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The Structural, Optical, and Electrical Properties of Vacuum Evaporated Cu-Doped ZnTe Polycrystalline Thin Films

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We have studied the structural, optical, and electrical properties of thermally evaporated, Cu-doped, ZnTe thin films as a function of Cu concentration and post-deposition annealing temperature. X-ray diffraction measurements showed that the ZnTe films evaporated on room temperature substrates were characterized by an average grain size of 300Å with a (111) preferred orientation. Optical absorption measurements yielded a bandgap of 2.21 eV for undoped ZnTe. A bandgap shrinkage was observed for the Cu-doped films. The dark resistivity of the as-deposited ZnTe decreased by more than three orders of magnitude as the Cu concentration was increased from 4 to 8 at.% and decreased to less than 1 ohm-cm after annealing at 260°C. For films doped with 6–7 at.% Cu, an increase of resistivity was also observed during annealing at 150–200°C. The activation energy of the dark conductivity was measured as a function of Cu concentration and annealing temperature. Hall measurements yielded hole mobility values in the range between 0.1 and 1 $cm^2/V \cdot s$ for both as-deposited and annealed films. Solar cells with a CdS/CdTe/ZnTe/metal structure were fabricated using Cu-doped ZnTe as a back contact layer on electrodeposited CdTe. Fill factors approaching 0.75 and energy conversion efficiencies as high as 12.1% were obtained.

Key words: II-VI semiconductor, polycrystalline thin films, ZnTe

INTRODUCTION

The formation of stable, low-resistance contacts to p-type CdTe is critical for the achievement of high efficiency and long-term stability of polycrystalline CdTe thin-film solar cells. Because of the rather high ionization energy of CdTe and the difficulty of achieving high doping levels in polycrystalline p-type CdTe, a low-resistance ohmic contact cannot be formed by a simple metallization. Chemical reactions between CdTe and some of the high work function metals (e.g., Au) also make it difficult to form a stable ohmic contact by metal evaporation. Several schemes have been developed for forming a stable ohmic contact in the course of developing high-efficiency polycrystalline thin-film CdTe solar cells. These include the use of Cu- or HgTe-doped graphite pastes,[1] Cu/Au bilayers or Cu-diffused junctions,[2] and Cu-doped ZnTe.[3,4] ZnTe was used because it is expected to have a small valence band discontinuity with CdTe and can be doped degenerately with Cu. The use of heavily doped ZnTe thin films as an intermediate layer between the high-resistivity CdTe and metal contact was first proposed by Meyers.[3,4] Incorporation of a thermally evaporated Cu-doped ZnTe contact in CdTe/CdS cells yielded 11.2% efficiency, a record efficiency for thin-film solar cells at that time.[4] Subsequently, several groups have investigated the deposition and properties of ZnTe thin films in relation to their application in thin-film CdTe solar cells.[5–9] In addition to films formed by thermal co-evaporation, rf-sputtering[6,7] and electrodeposition[5] have been used. Nitrogen doping was also investigated as an alternative to Cu-doping.[7] The specific contact resistance between rf-sputtered ZnTe and CdTe has also been reported.[6]

In this paper, we report the study of electrical, optical, and structural properties of vacuum evaporated ZnTe. The dependences of these properties on

