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DC Reactive Magnetron Sputtered $CuNiO_2$ Films: Structure, Electrical and Optical Characterization

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ABSTRACT

Copper nickel oxide ($CuNiO_2$) thin films were deposited on to glass and p- silicon substrates held at room temperature employing DC reactive magnetron sputtering at oxygen partial pressures in the range from 8×10^{-5} mbar to 6×10^{-4}mbar. Influence of oxygen partial pressure on the physical properties was investigated. The films formed at oxygen partial pressures $\leq 3\times10^{-4}$mbarwas of $CuNiO_2$ along with metallic copper and nickel. The films deposited at $\geq 3\times10^{-4}$ mbar were of single phase $CuNiO_2$. The films formed at low oxygen partial pressure 8×10^{-5} mbar were amorphous phase, and at 3×10^{-4} mbar were of (111) reflection with tetragonal $CuNiO_2$. Electrical resistivity of the films increased from 0.47 Ωcm to 6.4×10^{-1} Ωcm and optical band gap increased from1.92 eV to 2.16 eV with increase of oxygen partial pressure from 3×10^{-4} to 6×10^{-4} mbar.

Keywords:—*$CuNiO_2$ films, DC magnetron sputtering, structure, electrical, Optical properties*

I. INTRODUCTION

Transparent conducting oxides are widely used in thin film form for solar cells, transistors, light emitting diode, electrochromic devices and gas sensors. Transparent conducting coatings, indium tin oxide, fluorine doped tin oxide, indium and gallium doped zinc oxide are of n-type semiconductors. In order to meet the requirement for transparent thin films for optoelectronic devices, p-type transparent conducting thin films are required with electrical and optical properties. Most of the metal oxides are insulators or n-type semiconductors [1]. Copper oxide (CuO_2) and nickel oxide (NiO) are p-type semiconductors [2, 3]. Nickel oxide is a semitransparent p- type semiconductor with optical band gaps in the range 3.5 – 4.0 eV. Along with nickel oxide, copper oxide considered as prime semiconductor for application in solar cells since it is of high activity and selectivity in oxidation and reduction reactions [4]. It has direct band gap from 1.2 eV to 2.1 eV. Copper - nickel oxide thin films have been studied for

potential application in electrochromic devices [5, 6] and transparent coatings for light emitting diodes [7, 8]. It finds applications in photocatalytic performance of phenol degradation [9], antibacterial activity against Escherichia Coli [10] and corrosion resistance coatings [11]. It was also realizedp-Si/$CuNiO_2$/Al as photodiode [12], sensing of NO_2[13] and hydrogen gases [14, 15], and p-layer in solar cells [16]. Various thin films deposition techniques namely sol-gel [4], spray pyrolysis [10], electrochemical deposition [6], DC magnetron[11], RF magnetron sputtering [7, 12, 14], spin coating [16] and successive ionic layer absorption and reaction [17] were employed for preparation of copper nickel oxide films with different content of copper in nickel oxide. In this investigation, thin films of copper nickel oxide ($CuNiO_2$) films were deposited on to glass and p-silicon substrates by DC reactive magnetron sputtering of composite target of $Cu_{50}Ni_{50}$ at different oxygen partial pressures and sputter pressure of $1x10^{-2}$mbar. The effect of oxygen partial pressure on the structural, electrical and optical properties of the films was studied.

II. Experimentation

Thin films of copper nickel oxide ($CuNiO_2$) were deposited on to glass and p- silicon substrates by DC reactive magnetron sputtering method. Sputter system employed for deposition of films was pumped by diffusion pump backed by rotary pump. Oxygen was used as reactive gas and argon as sputter gas for deposition of the films. After obtaining the ultimate pressure 5×10^{-6}mbar, oxygen gas was introduced into the sputter chamber through fine controlled needle valve to achieve oxygen partial pressure in the range from 8×10^{-5}mbar to 6×10^{-4}mbar. Sputter gas of argon was admitted into the sputter chamber to reach sputter pressure of 1×10^{-2}mbar. Schematic of the sputter system employed for deposition of the films is shown in figure1. The films were deposited by sputtering the composite target of cupper-nickel ($Cu_{50}Ni_{50}$) with 99.95% purity on to glass and p-silicon substrates held at room temperatures (30°C). The deposited films were characterized for their chemical composition, structure, electrical and optical properties. Deposition parameters fix for the growth of the films were given in the table 1.Thickness of the deposited films measured with Dektak depth profilometer was in the range 90-110 nm. Chemical composition of the deposited films was determined with energy dispersive X-ray analyzer (Oxford Instruments Inca Penta FETX3) attached to the scanning electron microscope (Carl Zeiss model EVO MAIS). Crystallographic structure of the films was studied with X-ray diffractometer (X'pert Pro PAN Analytical) using copper Cu K_α radiation (λ = 0.15406 nm). Surface morphology of the films was analyzed with atomic force microscope. Electrical resistivity of the films was measured using van der Pauw method. Optical transmittance in the wavelength range 300 - 1000 nm was recorded with JASCO (model V570) UV-Vis-NIR spectrophotometer to determine optical band gap.

