

Structural, Optical and Electrical Characterizations of Cr-doped CuO Thin Films

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Abstract. The polycrystalline copper oxide (CuO) thin films have been produced using method of spin coating onto the soda lime glass (SLG) as well as substrate of p-type Si (1 0 0) wafers at 500 °C in furnace. The obtained undoped and Cr doped thin films of CuO have been comprehensively characterized via X-ray diffraction (XRD), ultraviolet–vis (UV–vis) spectroscopy, the current–voltage (*I–V*) and capacitance–voltage (*C–V*) characteristics for providing information on quality of the crystalline nature, change in energy band gap and electrical properties, respectively. Structural analysis results which obtained from XRD data demonstrate that CuO films conjunction with Cr doping indicated that all thin films have monoclinic polycrystalline nature, with two main peaks (002) and (111) with d_{hkl} about 2.52 and 2.32 Å, respectively. The transmittance and energy band gap value of undoped and Cr doped thin films of CuO ranging in varying concentration ratio have been determined in the wavelength region of 300 to 1100 nm. UV–vis spectrum analysis results indicate that both transmittance value and energy band gap of the CuO films is changed with increasing Cr doping ratio in CuO solution at room temperature. The *I–V* and *C–V* characteristic of Cr:CuO/p-Si diodes were associated with the CuO/p-Si diodes. It is seen that doping of Cr had a significant change onv the obtained devices’ performance. Thus, the Cr:CuO/p-Si diodes generated by 1% Cr doping using spin coating method had the highest light sensitivity compared with those of the other diodes.

Keywords: Cr, CuO, thin films, spin coating, Cr:CuO/p-Si diodes

1. Introduction

The metal oxide nanostructures’ extraordinary properties and structural difference started wide-ranging research focus in various nanoscale fields including electronics, catalysis, optics, optoelectronics, and biosensors [1-4]. As a metal oxide semiconductor view, CuO nanofilms are a major interest between other kinds of the metal oxide semiconductor. Copper oxide should be classified in two different stable forms which are known cupric oxide (CuO) and cuprous oxide (Cu₂O). CuO with nanostructures having semiconductor material of p-type conductivity exhibits intriguing properties such as direct energy band gap value (between 1.1 and 2.1 eV) [5,6], environment friendly and unique chemical stability and in contrast, Cu₂O has cubic structure that has 2–2.6 eV energy band gap with black color [7]. CuO as a semiconductor candidate is very promising for various application areas including H₂ gas sensors [8], CO₂ sensor [9], cross-point memory [10], solar selective absorber [11], solar cell [12], photoelectrochemical applications [13], perovskite solar cells [14] and electrochemical supercapacitors [15] owing to abundant availability in nature and low cost synthesis and easy preparation process of copper production [16,17]. It should be noted that, CuO has been both direct [18] and indirect energy band gap [19] more than cuprous oxide compound and fabrication methods strongly effect these values. Kuhaili indicated that cupric oxide for temperatures only below 300 °C is the stable phase at different partial pressure of oxygen (P(O₂)), and merely less than 1000 °C for atmospheric pressure, the equilibrium phase diagram of the Copper–Oxygen (Cu–O) system [20]. Otherwise, cuprous oxide is thermodynamically stable only in P(O₂) range of temperature, and that is obtained by heating of Cu with P(O₂) below 10 mTorr using a KrF excimer laser (248 nm) above 650 °C [21]. Nevertheless, nanocrystalline Cu₂O phase was additionally seen by annealing thin films of Cu in air at temperatures less than 300 °C [22,23]. A single monoclinic CuO phase was also obtained from the films annealed tubular furnace some increment in the healing temperature such as between 350 and 450 °C in air condition [22]. The research on CuO thin films has attracted extensive interest because of the fact that the p-type conducting oxide development [20] has significant importance in technology for p–n homo-junction based oxide materilas. Moreover, metal-semiconductor (MS) and metal-interlayer-semiconductor (MIS) type Schottky diodes’ electrical properties started considerable interest in experimental studies owing to metal and semiconductor interlayer’s different optical and electrical properties [24,25]. Since these devices’ performance and reliability is particularly based on the interlayer formation, these devices effect parameters of the device including the barrier height, interface-state density, series resistance as well as ideality factor.

Surface morphology, donor density, surface charge, oxygen vacancies’ presence and its catalytic effects in CuO can be significantly enhanced with doping with Cr [26,27]. Doping of Cr is preferred for the semiconductor materials owing to fact that the CuO material’s properties can be significantly changed by the doping of Cr such

as NH₃ sensing, transmittance value, and optical band gap [28-30]. Various methods have been used to fabricate CuO and Cu₂O thin films with dissimilar morphology. Monoclinic CuO and cubic Cu₂O thin films could be manufactured via copper's thermal oxidation at 250 and 350 °C in the air, respectively [31]. Samarasekera et al fabricated thin films of CuO using sol-gel spin coating technique and investigated Zn²⁺ doped CuO thin films' electrical properties. They found Zn²⁺ doped CuO films indicate electrochemical cell behavior only after illuminating [32]. Guillen and herrero fabricated thin films of Cu₂O and CuO via low-temperature oxidation processes and found that there is one level in the energy band gap of CuO which was attributed to oxygen's mono-vacancies and two defect levels next to the Cu₂O conduction band owing to vacancy complexes and mono-vacancies [31]. Shaban et al. employed spin-coating technique to investigate phase mixed with Cu₂O/CuO structural, optical and gas sensing properties and they found that the sensitivity of 6 % Cr and 3 % S doping of Cu₂O/CuO thin films significantly improved from 46 to 99.8 % towards flow rate of CO₂ increased from 30 to 150 sccm [33]. Pat et al. [2] deposited CuO thin film with Cr doping via technique of thermionic vacuum arc plasma and deposited they had high transparency, and dielectric constant [34].

Recently, transition metal oxides have been deposited [35-39] to improve crystalline nature of CuO thin films. Though different doped CuO thin films' physical and chemical properties have been examined by groups [16,40-43], CuO thin films with Cr doping are very limited in literature.

In the present study, CuO thin films with Cr doping were obtained through conventional, easy, environmentally friendly and suitable for the various size areas grown differently from among the above-mentioned method. The CuO thin films' structural, morphological and optical properties fabricated on glass and substrates of p-Si using spin coating technique. The obtained Cr doped films have been investigated employing XRD and UV-vis spectroscopy to provide data on the crystalline nature's quality and surface morphology change of the obtained films. Additionally, we have investigated the diodes' electrical properties to analyze the concentration effect on diode parameters of Cr:CuO/p-Si diodes by employing measurements of current-voltage (I-V) and capacitance-voltage (C-V) in the dark and light (100 mW/cm²).

2. Experimental

Cr doped CuO thin films with Cr/Cu ratios of 0, 1, 2 and 3% were prepared using spin coating method SLG and wafers of p-type Si (1 0 0) as substrate that have 1-10 Ω-cm resistivity. Before deposition process, SLG substrates were firstly boiled in 5:1:1 deionized water, ammonia and hydrogen peroxide mix for time of 20 min. at a temperature of 90 °C and in the solution of 5:1:1 deionized water, hydrogen peroxide and hydrogen chloride with same conditions. Then, these cleaned substrates were cleaned in acetone for 5 min each for two times to obtain clear surface. After this process, cleaned substrates cleaned by distilled water and dried under N₂ gas, respectively. Then, the Si wafers to obtain Cr:CuO/p-Si diode were boiled for 5 min in trichloroethylene, and later, stirred for 5 min in acetone each for two times and ethanol to obtain free of any organic contamination in ultrasonic bath. The wafers were etched in hydrofluoric acid (HF) solution: distilled water (H₂O) (1:10) two times for 30 s and then cleaned by distilled water to eliminate the native oxide and any chemical residues before inserting these Si wafers into the vacuum chamber to obtain Cr:CuO/p-Si diode. The rear contacts were made by evaporating an Al metal of 200 nm thickness on the Si wafers' unprocessed side, and that was continued by a speedy thermal annealing for 3 min at 570 °C under a N₂ gas.