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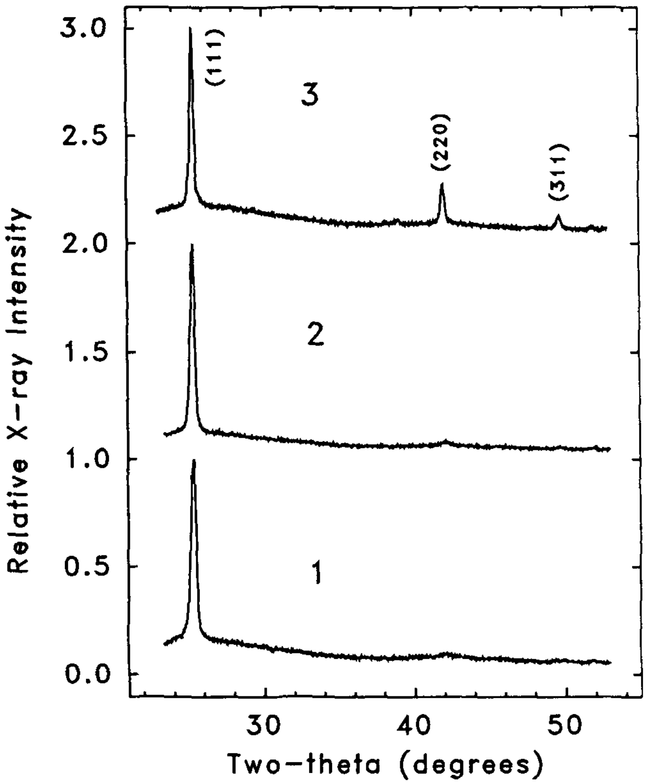

Fig. 1. XRD patterns of a vacuum evaporated ZnTe film with a Cu concentration of 7 at.%. 1: as-deposited, 2: annealed at 195°C for 30 min in vacuum, and 3: annealed at 275°C for 30 min in vacuum.

Cu concentrations and annealing temperatures were investigated. Because ZnTe is deposited as the last layer prior to final metallization when it is used as a contact layer in CdTe based solar cells, its processing is subjected to the most strict constraints. The deposition and annealing temperatures need to be kept low enough to avoid possible degradation of the CdTe/CdS junction and reactions between CdTe and ZnTe. Therefore, even though films with improved electrical and structural properties may be obtained at higher deposition and annealing temperatures, we have restricted our study to relatively low annealing temperatures.

EXPERIMENTAL PROCEDURES

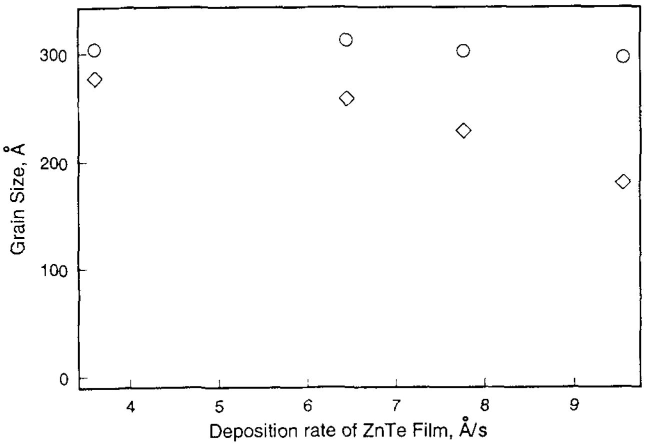

Fig. 2. Relationship between grain sizes and deposition rate of undoped ZnTe films. ◇ : as-deposited and ○ : after annealing at 260°C for 30 min in vacuum.

ZnTe films doped with Cu were deposited by vacuum evaporation. The vacuum system had a base pressure of 1 × 10^{-6} Torr and was partitioned into two sections: one for a ZnTe powder source (99.999%, Johnson-Matthey) and the other for a Cu source (99.9999%, Johnson-Matthey). The ZnTe and Cu deposition rates were measured by separate thickness monitors. The typical deposition rates of the ZnTe were 5–10Å/s. The deposition rate of the Cu was adjusted from 0 to 0.2Å/s to obtain different Cu atomic concentration in the ZnTe, varying between 0 and 10%. Microscope glass (soda-lime) slides were cleaned with Micro detergent and used as substrates for most measurements. During vacuum deposition, the substrates were held at room temperature. The ZnTe:Cu layer thickness was typically 1000Å for most structural and electrical measurements. For Hall measurements, thicker films (1 μm) were used in order to avoid sample heating during the measurement. 1 μm thick films were also used for the electron probe microanalysis (EPMA) to obtain an accurate measure of the film composition. The Cu concentrations we quote in this paper are the values obtained from the thickness monitors. Cu concentrations obtained from EPMA agree with the nominal values within 20%, indicating that the sticking coefficients of both ZnTe and Cu on room temperature substrates are similar and that the nominal Cu concentrations are close to the actual values.

