



ISSN: 2395-7852



International Journal of Advanced Research in Arts, Science, Engineering & Management

Volume 10, Issue 4, July 2023



INTERNATIONAL
STANDARD
SERIAL
NUMBER
INDIA

Impact Factor: 6.551

+91 9940572462

+91 9940572462

ijarasem@gmail.com

www.ijarasem.com

TO STUDY THE EFFECT OF DOPANT CONCENTRATION OF CdO IN STRUCTURAL AND OPTICAL PROPERTIES OF COPPER OXIDE NANO-COMPOSITES

DR. MONIKA, DR. RAJESH SHARMA, DR. ASTHA SINGH

PHYSICS DEPT. , CBLU, BHIWANI, HANSI, HARYANA, INDIA

ABSTRACT: CdO has been studied for decades as a prototypical wide band gap transparent conducting oxide with excellent n-type ability. Despite this, uncertainty remains over the source of conductivity in CdO and over the lack of p-type CdO, despite its valence band maximum (VBM) being high with respect to other wide band gap oxides. In this article, we use screened hybrid DFT to study intrinsic defects and hydrogen impurities in CdO and identify for the first time the source of charge carriers in this system. We explain why the oxygen vacancy in CdO acts as a shallow donor and does not display negative-U behavior similar to all other wide band gap n-type oxides. We also demonstrate that p-type CdO is not achievable, as n-type defects dominate under all growth conditions. Lastly, we estimate theoretical doping limits and explain why CdO can be made transparent by a large Moss–Burstein shift caused by suitable n-type doping. Copper oxide nanoparticles (CuO-NPs) were synthesized at room temperature via a green method that is easy, efficient, eco-friendly, and low-cost. The aqueous extract of Bougainvillea leaves was used as a reducing and capping agent. Pure polyvinyl alcohol (PVA) and CuO-PVA nano-composite thin films of 13 wt%, 30 wt%, 40 wt% and 51 wt% were prepared by the solution casting method. The optical and electrical properties of the prepared CuO-NPs, pure PVA, and CuO-PVA thin films were analyzed using a UV–visible spectrophotometer and Keithley electrometer.

The band-gap energy (E_g) value for the synthesized CuO-NPs was determined to be 2.74 eV. This band separation lies in a range that is suitable for a variety of optical and optoelectronic applications such as solar cells for energy conversion. Further, increasing the dispersion of CuO-NPs in a PVA matrix extended the absorption spectrum of PVA distinctly into the visible region and decreased the optical band gap exponentially from 4.42 eV for pure PVA to 3.34 eV for 51 wt% CuO-PVA. In addition, an increase in the DC electrical conductivity with CuO-NPs dispersion was observed. The decrease in the band gap energy was usually accompanied by an increase in the DC electrical conductivity making the CuO-PVA nanocomposite more applicable in thin-film solar cell applications.

KEYWORDS- CdO, CuO-nanoparticles, eco-friendly, nanoparticles, optical, dopant

I. INTRODUCTION

CdO has been shown to achieve a high electron concentration $N (>10^{21}\text{cm}^{-3})$ and at the same time a high mobility $\mu (>100\text{cm}^2/\text{Vs})$ when doped with conventional shallow dopants (In or Ga), and consequently making it a transparent conducting oxide with very low resistivity $\rho < 10^{-4}\Omega\text{cm}$. In this work, the properties of CdO thin films doped with a series of transition metal elements (CdO:TM) with partially filled 3d and 4d shells, including Sc, Ti, V, Cr, Fe, Y, Mo, and W, were investigated.[1,2,3] We find that doping with these TM elements can effectively increase the N in CdO to a maximum N (N_{max}) of $\sim(7-12)\times 10^{20}\text{cm}^{-3}$ with a dopant concentration x_{max} of 4–7%. However, unlike CdO:In, the μ of CdO:TM films drops rapidly from >100 to $<10\text{cm}^2/\text{Vs}$ as the dopant concentration x increases, so that they can only achieve a minimum ρ of $\sim(1-2)\times 10^{-4}\Omega\text{cm}$, \sim a factor of 2–3 higher than that in CdO:In. As a result, free-carrier absorption and plasma reflection effects limit their optical transparency to <1200 nm. For most 3d TM dopants, a qualitatively higher d-donor level $E_{d,\text{donor}}$ gives rise to higher $E_{F,\text{max}}$ or a higher N_{max} . Although at low x , the optical band gap E_{opt} of CdO:TM follows the calculated values due to free-carrier effects, as x increases, E_{opt} values are significantly higher than the calculated values. [4,5,6] This is believed to be an effect of the anticrossing interaction of the localized d-levels and the extended CdO conduction-band (CB) states, giving rise to a lower occupied E^- and an upper unoccupied E^+ subband. The restructured CBs have much flatter dispersion, which also results in a much higher effective



