

Structured ZnO films: Effect of copper nitrate addition to precursor solution on topography, band gap energy and photocatalytic activity

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Abstract. ZnO is a widely studied semiconductor material with interesting properties such as photocatalytic activity leading to wide range of applications, for example in the field of optoelectronics and self-cleaning and antimicrobial applications. Doping of photocatalytic semiconductor materials has been shown to introduce variation in the band gap energy of the material.

In this work, ZnO rods were grown on a stainless steel substrates using hydrothermal method introducing copper nitrate into the precursor solution. Zinc nitrate and hexamethylenetetramine were used as precursor materials and the growth was conducted at 90 °C for 2 h in order to achieve a well-aligned evenly distributed rod structure. Copper was introduced as copper nitrate that was added in the precursor solution in the beginning of the growth. The as-prepared films were then heat-treated at 350 °C and band gap measurements were performed for prepared films. It was found that increase in the copper concentration in the precursor solution decreased the band gap of the ZnO film. Methylene blue discolouration tests were then performed in order to study the effect of the copper nitrate addition to precursor solution on photocatalytic activity of the structured ZnO films.

1. Introduction

Zinc oxide is an n-type semiconductor with band gap energy of 3.37 eV. [1]Due to its unique electrical and optical properties, ZnO has a wide range of applications for example in gas sensors and solar cells. [2]In addition to its other interesting properties, ZnO is believed to have higher efficiency in photocatalytic performance than TiO₂. [3] Among many methods to synthesize ZnO nanostructures, hydrothermal synthesis is a relatively cheap and simple method to produce structured high surface area powders and thin films [4].

Copper has many physical and chemical properties similar to Zn and optical and morphological properties of ZnO can be changed via incorporation of Cu into the lattice of ZnO nanostructures. [5]Many studies have demonstrated incorporation of copper leading to reduced band gap energy of ZnO. [6-9] The band gap narrowing can increase the visible light photocatalysis of the material. This has been explained with the Cu 3d levels forming a new energy level below the conduction band of ZnO. [9]Despite the enhanced visible-light absorption leading to better visible-light photocatalysis [10], these intra-band levels can act as recombination centres decreasing the photocatalytic activity of the material [3].



In this study, we have used hydrothermal method to produce structured ZnO films with high surface area synthesized in a solution containing copper nitrate to study the effect of copper nitrate addition to precursor solution on bandgap energy and photocatalytic activity of the films.

2. Experimental

2.1. Preparation and characterization of zinc oxide films

Zinc oxide films were prepared by a hydrothermal method. Before the actual growth-step, a seed layer was formed on an AISI 304 stainless steel (SS) substrate (75mm x 25 mm) followed by the growth of ZnO nanorods. Before the process, substrates were cleaned by wiping with 2-propanol (C_3H_7OH , 99.5 %, VWR) and then rinsed with ethanol (C_2H_5OH , 99.5%, Altia Oyj). A solution for the seed layer was prepared mixing 2-methoxyethanol ($CH_3OCH_2CH_2OH$, $\geq 99.5\%$, Sigma-Aldrich) and ethanolamine ($NH_2CH_2CH_2OH$, $\geq 99.0\%$, Sigma-Aldrich) (96:4) and dissolving 0.23 M zinc acetate ($C_4H_6O_4Zn \cdot 2H_2O$, $\geq 98\%$, Sigma-Aldrich) into the mixture. Solution was then stirred at 60 °C for 2 h. After cooling down, the solution was spin coated (1500 rpm, 20 s) on the substrates and then the samples were heat treated at 350 °C for 20 min. The solution for growth of ZnO layer with tuned topography was prepared mixing hexamethylenetetramine ($C_6H_{12}N$, 99%, Sigma-Aldrich) and zinc nitrate ($Zn(NO_3)_2$, 98%, Sigma-Aldrich) volume ratio being 1:1. The concentrations of both HMTA and zinc nitrate were 0.05 M. Copper nitrate tri hydrate ($Cu(NO_3)_2 \cdot 3H_2O$) was added to the solution. Two synthesis with varying copper concentration were conducted: in the first synthesis, the Cu/Zn molar ratio in the solution was 0.005 and in the second synthesis, the Cu/Zn molar ratio was 0.05. The synthesis temperature was 90 °C. The plates were placed in the solution the seed layer side upside down and the growth was carried out for 2 hours. After removing the samples from the solution, they were rinsed with de-ionized water and dried in air. The samples were finally heat-treated at 300 °C for 30 min. The sample without Cu in the precursor solution is denoted as S1, the sample with lower Cu concentration in the precursor solution is denoted as S1_{Cu0,5%} and the sample with higher Cu concentration in the precursor solution is denoted as S1_{Cu5%}.

