Materials Science in Semiconductor Processing 71 (2017) 268–274

Contents lists available at ScienceDirect

Materials Science in Semiconductor Processing

journal homepage: www.elsevier.com/locate/mssp

Ni dependent structural, optical and electrical properties of CuO nanostructures

Sushil Kumar Kuanr, Shovan Nayak, K. Suresh Babu*

Centre for Nanoscience and Technology, Madanjeet of Green Energy Technologies, Pondicherry University (A Central University), Puducherry 605014, India

ARTICLE INFO

Keywords:
Powders
Microstructure
Electrical conductivity, Dielectric properties

ABSTRACT

The present work reports the synthesis of $Cu_{1-x}Ni_xO$ (x = 0%, 3%, 6% and 9%) nanoparticles by co-precipitation method and correlates the effect of nickel on structural, optical and electrical properties. A phase separation into cubic NiO was observed at the higher nickel concentration of 9%. The difference in ionic radii between copper and nickel resulted in the lattice contraction. The mean crystallite size and strain values were found to be varying with respect to nickel concentration. Raman spectroscopy studies exhibited the emergence of 1LO peak on 9% doping due to the phase separation into NiO. The band gap energy calculated using diffuse reflectance spectra indicated a narrowing of band gap with the increase in nickel content. AC impedance measurement showed a maximum conductivity of 2.13×10^{-2} S/cm at 600 °C for $Cu_{0.94}Ni_{0.06}O$. Further, a lower activation energy was noticed for 6% which increased at 9% Ni presence. The dielectric constant was found to be increasing till 6% and decreases with higher nickel content (9%). The present work clearly demonstrates the beneficial role of nickel in the form of a doped structure while it becomes detrimental upon phase separation.

1. Introduction

Nanostructured transition metal oxides have drawn considerable attention from both fundamental and technological aspects due to their unique optical, mechanical and electrical properties [1–6]. As a result of the higher surface to volume ratio at nano regime, oxides of transition metals show physico-chemical properties differing from their bulk counterparts [7–9]. Copper oxide (CuO) having a high dielectric constant and p-type semiconductor with a band gap of 1.4–2.1 eV have been utilised in solar cells, Li-ion battery, fuel cells, thermoelectrics, supercapacitors, magnetic storage media, gas sensor and various catalysis processes [10–15]. Various attempts have been made to improve the electrical properties of CuO nanostructures. The electrical performance of CuO can be influenced by its morphology, preparation method and chemical composition. Shao et al. reported that the typical value of electrical conductivity of a p-type CuO nanostructure as 7.8×10^{-4} S/cm [16]. Jeong et al. observed a higher electrical conductivity value for smaller grain sized CuO due to the dominance of conductivity in the grain rather than that of grain boundary [17]. Further, the presence of non-stoichiometric defect which is responsible for the modulation of charge carrier concentration can affect the electrical property. Drobny and Pulfrey have reported an enhancement in CuO conductivity as a result of non-stoichiometric defect produced by the increase in oxygen partial pressure [18].

The presence of dopant as well as its concentration in CuO may influence the chemical and physical properties. Further, the presence of dopant affects the stoichiometry and crystallinity of CuO and thereby having an impact on conductivity. Few reports are available on the preparation and structural changes associated with CuO on doping with transition metals, such as Mn [19], Fe [20–22], Cd and Zn [23]. However, limited investigations have been carried out to correlate the conductivity and the dopant nature in CuO [24,25]. Suda et al., examined the conductivity of pure and Li- or Al- doped CuO and reported the temperature dependent improvement in conductivity due to the enhancement in hole concentration [26]. Chiang et al., studied the effect of dopants such as Li, Ni, Co, Ag, Zn and Mg on the conductivity of CuO [27]. A relatively higher electrical conductivity of 1.8×10^{-5} S/cm was observed for Ni doped CuO even at a lower concentration of around 2.9 at%. In spite of the reports on the Ni-doped CuO nanostructure with respect to various properties, a systematic effort to unveil the evolution of electrical properties is absent to the best of our knowledge [28–30]. The optimum concentration of Ni doping required for the better conductivity needs to be ascertained in order to realize many potential applications.

