The Effect of Doping Thiourea In CdO Thin Films For Electronic Applications

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The effect of doping Thiourea in CdO thin films for electronic applications

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Abstract

Cadmium oxide (CdO) and Thiourea (Th) doped CdO thin films were deposited on soda lime glass (SLG) and crystalline p-type Si (100) substrates for various Th doping concentrations (0.3, 0.5, 0.7 at.%) using spin coating method. Some structural parameters such as the crystallite size, lattice constant, dislocation density (δ) and strain in the films were obtained from XRD analysis in which the polycrystalline structure with cubic nature and (111) prefential orientation was confirmed. CdO thin film has not shown any change in crystal phase after Th doping. The optical study emerged that the Th doping caused important changes in the transmittance, absorbance and reflectance spectra. A maximum optical transmittance (above 80%) have been obtained for 0.3% Th doped CdO thin films. Th doped CdO/p-Si heterojunctions exhibited low rectifying character and were not found to be the light sensitive.

Keywords: CdO, Thiourea doping, heterojunction

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1. Introduction

Semiconducting nanostructures are of great importance for device technology due to unique optical and electrical properties. The efforts have been made for the development of semiconductors for years. Compound semiconductors that are made from two or more elements have widespread applications. Transparent conducting oxides (TCOs) are an example of compound semiconductors [1-3]. TCOs have attracted a great attention of scientists in optoelectronic applications such as solar cells, phototransistors, flat panel field and manufacturing of gas-sensing.

CdO films are characterized by transparency in near-infrared (NIR) spectral analysis [4-6]. CdO shows n-type semiconductor property, which might be due to oxygen (O) vacancies (V\textsubscript{O}) and Cd interstitials (Cd\textsubscript{i}). CdO exhibits some features as the moderate indirect (1.98 eV) band gap, low resistivity of 10\textsuperscript{-2}–10\textsuperscript{-3} Ω cm, relatively high electrical conductivity (10\textsuperscript{2}–10\textsuperscript{3} S/cm) and rock salt crystal structure. [7]. This material stands out with synthesis methods as sol–gel–spin coating [8], successive ionic layer adsorption and reaction (SILAR) [9], spray pyrolysis [10], vacuum evaporation [11], radio frequency magnetron sputtering [12], chemical bath deposition [13]. Sol-gel method suggests some attractive features, such as low cost equipment, easy control of growth and amenability to large area coverage. Relatively small band gap of CdO is one of its disadvantages for the photovoltaic applications. CdO acts like a degenerate semiconductor (close to metal) at high level of doping. The absorption edge can be shifted by free carriers in the conduction band (Burstein–Moss effect) [14,15]. Ganesh et al. [16] prepared Nitrogen (N) doped (1-20%) cadmium oxide thin films on the glass substrates in their work using sol-gel spin coating method. They obtained the optical direct and indirect band gaps varying with the doping concentration in the range of 3.92-3.98 eV and 3.24-3.49 eV, respectively. In addition, several research groups reported that increasing doping concentrations decreased the band gap. Kabir et al. [17] carried out a work on strontium (Sr)
doped cadmium oxide (CdO) thin films by using spray pyrolysis technique. It is seen that the band gap of CdO decreases from 2.67 to 2.49 eV, as Sr quantity in CdO increases (1%, 2%, 3% to 4%).

Generally, there are studies in which single or co-doping of elements to TCOs are made in literature. But, Cho et al. [18] reported the synthesis of ZnO nanostructures by organosulfur compound thiourea (SC(NH₂)₂) with sulfur (S). Scanning electron microscopy (SEM) images show that the shape of the nanostructure changes with the concentration of thiourea. Density functional theory (DFT) suggests that sulfur atoms prefer to be found at the hexagonal vertices of ZnO, leading to a change in charge distribution. From the photoluminescence (PL) spectra, the emission peak shows a slight blue-shift with increasing the concentration of thiourea, visible light emission where there is a concept of interest in visible light emitting device applications. Blue-shifted or enhancement visible light emission is ascribed to the change of S doping in ZnO nanostructures [19,20].