A 0.1 M copper (II) acetate (Cu(CH₃COO)₂•H₂O) in ethanol solution was employed as the preliminary material and a 0.01 M solution of chromium (III) chloride (CrCl₃•6H₂O) in ethanol was used as the dopant source, respectively. The obtained solutions were firstly deposited on p-Si wafer with (100) orientation by spin coating method at 1500 rpm for 55 s for 3 layers of deposition. After this, the obtained films were annealed for 1 h in a furnace at 500 °C under air. Lastly, front contacts of Al were vaporized onto the Cr doped CuO thin films employing a shadow mask for investigating the heterojunctions' electrical properties. Then, obtained solutions were placed on substrates of SLG using the forementioned technique and conditions for 10 layers of deposition to investigate the Cr doped CuO thin films' structural and optical properties. During deposition process, each layer of the films was preheated to 230 °C on a hot plate for 10 minutes to obtain a homogenous surface.

The undoped and Cr doped CuO thin films' structural and phase purity analysis were determined by a Rigaku ultima III diffractometer with wavelength of 0.154 nm at 40 kV, and 30 mA for θ -2 θ range in the steps of 0.02° (θ) at room temperature. The conclusion of thin films' transmittance and energy band gap was analyzed by UV-Vis spectrophotometer between 300-1100 nm. I-V relations of all films were inspected by a source meter (Keithley 2400, Cleveland, USA) both in dark and under illumination with light with 100 mW/cm² light at room temperature to investigate the change of barrier height and ideality factor.

3. Structural properties

The prepared Cr doped CuO thin films' structural analysis was investigated by X-Ray diffraction, which was operated by Cu K α radiation source ($\lambda = 0.154187$ nm) and it produced 40 keV and 30 mA at room temperature for 2θ values ranging from 20° to 80° . The obtained samples' XRD patterns are displayed in Figure 1. The positions of peaks at 2θ angle that are around 35.6° , 38.8° , 48.8° , 53.5° , 68.07° , with d_{hkl} around 2.52, 2.32, 1.86, 1.71 and (1,38) Å were related to (JCPDS 05-6661 for CuO) (002), (111), (-202), (020) and (113) reflections planes, respectively. According to the XRD data, it is said that the samples' XRD patterns show a CuO single phase's existence with a monoclinic structure [1-3]. There are no signs of oxide phases associated with the impurity phase owing to the formation of the possible compounds containing chromium oxides and Cu₂O.

The diffraction data obtained from XRD including the values of peak orientations, strain (ϵ), grain sizes (D), dislocation density (δ), inter-planar spacing (d -spacing), and full width at half maximum (FWHM) for strong peaks are given in the Table 1. The intensities of peaks and FWHM values which employed to determine the grain size slightly change with increasing Cr concentration. Cr addition in the samples in air at temperature at 500°C change the composition and the crystal structure of the thin film; and also the peak intensities and orientation along (002) and (111) were higher. It is said that Cu ions' exchange changes the structure of crystal or crystallinity slightly owing to the fact that it is probably related to the Cr⁺ ion's atomic radius (0.62 Å) being smaller than Cu²⁺ ions' one (0.73 Å). When these results compared with previous studies, it was concluded that the given planes' orientation and intensity for CuO thin films mostly approve strong crystallinity with monoclinic structure [4]. Das and Alford revealed that that the Ag doped CuO thin film had preferential orientation along the line in the (111) [5]. Menazea and Ayman is indicated similar results and they showed that had a preferential orientation in the (200) direction [6]. Obulapathi et al. [44] indicated that similar XRD data. They indicated that the intensity of the peaks changed by the addition Cr into the CuO thin films.

Cr doped CuO thin film's crystallite size (D) was determined by the angular peak width at width at FWHM of (002) and (111) planes by employing the following expression [45].

$$D = \frac{0.94\lambda}{\beta \cos\theta} \quad (1)$$

where λ is 1.5418Å as the XRD wavelength, θ is the angle of Bragg diffraction and β is the angular peak width at FWHM and D is the crystallite size of the film of (002) and (111) planes. Calculation from X-ray diffraction data showed change in the crystallite size as a function of the Cr concentration. The calculation of Cr doped CuO thin films' crystallite size shows a change in D value as a Cr doping function at 500°C constant annealing temperature. Durai et al. [46] showed that the the D value of the Cr-doped CuO changes owing to a rise in absorbed atoms' mobility. d values of the obtained CuO film are determined by the Bragg's expression:

$$2d\sin\theta = n\lambda \quad (2)$$

where n is the diffraction order. Calculated d values of undoped and CuO thin films with Cr doping for (002) and (111) are around 2.52 and 2.32, respectively. The value of dislocation density (δ) that shows the defects' amount in samples is calculated using the formula below:

$$\delta = \frac{1}{D^2} \quad (3)$$

The change in the strain of the all films is determined using expression [27]:

$$\epsilon = \frac{\beta}{4\tan\theta} \quad (4)$$

The dislocation density value is changed between 56.87×10^{13} and $83.47 \times 10^{13} \text{ m}^{-2}$ for (002) plane and 13.88×10^{13} and $17.19 \times 10^{13} \text{ m}^{-2}$ for (111) plane owing to the fact that the δ values are inversely proportional to the D value square. Strain values of the (002) and (111) planes is changed with Cr dopant content. Therefore, it was said that the main effect of change in D is linked to change in strain. Durai et al. [46] showed Cr doped CuO films with as function of concentration change show change in strain value owing to strain relaxation with changed D value.

4. Optical Properties

The optical properties including absorbance, transmittance and band gap of undoped and CuO thin films with Cr doping via spin coating method were detailed analyzed to examine Cr doping effect by using UV-visible spectrophotometer data in the range of 300–1100 nm. The absorption coefficient and the undoped and Cr doped

CuO thin films' optical transmission spectra for four different doping concentration deposited on SLG substrate are given in figure 3 and 4, respectively. It was found that the CuO thin films' optical transmittance values increase in visible region as compared to undoped CuO film and the highest value has been found to be around 33 % related to 3% Cr doping in the visible range. This upsurge in the value of optical transmittance is assigned to the crystalline nature of the thin film characteristics because these changes are corresponding to the material properties of the thin films. The rise in the transmittance value of obtained CuO thin film could be ascribed to the Moss-Burstein (M-B) effect [47]. Thus, it is said that the CuO thin films' optical properties can be changed by Cr dopant content in the ultraviolet-visible range (401–750 nm) of the optical spectrum from 300 nm to 1100 nm. Thus, it is said that the optical properties including transmittance and absorbance of CuO thin films can be changed by different Cr dopant content in the ultraviolet-visible range region. The change in values of absorbance and transmittance indicates that CuO thin films could be applied to numerous applications including photovoltaic devices [48]. Menazea and Mostafa [49] are revealed that the CuO thin films' optical transmittance value is improved with Ag doping using Laser Deposition (PLD) technique. They also said that the enhancing in the transmittance value may be allocated to the structural properties of prepared thin films.

