

Development of rf Sputtered, Cu-Doped ZnTe for Use as a Contact Interface Layer to p-CdTe

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Cu-doped ZnTe films deposited by rf-magnetron sputtering have been analyzed with the intention to use this material as a contact interface in CdS/CdTe thin-film photovoltaic solar-cell devices. It is observed that unless careful attention is made to the pre-deposition conditioning of the ZnTe target, the electrical resistivity of thin films (~ 70 nm) will be significantly higher than that measured on thicker films (~ 1.0 μm). It is determined that N contamination of the target during substrate loading is likely responsible for the increased film resistivity. The effect of film composition on the electrical properties is further studied by analyzing films sputtered from targets containing various Cu concentrations. It is determined that, for targets fabricated from stoichiometric ZnTe and metallic Cu, the extent of Zn deficiency in the film is dependent on both sputtering conditions and the amount of metallic Cu in the target. It is observed that the carrier concentration of the film reaches a maximum value of $\sim 3 \times 10^{20} \text{ cm}^{-3}$ when the concentrations of Te and (Zn+Cu) are nearly equal. For the conditions used, this optimum film stoichiometry results when the concentration of metallic Cu in the target is ~ 6 at. %.

Key words: Contact interface layer, Cu-doped ZnTe, rf-magnetron sputtering

INTRODUCTION

In recent years, photovoltaic (PV) solar cells and modules incorporating thin-film CdTe absorber layers have achieved noteworthy conversion efficiencies, placing these device structures in the forefront of potential candidates for large-area, terrestrial applications.¹ However, to realize the full potential of this technology, issues relating to the fabrication of stable and low-resistance electrical contacts to p-CdTe must be addressed.² In materials such as p-CdTe, ohmic metal semiconductor contacts are not expected to form readily.³ In these cases, contact schemes that rely on quantum-mechanical tunneling at the contact interface are typically investigated. This type of contact is usually produced by doping the semiconductor heavily at the contact interface. Unfortunately, for p-

CdTe, this approach is limited by the inability to produce a CdTe layer with sufficiently high p⁺ doping. Because of these issues, identifying alternate contacting schemes continues to be a topic of considerable interest.

One possible technique to establish the required contact parameters is to utilize a separate interfacial layer between the metal contact and the CdTe. For this application, the interfacial layer must provide both a negligibly small valence-band discontinuity with the p-CdTe, and also be able to be doped highly p-type ($\sim 10^{20} \text{ cm}^{-3}$) at the outer metal contact in order to facilitate tunneling. Because of its electrical properties relative to CdTe, it is believed that an interface composed of thin-film, p⁺-ZnTe can meet these criteria.⁴ (See Fig. 1.) Nevertheless, relatively few studies have been undertaken to produce and analyze the type of material and deposition processes appropriate for this application. For example, although the deposi-

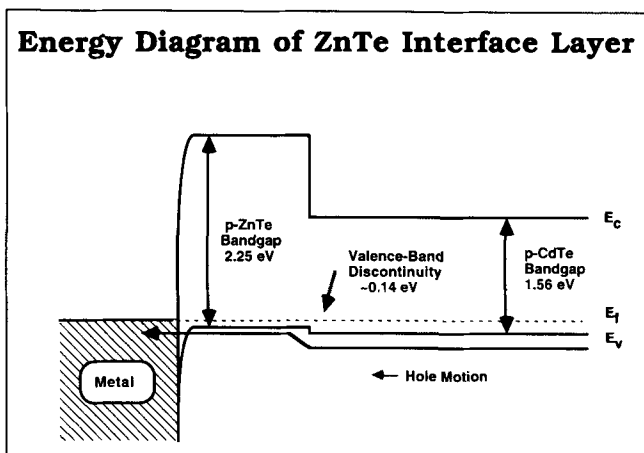


Fig. 1. Energy diagram illustrating main components and function of a p-ZnTe:Cu interface layer in a p-CdTe/metal contact.

