

Research Article

Sputter Power Influenced Structural, Electrical, and Optical Behaviour of Nanocrystalline CuNiO_2 Films Formed by RF Magnetron Sputtering

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Copper nickel oxide (CuNiO_2) films were deposited on glass and silicon substrates using RF magnetron sputtering of equimolar $\text{Cu}_{50}\text{Ni}_{50}$ alloy target at different sputter powers in the range of 3.1–6.1 W/cm^2 . The effect of sputter power on the chemical composition, crystallographic structure, chemical binding configuration, surface morphology, and electrical and optical properties of CuNiO_2 films was investigated. The films formed at sputter power of 5.1 W/cm^2 were of nearly stoichiometric CuNiO_2 . Fourier transform infrared spectroscopic studies indicated the presence of the characteristic vibrational bands of copper nickel oxide. The nanocrystalline CuNiO_2 films were formed with the increase in grain size from 75 to 120 nm as the sputter power increased from 3.1 to 5.1 W/cm^2 . The stoichiometric CuNiO_2 films formed at sputter power of 5.1 W/cm^2 exhibited electrical resistivity of 27 Ωcm , Hall mobility of 21 cm^2/Vsec , and optical bandgap of 1.93 eV.

1. Introduction

Cuprous oxide (Cu_2O) is a p-type semiconducting oxide material with a direct bandgap of about 1.9–2.2 eV and has a wide range of applications in the field of gas sensors, solar cells, thin-film transistors, and catalysts [1–4]. Cu_2O is the base for many p-type transparent conducting oxides (TCOs) to form CuMO_2 delafossites ($M = \text{Al, Cr, B, In, Ga, etc.}$), which are thought to retain the valence band features and conduction mechanism of Cu_2O [5]. Nickel oxide (NiO) thin films are very much attractive for the antiferromagnetic layers, electrochromic devices, and p-type transparent conducting oxide and functional layers in chemical sensors [6–8] because of their chemical stability along with suitable optical, electrical, and magnetic properties. Chen et al. [9] studied the change in the valence of Ni from Ni^{2+} to Ni^{3+} by incorporating copper into the NiO films formed by reactive sputtering of nickel target with varied copper concentrations of 10 and 18 at%. Moghe et al. [10] noticed that the crystallite size of the films decreased from 18.1 to 15.2 nm and that the optical bandgap decreased from 3.20 to 2.96 eV with

the increase of copper concentration from 0 to 10% in NiO films formed by spray pyrolysis. The electrical resistivity of the films also decreased with the increase in the content of copper in NiO films. Yang et al. [11] reported electrical resistivity of 0.19 Ωcm and optical bandgap of 3.7 eV in p-type $\text{Ni}_{0.9}\text{Cu}_{0.1}\text{O}$ films formed by pulsed plasma deposition. Miyata et al. [12] deposited p-type Cu_2O –NiO films with various concentrations of Cu_2O by RF magnetron sputtering and found electrical resistivity of $2 \times 10^4 \Omega\text{cm}$, hall mobility of 2.5 cm^2/Vsec , and optical bandgap of 2.9 eV in 50% of copper-doped NiO films. He et al. [13] achieved good electrochromic behaviour in sol-gel processed $\text{Cu}_{0.2}\text{Ni}_{0.8}\text{O}$ films in both the color and the bleached states with optical modulation of 7.5% at 633 nm and response time less than 1 sec. Chen et al. [14] found that the electrical resistivity and optical transmittance decreased with the increase of copper concentration from 10 to 18 at% in RF magnetron-sputtered Cu-doped NiO films. Recently, Ashok Kumar Reddy et al. [15] reported on the (30 at%) Cu-doped NiO films formed by DC magnetron sputtering and that the electrical resistivity decreased from

TABLE 1: Deposition conditions fixed for the growth of CuNiO_2 films.

Sputter target	$\text{Cu}_{50}\text{Ni}_{50}$
Target-to-substrate distance	50 mm
Ultimate pressure	5×10^{-4} Pa
Oxygen partial pressure (p_{O_2})	2×10^{-2} Pa
Sputtering pressure	4 Pa
Substrate temperature	523 K
Sputter power (P_w)	3.1–6.1 W/cm^2

64 to 18 Ωcm and found that optical bandgap increased from 2.20 to 3.30 eV with the increase of oxygen partial pressure from 9×10^{-3} to 4×10^{-2} Pa, respectively. Among the thin-film deposition techniques, the reactive magnetron-sputtering is one of the most widely used techniques for preparation of oxide films on large-area substrates by sputtering of metallic or metal oxide target in reactive gas of oxygen and sputter gas of argon. Nanocrystalline CuNiO_2 films with grain size of 95 nm, electrical resistivity of 1.5 Ωcm , and Hall mobility of 19 cm^2/Vsec were achieved by RF magnetron sputtering technique at a substrate bias voltage of -60 V [16]. In this paper, copper nickel oxide films were formed by RF reactive magnetron sputtering technique by sputtering of equimolar $\text{Cu}_{50}\text{Ni}_{50}$ alloy target at various sputter powers, and we studied the influence of sputter power on the chemical composition, crystallographic structure, surface morphology, chemical binding configuration, and electrical and optical properties of the deposited films.

