Effects of Vacuum and Air Annealing on Structural, Morphological, Optical, and Electrical Properties of Multilayer CdZnS Thin Films for Photovoltaic and Optoelectronic Applications

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ABSTRACT: Multilayer CdZnS (CZS) thin film was deposited on soda lime glass substrates. After deposition, the films were vacuum and air annealed at 100 °C, 200 °C, 300 and 400 °C for 1 h. Effects of vacuum and air annealing on structural, morphological, optical, and electrical properties of multilayer CZS films with increasing annealing temperature (IAT) were studied. The structural analysis revealed that the films were polycrystalline with hexagonal structure having a prominent/intensive peak along the (002) plane at 300 and 400 °C. The crystallite size of nanoparticles increased from 18.4 to 20.5 nm under air annealing and from 18.4 to 26.9 nm under vacuum annealing, showing the significance of annealing on nanoparticle grain growth. According to morphological analysis, the multilayer technique provides homogeneous film distribution over the substrate. The transmittance graphs of films revealed that it increased up to 92% in the visible and NIR regions under vacuum annealing and up to 52% under air annealing. Vacuum annealing enhanced the band gap energies more significantly than air annealing. The electrical resistivity increased with IAT, showing that structural, morphological, optical, and electrical properties of the multilayer thin films of CZS were strongly dependent on vacuum and air annealing.

INTRODUCTION

Ternary thin films have piqued attention in the fields of photovoltaic and optoelectronics due to their unique properties and wide range of applications. The structural, optical, electrical, and morphological characteristics of ternary semiconductor thin films may be adjusted using one or more variable components. The interest in the development of II–IV chalcogenide binary and ternary semiconductors is because of the potential for the researchers and scientists to enhance the efficiency of solar cells and optoelectronic devices by minimizing photon absorption energy losses and improving spectrum coverage of solar cells. Among such II–IV semiconductor materials, cadmium sulfide (CdS) has attractive properties like a high absorption coefficient, a wide band gap energy of 2.42 eV, a good transparency in the visible region of light, low resistivity, and photoconductive properties, making it a suitable candidate for light emitting diodes, diode lasers, photodetectors, and window layers in solar cells. When employed in solar cells, polycrystalline CdS has certain disadvantages due to its short band gap, thickness, and lattice mismatch, all of which contribute to a high defect density. Several properties are required to improve the performance of CdS as an effective window material for photovoltaic devices, including high conductivity to decrease solar cell electrical losses, reasonably high transparency, neither too thick to privilege absorption nor thin to avoid short circuiting, and higher photoconductivity to minimize changing the solar cell spectral response. This can be achieved by diffusing a suitable ratio of zinc (Zn) content into CdS, forming a ternary compound cadmium zinc sulfide (CZS), and the energy band gap can be tuned from 2.42 of CdS to 3.54 eV, the optimum band gap for ZnS. With the increase in band gap energy, CZS can be used as a window layer in photovoltaic cells. Using CZS instead of CdS as a window layer in the heterojunction photovoltaic device can decrease the absorption losses. There is an increase in voltage open circuit (voc) and short circuit current, in spite of a decrease in window absorption losses. Furthermore, CZS can lead to an increase in...
photocurrent in heterojunction devices.\textsuperscript{15} CZS thin films have a wide range of uses in the electronic, optical, and optoelectronic fields.\textsuperscript{16} 

CZS thin films have been fabricated using a variety of methods, including close space sublimation,\textsuperscript{17} spray pyrolysis,\textsuperscript{18} deep coating,\textsuperscript{19} metal organic chemical vapor deposition,\textsuperscript{20} screen printing,\textsuperscript{21} chemical bath deposition,\textsuperscript{22} and thermal evaporation.\textsuperscript{23} In the present study multilayer thin films of CZS have been fabricated by using a thermal evaporation technique and then vacuum and air annealed at different temperatures (100 to 400 °C), to study the annealing effect on optical, morphological, structural, and electrical properties of CZS films. Thermal evaporation is a common and the simplest method of physical vapor deposition (PVD). From this technique in a single run, with a very small amount of coating material, a large number of uniform thin film samples can be fabricated. Therefore, this technique is cost-effective and suitable for research and production of thin films as compared to other techniques. Combined postvacuum and air annealing effects on CZS films have not been previously reported.

