

# Optical properties of ZnO: Cu nanowires for optoelectronic applications

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**Abstract**—ZnO nanowires attract much attention for their applications in different kind of nano-devices. The control of size, shape and density of ZnO nanowires is of fundamental significance in modern science and engineering because the properties of ZnO highly depend on its morphology and structure. Doping is an important way to tailor the properties of semiconductor materials and among all Cu doped ZnO is very important recently because of its interesting properties, such as p-type, room temperature ferromagnetism and high efficient solar cells (SCs). We have prepared 0.1, 0.3, 0.5 and 0.8% of Cu doped ZnO nanowires using sol-gel spin coating techniques on the glass substrate. The coating solution was prepared using Zinc acetate as the dissolved precursor material, with the molarity of 0.2M and 2-methoxyethanol as the solvent, and the Copper acetate as the doping material. The stabilizer was mono-ethanolamine, and the molarity ratio of the stabilizer and zinc acetate was 1. In this research work we investigate the structure using micro Raman Spectroscopy and Micro-PL techniques of these nanowires transferred to a Si/SiO<sub>2</sub> substrate.

**Keywords**—ZnO, nanowires, semiconductor, solar cells.

## I. Introduction

ZnO is a semiconductor with a wide band gap of 3.2-3.4 eV. ZnO has a crystal structure called “wurtzite”, which is composed of alternating planes of tetrahedrally coordinated O<sup>2-</sup> and Zn<sup>2+</sup> ions as shown in Figure 1. Previous studies showed that when a portion of Zn ions in the ZnO lattice was replaced by other transition metal ions, M (M can be any transition metal available in a nitrate) to form a solid solution, Zn<sub>1-x</sub>M<sub>x</sub>O, the solid solution became able to absorb a portion of visible light. These investigations were made using either single crystals or pellets of ZnO. However, single crystals or pellets of ZnO are not suitable for use in electrochemical cells because growing single crystals is an expensive and time-consuming process and because it is difficult to ensure the homogeneity and reproducibility of the pellet samples. Therefore, it is desirable to produce these solid solutions by other synthetic methods. In addition, the synthetic method and experimental conditions can significantly vary

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the maximum amount of transition metal ions that can be incorporated into the wurtzite structure. These factors leave many opportunities to prepare and study Zn<sub>1-x</sub>M<sub>x</sub>O films with new optical properties [1]–[4].

## II. Fabrication technique

We have prepared 0.1, 0.3, 0.5 and 0.8 Cu doped ZnO thin films using sol-gel spin coating techniques. The coating solution was prepared using Zinc acetate as the dissolved precursor material, with the molarity 0.2M. and 2-methoxyethanol as the solvent, and the Copper acetate as the doping material, and the stabilizer was Monoethanolamine, the molarity ratio of the stabilizer and the zinc acetate was 1. Calculations of the Zinc acetate weight which required to get the molarity (m=0.2 M) ZnO solution. If we have 10 ml (V=0.1L) of the solvent, and if we know the molecular weight of the dissolved material zinc acetate (mw=219.5). We added 0.44 gm of the zinc acetate to 10ml of the solvent 2-methoxyethanol. Calculations of the Cupper acetate weight which required to get the concentrations (C=0.1%, 0.3%, 0.5% and 0.8%) of the ZnO solutions. If we have 10 ml (V=0.1L) of the solvent, and if we know the molecular weight of the doping material cupper acetate (mw=199.65), and the concentration of ZnO solution is 0.2M. Then we have stirred the solutions, and we kept the temperature maintained at 60°C. After 30 minutes we put the stabilizers [MEA]. Then, we have continued the stirring for 1hr at 60°C (Figure 1) [5], [6].



Fig. 1: Sol-gel spin coating technique

After aged the solutions for 24 hours, we uses them for coating. The rotation speed was around 2000RPM,

and the rotation time was 30sec. after coating we heated the samples at 150°C for 10mints before starting the next coating. We have made 7 layers after the last heating process; we annealed the samples at 400°C for 1 hour, so the surface of the samples will be more homogenous and uniform.

