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COMPREHENSIVE ANALYSIS OF MORPHOLOGY, STRUCTURE, AND PHOTOVOLTAIC PROPERTIES OF *CdTe* and *CdTe*:*In* THIN FILMS

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In this work, the photovoltaic properties and short-circuit current spectra of indium (In)-doped CdTe films were comprehensively investigated. The study covers the spectral sensitivity and light-absorption characteristics of undoped, freshly prepared, and thermally treated CdTe:In films. The effects of doping level and thermal treatment temperature on photovoltaic effect parameters were analyzed. The results showed that indium doping and subsequent thermal treatment significantly improve the photovoltaic efficiency of CdTe films. Using spectroscopic and electron microscopy methods, the chemical composition, surface morphology, and bandgap width of the films were determined, and their interrelation with optical and electrical properties was revealed. The obtained results indicate that $CdTe{:}In$ films are promising for applications in solar energy devices.

Keywords: CdTe:In *thin films; Photovoltaic effect; Short-circuit current spectra; Anomalous photovoltage (APV); Deep energy levels; Thermal treatment; Solar energy materials*

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INTRODUCTION

Thin-film semiconductor materials occupy an important place in modern optoelectronic and photovoltaic technologies. In this field, controlling the structural, optical, and electrical properties of materials is of decisive importance for improving the functional efficiency of devices. Cadmium telluride (CdTe) is widely studied as a promising semiconductor material due to its high light-absorption coefficient and suitable energy structure. Doping and post-deposition thermal treatment are important technological factors in modifying the properties of CdTe films. In particular, doping with indium (In) affects carrier concentration, defect compensation mechanisms, and the formation of internal electric fields [1, 2, 3]. Thermal treatment, in turn, governs grain growth, the redistribution of defect levels, and band alignment, as evidenced by short-circuit current spectra and anomalous photovoltage characteristics. At the same time, comprehensive studies of the relationships among short-circuit current spectra, spectral sensitivity, and photovoltaic efficiency in indium-doped CdTe thin films are limited. In this work, the spectral and photovoltaic properties of undoped, freshly prepared, and thermally treated CdTe:In films are analyzed in their interrelation. The research results have important scientific significance for optimizing semiconductor processing technologies and developing high-efficiency photovoltaic devices.

TECHNOLOGY AND MEASUREMENT METHODS

To obtain the films, we used the thermal vacuum evaporation method. A vacuum system was assembled based on a VUP-5M automatically controlled vacuum unit and a VAKMA 2NVR-5 DM fore-vacuum pump, together with a VAKMA NVDM-160 vapor-oil diffusion pump providing a pressure of ~10^{-2} Pa. The samples had dimensions of 7×25 mm² and a thickness of 0.8–1.5 µm. In this method, the films are formed as nanoscale polycrystalline layers; under vacuum conditions, the materials are heated to form a high-quality coating on the surface. Thickness and dimensions are precisely controlled, thereby improving the photovoltaic properties of the films [3, 4]. Using these methods, nanoscale polycrystalline films are produced under high-vacuum conditions. During preparation, the films were thermally treated in the 350–750 K range, resulting in a transition from the amorphous state to the polycrystalline state [5, 6]. The film thickness was accurately monitored using a special quartz crystal sensor of the equipment. At 77 and 300 K, the short-circuit current spectra and bandgap width of as-prepared and thermally treated $CdTe{:}In$ films were determined.

RESULTS

Short-circuit current spectra and bandgap width of CdTe:In films. Typical room-temperature spectra $I_{sc}(\nu)$ obtained for CdTe:In samples–undoped CdTe (curve 1), freshly prepared (2), and thermally treated (3)–are shown in Figure 1a. As can be seen from the curves, the spectral sensitivity of I_{sc} differs sharply for different samples. The spectral maxima are determined with an accuracy of ±0.05 eV and, with the same accuracy, correspond to the intrinsic absorption edge. The long-wavelength tail of the spectra is associated with impurity-related light absorption in the barrier regions of crystallites, i.e., anomalous photovoltage (APV), whose contribution increases significantly in the doped CdTe:In sample (curves 2 and 3 in Figure 1).