The increase of the value of transmittance corresponds to change of the energy band gap corresponding to valence electrons and conduction electrons. The direct energy band gap values of the all thin films are calculated via the Tauc's expression as stated below [50].

$$\alpha h\nu = A (h\nu - E_g)^m \quad (5)$$

where $h\nu$ is the radiation energy, E_g is the band gap of the used materials, A is the material's energy independent constant, n is constant that based on the transition nature, $m = 1/2, 2, 3/2, \text{ or } 3$ for direct, nondirect allowed transition, forbidden direct or forbidden nondirect transitions, respectively. α is a constant that gives the coefficient of absorption in cm^{-1} which is also calculated using the equation; $\alpha = 4\pi k/\lambda$; k is the absorption index of material and λ is the wavelength. Figure 4 indicates the plot of $(\alpha h\nu)^2$ versus incident energy of photon ($h\nu$) for undoped and Cr doped CuO films. Undoped CuO thin films' calculated band gap value is 1.60 eV, which increases to 2.30 eV after the doped by Cr in solution. The Cr doped CuO thin films are revealing both high transmittance as well as maximum energy band gap among the obtained thin films. Gülen et al indicated that the value of energy band gap was improved with Mn doping concentration in the thin film using SILAR method [51]. Pat et al. [34] revealed that energy band gap value of the Cr doped Cu_xO thin film was measured to be around 2 eV using thermionic vacuum arc plasma. Sajid et al [52] indicated that the pure CuO thin films' energy band gap is calculated to be 1.87 eV that is greater than bulk CuO (1.2 eV) because of confinement effects at quantum nanoscale level. Also they are showed that CuO thin film's energy band gap value has been increased up to 2.61 eV conjunctions with Cr doping owing to effects of band-filling as well as s-d and p-d exchange interactions. Das and Mitra [53] revealed that increase in energy band gap in doped films were seen up to 6% doping level owing to increase in carrier density in Ni doped CuO films.

It is said that increasing Cr concentration cause evaporation of oxygen and the obtained films become more Cu-rich owing to the fact that the O-rich samples usually have lower energy band gap value [54,55]. Relatively more Cu-rich thin films after Cr doping owing to the evaporation of excess oxygen from the film surface will have increase in the value of energy band gap as compared to the undoped CuO film. It is said that the change in the energy band gap conjunction with Cr doping might be capable for effect of band-filling. Thus, it is said that Cr could be used to regulate the CuO thin films' optical band gap for potential electronic equipment.

5. The Current-Voltage and Capacitance-Voltage Characteristics of the Cr:CuO/p-Si Diodes

To evaluate the fabricated heterojunction diodes' electrical properties, semi-logarithmic I-V plots were drawn from current-voltage measurements in the dark and under light (100 mw/cm^2). All diodes' I-V characteristics in the dark are shown in figure 5.

As seen in figure 5, although the best rectification ratio (RR) is seen in the 1% Cr doped diode ($RR=2.33 \times 10^3$ for $\pm 1\text{V}$), other diodes also have significant rectification behavior. At relatively low voltages, the Cr:CuO/p-Si heterojunction acts like a Schottky barrier diode [56]. Therefore, the Cr:CuO/p-Si diodes' I-V characteristics are explained by theory of Thermionic Emission (TE) which is well-known and stated in the following equations;

$$I = I_0 \exp\left(\frac{qV}{nkT}\right) \left[1 - \exp\left(-\frac{qV}{kt}\right)\right] \quad (6)$$

Where V is the applied voltage, n is the ideality factor, k is the Boltzmann constant, T is the absolute temperature in Kelvin, and I_0 is the saturation current which is given by:

$$I_0 = AA^*T^2 \exp\left(\frac{-q\phi_b}{kT}\right) \quad (7)$$

Where A is the diode area ($7.85 \times 10^{-3} \text{ cm}^2$), A^* is the effective Richardson constant and equal to $32 \text{ Acm}^{-2} \text{ K}^{-2}$ for p-type Si, q is the electron charge, and ϕ_b is the barrier height. The ideality factor n is related to the diode's conformity in the TE theory, and it is calculated from the linear region's slope of the forward bias in the plot of $\ln(I)$ - V characteristics via the following relation (for $V \geq 3kT/q$):

$$n = \frac{q}{kT} \left(\frac{dV}{d \ln I} \right) \quad (8)$$

The diode parameters n , ϕ_b , I_0 and RR are determined from the experimental I-V data at 300 K temperature and are given in Table 2. The results show that %1 Cr doping to CuO causes a slight improvement in the ideality factor. However, all produced the diodes' ideality factors are higher than unity, indicating that they demonstrate behavior of non-ideal diode. Ideality factors' higher values are associated to secondary mechanisms that involve dipoles of interface because of doped interface or structure of specific interface, and also defects of fabrication at the interface [57]. Furthermore, n 's large values may also be related to a wide distribution of low Schottky barrier patches due to the laterally inhomogeneous barrier [58]. Erdoğan and Güllü [57], calculated the ideality factor and barrier height being as 2.39 and 0.64 eV, respectively, in the Au/CuO/p-Si diode they constructed by the simple chemical method. Similarly, Ruzgar et al. [59] reported Au/(CuO:La)/n-Si photodiode's electrical performance that is formed with undoped CuO and La-doped CuO thin films produced by spin coating method. They calculated the best ideality value as 2.04 with 2% La doping CuO.

Another important parameter for Schottky barrier diodes is the barrier height (ϕ_b). Akin to the improving the diodes' ideality factor values, the height of barrier becomes optimum and maximum value reaching to 0.81 eV with 1% Cr doping. The 0.81 eV ϕ_b value we attained for the Al/%2Cr:CuO/p-Si device is considerably higher than both the barrier heights of the other diodes here and the conventional MS contacts diode's value such as the Al/p-Si diode, where ϕ_b is approximately 0.70 eV [60]. Some research have experimentally been carried out for the modification of barrier employing the thin films' interlayer [59]. Recently, Ruzgar et al. [8] have published a paper about the Au/Fe:CuO/n-si diode made by doping Fe to CuO. They reported that the barrier height changed with Fe doping to CuO and that the barrier height decreased as Fe doping increased. Similarly, Singh et al. [61] obtained 2.8 ideality factor and 0.82 eV barrier height for the n-CuO/p-Si diode, which they formed by method of sol-gel spin coating. In another study, Ruzgar et al. [59] stated that the height of barrier was the highest and optimum when the La contribution was 2% for the Au/La:CuO/n-Si diodes obtained by doping 2%, 5% and 10% La to CuO. Based on these, we can state that doping changes the barrier height of the diode and that the highest and optimum barrier height is achieved with 1% initial Cr doping to CuO in our work. The I-V graphs shown in Figure 5 deviate from linearity having relatively large forward biases associated with effects of series resistance. The diodes' series resistance can be investigated using Norde's method [62]. This includes a modified Norde function, and the function $F(V)$ is expressed as:

$$F(V) = \frac{V}{\gamma} + \frac{kT}{q} \ln\left(\frac{I(V)}{A^*AT^2}\right) \quad (9)$$

Where γ is a dimensionless arbitrary integer larger than idealty factor n and $I(V)$ is the diode's current in region of forward bias.

