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# Development of CdTe thin films on flexible substrates—a review

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## Abstract

In the recent years there has been an increased interest in photovoltaic structures on lightweight flexible substrates. Photovoltaic structures on lightweight substrates have several advantages over the heavy glass-based structures in both terrestrial and space applications. CdTe is one of the leading candidates for the solar cells due to its optimum band gap and the variety of film preparation methods. The development of CdTe thin films on flexible substrates is discussed. The film growth and characterization are reviewed.

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*Keywords:* CdTe; Thin film; Flexible substrate; Photovoltaic structure

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## 1. Introduction

During the last three decades considerable development has been achieved in the field of solar energy research, material development and fabrication of solar cells. Today the leading thin film photovoltaic materials are CdTe, Cu(In,Ga)Se<sub>2</sub> and a-Si. The reported efficiencies of these cells are lower than the predicted efficiencies. So much work is required to optimize the materials as well as the fabrication techniques. By the end of 1970s the reported efficiencies of CdTe-based solar cell devices were about 8% [1,2]. The work on CdTe thin films got much attention in the 1980s and

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efficiencies of about 13% were achieved [3,4]. The present status of thin film CdTe-based solar cell is about 16% efficiency for devices on glass substrates [5,6].

Thin film polycrystalline photovoltaics have been aimed at lower cost market where lower efficiency is acceptable [7,8]. The conventional cells are usually manufactured on glass substrates and offer no weight advantage over single crystal cells. Producing thin film cells on thin foil substrates (0.05 mm or less thick), however, offers several advantages for space as well as terrestrial applications. Since the substrate material can be as thin as 0.05 mm, the weight savings are significant in the case of thin film devices on flexible substrates. Furthermore, the photovoltaic devices on flexible substrates can be folded in any shape, and the supporting structure requirements are minimum compared to the heavy glass substrates. One of the major obstacles in the development of low cost and high efficiency solar cells is the use of glass substrates. Ordinary low cost soda lime glasses cannot be used since the annealing temperatures are more than 500°C. The poor thermal conductivity of glass makes it extremely difficult to maintain a constant annealing temperature across a large area panel and to avoid thermal stresses which cause breakage during fabrication. Thus, panel efficiency is much lower than would be expected from the efficiency of small devices. Hence metal foil mounted cells can both reduce weight and promise efficient cheaper cells.

The thin film cells are anticipated to have greater resistance to radiation degradation [7,8]. High efficiency can be achieved due to the high optical absorption coefficient. For example, in CdTe, light is absorbed within 2 μm and crystalline defects are relatively less important than in single crystal cells. Since the cells are so thin actual damage per unit radiation flux is less. Hence thin film solar cells should be less susceptible to radiation degradation than single crystal solar cells. Thus it appears that thin film solar cells on flexible metallic substrates offer several advantages over single crystal or glass mounted cells for both space and terrestrial applications.

The interest in CdTe-based devices on lightweight and flexible substrates gained interest in mid-90s and there are large number of reports on the film growth [8–24,27–34], post-deposition treatments [8–12,16,23,34], structural characterization [8,10–13,17,19,22–24,27,28,30–33], opto-electronic characterization [14–18,20–22,25–27,30,32,35], metal/CdTe junctions [14,16–18,20,22,25–27,30,35], electrolyte/CdTe junctions [9,10,33,34] and CdS/CdTe hetero-junctions [8,11,32]. In this review, we are discussing the growth of CdTe films on flexible stainless steel (SS) and molybdenum (Mo) foils, characterization of the films, Schottky junctions and hetero-junctions.

## **2. Growth of CdTe films on flexible metal substrates**

CdTe films can be prepared by a variety of techniques such as atomic layer epitaxy, electro deposition (ED), electroless deposition (ELD), spraying, close spaced sublimation (CSS), chemical vapor deposition (CVD), hot wall evaporation, screen printing, electron beam evaporation, laser ablation, thermal evaporation,

molecular beam epitaxy, metal organic chemical vapor deposition and sputtering. Among these techniques, the most popular methods are ED and CSS. To date the highest efficiency CdTe photovoltaic devices on glass substrates were prepared by these two techniques [5,36–38].