Recently, intense attention has been paid to understanding TCO-charge transport. Metallic oxide films might show rectifying property while brought into contact with a semiconductor. Therefore, CdO thin films as an electron transport layer are used at p–n heterojunctions, depositing on p-type silicon (Si) semiconductor. Research should include the mechanisms that are needed to explain the charge transport for construction of optoelectronic nanotechnology. CdO thin films grown on p-Si substrates were studied, forming p–n heterojunctions [21-23].

To the best of our knowledge, no an experimental investigation has been performed on Thiourea (Th) doped cadmium oxide (CdO) thin films.

In the present work, we report the growth of Th doped CdO on Si and glass substrates by sol-gel method. Th doped CdO thin film microstructure, crystal structure, optical and electrical properties are examined in detail with increasing doping level.
2. Experimental Details

To prepare CdO thin films, 2-methoxyethanol (C$_3$H$_8$O$_2$), monoethanolamine (MEA) (C$_2$H$_7$NO), Cadmium acetate dihydrate (CAD) (Cd(CH$_3$COO)$_2$.2H$_2$O) were used. The materials (precursor, solvent and stabilizer) were adjusted so that the molarity of the solution was 0.5 molar. CAD was dissolved in 2-methoxyethanol (C$_3$H$_8$O$_2$). The explanation of all the processing operations is presented in our previous work [24]. Molecular Formula of Thiourea is given as CH$_4$N$_2$S or H$_2$NCSNH$_2$. Fig. 1 shows a schematic representation of Thiourea. In fact, by adding Thiourea (Th), sulfur is added to CdO. CdO thin films with different proportions of Thiourea (Th$_{0.03}$Cd$_{0.99}$O, Th$_{0.05}$Cd$_{0.95}$O, Th$_{0.07}$Cd$_{0.93}$) were prepared. The solutions were coated on the ultrasonically cleaned soda–lime glass substrates with spin coating method. The spin speed was adjusted at 1500 rpm at a fixed spinning time of 60 s. Three samples obtained were thermally annealed at 1h in furnace, when the temperature reached 400 °C. p-Si (100) substrate was used to obtain the heterojunction. Chemically cleaned samples were exposed to pure nitrogen gas. The front face of p-type Si substrates was coated with Th doped CdO and the annealing process was applied. Coating/annealing parameters of soda–lime glass substrates were continued and then, to obtain Al/Th:CdO/p-Si device structures, circular shaped Al contact was made on Th doped CdO thin films. The atomic force microscopy (AFM) was used to measure the surface morphology of the CdO thin films. Crystallographic data of the CdO thin films are routinely characterized using x-ray diffraction (XRD, Rigaku) with Cu Kα radiation. The transmittance, absorbance and reflectance data were obtained by the aid of UV-vis spectrophotometer (Shimadzu UV-VISNIR 3600). The current-tension (I-V) relationship for Th:CdO/p-Si heterojunctions was supplied by a Keithley 2400 voltage source. Raman spectroscopy was evaluated to obtain the information about molecular vibrations.
3. Results and Discussion

3.1. Morphological, Structural and Optical Characteristics

Fig. 2a-c shows the AFM images of CdO thin films; 40x40 µm, 5x5 µm and three-dimensional (3D) for 0.3%, 0.5% and 0.7%, respectively. It appears that nanoclusters are formed in all three of the samples, but they do not show a homogeneous distribution on the surface. The surface distribution observed along the red line is also seen in the images of 40x40 µm. The roughness of the surface is in the order of nm for 0.5% Th doped CdO samples, while for CdO with 0.3% and 0.7% Th doping it is in the order of microns. Also, the Figs show statistics of the surfaces such as roughness average of the surface \(R_a\), peak to valley roughness \(R_{pv}\), root mean square roughness \(R_q\) and average maximum height \(R_z\). Moreover, Skewness \(R_{sk}\) and Kurtosis \(R_{ku}\) are related to the asymmetry and the peakedness according to the the mean line at the profile, respectively. The effect of doping Th is seen along the parameters of the surface morphology.

Fig. 3a-c shows the scanning electron microscope (SEM) images of CdO thin films at 17000 magnification. The images obtained with SEM show that each sample offers a different surface map. Energy-dispersive X-ray spectroscopy (EDX) data is also provided. The results include a large number of elements. The presence of unexpected elements other than the Th doped CdO composite structure is probably due to the glass used as substrate. Thiourea has the formula SC(NH₂)₂. It is organosulfur compound and contains sulfur. EDX results confirm the presence of the element sulfur (S). While sulfur content is not reported in CdO with 0.3% Th doping, S ratio is specified in CdO thin films with 0.5% and 0.7% Th doping. It is also noteworthy that the increasing Th ratio is parallel to the S ratio.