III. Results and Discussion

Deposition rate of the films depend on the oxygen partial pressure prevailed in the sputter chamber. Dependence of deposition rate of copper nickel oxide films on the oxygen partial pressure is shown in figure 2. The films formed at oxygen partial pressure of 8×10^{-5}mbar were 14.8 nm/min. and decreased to 9.4 nm/min with increase of oxygen partial pressure to 6×10^{-4} mbar. The decrease in the deposition rate with increase of oxygen partial pressure was due to decrease in the sputter yield of copper nickel due to reaction of oxygen and form $CuNiO_2$ films. Similar decrease in the deposition rate with increase of oxygen

partial pressure was noticed by Lu et al. in DC magnetron sputtered copper oxide films [18].

III (a). Chemical composition

Energy dispersive X-ray analysis spectra of copper nickel oxide films formed on silicon substrate at different oxygen partial pressures are shown in figure 3. The spectra of the films showed the kinetic energy peaks of copper, nickel and oxygen along with silicon. Silicon in the spectrum present was due to the signal from silicon substrate. EDAX spectra showed the intensity of oxygen peak enhanced with the increase of oxygen partial pressure. Chemical composition of the films was evaluated from the intensity of the kinetic energy peaks of copper, nickel and oxygen. Chemical composition of $CuNiO_2$ films deposited at different oxygen partial pressures are given in table 2. The films formed at low oxygen partial pressure of 8×10^{-5} mbar contained copper of 20.8 at. %, nickel of 21.4 at. % and oxygen of 57.8 at. % whereas those deposited at 3×10^{-4}mbar showed the content of copper 16.6 at. %, nickel 17.1 at. % and oxygen 66.3 at. %. The films formed at low oxygen partial pressure of 8×10^{-5} mbar was deficiency of oxygen because of insufficient quantity of oxygen prevail the sputter chamber to react with the sputter species and form oxide films. There these films were of metallic copper and nickel along with $CuNiO_2$. When the oxygen partial pressure increased to 3×10^{-4} mbar, required oxygen is available in the sputter chamber to react with copper nickel and form $CuNiO_2$. It indicated that oxygen partial pressure of 3×10^{-4}mbar is an optimum to form $CuNiO_2$ films by DC reactive magnetron sputtering.

III (b). Structural studies

Figure 4shows the X-ray diffraction profiles of copper nickel oxide films formed at different oxygen partial pressures. It is seen that the films formed at low oxygen partial pressure of 8×10^{-5} mbar were of X-ray amorphous. The films deposited at 1×10^{-4} mbar showed a weak diffraction peak 2θ at 37.2° related to the (111) reflection of tetragonal structured $CuNiO_2$ (JCPDS Card No. 06-0720) in the amorphous background. As the oxygen partial pressure increased to 3×10^{-4}mbar the intensity of the (111) reflection enhanced. At higher pressures there was decrement in the crystallinity of the films. The crystallite size determined from the (111) reflection of the films formed at oxygen partial pressure of 3×10^{-4}mbar was 6 nm and decreased to 4.5 nm at 6×10^{-4} mbar. The dislocation density and strain developed was calculated from the (111) reflection in the films. The dislocation density increased from 2.7×10^{16} lines/m^2 to 4.9×10^{16} lines/m^2 and the strain increased from 5.6×10^{-3} to 7.5×10^{-3} with increase of oxygen partial pressure from 3×10^{-4}mbar to 6×10^{-4}mbar respectively.