The prepared zinc oxide films were characterized using field emission scanning electron microscopy (FESEM, Zeiss ULTRAplus) for surface morphology studies and X-Ray diffraction (XRD, Panalytical Empyrean Multipurpose Diffractometer) to define the crystal structure of the samples. The band gap energies of the fabricated films were measured with UV-vis spectrophotometer (Shimadzu UV-3600 UV/Vis/NIR spectrophotometer) in the wavelength range of 300–500 nm.

Photocatalytic measurements were performed in an aqueous solution of methylene blue (MB). The sample plates were placed in a decanter glass with 30 ml of 0.0085 mM MB solution. In order to reach adsorption equilibrium, the test solution was first kept in the dark for 60 min after which the ultra violet (UV)-lamp was turned on. Illumination was done from above with a 100 W/m² power using Ledia NIS330U-M UV-Gun (peak maximum at 365 ± 5 nm). The concentration of MB in the solution was followed by UV-VIS spectroscopy (Shimadzu UV-2501PC Spectrophotometer). At one-hour intervals, a 3 ml MB solution was taken for absorbance measurement. The absorbance was measured at the wavelength of 665 nm. A dark experiment without any irradiation but under otherwise identical conditions was also conducted for comparison. The discoloration of MB under UV irradiation but without sample plates was also tested to confirm that irradiation does not decompose MB intrinsically.

3. Results and discussion

3.1. Morphology and crystal structure of ZnO films grown in different precursor concentration solutions and temperatures

The scanning electron microscopy images of the films prepared at different precursor solutions are shown in figure 1. The rod diameter was slightly increased with sample S1 compared to the samples S1_{Cu0,5%} and S1_{Cu5%}. Moreover, the rod diameter and density were equal for S1_{Cu0,5%} and S1_{Cu5%}. The

surface areas for the three samples were calculated from the SEM-images from the rod length, rod diameter and rod density for S1, S1_{Cu0,5%} and S1_{Cu5%}. The received values were 109 cm², 134 cm² and 127 cm², respectively. The rod lengths, densities and surface areas are given in Table 1. It is notable that addition of copper into the precursor solution impacted clearly the rod alignment making the structure more aligned compared to the sample synthesized without copper nitrate.

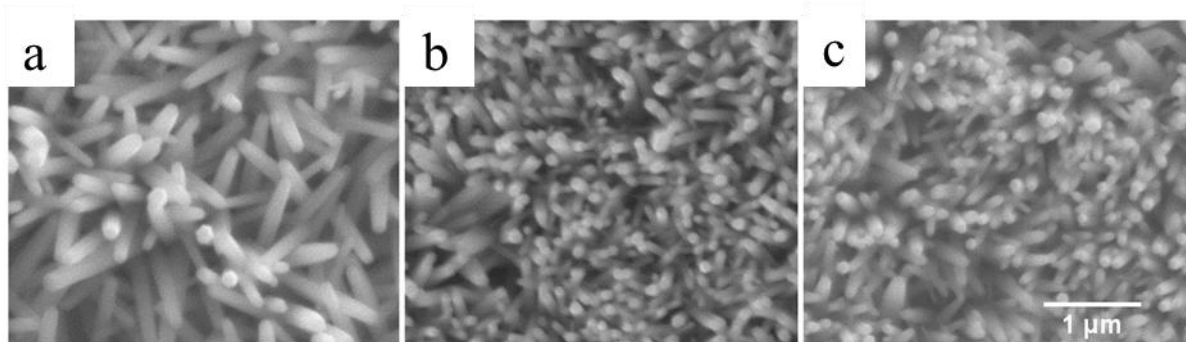


Figure 1 a–c. FESEM images of ZnO coatings prepared with a precursor solution a) without copper nitrate b) lower copper nitrate concentration and c) higher copper nitrate concentration

