Enhanced Opto-Electronic Properties Of X-Doped (X=Al, Ga, And In) CuO Thin Films For Photodetector Applications

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Abstract

Recent trends in optoelectronics still need a high efficient photodetector based on p-type metal oxide semiconductors. This work stands with the improvement in the performance of CuO thin films via doping with different metals into the thin films. The CuO thin films were successfully doped with 1 wt% of X (X=Al, Ga, and In) by spray pyrolysis technology. The prepared doped CuO thin films were characterized to interpret the structural, morphological, and elemental characteristics using advanced techniques. These doped CuO thin films were subjected to study the photodetection ability by analyzing optoelectronic properties. The doping also has tuned the optical and electrical properties. Among the fabricated photodetectors, the Al-doped CuO detector shows a maximum photocurrent. The CuO:Al(1.0%) thin film exhibits a high photocurrent of 2.59×10^{-6} A, the responsivity of 2.82×10^{-1} AW⁻¹, the external quantum efficiency of 66%, and detectivity of 1.45×10^{10} Jones. Compared to the other thin films, Al doping has remarkably reduced the bandgap and shows a good photosensing activity that may be due to an increase in charge carriers. These outcomes provide a way to assemble good photodetectors and tune their properties in a wide range.

1. Introduction

The nano-devices have been game-changing for the growing technology in the electronic era. Nanomaterials have been explored worldwide due to their demands in semiconductor devices. Cupric oxide (CuO), a p-type semiconductor with exclusive features has motivated researchers and industries. The abundance of availability and cost-effective CuO increases its implementation. The structural, chemical, and thermal stability of CuO leads to its application in supercapacitors, batteries, biosensors, gas sensors, etc. [1], [2]. The high current conductivity, high mobility, optical absorption, and narrow bandgap of CuO prompt its utilization in photodiodes, photocatalysis, and solar cells [3–6]. Interestingly, the properties of the CuO can be governed by various parameters like synthesis methods, morphology, nanocomposites, or doping of parental nanomaterials [7–9]. The CuO thin films have been the attractive approach to develop different morphologies for optical and electrical applications. The deposition and growth of thin films can be done in various methods like dip coating, spray pyrolysis, SILAR, CVD, or electrodeposition which vary the properties of thin films [10], [11]. Zang et al. has reported nitrogen-doped CuO thin films synthesized by radical oxidation at 500°C for reducing the resistance of thin films and enhancing optical properties [7]. The CuO thin films have been highly explored for photodetector application [11]. Quite recently, tuning of CuO thin films by dip-coating method has been reported by Das et al., for photodetector applications [10]. The photodetector prepared by CuO thin films (100-dip cycles) showed the best performance rather than 25, 75, and 125 dip cycles. Similarly, the spray pyrolysis method has been reported to improve the properties of CuO thin films [12]. The spray deposition is a facile and sustainable way to develop thin films. Further, the physical and chemical properties can be modified by controlling the amount/concentration of dopants [13], [14]. The CuO nanostructured with different dopants has been investigated for optoelectronic applications. The selected amount of La concentration is utilized while the synthesis process, enhance the photocatalytic property of CuO without destroying its

crystal structure [10]. Inass et al. has explored doping different amount of Li (2, 4, and 6%) to the CuO thin films by SILAR method for tuning the structural and optical nature [9]. The improved optoelectronic properties of CuO thin films after doping can be beneficial to consumer electronics. The CuO thin films also have been established with a better switching time of visible-light illumination with high photocurrent which depicts the quality of photo-sensing property [15]. Furthermore, the doping effect of metals such as Li, Al, Ga, Gd, In, La, Sb, Au, Fe, etc. has been investigated highly for improving optoelectronic properties [1, 3, 5, 6, 9, 13, 14, 16]. Interestingly, the doping of Ba, Sm, Au, and Pr have influenced the host structure, particle size, and optoelectronic characteristics [17]–[20]. The application of such doped thin films has resulted in enhanced photocurrent. Muhammad et al. have studied experimental and theoretical the effect of Al doping on CuO nanoparticles synthesized by combustion technique [21]. The DFT study has revealed the addition of impurity (Al doping) has reduced the bandgap of host CuO. The Al^{3+} doping has also modified the bond length and morphology of CuO nanoparticles. On other hand, indium doping to CuO thin films by the sputtering method has increased free charge concentration [22]. Single-phase monoclinic CuO:In thin films are generally used for a solar cell or LED applications. Similarly, Yin et al. have studied the effect of Ni-doped CuO films with high responsivity and external quantum efficiency photodetectors [23]. The effect of doping Al(1%), Sb(1%), and Sn(1%) to ZnS-thin film synthesized via spray pyrolysis method has been examined for photodetector applications [24].