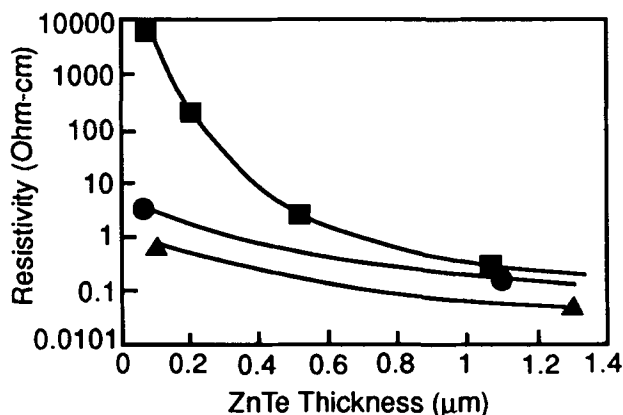


Fig. 2. Dependence of film resistivity on film thickness illustrating the effect of target preconditioning time and peak deposition rate. For all depositions: Cu concentration in ZnTe films = ~ 6 at.%, substrate temperature = 300°C . Squares: Deposition rate = 10 nm min^{-1} , preconditioning time = 5 min. Circles: Deposition rate = 10 nm min^{-1} , preconditioning time = 60 min. Triangles: Deposition rate = 40 nm min^{-1} , preconditioning time = 15 min.

tion of p⁺-ZnTe contact layers by molecular beam epitaxy has been investigated for use in ZnSe blue and blue/green laser diodes,⁵ the economics of PV manufacturing will likely preclude the use of this deposition technique for solar cells. In the case of PV devices, deposition techniques designed for large areas and high rates, such as sputtering or vapor transport, are more appropriate choices. Additionally, because the doped ZnTe will be deposited onto finished CdS/CdTe polycrystalline device structures, deposition processes that utilize relatively low deposition temperatures ($<300^\circ\text{C}$) may help to limit impurity diffusion through grain boundaries in the CdTe.

In this work, we report on recent investigations in which rf-magnetron sputtering is used to produce Cu-doped ZnTe (ZnTe:Cu). Two related studies are presented. The first examines the effect that predeposition conditioning of the sputtering target has on the electrical resistivity of very thin ZnTe:Cu films ($\sim 70 \text{ nm}$ thick). In the second study, the dependence of the compositional and electrical properties of thick ZnTe:Cu films ($\sim 1.0 \mu\text{m}$) on the concentration of

metallic Cu in the sputtering target are investigated. These studies suggest that ZnTe:Cu films formed by rf sputtering have potential for meeting the requirements of the CdTe-contact interface.

EXPERIMENTAL

The doped and undoped thin-film ZnTe layers used in these investigations are deposited by rf-magnetron sputtering at a frequency of 13.56 MHz. Except where otherwise noted, all depositions were performed on cleaned (soda-lime) glass. Substrate cleaning was accomplished by soaking the glass substrates for 60 min in an ultrasonically agitated solution of 5% detergent (Contrad 70) and deionized water maintained at $\sim 60^\circ\text{C}$. The samples were then rinsed in a tank of clean deionized water, maintained at 80°C for 5 min, and finally rinsed in a tank of cold deionized water. ZnTe deposition is performed in a Unifilm Technologies PVD 300, multi-source, planetary-motion sputtering system. The system is cryogenically pumped, and base pressures of $\leq 2 \times 10^{-7}$ Torr were established before each deposition (minimum system base pressure is $\sim 7 \times 10^{-8}$ Torr). Except as noted, sputtering is performed in a pure Ar ambient. Flow of research-grade Ar is set prior to throttling the cryopump and controlled via needle valves (Ar flow $\approx 70 \text{ cm}^3 \text{ min}^{-1}$). Ar (and N₂) flow is monitored with an ion gauge, and throttled chamber pressure is monitored with a Convectron gauge that has been calibrated against a capacitive manometer.

The sputtering source used for this study is a 5.08 cm US Gun II, fitted with $5.08 \times 0.635 \text{ cm}$ planar targets. The source operates in a sputter-down configuration in a voltage-control mode with voltages fixed at 59 or 117 V for peak rates of 10 or 40 nm min^{-1} , respectively. Source-to-substrate distance for all depositions is fixed at $\sim 2.86 \text{ cm}$, with the separation distance measured between the target (cathode) surface and the substrate. Although the system is capable of computer-controlling both the axial rotation and orbital motion of the substrate (used to achieve enhanced deposition uniformity), for these experiments, the axial rotation was disabled to permit the use of a substrate heater. Orbital motion involved moving the substrate every 50 s between positions located at $\pm 1.8 \text{ cm}$ from the axial center of the planar target. The substrate heater is composed of a solid Cu block embedded with cartridge heaters and a thermocouple. The targets are hot-pressed-powder mixtures of ZnTe (99.999% pure) and metallic Cu (99.9% pure), purchased from Cerac, Inc. (Milwaukee, WI). Additionally, a witness sample was fabricated simultaneously with one of the ZnTe:Cu targets (dimensions: $\sim 2.54 \text{ cm}$ diameter $\times \sim 0.2 \text{ cm}$ thick, nominally 6.2 at.% Cu). This witness sample was analyzed in order to determine if the Cu is uniformly distributed within the target, if the Cu concentration of the target is within specified limits, and if stoichiometry differences between the target and the film can be observed.