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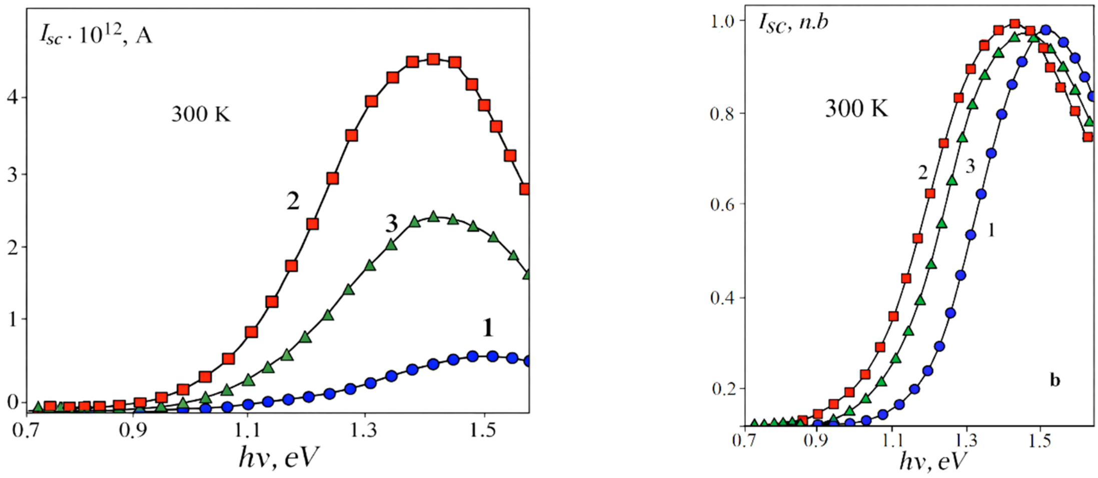

Figure 1. Short-circuit current Isc spectra of CdTe (curve 1) and CdTe:In films (curve 2 – freshly prepared; curve 3 – after thermal treatment) exhibiting AFK characteristics at T = 300 K, shown on (a) absolute and (b) normalized scales.

The short-wavelength decrease of the spectra appears to be due to light absorption in the quasi-neutral regions of the grains, which leads to bulk photoconductivity of the shunt layer and, consequently, to a decrease in the spectral value of the photovoltage, $V_{APV}(\nu)=I_{sc}(\nu)\cdot R_{pl}(\nu)$. The integral of the short-circuit current in doped films increases by more than two orders of magnitude compared to pure CdTe samples. This is achieved in the non-thermally treated CdTe:In case, where photoconductivity dominates in the films (V_{APV} is only 60–100 V/cm), and for thermally treated (TT) films, mainly due to the photovoltaic effect (V_{APV} =3·10^3 V/cm). From the standpoint of analyzing the APV formation mechanism, it was even more effective to compare the I_{sc} spectra for the three samples discussed above obtained at liquid nitrogen temperature, T=77 K (Figure 2).

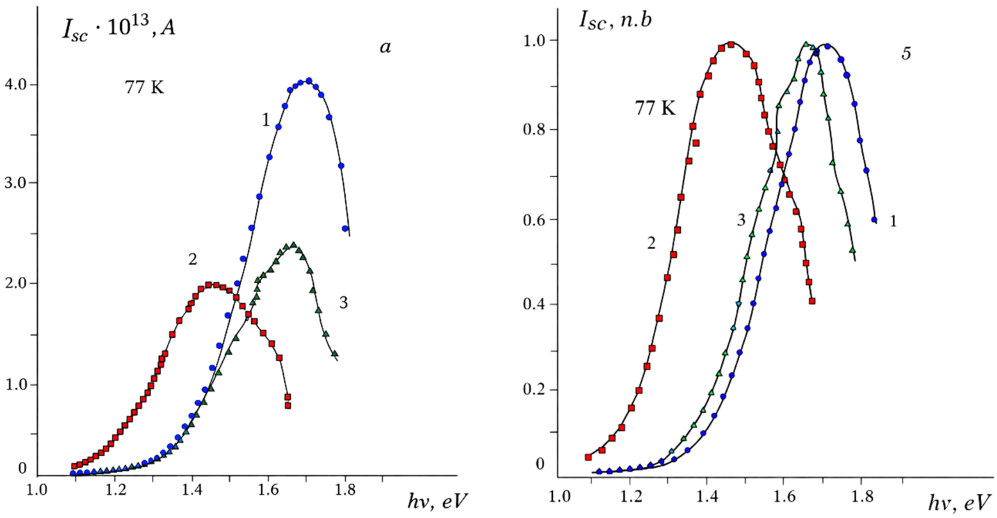

Figure 2. Short-circuit current I_{sc} spectra of CdTe (curve 1) and CdTe:In films (curve 2 – freshly prepared; curve 3 – after thermal treatment (TTE)) exhibiting AFK characteristics at T = 77 K, presented on (a) absolute and (b) normalized scales.