2. Experimentation

Copper nickel oxide (CuNiO_2) films were deposited on glass and p-silicon substrates using RF magnetron sputtering technique by sputtering of equimolar ($\text{Cu}_{50}\text{Ni}_{50}$) copper nickel alloy target of 50 mm diameter and 3 mm thickness. The films were formed on the substrates held at temperature of 523 K and at different sputter powers in the range of 3.1–6.1 W/cm^2 . The box-type sputter chamber was evacuated to ultimate pressure of 5×10^{-4} Pa using diffusion pump backed by rotary pump. Oxygen and argon gases were used as reactive and sputter gases and were admitted into the sputter chamber by fine control needle valves. The duration of the deposition of the films was 90 min. The deposition conditions maintained for the preparation of CuNiO_2 films are given in Table 1.

The thickness of the deposited CuNiO_2 films was determined by using the Veeco Dektak depth profilometer. The chemical composition of the deposited films was analyzed with energy-dispersive X-ray analysis (Oxford Instruments INCA Penta FETx3) attached to the scanning electron microscope (Carl Zeiss model EVO MA 15). The crystallographic structure of the films was determined by X-ray diffractometer (Siefert Diffractometer model 3003 TT) using monochromatic CuK_α radiation with wavelength of 0.15406 nm. The surface morphology of the deposited films was analyzed with atomic force microscope (Seiko Instruments model SPA 400). The chemical binding configuration of the films formed on

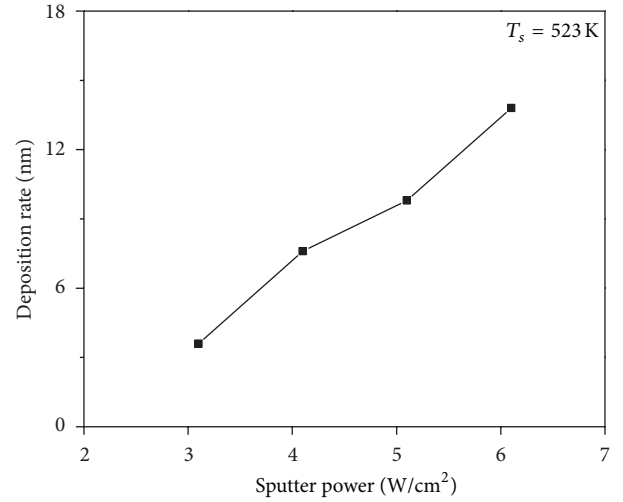


FIGURE 1: Variation of deposition rate with sputter power of CuNiO_2 films.

silicon substrates was analyzed by the Fourier transform infrared spectroscopy (Nicolet model 5700 FTIR). The electrical properties of the films were determined with a Hall measurement system (Ecopia HMS, 3000 VER 3.51.3). The optical transmittance of the films formed on glass substrate was recorded in the wavelength range of 300–2500 nm using the Perkin-Elmer double-beam spectrophotometer in order to determine the optical bandgap of the deposited films.

3. Results and Discussion

The deposition rate of the CuNiO_2 films was calculated from the thickness and duration of the deposition. Figure 1 shows the variation of deposition rate of the films with the sputter power applied to the target in the range of 3.1–6.1 W/cm^2 . The deposition rate of the deposited films increased from 3.6 to 13.8 nm/min with the increase of sputter power from 3.1 to 6.1 W/cm^2 , respectively. The deposition rate of the films increased almost linearly with the increase of sputter power. As the sputter power increased, the bombardment of argon ion on the sputter target increased; hence, the deposition rate of the films increased. Such an increase in the deposition rate with the increase of sputter power was observed by Gagaoudakis et al. [17] in indium oxide films and was observed by Sivasankar Reddy et al. [18] in copper oxide films deposited by DC reactive magnetron sputtering.

3.1. Chemical Composition. The chemical composition of the deposited films was determined by energy-dispersive X-ray analysis. The chemical constituents present in the films were influenced by the sputter power fed to the target during the growth of the films. The chemical composition of the deposited films was determined from the intensity of the constituent elements present in the EDAX spectra. Figure 2 shows the EDAX spectra of copper nickel oxide films formed at different sputter powers. The chemical composition of the films formed at different sputter powers is given in Table 2.