\section*{RESULTS AND DISCUSSION}

The physical appearance of the films was found to be smooth and continuous, and no pin holes or cracks were seen on them after deposition. The coatings showed satisfactory adherence with substrates after a tape test.

**Structural Analysis.** The RBS spectra of as deposited, vacuum, and air annealed multilayer CZS films at 300 °C are shown in Figure 1. The RBS results confirmed the layer formation and thickness of the films. According to RBS data, thin films were approximately stoichiometric. Thicknesses of the layers were found out to be 45–55 nm for 10 layers of CdS and 8–11 nm for Zn compared to the desired 50 and 10 nm, respectively.

Diffusion is clearly visible in Figure 1. The results revealed that with vacuum annealing the layers are partially diffused while in air annealing layers are completely/totally diffused. The presence of Si, Ca, and O\textsubscript{2} in the RBS spectrum could be attributed to the substrate.

XRD is performed in the 2 theta range of 20 to 60° to evaluate the crystalline structure of CZS multilayer thin films. Figure 2 and Figure 3 show XRD profiles, which revealed that the films are polycrystalline with a hexagonal structure, having a preferential orientation along (002), and additional planes (101), (102), and (103) were observed.\textsuperscript{24–29} Figure 3 illustrates the XRD profile of as-deposited and vacuum annealed films at different temperatures. The 2θ values for the (002) plane for as-deposited and vacuum annealed films were 26.63, 26.73, 26.76, 26.77, and 26.79°, so there was no substantial peak shift that was noticed during the annealing process. The intensities of the films were decreased at 100 and 200 °C but increased for the films vacuum annealed at 300 and 400 °C, and a new peak emerged along the (103) plane. Sharp peaks indicated that the films are polycrystalline, which means crystallinity increased as the temperature increased.

Figure 3 illustrates the XRD profile of as-deposited and air annealed films at different temperatures. The 2θ values for the (002) plane for as-deposited and air annealed films were 26.63, 26.66, 26.68, 26.81, and 26.85°. It was observed that the intensity of the air annealed films was decreased. The CZS composition of all the samples was confirmed by XRD, and the crystallinity increased after annealing.\textsuperscript{26,29} After the annealing treatment the increase in grain size might be attributed to the enhancement in the mobility of the surface adatoms and the cluster of small grains coalesced, which led to the formation of bigger grains with better crystallinity.\textsuperscript{26,29,30}

The following empirical formulas were used to determine crystallite size \( D \), lattice spacing \( d \), lattice parameters \( a \), \( c \), dislocation density \( \delta \), and strain \( \varepsilon \) for the CZS films.

\begin{equation}
D = \frac{K\lambda}{\beta \cos \theta}
\end{equation}

\begin{equation}
d = \frac{\lambda}{2 \sin \theta}
\end{equation}

\begin{equation}
\frac{1}{d^2} = \frac{4}{3} \left( \frac{h^2 + hk + k^2}{a^2} \right) + \frac{l^2}{c^2}
\end{equation}

\begin{equation}
\delta = \frac{1}{D^2}
\end{equation}

\begin{equation}
\varepsilon = \frac{\beta \cos \theta}{4}
\end{equation}

In the above formulas, \( K \) is the shape factor, and its approximated value is 0.92, \( \lambda \) is the wavelength of X-ray source (1.5406 Å), \( \beta \) is the full width at half-maximum, and \( \theta \) is the diffraction angle in degrees. (\( h, k, l \)) are the Miller indices.