According to the results reported in [7, 8, 9], in our experiments for CdTe films the I_{sc} value practically did not change within the studied temperature range T = 77÷300 K. However, in doped CdTe:In samples, when the temperature decreases from 300 K to 77 K, both the integral value of Iqt and the level of its spectral maximum decrease by approximately one order of magnitude. For freshly prepared CdTe:In films, a noticeable long-wavelength shift of the $I_{sc}(\nu)$ spectrum is observed, and a doublet structure appears (Figure 2a, curve 2). The latter is associated with a twofold contribution to the AFK integral, arising from impurity-related and intrinsic absorption, which dominates over the grain-related intrinsic contribution (see curve 2 in Figure 2 for hν < 1.6 eV).

However, it should be emphasized that in annealed CdTe:In films the "intrinsic" contribution to APV, similar to that in CdTe films, exceeds the "grain-related" contribution (curves 1 and 3), and the doublet structure of the oppositely signed shoulder spectrum is preserved compared to curve 2. The short-wavelength shift of the maxima in spectral curves 1 and 3 in Figure 2 is associated with the increase in the CdTe bandgap as the temperature decreases. Thus, in obliquely evaporated CdTe:In films, APV formation occurs due to light absorption in both the intrinsic and grain-related spectral regions. Depending on technological conditions, the "grain-related" contribution may exceed the "intrinsic" one and may even change its sign. To determine the impurity level involved in AFK formation, the long-wavelength tails of the $I_{sc}(\nu)$

spectra shown by curves 1–3 in Figure 2 were analyzed in more detail by studying the photon capture cross-section [10, 11]. From the comparison of the experimental and theoretical spectral curves (Figure 3), the following deep levels of local centers were identified at T=77 K: $E_1=E_c-(1.43\pm0.02)$ eV, $E_2=E_c-(1.05\pm0.02)$ eV, $E_3=E_c-(1.31\pm0.02)$ eV, $E_4=E_c-(1.18\pm0.02)$ eV, and $E_5=E_c-(0.9\pm0.02)$ eV.

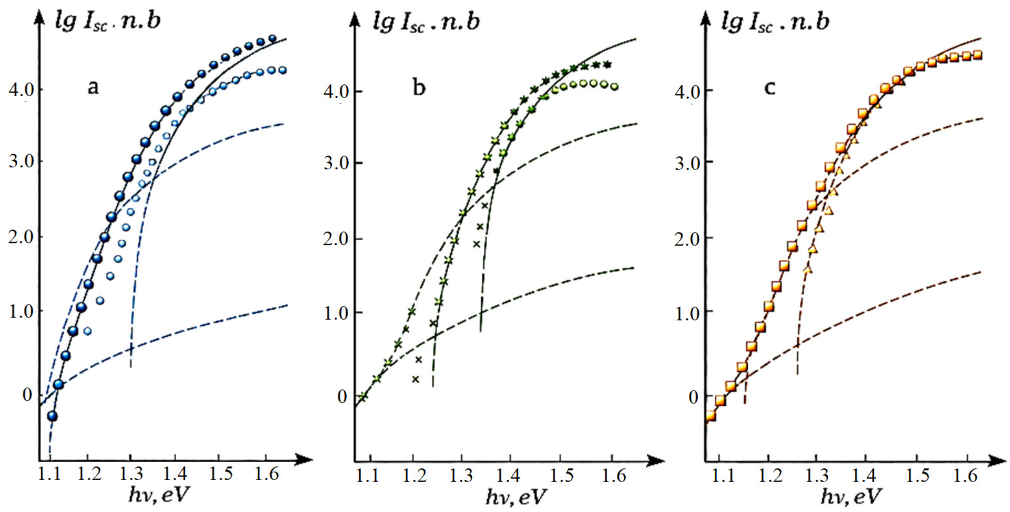

Figure 3. Short-circuit current spectra of CdTe (a) and CdTe:In films (b – freshly prepared; c – after thermal treatment) at T = 77 K (solid dots), and the theoretical spectra based on the photon capture cross-section (open dots, crosses, triangles, squares)

Surface morphology and crystal structure of the films studied by electron microscopy and spectroscopic methods

The surface morphology of CdTe polycrystalline thin films before and after thermal treatment was investigated using scanning electron microscopy (SEM). The obtained results clearly demonstrate that thermal treatment has a significant effect on the microstructural characteristics of the films.

The as-deposited (thermally untreated) CdTe film is characterized by an uneven and relatively disordered grain structure. The grains are irregular in shape, and their boundaries are poorly defined, with small particles and microdefects observed across the surface. This indicates a high density of grain boundaries and a relatively weakly compacted structure, which can increase the likelihood of charge carrier scattering and thus limit the film's electrophysical properties (Figure 4a).