Figure 6 shows the Cr:CuO/p-Si diodes' $F(V)$ - V graph for a few different concentrations of Cr doping. According to the Norde's method, the values of barrier height ϕ_b and series resistance R_s are expressed by the equations below:

$$\phi_b = F(V_0) + \frac{V_0}{\gamma} - \frac{kT}{q} \quad (10)$$

$$R_s = \frac{kT(\gamma-n)}{I_0} \quad (11)$$

where $F(V_0)$ is the $F(V)$'s minimum point, V_0 and I_0 are voltage and current corresponding to this point, respectively. ϕ_b and R_s values calculated by Norde's method are given in Table 1. From the results, diode of 2% Cr:CuO/p-Si exhibited the largest series resistance with 3,674 k Ω , while diode of 1% Cr:CuO/p-Si showed the smallest series resistance. The obtained ϕ_b values from the experimental I-V data and calculated from the Norde's expression have similar variation inclination but marginally different. This difference is generally associated with barrier inhomogeneity and the non-linear behavior of diode [57,59].

To evaluate the Cr doping effect on the CuO based diodes' photoelectric properties, the diodes' I-V measurements in the dark and under light were taken and their plots are shown in figure 7 (a-d).

As can be seen from figure 7 (a-d), the currents of all diodes under illumination are higher than currents in dark. However, when compared with the most of other diodes, the high light sensitivity was realized in the diode with 1% Cr doping. Overall, illumination does not significantly change the forward bias currents whereas the reverse bias current changed significantly with illumination. Higher energy photons compared with the materials' optical band gap energies that make up the diode provide electron-hole pairs. Since these photo-generated carriers contribute more to the current carriers in the reverse bias region, a significant increase in current occurs in this region. Thus, the diodes produced exhibit the typical photosensitive property. Table 3 demonstrates the ratio of diodes' dark and illuminated reverse bias currents (at -2V), open circuit voltage (V_{oc}) and short circuit current (I_{sc}).

For Schottky heterojunction diodes, measurements of capacitance are an important non-destructive technique to obtain information on constant charge concentration and barrier height. Figure 8 illustrates the %1 Cr:CuO/p-Si heterojunctions' C-V measurements at different frequencies (10 kHz-1 Mhz) at 300 K in dark.

The capacitance values of the %1 Cr:CuO/p-Si diode decrease with increasing frequency as given in Figure 8. In general, the reverse bias voltage and frequency strongly effects the capacitance measurement in the Schottky diode. The capacitance's dependence on voltage and frequency is due to certain properties of the heterojunction, such as interface states, pollution level, series resistance as well as layer interface between Cr:CuO and p-Si [63]. The capacitance's higher values at low frequencies may be associated with the interface states' continuous distribution and depletion capacitance of the diode [64]. On the other hand, charge carriers of high frequencies in the interface cannot contribute to the capacitance as they cannot track the signal of alternating current. As a result, the diode's capacitance value has a tendency to be the same while the frequency rises [65]. The a diode's depletion region capacitance is expressed as [66]:

$$\frac{1}{C^2} = \frac{2(V_{bi}+V)}{q\epsilon_s A^2 N_a}, \quad (12)$$

where A is the area of diode, V is the voltage of reverse bias, V_{bi} is the diffusion potential at zero bias and obtained from the C^{-2} -V plot's extrapolation to the axis of V, where ϵ_s is the the semiconductor's ($11.8\epsilon_0$ for p-Si) dielectric constant, N_a is the p-type semiconductor's acceptor concentration.

Figure 9 demonstrates the C^2 -V and C-V graphs of a 1% Cr:CuO/p-Si heterojunction diode at 1Mhz and temperature of 300 K. The values of V_{bi} and N_a were found to be 0.59 eV and $3.618 \times 10^{16} \text{ cm}^{-3}$, respectively. The height of barrier could be determined employing the C-V data by expression below:

$$\phi_{b(C-V)} = V_{bi} + \frac{kT}{q} \ln\left(\frac{N_v}{N_a}\right). \quad (13)$$

Where N_v is the valance band states' effective density for p-Si ($N_v=3.2 \times 10^{19} \text{ cm}^{-3}$) [7]. The 1% Cr:CuO diode's barrier height was calculated as 0.765 eV from the measurement of C-V. The diode's barrier height values attained from the I-V and C-V measurements are close. However, the values acquired by both methods are slightly different. This can also be described by the I-V and C-V measurements' different nature and the presence of semiconductor's interfacial layer as well as trap states [67,68].

6. Conclusion

In summary, Cr doped CuO thin films were grown on SLG substrate and CuO/p-Si and Cr:CuO/p-Si structures were produced by depositing thin films on p-type Si wafers using method of spin coating and annealed at 500 °C for 1h in air condition. The Cr doping effect on structural, optical, morphological and electrical properties of these films was comprehensively explored. The CuO films conjunction with Cr doping were monoclinic polycrystalline structure and with two main peaks (002) and (111) with d_{hkl} about 2.52 Å and 2.32 Å, respectively. The obtained thin film's XRD parameters including crystallite size, dislocation density and strain is slightly changed with increasing Cr concentration. The thin film's transmittance value was increased in the visible range as compared to undoped CuO thin film. The band gap energy was determined to be between 1.67 and 2.03 eV with increasing Cr concentration. The energy band gap was radically increased with an increase of Cr concentration in CuO. Additionally, CuO/p-Si and Cr:CuO/p-Si structures were obtained by depositing thin films on p-type Si wafers via method of spin coating. The devices' electrical properties were analyzed in details using $I-V$ measurement in the dark and under illumination employing a solar simulator. $C-V$ measurements were carried out in the dark with a frequency range of 1 to 500 Hz. The results reveals that Cr doping significantly altered the devices' electrical and photoelectrical parameters. The highest height of barrier, largest V_{OC} and I_{SC} were determined to be in 3% Cr doped CuO thin films. Moreover, the structures formed using 3% Cr-doped CuO films exhibited the smallest ideality factor and series resistance. Thus, the obtained thin films parameters could be employed for photovoltaic devices on the future studies.

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Competing Interests

The authors have no relevant financial or non-financial interests to disclose.

Author Contributions

All authors contributed to the study conception and design. Material preparation, data collection and analysis were performed by Silan BATURAY, Ilhan CANDAN and Cihat OZAYDIN. The first draft of the manuscript was written by Silan BATURAY and all authors commented on previous versions of the manuscript. All authors read and approved the final manuscript.

Research Data Policy and Data Availability Statements

Data will be made available on reasonable request.

Compliance with Ethical Standards

This article does not contain any studies involving animals performed by any of the authors. This article does not contain any studies involving human participants performed by any of the authors.

Highlights

- Undoped and Cr doped CuO thin films were deposited onto glass substrates and p-Si semiconductor by spin coating method.
- The Cr:CuO/p-Si heterojunctions were compared with undoped CuO/p-Si heterojunction.
- The Cr:CuO/p-Si diodes generated by 1% Cr doping using spin coating method had the highest light sensitivity compared with those of the other diodes.