Uniform, adherent ZnTe films were routinely obtained using the described procedure. Post-deposition annealing was performed in vacuum or in a N_2 environment. A strip heater was used for the annealing experiments and was composed of Mo sheet metal as the heating element and a graphite block as the sample holder. This system reached temperatures above 400°C in less than 1.5 min and cooling from 400 to 200°C took approximately 2 min. The temperature was maintained within 2°C of the set temperature. The post-deposition annealing temperatures were relatively low, in the range of 150 to 260°C.

The x-ray diffraction (XRD) measurements were performed with a Rigaku x-ray diffractometer using CuKα radiation. Electrical resistivity along the lateral direction was measured by depositing Au-stripes on the ZnTe films and performing two-point or four-point probe measurements. Hall measurements were also made for determining conductivity type and charge mobility. Wavelength-dispersive spectroscopy (WDS, Cameca model MBX electron microprobe) was used for compositional analysis. The WDS measurement was calibrated using an undoped, crystalline ZnTe standard acquired from Eagle Pitcher.

RESULTS AND DISCUSSION

Structural and Compositional Properties

We found that it was highly critical to pretreat the ZnTe source materials carefully before they were used for thin film depositions. XRD analysis of the source materials indicated that even high purity ZnTe powders (nominally 5N, obtained from several vendors) may contain up to several percent of metallic Te. Such metallic Te may produce a Te secondary phase in the deposited ZnTe films. By heating the ZnTe powder at a temperature that yields the typical sublimation rates (5–10Å/s) for more than 30 min in vacuum each time the source was recharged, the Te phase was suppressed and ZnTe films free of any secondary phase could then be obtained. The XRD pattern of a vacuum-evaporated ZnTe film is shown in Fig. 1. The as-deposited ZnTe film showed cubic phase with a preferred orientation such that the (111) planes tend to lie in the film plane. Upon annealing, grains with other crystal orientations [(220) and (311)] increased and the XRD peaks became sharper. From the linewidth of the XRD peaks, we estimated the average grain size of the ZnTe in the direction perpendicular to the substrate using Scherrer's formula. The results are shown in Fig. 2 for films deposited at different rates. As can be expected, larger grains were obtained at lower deposition rates. The grain size observed here, between 200 to 300Å, is much larger than that reported by Raju et al. (105Å) and Ako et al. (90Å) for their depositions on room temperature substrates.[10,11] This can be attributed to the low deposition rate we used. Both Raju and Ako used much higher deposition rates (30Å/s). The grain size of the 260°C-annealed film was relatively independent of the ZnTe deposition rate. Its value is also comparable to the value Raju and Ako reported (370Å) for their films deposited on heated (200°C) substrates. We did not observe any correlation between the grain size and the Cu doping concentration.

We measured the composition of 8 at.% Cu-doped ZnTe films using WDS. Both the as-deposited film and the film annealed at 190°C showed a Zn-deficiency of 5 at.%. We did not observe any preferential loss of Zn or Te for the annealed film. The Zn-deficiency we observed here is consistent with the results of previous studies of Cu-doped ZnTe.[9] The larger degree of Cu-excess in comparison to Zn-deficiency indicates that Cu in these films exists mostly in the Cu_2Te-like state. In this Cu_2Te-like bonding configuration, all the valence electrons are fully coordinated and consequently exhibit no electrical activity, consistent with our observation (discussed later) that few of the Cu dopants are electrically active in the as-deposited films. Upon annealing, conversion of a small amount of Cu from Cu_2Te-like to CuTe-like bonding configuration probably occurred. The latter corresponds to one Cu atom substituting for one Zn atom which acts as an acceptor in ZnTe and contributes to the increase of electrical conductivity. Because of the close proximity of the lattice constants of ZnTe (6.1026Å) and Cu_2Te (6.11Å), it was difficult to detect the incorporation of Cu in ZnTe and the formation of ZnTe-Cu_2Te ternary alloys by monitoring the changes in lattice constants obtained from XRD.