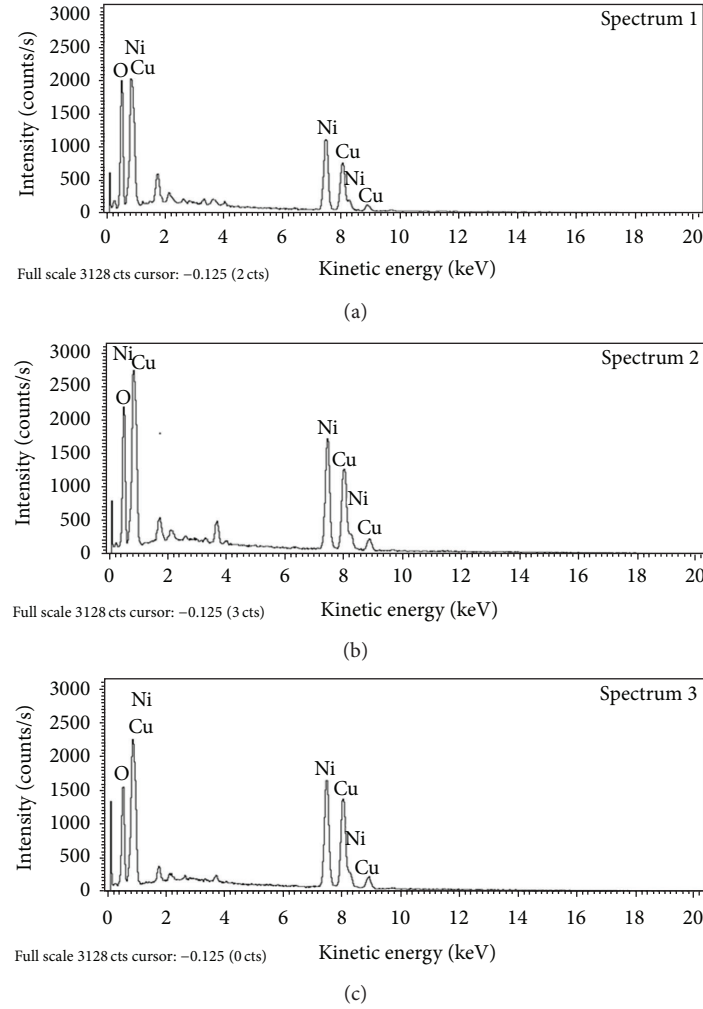


FIGURE 2: EDAX spectra of CuNiO_2 films formed at different sputter powers: (a) 3.1 W/cm^2 , (b) 5.1 W/cm^2 and (c) 6.1 W/cm^2 .

TABLE 2: Chemical composition of CuNiO_2 films formed at different sputter powers determined with the energy-dispersive X-ray analysis.

Sputter power (W/cm^2)	Atomic concentration (%)		
	Cu	Ni	O
3.1	24.2	22.9	52.9
4.1	24.8	23.6	51.6
5.1	25.2	24.0	50.8
6.1	31.1	30.7	38.2

It is seen from the table that the films deposited at sputter power of 5.1 W/cm^2 were of nearly stoichiometric, CuNiO_2 , that is with copper of 25.2 at%, nickel of 24.0 at% and oxygen of 50.8 at%. The films while deposited at higher sputter power of 6.1 W/cm^2 being contained excess of metallic content, that is, copper of 31.1 at%, nickel of 30.7 at%, and oxygen of 38.2 at%. At sputter power of 5.1 W/cm^2 , the sputter yield of metallic species was low, and the sputtered species of copper and nickel effectively react with the available oxygen in the

sputter chamber and form stoichiometric CuNiO_2 films. At higher sputter power of 6.1 W/cm^2 the ejected sputter atoms of copper and nickel were increased due to high sputter yield which reacts with the insufficient oxygen in the sputter chamber, hence achieving metal-rich oxide films. From these studies, it is revealed that the films formed at sputter power of 5.1 W/cm^2 , were of nearly stoichiometric CuNiO_2 .

3.2. X-Ray Diffraction Studies. X-ray diffraction profiles of the films deposited at different sputter powers recorded in the 2θ range of 15° – 80° are shown in Figure 3. It is seen from the figure that the films deposited at all sputter powers showed broad diffraction peak centered around $2\theta = 41.4^\circ$ related to the (002) reflection of CuNiO_2 [19]. The presence of broader diffraction peak indicated that the grown films were of nanocrystalline in nature. It is seen that the broadness of the peak slightly decreased with the increase of sputter power up to 5.1 W/cm^2 which revealed that the crystallite size of the films enhanced with the increase of sputter power. The films formed at sputter power of 5.1 W/cm^2 , exhibited another weak diffraction peak at about $2\theta = 36.9^\circ$ related to the (111)