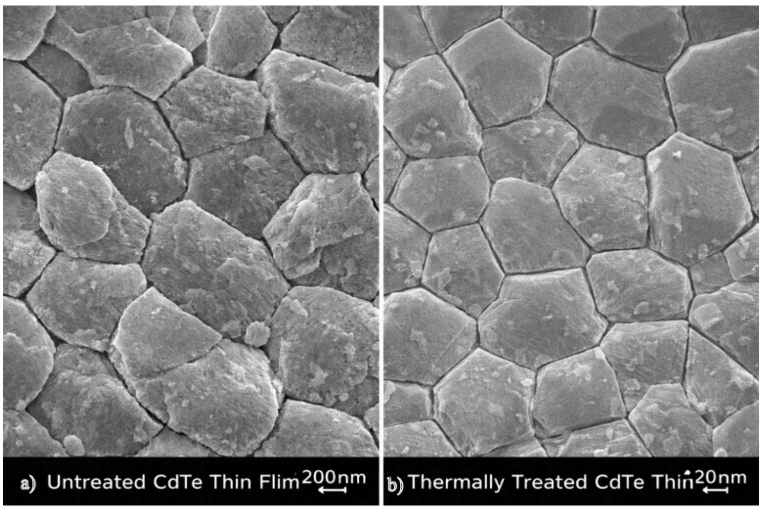

Figure 4. SEM images of CdTe films: (a) as-deposited and (b) after thermal treatment

In contrast, the thermally treated CdTe film exhibits a significantly improved microstructure. SEM images show an increase in average grain size, with grains appearing more regular and polyhedral. Grain boundaries are clear and smooth, and the film surface shows greater overall uniformity [12, 13]. This indicates that recrystallization and grain growth processes were activated during the thermal treatment (Figure 4b).

As a result of grain growth and structural densification, the number of grain boundaries decreases, thereby reducing charge-carrier recombination centers. Consequently, thermally treated CdTe films exhibit increased electrical conductivity, enhanced photosensitivity, and improved photoelectric properties. In addition, the reduction of surface defects can positively influence the film's optical absorption and interactions with photons.

Overall, the SEM results indicate that thermal treatment significantly improves the microstructural quality of polycrystalline CdTe thin films, promoting grain growth, structural densification, and enhanced surface uniformity. These microstructural changes are an important factor for increasing the efficiency of CdTe-based photovoltaic and photosensitive devices.

In the as-deposited CdTe:In sample (Figure 5a), the grains exhibit a relatively irregular and polygonal shape, with clearly defined grain boundaries. Numerous small spherical clusters (bright spots) are observed on the film surface. These clusters are associated with the uneven distribution of In dopants or the local formation of secondary phases. The non-uniform grain size and the high density of grain boundaries indicate a significant presence of structural defects in the film. As a result, strong charge-carrier scattering occurs at grain boundaries, leading to reduced electrical conductivity and an increase in recombination centers.

The morphological structure of thermally treated CdTe:In samples (Figure 5b) is significantly improved. The grains exhibit a more regular and larger polygonal shape, grain boundaries become smoother, and the surface density of the film increases [13, 14]. The reduction in the number of spherical clusters is explained by the redistribution of In atoms throughout the grain volume and the partial elimination of secondary phases. The increase in grain size reduces the number of grain boundaries, thereby enhancing charge-carrier mobility and decreasing resistivity.

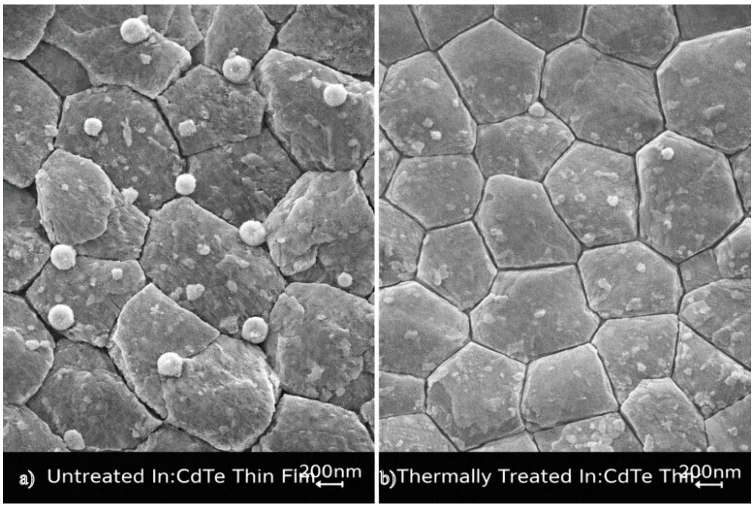

Figure 5. SEM images of as-deposited (a) and thermally treated (b) CdTe:In films

As a result of improved structural uniformity and reduced grain boundary effects in thermally treated CdTe:In samples:

- Charge carrier mobility increases;
- Resistivity decreases;
- Potential barriers at grain boundaries are reduced;
- Anomalous photovoltaic voltage is enhanced.

