

Comparative Structural, Optical, and Photovoltaic Characteristics of Ag and Sn-Doped Nanocrystalline CdS Thin Films Deposited by Vacuum Evaporation on FTO Substrates

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Abstract Silver (Ag, 1%) and tin (Sn, 1%) doped nanocrystalline cadmium sulfide (CdS) thin films were deposited on fluorine-doped tin oxide (FTO) glass substrates using vacuum evaporation aided by inert gas condensation (IGC) at room temperature (300 K). A hexagonal wurtzite phase with preferential orientation along the (002) plane and high crystalline purity was established by X-ray diffraction and Raman spectroscopy. Optical transmission investigations exhibited a red shift in the band gap to 2.23 eV (Ag) and 2.25 eV (Sn) from bulk CdS (2.42 eV) due to dopant-induced defect states resulting in band tailing. Electrical characterisation exhibited Schottky-type diode behaviour with increased rectification ratio and decreased series resistance for Ag-doped films. Ag-doped and Sn-doped devices illustrated better short-circuit current and fill factor from photovoltaic analysis, and double the sensitivity with ultrafast rise time of photoresponse (rise time $\approx 1.74 \mu\text{s}$) in Sn-doped films. The results demonstrate dopant-dependent optimisation of structural and optoelectronic properties in nc-CdS films and suggest Ag doping for photodetectors with high sensitivity and Sn doping for ultrafast optoelectronic switching devices.

Keywords: nanocrystalline, vacuum evaporation, Schottky-type diode, photodetector, optoelectronic switching devices

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1. Introduction

Photodetectors and photovoltaic devices are the most rapidly evolving fields in contemporary optoelectronics [1]. While photovoltaics form the core of renewable energy technologies, where maximising efficiency, stability, and low-cost fabrication are the primary challenges, high-speed photodetectors are central to optical communication, imaging, and real-time sensing applications that require ultrafast response and robust performance [2]. The creation of multifunctional materials that can tackle the needs of both energy harvesting and fast photonic detection is thus of extreme scientific and technological relevance [3].

Cadmium sulfide (CdS) is a direct band gap semiconductor (2.42 eV) and finds extensive optoelectronic applications in photodetectors, solar cells, and light sensors owing to its desirable optical and electrical characteristics [4]. Nanocrystalline CdS (nc-CdS) thin films have high surface area, band structure that can be engineered, and defect transport, which makes them promising candidate materials for future photonic devices.

Modification of CdS by doping with metal ions is a general approach used to engineer its properties for optimised device performance.

Silver (Ag) and tin (Sn) are significant dopants because their different ionic radii and valence states alter the CdS lattice differently via defect engineering and strain modulation [5,6]. Ag doping usually enhances photoconductivity by minimising recombination centres, whereas Sn doping can increase carrier scattering and alter band structure. Nevertheless, few comparative studies exist on how their influence affects nanocrystalline CdS films deposited under the same conditions.

The structural, optical, and photovoltaic characteristics of 1% Ag- and Sn-doped nc-CdS thin films grown on FTO substrates using vacuum evaporation coupled with inert gas condensation (IGC) are investigated in this study. Careful characterisation by X-ray diffraction (XRD), Raman spectroscopy, optical transmittance, and electrical measurements clarifies the influence of the dopant selection on device-related properties, offering insights for the optimisation of CdS-based optoelectronic devices.

2. Experimental Methods

2.1. Preparation of Ag and Sn-doped CdS Material

The melt quenching method was employed for the synthesis of CdS material. Element components (5 N pure) were put into a quartz ampoule following the measurement of the component amount, according to their atomic percentages. A vacuum of 2×10^{-5} mbar was maintained while sealing the quartz ampoule [7]. The ampoule was sealed and put in a furnace, and its temperature was increased to a maximum of 1200°C at a rate of 2 to 3 °C per minute. The ampoule was subsequently kept within the furnace at its highest melting point of elements for 24 hours to produce a homogeneous melt. The sealed ampoule was quenched in water at ice temperatures [7].