mass m^*e , hence it can also explain the much lower μ of CdO:TM films with high N. Transparent conducting oxides (TCOs) are widely used in optoelectronic devices such as flat panel displays, organic light emitting diodes, photovoltaics, heat reflectors, and energy-efficient windows because they are electrically conductive and optically transparent [1–3]. CdO is a promising transparent conducting oxide (TCO) due to its high electrical conductivity ($<10^3 \Omega^{-1} \cdot \text{cm}^{-1}$) and its direct band gap of 2.2 eV. It also has a nonstoichiometric composition, which is because of the presence of cadmium interstitial oxygen vacancies acting as donors [4]. The introduction of cobalt, which is a transition magnetic metal element, to CdO led to astonishing optical, electrical, and magnetic properties. This is mainly because of the interaction between the band electrons and the cobalt ion within the CdO lattice.

A review of the literature on pure and doped CdO films reveals a huge array of fabrication studies. In addition to vacuum evaporation, successive ionic layer adsorption and reaction technique, sol-gel technique, magnetron sputter, organic chemical vapour deposition system, chemical spray pyrolysis, chemical bath coating, successive ionic layer adsorption and reaction technique, pulsed laser deposition, and others, thin films deposition methods have been reported to produce undoped and metal-doped CdO thin films. A key consideration for selecting appropriate contributing materials is the ionic radius [5]. (Co^{2+}) is projected to be the optimal doping candidate for CdO films because it substitutes the Cd^{2+} sites in the lattice and contributes electrons to serve as charge carriers [6]. Structural, optical, and NLO properties of CdO film could be controlled with Co-doping because the ionic radius of Co being smaller than that of cadmium ions [7].

From the literature review, we found Al: CdO films and N: CdO films deposited by the SP technique with linear and nonlinear optical properties [8, 9]. As a result, we attempted to prepare and study the $\text{Cd}_{1-x}\text{Co}_x\text{O}$ films using this versatile technique. Furthermore, dilute concentration was chosen because we need homogeneous solutions in the SP technique so that during spray, chemical reactions take place in proportion, resulting in a homogeneous thin film in its entire volume. So far, there has been no discussion of the detailed report on NLO studies of $\text{Cd}_{1-x}\text{Co}_x\text{O}$ films. The present study aimed to prepare pure and [7,8,9] $\text{Cd}_{1-x}\text{Co}_x\text{O}$ thin films using the SP technique by varying the various contents of Co from 0 to 10 wt. % by volume and focused more on the enhancement of the structural, linear, and 3rd-order NLO properties by the Z-scan technique for optoelectronic device applications.

II. DISCUSSION

In recent years, with exponentially increasing energy demands, there has been a spurt in global efforts to efficiently harness solar energy. Among the various approaches, solar thermal techniques play a more and more important role in solar-energy harvesting, due to high energy-conversion efficiency and appealing energy storage functionality. The solar thermal system in concentrating solar power (CSP) convert solar energy into heat and then heat to electricity (thermophotovoltaics) for various applications, including solar water heating, space heating and cooling, refrigeration, industrial process heating and thermal power generation [1], [2], [3], [4].