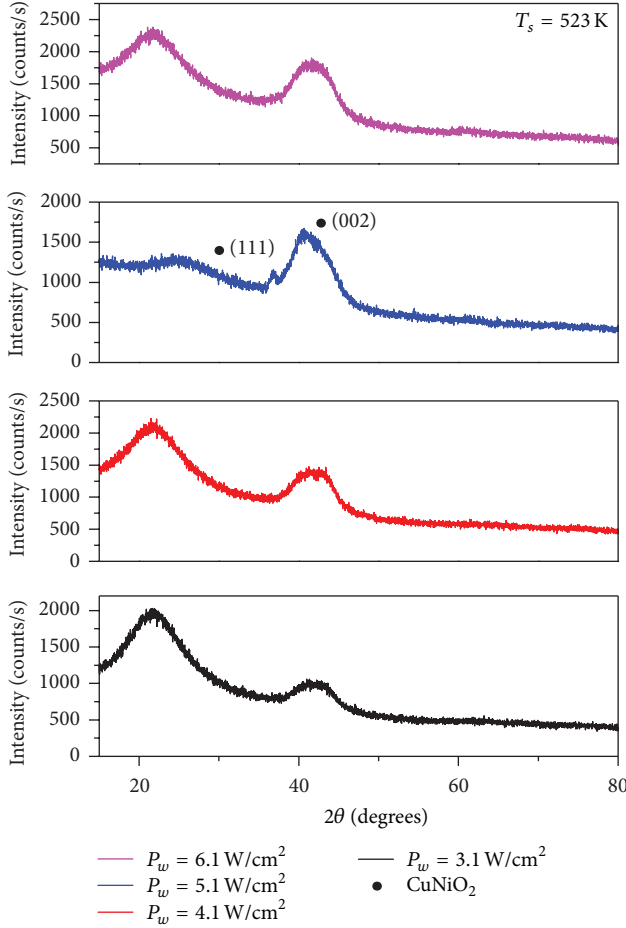


FIGURE 3: X-ray diffraction profiles of CuNiO₂ films formed at various sputter powers.

reflection of CuNiO₂. Further increase of sputter power to 6.1 W/cm², the sharpness of the (002) reflection decrease, whereas the (111) reflection disappeared. The reduction in the sharpness of the peak may indicate the presence of unreacted copper and nickel along with copper nickel oxide. This revealed that the films formed with sputter power of 5.1 W/cm² were of single-phase CuNiO₂, which was also confirmed by the chemical composition determined by the energy-dispersive analysis. It is to be noted that Miyata et al. [12] achieved the polycrystalline multicomponent Cu₂O–NiO films with the content of nickel in the range of 30–60 at% in RF magnetron-sputtered films by sputtering of Cu₂O–NiO powder targets.

The crystallite size (L) of the deposited CuNiO₂ films was calculated from the (002) reflection using the following Debye-Scherrer relation:

$$L = \frac{K\lambda}{\beta \cos \theta}, \quad (1)$$

where K is a constant with a value about 0.89 for copper target, β is the full width at half maximum (FWHM) of the peak measured in radians, and θ is the diffraction peak angle. The variation in full width at half maximum and the

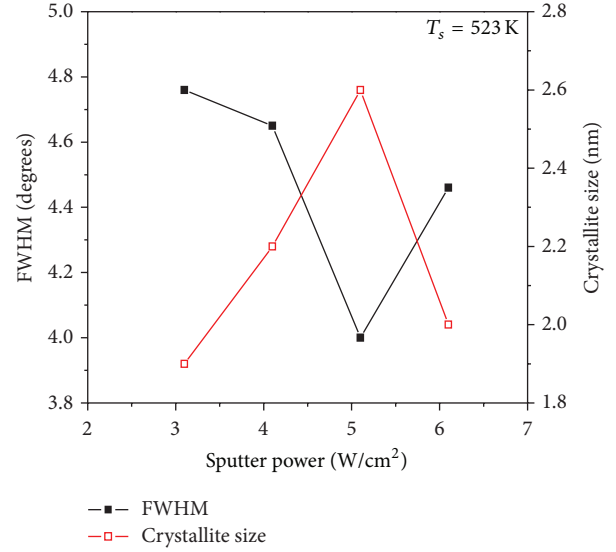


FIGURE 4: Variation of FWHM and crystallite size of CuNiO₂ films with sputter power.

crystallite size of the films formed at different sputter powers are shown in Figure 4. The full width at half maximum of the films decreased from 4.7 to 4.0° with the increase of sputter power from 3.1 to 5.1 W/cm²; thereafter, it increased to 4.46° at higher sputter power of 6.1 W/cm². The crystallite size of the films increased from 1.9 to 2.6 nm with the increase of sputter power from 3.1 to 5.1 W/cm², later, it decreased to 2.0 nm at higher sputter power of 6.1 W/cm². This clearly revealed that the grown films were of nanocrystalline CuNiO₂ with the crystallite size in the range of 1.9–2.6 nm.

The dislocation density (δ) is a measure of dislocations present in a unit volume of the film. The dislocation density of the films was calculated from the crystallite size using the following relation:

$$\delta = \frac{1}{L^2} \text{ (lines/m}^2\text{)}. \quad (2)$$

The strain (ϵ) developed in the films was determined from the full width at half maximum of X-ray diffraction peak using the following relation:

$$\epsilon = \frac{\beta \cos \theta}{4} \text{ (lines}^{-2}\text{/m}^4\text{)}. \quad (3)$$

The dislocation density and the strain of the films as a function of sputter power are shown in Figure 5. The dislocation density of the films decreased from 27×10^{16} to 15×10^{16} lines/m² with the increase of sputter power from 3.1 to 5.1 W/cm², respectively, and at higher sputter powers it further increased to 25×10^{16} lines/m². The strain developed in the films decreased from 1.6×10^{-2} to 1.3×10^{-2} lines⁻²/m⁴ with the increase of sputter power from 3.1 to 5.1 W/cm², and at higher sputter power of 6.1 W/cm² it increased to 1.45×10^{-2} lines⁻²/m⁴. From these studies, it is revealed that the increase of crystallinity is the main reason for the decrease of dislocation density and the strain in the films.

