

Studies on the structural, electrical and optical properties of thermally oxidized copper nickel oxide thin films

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Abstract

Thin films of copper nickel oxide (CuNiO_2) were prepared by thermal oxidation of metallic copper nickel film formed by DC magnetron sputtering of quimolar $\text{Cu}_{50}\text{Ni}_{50}$ target. The as-deposited copper nickel films were thermally oxidized in oxygen atmosphere at different temperatures in the range 250–350°C. The as-deposited and oxidized films were characterized for their chemical composition, structure and surface morphology, electrical and optical properties. The films oxidized at 350°C were of CuNiO_2 with polycrystalline nature and crystallite size of 38 nm. The influence of oxidation temperature on the physical properties was systematically investigated. The films oxidized at temperature of 350°C were CuNiO_2 with electrical resistivity of 7 Ωcm and optical band gap of 2.50 eV.

Introduction

Cuprous oxide is a p-type semiconducting oxide material finds potential applications in the field of gas sensor, solar cells, electrochromic devices and p-type transparent conductive coatings. Doping of nickel into copper oxide modifies the electrical properties by introducing acceptor levels in copper oxide [1]. CuO-NiO mixed metal oxide nanoparticles are potential as a catalyst for various organic reactions such as methanol synthesis and humidity and non-enzymatic glucose sensors [2-4]. Copper nickel oxide in thin film form find applications as NO_2 gas sensor, anode for fuel cells, solar selective coatings, solar cells, electrochromic devices, light emitting diodes, photodiodes, p-type gate in heterojunction field effect transistors, p-type transparent conducting coatings, antifungal coatings and super-capacitor coatings [5-19]. $\text{Cu}_x\text{Ni}_{1-x}\text{O}$ thin films with different copper compositions were deposited by various methods such as spray pyrolysis, sol-gel process electro-deposition, pulsed laser deposition, pulsed plasma deposition, co-evaporation, DC magnetron sputtering and RF magnetron sputtering [6-12,14,16,17,19-35]. In the literature, Yang et al. [27] reported that the p- $\text{Cu}_{0.1}\text{Ni}_{0.9}\text{O}$ thin films formed by pulsed plasma deposition showed the electrical resistivity of 0.19 Ωcm and optical band gap of 3.7 eV. Miyata et al. [31] noticed the electrical resistivity increased from 96 to $8 \times 10^5 \Omega\text{cm}$ and optical bands gap increased from 2.6 to 3.9 eV with increase of nickel content in RF reactive magnetron sputtered CuNiO ($\text{Ni} = 0-100 \text{ at.}\%$) films. Elsayed et al. [14] formed nanocrystalline CuNiO_2 films by sol-gel process with optical band gap of 2.4 eV. The electrical resistivity of 27 Ωcm and optical band gap of 2.0 eV were obtained by RF magnetron sputtering by using equimolar $\text{Cu}_{50}\text{Ni}_{50}$ target [34]. Menaka et al. [22] deposited $\text{Cu}_x\text{Ni}_{1-x}\text{O}$ ($x = 0.02 - 0.08$) films by spray pyrolysis and noticed that the electrical resistivity decreased from 250 to 88 Ωcm and optical band gap decreased from 3.94 to 3.58 eV with increase of copper content from 2 to 8 at.% respectively. In the present investigation, an attempt is made in the preparation of copper nickel oxide (CuNiO_2) thin films by thermal oxidation of metallic CuNi thin films formed by DC magnetron sputtering method. The thermally oxidized CuNiO_2 thin films were characterized for their composition, structure, electrical and optical properties.

Experimental

Thin metallic CuNi films were deposited by employing DC magnetron sputtering technique using the composite target of $\text{Cu}_{50}\text{Ni}_{50}$ (99.95% purity) with 50 mm diameter. The sputter chamber was evacuated to achieve the ultimate pressure of 1×10^{-5} mbar using diffusion pump backed by rotary pump. Pressure in the sputter chamber was measured with Pirani and Penning gauges. Before introducing the glass substrates in sputter chamber, the substrates were cleaned with degreasing solution followed by washing in deionized water. Later, the substrates were immersed in potassium dichromate solution for an hour and finally cleaned ultrasonically in a stainless steel tank for 15 minutes and dried with flow of nitrogen gas then transferred into chamber for deposition of copper nickel thin films. Target to substrate distance maintained was 50 mm. After achieving the ultimate pressure, argon gas was admitted into the sputter chamber through fine controlled needle valve to achieve sputter pressure of 3×10^{-2} mbar. The films were deposited on glass substrate held at room temperature and the DC power fed to the sputter target was 90 W. The duration of the deposition of the film was 10 min. As-deposited metallic CuNi films were thermally oxidized in oxygen atmosphere for three hours in the temperature (T_a) range 250°C to 350°C in order to transform in to copper nickel oxide films. The as-deposited and thermally oxidized films were characterized for their chemical composition, structure and surface morphology, electrical and optical properties. Thickness of the deposited CuNi film determined with Veeco Dektak (Model 150) was 220 nm. Chemical composition of the metallic and oxide films was determined with energy dispersive X-ray analysis (EDAX) (Oxford instruments Inca Penta FETX3). Crystallographic structure of the