TABLE I: Details of the fabricated samples

Sample	Method	Symbol
ZnCuO_1	Sol-gel	ZnCu <sub>0.1</sub> O
ZnCuO_2	Sol-gel	ZnCu <sub>0.1</sub> O
ZnCuO_3	Sol-gel	ZnCu <sub>0.3</sub> O
ZnCuO_4	Sol-gel	ZnCu <sub>0.3</sub> O
ZnCuO_5	Sol-gel	ZnCu <sub>0.5</sub> O
ZnCuO_6	Sol-gel	ZnCu <sub>0.5</sub> O
ZnCuO_7	Sol-gel	ZnCu <sub>0.8</sub> O
ZnCuO_8	Sol-gel	ZnCu <sub>0.8</sub> O

### III. Micro Raman characterization

Micro-Raman study was conducted to investigate the structural properties of ZnCu<sub>x</sub>O polycrystalline nanowires using the 325 nm He-Cd laser line. The nanowires for measurements were transferred to Si substrate to avoid the strong luminescence from glass substrate influencing measured spectra. Accumulation of Cu at the interstitial sites causes a distortion in ZnO lattice, breaks down its translational symmetry causing the increasing the intensity of the A1(LO) polar optical phonon modes near 570-580 cm<sup>-1</sup> as well as their broadening (Figure 2) [7], [8].

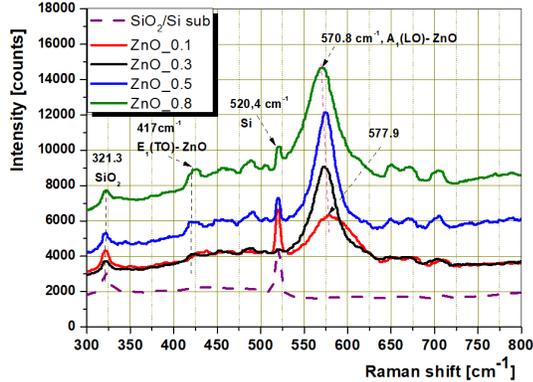


Fig. 2: Micro Raman spectra of ZnCu<sub>x</sub>O nanowires

### IV. Photoluminescence characterization

Photoluminescence study was conducted to investigate the optical properties of ZnCu<sub>x</sub>O nanowires. The Micro-photoluminescence (-PL) of the nanowires was studied using the 325 nm laser line of a He-Cd laser. Figure 4 shows the -PL spectrum of the polycrystalline nanowires. The PL spectrum shows a weaker peak near the UV region and a stronger broad peak in the visible region. The near-UV emission can be attributed to ZnO near-band-edge emission. The broad strong peak in the visible region is due to a defect level in the mid-gap region. The point

defects in a crystal include any foreign atom at a regular lattice site (i.e., substitutional site) or between lattice sites (i.e., interstitial site), antisite defects (e.g., Zn at O site or O at Zn site in the oxide), missing lattice atoms, and host atoms located between lattice sites and adjacent to a vacant site (i.e., Frenkel defects). The green emission from this oxide has been often related to O-vacancies (Figure 3) [8]

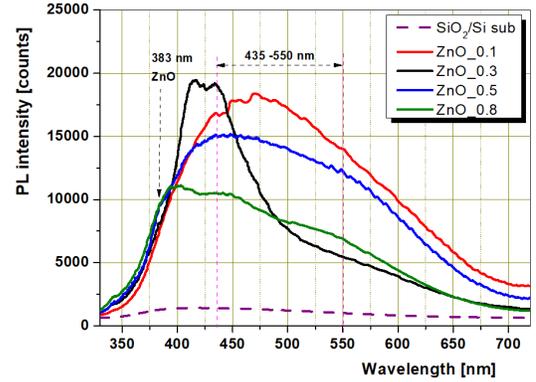


Fig. 3: Micro-Photoluminescence spectrum of ZnCu<sub>x</sub>O nanowires

### V. Conclusions

As can be seen, For a low concentration of doping, most of the incorporated Cu ions occupy ZnO lattice interstitial sites while for higher Cu ions concentrations modify the probability of excitonic transitions and hence the intensity of UV emission in the PL through an increase in the concentration of free excitonic states in the band structure of ZnO. In Raman spectra the accumulation of Cu at the interstitial sites causes a distortion in ZnO lattice, breaks down its translational symmetry, increasing the intensity of the A1(LO) polar optical phonon modes.

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