The samples prepared for this study were single

layers of Cu-doped and undoped ZnTe, nominally ~ 1.0 μm or ~ 70 nm thick and were deposited at various deposition conditions. Thickness measurements of the ~ 1.0 μm thick and the 70 nm thick samples were performed with a Veeco DekTak³ profilometer and a Rudolph Research Ellipsometer, respectively. Electrical characterization of the 1.0 μm thick samples was performed using Hall measurements (Van der Pauw technique). However, because of the high sheet resistance of the 70 nm thick samples, resistivity analysis for these samples was performed using a four-point probe. Compositional analysis was performed using wavelength-dispersive spectroscopy (WDS, Cameca Model MBX electron microprobe). This measurement was calibrated using an undoped, crystalline ZnTe standard (acquired from Eagle Pitcher), which was mechanically polished with 1 μm diamond grit. Depth-profiling compositional analysis was performed using secondary ion mass spectroscopy (SIMS, Cameca IMS3F). Analysis of the surface morphology was performed using scanning electron microscopy (SEM, JEOL Model JSM 840).

RESULTS AND DISCUSSION

Effects of Target Predeposition Conditioning on Film Electrical Resistivity

In previous work with ZnTe:Cu films, the primary motivation was to establish baseline electrical and structural properties for rf-sputtered films at thicknesses similar to that considered for use in PV devices (~ 1.0 μm). By studying these relatively thick films, an added advantage was gained in that Hall analysis could be employed because the greater film thickness significantly reduced the sheet resistance. Although this avenue of studying thick films added significantly to the basic understanding of the material properties, the need to perform optical analysis requires the fabrication of samples with much thinner films (~ 70 – 100 nm). Because, ultimately, data from both thick and thin films will be used in the same model, it is critical that the electrical properties of the thinner films be nominally identical to the thicker films. Additionally, because it is possible that current transport at a (polycrystalline) p-CdTe/p⁺-ZnTe interface may be assisted by tunneling, it is essential to be aware of differences in the electrical properties of the initial ZnTe layers (i.e., processes other than diffusion across the valence-band discontinuity may contribute to interface resistance). Unfortunately, once the thinner ZnTe:Cu films were deposited and analyzed, it was noted that the electrical resistivity of these films was more than 1000 times greater than those measured on thicker films. (See Fig. 2.) In light of these observations, we performed several specially designed experiments to identify the reason for this difference in resistivity.

The experiments were guided by the knowledge that, in addition to smaller grain size, the thinner ZnTe:Cu films will be more susceptible to contamination from the substrate and/or the target surfaces

than the thicker films. These possible sources of contamination were investigated by comparing depositions performed on both soda-lime and borosilicate (Corning 7059) substrates and by altering the target predeposition conditioning. Results indicated that, although the electrical properties of the first ~ 100 nm of ZnTe:Cu are not strongly dependent on the type of glass substrate used, they are critically dependent on the procedures used for target conditioning. As shown in Fig. 3, it is observed that by increasing the target predeposition time from 5 to 60 min, the electrical resistivity of a 70 nm thick ZnTe:Cu film is reduced from ~ 6000 to ~ 3 $\Omega\text{-cm}$ (6 at.% Cu, 10 nm min^{-1} , 300°C substrate temperature). It is also observed that, by incorporating both a similar predeposition treatment (i.e., predeposition rate \times predeposition time = constant) and a higher deposition rate (increasing the rate from 10 nm min^{-1} to 40 nm min^{-1}), the resistivity of a 70 nm thick film is reduced further to ~ 0.3 $\Omega\text{-cm}$. (See Fig. 2.) It is also noted in Fig. 2 that the effect of longer predeposition conditioning results in a slightly reduced resistivity for thicker films. However, even with a 60 min target predeposition time, the resistivity of the 70 nm thick films remains about an order of magnitude higher than that measured for a 1.0 μm thick film deposited under the same conditions. It is speculated that increased grain-boundary scattering and/or impurity compensation from residual contamination could lead to the observed higher resistivity. Unfortunately, because of the high sheet resistance of these thinner films, Hall measurements are not possible with the available apparatus.