Fig. 4 shows X-ray diffraction (XRD) pattern of Th:CdO thin films with various Th dopant concentrations (0.3%, 0.5%, 0.7%) deposited on the glass substrates. The preferred plane densities of the films are varied due to the increasing thiourea concentration. CdO thin
films show (111) and (200) preferential orientation in the thin film form, which has a cubic crystal structure. Peaks is in good agreement with the card number of Joint Committee on Powder Diffraction Standard (JCPDS) JCPDS: 05-0640. The CdO thin film has not shown any change in crystal phase after Th doping. Other crystalline orientations such as (220) and (311) have high intensity and well matched compared to literature [25,26]. The shifts change in the diffraction peaks, when Th is increased into the CdO lattice structure. Peaks appear to be more dominant at Bragg’s angle (2θ) of 33° to 38°. These are major diffraction peaks at various diffraction angles. The structure is indexed according to the face centred cubic (fcc) arrangement. Due to the addition, no phases (peaks) are revealed in the 0.5 and 0.7 wt% of Th doping. No structural deformation happens and all samples keep crystalline solid state. The peak of the crystalline orientation such as (311) loses dominance in 0.7% Th doped CdO thin film. It can be noticed that surface texture (orientation) characteristic depends on doping elements, including the stress, elongation and elasticity.

The texture coefficient \(TC_{(hkl)}\) value represents the growth surface and is given as follows [27],

\[
TC_{(hkl)} = \frac{I_{(hkl)} / I_{0(hkl)}}{\sum_n N^{-1} I_{(hkl)} / I_{0(hkl)}}
\]  

(1)

where \(N\) represents the diffraction peak number, \(I(hkl)\) is the observed relative intensity of the plane \((hkl)\), \(I_0(hkl)\) is the standard intensity. The (111) and (200) preferential plane growths show dominant peak intensity as in earlier reports [28,29]. Table I contains the texture coefficients for CdO films, depending on the amount of doping Th. Since CdO thin films include randomly oriented grains, the texture coefficient is important. The texture coefficient values close to 1 indicate the presence of randomly oriented grains [30]. It is observed that the
Th doping changes partially the texture coefficient values. It is seen that the textured CdO surface is especially dominant along (100) plane. The surface texture of the thin films reflects the mismatch of grain boundary. This is associated with porosity and plays an important role in the gas sensing mechanism [31].

The full width at half maximum (FWHM) is used as a tool to evaluate the peak intensity. The values of FWHM is given in Table I as a function of Th doping. FWHM gets smaller values for the (111) and (200) planes, which are the dominant peaks, increasing with doping concentration. The Scherrer equation is given to find the crystal size ($D$) of the particles [32]:

$$D = \frac{0.94\lambda}{\beta_{FWHM} \cos \theta}$$  \hspace{1cm} (2)

Where. 0.94 correlation coefficient is used. $\theta$, $\lambda$ represent the Bragg angle and the incident x-ray wavelength (1.5406 Å), respectively. Table II shows that the nm-scaled crystal size for the crystal plane (200) decreases with increasing Th concentration. The observed pattern is contrary to the previous report on Sr-doped CdO [17]. The decreasing nature of the XRD peaks with Th is due to the decreasing crystallite size [33]. The change in crystal boundaries also has an effect on crystal size. In addition, dislocation density ($\delta$) and strain ($\varepsilon$) (considering the crystallite size along c-axis) are some of other structural parameters, given as [34].

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

$$\varepsilon = \frac{\beta \cos \theta}{4}$$  \hspace{1cm} (4)
The values are given for the crystal plane (200) in Table II. The dislocation density (δ) is in order of $10^{14}$ lines/m$^2$ while it is obtained in $10^{15}$ lines/m$^2$ value for spray pyrolized strontium (Sr) doped cadmium oxide (SCO) thin films in Ref [17]. Both the δ and ε values increase with increasing Th doping concentration. Small dislocation density is associated with the crystalline quality or high degree of crystallinity of the film.