Concentrating solar power (CPS) technology which applies to solar- thermal power plants increases the availability of solar energy of the plants. As the core part of the concentrating solar power technology, selective solar absorbing coatings enhance the efficiency of the plants. Selective Solar absorbers (SSA) coatings demonstrate a high solar absorptance ($\alpha_s \geq 0.90$) in the UV–VIS–NIR region from 0.30 to 2.5 μm and a low thermal emittance ($\epsilon \leq 0.10$) in the IR region ($\lambda > 2.5 \mu\text{m}$) for solar thermal conversion [10,11,12] applications [5], [6], [7], [8], [9], [1], [10]. The optical properties and thermal stability of the coatings determine the features of the solar selective absorbing coatings in actual engineering applications, including its solar-thermal conversion efficiency, operating temperature and working lifetime [2], [7], [11], [12], [13], [14]. A variety of selective coatings have been reported for solar thermal applications such as metal-oxides composites (e.g. Cr-Cr₂O₃, Co-Al₂O₃, W- Al₂O₃) [15], [16], [17], transition metal nitrides (e.g. TiN, TiAlN, HfNx) [18], [19], transition metal oxynitrides (e.g. TiNxOy, NbTiON), and alternative layers of metal and oxide layers (MgO/Zr/MgO, AlxOy/Pt/AlxOy, Cr₂O₃/Cr/Cr₂O₃, ZrOx/Zr/ZrOx/AlxOy) [1], [16] have been widely studied.

Among metal oxides semiconductors, copper oxide (CuO) is one of the promising SSA materials which have combination of interesting properties for good solar selectivity. CuO is p-type semiconductor with a direct band gap of 1.2 eV and high optical absorption coefficient. CuO thin films have wide range of applications in energy harvesting and storage, such as solar cells, photoelectro-chemical cells, photocatalysts, and lithium ion batteries [9], [13,14,15] So far different CuO nanostructures have been obtained by different methods such as reactive sputtering, chemical vapor deposition (CVD), anodizing, chemical conversion and thermal oxidization [16]. S. Karthick et al.[17], reported that CuO was synthesised on Cu substrate as selective solar absorber by using NaOH and NH₄OH through solution based oxidation reaction and 90% absorptance (α) value and 7% thermal emittance (ϵ) value in the range of 0.3–2.0 nm wavelength was reported. X. Zhang et

al. [18], also reported that CuO was synthesised on Cu substrate as selective solar absorber by using KOH and $K_2S_2O_8$ through chemical oxidation process. However, detailed optical properties and chemical composition of CuO thin films were not studied. L. Yalin et al.[19], also reported that CuO was synthesised on Cu substrate as selective solar absorber by using KOH and $K_2S_2O_8$ through chemical oxidation process and 90% solar absorptance value in the solar spectrum region and 11% of emittance value in the infrared region was reported. However, detail in terms of structural properties of the CuO thin films synthesised by chemical oxidation process for different oxidation reaction is lacking. In this work, CuO nanocoatings were synthesized in aqueous solution of alkaline (KOH) and ($K_2S_2O_8$) on Cu substrates through solution based chemical oxidation process for different reaction time for selective solar absorber applications. The structural and optical properties of the synthesised CuO nanocoatings were studied.

III. RESULTS

The optical constants and optical energy gap of (PVA-PEG-CuO) nano-composite films have been studied in the present paper. The nano-composite films was prepared by casting technicality, where, (PVA-PEG) blends used as matrix while the Copper oxide nanoparticles were (0, 2, 4, 6, 8) wt% as a filler. The present study is aimed to modification of the optical properties of blends with different concentrations of (CuO) nanoparticles and for achieves a new class of material. The absorption and transmission spectra have been recorded at the wavelength range 220-800 nm. The experimental results illustrate that the absorbance of pure blend was increased with increase of Copper oxide concentrations and vice versa with transmission. On the other hand, the optical constants and optical energy gap were changed with the addition of Copper oxide nanoparticles concentrations. Crystalline size and particle structure of obtained nanoparticles was examined by using XRD analysis. CuO nanoparticles has Monoclinic structure. The average crystalline size was calculated from the Full Width Half Maximum (FWHM) of the diffraction peaks using the Scherrer Debye formula. The morphology of 0.02 of CuO nanoparticles shows good homogeneity and uniform distribution due to increased substitution of various copper ions. The absorption spectrum generally depends on factors such as band gap, oxygen deficiency, grain size, lattice strain, impurity centers and surface roughness. Band gap of CuO nanoparticles is calculated through tauc plot. Fourier transform infrared (FTIR) spectroscopy investigated the compositional properties of the prepared CuO nanoparticle. [17,18,19]