Optical Properties

The optical transmission of the ZnTe films was studied as a function of Cu doping concentration. The results are shown in Fig. 3. The undoped film shows a sharper absorption edge than the Cu-doped films.

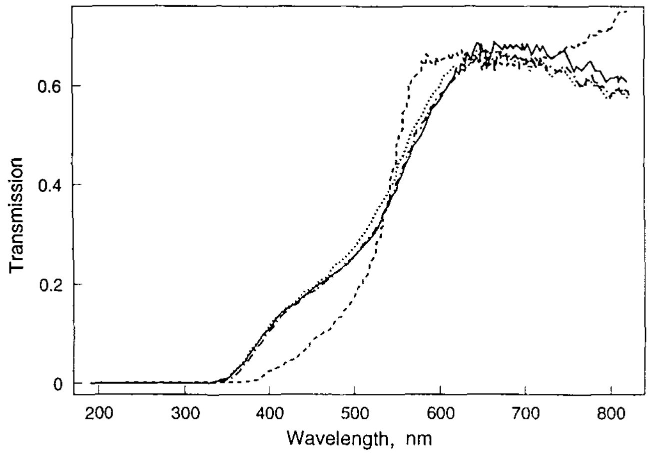

Fig. 3. Optical transmission of as-deposited ZnTe films with different Cu doping concentration: dashed: undoped, dotted: 5 at.% Cu doping, solid: 6 at.% Cu, and dot-dashed: 7 at.% Cu.

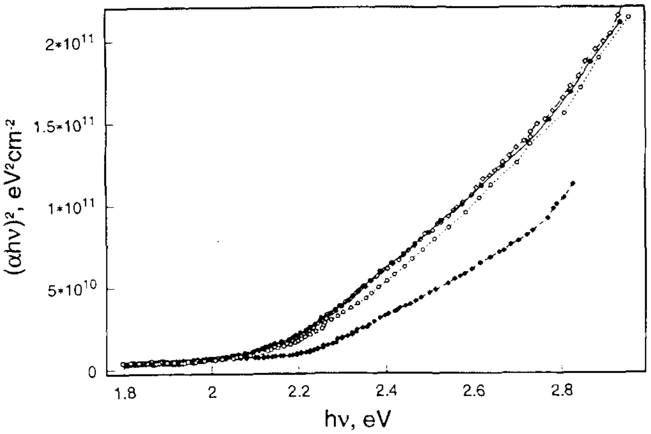

Fig. 4. Absorption edge of as-deposited ZnTe films with different Cu concentrations. ◆: undoped,   : 5 at.% Cu doping, ●: 6 at.% Cu, and   : 7 at.% Cu.

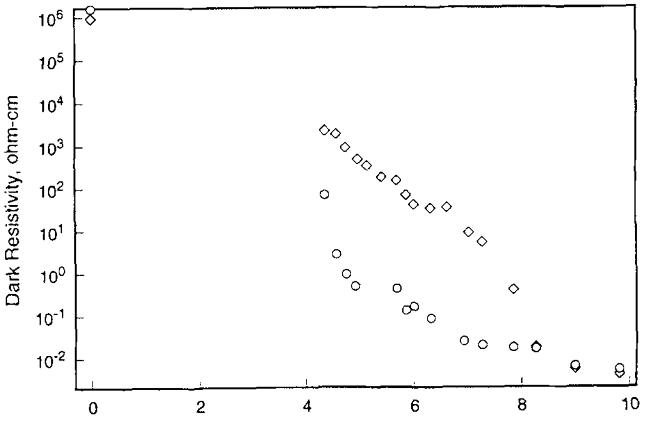

Fig. 5. Dark resistivity of ZnTe films with different Cu concentrations.   : as-deposited, and   : after annealing at 260°C for 30 min in vacuum. The deposition rate of ZnTe was 10Å /s.