III(c). Surface morphology

Surface morphology of the deposited films was analyzed with atomic force microscope. Figure 5 shows the two- and three-dimensional atomic force micrographs of the films formed at different oxygen partial pressures. Grown grains were of spherical shape with uniform distribution on the surface of the films. Size of the grains increased from 56 nm to 89 nm with increase of oxygen partial pressure from 8×10^{-5} mbar to 3×10^{-4} mbar respectively. At higher partial pressures the grains were segregated and form as clusters. The root mean square roughness of the films formed at low partial pressure of 8×10^{-5} mbar was 2.0 nm. As the pressure increased roughness increased and reached to 4.6 nm at oxygen partial pressure of 3×10^{-4} mbar.

III(d). Electrical properties

Electrical resistivity of the $CuNiO_2$ films formed at different oxygen partial pressures is given in figure 6. The electrical resistivity increased with increase of oxygen partial pressure. The films formed at low oxygen partial pressure of 8×10^{-5} mbar were 6.4×10^{-2} Ωcm. The electrical resistivity of the films formed at oxygen partial pressure of 6×10^{-4} mbar increased to 0.64 Ωcm. Low electrical resistivity of the films formed at low oxygen partial pressure of 8×10^{-5} mbar was due to deficiency of oxygen and those deposited at oxygen partial pressure of 3×10^{-4}mbar were of $CuNiO_2$. Increase in the resistivity with increase of oxygen partial pressure was due to increase in the content of oxygen that is filling of oxygen ion vacancies in the films. The electrical resistivity of the films formed at oxygen partial pressure of 3×10^{-4}mbar was achieved was 0.47 Ωcm. Miyata et al. [19] reported high electrical resistivity of 3×10^{4} Ωcm in RF magnetron sputtered $CuNiO_2$ films because of low hole concentration. Chen et al. [5] reported the electrical resistivity of 0.02 Ωcm in Cu (18 at. %) doped NiO films formed by RF magnetron sputtering. Hall mobility measurements indicated that the films were of p- type in electrical conduction. The hole mobility of the films decreased from 2.03 cm^2/V.sec. to 1.16 cm^2/V.sec. with increase of oxygen partial pressure from 8×10^{-5}mbar to 6×10^{-4} mbar. The hole concentration decreased from 4.2×10^{19} $cm^3$to $8.4\times10^{17}cm^3$ with increase of oxygen partial pressure from 8×10^{-5} mbar to 6×10^{-4} mbar.

III(e). Optical properties

Optical transmittance of the films formed on glass substrates was studied to understand the optical absorption and to determine the optical band gap. The optical transmittance of the films was influenced by the oxygen partial pressure maintained during the deposition of the films. Figure 7 shows the optical transmittance spectra of $CuNiO_2$ films formed at different oxygen partial pressures. Optical transmittance of the films deposited at oxygen partial pressure of 8×10^{-5} mbar was 40%. As the oxygen partial pressure increased the transmittance of the films increased to 65% at oxygen partial pressure of 6×10^{-4} mbar. Low transmittance at low oxygen partial pressures was due to the scattering of photons by oxygen vacancies that is metallic copper and nickel. When oxygen partial pressure increased to 3×10^{-4} mbar the oxygen ion vacancies reduced hence increase in the transmittance in the $CuNiO_2$ films. The fundamental optical absorption edge of the films shifted towards lower wavelength side with increase of oxygen partial pressure. The optical absorption coefficient (α) was determine from the optical transmittance (T) and thickness of the films (t) using the relation

$$A= -(1/t)\ln(T) \quad \text{..... (1)}$$

The optical band gap (E_g) of the films was determined by fitting the absorption to the Tauc's relation [20]

$$(\alpha h\nu)^2 = A(h\nu - Eg) \quad \text{..... (2)}$$

Plots of $(\alpha h\nu)^2$ versus photon energy of the films formed at different oxygen partial pressures are shown in figure 8. Optical band gap of the films increased from 1.92 eV to 2.22 eV with increase of oxygen partial pressure from 8×10^{-5} mbar to 6×10^{-4} mbar respectively. Optical band gap of the films formed at low oxygen partial pressure of 8×10^{-5} mbar was 1.92 eV. The $CuNiO_2$ films deposited at oxygen partial pressure at 3×10^{-4}mbarincreased to 2.16 eV. Tasdemirci achieved optical band gap of 2.37 eV in successive ionic layer absorption and reaction processed $CuNiO_2$ films [17].