In this work, CuO and X-doped (X = Al, Ga, and In) CuO thin films were prepared on glass substrates using simple and low-cost spray method together with studying the structural, surface morphology, optical and electrical characterizations.

2. Experimental

Analytical grade precursors such as copper chloride (CuCl_2 , 0.1M), AlCl_3 , GaCl_3 , and InCl_3 were used in this work. Distilled water was used as a solvent throughout the experimental procedures. The nebulizer spray pyrolysis (NSP) method with an automated x-y movement system was used to prepare the films. The process of spray deposition was optimized for the best deposition of thin films such as the substrate temperature was fixed at 450°C and air pressure of 1.5 kg/cm^2 . The distance from the substrate to the nozzle was kept constant at 5 cm. Figure 1 illustrates the schematic for the synthesis of the CuO and X-doped CuO thin films where the X is Al(1%), Ga(1%), and In(1%). The Al, Ga, and In doping thin films are named as CuO:Al(1%), CuO:Ga(1%), and CuO:In(1%), respectively.

The synthesized thin films were subjected to characterizations using advanced techniques. To understand the thin films' purity, phase, and crystallization, an X-ray diffractometer (Bruker AXS with Cu-K α source, $\lambda = 1.5406 \text{ \AA}$) was used. The surface morphology of the coated films on glass substrate was studied by field emission-scanning electron microscope (Carl Zeiss Ultra 55). Perkin Elmer LS-55 fluorescence spectrophotometer is used for optical studies such as photoluminescence. UV-spectrophotometer (Perkin Elmer 4 Lambda 35) was used to collect the absorption data in the wavelength range of 300–900 nm. A Keithley source meter (Model 2450) was used to measure the photocurrent characteristics of the prepared thin films. A stylus profilometer (Mitutoyo SJ-301) was used

for film thickness measurements of the prepared films. The measured average film thickness values are around 500 nm.

3. Results And Discussion

3.1. Structural studies

Figure 2 shows the XRD patterns of CuO, CuO:Al(1%), CuO:Ga(1%), and CuO:In(1%) thin films, which reveals a typical monoclinic CuO structure with a space group of $C_{2/c}$. The diffraction peaks at (110), (002), (111), (020), (202), and (113) are indexed to the pure CuO phase (as per JCPDS file No: 89-5899). The observed high-intensity diffraction peaks suggest the crystallinity nature of CuO of the thin films. Further, the doping does not change the XRD pattern of the host CuO thin films stating that there is no change of structure on doping of Al(1%), Ga(1%), and In(1%). It is seen that doping of Al to the CuO thin films has resulted in sharp intense peaks whereas doping of Ga and In has reduced the intensity. The increase of peak intensity at (002) plane for Al doped CuO when compared to other samples, this might be due to the lower ionic radius of Al^{3+} (0.54 Å) than Ga^{3+} (0.62 Å) and In^{3+} (0.94 Å); while the host Cu^{2+} ionic radius is (0.74 Å). Therefore, the solubility limit of Al ions is higher than other dopants and hence effortlessly substitute in the Cu sites. However, the dopant of In^{3+} ions may segregate around the grain boundaries of CuO due to its higher atomic size than host Cu^{2+} ions, as resulting there is a reduction peak intensity occurs. With reference to XRD patterns, the lattice parameter, the crystallite size (D), and strain (ϵ) values of all the films are calculated by given Scherer and Williamson-Hall equations and summarized in Table 1.

Table 1
Crystallite size, Strain, Lattice constant, and cell volume of the CuO, CuO:Al(1%), CuO:Ga(1%), and CuO:In(1%) thin films.

Samples	Crystallite size (nm)	Strain $\times 10^{-3}$	Lattice constant			Cell Volume $V(\text{\AA}^3)$
			a(Å)	b(Å)	c(Å)	
CuO	33	3.18	4.674(4)	3.426(3)	5.117(4)	80.87(11)
CuO:Al(1.0%)	41	2.54	4.663(6)	3.424(4)	5.118(7)	80.66(18)
CuO:Ga(1.0%)	36	2.89	4.668(5)	3.423(4)	5.119(6)	80.76(15)
CuO:In(1.0%)	34	3.07	4.686(7)	3.424(5)	5.073(7)	80.30(2)