The ED kinetics of the CdTe from aqueous solution containing CdSO<sub>4</sub>, TeO<sub>2</sub> and H<sub>2</sub>SO<sub>4</sub> has been extensively investigated [36,39–41]. Deposition of CdTe can occur through two possible ways: Cd<sup>2+</sup> ion can react with H<sub>2</sub>Te produced during the reduction of HTeO<sub>2</sub><sup>+</sup> yielding CdTe, or tellurium deposited on the working electrode can react with Cd<sup>2+</sup> to give CdTe. In either case the deposition process occurs through the transfer of six electrons. The ED is normally done in glass beakers having a vapor-tight lid. The electrolyte is 0.5–1.5 M CdSO<sub>4</sub> containing 100–300 μM TeO<sub>2</sub>. The solution is continuously stirred at the rate of 50–100 rpm and the temperature of the electrolyte is maintained at 80–90°C. Under these conditions stoichiometric films are obtained at a potential of –370 to –390 mV with respect to SHE [20,26,28]. The counter electrode can be pure platinum wire/mesh or graphite. It is observed that the substrate material has an influence on the deposition current. At the initial stage when the nucleation of CdTe on the substrate is not complete, it is observed that the deposition current is high for the metallic substrates compared to the tin oxide coated glass [19].

Fig. 1 shows current versus time curve for CdTe deposition on SS substrate (see Ref. [17]). At the initial stage of ED, the cell current is high and rapidly decays to a level determined by the concentration of the HTeO<sub>2</sub><sup>+</sup> ions. This is explained as follows: at the initial stage, when the nucleation of the CdTe on the substrate is not complete, the current is high, and once the substrate surface has been passivated with layers of CdTe, the rate of reaction depends on the availability of free tellurium ions. So after the initial fast decay, the deposition is controlled by the diffusion of

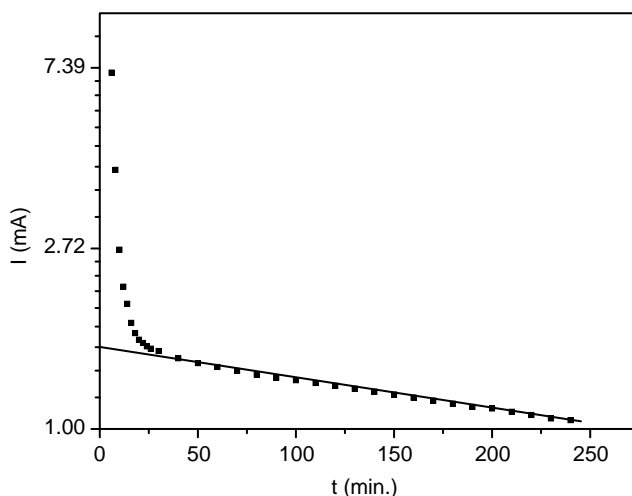


Fig. 1. A graph of the cell current against time for the electro deposition of CdTe on SS substrate. The solution pH was 2 and the bath temperature was 80°C (see Ref. [17]).

tellurium [39]. During this deposition no additional Te is supplied and the solution was being depleted of tellurium with time as is evident from Fig. 1. After the initial decay the current falls exponentially with time. Using Faraday's law and the total charge, the number of transferred electrons ( $N$ ) was determined as more than 7. But if the charge is calculated from the area under the straight line extrapolated to  $t = 0$ ,  $N$  value close to the predicted value of 6 is obtained. This indicates that at the initial stage of deposition a certain amount of charge flows, which does not contribute to the formation of stoichiometric CdTe [17]. Good quality films with thickness 1.5–2  $\mu\text{m}$  thickness on large area substrates ( $7 \times 3 \text{ cm}^2$ ) were electrodeposited in 4–6 h [16–20]. The films are microcrystalline with strong preferred orientation in the (1 1 1) plane. The grain size of the crystallites is about 0.2–0.5  $\mu\text{m}$ .