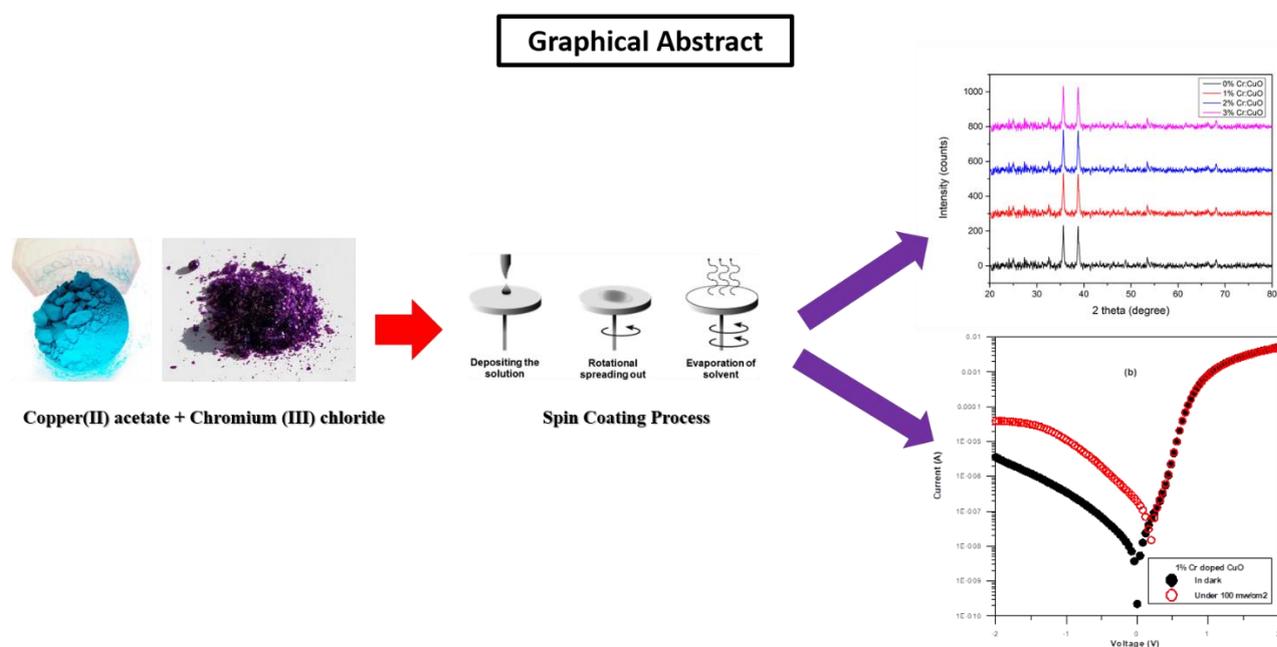


Fig. Graphical abstract.

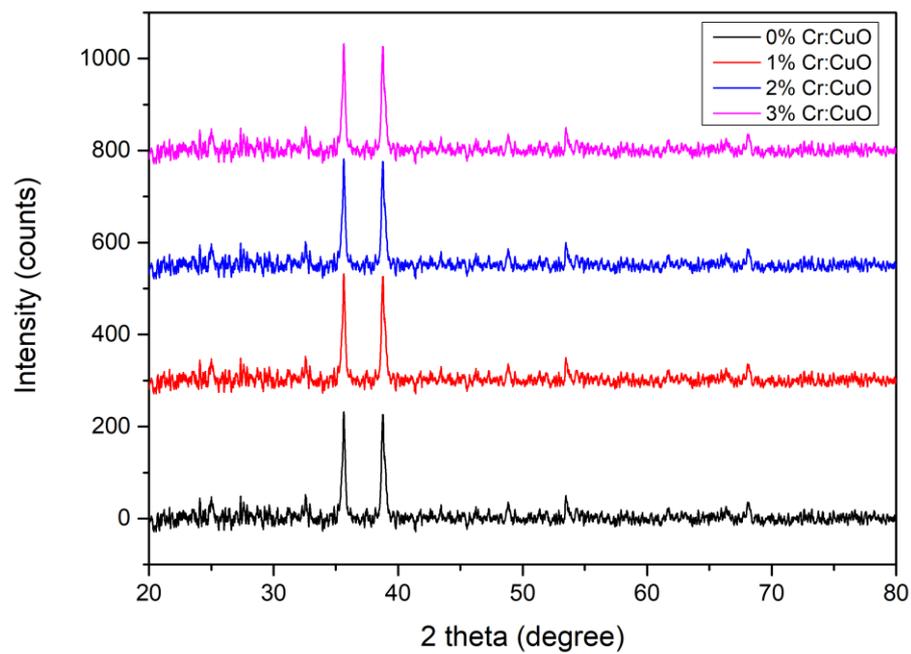


Fig. 1 XRD patterns CuO thin films with Cr doping.

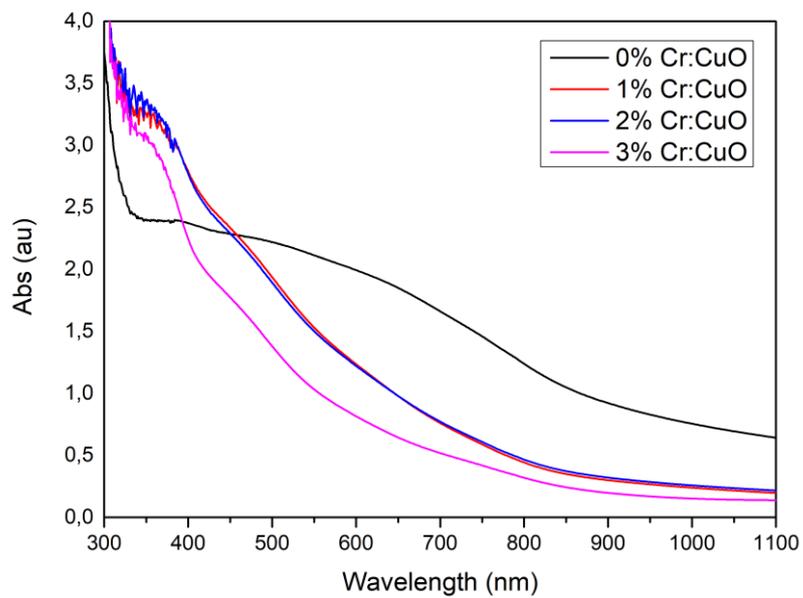


Fig. 2 Absorbance spectrum of CuO thin films for different Cr concentrations.

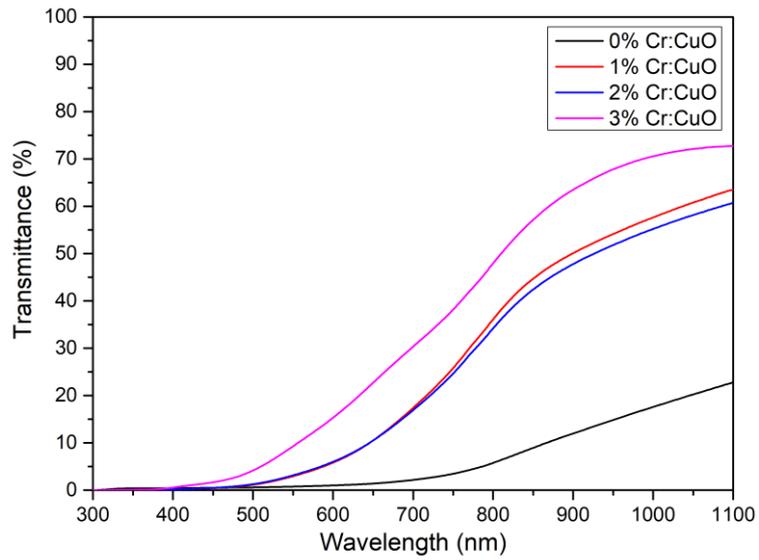


Fig. 3 Transmittance spectrum of CuO thin films for different Cr concentrations.