$$D = \frac{0.9\lambda}{\beta \cos \theta} \quad (1)$$

$$\epsilon = \frac{\beta \cot \theta}{4}$$

2

where, λ - X-ray wavelength, θ - Bragg angle, β – full width half maximum (FWHM). The crystallite size of CuO, CuO:Al(1%), CuO:Ga(1%), and CuO:In(1%) thin films was found to be 33, 41, 36, and 34 nm, respectively. The strain value decreases by adding impurities with CuO. The maximum crystallite size and minimum strain values obtained by Al-doping with CuO are expected to be potential for photo-sensing applications. Rietveld refinement was performed using DIFFRAC.TOPAS v.6.0 (Bruker-AXS, Karlsruhe, Germany) software for analysis the structural parameters which is shown in supplementary Fig. 1. The value of lattice parameters (a, b, c) well matches with early reports for pure CuO thin films[15]. There is a minor variation of lattice parameters after doping of Al, Ga, and In, that reflects in nearly a constant cell volume. Thus, the XRD results confirmed the incorporation of Al, Ga, and In into the CuO lattice and the effect of doping on the structural pattern of host thin films. The change in a lattice structure and strain by doping metals into CuO have been earlier reported by various research groups[4], [25]–[27].

3.2. Morphology studies

Figure 3 represents the SEM micrographs of the CuO, CuO:Al(1%), CuO:Ga(1%), and CuO:In(1%) thin films. The thin film morphology plays a vivacious role in determining the optoelectronic properties. A flaky morphology is seen that Fig. 3(a, b) whereas agglomerated morphology is seen in Fig. 3(c, d). It is clearly seen in CuO (Fig. 3a) and Al-doped of CuO thin films (Fig. 3b) are nearly similar which substantiate the XRD pattern of CuO and Al-doped CuO thin films. The doping of Ga and In into CuO thin films seems to be slightly changed from the host CuO morphology, which corroborates the XRD analysis. A clear agglomeration of particles seen for CuO:Ga(1%) and CuO:In(1%) thin films evident a little change in the growth of CuO thin films, so as seen in XRD of thin films. Fascinatingly, the Al doping with CuO thin films has formed homogeneous nanoparticles grown on the substrate. The flaky ribbon-type nanoparticles have been widely distributed over the surface of the substrate forming a uniform thin film. Such surfaces that resulted after doping of CuO thin film are expected to show remarkable optoelectronic properties. To understand the elemental composition and amount of doping, the EDX analysis was performed on thin films. The EDX spectra of the fabricated thin films are shown in Fig. 4. The insets of Fig. 4 show the elemental composition of the fabricated thin films. The Al, Ga, and In doping contents are about 0.94%, 0.87%, and 0.91%, respectively.

3.3. Optical studies

The fabricated thin films were subjected to optical properties investigations. The optical absorbance of all thin films in the wavelength range of 300–900 nm is shown in Fig. 5(a). The UV-vis spectra show a sharp peak in the range of 350–380 nm for all the thin films. Usually, an intense peak with plateau-type UV-absorption spectrum is seen in well crystalline CuO thin films [28], [29]. There is a slight variation of peaks for doping into CuO thin films. The CuO:Al thin film has shown an absorbance peak with high

intensity compared to other thin films. It is observed from Fig. 5(a) that the doping of Al, Ga, and In into the CuO lattice considerably hike the absorbance than pure CuO thin film, which confirms the improved optical response. The direct band-gap has been calculated by given Tauc's relation[13]:

$$\alpha h\nu = B(h\nu - E_g)^n \quad (4)$$

where α denotes the absorption coefficient, $h\nu$ is the incident photon energy, B is a constant, n is an index depending upon the nature of the electronic transition responsible for the absorption, and E_g denotes the bandgap. Figure 5(b) shows the $(\alpha h\nu)^2$ vs. photon energy ($h\nu$) plots for the thin films. The E_g values of thin films are estimated by extrapolating the linear fit onto the photon energy axis in the high slope region and given in Table no. 2. The band-gap of pure CuO thin film is found to be 2.14 eV, where doping has reduced the band-gap. The E_g values for CuO:Al(1%), (c) CuO:Ga(1%), and (d) CuO:In(1%) thin films is found to be 1.89, 1.78, and 2.11 eV, respectively. The doping of Al and Ga has extraordinarily reduced the bandgap. Similar doping of trivalent Nd^{3+} rare-earth to CuO thin films has reduced bandgap from 2.04 to 1.89 eV [4]. Such doping can affect the optical properties of CuO thin films and be beneficial for light-dependent applications [14], [18].