IV. Figures and Tables

Table 1. Deposition conditions for preparation of $CuNiO_2$films

Deposition method	DC magnetron sputtering
Sputter target	Cu50Ni50 target (50 mm diameter)
Target - substrate distance	60 mm
Substrates	Glass and p- silicon
Substrate temperature	30°C
Sputter power	90 Watt
Ultimate pressure	$5x10^{-6}$mbar
Oxygen partial pressure (pO_2)	$8x10^{-5}$- $6x10^{-4}$mbar
Sputter pressure	$1x10^{-2}$mbar

Table 2. Chemical composition of $CuNiO_2$ films evaluated from EDAX

Oxygen partial pressure (mbar)	Chemical composition (at. %)		
	Copper (at. %)	Nickel (at. %)	Oxygen (at. %)
$8x10^{-5}$	20.8	21.4	57.8
$1x10^{-4}$	17.7	18.1	63.6
$3x10^{-4}$	16.6	17.1	66.3

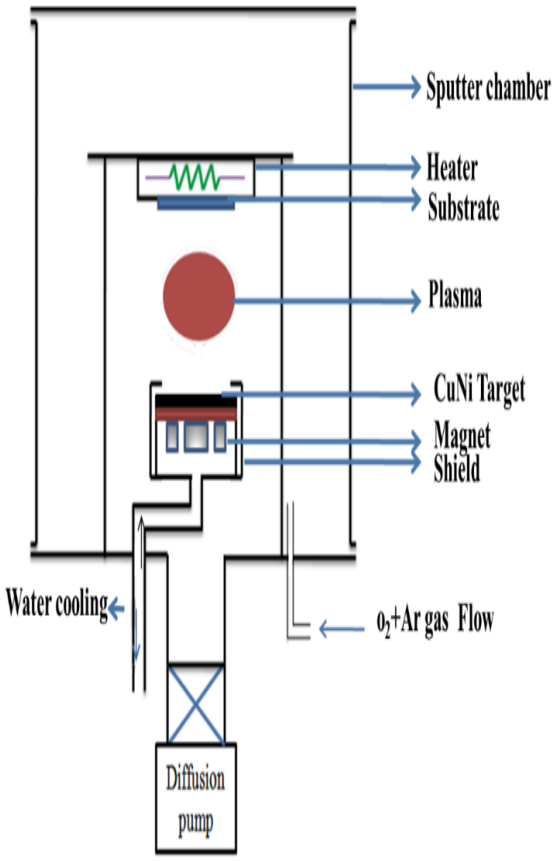

Figure 1: Schematic diagram of DC magnetron sputtering system for deposition of copper nickel oxide films

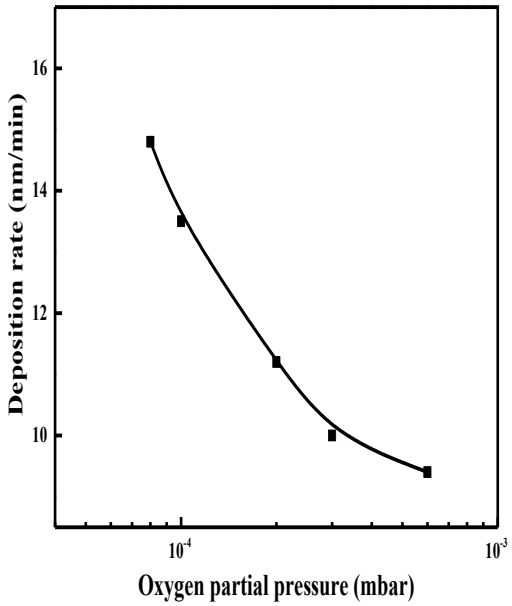

Figure 2: Dependence of deposition rate on the oxygen partial pressure of $CuNiO_2$ films