2.2. Thin-Film Deposition

Thermal vacuum evaporation was employed to deposit thin films on well-degassed clear fluorinated tin oxide (FTO) glass substrates by the inert gas (Ar) condensation (IGC) method using a vacuum coating unit known as HINDHIVAC with model VS-65D. The entire process was carried out at a base pressure of 2×10^{-5} mbar and ambient temperature. To achieve thermodynamic equilibrium, thin films were left in darkness in a deposition chamber for 24 hours before measurement [7].

2.3. Structural and Optical Characterisation

The structural properties of the nanocrystalline CdS (nc-CdS) thin films were characterised by X-ray diffraction (XRD) measurements carried out using a Spinner 3064 XPERT-PRO X-Ray diffractometer with CuK α radiation ($\lambda=1.54056\text{\AA}$) [7]. The scans were collected at a scan rate of 0.02° per second in a 2 θ range of 20° to 70° [8]. Crystallite size and micro-strain were calculated from the peak positions and widths using the Debye–Scherrer formula and strain formulas, respectively. Raman spectroscopy measurements were performed on a Spex Model Ramalog 1403 double monochromator with an RCA 31034A photomultiplier tube, under laser excitation at 532 nm to investigate phonon vibrational modes and crystal quality [9]. Optical transmission and absorption spectra were measured through a Perkin Elmer LAMBDA 750 UV/VIS/NIR computer-controlled spectrophotometer over a wide wavelength range from 300 nm to 2500 nm at room temperature (300 K). The measured spectra permitted the determination of the optical band gap from the conventional Tauc's approach and Lambert–Beer's law for quantitative estimation of the absorption coefficient. The surface microstructure and morphology of the films were investigated by a FE-SEM (SU-8000 Scanning Electron Microscope, model HI-0876-0003) and insights into grain size and film homogeneity were gained.

2.4. Electrical and Photovoltaic Characterisation

Current–voltage (I–V) characterisation in the dark and under illumination by white light at various intensities was

conducted using a Keithley electrometer 6517A, which offered both voltage source and current measurement functions. From the measured I–V curves, important diode parameters were determined using the thermionic emission model, such as series resistance (R_s), ideality factor (n), reverse saturation current (I_0), and the Schottky barrier height (Φ_B). Photovoltaic performance parameters like open-circuit voltage (V_{oc}), short-circuit current (I_{sc}), fill factor (FF), and maximum output power (P_{max}) were determined from illuminated I–V data.

2.5. Temporal Response Measurement

The time -resolved photoresponse of the doped CdS thin-film devices was recorded with a pulsed nanosecond Nd: YAG laser at a wavelength of ~ 1064 nm. The duration of the laser pulse was ~ 10 ns, and the output energy was ~ 10 mJ/pulse. In order to improve the signal-to-noise ratio, the sample was embedded in a metallic sample holder specially designed to offer electromagnetic shielding as well as mechanical stability. The electric field-induced photocurrent produced by the devices in response to the laser pulses was recorded with a Digital Phosphor Oscilloscope (Tektronix DPO 4054) that has the Tekvisa interface software for data analysis and acquisition. This configuration allowed accurate measurement of the rise time and fall time of the photodetector signal, key parameters for assessing device speed and its suitability for high-frequency photonic applications.

3. Results and Discussion

3.1. Structural Properties

The SEM micrograph of the prepared samples is shown in Figure 1 (a-b). It is observed from the SEM micrograph that the deposited film consists of spheroid-like grains, which cover the glass substrate well. There are no cracks or pinholes in the micrograph [10].

Figure 1 (c) indicates the XRD patterns of the FTO substrate and Ag- and Sn-doped CdS thin films. The films show well-resolved diffraction peaks of the hexagonal wurtzite phase of CdS (JCPDS card No. 06-0314) with preferred orientation along the (002) plane. There are no secondary or impurity phases, indicating high phase purity.