3.4. Photoluminescence studies

Figure 6 shows the photoluminescence spectra of as-prepared CuO and doped CuO thin films recorded in the range of 370–600 nm with the excitation wavelength of 350 nm. The doped and undoped thin films exhibited spectra of four peaks around 410, 450, 475, and 525 nm. The violet emission peak around ~ 410 nm might be because of the recombination of electron-hole pairs due to free-excitons [30]. The blue emission peak around 450 nm and a broad peak at ~ 475 nm could be due to electronic transition between the oxygen interstitials and Cu vacancies [31]. A green emission peak around ~ 525 nm might be attributed to the CuO band-band transition, trapped electrons at the defect sites, copper interstitials, oxygen vacancies, and electron transition near the conduction band (CB) [32]. The shift in peaks can be ascribed to the addition of impurities to CuO thin film which alters the structure and morphology. The doping La to the CuO thin film has generated defects in the CuO lattice structure [28]. Muthukrishnan et al. has reported PL variation with a change of concentration of CuO thin films prepared by spray pyrolysis method [12]. The Au-doping to CuO thin films cause a change in the grain boundary and microstrain defects have led to change in PL [18]. The doping also improves the morphology and thickness of the film deposited on the substrate result in photoresponse/current of the thin film [20].

3.5. Photo-sensing properties

The photo-sensing properties determine the practical applications of thin film semiconductors in photodetectors. Figure 7 shows the schematic illustration of device fabrication for optoelectronic studies performed on the fabricated thin films. The I–V characteristics studied for all the thin films are shown in Fig. 8. The I–V curves are drawn by changing the bias voltages from + 5 to – 5 V under dark and visible-

light illumination (532 nm) conditions. The linear trend in I-V curves is found in the CuO and doped CuO thin films. Such a trend has been seen in other semiconductor thin films suggesting the ohmic nature of thin film due to doping, defects, or impurities added to the host. Ni-doped CuO thin films are reported with low resistivity due to vacancies generated [27]. Similarly, doping CuO thin films with the chemical spray method has displayed high absorption of light leading to high photocurrent [4]. The I-V curves of dark current (I_{dark}) and photocurrent (I_{photo}) for the fabricated thin films are recorded in Table 2. The photocurrent is higher than the dark currents that indicate the generation of charge carriers on activation of the light. Different illumination effect is seen with the variation of doping to the CuO thin films, which may be a consequence of the different structure and morphological distribution of parent thin films occurred on doping. However, the doping Al, Ga, and In have successfully enhanced both dark and photocurrent of CuO thin films. The photo-current of CuO:Al(1%) is found to be the highest as compared to CuO, CuO:Ga(1%), and CuO:In(1%).

Table 2

Comparison table showing the photocurrent, dark current, responsivity, external quantum efficiency, detectivity, rise and fall time for CuO, CuO:Al(1%), CuO:Ga(1%), and CuO:In(1%) thin films with other reported works.

Samples	I_{dark} (A)	I_{photo} (A)	R (AW ⁻¹)	EQE (%)	D^* (Jones)	Rise Time (s)	Fall Time (s)	Ref.
CuO/Si	3.50 E-11	2.23 E-07	-	-	-	0.85	0.83	[33]
SiO ₂ @ CuO/Si	4.78 E-06	1.00 E-04	2.59 E-01	100.7	1.71 E+12	-	-	[34]
Ni doped CuO	-	6.00 E-07	26.4 E-00	5176	-	-	-	[23]
CuO-ZnO core shell nanowires	3.43 E-12	~ E-09	8.74 E-00	26.56	40.5E+09	~ 35	~ 35	[35]
SnO ₂ /CuO	~ E-08	~ E-05	10.3 E-00	-	-	-	-	[36]
CuO@CuS/Si	-	-	7.98 E-01	309.66	8.19 E+11	-	-	[37]
CuO	1.35E-06	1.79E-06	8.71E-02	20.0	4.19E+09	4.6	4.1	
CuO:Al(1.0%)	1.18E-06	2.59E-06	2.82E-01	66.0	1.45E+10	4.3	4.0	This work
CuO:Ga(1.0%)	1.27E-06	1.73E-06	9.25E-02	22.0	4.59E+09	4.4	3.9	
CuO:In(1.0%)	1.19E-06	1.78E-06	1.17E-01	27.0	5.99E+09	4.4	4.0	

Furthermore, the sensitivity of photodetector fabricated by all the thin films was examined by the parameters viz. responsivity (R), detectivity (D^*), and external quantum efficiency (EQE). These parameters are calculated by the following formulae (6,7 and 8) and tabulated in Table No.3.