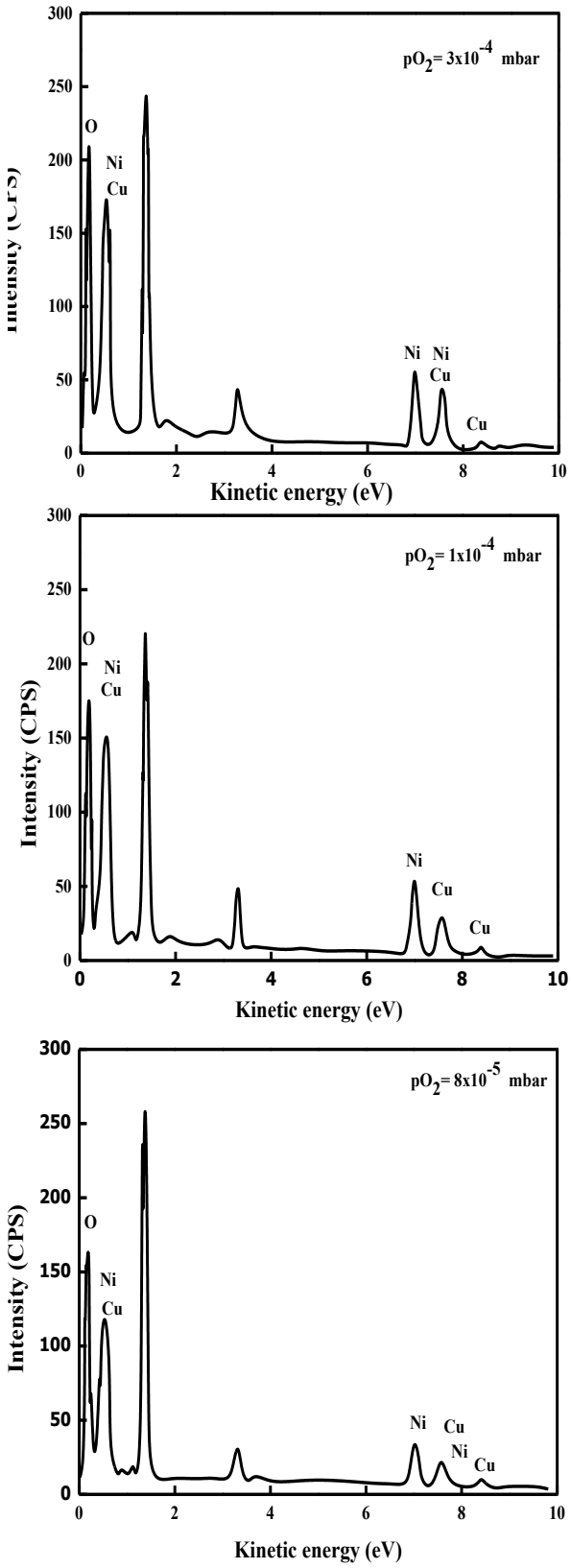

Figure 3: EDAX spectra of copper nickel oxide films formed at different oxygen partial pressures

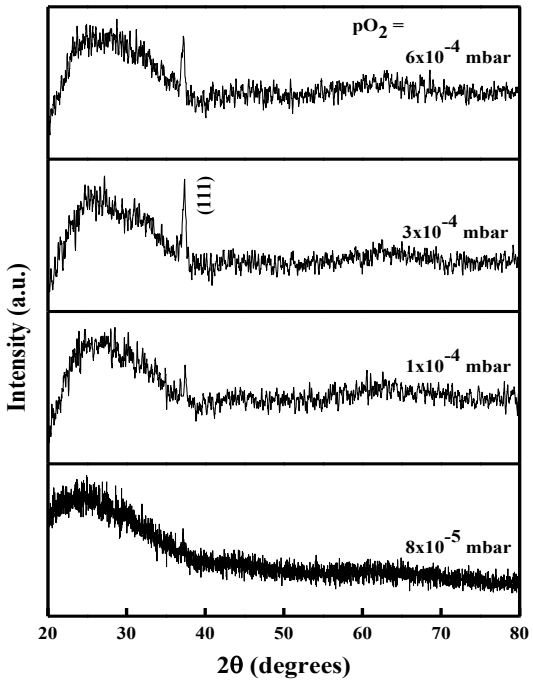

Figure 4: XRD profiles of copper nickel oxide films formed at different oxygen partial pressures