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films was determined with X-ray diffraction (XRD) (RigakuMiniflexII) X-ray diffractometer using copper K_α radiation with wavelength of 0.15406 nm. The surface morphology of the films was analyzed with atomic force microscope (AFM) (Seiko Instruments). Electrical resistivity, Hall mobility and carrier concentration were determined by using a Hall effect measurement system (ECOPIA HMS-3000 VER3.51.3). Optical transmittance of the films was recorded with Perkin - Elmer double beam spectrophotometer in the wavelength range 300 - 800 nm in order to understand the optical absorption and to determine the optical band gap. The influence of oxidation temperature on the physical properties was systematically investigated on the copper nickel oxide films.

Results and discussion

Chemical composition

Chemical composition of the as-deposited metallic copper nickel films formed on silicon substrates and thermally oxidized copper nickel oxide films were analyzed with energy dispersive X-ray analysis. Figure 1a shows the EDAX spectrum of copper nickel films. The film showed the characteristic constituent peaks of copper and nickel. The chemical composition of the film was calculated from the intensities of copper and nickel peaks. The copper nickel film contained the copper content of 50.7 at. % and nickel 49.3 at. %. There was no peak related to oxygen which indicated that the as-deposited were of copper nickel films. The EDAX spectra exhibited that the intensity of oxygen peak increased with increase of oxidation temperature. It revealed that the oxidation of copper nickel films leads to transform into the copper nickel oxide.

The increase in the intensity of characteristic peak of oxygen indicated the increase of oxygen content in the films due to convert into copper nickel oxide with the increase of temperature of oxidation as shown in figure 1b, c, and d. The ratio of peak intensity of copper to nickel remains almost constant to unity. The chemical composition of the as-deposited and thermally oxidized films is given table 1. It is seen from the table that the content of oxygen in the films increased from 44.8 at. % to 49.4 at. % with increase of temperature from 250°C to 350°C respectively. It clearly indicated that the CuNi films oxidized at temperature of 350°C were of stoichiometric CuNiO_2 .

It revealed that the temperature of 350°C is an optimum to oxidize metallic copper nickel films into copper nickel oxide (CuNiO_2). It is to be noted that CuNiO_2 thin films were also achieved by RF reactive magnetron sputtering of equimolar $\text{Cu}_{50}\text{Ni}_{50}$ target at an oxygen partial pressure of 2×10^{-4} mbar [34].

Structural Properties

X-ray diffraction profile of as-deposited copper nickel film is shown in figure 2. The diffraction pattern of the films was polycrystalline nature. The film exhibited weak diffraction peaks at 22.1° , 29.2° and strong peaks at 37.4° , 44.2° and 51.3° . A weak peak located at 22.1° was related to the (200) reflection of NiO [36,37]. Another diffraction reflection seen at 29.2° related to copper nickel / Cu_2O [38,39]. The peak seen at 37.4° corresponds to the (222) reflection of NiO and the peaks situated at 44.2° and 51.3° were connected to the CuNi alloy [7,40]. It revealed that the as-deposited film was of CuNi along with traces nickel oxide. The presence of nickel oxide phase and copper oxide was mainly due to

