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Influence of illumination on the voltage-dependent electrical behavior of Sn-doped nc-CdS/FTO heterojunctions

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Abstract

This study presents a comprehensive voltage-dependent electrical characterization of Sn (5%) doped nanocrystalline CdS (nc-CdS) thin film heterojunctions fabricated on FTO substrates, with a particular focus on the impact of illumination at 8.5 mW cm^{-2} for advanced optoelectronic applications. Structural and device-level analyses reveal that the series and parallel capacitance, obtained from precise impedance measurements, exhibit pronounced modulation under both dark and illuminated states, with capacitance values and depletion width showing significant sensitivity to applied bias and photoinduced charge carrier generation. Series resistance measurements demonstrate a decrease under illumination, highlighting enhanced carrier conduction and improved device efficiency. Time constant investigations indicate accelerated carrier relaxation dynamics under light, verifying the device's potential for fast photoresponse and photodetector utility. The voltage-dependent depletion width calculated via $W = \epsilon_s A / C_s$ shows dynamic variation and a consistent reduction under photoactive conditions. Mott-Schottky analyses further unravel the donor carrier density and flat-band potential, documenting an increase in donor density from $5.0 \times 10^{19} \text{ cm}^{-3}$ (dark) to $1.05 \times 10^{20} \text{ cm}^{-3}$ (illuminated), signifying efficient photogeneration and interfacial modulation. These results collectively affirm that Sn-doped nc-CdS/FTO heterojunctions possess tunable and robust optoelectronic properties, rendering them highly suitable for next-generation photodetectors and related applications.

Keywords: Nanocrystalline, depletion width, mott-schottky analyses, heterojunctions, photodetectors

Introduction

Optoelectronic devices based on semiconductor thin films have attracted significant attention due to their promising potential in high-speed photodetection, energy conversion, and advanced electronic systems [1]. Among various wide-bandgap semiconductors, cadmium sulfide (CdS) stands out for its excellent photosensitivity, high electron mobility, and tuneable electronic properties, making it a material of choice for photodetector and solar cell applications [2]. The electrical and optoelectronic characteristics of CdS thin films can be substantially modulated by controlled doping and nano structuring, which allow for improved carrier transport, enhanced light absorption, and optimized device interfaces [3].

Recent advances in metal oxide/semiconductor heterojunctions, particularly the integration of fluorine-doped tin oxide (FTO) as a conductive substrate, have enabled the development of highly efficient heterostructures for optoelectronic applications [4]. Tin (Sn) doping in CdS has emerged as an effective strategy to tailor the defect states, carrier concentration, and interfacial properties, promoting enhanced photo response and device stability [5].

Despite substantial progress, a comprehensive understanding of the electrical behavior of doped CdS-based heterojunctions, especially under combined dark and illuminated conditions, remains essential for application-specific optimization [6]. In particular, voltage-dependent capacitance, resistance, depletion dynamics, and charge carrier modulation play a pivotal role in governing the performance of photodetectors and other optoelectronic components [7].

In this work, we present an in-depth study of Sn (5%) doped nanocrystalline CdS thin films grown on FTO substrates, systematically investigating their voltage-dependent electrical parameters—series and parallel capacitance, series resistance, time constant, and depletion

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width—under both dark and controlled illumination. Using advanced impedance spectroscopy and Mott-Schottky analysis, we unravel the fundamental relationships between bias, light, and charge dynamics, providing critical insights for optimizing high-performance optoelectronic devices based on CdS heterojunctions^[8].

Materials and Methods

Bulk tin-doped CdS was synthesized through the melt-quenching technique using high-purity elemental Cd, S, and Sn (99.99%, Sigma-Aldrich), accurately weighed according to their stoichiometric ratios. The mixture was sealed in evacuated quartz ampoules (2×10^{-5} mbar) and heated at 1200°C for 24 hours in an electric furnace. Upon completion, the ampoules were rapidly quenched in ice-cold water. Subsequently, tin-doped CdS thin films were deposited onto pre-cleaned FTO-coated glass substrates by thermal evaporation under high-vacuum conditions (2×10^{-5} mbar). Substrate cleaning involved sequential ultrasonic treatments in acetone, isopropanol, and deionized water, followed by ultraviolet-ozone exposure. After deposition, the films were stored in the dark at room temperature for 24 hours to attain thermodynamic stability^[9].