For the (002) peak, Tables 1 and 2 illustrate the structural parameters \( \delta \), \( D \), \( d \), \( a \), \( c \), and \( \varepsilon \) for the air and vacuum annealed films at different temperatures. The crystallite size of CZS films under air annealing increased from 18.4 to 20.5 nm, whereas under vacuum annealing it increased from 18.4 to 26.9 nm with increasing temperatures. According to the findings reported in Tables 1 and 2, the lattice parameters \( a \) and \( c \) decreased for air and vacuum annealing with increasing temperature. The strain increases, but the dislocation density decreases in both cases. The results of this study’s structural analysis are comparable with those of prior studies on CZS films made using closed space sublimation,\textsuperscript{31} chemical bath deposition,\textsuperscript{32} acidic chemical bath deposition,\textsuperscript{33} and diluted chemical bath deposition.\textsuperscript{34}
Figure 2. XRD analysis of vacuum annealed thin films.

Figure 3. XRD analysis of air annealed thin films.

Table 1. Variational Data in Structural Parameters of Air Annealing CZS Thin Films

| sample         | d  (Å) | a  (Å) | c  (Å) | D  (nm) | $\delta = 1/D^2$ (nm)$^{-2}$ | $\epsilon = \beta \cos \theta/4$ (lin-m)$^{-2}$ |
|----------------|--------|--------|--------|---------|-----------------------------|--------------------------------------------|
| CZS (as-deposited) | 3.345  | 4.151  | 6.690  | 18.4    | 0.00279                     | 0.002215                                  |
| CZS 100 °C       | 3.343  | 4.141  | 6.686  | 19.3    | 0.00268                     | 0.002222                                  |
| CZS 200 °C       | 3.341  | 4.125  | 6.672  | 20.2    | 0.00245                     | 0.003165                                  |
| CZS 300 °C       | 3.330  | 4.115  | 6.661  | 20.4    | 0.00241                     | 0.003793                                  |
| CZS 400 °C       | 3.330  | 4.114  | 6.660  | 20.5    | 0.00238                     | 0.003706                                  |

Table 2. Variational Data in Structural Parameters of Vacuum Annealing CZS Thin Films

| sample         | d  (Å) | a  (Å) | c  (Å) | D  (nm) | $\delta = 1/D^2$ (nm)$^{-2}$ | $\epsilon = \beta \cos \theta/4$ (lin-m)$^{-2}$ |
|----------------|--------|--------|--------|---------|-----------------------------|--------------------------------------------|
| CZS (as-deposited) | 3.345  | 4.151  | 6.690  | 18.4    | 0.00279                     | 0.002215                                  |
| CZS 100 °C       | 3.335  | 4.150  | 6.671  | 20.2    | 0.00245                     | 0.004078                                  |
| CZS 200 °C       | 3.332  | 4.146  | 6.665  | 25.5    | 0.00153                     | 0.004327                                  |
| CZS 300 °C       | 3.331  | 4.144  | 6.651  | 26.6    | 0.00141                     | 0.004430                                  |
| CZS 400 °C       | 3.331  | 4.142  | 6.650  | 26.9    | 0.00138                     | 0.004503                                  |
**Morphological Analysis.** The micrographs of CZS thin films air and vacuum annealed at 100 °C, 200 °C, 300 °C, and 400 °C were examined using scanning electron microscopy (SEM). In Figure 4a–e and Figures 5a–d, SEM micrographs revealed that films are uniform, crack free, and homogeneous. The micrographs also showed that the grain size increased

![Figure 4. SEM and EDAX of (a) as-deposited, (b) 100 °C, (c) 200 °C, (d) 300 °C, and (e) 400 °C air annealed CZS films.](image-url)
during the annealing process as the temperature increased. Transparency and higher light transmission result from a smooth surface, whereas uneven coatings scatter light. Significant study has shown that a nonsmooth surface can produce light scattering. The existence of compact films and smooth grains is seen in SEM scans of the films, resulting in improved transmission efficiency. More energy is available for crystallite growth with the increase in the annealing temperature, which improves surface uniformity and crystallinity, resulting in a decrease in defects and surface roughness.

EDAX analysis is used to examine the elemental compositions of the thin films. Cadmium, zinc, and sulfur are present in the usual EDAX pattern of the CZS, as well as silicon, calcium, and oxygen attributed to soda lime glass substrates. EDAX results are in good agreement with RBS results. Due to the high concentrations of Cd and S in comparison to Zn, the EDAX spectrum displayed significant peaks for these elements. Tables 3 and 4 reflect the EDAX results of air and vacuum annealed CZS films, which indicate that sulfur content is higher in all deposited films.