The interplanar spacing of the (002) plane, d_{002} , is calculated from the respective peak position by using the relation [7]:

$$\lambda = 2d_{002} \sin \theta$$

The crystallite size (D) corresponding to the predominant peak (002) is calculated by using Debye–Scherrer's formula [7]:

$$D = \frac{0.94\lambda}{\beta \cos \theta}$$

where θ is the Bragg's diffraction angle, λ (~ 1.54 Å) is the wavelength of X-ray, and β is the full width at half maxima (FWHM) in radian along the (002) plane. The micro-strain (ϵ) is estimated by using the formula [7]:

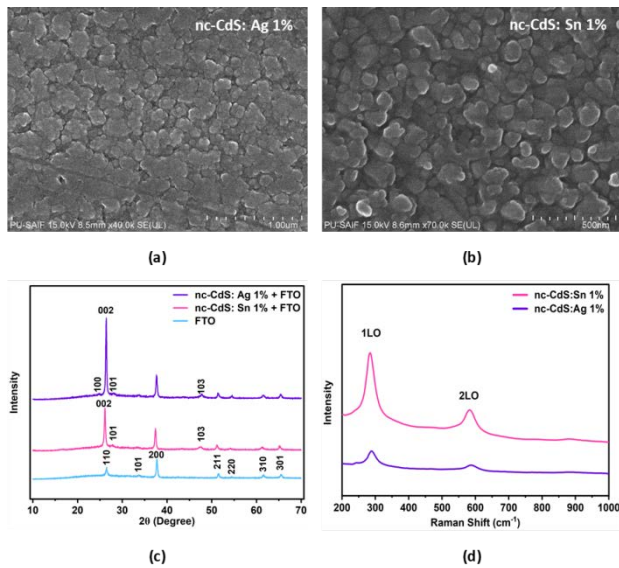


Figure 1. (a-b) SEM images (c) X-ray diffraction patterns (d) Raman spectra of nc-CdS: Ag 1% and nc-CdS: Sn 1% thin films

$$\varepsilon = \frac{\beta \cos \theta}{4}$$

Tabulated in Table 1 are the calculated d_{002} , D and ε values. The calculated values of d_{002} , D and ε are tabulated in Table 1. Crystallite size derived from the (002) peak is greater for Ag-doped films (38 nm) than for Sn-doped films (29 nm), agreeing with growth-induced strain differences.

Raman spectroscopy (Figure 1 (d)) indicates dominant peaks at 289 cm^{-1} and 585 cm^{-1} in the CdS: Ag (1%) spectrum and likewise at 284 cm^{-1} and 583 cm^{-1} in the CdS: Sn (1%), both of which are characteristic of first and second-order longitudinal optical (LO) phonon modes in CdS [11]. The absence of defect or impurity-related modes indicates preservation of the crystal structure upon doping.

3.2. Optical Properties

Figure 2 presents the optical transmission spectra for the nc-CdS: Ag 1% and nc-CdS: Sn 1% (thin films deposited at room temperature (300 K) in the wavelength range of 300–2500 nm. The transmittance (T) is related to the absorption coefficient (α) according to Lambert–Beer’s law as:

$$T = e^{-\alpha d}$$

where d is the thickness of the film. For the direct band gap semiconductors such as CdS, the fundamental edge of absorption can be modelled using the Tauc relation [12]:

$$h\nu\alpha = A(h\nu - E_g)^{\frac{1}{2}}$$

where h is Planck’s constant, ν is the frequency of a photon, E_g is the optical band gap, and A is a constant independent of photon energy. The value of E_g is determined by extrapolating the linear portion of the $(\alpha h\nu)^2$ vs. $h\nu$ plot to $\alpha=0$ (insets of Figure 2).