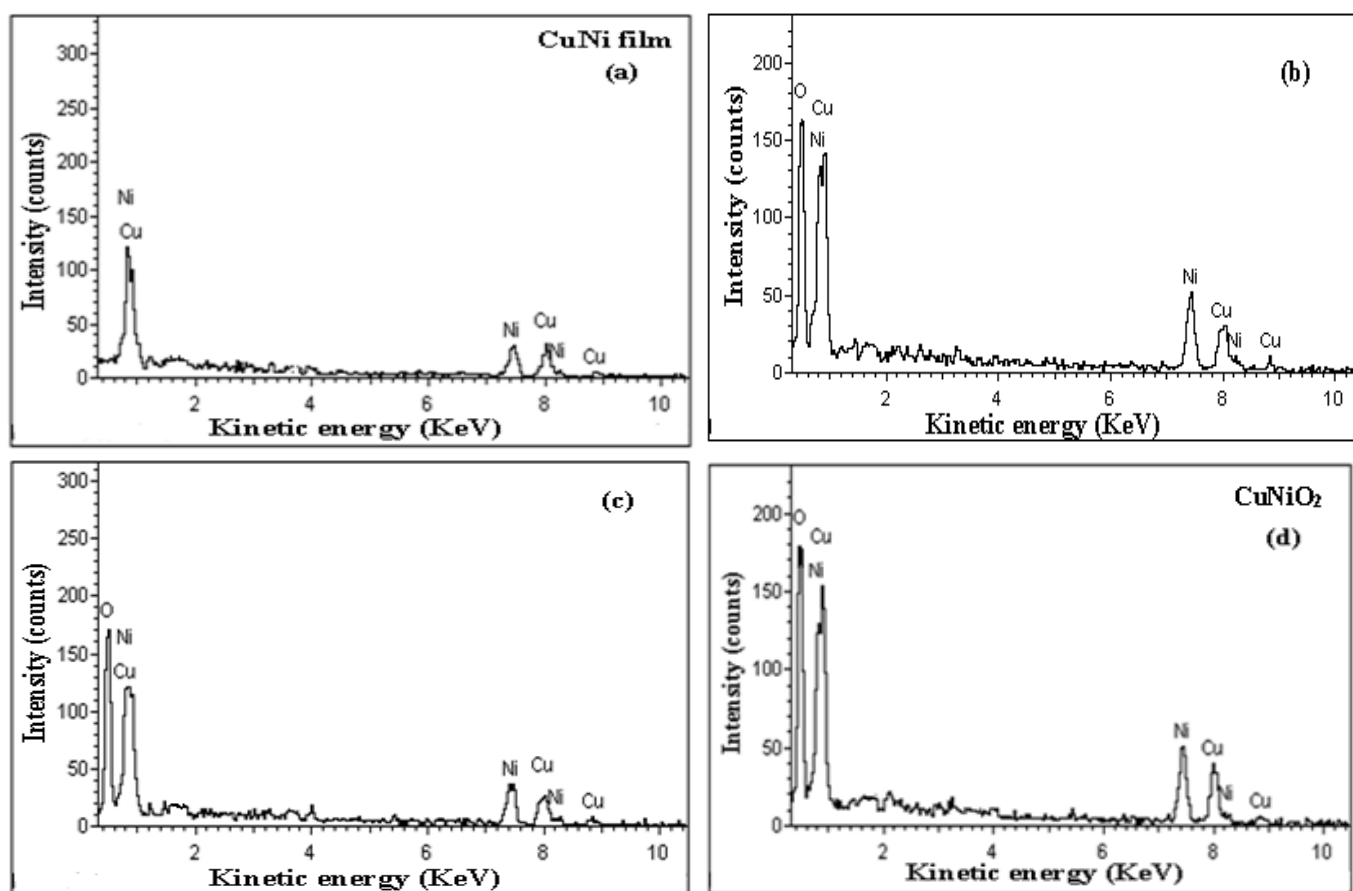


Figure 1. S Energy dispersive X-ray of (a) as-deposited copper nickel thin film and the films oxidized at temperatures: (b) 250°C, (c) 300°C and (d) 350°C

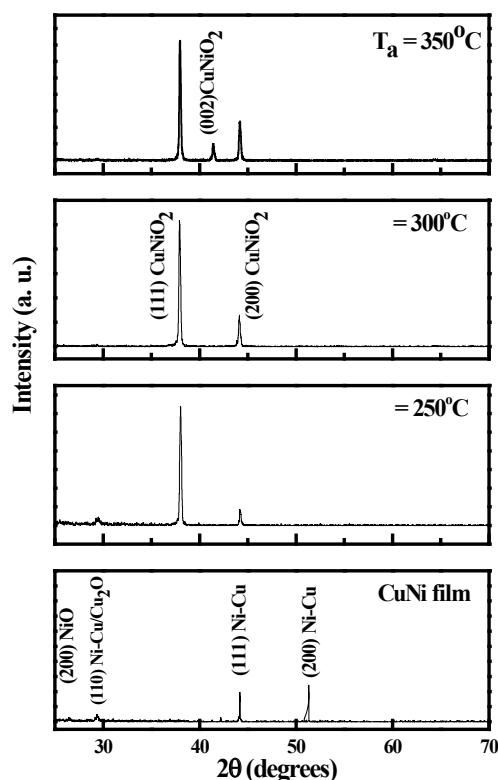


Figure 2. X-ray diffraction profiles of (a) as-deposited copper nickel film and thermally oxidized copper nickel oxide films: (b) 250°C, (c) 300°C and (d) 350°C.

Table 1. Chemical composition of copper nickel oxide films oxidized at different temperatures.

Film	Oxidation temperature (°C)	Chemical composition (at. %)		
		Copper	Nickel	Oxygen
CuNi	As-deposited	48.9	51.1	----
	250	28.2	26.9	44.8
	300	26.9	25.8	47.3
	350	25.0	25.6	49.4