CdTe has been successfully electrodeposited on various foils such as SS, Mo, Ni and Cu; among these Mo is considered as the appropriate material due to its matching thermal coefficient of expansion with that of CdTe. The as deposited films are n-type with resistivities in the range  $10^4$ – $10^6 \Omega \text{ cm}$ , the higher resistivity is due to the compensation effect involving the imperfections and native defects [36]. The n-type conductivity of the ED films is evident from the AUGER depth profile analysis, which shows that the film is rich in Cd throughout the thickness of the film (Fig. 2). The slight difference in stoichiometry of the film surface can be explained as due to the formation of an oxide layer.

The investigation of the influence of deposition potential and temperature on the film characteristics revealed that these parameters influence both the structure and the composition of the film [22,24,28]. The doping of the deposition solution has no influence on the deposition mechanism [22]. The Fermi energy level in films deposited from Cl-containing solutions was lower compared to that deposited from undoped solutions. This lowering in Fermi energy is due to the influence of Cl-related shallow levels [25].

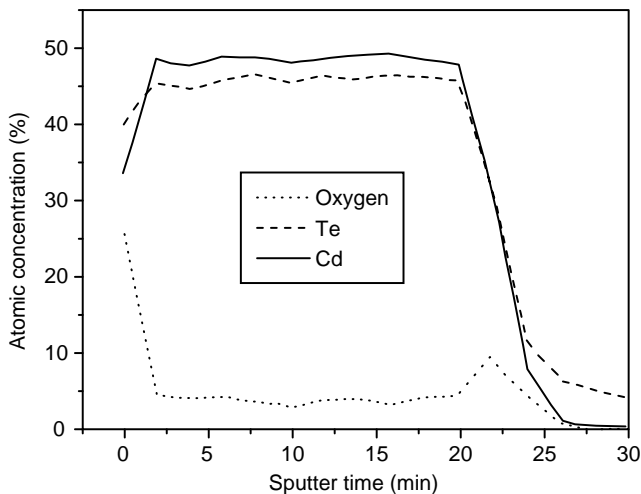


Fig. 2. The AUGER depth profile of a CdTe film electrodeposited on SS substrate.

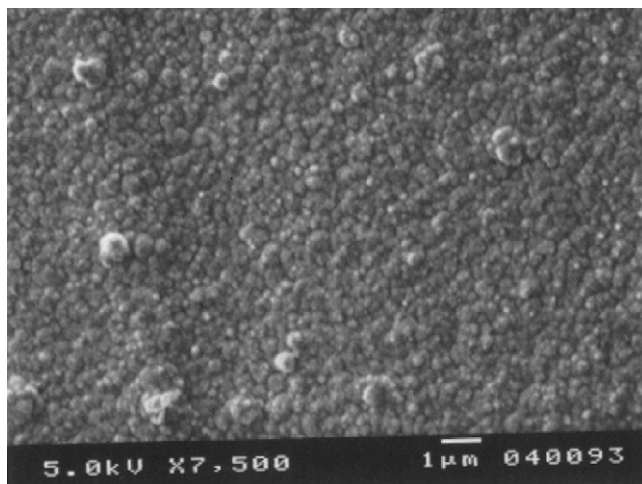


Fig. 3. SEM picture of an electrodeposited CdTe film on SS substrate (see Ref. [27]).

CSS is an efficient technique for the preparation of high quality large area films. The typical experimental parameters to obtain good quality films are as follows, source temperature—660°C, substrate temperature—600°C, oxygen pressure—1 Torr, helium pressure—15 Torr and deposition time—4 min. Under these conditions uniform films of about 8 μm thickness were obtained [27]. The XRD analysis showed identical characteristics with the ED films [27]. The SEM analysis showed that the CSS films on SS substrates are superior to the ED films on SS substrate, the average grain size of the CSS films is about 4 μm, much larger than the 0.3 μm size of the ED film. For a comparison, the SEM pictures of CdTe films prepared by CSS and ED are shown in Figs. 3 and 4. It is clear that the CSS prepared films are more closely packed compared to the ED films.

There is not much work reported on the development of CdTe films on metallic substrates using CSS. Since CSS is a high temperature process, there is possibility for the formation of an oxide layer on the metallic substrate and this can deteriorate the electrical contact between CdTe and the metallic substrate. The development of a conducting interlayer between the CdTe and the metallic substrate is an area which requires more attention in order to give a stimulus for the development of CdTe-based photovoltaic devices on metallic substrates. There have been reports about the attempts made to develop an interlayer between CdTe film and the metallic substrate in CSS and ED films [8,23,24].