From this study, the optical band gap values were derived and tabulated in Table 1. The optical transmission

spectra suggest a red shift of the absorption edge as compared to bulk CdS (2.42 eV), with band gaps reduced to 2.23 eV and 2.25 eV for the Ag and Sn-doped films, respectively. The red shift can be related to defect states near the band edges being induced by the dopants and the resultant lattice strain leading to Urbach tailing. The similar bandgap values suggest that the dopants have a similar influence on the change in electronic structure of the films with slight variations due to ionic size and site occupancy in the CdS matrix.

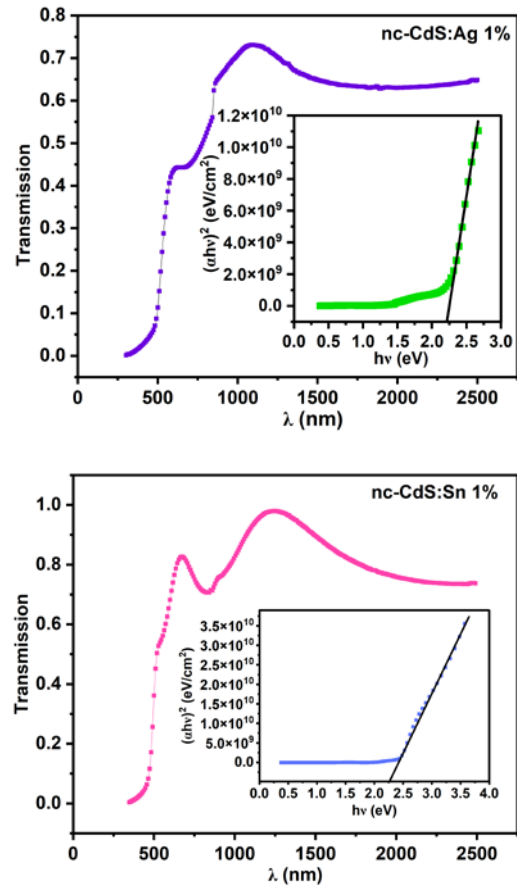


Figure 2. Optical transmission spectra for the nc-CdS: Ag 1% and nc-CdS: Sn 1% thin films deposited at room temperature (300 K). The inset shows the graph plotting $(h\nu\alpha)^2$ against $h\nu$

Table 1. Structural, Vibrational, and Optical Properties of Doped CdS Thin Films

Parameter	CdS: Ag (1%)	CdS: Sn (1%)
Interplanar spacing (d_{002} , Å)	3.37	3.41
Crystallite size (D , nm)	38	29
Micro-strain (ε , Lines $^{-2}$ m $^{-4}$)	0.000956	0.001268
1LO (cm^{-1})	289	284
2LO (cm^{-1})	585	583
Band gap (E_g , eV)	2.23	2.25

3.3. Electrical and Photovoltaic Behaviour

Figure 3 shows the dark and under white light illumination I-V curves at different intensities for the devices of FTO/nc-CdS: Ag 1% and FTO/nc-CdS: Sn 1%. Both devices show an increase in the current with illumination, and this current improves as we increase the intensity of the light. These behaviours confirm their photoconductive nature not only by increasing the current

in both devices under illumination, the I-V curves showing a rectifying behaviour, with rectification ratios evaluated as 1.83 (Ag) and 1.96 (Sn) at ± 3 V, supporting the formation of Schottky-type junctions between the FTO and CdS thin films.