**Optical Properties.** The optical parameters like absorption coefficient, energy band gap, refractive index, etc. can be calculated by using transmission data (300 to 2500 nm) in the UV–vis–NIR range and fitting the transmission curve by the following equation:

\[
T = \frac{Ax}{B - Cx \cos \phi + Dx^2}
\]
The parameters used in the above equation are defined as

\[ A = 16n^2s, \quad B = (n + 1)^3(n + s^2), \quad C = 2(n^2 - 1)(n^2 - s^2), \quad D = (n - 1)^3(n - s^2), \quad \text{and} \quad \Phi = 4\pi n d / \lambda, \quad x = \exp(-\alpha d). \]

Here, \( n, \alpha, \lambda, \) and \( d \) describe the refractive index, absorption coefficient, wavelength, and thickness of the film. \( s \) is the refractive index of a glass substrate. The refractive index \( n \) of a film can be calculated as

\[ n = a + \frac{b}{\lambda^2}, \quad a \text{ and } b \text{ are constants} \tag{7} \]

The absorption coefficient \( \alpha \) of the films can be calculated as

\[ \alpha = c + \frac{f}{\lambda} + \frac{g}{\lambda^2}, \quad c, f, \text{ and } g \text{ are constants} \tag{8} \]

The typical fitted curve of the vacuum annealed CZS film at 400 °C is shown in Figure 6. It showed that the measured transmission and fitted data coincide each other. The absorption coefficient \( \alpha \) in the high absorption region can be calculated by using the values of \( n \) and \( d \) from the fitted curve. The exact solution of eq 7 can be calculated as

\[ x = \frac{[C \cos(\phi) + A/T] - [(C \cos(\phi) + A/T)^2 - 4BD]^{1/2}}{2D} \tag{9} \]

\[ \alpha = -\frac{1}{d}\ln(x), \text{ as these factors are explained above.} \]

In the design and study of optoelectronic devices as well as photovoltaic applications, the optical characteristics of the materials are important. Figure 7 and Figure 8 show transmittance plots as a function of wavelength in the range of 300–2500 nm for air and vacuum annealed CZS films. The transmittance plots show the presence of interference fringes, which confirm the homogeneous and smooth nature of deposited films. A remarkable difference in transmittance plots between air and vacuum annealing has been observed. Near the UV range, the decrease in transmittance is due to the glass absorption edge. As the temperature increases from 100 to 400 °C, there is a remarkable increase in transmittance in the visible (VIS) and infrared (IR) region from 9% to 93% under vacuum annealing. Especially, the sample annealed at 300 and 400 °C shows a 92% transmittance, which is required in photovoltaic applications. The high transmittance of the films is an indication for their improved crystalline nature and

| Table 3. Elemental Composition (EDAX) of Air Annealed CZS Films |
|------------------|------------------|------------------|------------------|------------------|------------------|
| element          | atom % as-deposited | atom % at 100 °C | atom % at 200 °C | atom % at 300 °C | atom % at 400 °C |
| cadmium          | 36.30             | 37.41            | 38.23            | 38.34            | 39.12            |
| sulfur           | 49.50             | 49.49            | 49.52            | 50.10            | 50.07            |
| zinc             | 14.20             | 13.10            | 12.25            | 11.56            | 10.81            |
| total            | 100               | 100              | 100              | 100              | 100              |

| Table 4. Elemental Composition (EDAX) of Vacuum Annealed CZS Films |
|------------------|------------------|------------------|------------------|------------------|------------------|
| element          | atom % as-deposited | atom % at 100 °C | atom % at 200 °C | atom % at 300 °C | atom % at 400 °C |
| cadmium          | 36.30             | 39.09            | 40.83            | 42.29            | 43.42            |
| sulfur           | 49.50             | 49.69            | 49.82            | 50.15            | 50.27            |
| zinc             | 14.20             | 11.22            | 9.35             | 7.56             | 6.31             |
| total            | 100               | 100              | 100              | 100              | 100              |

Figure 6. Fitted plot of vacuum annealed CZS film at 400 °C.