The above observations suggest that the primary cause of the high resistivity initially noted in the thinner ZnTe:Cu films is linked to contamination of the sputtering target by air during sample loading procedures. To investigate this further, comparative SIMS analysis was performed on two test samples. Both samples were sputtered from the same target (i.e., nominally identical Cu concentration of ~ 6 at.%). However, for one sample, the target was predeposited for 5 min (Sample #1, $\rho \cong 6000$ $\Omega\text{-cm}$), while the other sample target was predeposited for 60 min

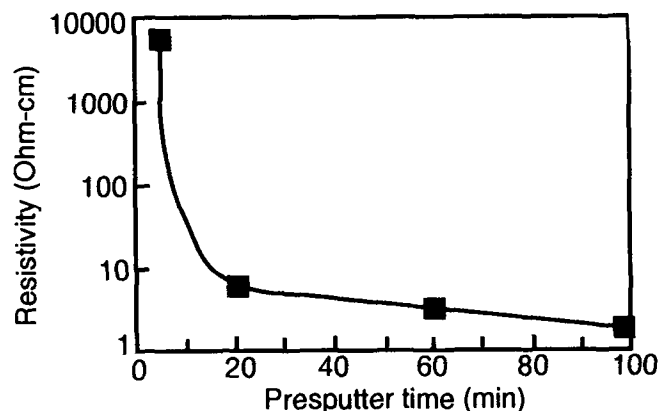


Fig. 3. Dependence of thin ZnTe:Cu film resistivity on target predeposition time. Film thickness ~ 70 nm, Cu concentration in film ~ 6 at.%, deposition rate = 10 nm min^{-1} , substrate temperature = 300°C .

(Sample #2, $\rho \approx 3 \Omega\text{-cm}$). Depth-profiling SIMS analysis indicates that Sample #1 contains more N than observed in Sample #2. Assuming that N contamination contributes to the high resistivity of the thinner films, several ZnTe:Cu sputter depositions were performed in a N-containing ambient. Results indicate that, even at the smallest N_2 flow that could be controlled, the presence of N increases the resistivity of the ZnTe:Cu film from $\sim 3 \Omega\text{-cm}$ to $\sim 25,000 \Omega\text{-cm}$ ($\sim 1 \times 10^{-5}$ Torr N_2 [UHP-grade N_2] mixed with 7.8×10^{-4} Torr Ar, pressures measured before throttling to 1×10^{-2} Torr). Higher N_2 flows produce films with resistivities too high to measure using available equipment. Although this observation provides strong support for the possibility of N contamination from the target surface increasing film resistivity, it is a curious result in view of the success of N-dopant incorporation in molecular beam epitaxy (MBE) grown ZnTe.⁵ However, considering the process differences between ZnTe:N films grown by sputter deposition and MBE, the possibility of significant material differences remains reasonable.

Effects of Cu-Doping Level on Film Compositional and Electrical Properties

In earlier work, it was reported that sputtered ZnTe films tend to be Zn-deficient relative to the specified target stoichiometry. It was also reported that the extent of Zn deficiency can be modified slightly by the choice of sputtering conditions (e.g., chamber pressure, source-to-substrate distance, and substrate temperature).² Although any Zn deficiency would be undesirable in the fabrication of high-resistivity, stoichiometric ZnTe films, it is believed that a limited amount of Zn deficiency could be used advantageously to produce p^+ ZnTe. In this case, a Group I acceptor (such as Cu) could substitute for the missing Zn. It follows that optimum electrical activation of the dopant should occur at a Cu-dopant concentration approximately equal to the level of Zn deficiency. At higher or lower Cu concentrations, excess Te or Cu would likely reduce the electrical quality of the film and also increase the possibility of (unwanted) diffusion of Cu toward the CdS/CdTe junction region.