the oxidation of nickel and copper with residual oxygen in the sputter chamber during the growth of the films. Figure 2 shows the X-ray diffraction profiles of thermally oxidized copper nickel oxide films at temperatures of 250°C, 300°C and 350°C. It is seen from the diffraction profiles that the thermally oxidized films were also of polycrystalline in nature. The films oxidized at 250°C showed the X-ray diffraction peaks at 37.1° and 43.9° related to the (111) and (200) reflections of CuNiO₂ [27]. As the oxidation temperature increased to 300°C the intensity of diffraction peaks increased which indicated the improvement in the crystallinity of the films. Further increase of oxidation temperature to 350°C, there was enhancement in the peak intensities of (111) and (200) along with the appearance of diffracted peak at 41.4° related to the (002) reflection of CuNiO₂. From the X-ray diffraction peaks the interplanar distance and the lattice parameters were calculated. The structure of the films oxidized at temperature of 350°C was tetragonal with lattice parameters, $a = 0.4112$ nm and $c = 0.4361$ nm. The given thermal energy to the copper nickel films in presence of oxygen leads to transform the copper nickel films into copper nickel oxide. It revealed that the increase of oxidation temperature to 350°C the metallic copper nickel films were transformed into CuNiO₂ with enhanced crystallinity. The crystallite size (D) of the as-deposited and thermally oxidized films was calculated from the full width at half maximum intensity (β), the

diffraction angle (θ) of the (111) peak, and the wavelength of copper X-rays using Debye-Scherrer's relation [41]

$$D = K\lambda / \beta \cos\theta \quad (1)$$

where K is a constant with a value of 0.89 for X-ray target of copper and θ the diffraction angle. The full width at half maximum intensity of peak decreased with increase of oxidation temperature which indicated the crystallite size increased with the oxidation temperature. The crystallite size of the as-deposited copper nickel film was 13 nm. As the temperature of oxidation increased to 350°C the crystallite size increased to 38 nm as shown in figure 3. It was reported low crystallite size of 32 nm in spray deposited copper nickel oxide films [21]. The dislocation density (δ) of the films was determined from the crystallite size using the relation [42].

$$\delta = 1/D^2 \quad (2)$$

The dependence of dislocation density on the oxidation temperature of the films are shown in figure 3. The dislocation density of the as-deposited metallic copper nickel film was 7.5×10^{16} lines/m². As oxidation temperature increased the dislocation density decreased to 4.1×10^{16} lines/m² in copper nickel oxide films oxidized at temperature of 300°C. Further increase of oxidation temperature to 350°C the dislocation density decreased to 1.2×10^{16} lines/m². The low value of dislocation density in the CuNiO₂ films oxidized at higher temperature was mainly due to the larger crystallite size. It is to be noted that the dislocation density reported in the CuNiO₂ films was high value of 15×10^{16} lines/m² in bias magnetron sputtered CuNiO₂ films [34]. The strain (ϵ) developed in the films was calculated from the X-ray diffraction peak and full width at half maximum intensity using the relation [43].

$$\epsilon = \beta \cos\theta / 4 \quad (3)$$

Figure 4 shows the dependence of strain on the oxidation temperature of the copper nickel oxide films. It is seen from the figure that the strain in the metallic copper nickel films was 9.4×10^{-4} lines²/m⁴. The strain in the films decreased with oxidation temperature. The films oxidized at 250°C exhibited the strain of 7.4×10^{-4} lines²/m⁴. The number of crystallites (N) were calculated from the crystallite size and thickness of the film using the relation [44].

$$N = t/D^3 \quad (4)$$

The number of crystallites in metallic CuNi films 0.100 nm². In the case copper nickel oxide films the number of crystallites decreased

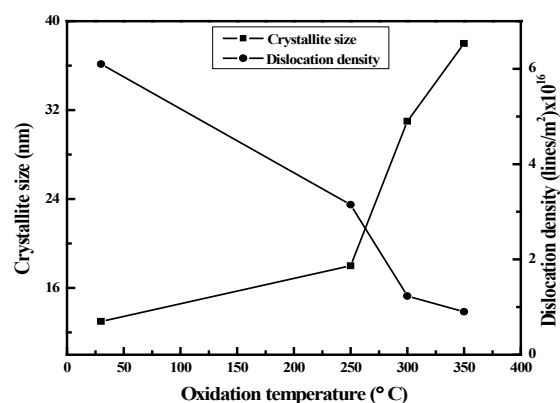


Figure 3. Variation in Crystallite size and dislocation density of copper nickel oxide films with oxidation temperature.

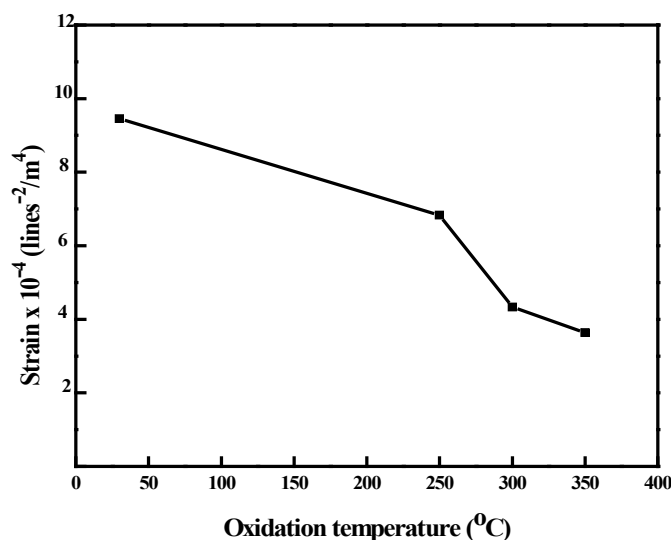


Figure 4. Dependence of strain on the thermal oxidation temperature of copper nickel oxide films.

from 0.037 to 0.004 nm⁻² with increase of oxidation temperature from 250°C to 350°C respectively.