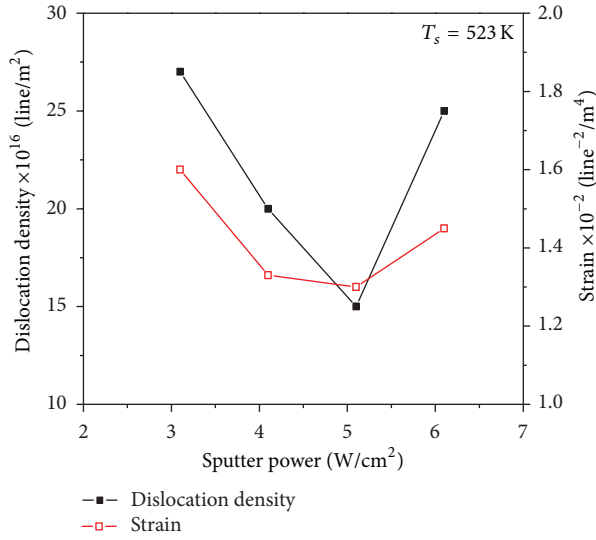


FIGURE 5: Variation of dislocation density and strain of CuNiO₂ films with sputter power.

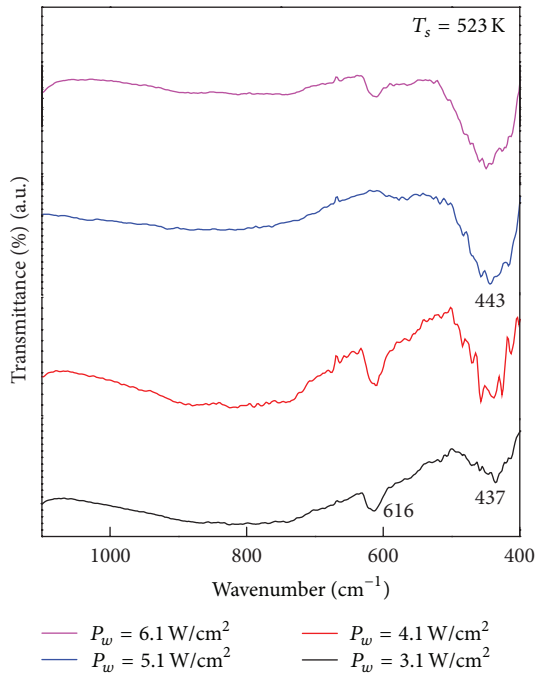


FIGURE 6: FTIR transmittance spectra of CuNiO₂ films formed at different sputter powers.

3.3. The Fourier Transform Infrared Spectroscopic Studies.

A Fourier transform infrared spectroscopic study gives the information about the chemical binding configuration in the films. Figure 6 shows the Fourier transform infrared transmittance spectra of CuNiO₂ films formed at different sputter powers. The films formed at low sputter power of 3.1 W/cm² exhibited an absorption band at 616 cm⁻¹ and a broad absorption peak at 437 cm⁻¹. Further increase of sputter power to 4.1 W/cm² made the absorption band intensity increase. The band observed at 616 cm⁻¹ was related to the vibration of

Cu₂O [20]. To be noted are the vibrations of CuO and Cu₂O located at 510 and 630 cm⁻¹, respectively, the vibration of nickel oxide (Ni₂O₃), located at 450 cm⁻¹ [21], and the vibration of NiO located at 426 cm⁻¹ [22]. Hence, the vibration band seen at 616 cm⁻¹ was related to the Cu₂O. The band located at 437 cm⁻¹ was related to the copper nickel oxide phase. This revealed that the films formed up at sputter power of 4.1 W/cm² contained the vibration bands of Cu₂O and copper nickel oxide. The films formed at 5.1 W/cm² exhibited copper nickel oxide without the presence of Cu₂O. Further increase of sputter power to 6.1 W/cm² once again made the vibration band related to Cu₂O observable. It is to be noted that the vibration band related to copper nickel oxide shifted from 437 to 443 cm⁻¹ with the increase of sputter power from 3.1 to 5.1 W/cm². Shobha et al. [23] also noticed the absorption band at 447 cm⁻¹ in the electrodeposited Ni-Cu oxide films. From these studies, it is revealed that the films formed at sputter power of 5.1 W/cm² were of single-phase CuNiO₂ without presence of the additional phase of Cu₂O.