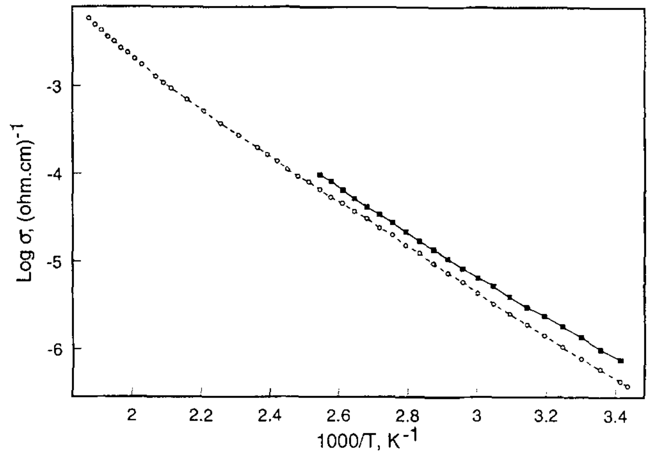

Fig. 6. The temperature dependence of conductivity of an undoped ZnTe film. ○: during warming, and ■: during cooling.

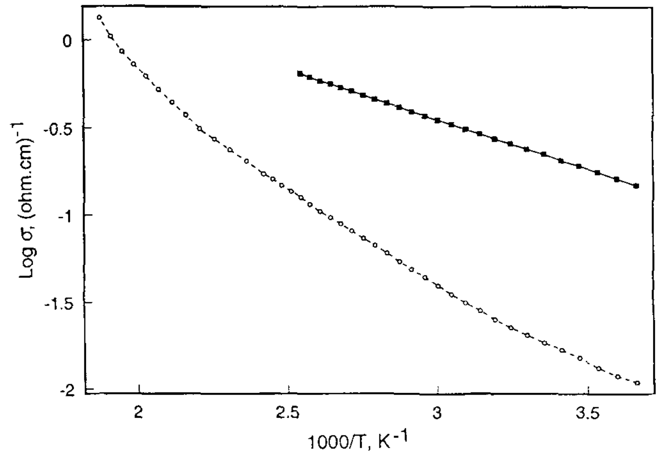

Fig. 7. The temperature dependence of conductivity of a ZnTe film with a Cu concentration of 4.3 at.%. ○ during warming, and ■: during cooling. Annealing in vacuum or in nitrogen yielded the same result.

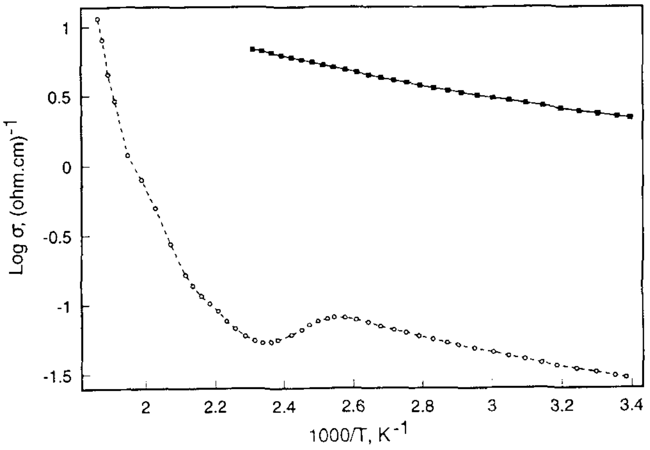

Fig. 8. The temperature dependence of conductivity of a ZnTe film with a Cu concentration of 6.0 at.%. ○: during warming, and ■: during cooling.