The lattice constant (a) for cubic structured CdO is given as [35]:

$$\frac{1}{d^2} = \left(\frac{h^2 + k^2 + l^2}{a^2}\right)$$  \hspace{1cm} (5)

The lattice constant values of samples annealed 400 °C for (200) preferential peak are give in Table II. The values obtained were found very close to the standard lattice constant value of CdO (4.69 Å). It can also be deduced from the experimental results that the Th contribution and its varying amount have an effect on the lattice constant.

Fig. 5a shows the optical transmittance measurements for 0.3%, 0.5% and 0.7% Th doped CdO thin films in the wavelength range of 280–800 nm. While the transmittance increases at about 300 nm, it shows a fluctuating trend, increasing again at around 480 nm with increasing wavelength. It does not change significantly in longer wavelengths. It is seen that the transmittance of 0.3% Th doped CdO thin films is lowest in the UV region up to the visible region limit and the transmittance increases with increasing Th contribution. However, 0.3% Th CdO thin films show the highest transmittance at long wavelengths with a value above 80%. There are reports in the literature that the transmittance of CdO thin films decreases with increasing amount of additive element. [36,37]. The effect of S$^{2-}$ ions, which can replace the oxygen vacancies or Cd$^{2+}$ ions, can be considered. It is relevant to state that transmittance reduction due to increased doping is not related to scattering.
Fig. 5b shows the absorption spectra of Th:CdO thin films. It is seen that the absorbance edge decreases as doping concentration increases. The spectrum shows two different absorption discontinuities (absorption edge) at about 300 nm and the other at about 500 nm. While the absorbance is almost constant in the spectrum of visible region, the increase in the UV-region that starts with a bump turns into a peak as the wavelength decreases. Similar behavior was also observed in the study examining the optical characteristics of Indium-doped cadmium oxide thin films prepared by Ganesh et al. [33]. Touch technique can be used to obtain the optical band gap ($E_g$) [38]:

$$\alpha h\nu = B_{op} (h\nu - E_g)^n$$

(6)

where $\alpha$ absorption coefficient, $B_{op}$ is a constant coefficient, $n$ is an exponent (index) associated with the character of the optical transition and $h\nu$ is the photon energy. This index follows the allowed direct, forbidden direct, allowed indirect, forbidden indirect transition as $1/2$, $3/2$, 2 and 3, respectively. The value of $n$ is determined as $1/2$ for CdO with direct transition.

Fig. 5c shows $(\alpha h\nu)^2$ vs. $h\nu$. The value of optical band gap is determined using the extrapolation of the straight-line portion, corresponding to an approximate accuracy of 0.05 eV (Table II). The obtained bandgap values were found within the standard range of $E_g$ (CdO) (2.2–2.6 eV) [39,40]. The bandgap of CdO thin film was found to be blue-shifted as Th incorporation level increases (band-gap widening-BGW). This is attributed to Burstein-Moss (BM) band gap widening on varying doping of Th from 0.3% to 0.7% [41,42]. The variation in band gap is due to more O-vacancies resulting from the presence of S content in Th doped CdO nanostructures. Moss–Burstein BGW could be resulted by the variation of carrier concentration. The band gap change is phenomenologically affected by the carrier
concentration. The band gap for a semiconductor consisting of conduction electrons \( (N_{el}) \) is given by the following equation [42]:

\[
E_g = E_{g}^{int} + S_{BGV}N_{el}^{2/3}
\]  

(7)

The \( \Delta E_g^{BM} \) is related to the band-gap widening (BGW) [43].

\[
\Delta E_g^{BM} = S_{BGW}N_{el}^{2/3}
\]  

(8)

\[
S_{BGW} = \left( \frac{n_e^2}{2\gamma m_e} \right)(3\pi^2)^{1/3}
\]  

(9)

Where \( \gamma \) is equal to \( m_{vc}^*/m_e \) as the ratio. \( m_{vc}^* \) the reduced effective mass and \( m_e \) is free-electron mass.

\[
\frac{1}{m_{vc}^*} = \frac{1}{m_v} + \frac{1}{m_c}
\]  

(10)