Figure 7. Transmittance plot of air annealed films.

Figure 8. Transmittance plot of vacuum annealed films.
high degree of stoichiometry.\textsuperscript{39} Light is less dispersed by decreasing grain boundaries as the surface grain size grows. As a result, the transmittance of the material increases as the temperature increases.\textsuperscript{40} The obtained spectra revealed the impacts of temperature annealing on optical parameters such as band gap energy, absorption coefficient, etc.\textsuperscript{40,41} In the visible range, CZS films were transparent, but in the infrared range, they were much more transparent. These results are comparable with the results reported in refs\textsuperscript{29} and \textsuperscript{33} and are found to be better than those reported in refs\textsuperscript{31} and \textsuperscript{32}. Because of the significant absorption in the UV region, film transmittance in this region is low. On the other hand, samples under air annealing showed overall 52% transmittance between 100 to 400 °C. Only 30% transmittance was achieved in the visible and IR regions for the sample annealed at 300 and 400 °C, respectively.

The Tauc equation \( \alpha h\nu (\nu - E_g)^{1/2} \) was used to compute the energy band gap \( E_g \) of the films.\textsuperscript{42} This can be done by drawing a graph between the \( (\alpha h\nu)^2 \) vs \( (h\nu) \) curves to \( (\alpha h\nu)^2 = 0 \). Zn ions have smaller radii than Cd ions. When Zn ions replaced Cd ions in films, the size of the lattice constants reduced. As the lattice constants reduced, the interaction between the wave functions associated with the valence electrons increased, resulting in an increase in the energy band gap.\textsuperscript{43} Figure 9a,b shows that the resulting energy band gaps for vacuum and air annealed samples between 100 and 400 °C are (1.96 eV, 2.22 eV, 3.05 eV, 3.16 eV) and (1.38 eV, 1.43 eV, 2.14 eV, 2.50 eV), respectively. Since ZnS has a larger band gap than CdS, the increase in the optical band gap is attributed to expansion of the energy band provided by ZnS. The energy band gap finding showed that these results are comparable with those of refs\textsuperscript{33} and \textsuperscript{36}.

**Electrical Properties.** Figure 10a,b depicts the electrical resistivity of CZS multilayer thin films under air and vacuum annealing as a function of increasing temperature from 100 to 400 °C. Figure 10a,b shows clearly that the electrical resistivity under air and vacuum annealing increases as the temperature increases. In the case of vacuum annealed films, resistivity is larger than that of air annealed films. For vacuum annealed samples we have found the resistivity of 2.99 × 10^5 Ω cm to 1.88 × 10^6 Ω cm is less than that reported by ref\textsuperscript{11}, whereas it is found to be 7.13 × 10^2 Ω cm to 6.7 × 10^4 Ω for air annealed...
samples, comparable with the results reported by ref 33. The increase in resistivity could be related to the increase in the band gap energy as the temperature rises. Furthermore, the increase in crystallinity, the stoichiometry, and the reduction of residual stresses associated with multilayer films could also be responsible. Other factors that may contribute to an increase in resistivity include oxygen vacancies in air annealing, a decrease in the Zn interstitial site in the films, and the CZS film fabrication technique.