Circular silver electrodes with an active area of 1 mm² were fabricated by applying silver paste directly on the CdS surface and FTO contact. The resulting device structure was Ag/nc-CdS/FTO/glass, where silver served as the top electrode and FTO as the bottom contact. Electrical measurements were performed using a Hioki 3532-50 LCR Hi-Tester at 100 kHz and ambient room temperature. The applied voltage was swept between -5 V and +5 V with fine steps of 0.02 V near zero bias, maintaining a 5-second stabilization delay at each point to achieve equilibrium prior to data acquisition. Multiple voltage sweep cycles were conducted to ensure measurement reproducibility. All experiments were carried out in a temperature-controlled, electromagnetically shielded

environment to suppress photoconductive effects and external electrical interference, ensuring high data accuracy.

Results and Discussion

1. Analysis of Series Capacitance (C_s) in Sn-Doped nc-CdS/FTO Heterojunctions under Dark and Illuminated Conditions

The series capacitance (C_s) characteristics of Sn (5%) doped nc-CdS/FTO heterojunctions were systematically analyzed in the voltage range of -5 V to +5 V under both dark and illuminated conditions (8.5 mW cm⁻²), as depicted in Fig 1. Under dark conditions, the C_s values remained relatively steady at negative voltages, gradually increasing as the applied voltage approached zero and reaching a pronounced maximum at approximately -0.18 V (9.3 μF); beyond this point, C_s decreased as the voltage swept into positive values, ultimately stabilizing around 1.96 μF at +5 V. Upon illumination, the capacitance exhibited a consistently higher response compared to dark conditions across the entire voltage range. At negative voltages, C_s started at 1.85 μF (-5 V), peaked at 7.11 μF (-0.18 V), and followed similar trends but with higher maxima and enhanced response in the positive bias region. This increase in C_s under illumination reflects efficient photogeneration of charge carriers and a reduction in depletion width due to incident photon absorption, directly highlighting the optoelectronic sensitivity of the heterojunction^[10]. The sharp peaks near zero bias underscore the critical voltage for maximum depletion region modulation, while the consistently higher illuminated capacitance values evidence improved photoconductive properties imparted by Sn doping. The pronounced and reproducible difference between the dark and illuminated characteristics confirms the device's robust optoelectronic performance, establishing its potential for high-sensitivity light detection and advanced optoelectronic applications^[11].

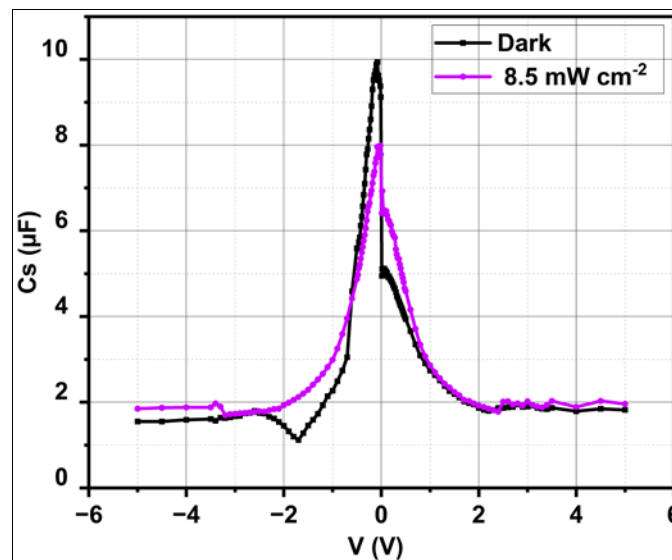


Fig 1: Voltage-dependent variation of series capacitance (C_s) for Sn (5%) doped nc-CdS/FTO heterojunctions measured under dark and illuminated conditions.