\( m_c^* \) the conduction band effective mass and \( m_v^* \) the valence-band. \( m_{vc}^* \) is equal to 0.274\( m_e \) [44]. \( E_{g}^{int} \) as the optoelectronic function is the intrinsic bandgap due to the Cd-Cd and e\(^-\) lattice interactions (2.1 eV) [44]. \( S_{BGW} = 1.348 \times 10^{-18} \text{ eV m}^2 \) for CdO [45]. The carrier concentrations for 0.3 and 0.7 wt% of Th doping were estimated to be 1.x\( 10^{20} \) and 2.3x\( 10^{20} \) \( \text{cm}^3 \), respectively. It is seen that the carrier concentration increases as Th incorporation increases.
Fig. 5d shows the reflectance characteristics of Th:CdO thin films with various Th dopant concentrations (0.3%, 0.5%, 0.7%) deposited on the glass substrates. It is seen that the reflectance increases in the visible region as Th doping concentration increases, but, this reverses after about 500 nm and it decreases with increasing Th doping concentration in the IR region.

The exponential edge region is characterized by Urbach-Martienssen rule:

\[ \alpha = \alpha_0 \exp \left( \frac{E}{E_u} \right) \]  

where \( E_u \) and \( \alpha_0 \) are Urbach energy and a constant, respectively. Fig. 6 shows the plots of \( \ln(\alpha) \) vs. photon energy (hv) for CdO thin films with Th (0.3%, 0.5%, 0.7%). The obtained values are given in Table II. The absorption is due to localized-to-extended-states transitions in the exponential tail. Urbach energy decreases as Th-content in CdO thin films increases, and then it increases.

Fig. 7a shows the variation of absorption index or extinction coefficient (\( k \)) vs wavelength (\( \lambda \)) for Th doped CdO thin films. The absorption index is given as following relation:

\[ k = \frac{\alpha \lambda}{4\pi} \]  

As it is seen, the absorption index (extinction coefficient) shows a similar character to the absorption plot. The absorption index also changes depending on Th doping concentration. Fig. 7b shows the plots of refractive index (\( n \)) vs wavelength (\( \lambda \)) for Th doped CdO thin films. The exciton coefficient (\( k \)) constitutes the imaginary part of the complex refractive index (\( n \)): 
\[ n^2(\lambda) = n(\lambda) + ik(\lambda) \quad \text{(13)} \]

\[ R = \frac{(n-1)^2 + k^2}{(n+1)^2 + k^2} \quad \text{(14)} \]

\[ n = \left( \frac{1 + R}{1 - R} \right) + \sqrt{\frac{4R}{(1-R)^2}} - k^2 \quad \text{(15)} \]

The refractive index also behaves like reflectance curves and the characteristics change depending on the concentration. Moreover, the refractive index first increases and then decreases with increasing wavelength. In particular, the region of reduction is known as normal dispersion and the region of increase as abnormal dispersion region [46]. Refractive index values of 1.90, 1.74 and 1.60 (0.3, 0.5, 0.7 at.%) at 600 nm are smaller than the values obtained for In:CdO samples [47]. The changing polarization after reflection and the change in thickness of the doped films have an effect on the refractive index.

The dispersion is given considering the single oscillator model [48]:

\[ n^2 - 1 = \frac{E_d E_0}{E_0^2 - (h\nu)^2} \quad \text{(16)} \]

where \(E_d\) is the dispersion energy due to oscillator and represents to the band-to-band electronic transitions, \(E_0\) is the oscillator's energy. The variation of \(1/(n^2-1)\) vs. \((h\nu)^2\) for the Th:CdO thin films is given in Fig. 8. The values of \(E_0\) and \(E_d\) are determined from the region of straight line. As seen in Table II, the dispersion energy and excitation values of the CdO thin films change with the doping of Th, but, do not show a certain trend. A similar work was
made for Boron doped CdO thin films. It was found a relation for the dispersion energy with doping of Boron [49].

Also, the static refractive index \( n_0 \) can be found as the \( E_d \) to \( E_0 \) ratio \( (E_d/E_0) \) and is given as follows:

\[
n_0 = \sqrt{1 + \frac{E_d}{E_0}}
\]  

(17)

The values of static refractive index are were found to be 1.63 and 1.54 and 1.46 (0.3, 0.5, 0.7 at.%), respectively. Also, the static dielectric constant can be determined by expressing \( \varepsilon_s = n^2(0) \).