In order to test this speculation further, in this work the dependence of film stoichiometry on target composition is investigated in more detail. First, WDS compositional analysis is used to compare the composition of a ZnTe:Cu witness target to the composition measured in a film sputtered from a nominally identical sputtering target (e.g., the witness target is pressed from the same powder mixture as the sputtering target). These comparisons are used to check the target composition resulting from the fabrication procedures, as well as to investigate previous speculation that the films are Zn-deficient relative to the target. Second, effects due to the amount of Cu concentration in the target are studied by depositing a series of ZnTe films from a set of targets fabricated to include various Cu concentrations (six targets: ~ 0 , 1.4, 3.7, 6.2, 9.4, 10.9 at.% Cu, measured in film). For

this set of depositions, sputtering conditions previously found to provide material properties optimal for electrical measurements are used (sputtering rate = 40 nm min^{-1} , substrate temperature 300°C , thickness = $\sim 1.0 \mu\text{m}$ target preconditioning time = 60 min).

Wavelength dispersive spectroscopy analysis of the witness target indicates that a direct comparison of the composition of a ZnTe:Cu film with the composition of a target is difficult because of several issues. First, unlike a sputtered ZnTe:Cu film, which is composed of *Cu-doped ZnTe*, the witness target is composed of *individual particles* of ZnTe and Cu. Furthermore, the particles used to fabricate the targets are large (~ 325 mesh; particles $\geq 75 \mu\text{m}$ diameter) compared to the typically used WDS spot size ($\sim 20 \mu\text{m}$). For these reasons, the point-to-point variation of the WDS measurement on the witness target is much greater than the variation typically observed from measurements on the surface of a sputtered film. In order to limit the effect of these differences, the spot size and beam energy were varied in order to achieve maximum WDS counting statistics. Next, using these optimal beam conditions ($20 \mu\text{m}$ beam size, 10 kV beam energy), a large number (100 points) of randomly chosen locations on the target surface were analyzed in order to reduce the statistical uncertainty in the measurement. Finally, in order to determine the spatial distribution of surface species, a 9000-point WDS map was produced indicating the relative concentrations of Zn, Te, and Cu within the near-surface region ($1\text{--}2 \mu\text{m}$ from the surface).

Wavelength dispersive spectroscopy analysis of the Cu concentration on the surface of the witness target indicated that, as expected, the Cu is contained in small regions of nearly pure metallic Cu that are uniformly distributed across the surface of the target (Cu-region diameter $\approx 5\text{--}20 \mu\text{m}$). Averaging the results of the 100-point measurement, the concentration of Cu in the witness target was found to be 8.6 ± 2.7 at.%. This range includes the measured concentration of Cu in films sputtered from the nominally identical target (6.2 ± 0.4 at.%). However, it is noted that the overlap is partly due to the large uncertainty of Cu concentration in the target.

Wavelength dispersive spectroscopy analysis of the Zn and Te concentrations on the surface of the witness target also indicate large uncertainties. However, in this case the 100-point measurement suggests that the surface of the unsputtered target is Te-rich (42.4 ± 3.5 at.% Zn and 49.0 ± 2.3 at.% Te). Comparing WDS analysis of the Zn and Te concentrations from the 9000-point map to an SEM image of the same region on the witness target reveals that Zn tends to decorate surface artifacts such as scratches, while the Te concentration is relatively unaffected by surface features. This observation suggests, prior to sputtering, the target's surface is preferentially covered with a Te layer that may be formed during target fabrication. Because the surface concentration of Zn is affected by (post-target-fabrication) features that penetrate deeper into the surface, it is likely that the regions of

the target beyond the x-ray penetration depth (~1–2 μm) are more stoichiometric in Zn and Te than the surface. In order to test this speculation, depth-profiling SIMS has been performed on the witness target. Unfortunately, thus far these results are inconclusive because the dynamic range of the SIMS instrument in the Zn and Te concentration range is not sufficiently sensitive to reveal the small variations in Zn and Te predicted as a function of depth. Therefore, the above analysis leaves open the possibility that proper conditioning of the ZnTe:Cu target will yield equal concentrations of sputtered Zn and Te species. However, because of the complicating factors associated with measurements on target material, questions remain on this point.