3.4. Atomic Force Micrograph Studies. The surface morphology of CuNiO₂ films was influenced by the sputter power fed to the sputter target. Figure 7 shows three- and two-dimensional atomic force micrographs of films formed at different sputter powers. The films formed at low sputter power of 3.1 W/cm², showed fine grains uniformly spread on the surface of the substrates. As the sputter power increased to 5.1 W/cm² the shape of the grains were spherical and larger in size. In the case of the films deposited at higher sputter power of 6.1 W/cm², the shapes of the grains were in rod like with decrease in the size of the grains. The grain size increased from 75 to 120 nm with the increase of sputter power from 3.1 to 5.1 W/cm² due to the increase of crystallinity of the films. The films formed at higher sputter power exhibited smaller size grains (90 nm) with needle-like shape which may be due to the presence of CuNiO₂ along with metallic copper and nickel as noticed in the EDAX data. The root mean square (RMS) roughness of the films increased from 2 to 8 nm with the increase of sputter power from 3.1 to 5.1 W/cm² and then it decreased to 4.7 nm at sputter power of 6.1 W/cm². Such a variation in the surface morphology was observed by Jin et al. [24] in DC magnetron-sputtered titanium films.

3.5. Electrical Properties. Figure 8 shows the variation of electrical resistivity (ρ) of the CuNiO₂ films with the sputter power. The electrical resistivity was highly influenced by the sputter power maintained during the growth of the films. It is seen that the electrical resistivity of the films decreased with the increase of sputter power. The electrical resistivity of the films formed at low sputter power of 3.1 W/cm², was 130 Ω cm. As the sputter power increased to 5.1 W/cm² the electrical resistivity decreased to 27 Ω cm. The decrease in the electrical resistivity with the increase of sputter power was due to improvement in the crystallinity of the films. The electrical resistivity of the films reduced to 21 Ω cm in the case of the films formed at high sputter power of 6.1 W/cm², which may be due to presence of metallic nickel and copper in copper nickel oxide. It is to be mention that the reported

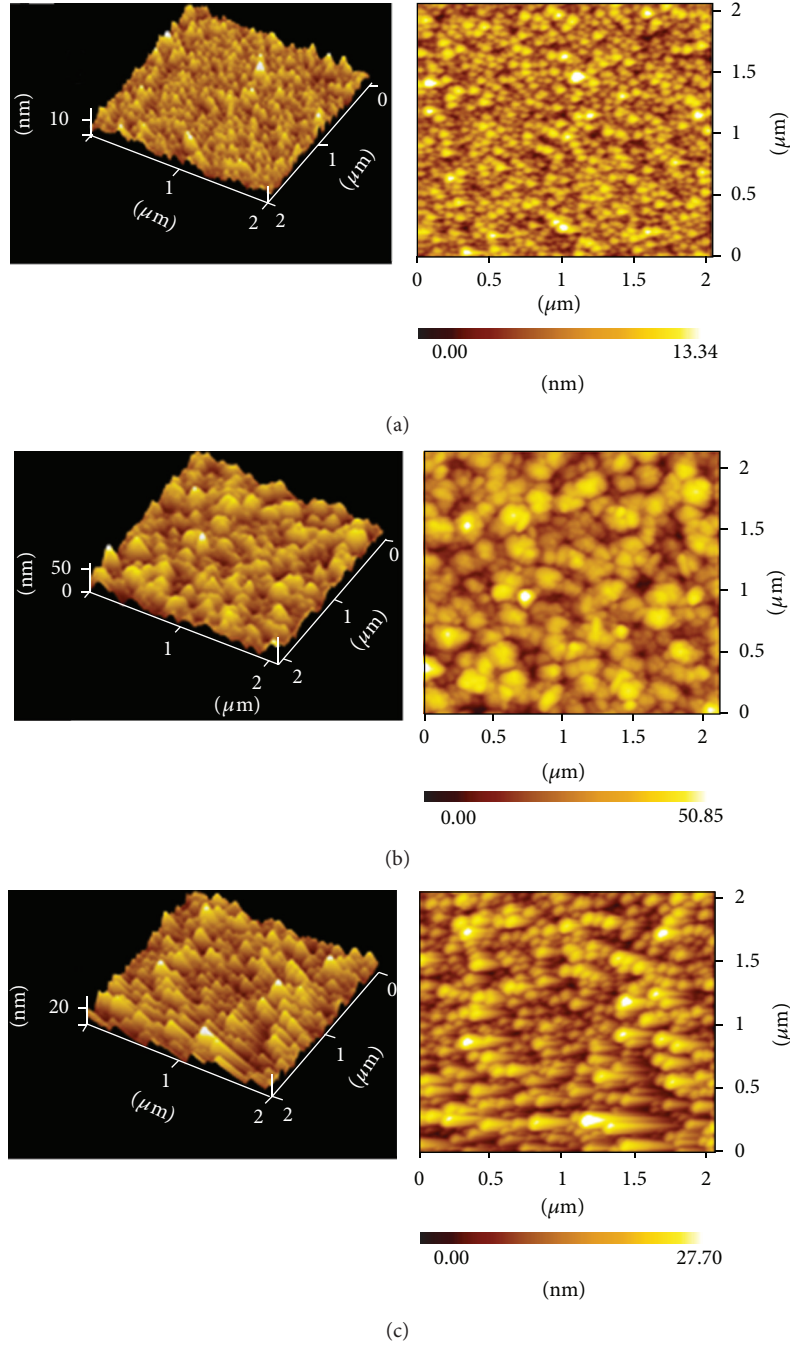


FIGURE 7: Three- and two-dimensional atomic force micrographs of CuNiO_2 films formed at different sputter powers: (a) 3.1 W/cm^2 , (b) 5.1 W/cm^2 , and (c) 6.1 W/cm^2 .