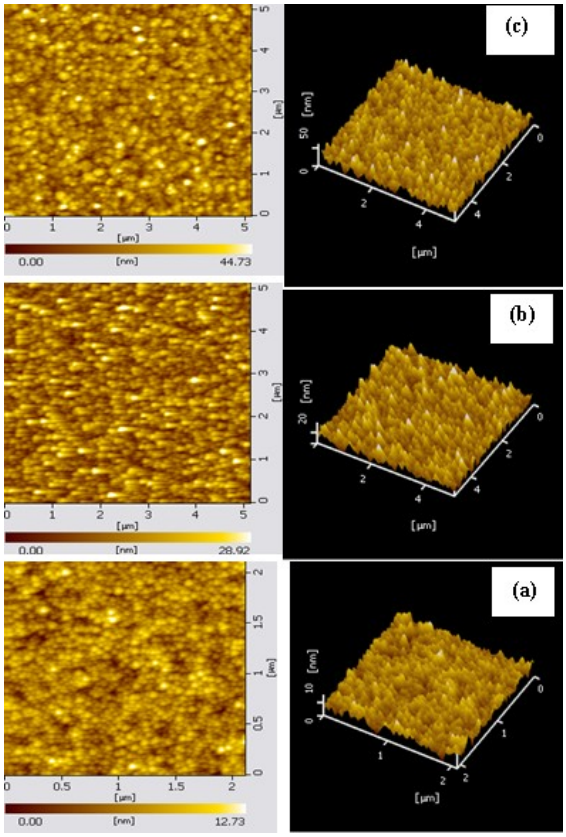

Figure 5: AFM micrographs of copper nickel oxide films formed at oxygen partial pressures: (a) 8×10^{-5} mbar (b) 1×10^{-4}mbar and (c) 3×10^{-4}mbar.

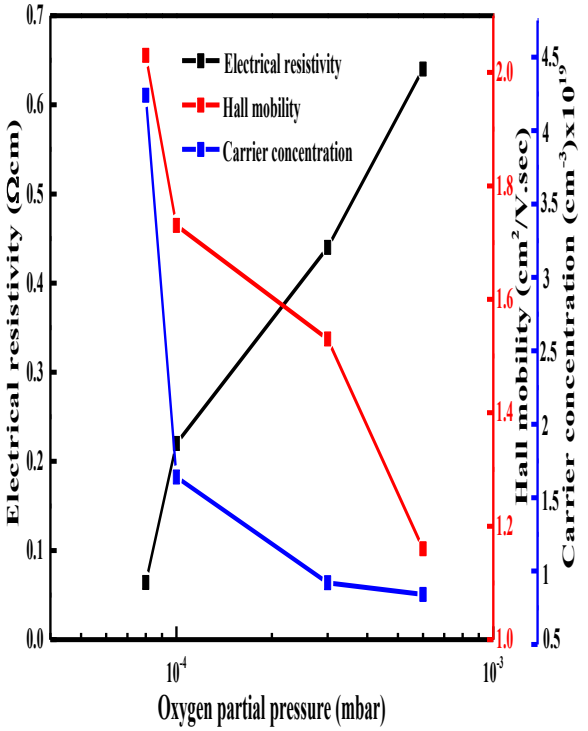

Figure 6: Dependence of Variation of electrical resistivity of $CuNiO_2$ films with oxygen partial pressures

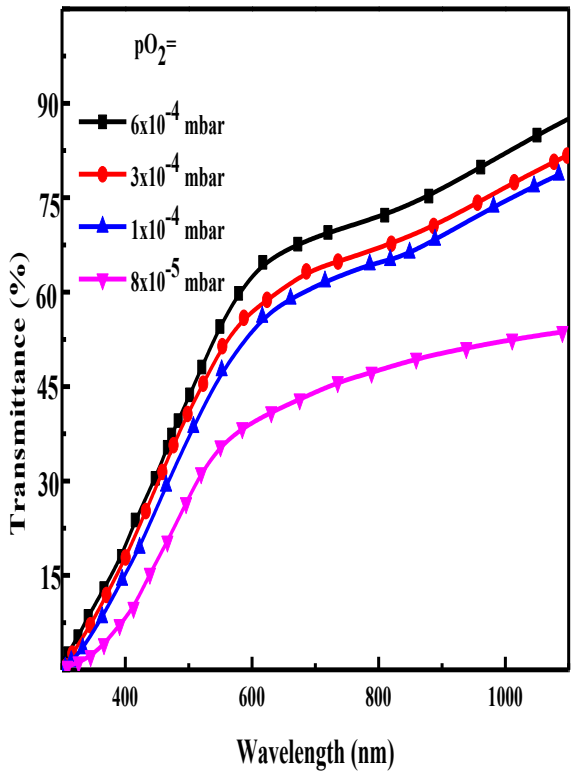

Figure 7: Optical transmittance spectra of $CuNiO_2$films formed at different oxygen partial pressures