Figure 4 shows SEM photographs illustrating changes in surface morphology as a function of Cu concentration in ~1.0 μm thick ZnTe:Cu films. It is noted in Figs. 4a–4c that the film surface is essentially featureless for Cu concentrations of 0, 1.4, and 3.7 at.%. This apparent lack of structure is often

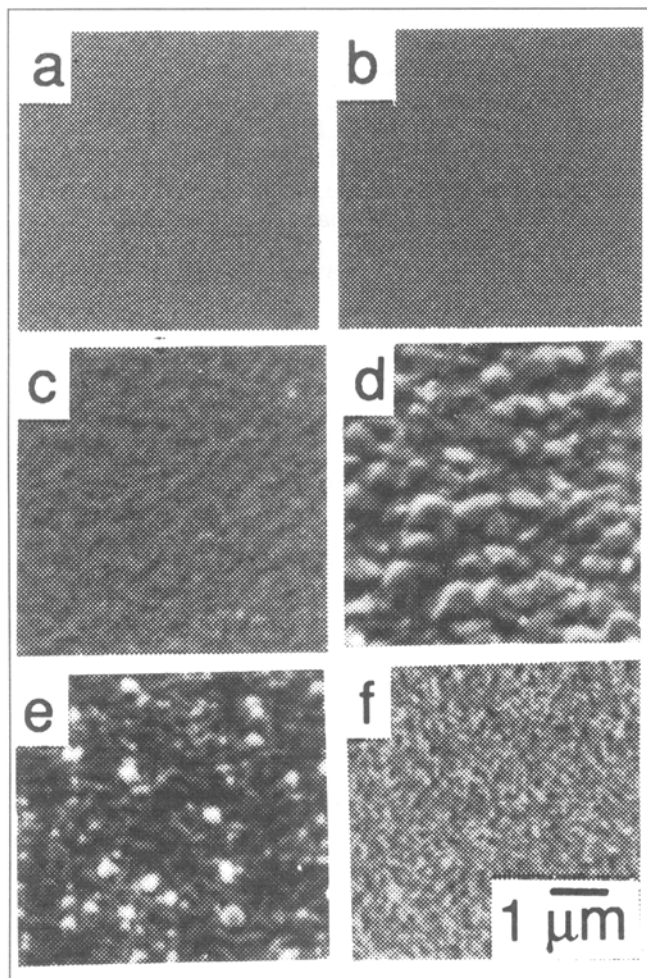


Fig. 4. Scanning electron microscopy photographs illustrating changes in surface morphology as a function of increasing Cu concentration. For all depositions, film thickness ~1.0 μm, substrate temperature = 300°C, deposition rate = 40 nm min⁻¹, preconditioning time ≥ 15 min. Cu concentrations measured in films: (a) 0.04 at.% (nominally undoped ZnTe film), (b) 1.41 at.%, (c) 3.68 at.%, (d) 6.15 at.%, (e) 9.44 at.%, and (f) 10.93 at.%.

observed for films deposited onto low-temperature substrates and results from the surface features being too small to resolve with SEM. The actual microstructure is likely composed of small, fibrous, upright columns.⁶ At a Cu concentration of 6.2 at.% (Fig. 4d), a dramatic change occurs in the surface morphology. At this point, the structure appears to be composed of ~0.5–1.0 μm diameter, grain-like features, suggesting that the deposition parameters have provided conditions suitable for three-dimensional grain growth. Although not shown, depth-profiling SIMS analysis indicates that the Cu is distributed uniformly throughout the bulk of these ZnTe:Cu films. Therefore, the grain-like surface features observed in Fig. 4d are probably not due to surface segregation of the Cu (which could lead to the formation of Cu-Te compounds). At higher Cu concentrations of 9.4 and 10.9 at.% (Fig. 4e, 4f), the grain-like features are no longer present, and a morphology suggesting the growth of larger columns is observed.

Figure 5 shows the variation of measured Zn, Te, and (Zn+Cu) concentration as a function of measured Cu concentration in the sputtered ZnTe film. Here one notes that the variations in stoichiometry at high Cu concentrations (> 6 at.%) are generally consistent with that expected from targets fabricated from stoichiometric-ZnTe and metallic-Cu powder (see Fig. 5, dashed lines). However, the measured concentrations of Zn between 0 and ~5–6 at.% Cu are more consistent with a film that is becoming increasingly Zn deficient with increasing Cu concentration. This dependence was not expected and is not well understood at this

