



Heavily nickel-doped zinc oxide nanostructures prepared by hydrothermal oxidation of electro-deposited alloy films and their photoluminescence properties

Naeem-ur- Rehman^a, Mazhar Mehmood^{a,*}, Farhat Ali^a, Muhammad Asim Rasheed^a, Muhammad Younas^b, Francis C.C. Ling^b, Syed Mansoor Ali^c

^a National Centre for Nanotechnology, Department of Metallurgy and Materials Engineering, Pakistan Institute of Engineering and Applied Sciences (PIEAS), Islamabad 45650, Pakistan

^b Department of Physics, The University of Hong Kong, Pokfulam Road, Hong Kong, China

^c Department of Physics and Astronomy, King Saud University, Riyadh, Saudi Arabia

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ABSTRACT

Wurtzite ZnO nanostructures doped with up to 17 at% Ni have been formed by hydrothermal oxidation of electrodeposited Zn–Ni alloy films. The wire diameter decreases with Ni content, up to about 20–50 nm for the Zn_{0.83}Ni_{0.17}O nanowires formed in NaCl solution. A strong ultra-violet emission is seen in the photoluminescence spectra obtained at 10 K and room temperature. A substantial visible emission exhibited by un-doped ZnO nanostructures formed in pure water becomes negligible by nickel doping and almost completely vanishes for the samples prepared in chloride solution, due to higher crystalline quality.

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1. Introduction

Functional nanomaterials exhibiting interesting optical, electrical and magnetic properties have recently gained huge interest of the researchers because of novel properties related with nano-scale dimensions and large surface area. ZnO nanostructures are interesting for their exceptional physical properties, e.g., high electrical conductivity, transparent nature, photoluminescence in ultra-violet and visible region, etc., in addition to ability to form various morphologies [1–4].

ZnO nanostructures are synthesized by a diverse range of techniques including chemical vapour deposition [5–7], vapour transport [8,9], thermal oxidation [10], vapour–liquid–solid growth [11,12], precipitation [13], sol–gel [14] and hydrothermal processes [15], etc. Variation in synthesis parameters affects the crystallinity and optical properties of ZnO nanostructures [3,16,17]. Nevertheless, defect-free ZnO nanostructures are very difficult to form as photoluminescence spectra almost always exhibit defect-related emissions in the PL spectra [3,17–20]. Some degree of control is however exercised by post heat treatments in highly controlled atmospheres [21].

Doping of transition metals in ZnO nanostructures is of considerable interest. Nickel is considered to be the most efficient transition metal dopant due to its exceptional chemical stability and ability to tune electrical, optical and magnetic behaviour of ZnO nanostructures [22]. Nickel has been successfully doped up to about 5% in wurtzite ZnO nanostructures by co-precipitation [13,14,22,23]. At 10% and higher nickel content in the sample, segregation of some nickel to form NiO has been seen inevitable.

In an earlier work [24], the present authors prepared ZnO nanostructures by hydrothermal oxidation of electrodeposited zinc in NaCl solution. The structures exhibited interesting optical properties. For instance, green emission was almost absent, although prominent blue emission was seen in some cases, with strong UV emission.

In the present work, un-doped and heavily Ni-doped ZnO nanostructures have been formed by hydrothermal oxidation of electrodeposited Zn and Zn–Ni alloys. Comparative study of hydrothermal oxidation in water and in NaCl solution has been performed. Particular emphasis has been laid on the structural and morphological changes and photoluminescence properties of ZnO nanostructures as a function of oxidation environment and nickel doping.

2. Experimental

Analytical grade ZnCl₂, NiCl₂·6H₂O and boric acid were used for electrodeposition bath. The pH of the bath was 3.6 ± 0.1 (measured

* Corresponding author.

E-mail address: mazhar@pieas.edu.pk (M. Mehmood).