Because the average grain size of the undoped and doped films is similar, the soft absorption edge observed with Cu-doped films is attributed to a heavy doping effect (i.e., relaxation of momentum conservation requirement, potential fluctuations caused by impurities), not to a grain boundary effect. The absorption coefficient (α) of the ZnTe films was calculated based on the measured transmission. The ZnTe bandgap was then determined by plotting $(\alpha h\nu)^2$ as a function of photon energy ($h\nu$) (Fig. 4). Both undoped and Cu-doped films showed well-defined absorption edges. The band gap of the undoped ZnTe was 2.21 eV. With increasing Cu doping concentration, the absorption edge shifted to lower energy, suggesting a decrease of the ZnTe bandgap. For Cu concentrations of 5, 6, and 7 at.%, the ZnTe band gap was 2.17, 2.15, and 2.15 eV, respectively. In all cases, the bandgap observed was smaller than that of single crystal ZnTe (2.26 eV). The decrease of bandgap with Cu doping concentration can be explained by the many-body interaction among the charge carriers in the degenerately doped ZnTe film.[12] The Burstein-Moss shift associated with band filling is less important for the p-type ZnTe because of the large effective mass of holes. The results shown in Fig. 4 are for as-deposited films. Post-deposition annealing did not affect significantly the positions of the absorption edges.

Electrical Properties

Figure 5 shows the change of the electrical resistivity (ρ) of ZnTe films with different Cu contents [Cu]. The resistivity of the as-deposited ZnTe films decreased with increasing [Cu], from 10^6 Ω-cm for the undoped film to 5×10^{-3} Ω-cm for films doped with 10 at.% Cu. At the intermediate doping concentrations (4 to 7 at.%), the resistivity was in the range between 10^1 to 10^3 W-cm. After annealing at 260°C for 30 min, ρ decreased dramatically, as a result of the activation of the Cu dopant. A large decrease in resistivity by nearly three orders of magnitude was observed after annealing films with medium Cu doping. Very small changes were observed in the undoped and heavily doped samples.

The conductivities (σ) of the films were measured as a function of temperature. A typical result is presented in Fig. 6 for an undoped film. Both as-deposited and annealed samples showed the predicted behavior, i.e., a linear log(σ) vs 1/T relationship. Also, the conductivity vs temperature curves measured during the annealing and cooling process were nearly identical for the undoped film. For Cu-doped films, the conductivity vs temperature plots showed more complicated behavior. As shown in Fig. 7 for a film doped with 4.3 at.% of Cu, the conductivity exhibited irreversible changes as a result of annealing during the measurement. The conductivity increased and its activation energy decreased after annealing at 260°C. Such a drastic decrease of resistivity at the annealing temperature of 260°C is consistent with the results of Gessert et al.[6]

An abnormal conductivity vs temperature behavior was observed for films doped with 6–7 at.% Cu. As shown in Fig. 8, a decrease in conductivity was observed with increasing temperature between 150 to 200°C for the as-deposited film. After annealing above 260°C, the conductivity increased and the conductivity vs temperature exhibited the normal behavior, i.e., similar to the film with 4.3 at.% Cu.

The activation energy of conductivity of ZnTe films was deduced from the temperature dependence of dark conductivity between 20–120°C. The activation energy of conductivity was rather high (0.5 eV) for the undoped film. This high activation energy is consistent with the values others have reported for undoped ZnTe.[7,13] The ionization energy of the second level of Zn-vacancy is one possible interpretation for this energy. For Cu-doped films, the activation energy was much smaller than that of undoped film (Fig. 9). E_a decreased with increasing [Cu] as a result of increased doping concentration and stronger interactions among impurities. For medium Cu doping, the activation energy was in the range between 0.1 and 0.2 eV, in general agreement with values reported for the ionization energy of the Cu_{Zn} acceptor level (0.12, 0.15 eV).[14,15] For higher Cu doping, the activation energy diminished as the carrier concentration became degenerate. For the same reason, the activation energy of the annealed films was also much lower for medium doped samples. For annealed films with 4–8 at.% concentration, the activation energy was less than 50 meV. We have performed Hall measurements on Cu-doped ZnTe films to obtain the carrier concentration and mobility. Hall measurements of undoped ZnTe film could not be performed on the apparatus used because of the high resistivity and low mobility of the films. For Cu-doped films, the carrier concentration was on the order of 10^{20} cm^{-3} and the carrier mobility was in the range between 0.1 and 1 cm^2/V·s. Mobility values in this range are in general agreement with others[16,17] reported for polycrystalline ZnTe formed by various methods. The degenerate doping in the annealed ZnTe films suggests that the Fermi level lies in the valence band for the Cu-doped films. In this case, the activation energy we measured for the annealed film is probably associated with the potential barriers at grain boundaries.[18]