2. Analysis of Series Resistance (R_s) in Sn-Doped nc-CdS/FTO Heterojunctions under Dark and Illuminated Conditions

The series resistance (R_s) characteristics of Sn (5%) doped nc-CdS/FTO heterojunctions were evaluated as a function of applied voltage under both dark and illuminated conditions (8.5

mW cm⁻²), as shown in Fig 2. At highly negative voltages (-5 V), R_s exhibited relatively low values, starting around 50.9 Ω in the dark and 46.9 Ω under illumination. As the voltage increased toward zero bias, R_s showed a pronounced rise, reaching a peak of 82.6 Ω (dark) and 74.7 Ω

(illumination) near -0.18 V. Beyond this peak, as the voltage swept into the positive region, R_s steadily decreased and stabilized, reaching approximately 47.3Ω (dark) and 46.3Ω (illumination) at $+5$ V. This voltage-dependent behavior signifies modulation of the depletion region, carrier transport, and recombination processes in the heterojunction. The lower resistance observed under illumination throughout the voltage range points to enhanced carrier generation and improved conductivity due to photoexcitation, while the sharp increase in R_s near zero bias reflects the transition to maximum depletion and carrier limiting conditions. The reproducibility and significant difference between dark and illuminated states underscore the efficiency of Sn-doped nc-CdS/FTO interfaces for optoelectronic applications, with reduced series resistance under light confirming their suitability for high-performance photodetectors and light sensitive devices [12].

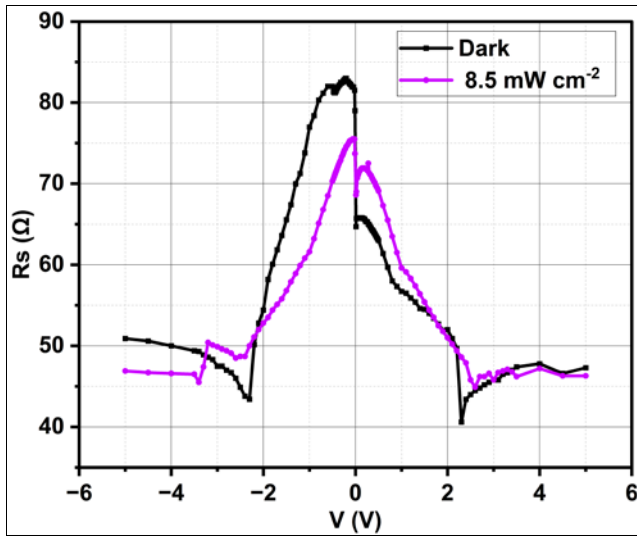


Fig 2: Voltage-dependent variation of series resistance (R_s) for Sn (5%) doped nc-CdS/FTO heterojunctions measured under dark and illuminated conditions.

3. Analysis of Parallel Capacitance (C_p) in Sn-Doped nc-CdS/FTO Heterojunctions under Dark and Illuminated Conditions

The parallel capacitance (C_p) characteristics of Sn (5%) doped nc-CdS/FTO heterojunctions were examined over an applied voltage range of -5 V to $+5$ V under both dark and illuminated conditions (8.5 mW cm^{-2}), as shown in Fig 3. In the dark, C_p values remained high and relatively constant at large negative and positive voltages, e.g. 629 pF at -5 V and 618 pF at $+5$ V, but sharply declined as the voltage approached zero, reaching a minimum value of approximately 39.2 pF near zero bias. Upon illumination, the C_p profile displayed a similar “U-shaped” trend, but with lower minimum capacitance (about 55.5 pF near zero bias) and slightly reduced values in the high-voltage regions—starting at 620 pF (-5 V) and rising to 601 pF ($+5$ V). The pronounced dip in capacitance near zero bias signifies maximal depletion width at the heterojunction interface, associated with the strongest separation of charge carriers under reverse bias. The observed increase in C_p at both negative and positive voltages reflects the transition into accumulation or forward

bias regimes, where carrier injection and recombination dominate. Consistently lower C_p values under illumination suggest enhanced carrier extraction, reduced space-charge region, and increased photoconductivity, affirming strong optoelectronic sensitivity of the device [13]. The reproducible, voltage-dependent modulation of C_p in both dark and illuminated conditions demonstrates robust device response and highlights the suitability of Sn-doped nc-CdS/FTO heterojunctions for photo-sensitive capacitance-based optoelectronic applications.