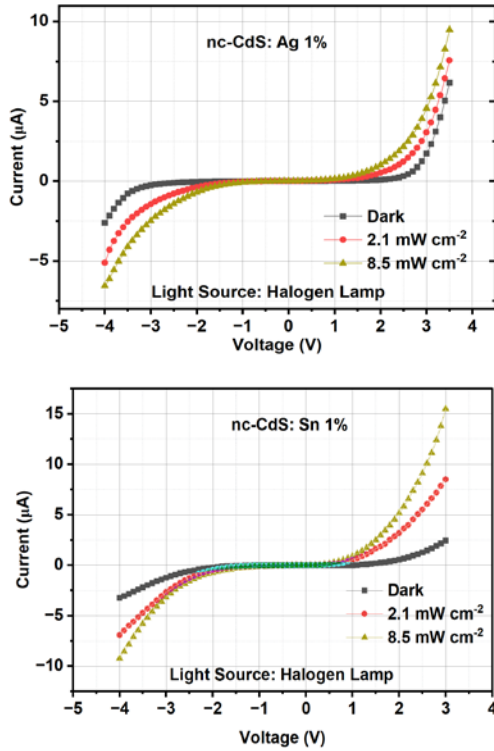


Figure 3. I-V characteristics of FTO/nc-CdS: Ag 1% and FTO/nc-CdS: Sn 1% Schottky diode heterojunctions measured in dark and under light illumination of different intensities

For an ideal Schottky junction, the thermionic emission model describes the forward current in the following manner:

$$I = I_0 \left\{ e^{\frac{q(V-IR_s)}{nk_B T}} - 1 \right\}$$

where I_0 is the reverse saturation current, R_s is the series resistance, n is the ideality factor, k_B is the Boltzmann constant, and T is the absolute temperature [13]. For $qV \gg k_B T$, the term -1 becomes negligible. Therefore,

$$V = \frac{nk_B T}{q} \ln I - \frac{nk_B T}{q} \ln I_0 + IR_s$$

In the high forward bias region, where series resistance dominates, the slope of V vs. I give R_s :

$$R_s = \frac{dV}{dI}, \text{ for } \left[V \gg \frac{k_B T}{q} \right]$$

The extracted values are tabulated in Table 2. The larger resistance for Sn-doped films suggests stronger carrier scattering or inferior contact quality compared to Ag-doped films.

At low forward bias, the diode equation reduces to:

$$I \approx I_0 e^{\frac{qV}{nk_B T}} \Rightarrow \ln I = \frac{qV}{nk_B T} + \ln I_0$$

The $\ln I$ vs. V plot gives I_0 from the intercept at $V = 0$ (Figure 4). The greater I_0 in Sn-doped films indicates greater leakage, possibly due to an increased defect density or poorer barrier control. The ideality factor n values are derived from the slope of $\ln I$ vs V (Figure 4). Both ideality factors are well above the theoretical range (1-2), indicating significant non-ideal transport, likely dominated by recombination at grain boundaries, high interface state density, and tunnelling paths in the defect-rich nanocrystalline structure.

The Φ_B barrier height is extracted by using the equation [14]:

$$I_0 = AA^* T^2 \exp\left(\frac{-q\Phi_B}{k_B T}\right)$$

Where A is the contact area and A^* the Richardson constant ($\approx 24 \text{ A K}^{-2} \text{ cm}^{-2}$ for CdS). The calculated values are shown in Table 2. Both values for the barrier height are below the band gap of CdS, as expected for Schottky diodes; the slightly lower value for Sn films indicates more band tailing and interfacial states.