Table 1. Rod diameters, densities, lengths and surface areas of S1, S1Cu_{0,5%} and S1Cu_{5%}

	S1	S1Cu0,5%	S1Cu5%
Rod diameter (nm)	141	101	104
Rod density (rods/μm ²)	10	25	24
Rod length (nm)	1270	891	840
Surface area (cm ²)	109	136	127

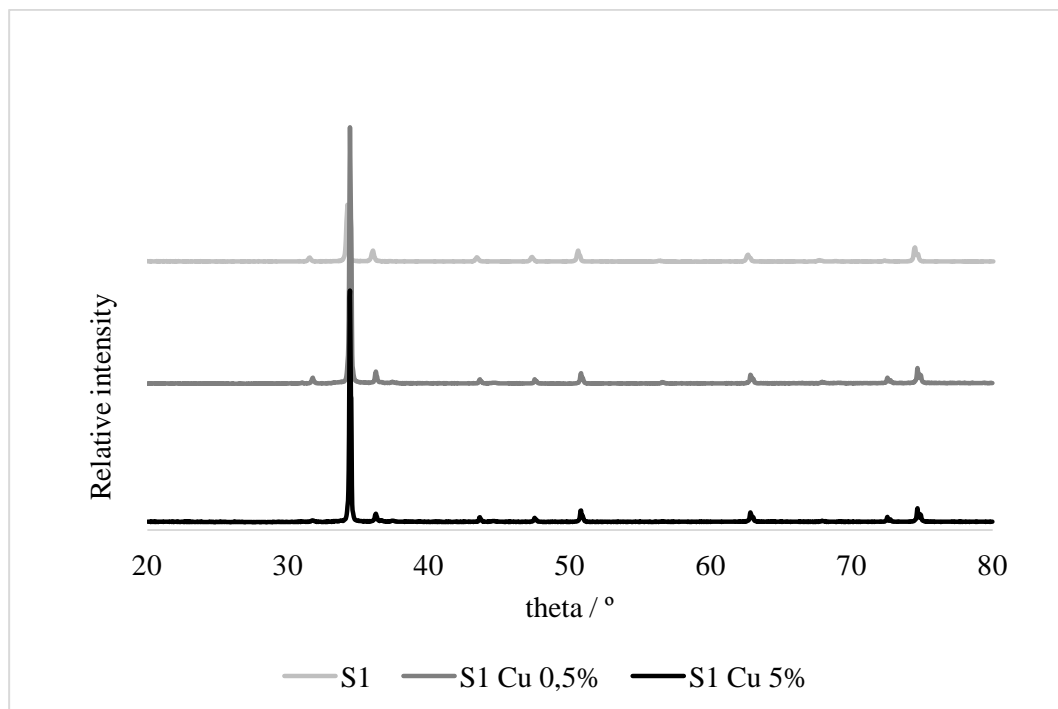


Figure 2. XRD analysis of the ZnO films with and without copper nitrate in the precursor solution

XRD analyses were conducted for all four coatings and all of them showed clear peaks of hexagonal wurtzite structure. Apart from peaks of wurtzite and iron from stainless steel substrate, no other peaks could be detected. The XRD patterns for each coating are shown in Fig. 2.

3.2. MB degradation results

The band gap energy values for samples synthesized without and with varying amount of copper nitrate in the precursor solution are listed in table 2. The increased amount of copper in the precursor solution was observed to decrease the band gap energy of the prepared films. The decrease of band gap energy could result from the increase of the lattice constant between Cu-O and Zn-O bonds. It can be assumed that copper forms a new energy level below the conduction band of ZnO which narrows the band gap.