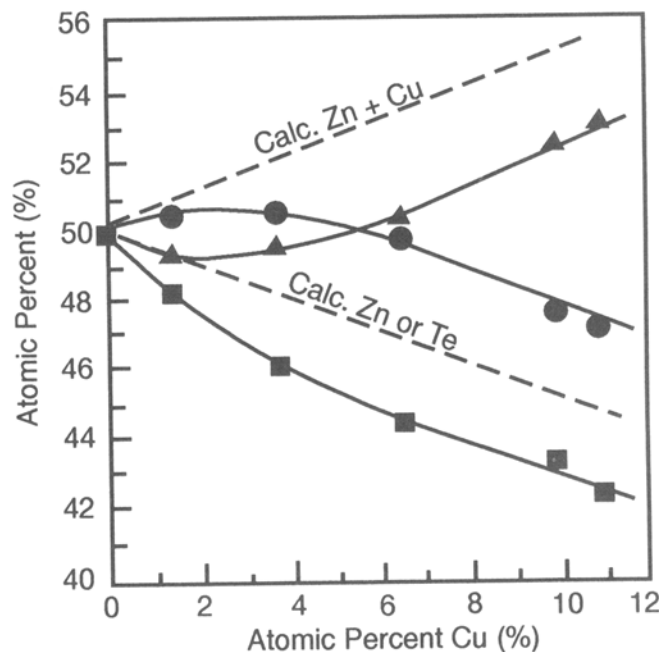


Fig. 5. Measured composition of Te, Zn, and (Zn+Cu) in ZnTe:Cu films as a function of measured Cu concentration in film. Squares indicate at.% Zn. Circles indicate at.% Te. Triangles indicate at.% (Zn+Cu). Dashed lines indicate what would be expected if the film concentrations exactly matched the specified target concentrations. For all depositions, film thickness ~1.0 μm substrate temperature = 300°C, deposition rate = 40 nm min⁻¹, preconditioning time ≥ 15 min.

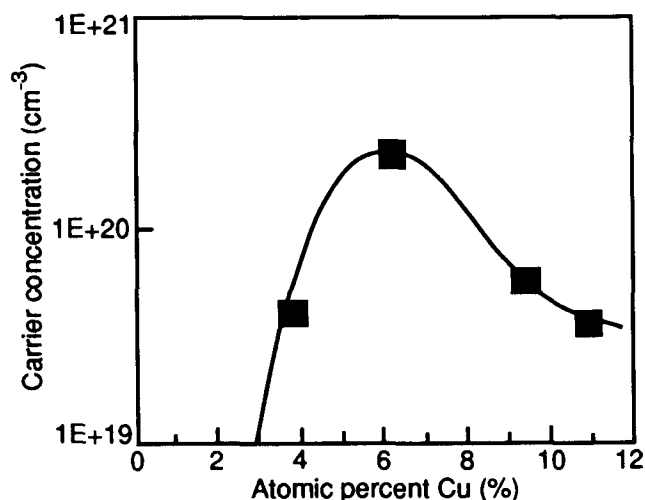


Fig. 6. Measured carrier concentration in ZnTe:Cu films as a function of measured Cu concentration. All measurements indicated p-type carriers in ranges shown. For all depositions, film thickness $\sim 1.0 \mu\text{m}$, substrate temperature = 300°C , deposition rate = 40 nm min^{-1} , presputter time $\geq 15 \text{ min}$.

time. Reasons for this dependence include the possibility of Cu recoil neutrals from the target re-sputtering Zn from the growing film. Regardless of the reason for this variation, the result remains that, for these sputtering conditions and target fabrication procedures, the concentrations of (Zn+Cu) and Te in the film reach nearly equal values at a Cu concentration of 5–6 at.%. At concentrations greater than ~ 6 at.%, the films contain an increasing amount of excess Cu, which will likely coordinate interstitially or possibly form uniformly distributed, microcrystalline phases of CuTe or Cu_2Te .

Figure 6 shows the effect of increasing Cu concentration on the Hall-measured carrier concentration. Here one notes that the (hole) carrier concentration reaches a maximum value of $\sim 3 \times 10^{20} \text{ cm}^{-3}$ at a Cu concentration of ~ 6 at.%. Combined with Fig. 5, these observations indicate that the activation of p-type carriers reach a maximum when the concentrations of Te and (Zn+Cu) are roughly equal. Further, comparisons with Fig. 5 indicate that, although the concentrations of Te and (Zn+Cu) in the films are nearly equal below Cu concentrations of ~ 6 at.%, the small difference in stoichiometry is apparently sufficient to severely limit carrier activation. Comparing this compositional analysis with the SEM data of Fig. 4 suggests that the grains observed at Cu concentrations of ~ 6 at.% may be a $\text{Cu}_x\text{Zn}_{1-x}\text{Te}$ alloy where $x \approx 0.06$. In this situation, the high carrier concentration observed at Cu concentrations ~ 6 at.% may be due to improved intra-grain quality of the $\text{Cu}_x\text{Zn}_{1-x}\text{Te}$ alloy compared to films that contain excess Te or Cu. Although not shown, the measured mobilities of these sputtered ZnTe:Cu films are very low—typically $< 1 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$. However, slightly higher mobilities of $1\text{--}3 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ were observed for the films deposited with Cu concentrations of 9–11 at.%. Although it is speculated that excess Cu may assist in grain-boundary passivation at this time, the reason for the trend of increased