The abnormal decrease of conductivity depicted in Fig. 8 was further investigated by performing the conductivity measurements with temperature cycling after the drop in conductivity occurred. The results are shown in Fig. 10. The conductivity increased with increasing temperature for annealing temperatures below 130°C, as is commonly expected for the thermal activation of charge carriers. After the decrease of conductivity was observed at medium annealing temperatures (between 150 and 170°C), the annealing was stopped. The activation energy and the dark conductivity were then measured as the sample temperature decreased. The room temperature conductivity was found to decrease by three orders of magnitude in comparison with the as-deposited film. The activation energy was also much larger (0.3 eV) than that of the as-deposited film (0.06 eV). Annealing at higher temperatures (>240°C) led to the recovery and further increase of conductivity, accompanied by a decrease of the activation energy. Hall measurements were performed on samples that had been annealed at different temperatures corresponding to the minimum and maximum conductivity. No significant difference in the carrier mobility was observed, indicating that the abnormal decrease of conductivity at intermediate annealing temperatures was caused by a decrease in carrier concentration. It appears that a certain compensation mechanism occurred in the temperature range between 150 and 170°C. The exact mechanism is, however, not clear. Abnormal decreases of conductivity at low annealing temperatures have been observed in the past in other II-VI compound semiconductors. For example, a decrease in hole concentration by nearly one order of magnitude was observed in Au-doped CdTe after annealing at 100°C for 1 h.[19] The author interpreted the abnormal decrease in terms of the relocation of Au atoms from Cd-substitutional sites to interstitial sites. The interstitial Au atoms act as donors and compensate the Au_{Cd} acceptors, leading to a decreased hole concentration. We suspect that a similar mechanism may have caused the abnormal conductivity decrease observed in this work. The activation energy of 0.3 eV observed

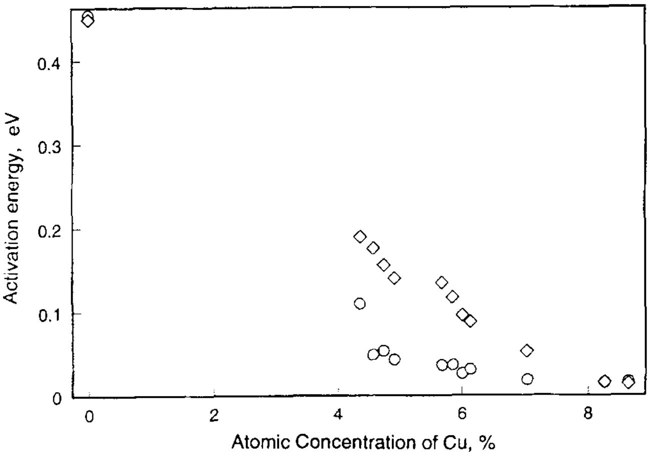

Fig. 9. The activation energy of dark conductivity of Cu-doped ZnTe films as a function of Cu concentration. ◇ : as-deposited, and ○ : after annealing at 260°C for 30 min in vacuum.