### 3. Characterization of the films

The CdTe films on metallic substrates have been characterized using a number of tools such as XRD, SEM, AUGER, AFM, ICP, EDS, photoluminescence (PL),

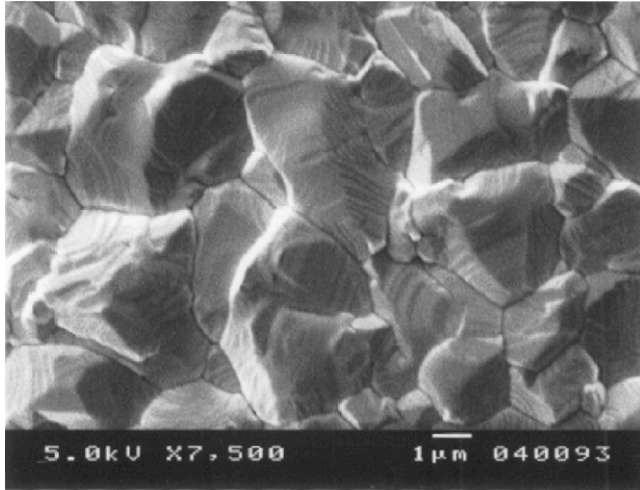


Fig. 4. SEM picture of an 8 μm thick CdTe film on SS substrate, the film was prepared by close spaced sublimation (see Ref. [27]).

photo-induced current transient spectroscopy (PICTS) and optical transmittance. The physical as well as the opto-electronic characteristics of the CdTe films on metallic substrates have been observed to be independent of the substrate material. The XRD analysis revealed that in all the cases the preferential orientation of the grains in the film is along the (1 1 1) plane [17,19,23,24,27,28,30]; the SEM analysis showed the grain sizes of ED films are ranging from 0.2 to 0.5 μm [17,19,22,24] where as the CSS prepared films have larger grains of the order of 3–6 μm in size [23,27]. The morphological studies showed that the CSS prepared films have a compact surface structure with closely packed grains compared to the surface of the ED films having voids. The ICP, EDS and AUGER composition analysis showed that the ED films are Cd-rich where as the CSS films are rich in Te [17,20,28]. This is not unexpected since the ED films are n-type and the CSS films are p-type. The AUGER depth profile analysis indicates that in all the cases, whether the conductivity type of the film is n or p, the atomic composition is constant throughout the thickness of the film (Figs. 2 and 5). From Figs. 2 and 5 it can be observed that there is a certain amount of oxygen in the film. In CSS films the presence of oxygen is expected since the films were prepared in a mixture of helium and oxygen. In ED films the source of oxygen is the electrolyte itself, since there is always dissolved oxygen in the solution. The PL studies revealed that the samples present PL emission regardless of the way in which they were prepared [27]. In both ED and CSS cases the PL spectra show an emission line corresponding to the well-known defect band of CdTe in the region of 1.4–1.5 eV. This behavior is indicative of a defect or impurity-dominated CdTe surface, which normally gives rise to transitions PDA, BI, IB and their respective phonon transitions [27]. The PL emission intensity increased after annealing the samples and further additional shoulder peaks also appeared as a result of annealing. In general, the additional features in the CdCl<sub>2</sub> treated films suggest that the CdCl<sub>2</sub>

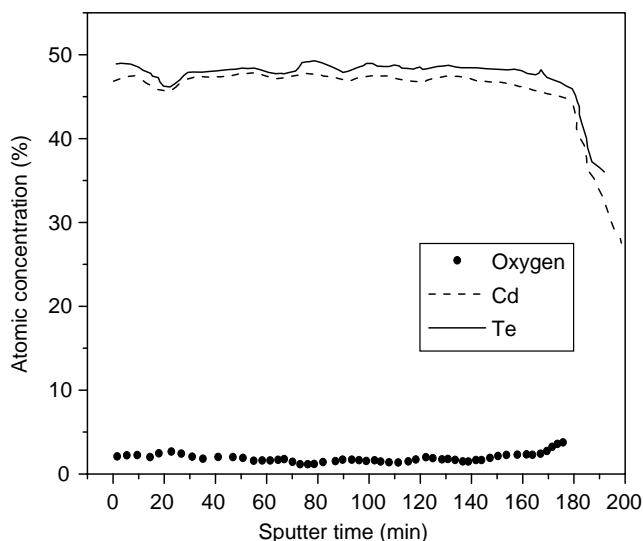


Fig. 5. The AUGER depth profile of a CdTe film prepared by close-spaced sublimation on SS substrate.