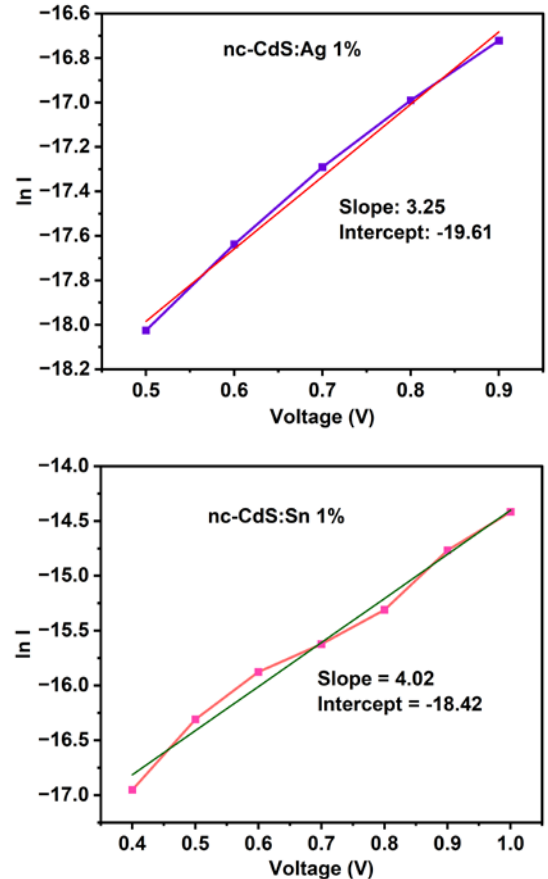


Figure 5. ln I-V plots under forward-bias condition

The potential of nc-CdS: Ag 1% and nc-CdS: Sn 1% devices as photodetectors is confirmed by their rectifying and photosensitive characteristics. The Sn-doped CdS device shows a slightly higher rectification ratio and a lower ideality factor compared to the Ag-doped device. The slightly higher barrier height, much lower series resistance, and lower leakage current of Ag-doped CdS, in contrast, indicate improved junction quality and more efficient charge transport. The high ideality factors in both cases clearly demonstrate non-ideal transport, which is

typical of nanocrystalline thin films where grain boundaries and defect-mediated conduction are predominant.

3.4. Photovoltaic and Photodetector Performance

In the presence of light, both devices exhibited photovoltaic behaviour with an open-circuit voltage (V_{oc}), short-circuit current (I_{sc}) and fill factor (FF). The fill factor is given by [15]:

$$FF = \frac{V_m I_m}{V_{oc} I_{sc}}$$

Where V_m and I_m are the voltage and current corresponding to the maximum useful power. Both devices showed open-circuit voltages approximately equal to 0.022–0.023 V. Ag-doped films exhibit a fivefold increase in short-circuit current (2.05 μ A) with a marginally (2.12%) improved fill factor (31.46%) as compared to the Sn-doped films (0.4168 μ A, 29.5%) (Figure 5, Table 2). This indicates a more efficient charge generation and extraction mechanism in the CdS: Ag 1% device, which is likely due to a lower series resistance and better interface properties. However, both systems exhibited relatively high ideality factors and low open circuit voltages when compared with optimised inorganic solar cells, emphasising the impact of grain boundaries, defect states, and interface traps that are common in nanocrystalline thin films.

Table 2. Photovoltaic and Photodetector Parameters of Ag and Sn-Doped CdS Devices

Parameter	nc-CdS: Ag 1%	nc-CdS: Sn 1%
Rectification Ratio (± 3 V)	1.83	1.96
Series Resistance (R_s , k Ω)	110	432
Ideality factor (n)	11.9	9.63
Reverse saturation current (I_s , A)	3.08×10^{-9}	9.95×10^{-9}
Barrier height (Φ_B , eV)	0.884	0.853
Open-Circuit Voltage (V_{oc} , V)	0.023	0.022
Short-Circuit Current (I_{sc} , μ A)	2.05	0.4168
Voltage at Maximum Power (V_m , V)	0.015	0.01
Current at Maximum Power (I_m , μ A)	0.972	0.267
Maximum Power (P_{max} , nW)	1.46	2.7
Fill Factor (FF)	31.46%	29.5%
Sensitivity (S)	≈ 0.198	≈ 0.39
Responsivity (R, A/W)	$\approx 4 \times 10^{-5}$	$\approx 1.39 \times 10^{-5}$
Detectivity (D^* , Jones)	$\approx 1.7 \times 10^7$	$\approx 1.42 \times 10^5$
Rise Time (t_r , μ s)	~ 17	~ 1.74
Fall Time (t_f , μ s)	~ 204	~ 110