**CONCLUSIONS**

A comparative study for the vacuum and air annealing effect on multilayer CZS thin films in the temperature range of 100–400 °C was performed for 1 h. The multilayer CZS thin films fabricated on a glass substrate were found to be polycrystalline in nature, having hexagonal structure with a prominent peak along the (002) plane. The crystallinity and broadening of peaks improved with the increase of the annealing temperature. The Rutherford backscattering technique confirmed the layer formation and thickness of the multilayer CZS thin films. SEM micrographs revealed that the grain size of CZS films enhanced as the annealing temperature was increased. Annealing significantly enhanced the transmission and overall feature of the films. A remarkable difference in transmittance plots between air and vacuum annealing has been observed. Overall, 92% transmittance in the visible/IR range under vacuum annealing and 52% transmittance in air has been observed. The band gap has been found in the range of 1.96 eV to 3.16 eV and 1.38 eV to 2.50 eV for vacuum and air annealing, respectively. The band gap energy increased as the annealing temperature rose, which could be related to quantum confinement phenomena. The electrical resistivity of multilayer CZS films under vacuum or air annealing increased as the temperature increases. In the case of vacuum annealed films, resistivity is larger than that of air annealed films. We have elaborated a comparative study on multilayer CZS films for the prospective of vacuum and air annealing in thin film fabrication for researchers and scientists to enhance the effectiveness of thin films in photovoltaic and other optoelectronic devices. The results are potentially useful for window layers in CIGS and CdS/CdTe photovoltaic cells.

**EXPERIMENTAL PROCEDURE**

Highly pure (99.999%) CdS and (99.999%) Zn materials were used as the source materials for the deposition of the CdS and Zn multilayer thin film on soda lime glass substrates using the thermal evaporation (resistive heating) technique. The multilayer thin film comprised 20 layers, 10 each of CdS and Zn as shown in Figure 11.

**Sample Preparation.** Before deposition, the substrates were cleaned with detergent and then washed in running water. These substrates were cleaned in an ultrasonic bath with isopropyl alcohol. A high vacuum coating system (Edward 610A) was used for the deposition of the films. The chamber was maintained at a vacuum of ~1 × 10⁻⁵ mbar during film deposition. The substrates were heated to 150 °C (30 min) for degassing and then cooled to room temperature (25 °C) before deposition. During deposition, the substrates were held at an ambient temperature (25 °C). FTM7, a fine crystal quartz thickness monitor, was used to analyze the film thickness and deposition rate. The deposition rate for CdS was 0.70 nm/s, and for Zn it was 0.15 nm/s. The distance between the source and the substrate was fixed at 30 cm, and the substrate holders were rotated at 10 rpm.

The as-deposited films were first vacuum annealed while maintaining a vacuum of 1 × 10⁻⁵ mbar, and later as-deposited films were air annealed at various temperatures ranging from 100 to 400 °C respectively.

**Experimental Techniques.** X-ray diffraction (XRD) was used to reveal structural analysis carried out at room temperature employing an X-ray diffractometer (Bruker D8 Discover) instrument using a Cu Kα source having a wavelength of λ = 0.15418 nm. Optical parameters at room temperature in the wavelength range of 300 to 2500 nm were recorded by using an ultraviolet, visible, and near-infrared (UV–vis–NIR) spectrophotometer (PerkinElmer Lambda 19) equipped with UV Win software. The band gap energies of these films were estimated by fitting transmission data. The surface morphology of the films was investigated using a field emission scanning electron microscope (TESCANMAIA3) equipped with an Octane Elite EDAX detector. At a voltage of 20 kV, the energy-dispersive X-ray spectroscopy (EDAX) investigation was carried out. The multilayer film’s layer structure was confirmed by using the Rutherford back scattering (RBS) technique. Incident He⁻ ions having energy of 1.995 MeV were used, and the backscattering angle was fixed at 170°. Backscattered particles were detected using an SSB detector with a resolution of 13 keV. The software XRUMP and SIMNRA were applied for analysis. The electrical resistivity of the films was measured with a Keithly 2410-C, 1100, source analyzer using a two-probe method.

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**Figure 11.** Schematic diagram of the prepared CZS films.
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Author Contributions
This work was carried out in collaboration among all authors. Khalid Bashir prepared samples and wrote the original draft of the manuscript. Muhammad Ashraf and Nasir Mehbbo supervised this research. Abid Zaman, Vineet Tirth, and Ali Algahtani did the final writing review, corrections, and editing. Asad Ali and Turab Ali helped with the methodology and measurements. Muhammad Mushtaq prepared content analysis and graphical arrangements. Khaled Althubeiti helped with software, formal analysis, and funding acquisition. All authors read and approved the final manuscript.

Notes
The authors declare no competing financial interest.

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