treatment improves the quality of the films and the CSS prepared films are better than the electrodeposited films [27].

There are a number of articles on the PICTS investigation of the CdTe films developed on metallic substrates [21,22,25,27]. PICTS is an efficient tool in investigating the deep and shallow levels in high resistivity films. Using a highly absorptive radiation in PICTS measurements, the nature of the traps can be determined. Since the CdTe has a high absorption coefficient in the region above the band gap energy, most of the incident radiation below 500 nm will be absorbed in the top layer of the material and the electron hole pairs will be created in this layer. Depending on the polarity of the applied bias, either electrons or holes will be injected into the bulk of the material and are trapped. The transient during the dark interval contains information about the traps [21,27].

The transmittance measurements of the CdTe films were achieved by successfully transferring the films from the opaque substrates on to glass slides using transparent epoxy. The epoxy was found to be stable over a long period of time and highly transparent in the visible region. Various direct and indirect allowed optical transitions in CdTe films have been detected using the absorption coefficient calculated from the transmittance spectra [15,16].

#### 4. Molybdenum/CdTe interface

Even though Mo is considered as one of the possible substrates for the CdTe-based devices, the p-CdTe can form a rectifying junction with Mo. Fig. 6 shows the ideal energy band diagram for a Mo/p-CdTe junction. Since the electron affinity of

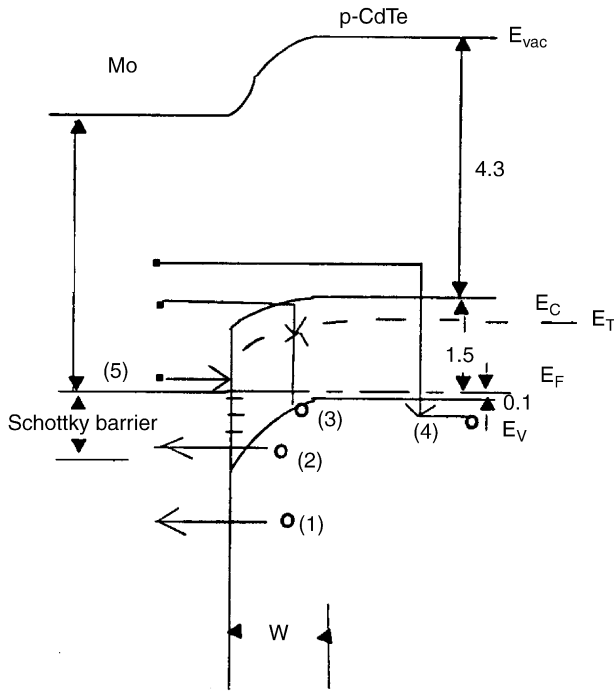


Fig. 6. The energy-band diagram for a Mo/p-CdTe junction.

CdTe is 4.3 eV and its band gap is 1.5 eV, the work function of p-CdTe (depending upon its acceptor concentration) lies between 5.05 and 5.8 eV. The work function of Mo, however is less than 5 eV. Thus the Mo/p-CdTe junction is a Schottky diode (Fig. 6).

The current transport in metal–semiconductor contacts is mainly due to majority carriers (holes in a p-type material). The current flow across the metal–semiconductor contacts can take five paths [42]:

- (1) thermionic emission current from the semiconductor over the potential barrier into the metal (the dominant process for Schottky diodes with moderately doped semiconductor operated at moderate temperature (e.g. 300 K)),
- (2) quantum-mechanical tunneling current through the barrier (the dominant process for contact with a heavily doped semiconductor),
- (3) recombination current in the space-charge region,
- (4) injection current from the metal to the semiconductor,
- (5) recombination current via interface states.