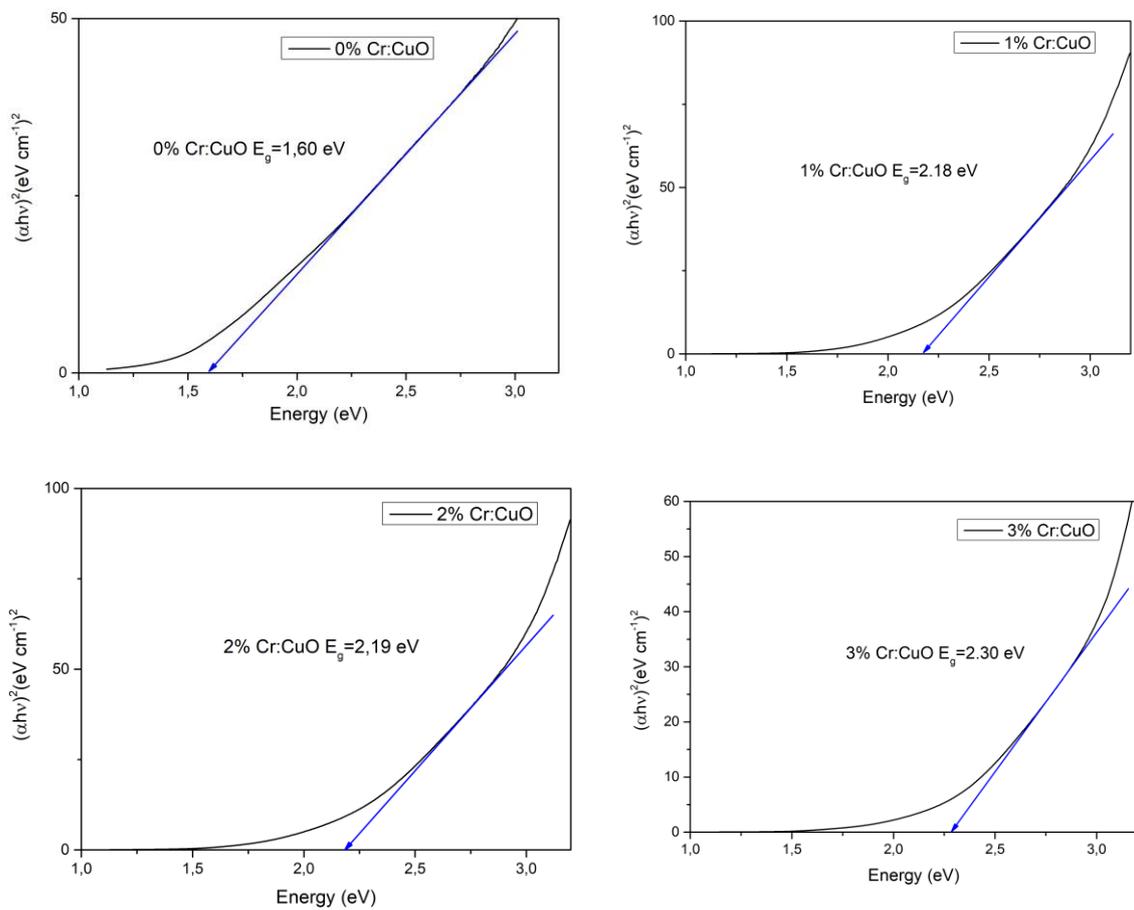


Fig. 4 $(ah\nu)^2$ vs. $h\nu$ plot of Cr doped CuO thin film on sodalime glass substrate.

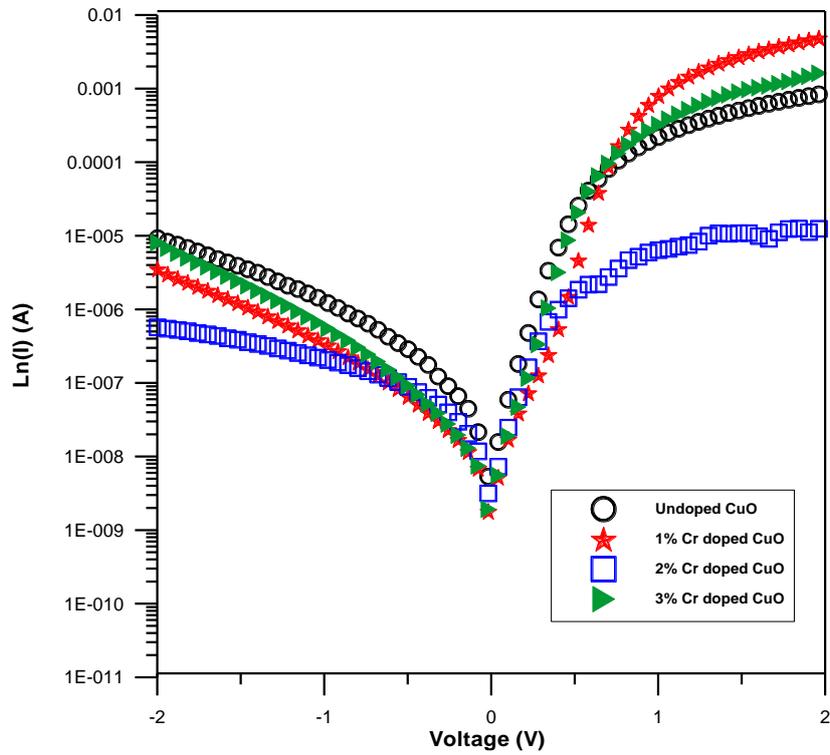


Fig 5. Semi-logarithmic I-V plots of the Cr:CuO diodes in dark.