Surface Morphology

Atomic force microscope was used to analyze the surface morphology of as-deposited CuNi films and thermally oxidized copper nickel oxide films. Figure 5 shows the three dimensional and two dimensional atomic force micrographs of as-deposited copper nickel (figure 5a), thermally oxidized copper nickel oxide films (figure 5b, c, and d) respectively. As-deposited films were of fine grain structure while those oxide films were of larger in grain size. The variation in grain size with the oxidation temperature of CuNiO₂ films is shown in figure 6. The grain size of the as-deposited copper nickel films was 55 nm. As the oxidation temperature increased, the thermal energy accelerates the coalescence of small grains into larger ones, and also reacts with oxygen to form copper nickel oxide. The grown grains were of almost spherical in shape. The root mean square (RMS) roughness of the metallic CuNi films was 2.0 nm. In copper nickel oxide films oxidized at temperature of 350°C of high roughness of 12.1 nm as shown in figure 6. Such an increase in the roughness with deposition temperature was noticed in aluminum oxide thin films formed by DC magnetron sputtering [45] and Cu₂O films deposited by DC magnetron sputtering [46].

Electrical Properties

The electrical properties of the films are strongly influenced by the oxidation temperature. The dependence of electrical resistivity on the oxidation temperature of copper nickel oxide films is shown in figure 7. Electrical resistivity of metallic copper nickel films was 4×10^{-3} Ωcm. As the temperature increased the oxidation of copper nickel films takes place. The films oxidized at 250°C were partially oxidized and showed the electrical resistivity of 5×10^{-1} Ωcm. Further increase of oxidation temperature to 350°C the films were fully oxidized and form CuNiO₂. These oxide films showed the electrical resistivity of 7 Ωcm. The oxide films are in general of high electrical resistivity when compared to mixed phase oxide films. In the literature, it was reported that the electrical resistivity in pulsed laser deposited Ni_{0.9}Cu_{0.1}O films was 0.19 Ωcm [27]. Miyata et al. [31] achieved electrical resistivity of 70 Ωcm and 4×10^4 Ωcm in RF magnetron sputtered Cu₂O and NiO films respectively, while equimolar Cu-Ni oxide films showed the value of

2×10^4 Ωcm. Chen et al. [32] reported low electrical resistivity of 36 Ωcm in 9 at. % copper doped nickel oxide films. The variation in the electrical resistivity of the copper nickel oxide films was mainly due to the difference in the chemical composition and the deposition method of the films. Hall effect measurements indicated that the metallic copper nickel films were of n-type while copper nickel oxide films were of p-type in electrical conduction. When the films oxidized the type of charge carrier transport changed from electronic to hole conduction. Figure 8 shows the variation of Hall mobility of the copper nickel oxide films with the oxidation temperature. The metallic copper nickel films showed electron mobility of 0.4 cm²/V.sec. As the oxidation temperature