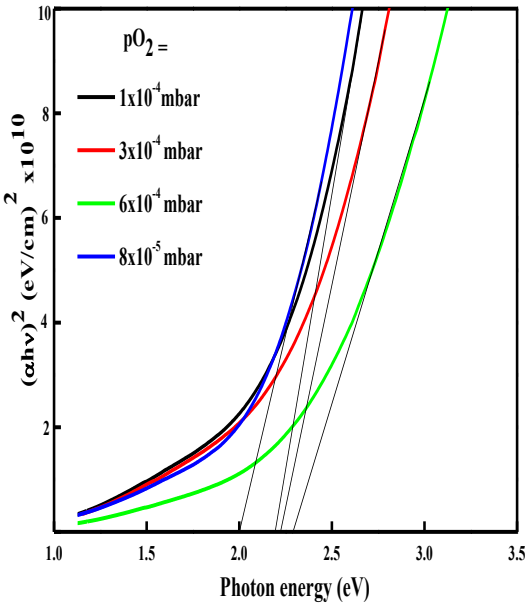

Figure 8: Plots of $(\alpha hv)^2$ versus photon energy of $CuNiO_2$ films formed at different oxygen partial pressures

V. CONCLUSION

Copper nickel oxide films were deposited by DC magnetron sputtering of composite target of $Cu_{50}Ni_{50}$ on to glass and p- silicon substrates held at 30°C at different oxygen partial pressures in the range 8×10^{-5}- 6×10^{-4} mbar and at sputter pressure of 1×10^{-2} mbar. The chemical composition, structure, surface morphology, electrical and optical properties were investigated. Energy dispersive X-ray analysis indicated that the films formed at oxygen partial pressures < 3×10^{-4} mbar were of $CuNiO_2$ along with metallic copper and nickel and those deposited ≥ 3×10^{-4} mbar were of $CuNiO_2$. The films deposited at oxygen partial pressures less than 3×10^{-4} mbar were amorphous phase and at 3×10^{-4} mbar and above were showed (111) reflection related to tetragonal $CuNiO_2$. Atomic force microscope studies revealed that the grain size of the films increased from 56 nm to 89 nm and surface roughness increased from 2.0 nm to 4.6 nm with increase of oxygen partial pressure from 5×10^{-5} mbar to 6×10^{-4}

mbar. Electrical resistivity of the films increased from 0.47 Ωcm to 6.4×10^{-1} Ωcm and optical band gap with increase from 1.92 eV to 2.26 eVwith increase of oxygen partial pressure from 3×10^{-4} mbar to 6×10^{-4} mbar. In conclusion, Tetragonal structured $CuNiO_2$ films were deposited at oxygen partial pressure of 3×10^{-4} mbar were with crystallite size of 6 nm, electrical resistivity of 4.7×10^{-1} Ωcm and optical band gap of 2.22 eV.

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REFERENCES:

[1] M.A. Laughton and D.F. Warne, "Electrical Engineers Reference Book", 6th Ed. Elsevier Science, Oxford, pp 10-43, 2003.

[2] Z. He, Z. Ji, S. Zhao, C. Wang, K. Liu and Z. Ye, Characterization and electrochromic properties of $Cu_xNi_{1-x}O$ films prepared by sol-gel coating, Solar Energy, vol. 80, pp 226, 2006.

[3] J. Zhang, A.H. Baillie and S. Bremne, "Pulsed laser deposited nickel oxide on crystalline silicon as holeselective contacts," J. Vac. Sci. Technol. B, vol. 38, pp 014013-8, 2020.

[4] V. Ramya, K. Neyvasaga, R. Chandramohan, S. Valanarasu, A.M.F. Benail, J. Mater. Sci: Mater. Sci. Electron., vol. 26, pp 8489 – 8496, 2015.