IV. CONCLUSION

The increasing energy demand and environmental problems, such as contamination from the combustion of fossil fuels, [1] have brought the need to use alternative energy sources for energy production [2, 3]. Cu_2O is a promising candidate for photovoltaic applications as a possible solution to the global energy crisis [1, 4], providing alternative, safe, and sustainable energy sources [3]. Examples of this are the conversion of solar energy into electrical energy [5–7] and the generation of hydrogen from the photoelectrochemical conversion of the sun [3, 8].

In recent years, the research has been focused on the search for emerging cheap materials that are abundant in the Earth's crust, non-toxic, and have structural, optical, and electrical properties that make them adequate as light-absorbing materials [9]. Cu_2O is a p-type semiconductor due to the negatively charged Cu vacancies [10]. It has a direct band gap between 1.9 and 2.2 eV [11, 12] and a significant absorption coefficient from violet to green in the range of the solar spectrum (at 600 nm) [13, 14].

Cuprous oxide is used in electrodes for lithium-ion batteries, photochemical cells, hydrogen production, sensors, photocatalysts, supercapacitors, magnetic storage, and water splitting [15,16], as well as a bactericide, colorant, and additive for corrosion-proof coatings [17,18]. Various methods have been developed to obtain Cu_2O , such as the water bath method, the SILAR (Successive Ionic Layer Absorption and Reaction) method, the polyol method, chemical reduction, and sol-gel [4, 10, 17, 18]; however, some of these methods require special equipment [17, 18], catalysts, organic additives, or expensive surfactants [18].

Among the available methods, the reduction of copper salts with some reducing agents has been identified as a simple process with a quick reaction rate [4, 18]. The use of glucose as a reducing agent has the advantage of being environmentally friendly, resulting in green chemical synthesis. Besides, glucose is cheap and highly selective in producing Cu_2O [19], and its use is suitable for the development of Cu_2O particles with different morphologies like spheres, cubes, beveled cubes, octahedrons, flower shapes, nanowires, nanorods, hierarchical structures, cages, and hollow structures [17, 18] by changing the temperature, pH, reagents, solvents, reaction times, and surfactants control [16,17].



Over the years, several works have reported the formation of Cu_2O using glucose as a reducing agent. In 2009, for example, Cao and colleagues investigated the effect of the synthesis temperature on the morphological evolution of Cu_2O particles. Their study focused on synthesis temperatures from 95°C to 180°C using an autoclave system and reaction times from 6 to 36 hours. They found qualitatively that at synthesis temperatures above 180°C , they obtained a mixture of Cu_2O and metallic copper [15,16]. On the other hand, Cao et al. [12,13] reported the formation of different morphologies of Cu_2O by varying the glucose concentration at a synthesis temperature of 50°C . They observed qualitatively the appearance of CuO peaks in their diffraction patterns when the glucose concentration is deficient, suggesting that the reduction of Cu^{+2} ions into Cu^{+1} ions is not complete under low glucose conditions [10,11].

In this work, Cu_2O was obtained by reducing Benedict's solution with glucose in an alkaline medium without any surfactants, additives, or templates. Our work avoids using sulfur-containing reagents or any special equipment; instead, we developed a rapid and simple synthesis at a low temperature of 65°C . The present study mainly focuses on the effects of the glucose content and the temperature on structural and optical properties. A detailed quantitative analysis was carried out using the Rietveld refinement and the Williamson-Hall (W-H) approach to quantify the composition of the samples and to obtain structural information such as the variation of lattice parameters, crystallite size, unit cell volume, and microstrains.[9,10] The results showed a mixture of phases in the composition of the samples. In addition, when the glucose content increased, the crystallite size decreased, and the microstrains increased. Various morphologies were obtained when the amount of reducing agent was changed. However, all morphologies showed an absorption broad almost constant in the range of 200 nm to 570 nm. The in-situ X-ray diffraction showed that Cu_2O transforms to Cu at temperatures above 300°C and CuO at temperatures above 320°C . These properties make Cu_2O a candidate for solar cell applications as a light absorber material.[19]