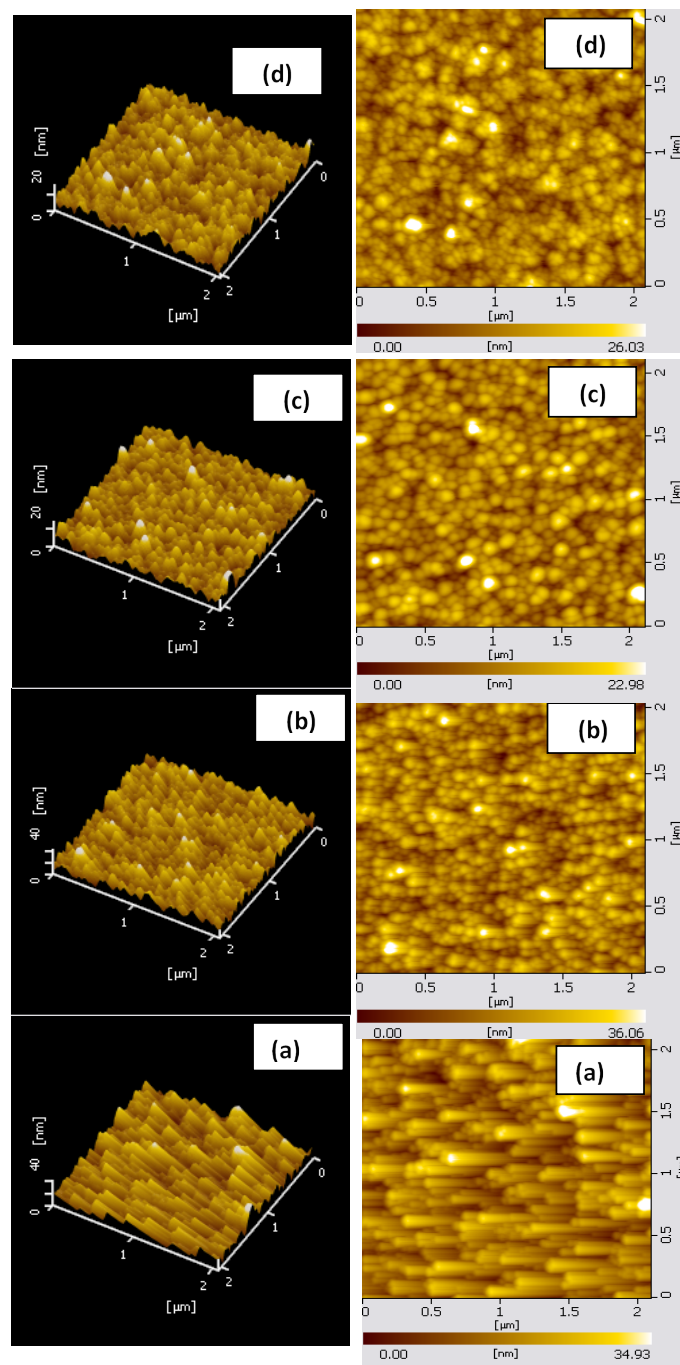


Figure 5. Two and Three dimensional AFM images of (a) copper nickel film and copper nickel oxide films oxidized at temperatures: (b) 250°C, (c) 300°C and (d) 350°C.

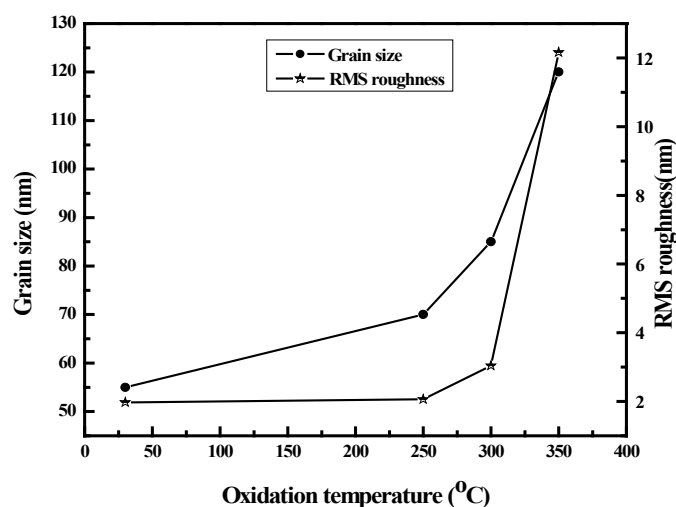


Figure 6. Variation in Grain size and root mean square roughness of copper nickel oxide films with oxidation temperature.

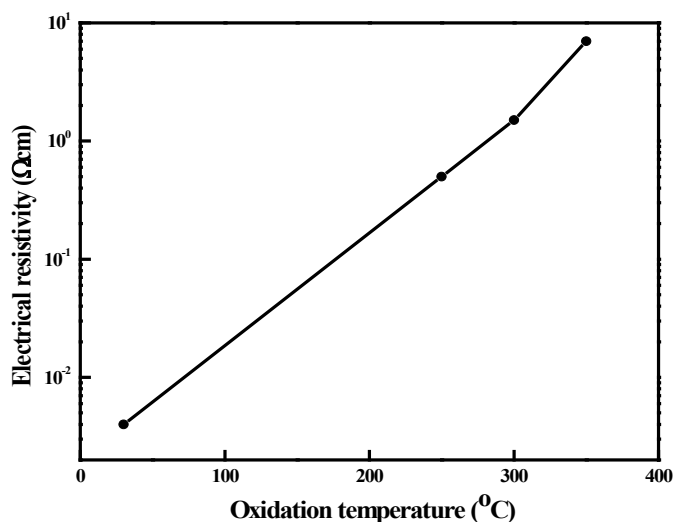


Figure 7. Dependence of electrical resistivity on oxidation temperature of copper nickel oxide films.

increased the hole mobility increased from 3.1 cm²/V.sec and reached a value of 7.8 cm²/V.sec with increase of oxidation temperature from 250°C to 350°C in CuNiO₂ films. The electron concentration in metallic copper nickel film was 3.9x10¹⁸ cm⁻³. Hole concentration in the films decreased from 4.0x10¹⁷ to 1.1x10¹⁶ cm⁻³ with increase of oxidation temperature from 250°C to 350°C respectively as shown in figure 8. Miyata et al. [31] reported low Hall mobility of 2 cm²/V.sec and low carrier concentration of 8x10¹³ cm⁻³ due to high electrical resistivity of copper nickel oxide films. In contrast to this, Chen et al. [32] obtained Hall mobility of 1 cm²/V.sec and carrier concentration of 2x10²⁰ cm⁻³ in 18 at. % of copper doped NiO films formed by RF magnetron sputtering.