electrical resistivity of RF magnetron-sputtered Cu_2O and NiO films was $9.6 \times 10^1 \Omega\text{cm}$ and $8.0 \times 10^5 \Omega\text{cm}$, and the equimolar Cu-Ni oxide films, it was $3.0 \times 10^4 \Omega\text{cm}$ [12]. Yang et al. [11] achieved low electrical resistivity of $0.2 \Omega\text{cm}$ in $\text{Ni}_{0.9}\text{Cu}_{0.1}\text{O}$ films formed by pulsed plasma deposition and Chen et al. [9] noticed that the resistivity decreased from 0.12 to $0.07 \Omega\text{cm}$ with the increase of copper from 10 to 18 at% in RF magnetron-sputtered NiO films. In contrast to this, Kikuchi et al. [25] reported that the electrical resistivity of

the Cu_2O films increased from 2×10^2 to $8 \times 10^2 \Omega\text{cm}$ with the increase of the Ni content from 0 to 2 at%. The large variations in the electrical resistivity with the doping concentration of the Ni in CuO films were mainly due to the deposition method employed and the process parameters fixed during the formation of the films.

The Hall measurements indicated that the deposited films were of p-type in electrical conduction. The Hall mobility (μ) of the films increased from 3.9 to $21 \text{ cm}^2/\text{Vsec}$ with the

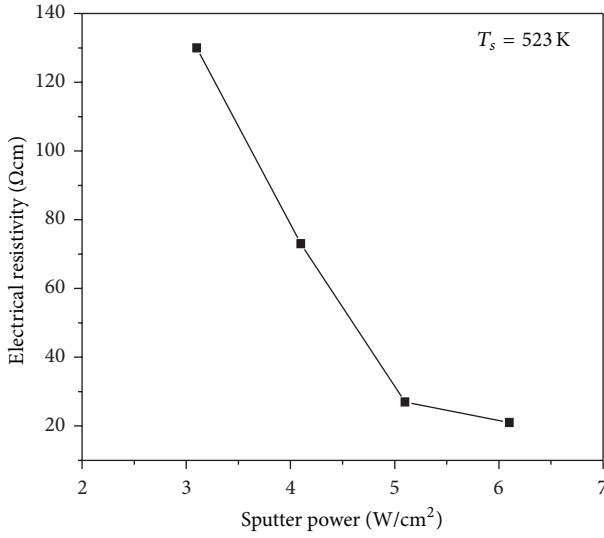


FIGURE 8: Variation of electrical resistivity of CuNiO₂ films with sputter power.

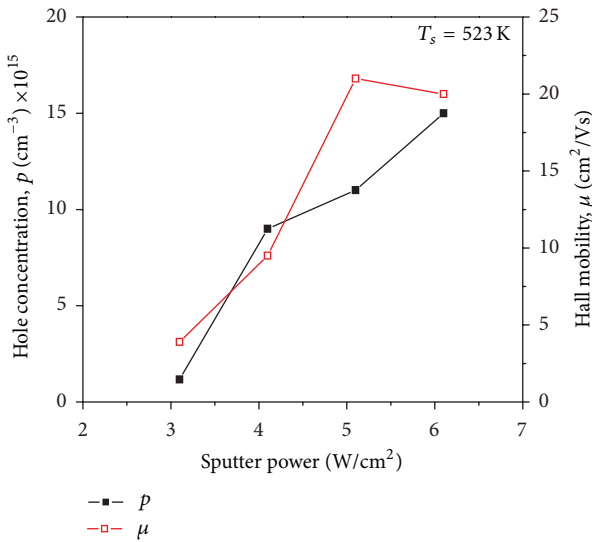


FIGURE 9: Variation of hole concentration and Hall mobility of CuNiO₂ films with sputter power.

the increase of sputter power from 3.1 to 5.1 W/cm², thereafter, it decreased to 20 cm²/Vsec at higher sputter power of 6.1 W/cm² as shown in Figure 9. The increase in the Hall mobility with the increase of sputter power was due to, improvement in the crystallinity and maybe substitution of Ni²⁺ by Cu⁺ lead to dislocation of holes in the valance band hence increase in the Hall mobility [26]. The hole concentration (p) in the films increased from 1.1×10^{15} to 1.5×10^{16} cm⁻³ with the increase of sputter power from 3.1 to 5.1 W/cm² while at higher sputter power of 6.1 W/cm² it further enhanced to 1.5×10^{16} cm⁻³ due to the presence of metallic phase along with CuNiO₂. Miyata et al. [12] achieved low Hall mobility of 2 cm²/Vsec and low carrier concentration of about 8×10^{13} cm⁻³ due to high resistivity of