Thermal treatment significantly improves the morphological quality of In-doped CdTe polycrystalline films and optimizes their electrophysical and photoelectric properties. This makes these films a promising material for use in photodetectors and photovoltaic devices.

1. ***Phase identification:*** The main diffraction peaks in the experimental spectrum are located approximately at the following 2θ positions: ~23.8°, ~39–40°, ~46–47°, ~56°, and ~62–66° (Figure 6). These reflections correspond to the cubic CdTe crystal structure (zinc-blende, space group F-43m). By comparison with the ICDD reference card for CdTe (PDF 96-900-8841), the following crystallographic planes are identified:

2θ (°)	Miller indices (hkl)	Phase attribution
~23.8°	(111)	CdTe
~39.3°	(220)	CdTe
~46.5°	(311)	CdTe
~56.2°	(400)	CdTe
~62–66°	(331)/(422)	CdTe

2. ***Crystal structure and texture (preferential orientation):*** The (111) reflection exhibits the highest intensity in the diffraction pattern, indicating the presence of a strong (111) texture. This suggests that the crystallites predominantly grow along the (111) direction and that grain orientation is largely aligned with this energetically favorable plane. Such behavior reflects epitaxial or semi-oriented growth along the most thermodynamically stable crystallographic plane. For CdTe, the (111) plane possesses the lowest surface energy; therefore, this orientation is commonly dominant in polycrystalline thin films.

3. ***Presence of secondary phases:*** The lower panels also include separate reference cards for Cd and Te. In the experimental diffraction pattern, no distinct diffraction peaks corresponding to metallic Cd are detected. Likewise, no

dominant reflections attributable to the hexagonal Te phase are observed. This indicates that the segregation of free Cd or free Te is minimal, and the film is essentially composed of a single CdTe phase with well-controlled stoichiometry. If minor low-intensity additional peaks are present, they may be associated with micro-Te segregation or slight traces of Cd oxidation. Nevertheless, the dominant and clearly identified phase is CdTe.

4. ***Crystallite size estimation (Scherrer analysis):*** If the full width at half maximum (FWHM) of the (111) diffraction peak is known, the average crystallite size can be calculated using the Scherrer equation:

$$D = \frac{0.9\,\lambda}{\beta\cos\theta}. \tag{1}$$

Here: λ=1.5406 Å is the X-ray wavelength (CuKα radiation), β is the full width at half maximum (FWHM) of the diffraction peak expressed in radians, and θ is the Bragg angle corresponding to the diffraction peak position [15, 16].

The relatively narrow diffraction peaks observed in the spectrum indicate good crystallinity and the formation of relatively large crystallites, typically in the range of 30–100 nm.

5. ***Internal mechanical strain (IMS) and lattice parameter:*** If the (111) diffraction peak slightly shifts from its ideal position, this indicates the presence of internal mechanical strain in the film:

- A shift toward lower 2θ values (left shift) corresponds to lattice expansion (tensile strain).
- A shift toward higher 2θ values (right shift) corresponds to lattice contraction (compressive strain).

For cubic CdTe, the lattice parameter is approximately: $\alpha \approx 6.48$ Å

If the interplanar spacing d d is calculated from the experimental 2θ value using Bragg's law:

$$d = \frac{\lambda}{2\sin\theta} \tag{2}$$

where λ is the X-ray wavelength and $\theta = \frac{2\theta}{2}$, then the lattice parameter for cubic CdTe can be determined using:

$$a = d\sqrt{h^2 + k^2 + l^2} \tag{3}$$

Once calculated, the internal mechanical strain (IMS) in the film can be determined by comparing the experimentally obtained lattice parameter with the standard value.

6. ***Background level and amorphous component:*** The diffraction pattern exhibits a low background intensity along with well-defined and sharp crystalline peaks. This indicates a negligible amorphous component in the film and a high degree of crystallinity.

7. ***Photovoltaic significance:*** The strong (111) texture and high degree of crystallinity provide several important advantages, including reduced carrier recombination, a lower density of grain boundary defects, enhanced charge carrier mobility, and improved photoelectric response (optical response). These structural features are critical factors for enhancing the performance of CdTe-based solar cells.