Optical Properties

Optical transmittance of metallic copper nickel and thermally oxidized copper nickel oxide films was recorded in order to study the optical absorption and to determine the optical band gap. Figure 9 shows the optical transmittance spectra of copper nickel and copper nickel oxide thin films oxidized at different temperatures. It is seen

from the figure that the transmittance of copper nickel thin film was very low (< 3%) since the metal films reflect the incident radiation. As the oxidation temperature increased to 250°C the transmittance of the films increased and showed about 19% (at wavelength of 600 nm). This is due to partially oxidation of CuNi films into copper nickel oxide. Further increase of oxidation temperature to 350°C the transmittance enhanced to about 30 % due to the formation of copper nickel oxide films. The fundamental optical absorption edge of the films shifted towards lower wavelength side with increase of oxidation temperature. Absorption coefficient (α) of the films calculated from the thickness of the film (t) and optical transmittance (T) data using the relation.

$$\alpha = - (1/t) \ln T \quad (5)$$

The optical band gap (E_g) of the films was determined from the absorption coefficient and the photon energy using Tauc's relation [47] assuming the direct transitions take place from the top of the valence band to the bottom of conduction band.

$$(\alpha h\nu) = A (h\nu - E_g)^{1/2} \quad (6)$$

Figure 10 shows the plots of $(\alpha h\nu)^2$ versus photon energy ($h\nu$) of the copper nickel oxide films oxidized at different temperatures.

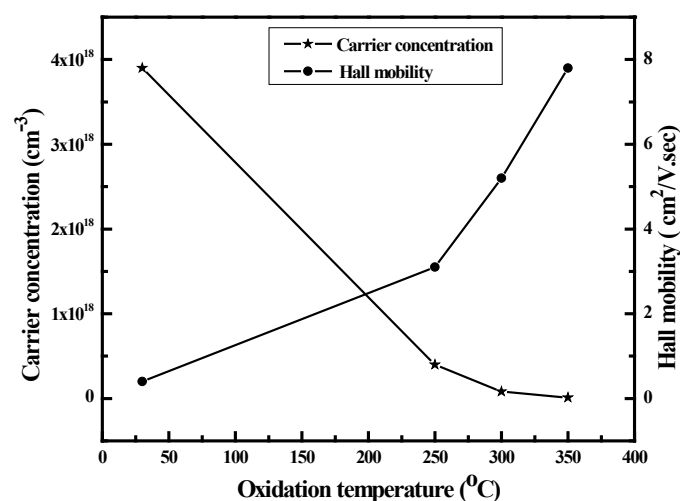


Figure 8. Variation in Carrier concentration and Hall mobility of copper nickel films with oxidation temperature.

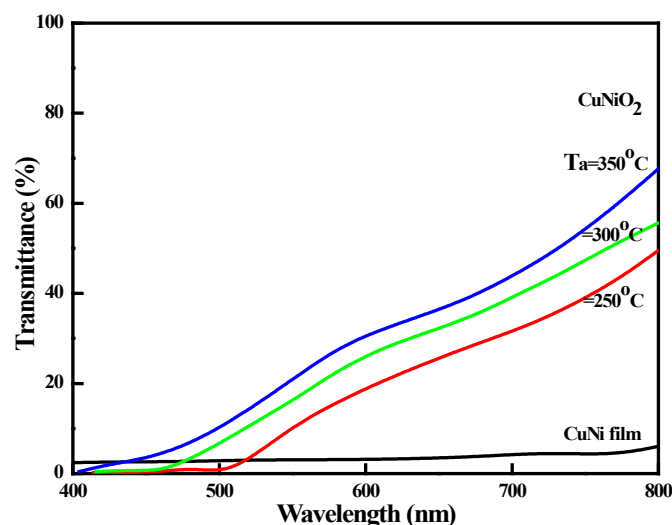
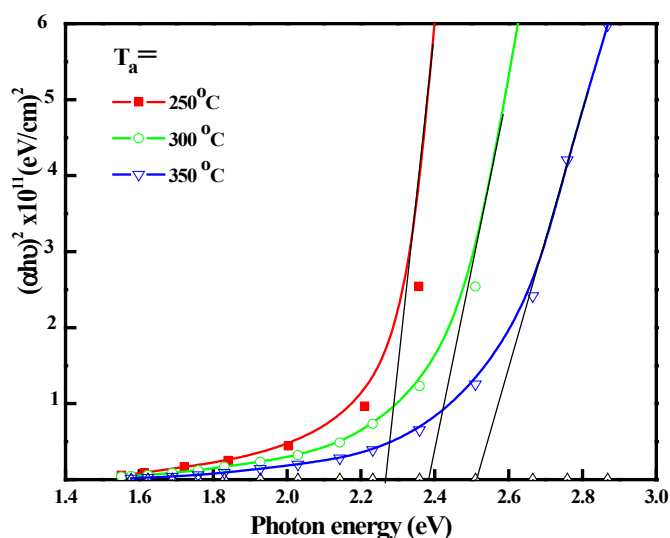


Figure 9. Optical transmittance spectra of thermally oxidized copper nickel oxide films.