The photodetector performance can be measured in terms of sensitivity (S), responsivity (R) and relative detectivity (D^*). The S indicates the relative increase in current, due to illumination and is often utilised as a merit value to indicate signal improvement or photocurrent gain with respect to the dark current. The R is simply defined as the photocurrent per unit incident power per unit area of the photodetector. The D^* defines the minimum detectable optical signal, and larger values represent better detection in the presence of noise [16].

$$S = \frac{(I_p - I_d)}{I_d}$$

$$R = \frac{(I_p - I_d)}{PA}$$

$$D^* = \frac{RA^{1/2}}{(2eI_d \Delta f)^{1/2}}$$

Where I_p is the photocurrent, I_d the dark current, P the incident light intensity, A the effective device area and e the electronic charge [17]. S, R and D^* were calculated for a white light source with an incident intensity of 8.5 mW cm^{-2} at zero bias operating voltage using the equations previously mentioned. The estimated values are presented in Table 2. Sn doping doubles the sensitivity compared to Ag doping (0.39 vs. 0.198), suggesting that Sn-doped nc-CdS has a greater current enhancement under illumination. Both materials show low responsivity. The Ag-doped CdS has a much higher detectivity ($\sim 10^7$ Jones) compared to Sn-doped ($\sim 10^5$ Jones). This means Ag doping improves the ability to detect weak signals, whereas Sn doping increases current response but adds more noise, reducing detectivity.

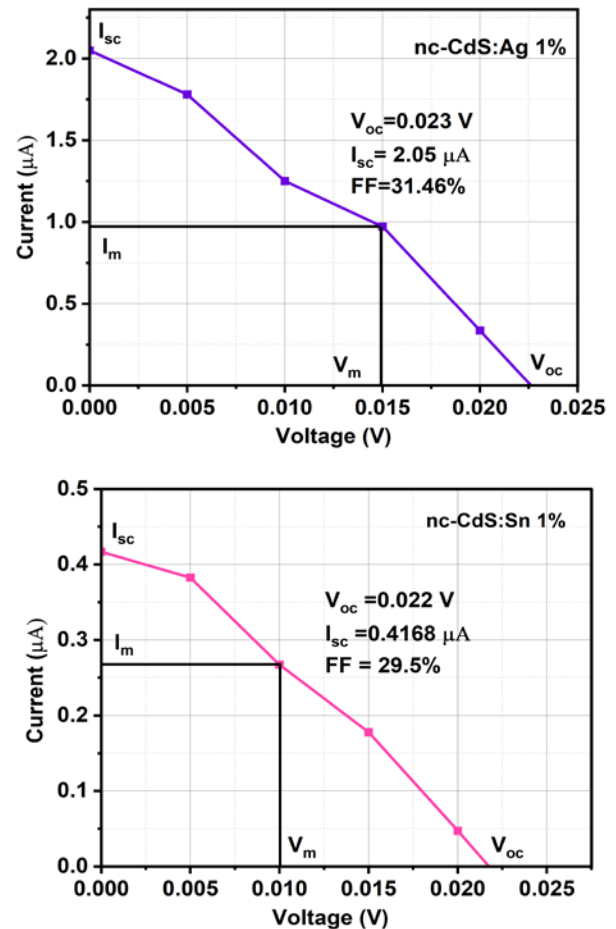


Figure 6. The photovoltaic characteristics of the devices under halogen light illumination with an intensity of 8.5 mW/cm²

Photodetector's temporal behaviour is evaluated by rise time (t_r) and fall time (t_f) parameters. The rise time is characterised by the time the photocurrent takes to rise by

10% to 90% level of I_{peak} , and the fall time by the time the photocurrent takes to decrease by 90% to 10% level of I_{peak} [18]. An Nd-YAG laser operating at the wavelength of approximately 1064 nm and pulse width and power of approximately 10 ns and 10 mJ, respectively, served as the excitation radiation source. Temporal response analysis reveals Sn-doped films have by far the shortest rise (1.74 μs) and fall (110 μs) times among the Ag-doped films (17 μs rise and 204 μs fall). This exhibits the merits of Sn doping for ultrahigh-speed photonic switching, while Ag doping favours applications requiring a long lifetime of carriers.