$$R = \frac{I_p}{P_{in} \times A} \quad (6)$$

$$EQE = R \frac{hc}{e\lambda} \quad (7)$$

$$D^* = R \sqrt{\frac{A}{2eI_{dark}}} \quad (8)$$

where I_p , A , and P_{in} denote the photocurrent, effective area, and intensity of the light, respectively whereas h , c , and λ represent Planck's constant, velocity of light, and wavelength of the incident light, respectively. The symbols e and I_d denote the charge of the electron and dark current, respectively. The calculated values for R , D^* , and EQE for all the thin films are shown in Fig. 8. The plotted graph infers the values of responsivity of the thin films are found to be 8.71×10^{-2} , 2.82×10^{-1} , 9.25×10^{-2} , and $1.17 \times 10^{-1} \text{ AW}^{-1}$ for CuO, CuO:Al(1%), CuO:Ga(1%), and CuO:In(1%), respectively. Similarly, the EQE values follow the values of 20, 66, 22, and 27% for the above thin films, respectively. The values of D^* for CuO:Al(1%) is found to be 1.45×10^{10} Jones. Thus, the photodetector parameters elucidate the effect of doping on CuO thin films. The Al(1%) doping affects the CuO thin films significantly whereas the doping of Ga(1%) and In(1%) shows quite a lower effect.

The transient photoresponse has been recorded for fabricated CuO-based thin films and is shown in Fig. 9. The photoresponse gives the current response of the thin films with time on UV illumination. The CuO, CuO:Al(1%), CuO:Ga(1%), and CuO:In(1%) photodetectors switched at a 532 nm visible light illumination with the power of $1-5 \text{ mW/cm}^2$. The systematic rise and fall times have been recorded and tabulated in Table 3. The photocurrent response increases with the increasing intensity of the laser light, indicating that more charge carriers were obtained for more intensity of light. The rise time/decay time of the photocurrent for CuO and Al, Ga, In –doped CuO films were found to be 4.6s/4.1s, 4.3s/4.0s, 4.4s/3.9s and 4.4s/4.0s, respectively. The Al-doped CuO thin film has a minimum value of rise/decay time as compared to other thin films that are designated to the improved crystallinity and well-grown thin film. The mechanism for the observed changes in the photosensitive properties of present thin films as a function of composition can be explained and is attributed to the number of oxygen molecules available for the adsorption and desorption process at the surface of the films as well as carrier concentration differences caused by the intrinsic nature of dopant elements. Since CuO:Al(1%) exhibits a highly crystalline nature and surface homogeneity as compared to the other films, which suggests the decrement of oxygen vacancies due to the increased oxygen ions at the surface of the films. As a result, CuO:Al(1%) exhibits relatively better photo-sensing properties among all the fabricated thin films. The photodetector thin film is reported with high photocurrent due to high charge carriers [10]. The oxygen vacancies lead to excellent visible light absorption and electron-hole pair generation/recombination. Similar, doping effect is seen in C and Au doped CuO thin film [5], [6]. The Comparison of photocurrent, dark current, responsivity, external quantum efficiency, detectivity, rise and fall time for CuO, CuO:Al(1%), CuO:Ga(1%), and CuO:In(1%) thin films with other reported works was given in Table 2. Thus, the present study reveals the significance of doping elements on the structural, optical and photo-sensing properties of CuO thin films.

3.6. Mechanism of CuO thin film photodetector

The photoresponse of the fabricated photodetector could be explained using the mechanism shown in Fig. 10. The explanation of the charge transfer process of the metal oxide-based photodetector was

carried out in dark and light conditions at a bias voltage of 5V. During the dark conditions, oxygen atoms are adsorbed to the surface of CuO creating electron trap sites ($O_2 + e^- = O_2^-$). These trap sites result in the formation of a wider depletion layer in turn reducing the electrical conductivity resulting in the decrease of dark current value. Moreover, when the photodiode was exposed to visible light, the photogenerated carriers (i.e holes) neutralize the surface oxygen ions ($h^+ + O_2^- = O_2$) making the electrons free from recombination with holes. This phenomenon increases the lifetime of the electrons and in turn, increases the photocurrent value. When the light is cut off, the oxygen ions are again adsorbed to the CuO surface and the resultant current value decreases.

4. Conclusions

The effect of Al, Ga, and In doping in structural, morphological, optical, and photosensing properties of pure CuO thin films fabricated by spray technology. The doped CuO thin films were optimized for photosensing applications. The CuO, CuO:Al(1%), CuO:Ga(1%), and CuO:In(1%) thin films are found to be crystalline and flaky morphology. The optical properties revealed the CuO:Al(1%) thin film's highest optoelectronic property in comparison to the CuO, CuO:Ga(1%), and CuO:In(1%) thin films. The doping of Al with CuO thin films has improved optoelectronic properties, which can be utilized for photodetectors. This work opens the scope for the investigation of other parameters to boost the performances of photodetectors.