[5] Y.E. Firat and A. Peksoz, "Efficiency enhancement of electrochromic performance in NiO thin films via Cu doping for energy saving potentials," Electrochemica Acta, vol. 295, pp645-652, 2019.

[6] L. Zhao, G. Su, W. Liu, L. Cao, J. Wang, Z. Dong and M. Song, "Optical and electrochemical properties of Cu doped nickel oxide films prepared by electrochemical deposition," Appl. Surf. Sci., vol. 257, pp 3974-3979, 2011.

[7] S.C. Chen, T.Y. Kuo, Y.C. Lin and H.C. Lin, "Preparation and properties of p-type transparent conductive Cu doped NiO films, Thin Solid Films, vol. 512, pp 4944-4947, 2011.

[8] A. Liu, H. Zhu, Z. Guo, Y. Meng, G. Liu, E. Fortunato, R. Martins and R. Shen, "Solution combustion synthesis: Low temperature processing for p-type Cu:NiO thin films for transparent electronics," Adv. Mater., vol. 29, pp 1701599, 2017.

[9] S.E. Anita, U. Prateek, K. Varun Kumar, F.C. Kwok and G.A.M. Ali, "Photocatalytic performance of anovel semiconductor nanocatalyst copper doped nickel oxide for phenol degradation," Mater. Chem.Phys.,2019, Doi.10.1015/ j.matchemphy.2019.122520.

[10] M. Aftab, M.Z. Butt, D. Ali, F. Bashir and Z.H. Aftab. "Impact of copper doping in NiO thin films on their structure, morphology and antibacterial activity against EscherichiaColi, Ceram. Int., 2019,Doi: 10.1016/j.ceramint. 2019.10.247.

[11] W.Burgstaller, M. Hafner, M. Voith, A. Ionut, A.I. Mardare and A.W.

Hassel, "Copper nickel oxidethin films library reactively co-sputtered from a metallic sectional cathode," J. Mater. Res., vol. 29, pp 148-157, 2014.

[12] I.A.Elsayed, M. Cavas, R.K. Gupta, T. Fahmy, A.A.A. Ghamdi, F. Yakuphanoglu, "Photo-conducting and photo-capacitance properties of Al/p-$CuNiO_2$ on p-Si isotype heterojunction photodiode," J. Alloy. Compd., vol. 638, pp 166-171, 2015.

[13] S.J. Merher, M.O. Dawood, O.M. Abdulmunem, M.K. Mejbel, "Copper doped nickeloxide Gas sensor," Vacuum, vol 172, pp 109074, 2019.

[14] D. Abubakar, N.M. Ahmed, S. Mahmud and N.A. Algadri, "Properties of NiOnano structured growth using thermal dry oxidation of nickel metal film for hydrogen gas sensing at room temperature," Mater. Res. Express, vol. 4, pp 07500, 2017.

[15] C.H. Wu, Z. Zhu, H.M. Chang, Z.X. Jiang and C.Y. Hsieh, "Pt@NiO core-shell nanostructure for hydrogen gas sensor," J. Alloy. Compd., vol. 814, pp 151815, 2020.

[16] J.H. Kim, P.W. Liang, S.T. Williams, N. Cho, C.C. Chueh, M.S. Glas, D.S. Ginger and A.K.Y. Jen, "High performance and environmentally stable planer heterojunction perovskite solar cells based on a solution processed copper doped nickel oxide hole transport layer," Adv. Mater., vol.27, pp 695-701,2015.

[17] T.C. Tasdemrci, "Synthesis of copper doped nickel oxide thin films: Structural and optical properties." Chem. Phys. Lett., vol. 738, pp 136884, 2020.

[18] H.C. Lu, C.L. Chu, C.Y. Lai, Y.H. Wang, Thin Solid Films, vol. 517, pp 4408-4412, 2009.

[19] T. Miyata, H. Tanaka, H. Sato and T. Minami, "P-type semiconducting Cu2O-NiO thin films prepared by magnetron sputtering," J. Mater. Sci., vol. 41, pp 5531-5537. 2006.

[20] J. Tauc, Amorphous and Liquid Semiconductor, Plenum Press, NY, 1974.

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