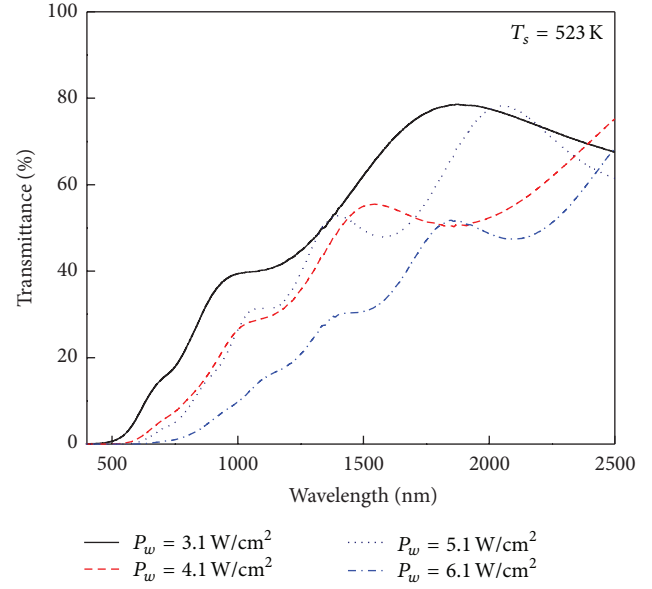


FIGURE 10: Optical transmittance spectra of CuNiO₂ films formed at different sputter powers.

the films. Chen et al. [14] obtained Hall mobility of 1 cm²/Vsec and carrier concentration of 2.5×10^{20} cm⁻³ in 18 at% copper doped NiO films formed by RF magnetron sputtering.

3.6. Optical Properties. Figure 10 shows the wavelength dependence optical transmittance of the CuNiO₂ films formed at different sputter powers. it is seen from the figure that the optical transmittance of the films decreased with the increase of sputter power. The optical absorption edge of the films shifted towards higher wavelengths side with the increase of sputter power. The decrease in the transmittance at higher sputter power of 6.1 W/cm² may be due to the clusters (growth of copper and nickel) reflecting the incident photons or scatter by the grain boundaries [15]. It is to be noted that the optical transmittance of Cu doped NiO films decreased from 72 to 43% with the increase of Cu content from 2.3 to 18.2 at% respectively in RF sputter deposited from Cu₂O–NiO mixed powder target [14]. The absorption coefficient (α) of the films was calculated from the optical transmittance (T) data using the following relation [27]:

$$\alpha = -\left(\frac{1}{t}\right) \ln T, \quad (4)$$

where t is the film thickness. The optical bandgap of the films was determined from the absorption coefficient (α) and photon energy ($h\nu$) by using the following Tauc relation:

$$(\alpha h\nu) = A(h\nu - E_g)^{1/2} \quad (5)$$

assuming that the direct transitions take place from the valance band to the conduction band. The optical bandgap of the films decreased from 2.0 to 1.41 eV with the increase of sputter power from 3.1 to 6.1 W/cm² respectively. The decrease of bandgap with the increase of sputter power may

be due to improved crystallinity. Miyata et al. [12] achieved an optical bandgap of 2.75 eV in 50 at% Ni in Cu–Ni–O films formed by RF magnetron sputtering, whereas Moghe et al. [10] reported a value of 3.04 eV in 50 at% copper-doped NiO films formed by spray pyrolysis. The different values of optical bandgap achieved in the films are maybe due to the difference in the formation of the compound.

4. Conclusions

Thin films of CuNiO₂ were formed on glass and silicon substrates held at 523 K by sputtering of equimolar (Cu₅₀Ni₅₀) target at various sputter powers in the range of 3.1–6.1 W/cm² employing RF magnetron sputtering method. The influence of sputter power on the chemical composition, chemical binding configuration, structure, and electrical and optical properties was systematically investigated. The deposition rate of the films was almost linearly increased with the increase of sputter power. The energy-dispersive X-ray analysis indicated that the films formed at sputter power of 5.1 W/cm², were of nearly stoichiometric CuNiO₂. The grown films were of nanocrystalline with the crystallite size of about 3 nm. The atomic force micrographs exhibited that the grains size of the films increased from 75 to 120 nm with the increase of sputter power from 3.1 to 5.1 W/cm² and the shape of the grains depends on the sputter power. The Fourier transform infrared spectroscopic studies showed the characteristic vibration bands of CuNiO₂ in the films. electrical resistivity and Hall mobility of the films increased with the increase of sputter power. The deposited films were of p-type electrical conductivity. The optical transmittance of the films decreased and the absorption edge shifted towards higher wavelengths side with the increase of sputter power. The optical bandgap decreased from 2.0 to 1.41 eV with the increase of sputter power from 3.1 to 5.1 W/cm². In conclusion, the films deposited at sputter power of 5.1 W/cm² were nearly stoichiometric CuNiO₂ with nanocrystalline in nature with crystallite size of 2.6 nm. These films showed the electrical resistivity of 27 Ωcm, Hall mobility of 21 cm²/Vsec, and optical bandgap of 1.93 eV.

Acknowledgments

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