Declarations

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References

- [1] R. Molavi and M. H. Sheikhi, "Facile wet chemical synthesis of Al doped CuO nanoleaves for carbon monoxide gas sensor applications," *Mater. Sci. Semicond. Process.*, vol. 106, no. October 2019, p. 104767, 2020, doi: 10.1016/j.mssp.2019.104767.
- [2] T. E. Balaji, H. Tanaya Das, and T. Maiyalagan, "Recent Trends in Bimetallic Oxides and Their Composites as Electrode Materials for Supercapacitor Applications," *ChemElectroChem*, vol. 8, no. 10. John Wiley and Sons Inc, pp. 1723–1746, May 2021, doi: 10.1002/celc.202100098.
- [3] B. Yan, Y. Wang, T. Jiang, and X. Wu, "Synthesis and enhanced photocatalytic property of La-doped CuO nanostructures by electrodeposition method," *J. Mater. Sci. Mater. Electron.*, vol. 27, no. 5, pp. 5389–5394, 2016, doi: 10.1007/s10854-016-4439-z.

- [4] D. Naveena, T. Logu, R. Dhanabal, K. Sethuraman, and A. C. Bose, "Comparative study of effective photoabsorber CuO thin films prepared via different precursors using chemical spray pyrolysis for solar cell application," *J. Mater. Sci. Mater. Electron.*, vol. 30, no. 1, pp. 561–572, 2019, doi: 10.1007/s10854-018-0322-4.
- [5] M. M. Koc, "Photoelectrical properties of solar sensitive CuO doped carbon photodiodes," *J. Mol. Struct.*, vol. 1208, p. 127872, 2020, doi: 10.1016/j.molstruc.2020.127872.
- [6] S. RUZGAR, Y. CAGLAR, O. POLAT, D. SOBOLA, and M. CAGLAR, "The tuning of electrical performance of Au/(CuO:La)/n-Si photodiode with La doping," *Surfaces and Interfaces*, vol. 21, no. August, p. 100750, 2020, doi: 10.1016/j.surfin.2020.100750.
- [7] Z. Zang, A. Nakamura, and J. Temmyo, "Nitrogen doping in cuprous oxide films synthesized by radical oxidation at low temperature," *Mater. Lett.*, vol. 92, pp. 188–191, 2013, doi: 10.1016/j.matlet.2012.10.083.
- [8] C. Ravichandiran *et al.*, "The effect of rare earth Nd³⁺ doping on physical characteristics of Cu₂O thin films derived by electrodeposition technique," *Thin Solid Films*, vol. 683, no. August 2018, pp. 82–89, 2019, doi: 10.1016/j.tsf.2019.05.008.
- [9] I. A. Zgair, A. H. Omran Alkhayatt, A. A. Muhmood, and S. K. Hussain, "Investigation of structure, optical and photoluminescence characteristics of Li doped CuO nanostructure thin films synthesized by SILAR method," *Optik (Stuttg.)*, vol. 191, no. June, pp. 48–54, 2019, doi: 10.1016/j.ijleo.2019.06.008.
- [10] S. K. Shaikh, V. V. Ganbavle, S. I. Inamdar, and K. Y. Rajpure, "Multifunctional zinc oxide thin films for high-performance UV photodetectors and nitrogen dioxide gas sensors," *RSC Adv.*, vol. 6, no. 31, pp. 25641–25650, 2016, doi: 10.1039/c6ra01750a.
- [11] W. Q. Liang *et al.*, "A solution-processed ternary copper halide thin films for air-stable and deep-ultraviolet-sensitive photodetector," *Nanoscale*, vol. 12, no. 33, pp. 17213–17221, 2020, doi: 10.1039/d0nr03630g.
- [12] S. Muthukrishnan, V. Subramaniam, T. Mahalingam, S. J. Helen, and P. Sumathi, "Improved properties of spray pyrolysed CuO nanocrystalline thin films," *J. Mater. Sci. Mater. Electron.*, vol. 28, no. 5, pp. 4211–4218, 2017, doi: 10.1007/s10854-016-6043-7.
- [13] P. Gu, X. Zhu, and D. Yang, "Structural, optical and photoelectric properties of Mn-doped ZnO films used for ultraviolet detectors," *RSC Adv.*, vol. 9, no. 14, pp. 8039–8047, 2019, doi: 10.1039/c9ra01099h.
- [14] M. Shkir *et al.*, "An effect of Fe on physical properties of nanostructured NiO thin films for nonlinear optoelectronic applications," *Appl. Phys. A Mater. Sci. Process.*, vol. 126, no. 2, pp. 1–14, 2020, doi: 10.1007/s00339-020-3293-2.