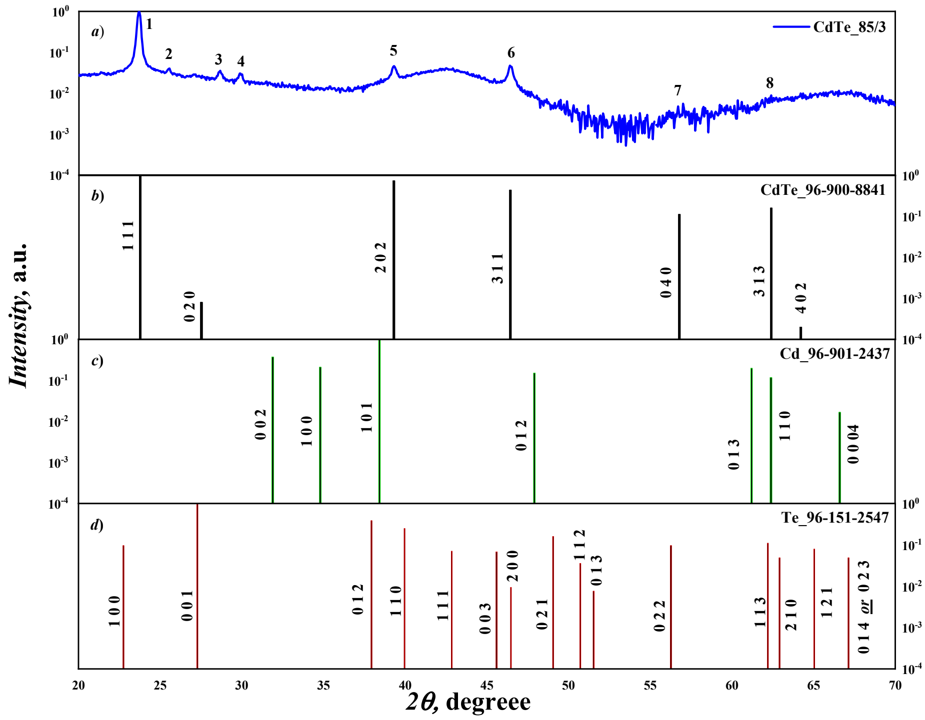

Figure 6. X-ray diffraction (XRD) patterns of the polycrystalline CdTe thin film: (a) experimental diffraction spectrum; (b) reference ICDD card for cubic CdTe (zinc-blende structure, PDF 96-900-8841); (c) Cd reference (PDF 96-901-2437); and (d) Te reference (PDF 96-151-2547).

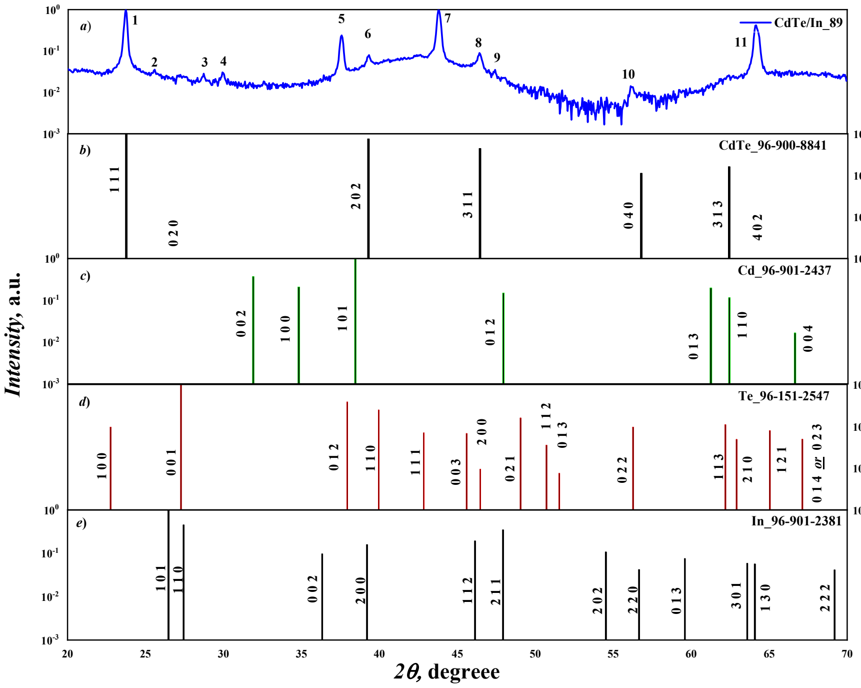

Figure 7. X-ray diffraction (XRD) patterns of the polycrystalline CdTe:In thin film: (a) experimental diffraction spectrum; (b) reference ICDD card of cubic CdTe (zinc-blende structure, PDF 96-900-8841); (c) Cd reference (PDF 96-901-2437); (d) Te reference (PDF 96-151-2547); and (e) In reference (PDF 96-901-2381).