Various methods have been employed for the synthesis of copper oxide such as colloid thermal synthesis [31], reflux condensation [32], solid state reaction [33], thermal decomposition [34], sol-gel [35], sonochemical [36], hydrothermal [37], etc. Out of all these methods,

---

* Corresponding author.
E-mail address: sureshbabu.nst@pondiuni.edu.in (K. Suresh Babu).

http://dx.doi.org/10.1016/j.mssp.2017.08.012
Received 1 July 2017; Received in revised form 3 August 2017; Accepted 5 August 2017

co-precipitation provides a simple, fast and economical route for the preparation of CuO nanostructures. The present work deals with the synthesis of $Cu_{1\text{-}x}Ni_xO$ nanoparticles and its influence on structural, optical and electrical properties. Thus, present work shows that the doping of Ni^{2+} in CuO only up to a certain limit can enhance its electronic conductivity.

2. Experimental detail

2.1. Preparation of $Cu_{1\text{-}x}Ni_xO$ nanoparticles

$Cu_{1\text{-}x}Ni_xO$ (x = 0, 3, 6 and 9 at%) nanoparticles were prepared by co-precipitation method using copper nitrate trihydrate ($Cu(NO_3)_2{\cdot}3H_2O$, Himedia) and nickel nitrate hexa hydrate ($Ni(NO_3)_2{\cdot}6H_2O$, Himedia) as precursors. Typically, to 500 ml of 1 M aqueous $Cu(NO_3)_2{\cdot}3H_2O$ solution, calculated amount of $Ni(NO_3)_2{\cdot}6H_2O$ was added. After stirring at 600 rpm for 30 min, 1 M NaOH solution was added drop wise in order to maintain the pH at 11 which changes the colour from transparent deep blue to opaque sky blue. After stirring the solution for 6 h, the precipitate was centrifuged and washed four times with deionized water to remove any impurities. Subsequently, the resultant precipitate was filtered, dried at 80 °C overnight and calcined at 350 °C for 2 h. The detail of the synthesis procedure of Ni doped CuO nanoparticles is shown schematically in Fig. 1. The calcined powder was uniaxially pressed at 7 t into cylindrical pellets to form 13 mm diameter and 2.5 mm thickness. The green pellet was sintered at 600 °C for 5 h at a heating rate of 5 °C per minute.

2.2. Characterization techniques

The crystal structure of the material was investigated using Rigaku Ultima IV X-Ray diffractometer (XRD) using Cu Kα radiation (λ = 0.15418 nm). Raman spectroscopic studies were carried out with Renishaw Laser confocal Raman Microscope RM 2000 using 514 nm laser excitation. Optical properties were analysed by UV–visible Diffused Reflectance Spectrophotometer (DRS, Varian, 5000). The surface morphology and elemental composition were investigated by a Field Emission-Scanning Electron Microscope (FE-SEM), Zeiss Gemini Ultra-55 with Oxford EDX attachments operating at 5 kV. The cylindrical pellets of 13 mm diameter and 1 mm thickness were used as a dielectric medium by using platinum mesh on both sides of the sample as electrodes. The frequency dependent of dielectric constant and the electrical behaviour were studied using a Broadband dielectric spectrometer (Novocontrol Technologies, Concept 80) from room temperature to 600 °C in the frequency range of 1 Hz to 10 MHz at the bias potential of 1 V.