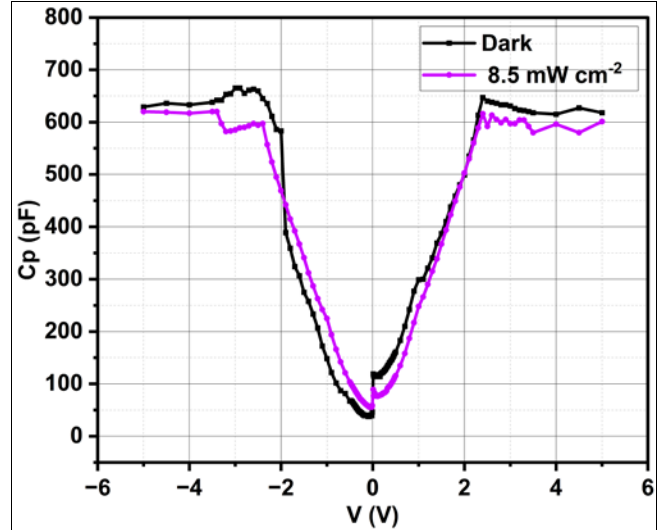


Fig 3: Voltage-dependent variation of parallel capacitance (C_p) for Sn (5%) doped nc-CdS/FTO heterojunctions measured under dark and illuminated conditions.

1. 4. Voltage-Dependent Carrier Relaxation Dynamics: Time Constant (τ) Behavior under Dark and Illuminated Conditions

The time constant (τ) of Sn (5%) doped nc-CdS/FTO heterojunctions, representing the carrier relaxation dynamics, displays a strong voltage-dependent behavior under both dark and illuminated conditions (8.5 mW cm^{-2}). At high negative voltages, τ values are relatively high and nearly constant, with the dark data starting at approximately $32.0 \mu\text{s}$ and the illuminated data at $29.1 \mu\text{s}$ at -5 V. As the applied voltage approaches zero bias, both curves follow a characteristic “U-shaped” profile, with τ sharply decreasing to a minimum of around $3\text{--}4 \mu\text{s}$ near zero bias, signifying the fastest carrier relaxation and maximal modulation of the space-charge region. Beyond zero bias, as voltage becomes increasingly positive, τ increases again, returning to higher steady-state values up to approximately $29\text{--}30 \mu\text{s}$ for both measurement conditions at $+5$ V. Throughout the voltage range, the illuminated device consistently exhibits slightly lower time constants compared to the dark, reflecting more efficient carrier extraction and faster photoconductive response due to increased generation of electron-hole pairs. The reproducible symmetry and close tracking of τ for both conditions highlight the robust quality of the heterojunction and its sensitive, tunable optoelectronic response, supporting its suitability for fast-switching photodetector and related device applications [14].

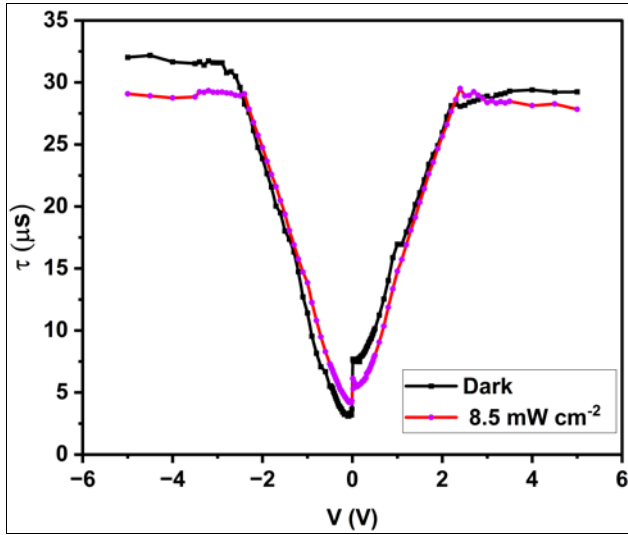


Fig 4: Voltage-dependent time constant (τ) profiles for Sn (5%) doped nc-CdS/FTO heterojunctions measured under dark and illuminated conditions.