1. ***Phase identification:*** In the experimental pattern (a), the main diffraction peaks are observed at approximately the following 2θ values: ~23.7° corresponding to (111), ~39.3° to (220), ~46.5° to (311), ~56° to (400), and ~62–66° to (331)/(422) (Figure 7). These reflections are fully consistent with the cubic zinc-blende crystal structure of CdTe (space group F-43m), in agreement with the ICDD reference card (PDF 96-900-8841). Therefore, the indium-doped film preserves the cubic CdTe phase as the dominant structural phase.

2. ***Effect of indium doping on the crystal structure:*** The lower panel includes the reference card for In (PDF 96-901-2381). In the experimental diffraction pattern, no distinct peaks corresponding to metallic indium are detected. Furthermore, no strong reflections associated with In_2Te_3 or other intermetallic phases are observed. This indicates that indium is incorporated substitutionally into the CdTe lattice, without phase segregation, leading to the formation of a single-phase solid solution.

3. ***Peak shift and lattice deformation:*** The atomic radius of indium is not smaller than that of cadmium (In ≈ 0.156 nm, Cd ≈ 0.148 nm). Therefore, when In atoms substitute Cd sites in the lattice, changes in the lattice parameter may occur, leading to slight shifts in the diffraction peak positions [17].

If the (111) diffraction peak shifts relative to that of pure CdTe: A shift toward lower 2θ values (left shift) indicates lattice expansion (tensile strain). A shift toward higher 2θ values (right shift) indicates lattice contraction (compressive strain).

Such peak shifts confirm the presence of internal mechanical strain (IMS) within the film.

4. ***Degree of crystallinity:*** In the diffraction pattern, the peaks are sharp and intense, the background level is relatively low, and the (111) reflection is dominant. These features indicate good crystallinity, a strong preferential texture, and oriented grain growth.

5. ***Texture:*** The (111) diffraction peak is significantly more intense than the other reflections, indicating preferential growth along the energetically stable (111) plane. This suggests a reduced grain boundary density and a lower concentration of recombination centers. Such structural characteristics positively influence the photovoltaic properties of the material.

6. ***Additional peaks:*** In the experimental diffraction pattern, additional peaks labeled 5, 6, 8, 9, 10, and 11 are observed. These features may be associated with lattice distortion induced by indium incorporation, microstrain effects, minor interstitial defects, or stress localized at grain boundaries. However, these peaks do not correspond to independent secondary phases, indicating that no separate crystalline phase is formed.

7. ***Structural quality assessment:*** The CdTe:In thin film is phase-pure, retains the cubic crystal structure, and exhibits a strong (111) preferential orientation. Indium is successfully incorporated into the lattice, and the film demonstrates a high degree of crystallinity.

8. ***Correlation with photovoltaic and electrical properties:*** Indium acts as a donor dopant in CdTe. Due to the improved structural quality, electrical conductivity increases, carrier concentration is enhanced, recombination processes are reduced, and the optical response is improved [18, 19].

DISCUSSION

In the CdTe photovoltaic sample, three defect levels are active: E_1, E_2, and E_3, which are associated with singly and doubly charged cadmium vacancies and excess tellurium, respectively [9]. In the as-prepared CdTe:In film, the E_1 level is not observed (Figure 3b), which is most likely attributed to charge-state saturation V_{Cd}^{--} and the formation of donor–acceptor pairs $I_n^+V_{Cd}^-$, with an electron transition energy to the conduction band of 1.18 eV. During heat treatment (HT) of the doped film, self-compensation between interstitial donors In^{+i} and vacancy-type acceptors V_{Cd}^{-j} occurs [3, 9], and the E_5 level appears in the Iqt spectrum (Figure 3c). This is most likely associated with the formation of defect pairs ($I_n^+V_{Cd}^-$) in the barrier region near the surface of the crystal grains. This is accompanied by a sharp increase in photoresistance and a simultaneous one-order-of-magnitude rise in U_{APV}. The contribution of the E_5 level to APV is associated with light absorption in the barrier region, which induces electron transitions from the E_5 level to the conduction band. Since the occupancy of this level decreases exponentially toward the grain surface, the contribution of E_5 centers to impurity-related APV is insignificant compared to that of the localized E_2, E_3, and E_4 centers (see Figure 3).