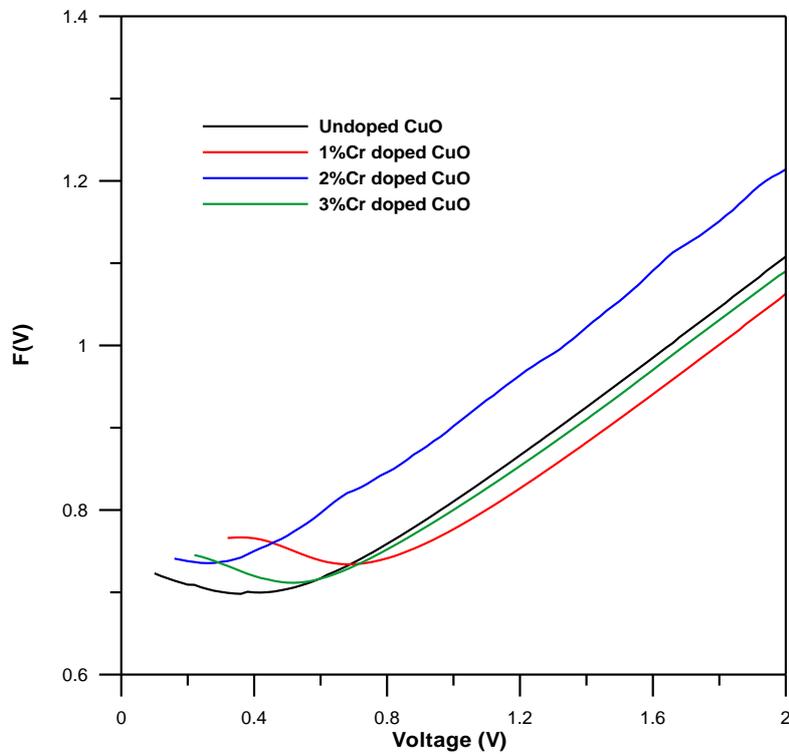
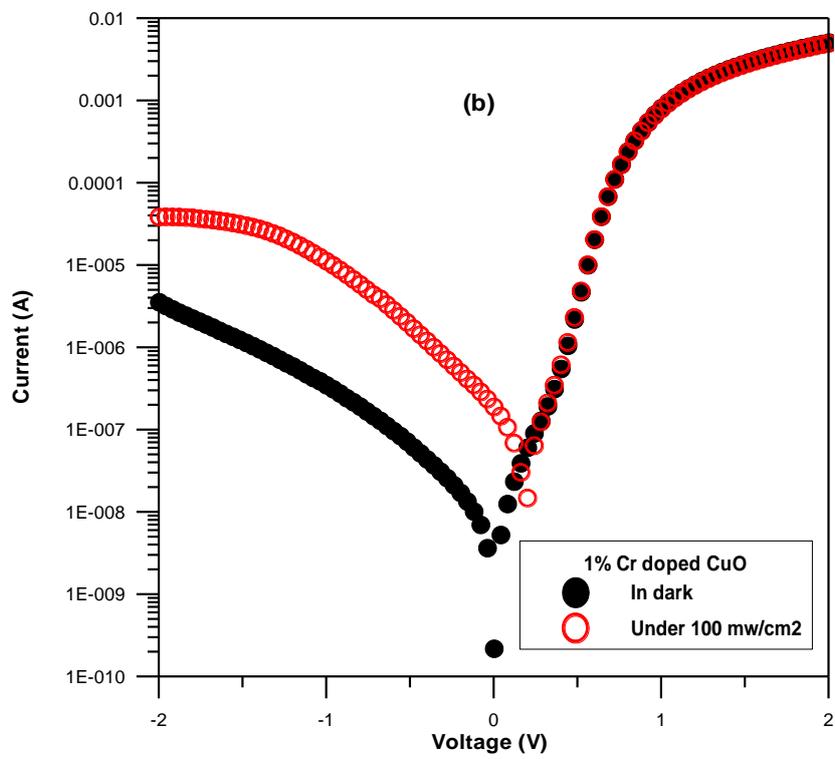
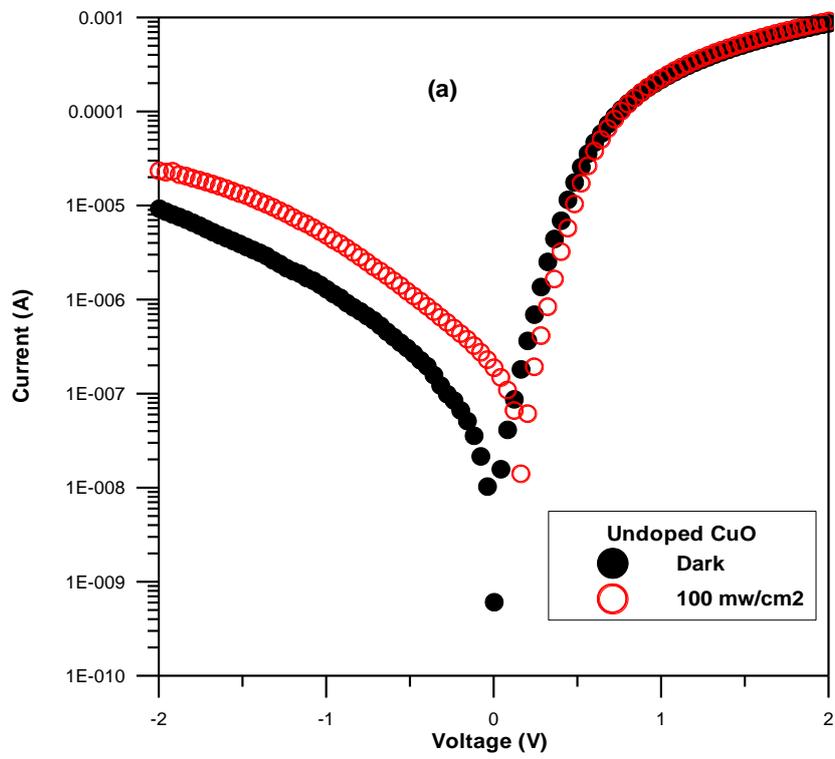


Fig. 6 Norde plots of the CuO/p-Si and Cr:CuO/p-Si heterojunctions.



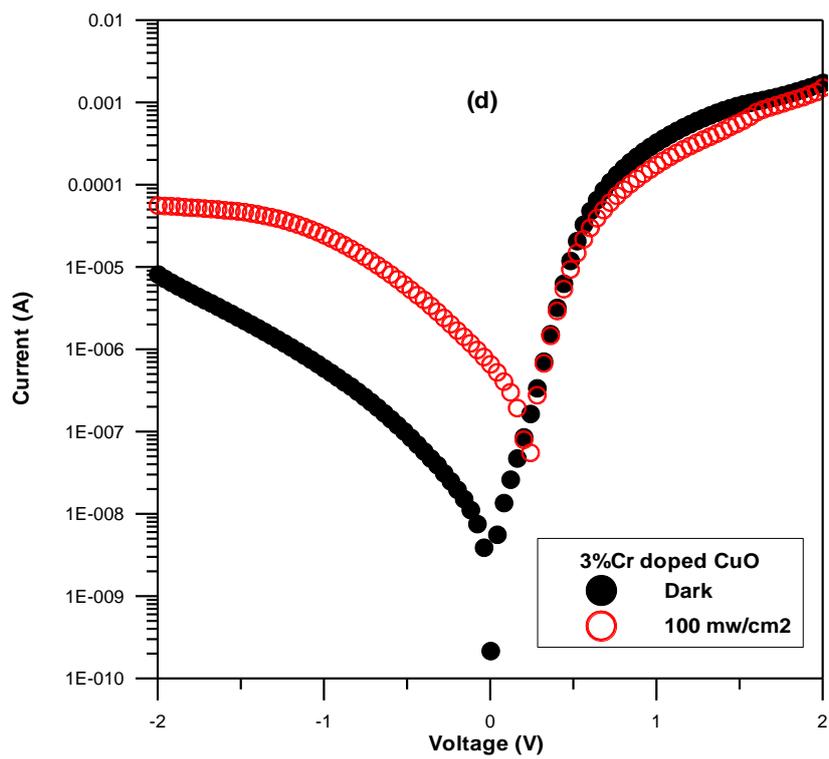
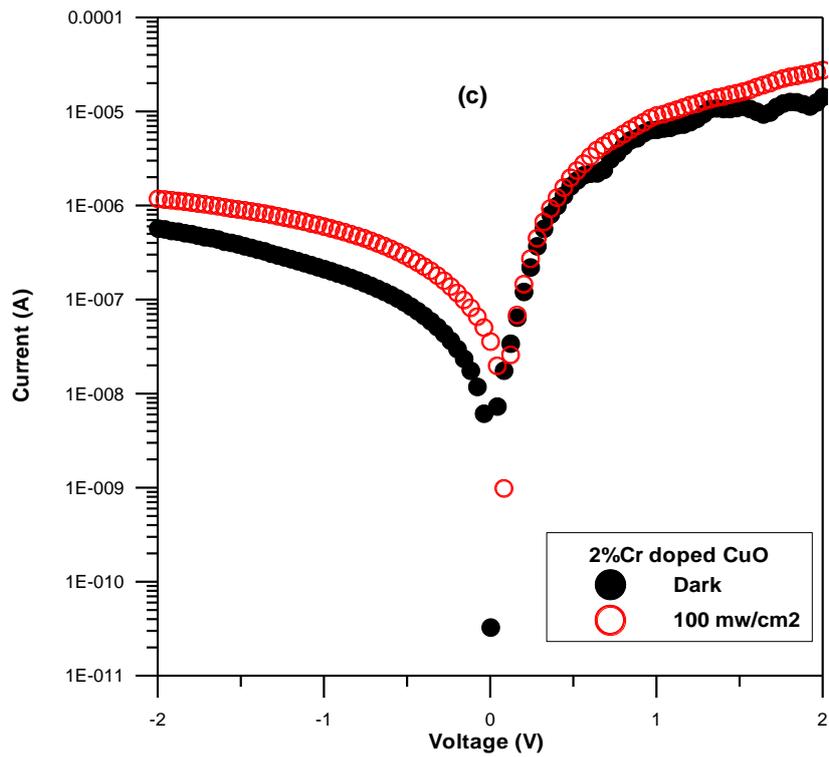


Fig. 7(a-d) In I–V plots of the CuO/p-Si and Cr:CuO/p-Si heterojunctions in the dark and under light (100 mW/cm²).