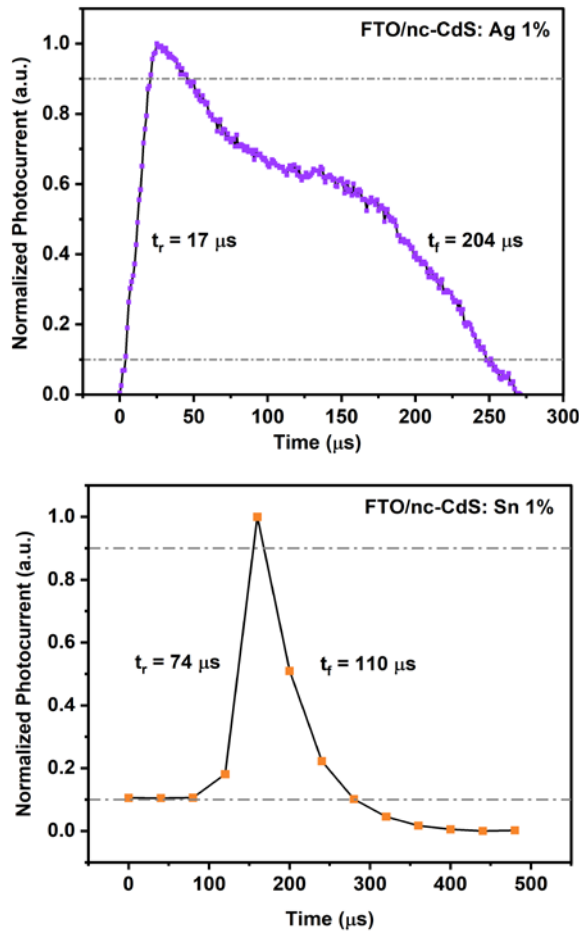


Figure 7. Rising and falling edges for estimating rise and fall times

4. Conclusion

Nanocrystalline CdS thin films doped with Sn 1% and Ag 1% were successfully prepared onto FTO substrates by vacuum evaporation using the inert gas condensation technique. The two series of films retained the hexagonal CdS crystal structure, but the dopants extensively transformed their microstructural, optical, and electronic behaviours. Ag-doped films show larger grain size, reduced series resistance, higher barrier height, and superior detectivity and photovoltaic performance, making them ideal for sensitive photodetection and low-noise applications. Sn doping, on the other hand, reduces grain size and micro-strain, adds greater series resistance and leakage current, and lowers overall detectivity and responsivity, balanced by strongly accelerated rise and fall

time, suitable for ultrafast optoelectronic switching device applications. The research shows that dopant selection offers a tuneable approach to tailoring CdS nanocrystalline thin films to provide specific device roles, such as very sensitive photovoltaic sensors or very fast photonic switches. Future studies can be directed at the enhancement of doping concentrations and exploration of heterojunction geometries to obtain greater functionality.

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Statement of Competing Interests

The authors have no competing interests.

List of Abbreviations

nc: Nanocrystalline
CdS: Cadmium Sulfide
Ag: Silver
Sn: Tin
FTO: Fluorine-doped Tin Oxide
SEM: Scanning Electron Microscopy
XRD: X-ray Diffraction
Rs: Series Resistance
 I_0 : Saturation Current
 Φ_B : Barrier Height
 V_{oc} : Open-circuit Voltage
 I_{sc} : Short-circuit Current
FF: Fill Factor
R: Responsivity
S: Sensitivity
 D^* : Detectivity
 t_r : Rise Time
 t_f : Fall Time
nm: Nanometer

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