Table 2. Summary of electrical and optical properties of Cu-Ni-O films prepared by different methods.

S.No.	Deposition method	Target composition	Film composition	Substrate temperature/ Annealing temperature (°C)	Electrical resistivity (Ωcm)	Optical bandgap (eV)	Ref.
1	Spray pyrolysis	--	$\text{Cu}_x\text{Ni}_{1-x}\text{O}$ ($x=0-0.10$)	350	---	3.2-2.96	20
2	Spraypyrolysis	--	$\text{Cu}_x\text{Ni}_{1-x}\text{O}$ ($x = 0.02-0.08$)	450	³ 250 - 88	3.94-3.58	22
3	Sol-gel process	---	CuNiO_2	150	---	2.4	14
4	Sol-gel process	---	$\text{Cu}_{0.05}\text{Ni}_{0.95}\text{O}$	550	0.23	3.69	24
5	RF Magnetron sputtering	Cu:NiO (Cu=0-9.8%)	Cu-Ni-O	100	8.7	3.3	17
6	RF magnetron sputtering	CuO-NiO Cu= 0-100%)	Cu-Ni-O	30	$70-4 \times 10^4$	2.6 -3.9	31
7	RF magnetron sputtering	NiO-Cu	$\text{Cu}_{0.09}\text{Ni}_{0.91}\text{O}$	30	36	---	32
8	RF magnetron sputtering	$\text{Cu}_{50}\text{Ni}_{50}$	CuNiO_2	250	27	2.0	33
9	RF Magnetron sputtering	CuO : NiO (0.18:0.82)	Cu-Ni-O	30	0.12	2.41	35
10	RF Magnetron sputtering	Cu:NiO (Cu=0-12%)	Cu-Ni-O	30	-----	3.86 - 3.63	38
11	Pulsed plasma deposition	NiO-CuO	$\text{Cu}_{0.1}\text{Ni}_{0.9}\text{O}$	30	0.19	3.7	27
12	DC magnetron sputtering	$\text{Cu}_{0.3}\text{Ni}_{0.7}$	$\text{Cu}_{0.3}\text{Ni}_{0.7}\text{O}$	100	81	2.2	29
13	DC magnetron sputtering	$\text{Cu}_{50}\text{Ni}_{50}$	CuNiO_2	250 - 350	0.5 – 7.0 -7	2.25 -2.50	Present work

**Figure 10.** Plots of $(\alpha h\nu)^2$ versus photon energy of copper nickel oxide films.

By extrapolating the linear portion of the plots to $\alpha = 0$ resulted the optical band gap. Optical band gap of the films increased from 2.25 to 2.50 eV with increase of oxidation temperature from 250°C to 350°C respectively. Summary of the electrical and optical properties of copper nickel oxide films of different compositions formed by various deposition techniques are given in table. The low value of optical band gap of the films oxidized at low temperatures was mainly due to the partial oxidation of the films. It is to be noted that the optical band gap of 50% Cu in copper nickel oxide films was 2.75 eV in RF magnetron sputtered and 3.04 eV in spray deposited films [20,31]. It is to be noticed that the optical band gap of 2.0 eV was obtained in RF magnetron sputtered and 2.4 eV in sol-gel processed CuNiO_2 films. It is seen from the table that the large variations in the electrical resistivity and optical

band gap depends on the deposition method and deposition parameter [14,30]. The low electrical resistivity and small band gaps were due to the mixed phase films.

Conclusions

Thermal oxidation process was employed for the growth of copper nickel oxide thin films. Metallic copper nickel films were deposited by DC magnetron sputtering of equimolar target of $\text{Cu}_{50}\text{Ni}_{50}$ on to glass substrates held at room temperature. As-deposited copper nickel film was thermally oxidized in oxygen atmosphere at different temperatures in the range 250 – 350°C. These films were characterized for chemical composition, structure, electrical and optical properties. The films oxidized at temperatures less than 350°C were deficiency in the oxygen content where as those oxidized at 350°C were of CuNiO_2 . These CuNiO_2 films were of polycrystalline in nature with tetragonal structure with crystallite size of 38 nm. The electrical resistivity of the films decreased with increasing of oxidation temperature and exhibited a value of 7 Ωcm. Hall effect studies indicated that the oxide films were of p-type in electrical conduction with Hall mobility of 7.8 $\text{cm}^2/\text{V}\cdot\text{sec}$. The optical absorption edge shifted towards lower wavelength side with increase of oxidation temperature. Optical band gap of the CuNiO_2 films oxidized at temperature of was 2.25 eV.

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