The depletion layer width  $W$  is given by

$$W = \sqrt{\frac{2\epsilon_s(V_{bi} - V_1)}{qN_A}}, \quad (1)$$



where  $N_A$  is the acceptor concentration at the CdTe surface,  $q$  is the charge of an electron,  $\epsilon_s$  is the dielectric constant of CdTe,  $V_{bi}$  is the junction potential of the contact in equilibrium and  $V_1$  is the forward bias. The doping concentration  $N_A$  can be measured from the capacitance–voltage characteristics:

$$N_A = \frac{2}{q\epsilon_s} \left[ -\frac{1}{d(1/C^2)/dV} \right], \quad (2)$$

where  $C$  is the capacitance.

Modeling the diode  $D$ , as a Schottky diode and assuming that path (1) thermionic emission current is the dominant current mechanism, its current–voltage characteristics can be expressed as [43,44]

$$J_{te} = J_{ote} [e^{qV/nkT} - 1], \quad (3)$$

where

$$J_{ote} = BT^2 e^{-\phi_b/kT}, \quad (4)$$

$$\phi_b = (\chi + E_g)_{CdTe} - W_{m'}, \quad (5)$$

where the barrier height  $\phi_b$  depends on the band gap ( $E_g$ ), electron affinity ( $\chi$ ) and the metal work function ( $W_m$ );  $n$  is the diode ideality factor;  $T$  is the temperature;  $k$  is Boltzmann's constant;  $q$  is the electron charge and  $B$  is the effective Richardson constant.

If path (2), quantum-mechanical tunneling current through the barrier becomes the dominant transport process for a heavily doped CdTe, then we can model MS junction as a good conductivity contact. In this case, the doping concentration  $N_A$  must be very large so that the depletion into the semiconductor ( $W$ ) is small enough to allow carriers to tunnel across the barrier. The tunneling current can be increased by (i) reducing the Schottky barrier height and thus increasing the probability of majority carrier tunneling, (ii) increasing the number of majority carriers at the semiconductor surface.

## 5. Photovoltaic devices

The CdTe films have been extensively studied using Schottky devices. The majority of the opto-electronic characterizations were carried out with metal/n-CdTe devices. These investigations include charge transport mechanism, activation energy, spectral response and band gap states. Valuable information such as junction transport mechanism [14,26,30], deep and shallow levels [14,17,21,22,25–27], barrier height [14,20,30,35], carrier concentration [14,17,30,35], band gap and its temperature dependence [18] and voltage-dependent collection functions were obtained from these studies [20].

The prominent charge transport mechanisms have been described as space charge limited (SCLC), thermionic emission and Poole–Frenkel type [14,17,26,30], and it was reported that the SCLC conduction was controlled by a donor type deep level

whose ionization energy varies with the applied bias [14]. The activation energy measurements from the current–temperature studies revealed the presence of different band gap states with energies 0.05, 0.137, 0.263, 0.31, 0.5, 0.65 and 0.76 eV [14,17,25,26]. The PICTS and PL measurements brought further insight into the various deep and shallow levels [21,22,25,27]. The spectral response measurements brought out interesting information about the band gap and its temperature dependence. The value of the band gap at absolute zero temperature was estimated as 1.61 eV and the band gap shrinks as temperature increases at the rate of 0.4 meV/K [18]. The voltage-dependent collection functions influence the photocurrent of the devices in both short and long wavelength regions of the spectrum. It was observed that the contribution of the voltage-dependent collection functions depends on the open circuit voltage ( $V_{oc}$ ) of the device [20]. The  $V_{oc}$  dependence of the long wavelength response causes a systematic dependence of the band gap calculated from the photocurrent on the open circuit voltage of the devices [20].

There is not much work done on the fabrication of CdTe/CdS junctions on flexible substrates. The attempts to develop an unconventional CdTe/CdS back wall structure on metallic substrate faces challenges in forming an ohmic contact between the CdTe and the metallic substrate. Another obstacle is the formation of the heterojunction partner CdS on the rough CdTe surface. The reported CdTe/CdS back wall device has an open circuit voltage 580 mV [8].

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