Two components, surface and bulk energy change through the dielectric as the total power loss. Dielectric materials include a dissipation factor (tan\( \delta \)), which is characterized by the real \( (\varepsilon_1) \) and imaginary \( (\varepsilon_2) \) parts dependent complex dielectric constant \( (\varepsilon) \) [50]:

\[
\tan \delta = \frac{\varepsilon_2}{\varepsilon_1}
\]  

(18)

Dielectric with low dissipation factor is required to minimize power losses for high energy efficiency. Fig. 9 shows the variation of tan\( \delta \) vs. \( \lambda \). The dissipation factor decreases as the doping Th increases.

Bulk and surface energy loss functions (BELF and SELF) are derived by [51]:

\[
-\text{Im} \left[ \frac{1}{\varepsilon} \right] = \frac{\varepsilon_2}{\varepsilon_1^2 + \varepsilon_2^2}
\]  

(19)
\[
- \text{Im}\left[\frac{1}{\varepsilon^* + 1}\right] = \frac{\varepsilon_2}{(\varepsilon_1 + 1)^2 + \varepsilon_2^2}
\] 

Fig. 10a,b shows the variation of the BELF and SELF vs. \(h\nu\). The probability of electrons to be excited in bulk and surface is characterized in REELS analysis. The bulk energy loss takes smaller values than the surface energy loss. It is seen that the energy losses decrease with increasing Th concentration.

Analysis of the vibration modes is associated with transport properties and phase orientation. Fig. 11 shows the Raman spectra of CdO thin films. Data with backscattering geometry includes the incidence of wavelength 532 nm. Raman spectroscopy was activated into the range of 100 to 4000 wave number. Location and shape of peaks are almost unchanged for three samples, while peak maxima increase with increasing Th. Weak peak is observed at 385 cm\(^{-1}\). The major Raman peaks correspond to transverse optical (TO) and longitudinal optical (LO) modes of CdO within the range of 291 to 1000 wave number [51,52]. More intense band is presented at \(\sim 1381\) cm\(^{-1}\). Moreover, the peaks are centered at 1850 cm\(^{-1}\) and 3269 cm\(^{-1}\), respectively. Peaks appear to be centered at larger wavelengths compared to the literature [53-55]. Additional peaks are might be related to the vibration modes, which can be attributed to the internal stress due to Th and surface influence.

### 3.2. Current-Voltage (I–V) Characteristics of Th:CdO/p-Si Heterojunction Diodes

Fig. 12a shows the schematic configuration of Th:CdO/p-Si heterojunction. A voltage of \(\pm 2\) V was applied to the heterojunction structure. Fig. 12b shows the current-voltage (I-V) characteristics obtained as a result of the applied voltage. As it is seen, the heterojunction exhibits rectifying property, including a low rectification ratio in dark condition. The rectifying nature increases with increasing Th content in CdO. It is thought that there is a barrier between CdO and p-Si in junction. CdO is considered to have the appropriate Fermi
level with p-Si. It introduces a relevant layer for charge carrier transport. No a saturation is observed in the reverse saturation current. Th: CdO/p-Si diodes do not exhibit a photovoltaic response to the illumination.

The conduction mechanism of the heterojunction is described by thermionic emission theory (TET) [56]:

\[
J = J_0 \exp \left( \frac{q(V - JR_s A)}{nkT} \right) \left[ 1 - \exp \left( - \frac{q(V - JR_s A)}{kT} \right) \right]
\]

(21)

where, \( A, A^*, k, q, n, T \) and \( R_s \) have well-recognized meanings as characterized in our previous work [57]. \( V - JR_s A \) is electrical potential loss across the heterojunction (voltage drop). \( J_0 \) is the saturation current density and given by below equation:

\[
J_0 = AT^2 \exp \left( - \frac{q\phi_b}{kT} \right)
\]

(22)

The values of \( I_o \) for Th doped CdO/p-Si heterojunction diodes are in order of \( 10^{-6} \) A (Table III), which is initially decreased, then increased with increasing Th doping. The saturation current flow of the diode seems to vary by Th doping. The barrier height (\( \phi_b \), BH) and ideality factor (\( n \)) are expressed by below equations:

\[
\phi_b = \frac{kT}{q} \ln \left( \frac{AT^2}{J_0} \right)
\]