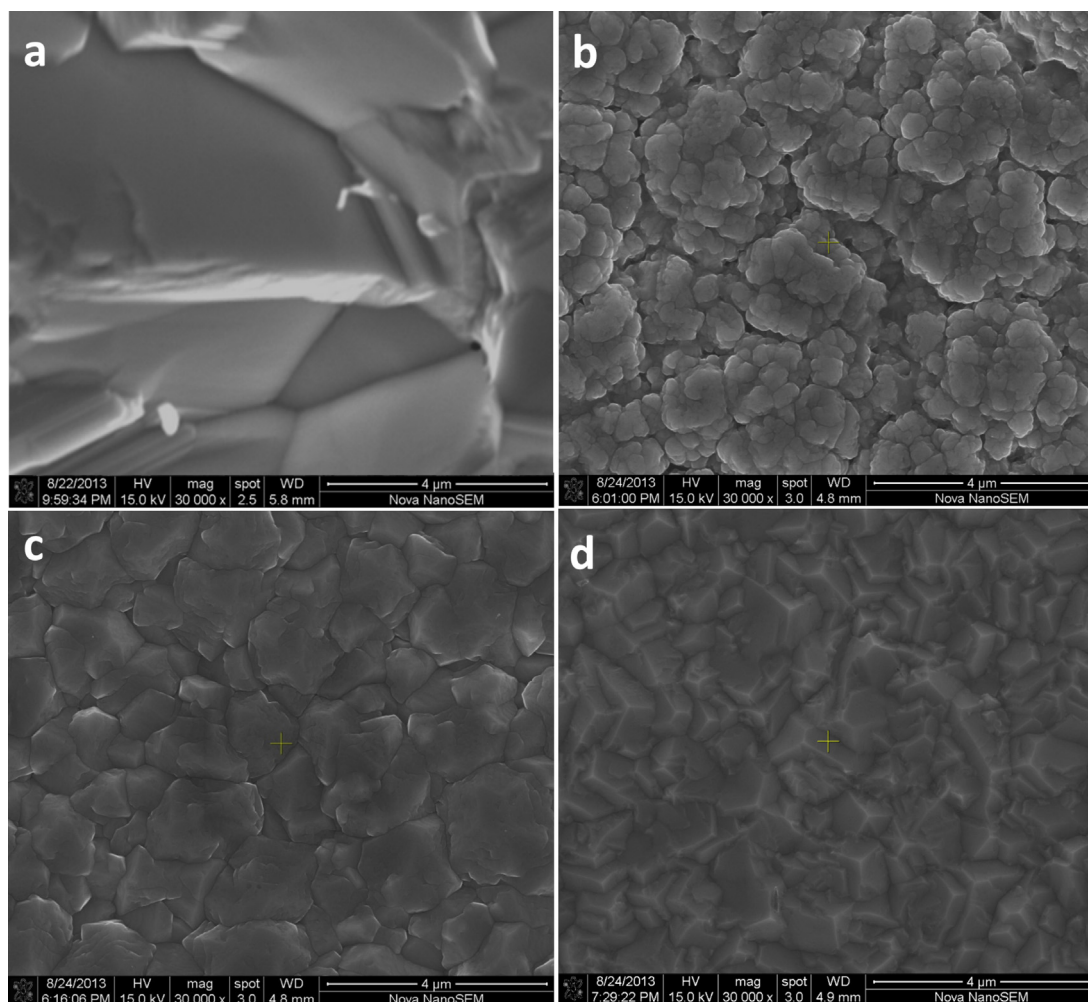


Fig. 1. SEM images of the electrodeposited films; (a) Zn, (b) Zn–7%Ni, (c) Zn–12%Ni, (d) Zn–17%Ni. (Percentage of nickel is in atomic percent.).

by pH meter Model PH 330/SET – 0, 82362 WTW, Germany). Electro-deposition of metal and alloy films was performed (on copper substrate) at a constant current density of 350 A m^{-2} for a period of 10 min using Potentiostat/Galvanostat AMEL Model-2051. Other details can be seen elsewhere [25].

Electrodeposited Zn and Zn–Ni films were immersed in 70 ml of pure water or 3.5% NaCl solution in a Teflon-lined Stainless Steel (SS) autoclave. The autoclave was then placed in an electric oven (Heraeus vacutherm VT 6130P). The temperature of the oven was slowly increased to 100°C , which was maintained for a period of 24 h followed by slow cooling to room temperature. The sample was then removed from the autoclave and thoroughly washed with distilled water.

X-ray diffraction (XRD) was performed by Bruker D8 Discover diffractometer with $\text{Cu K}\alpha$ radiations. Scanning electron microscopy (SEM) and compositional analysis was performed by using field emission scanning electron microscope (FEI Nova NanoSEM 430) equipped with EDX system (EDAX). High resolution transmission electron microscopy (HRTEM) was performed by FEI Technai G2 20 Scanning TEM. Photoluminescence (PL) spectra were obtained at room temperature (RT) and 10 K using 325 nm He–Cd laser line (Melles Griot Series 56) at 15 mW.

3. Results and discussion

Figure 1 shows SEM images of zinc and zinc–nickel alloy films electrodeposited on copper substrate in various chloride baths at a

current density of 350 A m^{-2} . Composition of these alloy films, as determined by EDX analysis, is shown in Table 1. (Percentage refers to atomic percent in this manuscript.) It has been reported by some of the present authors that the concentration of zinc and nickel chlorides in the bath has pronounced effect on the composition and morphology of alloy deposits, although the deposits remain rich in zinc due to anomalous co-deposition [25].

Figure 2 shows XRD patterns of ZnO nanostructures formed by hydrothermal oxidation of zinc and zinc–nickel alloy films in pure water and NaCl solution. After hydrothermal oxidation, wurtzite ZnO is formed. The electrodeposited alloy film is almost completely oxidized in NaCl solution (Figure 2(a–c)), except for the alloy containing 17% Ni (Figure 2(d)). In pure water, metal film is completely oxidized to ZnO (Figure 2(a)); XRD patterns for the alloy films indicate some un-consumed alloy phase ($\text{Ni}_2\text{Zn}_{11}$) (Figure 2(b–d)). The oxide layer formed on the alloy deposits seems to passivate the underlying metal/alloy and resist further oxidation in water. In NaCl

Table 1

Composition of precursor solution for electrodeposition and resulting Ni contents in deposited alloy films.

Sr. no	ZnCl ₂ in sol. (g/L)	NiCl ₂ ·6H ₂ O in sol. (g/L)	Ni contents in alloy (at%)
1	200	0	0
2	200	50	7
3	200	200	12
4	50	200	17

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