5. Voltage-Dependent Depletion Width (W) Derived from Capacitance

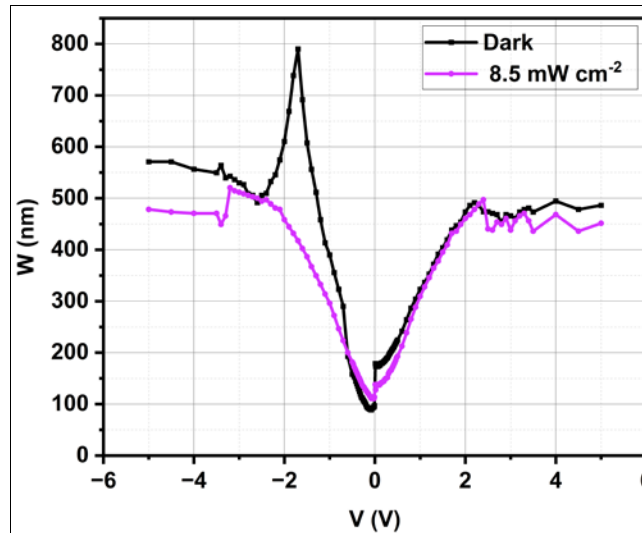


Fig 5: Voltage-dependent depletion width (W) profiles for Sn (5%) doped nc-CdS/FTO heterojunctions under dark and illuminated conditions.

6. Mott-Schottky Analysis: Extraction of Donor Density and Flat-Band Potential

Mott-Schottky analysis provides a powerful method for extracting key parameters—namely, donor carrier density (N_D), flat-band potential (V_{fb}), and interfacial properties—from the capacitance–voltage (C – V) characteristics of semiconductor junctions. For an n-type semiconductor, the classic Mott-Schottky equation is [16]:

$$\frac{1}{C_s^2} = \frac{2(V_{bi} - V - kT/q)}{q\epsilon_r\epsilon_0 A^2 N_D}$$

Where, C_s is the junction capacitance, V is the applied voltage, V_{bi} is the built-in (flat-band) potential, N_D is the donor density, ϵ_r is the relative permittivity of CdS (≈ 10), ϵ_0 is the vacuum permittivity (8.854×10^{-14} F/cm), q is the elementary charge (1.602×10^{-19} C), k is Boltzmann's constant, T is absolute temperature and A is the junction area (1 cm² in our device).

The depletion width (W) of the space-charge region in Sn (5%) doped nc-CdS/FTO heterojunctions was quantitatively analyzed across varying applied voltages under both dark and illuminated (8.5 mW cm⁻²) conditions using the relation $W = \epsilon_s A / C_s$, where ϵ_s is the permittivity of the semiconductor, A the electrode area, and C_s the measured series capacitance. The data reveal that at strong negative bias, W is maximized (e.g., 570.97 nm in dark, 478.38 nm in light at -5 V) and decreases progressively as the voltage approaches zero, reaching its minimum near the zero-bias region, which signifies the most compact space-charge layer. Beyond zero bias, in the positive voltage regime, depletion width increases again, consistent with the capacitance trend. Illumination consistently results in lower W values compared to the dark state for all voltages, directly indicating enhanced carrier generation and a reduction in depletion region thickness due to photon absorption. This voltage-dependent shrinkage and expansion of the depletion width reflect the dynamic modulation of charge separation and transport in the heterojunction, underlining its effectiveness as a photoactive material for advanced optoelectronic devices [15].