(23)
\[ n = \frac{q}{kT} \left[ \frac{dV}{d \ln(J)} \right] \]  \hspace{1cm} (24)

The \( \phi_b \) and \( n \) are found from the intercept and the slope of the straight-line region of the log \( I \) vs. \( V \) plot, respectively. The values of \( \phi_b \) were determined to be 0.64 eV, 0.63 eV and 0.64 eV for Si diodes based on Th:CdO thin films with Th doping (0.3\%, 0.5\%, 0.7\%), respectively, in dark conditions. Also, it is seen that the ideality factor increases as Th doping increases. The ideal factor (>1) is attributed to the presence of other current transport mechanisms [58]. The determined values were obtained from a specific (linear) region of the forward bias \( I-V \) curves. However, Norde proposed a method that allows to find diode parameters from data that takes into account whole forward \( I-V \) data [59]:

\[ F(V) = \frac{V_0}{\gamma} - \frac{kT}{q} \left( \frac{I(V)}{AA'T^2} \right) \]  \hspace{1cm} (25)

where \( \gamma \) is a dimensionless quantity. The Norde function, which allows to find the \( \phi_b \) and series resistance \( (R_s) \) is rewritten as follows:

\[ \Phi_b = F(V_0) + \frac{V_0}{\gamma} - \frac{kT}{q} \]  \hspace{1cm} (26)

\[ R_s = \frac{kT(\gamma - n)}{ql_0} \]  \hspace{1cm} (27)
Fig. 13 shows the F(V) vs. V curves. Results are determined by using the points corresponding to the minimum of plot and given in Table III. The $R_s$ value is high for Al/p-Si heterojunction with 0.7% Th:CdO thin film layer.

In the forward bias region of Fig. 14a-c, while the capacitance do not show any variation, it decreases with increasing frequency in the reverse bias region. This is attributed to the presence of interfacial states that cannot follow a.c. (alternating current) signal. It seems that the doping Th partially affects the capacitance values.

5. Conclusions

CdO thin films with different Th-doping contents could be obtained by a simple and cost-effective sol-gel spin coating method on to glass and p-Si (100) substrates. The AFM results show that the surface is composed of nano-clusters with the roughness in the order of nm for 0.5% Th doped CdO sample. SEM (EDX) results confirm the presence of the element sulfur (S) in the thiourea and the Cd/O in the CdO. While XRD results correspond to dominant preferential orientation with peaks (111) and (200), the doping Th has no effect on the crystal character, affecting some structural parameters. The increasing Th contribution increases the optical band gap. Th:CdO/p-Si heterojunction exhibits rectifying property, including a low rectification ratio in dark condition. However, it is seen that Th:CdO/p-Si diodes do not show any response to the illumination. All devices show relative capacitance changing depending on the voltage and frequency in the order of nF, which is partially affected by the Th contribution.

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Authors’ Contribution All authors contributed to the study conception and design.

Data Availability The above-mentioned authors have all the relevant data associated with this research work and will be dedicated to share that, if they will be asked to do so in future.

Compliance with Ethical Standard All the Ethical Standards have been seen by the authors and will supposed to follow them in future as well.

Conflict of Interests The authors declare that they have ‘no known conflict of interests or personal relationships’ that could have appeared to influence the work reported in this paper.

Consent to Participate & for Publication Since, the concerned research paper is based for the ‘non-life science journal’. So, ‘Not Applicable’ here. However, the authors have gone through all policies of journal and consent the authorities for further processing.

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Table I Some structural parameters for Th doped CdO thin films

| Th at.% | 2θ (°) | FWHM | hkl | I₀ | Iₜhkl | TCₜhkl |
|---------|--------|------|-----|----|-------|--------|
| 0.3     |        |      |     |    |       |        |
| 33.35   | 0.270  | 111  | 20.0 | 21.71 | 3.350 |
| 38.18   | 0.336  | 200  | 10.0 | 12.32 | 2.960 |
| 66.20   | 0.770  | 311  | 10.0 | 8.65  | 1.720 |
| 0.5     |        |      |     |    |       |        |
| 33.25   | 0.285  | 111  | 20.0 | 35.75 | 3.560 |
| 38.28   | 0.360  | 200  | 10.0 | 16.47 | 2.700 |
| 55.55   | 0.790  | 220  | 20.0 | 8.39  | 1.890 |
| 0.7     |        |      |     |    |       |        |
| 33.28   | 0.292  | 111  | 20.0 | 28.26 | 3.656 |
| 38.22   | 0.388  | 200  | 10.0 | 14.29 | 2.896 |
| 55.38   | 0.853  | 220  | 20.0 | 8.61  | 1.830 |