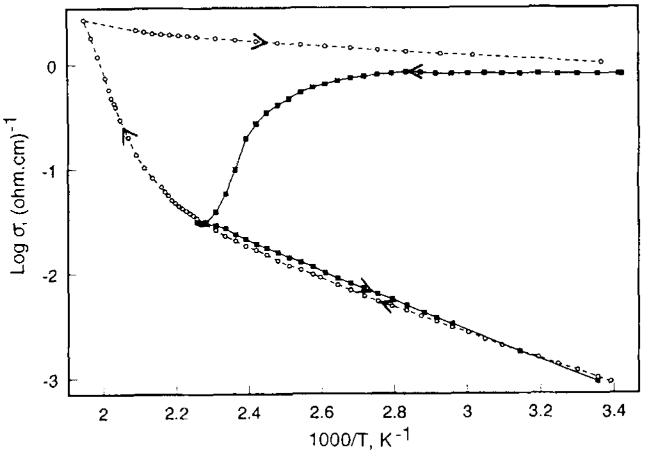

Fig. 10. The temperature dependence of conductivity of a ZnTe film with a Cu concentration of 6.0 at.%. The arrows indicate the directions of temperature change during the measurements.

with samples annealed at intermediate temperatures is much larger than the ionization energy of Cu_{Zn} acceptor levels (0.12, 0.15 eV).[14,15] However, it is rather close to the ionization energy reported for intrinsic defect levels in ZnTe (0.25 eV),[14] suggesting that the acceptor levels dominating electrical conduction are most likely the levels originating from Zn vacancies.

Application of Cu-Doped ZnTe in CdTe/CdS Solar Cells

Complete solar cells were fabricated using the thermally evaporated ZnTe films. The structure of the cell consisted of electrodeposited CdTe on chemical-bath-deposited CdS on SnO_2-coated glass substrates. Details of the CdTe and CdS deposition and annealing procedures have been described in our previous publications.[20] We investigated the effects of Cu concentration, ZnTe annealing temperature, and metals (Au, Ni, Co) used for contacting ZnTe, on the ZnTe/CdTe/CdS solar cell performances. Cu concentrations between 4 and 7 at.%, annealing temperatures in the range of 155–185°C, and Au contact to the ZnTe have been found to yield the most efficient devices.[21] Annealing at temperatures over 200°C always leads to a drastic decrease in cell efficiencies, in agreement with the early work of Meyers.[4] Using the ZnTe back contact, we have obtained cells with high energy conversion efficiencies. CdS/CdTe/ZnTe cells which yielded a V_{oc} of 0.79 V, a J_{sc} of 20.8 mA/cm^2, a FF of 0.73, and an efficiency of 12.1% have been obtained. In terms of individual parameters, we have obtained V_{oc} values of over 0.8 V, and FFs of 74% on other cells. Based on the analysis of the light I-V data, we evaluated the series resistance in the cells to be less than 1 Ω-cm^2, which is in the same range as the series resistance observed in CdTe thin-film cells using Cu-doped graphite contacts.

SUMMARY

Cu-doped ZnTe was studied as a promising material for forming low-resistance contacts to p-type CdTe. The ZnTe was formed by vacuum co-evaporation of Cu and ZnTe. The structural, optical, and electrical properties were studied systematically as functions of Cu concentration and annealing temperature. XRD measurements indicate that the ZnTe films are characterized by an average grain size of 300Å with a (111) preferred orientation. Optical absorption measurements yielded a bandgap of 2.21 eV for undoped ZnTe and a reduced bandgap for Cu-doped films. The dark resistivity and its activation energy were measured as a function of Cu concentration and annealing conditions. A decrease of dark resistivity by more than three orders of magnitude was observed for as-deposited ZnTe films as the Cu concentration was increased from 4 to 8 at.%. Resistivity values less than 1 ohm-cm were obtained after annealing the Cu-doped film at 260°C for 30 min. For films doped with 6–7 at.% of Cu, an increase of resistivity was observed during annealing at 150–200°C. Application of the Cu-doped ZnTe thin films in CdTe based solar cells yielded low series resistance and high conversion efficiency.

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