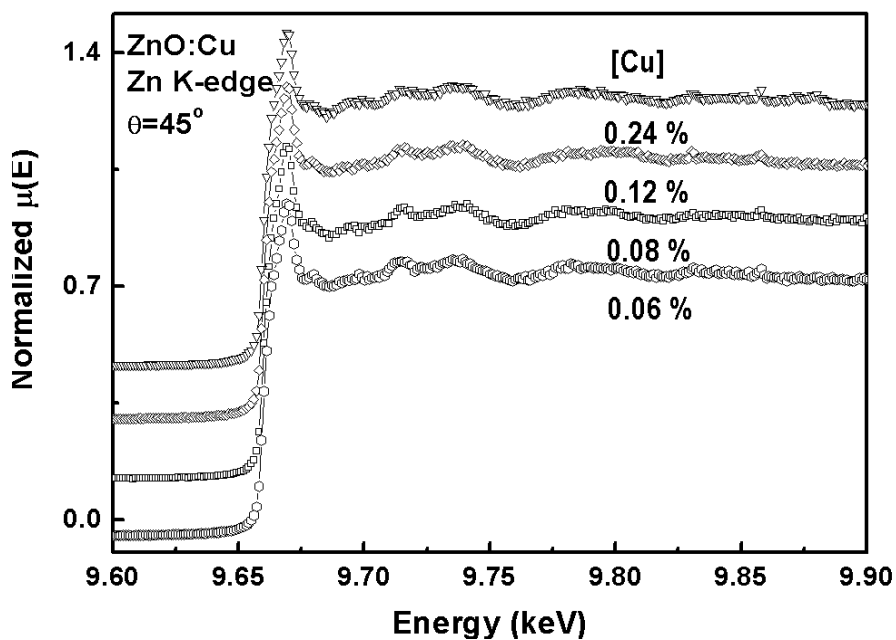


Fig. 2 XANES recorded at the Zn K edge from ZnO nanowires with different Cu concentrations, shifted for clarity.

References:

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