SEM analysis reveals that the surface morphology of CdTe and CdTe:In polycrystalline thin films is highly sensitive to heat treatment (HT). The as-deposited CdTe films exhibit irregular grains, indistinct grain boundaries, and dispersed microdefects, indicating insufficient structural compaction and a high grain boundary density. Such a microstructure promotes strong carrier scattering at grain boundaries, reduces mobility, enhances recombination, and consequently degrades electrical conductivity and photoelectric performance.

After HT, CdTe films exhibit significant grain growth, improved grain uniformity, and enhanced surface homogeneity, consistent with recrystallization processes. The increase in grain size reduces grain boundary density and recombination centers, thereby improving electrical conductivity and photosensitivity. Additionally, reducing surface defects stabilizes light absorption and enhances photon–matter interactions.

In CdTe:In films, the HT effect is more complex, influencing both grain morphology and the spatial redistribution of In dopants. In untreated samples, spherical clusters likely originate from non-uniform In distribution or localized secondary phases, acting as trap and recombination centers. HT significantly reduces these clusters, promotes grain enlargement, and enhances structural densification due to dopant redistribution toward energetically favorable configurations. The smoothing and reduction of grain boundaries decrease potential barriers, increase carrier mobility, and lower resistivity. This reduction in grain boundary density plays a crucial role in enhancing the anomalous photovoltage (APV).

XRD analysis confirms the preservation of the cubic CdTe lattice with strong (111) preferential orientation and high phase purity in both CdTe and CdTe:In films. Indium incorporation does not disrupt the crystal structure; instead, it maintains the structural quality required for efficient photovoltaic and optoelectronic applications. Overall, thermally treated CdTe:In thin films demonstrates improved structural, electrical, and photoelectric properties, confirming their strong potential for high-performance photodetectors and photovoltaic devices (Figure 6, 7).

CONCLUSIONS

XRD analysis confirms that both CdTe and CdTe:In thin films crystallize in the cubic zinc-blende structure (F-43m) with a strong (111) preferential orientation. The dominant (111) reflection and well-defined higher-order peaks ((220), (311), (400)) verify high phase purity and good crystallinity. No secondary phases related to metallic Cd, Te, or indium compounds were detected, indicating effective stoichiometric control and successful substitutional incorporation of In into the CdTe lattice. Slight peak shifts in CdTe:In suggest lattice distortion induced by indium doping.

Electrical and spectral measurements reveal a significant enhancement in photosensitivity and photoelectric response for CdTe:In films. Thermally treated samples exhibit a pronounced increase in short-circuit current and anomalous photovoltage (APV), confirming the dominance of the photovoltaic mechanism. Low-temperature (77 K) spectral analysis identifies deep energy levels (E_1–E_5) contributing to APV formation.

SEM observations demonstrate that thermal treatment promotes grain growth, structural densification, and improved surface uniformity. The reduction in grain boundary density enhances carrier mobility and suppresses recombination processes.

Overall, thermally treated polycrystalline CdTe:In thin films exhibit improved structural, electrical, and photoelectric properties, confirming their strong potential for high-efficiency photodetectors and photovoltaic applications.

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КОМПЛЕКСНИЙ АНАЛІЗ МОРФОЛОГІЇ, СТРУКТУРИ ТА ФОТОЕЛЕКТРИЧНИХ ВЛАСТИВОСТЕЙ ТОНКИХ ПЛІВОК CdTe та CdTe:In

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У цій роботі було всебічно досліджено фотоелектричні властивості та спектри струму короткого замикання плівок CdTe, легованих індієм (In). Дослідження охоплює спектральну чутливість і характеристики поглинання світла нелегованих, свіжоотриманих і термічно оброблених плівок CdTe:In. Було проаналізовано вплив рівня легування та температури термічної обробки на параметри фотоелектричного ефекту. Отримані результати показали, що легування індієм і подальша термічна обробка суттєво підвищують фотоелектричну ефективність плівок CdTe. Використовуючи спектроскопічні методи та електронну мікроскопію, було визначено хімічний склад, морфологію поверхні та ширину забороненої зони плівок, а також встановлено їх взаємозв'язок з оптичними та електричними властивостями. Отримані результати свідчать про те, що плівки CdTe:In є перспективними для застосування в сонячній енергетиці.

Ключові слова: *тонкі плівки CdTe:In; фотоелектричний ефект; спектри струму короткого замикання; аномальна фотонапруга (APV); глибокі енергетичні рівні; термічна обробка; матеріали для сонячної енергетики*