REFERENCES

- [1] M. Kaur et al., Growth and branching of CuO nanowires by thermal oxidation of copper, *Journal of Crystal Growth* 289(2), 670 (2006).
- [2] J. Zhu et al., Synthesis of flower-like CuO nanostructures via a simple hydrolysis route, *Materials Letters* 61(30), 5236 (2007).
- [3] J. K. Sharma et al., Green synthesis of CuO nanoparticles with leaf extract of *Calotropis gigantea* and its dye-sensitized solar cells applications, 632, 321 (2015).
- [4] S. Gunalan et al., *Aloe barbadensis* Miller mediated green synthesis of mono-disperse copper oxide nanoparticles: optical properties, *Journal of Alloys and Compounds* 97, 1140 (2012).
- [5] J. Chen et al., CuO nanowires synthesized by thermal oxidation route 454(1-2), 268 (2008).
- [6] Y.-K. Su et al., Controlled synthesis of highly ordered CuO nanowire arrays by template- based sol-gel route, *Journal of Alloys and Compounds* 17(4), 783 (2007).
- [7] L. Yu et al., Cupric oxide nanoflowers synthesized with a simple solution route and their field emission, *Journal of Crystal Growth* 310(12), 3125 (2008).
- [8] G.-Q. Yuan et al., Shape-and size-controlled electrochemical synthesis of cupric oxide nanocrystals, *Journal of Crystal Growth* 303(2), 400 (2007).
- [9] W.-T. Yao et al., Formation of uniform CuO nanorods by spontaneous aggregation: Selective synthesis of CuO , Cu_2O , and Cu nanoparticles by a solid- liquid phase arc discharge process, *The Journal of Physical Chemistry B* 109(29), 14011 (2005).
- [10] Y. Liu et al., In situ synthesis and assembly of copper oxide nanocrystals on copper foil via a mild hydrothermal process, *Journal of Materials Chemistry* 16(2), 192 (2006).
- [11] A. Musa et al., Production of cuprous oxide, a solar cell material, by thermal oxidation and a study of its physical and electrical properties, *Solar Energy Materials and Solar Cells* 51(3-4), 305 (1998).
- [12] P. Poizot et al., Nano-sized transition-metal oxides as negative-electrode materials for lithium-ion batteries, *Nature* 407(6803), 496 (2000).
- [13] Z. Yang et al., Controlled synthesis of CuO nanostructures by a simple solution route, *Journal of Solid State Chemistry* 180(4), 1390 (2002).
- [14] H. Wang et al., Preparation of CuO nanoparticles by microwave irradiation, *Journal of Crystal Growth* 244(1), 88 (2002).
- [15] K. Ali et al., Analysis of Non-Uniform Doping in Silicon Solar Cell and Optimization Using PC1D, *Journal of Ovonic Research* 15(4) 215 (2019). 412



- [16] W. Wang et al., Synthesis and characterization of CuO nanowhiskers by a novel one-step, solid-state reaction in the presence of a nonionic surfactant, *Materials Research Bulletin* 37(6), 1093 (2002).
- [17] D. Prabhakaran et al., Morphology and etching studies on YBCO and CuO single crystals *Physica C: Superconductivity and its Applications* 319(1-2), 99 (1999).
- [18] J. Zhang et al., Nearly monodisperse Cu₂O and CuO nanospheres: preparation and applications for sensitive gas sensors, *Chemistry of Materials* 18(4), 867 (2006).
- [19] H. Kidowaki, T. Oku, T. Akiyama. Fabrication and characterization of CuO/ZnO solar cells. in *Journal of Physics: Conference Series*, 2012, IOP Publishing.



INTERNATIONAL
STANDARD
SERIAL
NUMBER
INDIA



International Journal of Advanced Research in Arts, Science, Engineering & Management (IJARASEM)

| Mobile No: +91-9940572462 | Whatsapp: +91-9940572462 | ijarasem@gmail.com |

www.ijarasem.com