Table II Some optical and structural parameters for Th doped CdO thin films

| CdO      | Th (0.3 at.%) | Th (0.5 at.%) | Th (0.7 at.%) |
|----------|---------------|---------------|---------------|
| Eₑ (meV) | 346           | 243           | 356           |
| Eᵧ (eV)  | 2.41          | 2.53          | 2.61          |
| dₜhkl (200) | 2.3510    | 2.3560        | 2.3440        |
| Crystallite size (D) (nm) | 44.35 | 41.96 | 38.61 |
| Lattice constant, a (Å) | 4.702 | 4.712 | 4.688 |
| Dislocation density (δ) x10¹⁴ lines/m² | 5.082 | 5.677 | 6.708 |
| Strain (ε) x10⁻² | 8.158 | 8.623 | 9.373 |
| Eₛ (eV) | 2.721         | 2.799         | 2.962         |
| Eᵧ (eV) | 4.575         | 3.854         | 3.399         |
**Table III** Some diode parameters of the heterojunctions

|                | CdO       | Th (0.3 at.%) | Th (0.5 at.%) | Th (0.7 at.%) |
|----------------|-----------|---------------|---------------|---------------|
| $\Phi$ (eV)    | 0.64      | 0.63          | 0.64          |               |
| $I$ - $V$      |           |               |               |               |
| $n$            | 1.43      | 1.44          | 1.45          |               |
| $\Phi$ (eV)    | 0.58      | 0.58          | 0.60          |               |
| Norde          |           |               |               |               |
| $R_s$ (ohm)    | 289.54    | 252.15        | 433.37        |               |
| $I_o$ (A)$\times 10^6$ | 1.30    | 1.75          | 1.05          |               |
**Figure Caption**

**Fig. 1.** The schematic representation of Thiourea.

**Fig. 2(a-c).** AFM images of Th:CdO thin films at 40x40 µm, 5x5 µm and three-dimensional (3D): (a) 0.3%, (b) 0.5%, (c) 0.7%.

**Fig. 3(a-c).** SEM images and EDX results of Th:CdO thin films: (a) 0.3%, (b) 0.5%, (c) 0.7%.

**Fig. 4.** XRD spectra of Th:CdO thin films deposited on glass substrates.

**Fig. 5(a-d).** (a) Transmittance spectra of Th:CdO thin films, (b) absorption spectra of Th:CdO thin films, (c) Plots of \((ahv)^2\) vs. \(hv\) (d) Reflectance spectra of Th:CdO thin films.

**Fig. 6.** Dependence of \(\log \alpha\) on the photon energy \(h\nu\) for the films.

**Fig. 7a,b.** Plots of (a) extinction coefficient (b) the refractive index for Th:CdO thin films.

**Fig. 8.** The variation of \(1/(n^2-1)\) vs. \(\lambda\) for Th:CdO thin films.

**Fig. 9.** Dependence of dissipation factor (\(\tan \delta\)) on the wavelength.

**Fig. 10a,b.** (a) Volume energy loss and (b) surface energy loss as functions of \(h\nu\) for the films.

**Fig. 11.** Raman spectra of Th:CdO thin films.

**Fig. 12a,b.** (a) The schematic configuration of Th:CdO/p-Si heterojuction, (b) the \(I-V\) characteristics of Th:CdO/p-Si heterojunctions.

**Fig. 13.** The plots of \(F(V)\) vs. \(V\) for Th:CdO/p-Si heterojunctions.

**Fig. 14.** The \(C-V\) characteristics of Th:CdO/p-Si heterojunctions.
Figures:

Fig. 1.
Fig. 2(a-c).
Fig. 3(a-c).
Fig. 4.
Fig. 5a-d.
Fig. 6.

Fig. 7a,b.
Fig. 8.

Fig. 9.
Fig. 10a,b.

Fig. 11.
Fig. 12a,b.

Fig. 13.
Fig. 14a-c.