- [15] H. T. Das *et al.*, "Tuning the Optical, Electrical, and Optoelectronic Properties of CuO Thin Films Fabricated by Facile SILAR Dip-Coating Technique for Photosensing Applications," *J. Inorg. Organomet. Polym. Mater.*, vol. 31, no. 6, pp. 2606–2614, 2021, doi: 10.1007/s10904-021-01928-z.
- [16] A. Badawi *et al.*, "Structure investigation and optical bandgap tuning of La-doped CuO nanostructured films prepared by spray pyrolysis technique," *Appl. Phys. A Mater. Sci. Process.*, vol. 127, no. 4, pp. 1–9, 2021, doi: 10.1007/s00339-021-04387-y.
- [17] S. S. K. Jacob *et al.*, "Investigation on structural, optical and photovoltaic properties of Barium doped cuprous oxide thin films by nebulizer spray technique," *Mater. Res. Express*, vol. 6, no. 11, 2019, doi: 10.1088/2053-1591/ab485f.
- [18] R. A. Ismail and R. S. Abdul-hamed, "Laser ablation of Au – CuO core – shell nanocomposite in water for optoelectronic devices Laser ablation of Au – CuO core – shell nanocomposite in water for optoelectronic devices."
- [19] C. Ravichandiran *et al.*, "Effect of rare earth Pr doping on core characteristics of electrodeposited nanocrystalline Cu₂O films: a film for optoelectronic technology," *J. Sol-Gel Sci. Technol.*, pp. 578–588, 2019, doi: 10.1007/s10971-019-04934-3.
- [20] C. Ravichandiran *et al.*, "Influence of rare earth material (Sm³⁺) doping on the properties of electrodeposited Cu₂O films for optoelectronics," *J. Mater. Sci. Mater. Electron.*, vol. 30, no. 3, pp. 2530–2537, 2019, doi: 10.1007/s10854-018-0527-6.
- [21] M. R. Islam, J. E. Obaid, M. Saiduzzaman, S. S. Nishat, T. Debnath, and A. Kabir, "Effect of Al doping on the structural and optical properties of CuO nanoparticles prepared by solution combustion method: Experiment and DFT investigation," *J. Phys. Chem. Solids*, vol. 147, p. 109646, 2020, doi: 10.1016/j.jpcs.2020.109646.
- [22] Y. Du, X. Meng, and X. Gao, "Variations of the microstructure and the optical and electrical properties with sputtering power for direct-current-magnetron-sputtered indium-doped CuO thin films at room temperature," *Thin Solid Films*, vol. 684, no. November 2018, pp. 53–58, 2019, doi: 10.1016/j.tsf.2019.05.056.
- [23] W. Yin *et al.*, "High Responsivity and External Quantum Efficiency Photodetectors Based on Solution-Processed Ni-Doped CuO Films," *ACS Appl. Mater. Interfaces*, vol. 12, no. 10, pp. 11797–11805, 2020, doi: 10.1021/acsami.9b18663.
- [24] A. J. Jebathew, M. Karunakaran, R. Ade, D. Jayram, and V. Ganesh, "Optical manipulation of nebulizer spray pyrolysis fabricated ZnS thin films for photo detector applications: An effect of Al, Sn, Sb doping," no. April, 2021.