Table 2. Band gap values of S1, S1_{Cu0,5%} and S2_{Cu5%}

Sample	Band gap (eV)
S1	3.204
S1 _{Cu0,5%}	3.171
S2 _{Cu5%}	3.163

3.3. MB discolouration results

The dark tests were performed before the actual measurements for one hour during which the concentration of the solution did not change and thus the samples did not adsorb methylene blue. The MB solution was also irradiated without the samples and no change in the concentration of MB was observed, which means that irradiation did not intrinsically decompose MB. Based on MB degradation test results, the sample prepared without copper nitrate in the precursor solution (S1) had the highest photocatalytic activity although all the prepared coatings showed photocatalytic activity (Fig. 3). The sample S1_{Cu0,5%} with lower copper concentration in the precursor solution showed better photocatalytic performance compared to the sample S1_{Cu5%} that had higher copper concentration of the precursor solution. The lower photocatalytic activity of the samples prepared in the copper nitrate containing precursor solution could result from copper ions in the ZnO lattice acting as recombination centres. The reduced photocatalytic activity may also be due to the reduced band gap energies, which can be beneficial when only longer wavelengths of light are available. However, when artificial excitation is used the narrowing of the band gap may not be beneficial.

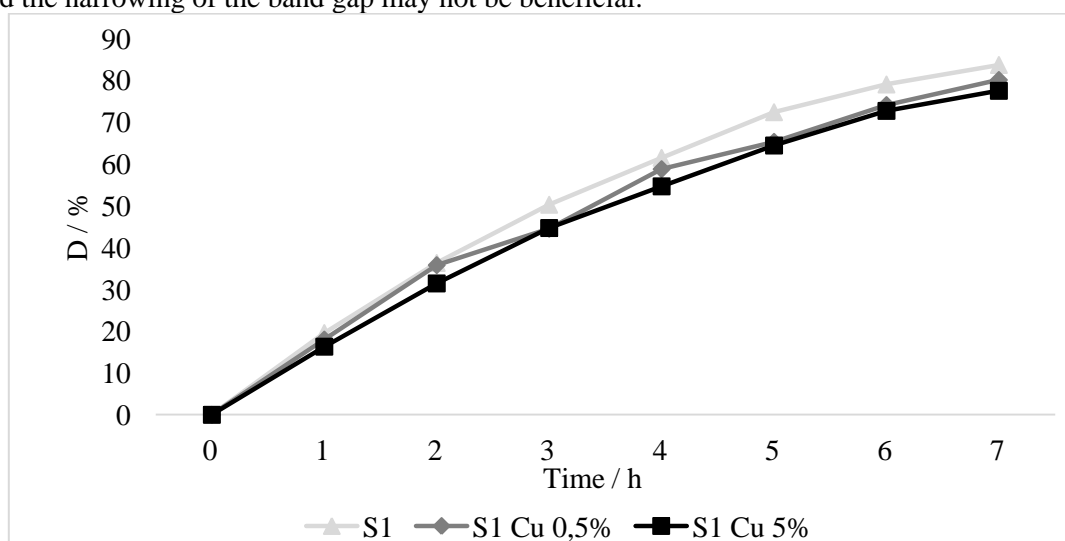


Figure 3. Percentage of degraded methylene blue as a function of time for samples S1, S1_{Cu0,5%} and S1_{Cu5%}

4. Conclusions

In this paper, we prepared ZnO films with varying amount of copper nitrate in the precursor solution. It was shown that addition of copper nitrate resulted in well-aligned nanorod structure compared to the less aligned structure obtained via synthesis without copper nitrate. It was also demonstrated that addition of copper nitrate to the precursor solution of hydrothermally grown ZnO nanorods lead to decrease in the band gap energy of the coating. The photocatalytic activity of the coatings was also reduced when copper nitrate was used as a precursor despite the increased surface area that was obtained in the synthesis with copper nitrate. The reduced photocatalytic activity may have resulted from recombination centres formed by Cu but also from decreased band gap energy since artificial excitation was used in this study.

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