mobility at high Cu concentrations is not clear.

The above analysis indicates that ZnTe:Cu films with the highest electrical quality are produced when the target constituents combine at the surface of the film to form a stoichiometric $\text{Cu}_x\text{Zn}_{1-x}\text{Te}$ alloy. Unfortunately, even for the highest-quality films produced here, calculations suggest that a significant amount of Cu remains electrically inactive. Specifically, for films produced with ~ 6 at.% Cu, it is likely that $> 50\%$ of Cu is coordinated interstitially, and/or located along grain boundaries. It is possible that this electrically inactive Cu would be free to diffuse toward the CdS/CdTe junction, and there cause junction degradation and/or reduce long-term device stability. Although these potential issues related to Cu diffusion and CdS/CdTe device performance still need to be studied, future work should also be directed toward finding methods to produce p⁺-ZnTe films that contain lower overall Cu concentrations. In the study presented here, the optimum Cu concentration is linked to the fact that metallic Cu is used during target fabrication. Additionally, the study suggests that targets composed of the desired $\text{Cu}_x\text{Zn}_{1-x}\text{Te}$ alloy will not form the same film stoichiometry because of preferential Zn loss during sputtering. Therefore, in order to produce films of high electrical quality at lower Cu concentrations, it may be necessary to fabricate targets that include excess Zn. It is presently speculated that this may be accomplished by employing co-sputtering procedures, or by hot-pressing targets from combinations of stoichiometric ZnTe and Zn-Cu alloys.

CONCLUSIONS

Electrical properties of Cu-doped ZnTe thin films formed by rf-magnetron sputtering have been studied. It is observed that the resistivity of very thin ZnTe:Cu films ($\sim 70 \text{ nm}$ thick) can be more than 1000 times greater than measured for thicker films ($\sim 1.0 \mu\text{m}$ thick). It is found that this difference in resistivity is caused by insufficient target preconditioning prior to film deposition. Although less pronounced, the benefits of longer target preconditioning times can also be observed in thicker films. Electrical and SIMS analysis of reactively sputtered ZnTe:Cu films deposited in a N-containing ambient indicate that this variation in film resistivity may be caused by N contamination of the target surface during sample loading.

It is observed that the amount of electrically active Cu in a sputtered ZnTe:Cu film is a function of both metallic Cu concentration in the sputtering target and the extent of Zn deficiency resulting from the sputtering conditions. It is also observed that the extent of Zn deficiency in the film depends on the amount of Cu in the sputtering target. For the sputtering conditions employed in this study, compositional analysis indicates that the concentrations of Te and (Zn+Cu) in the film are nearly equal at a Cu concentration of ~ 6 at.%. At this composition, SEM analysis indicates that three-dimensional grain

growth is occurring, and Hall analysis indicates that the maximum level of carrier activation is reached ($\sim 3 \times 10^{20} \text{ cm}^{-3}$). These results imply that a $\text{Cu}_x\text{Zn}_{1-x}\text{Te}$ alloy with enhanced electrical quality is formed at a Cu concentration of ~ 6 at. %.

Taken together, the analysis indicates that the extent of Cu activation in a ZnTe:Cu film is very sensitive to the extent of excess Te or Cu. It is further noted that the highest level of Cu dopant activation is achieved when the composition of Te and (Zn+Cu) are nearly equal. Because optimum Cu concentration is limited to the fact that pure (metallic) Cu powder is used during target fabrication, it may not be possible to use this target fabrication process to produce high quality ZnTe:Cu films with lower Cu concentration. However, it may be possible to produce the desired films by employing co-sputtering procedures, or by

fabricating the targets from powders of stoichiometric ZnTe combined with either mixtures of metallic Zn and Cu, or with Zn-Cu alloys.

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