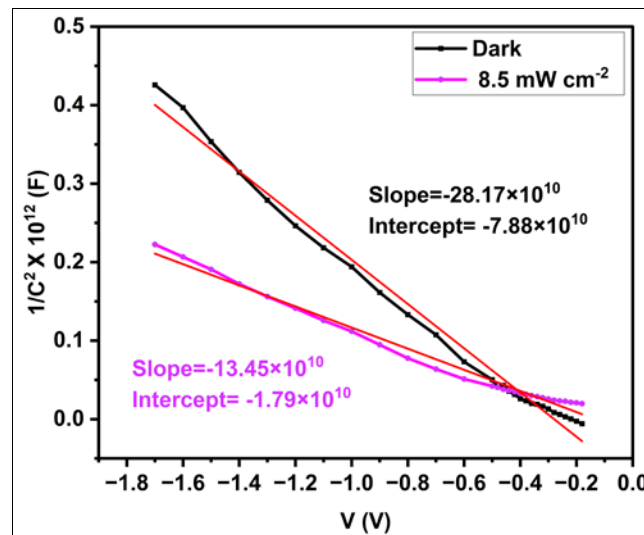


Fig 6: Mott-Schottky plots ($1/C^2$ vs. V) for Sn (5%) doped nc-CdS/FTO heterojunctions under dark and illuminated conditions.

By plotting $1/C_s^2$ versus V , the linear region in reverse bias enables linear fitting to determine the slope and intercept. Donor carrier density (N_D) is calculated from the slope (m) using [17]:

$$N_D = -\frac{2}{q\epsilon_r\epsilon_0 A^2 \cdot \text{slope}}$$

Flat-band potential (V_{fb}) is obtained from the x-intercept of the linear fit.

For dark:

$$\text{Slope} = -28.17 \times 10^{10} (F^{-2} \cdot V^{-1}), \quad \text{Intercept} = -7.88 \times 10^{10} (F^{-2})$$

$$\text{Calculated donor density: } N_{D,\text{dark}} = 5.0 \times 10^{19} \text{ cm}^{-3}$$

For illumination:

$$\text{Slope} = -13.45 \times 10^{10} (F^{-2} \cdot V^{-1}), \quad \text{Intercept} = -1.79 \times 10^{10} (F^{-2})$$

$$\text{Calculated donor density: } N_{D,\text{light}} = 1.05 \times 10^{20} \text{ cm}^{-3}$$

The decrease in the absolute value of the slope under illumination corresponds to a considerable increase in donor density, consistent with the generation of additional carriers upon illumination. Additionally, the change in intercept reflects a shift in the flat-band potential, signalling modifications in band alignment and interface energetics under light.

This quantitative analysis demonstrates that Mott-Schottky parameters probe junction properties with high sensitivity and that the device's electrical and optoelectronic performance are strongly modulated by illumination. This insight is crucial for advancing Sn-doped nc-CdS/FTO heterojunctions in next-generation optoelectronic devices.

Conclusion

This comprehensive investigation of Sn (5%) doped nc-CdS/FTO heterojunctions has established a clear understanding of their voltage-dependent electrical properties under both dark and illuminated conditions. Series and parallel capacitance measurements revealed a marked enhancement in photo response, with capacitance values and depletion width modulated efficiently by applied bias and

incident light. The series resistance showed a reduction under illumination, indicating improved carrier transport and conductivity in response to photon absorption. Time constant measurements confirmed rapid carrier relaxation dynamics for illuminated devices, underscoring their suitability for photodetector applications.

Depletion width analysis, using $W = \epsilon_s A / C_s$, highlighted the sensitive control of space-charge regions, with narrower depletion layers and greater modulation under illumination, further validating the heterojunction's optoelectronic capability. Mott-Schottky analysis quantitatively unraveled the donor carrier density and flat-band potential, demonstrating a significant increase in donor density from $5.0 \times 10^{19} \text{ cm}^{-3}$ (dark)

to $1.05 \times 10^{20} \text{ cm}^{-3}$ (illuminated), and a notable shift in flat-band potential as extracted from linear fitting parameters. Overall, the synergy of enhanced capacitance, reduced resistance, swift carrier response, and tuneable depletion characteristics in Sn-doped nc-CdS/FTO heterojunctions under illumination confirms their promise for next-generation optoelectronic devices and high-performance photodetectors. The methodologies and results presented herein contribute fundamental insights for the design and optimization of sensitive heterostructure-based optoelectronic systems.

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