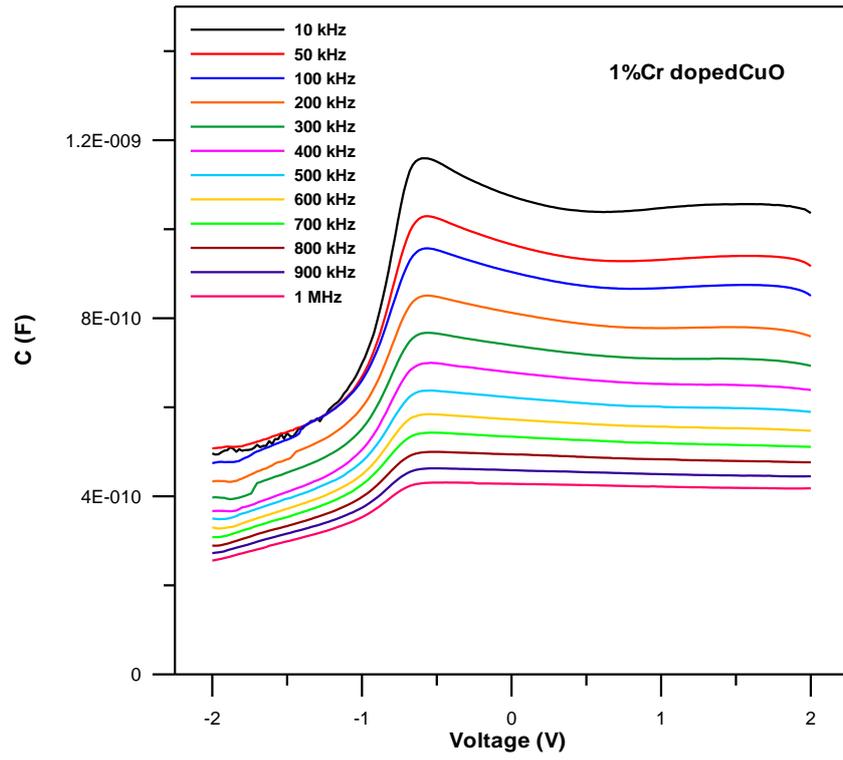


Fig. 8 The C–V measurements of the 1 % Cr:CuO/p-Si heterojunctions at different frequencies (10 kHz-1 Mhz)

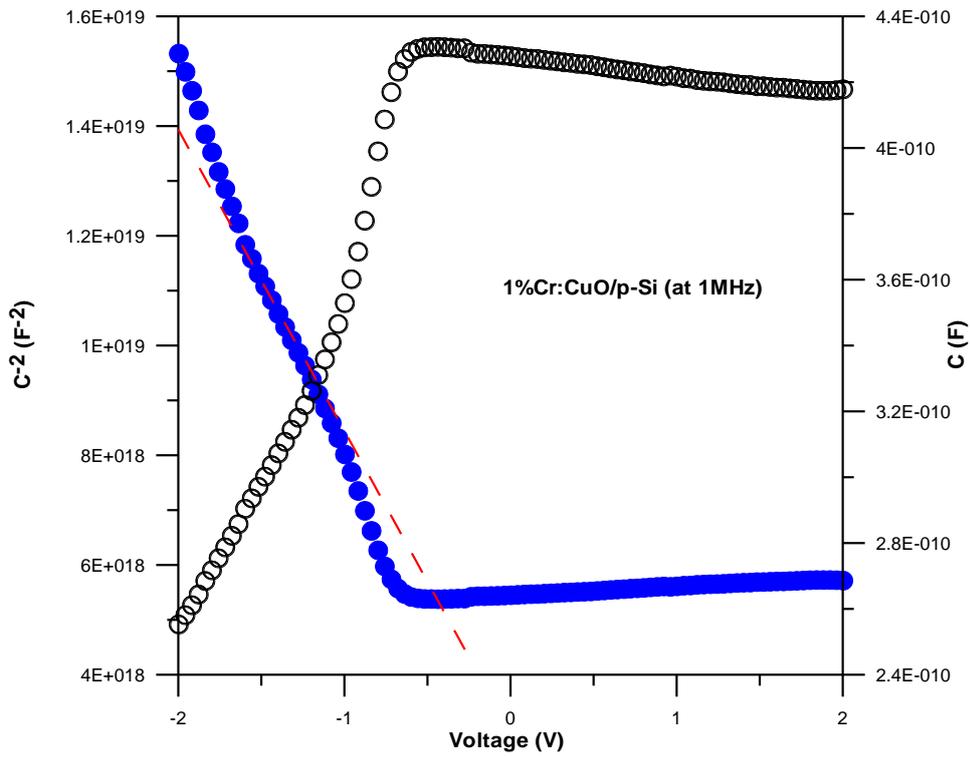


Fig. 9 C^2 –V and C-V plots of 1%Cr:CuO/p-Si heterojunctions at 1 MHz.

Table 1. Crystallite size, dislocation density and strain value of the undoped and Cr-doped CuO films obtained by XRD

	Theta peaks (θ)	Grain size (nm)	d-spacing (Å°) (calculated)	d-spacing (Å°) (standart)	Orientation	Dislocation density ($\times 10^{15} \text{ m}^{-2}$)	strain
Undoped	35.63	27.35	2.52	2.520	(002)	1.34	0.25
	38.79	19.61	2.32	2.319	(111)	2.60	0.32
1 % Cr-doped	35.64	19.25	2.52	2.519	(002)	2.70	0.35
	38.77	26.20	2.32	2.323	(111)	1.46	0.24
2 % Cr-doped	35.64	25.73	2.52	2.521	(002)	1.51	0.26
	38.78	20.10	2.32	2.323	(111)	2.48	0.31
3 % Cr-doped	35.65	16.94	2.52	2.519	(002)	3.49	0.40
	38.77	15.31	2.32	2.323	(111)	4.27	0.41

Table 2. The electrical parameters of Cr:CuO/p-Si diodes with different doping ratios (0%, 1%, 2% and 3%) at 300 K and dark conditions.

Sample	n	ϕ_b (I-V) (eV)	I_0 (A)	RR (for $\pm 1V$)	ϕ_b (Norde) (eV)	R_s (k Ω) (Norde)
0%Cr:CuO/p-Si	2.28	0.73	1.16×10^{-8}	170.7	0.791	4.173
1%Cr:CuO/p-Si	2.17	0.81	4.55×10^{-10}	2335.4	0.734	0.312
2%Cr:CuO/p-Si	2.47	0.75	5.26×10^{-9}	30.4	0.803	36.74
3%Cr:CuO/p-Si	2.14	0.77	2.22×10^{-9}	557.2	0.859	1.064

Table 3 Photoelectrical parameters of CuO/p-Si and Cr:CuO/p-Si diodes under illumination with 100 mW/cm² light

Diode	Photo sensitivity ratio	V_{oc} (mV)	I_{sc} (μA)
CuO/p-Si	3.30	160	0.190
1% Cr doped cuO/p-Si	33.74	180	0.191
2% Cr doped cuO/p-Si	2.06	80	0.036
3% Cr doped cuO/p-Si	27.82	220	0.663