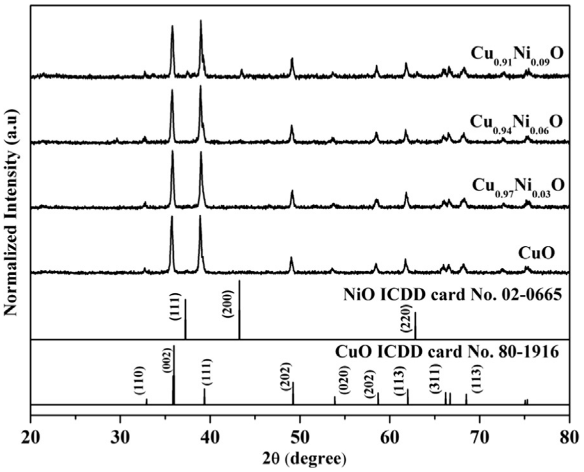

Fig. 2. XRD spectra of pure CuO and Ni doped CuO nanoparticles.

3. Results and discussion

3.1. Structural analysis

Fig. 2 shows the XRD pattern of $Cu_{1\text{-}x}Ni_xO$ nanoparticles prepared by co-precipitation method. The major peaks observed at 2θ values of 32.58, 35.47, 38.97 and 48.74° correspond to the (110), (002), (111) and (202) reflection planes of monoclinic CuO (ICDD card no. 80-1916), respectively. Only single phase CuO was observed for the addition of nickel up to 6% indicating the presence of nickel as the dopant in CuO matrix. However, in the case of $Cu_{0.91}Ni_{0.09}O$ additional peaks were observed at 2θ values of 37.24, 43.27° which correspond to (111) and (200) diffraction planes, respectively, of cubic phased NiO (ICDD card no. 02-0665). A progressive shift towards higher 2θ value was observed for (002) and (111) planes with the increase in dopant concentration due to the substitution of Cu^{2+} (ionic radius: 0.73 Å) with Ni^{2+} (ionic radius: 0.70 Å) ions. Therefore, it can be speculated that the Ni^{2+} ions are incorporated into CuO lattice by replacing the Cu ions to form doped structures.

The lattice parameter ($a \neq b \neq c$, $\alpha = \gamma = 90^\circ \neq \beta$) and the unit cell volume of CuO lattice was calculated by using the following equation:

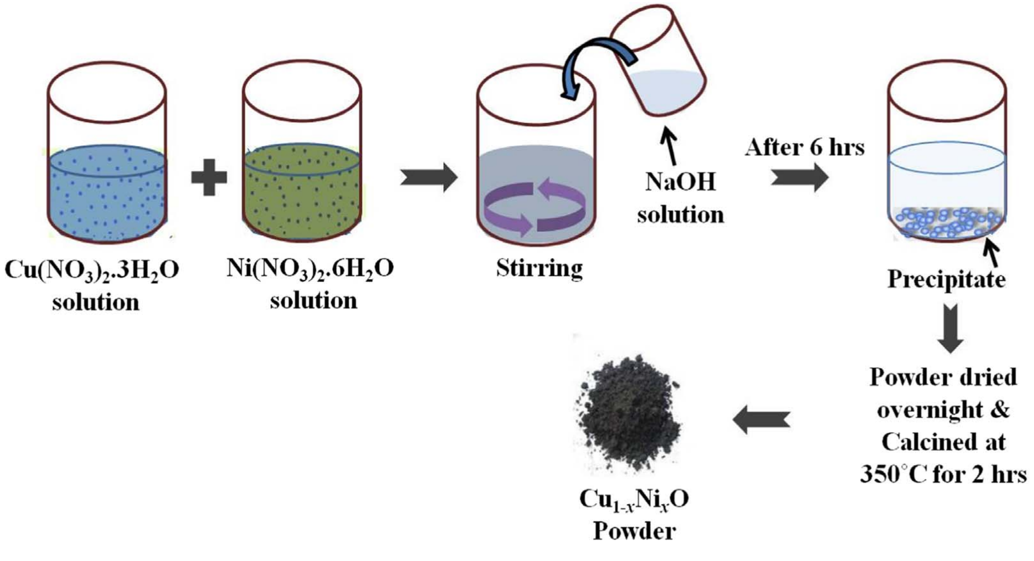

Fig. 1. Schematic representation of the synthesis of Ni doped CuO nanoparticles.