- [25] Ş. Baturay, A. Tombak, D. Batibay, and Y. S. Ocak, "n-Type conductivity of CuO thin films by metal doping," *Appl. Surf. Sci.*, vol. 477, pp. 91–95, 2019, doi: 10.1016/j.apsusc.2017.12.004.
- [26] W. Z. Tawfik, Z. S. Khalifa, M. S. Abdel-wahab, and A. H. Hammad, "Sputtered cobalt doped CuO nano-structured thin films for photoconductive sensors," *J. Mater. Sci. Mater. Electron.*, vol. 30, no. 2, pp. 1275–1281, 2019, doi: 10.1007/s10854-018-0395-0.
- [27] S. Baturay *et al.*, "Modification of electrical and optical properties of CuO thin films by Ni doping," *J. Sol-Gel Sci. Technol.*, vol. 78, no. 2, pp. 422–429, 2016, doi: 10.1007/s10971-015-3953-4.
- [28] L. V. Devi, T. Selvalakshmi, S. Sellaiyan, A. Uedono, K. Sivaji, and S. Sankar, "Effect of La doping on the lattice defects and photoluminescence properties of CuO," *J. Alloys Compd.*, vol. 709, pp. 496–504, 2017, doi: 10.1016/j.jallcom.2017.03.148.
- [29] A. Tombak, M. Benhaliliba, Y. S. Ocak, and T. Kiliçoglu, "The novel transparent sputtered p-type CuO thin films and Ag/p-CuO/n-Si Schottky diode applications," *Results Phys.*, vol. 5, pp. 314–321, 2015, doi: 10.1016/j.rinp.2015.11.001.
- [30] P. Chand, A. Gaur, A. Kumar, and U. Kumar Gaur, "Structural and optical study of Li doped CuO thin films on Si (1 0 0) substrate deposited by pulsed laser deposition," *Appl. Surf. Sci.*, vol. 307, pp. 280–286, 2014, doi: 10.1016/j.apsusc.2014.04.027.
- [31] A. R. Ansari, A. H. Hammad, M. S. Abdel-wahab, M. Shariq, and M. Imran, "Structural, optical and photoluminescence investigations of nanocrystalline CuO thin films at different microwave powers," *Opt. Quantum Electron.*, vol. 52, no. 10, pp. 1–16, 2020, doi: 10.1007/s11082-020-02535-x.
- [32] C. R. Gobbiner, G. R. Dillip, S. W. Joo, and D. Kekuda, "Heterogeneity of photoluminescence properties and electronic transitions in copper oxide thin films: A thickness dependent structural and optical study," *Ceram. Int.*, vol. 44, no. 14, pp. 16984–16991, 2018, doi: 10.1016/j.ceramint.2018.06.140.
- [33] J. Sultana, S. Paul, A. Karmakar, G. K. Dalapati, and S. Chattopadhyay, "Optimizing the thermal annealing temperature: technological route for tuning the photo-detecting property of p-CuO thin films grown by chemical bath deposition method," *J. Mater. Sci. Mater. Electron.*, vol. 29, no. 15, pp. 12878–12887, 2018, doi: 10.1007/s10854-018-9407-3.
- [34] S. Gunasekaran *et al.*, "Fabrication of high-performance SiO₂@p-CuO/n-Si core-shell structure based photosensitive diode for photodetection application," *Surfaces and Interfaces*, vol. 20, no. July, p. 100622, 2020, doi: 10.1016/j.surfin.2020.100622.
- [35] A. Costas, C. Florica, N. Preda, A. Kuncser, and I. Enculescu, "Photodetecting properties of single CuO–ZnO core–shell nanowires with p–n radial heterojunction," *Sci. Rep.*, vol. 10, no. 1, pp. 1–12, 2020, doi: 10.1038/s41598-020-74963-4.

- [36] T. Xie *et al.*, "High-performing visible-blind photodetectors based on SnO₂/CuO nanoheterojunctions," *Appl. Phys. Lett.*, vol. 107, no. 24, 2015, doi: 10.1063/1.4938129.
- [37] S. Gunasekaran *et al.*, "Photosensitive activity of fabricated core-shell composite nanostructured p-CuO@CuS/n-Si diode for photodetection applications," *Sensors Actuators, A Phys.*, vol. 317, p. 112373, 2021, doi: 10.1016/j.sna.2020.112373.

Figures

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Figure 1

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Figure 2

XRD patterns of (a) CuO, (b) CuO:Al(1%), (c) CuO:Ga(1%), and (d) CuO: In(1%) thin films prepared by spray method.

Figure 3

FESEM images of (a) CuO, (b) CuO:Al(1%), (c) CuO:Ga(1%), and (d) CuO:In(1%) thin films.

Figure 4

EDX spectra of (a) CuO, (b) CuO:Al(1%), (c) CuO:Ga(1%), and (d) CuO:In(1%) thin films (Insets show the corresponding elemental composition).

Figure 5

(a) Absorption spectra and (b) $(\alpha h\nu)^2$ vs. photon energy ($h\nu$) curves with linear fits of (a) CuO, (b) CuO:Al(1%), (c) CuO:Ga(1%), and (d) CuO:In(1%) thin films.

Figure 6

Photoluminescence spectra of CuO, CuO:Al(1%), CuO:Ga(1%), and CuO:In(1%) thin films.

Figure 7

Schematic illustration for fabrication of photodetectors with the CuO-based thin films grown over a glass substrate and its analysis.

Figure 8

Current (I)-voltage (V) curves of CuO, CuO:Al(1%), CuO:Ga(1%), and (d)

CuO:In(1%) photo-detectors measured in dark and presence of light.

Figure 9

Time-dependent photo-response (Current vs. time) of CuO, CuO:Al(1%), CuO:Ga(1%) and CuO:In(1%) photo-detectors switched at a 532 nm visible light illumination with the power of 1-5 mW/cm². ON and OFF periodically at a fixed bias field of 5 V.

Figure 10

Mechanism showing the photoresponse of the fabricated metal oxide-based photodetector