

CdTe/CdS solar cells on flexible substrates

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Abstract

The development of CdTe/CdS solar cells on flexible substrates is reviewed in this article. Photovoltaic structures on lightweight and flexible substrates have several advantages over the heavy glass based structures in both terrestrial and space applications. The cells mounted on flexible foil are not fragile, the requirements of the supporting structures are minimum and they can be wrapped onto any suitably oriented or curved structures. The specific power of the solar cells is an important factor in space applications and hence development of photovoltaic devices on light weight substrates is interesting. CdTe is one of the leading candidates for photovoltaic applications due to its optimum band gap for the efficient photo-conversion and robustness for industrial production with a variety of film preparation methods. Flexible solar cells with conversion efficiencies exceeding 11% have been developed on polyimide foils. The development of CdTe devices on metallic substrates is impeded due to the lack of a proper ohmic contact between CdTe and the substrate. The polymer substrate has the advantage that the devices can be prepared in both “superstrate” and “substrate” configurations.

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1. Introduction

Solar energy is one of the abundant, non-polluting renewable energy of our planet. During the last three

decades considerable progress has been made in developing technologies to harness electricity from solar radiation. The most commonly used solar cell material is crystalline silicon (Si) and naturally the cost is an obstacle to terrestrial applications. In the last two decades considerable work has been done in developing thin film solar cells to replace the costly single crystal and wafer based solar cells and the progress achieved is encouraging.

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The conventional polycrystalline thin film solar cells are usually manufactured on transparent conducting oxide (TCO) coated 3–5 mm thick glass substrates and offer no weight advantage or shape adaptability for curved surfaces. Producing thin film solar cells on flexible metal foil or polymer substrates however offers several advantages for space as well as terrestrial applications. Since the solar cell can be as thin as 5 μm and the flexible substrate is 5–10 μm thick, weight savings compared to glass substrates are significant. Further, the high stability of CdTe solar cells under proton and electron irradiation makes it suitable for space applications. The specific power of the solar cells is an important factor in space applications and hence development of photovoltaic devices on light weight and flexible substrates is interesting. For terrestrial applications, cells mounted on flexible foil have a special advantage since they can be wrapped onto any suitably oriented structure.

Today, CdTe is one of the leading thin film photovoltaic materials due to the optimum band gap of 1.5 eV for the efficient photo conversion, high optical absorption coefficient and successful development of high efficiency solar cells and modules. Amongst several attractive features, high chemical robustness and a simple phase diagram are the most important ones for large area production of CdTe solar modules at industrial scale. The work on CdTe/CdS thin film solar cell started in 1970s, but the progress in R&D got real impetus in 1980s with the development of various techniques such as electro deposition (ED), screen printing, vacuum evaporation and close spaced sublimation (CSS) and efficiencies exceeding 10% were achieved for CdTe/CdS hetero-junction solar cells (Basol, 1988; Chu, 1988; Mitchell et al., 1988). The pioneering work of different groups in the 1990s pushed the efficiency to above 15%, and the present status of the thin film CdTe/CdS solar cell is more than 16.5% efficiency for devices on TCO coated glass substrates (NREL, 2001), more than 7% efficiency for devices on flexible metallic substrates (Matulionis et al., 2001) and 11% efficiency for devices on flexible polymer substrates (Romeo et al., 2002, 2004). The commercialization of the CdTe photovoltaic technology started in 2001 and the CdTe photovoltaic modules with output power ranging from 45 to 55 W at a size of 60 cm \times 120 cm are available in the market. The efficiency of the commercial CdTe solar module is about 8% for 55 W modules (First Solar, 2004).

Even though considerable effort has been spared to optimize the fabrication technology of CdTe solar cells, efficiencies of small area CdTe solar cells have stagnated at 15–16.5% for the last 10 years although the predicted efficiency of a photovoltaic device based on this material is about 30%. In CdTe and CdS thin films, the random grain boundaries and the inherent non-uniform grain sizes cause different problems such as non-uniform CdTe

doping, device shunting and high surface recombination velocities (Zubia, 1993). The non-uniformity is an inherent problem in polycrystalline films and is one of the causes preventing further increase in cell efficiency.

Even though the CdTe solar cells on glass substrates have efficiencies exceeding 16%, not much efforts were reported on the development of these devices on flexible substrates. CIGS solar cells on flexible polymer substrates have demonstrated 12.8% efficiency (Tiwari et al., 1999). The reported efficiency of the CdTe/CdS solar cells on polymer substrates is 7.3% in substrate configuration and 11% efficiency in superstrate configuration. Attempts were made to develop CdTe/CdS solar cells on flexible metal foils in a substrate configuration and efficiencies in the range 3.5–8% were reported (Enríquez et al., 2004; Matulionis et al., 2001; Vijay et al., 1999). One of the hurdles in the development of CdTe devices on metallic substrates is that most of the metal foils do not form an efficient ohmic contact with CdTe and it is difficult to incorporate an additional buffer layer as ohmic contact to increase the cell efficiency. The criteria of matching thermal expansion coefficients and work function, limit the choice of available substrate materials. Another reason is that during CdCl₂ annealing treatment, diffusion of impurities changes the ohmic contact properties.

In this article we review the work on the fabrication technology of CdTe/CdS solar cells on both flexible metallic and polymer substrates. Special attention is given to the development of CdTe films by ED and CSS. The polymer substrate has an advantage that the devices can be prepared both in the superstrate and substrate configurations where as in the case of metallic substrates only substrate configuration is possible. Development of superstrate CdTe/CdS devices on polymer substrates is highly interesting, but the scarcity of a transparent polymer which can withstand the high processing temperature is the hurdle in this direction.

2. Flexible metal foil supported devices (substrate configuration)

CdTe films can be developed by a variety of techniques such as electro deposition (ED), electroless deposition (ELD), spraying, close spaced sublimation (CSS), vapor transport deposition (VTD), screen printing, electron beam evaporation, laser ablation, thermal evaporation, metal organic chemical vapor deposition and sputtering. Among these techniques, ED is popular due to simplicity and the economical technology, VTD is suitable in large scale manufacturing and CSS has the advantage of obtaining larger grain polycrystalline films. To date the highest efficiency CdTe photovoltaic devices on glass substrates were prepared by CSS. The schematic diagram of a CdTe/CdS device in the sub-

strate configuration is shown in Fig. 1. Molybdenum (Mo) is considered as the suitable substrate material from the point of view of the matching thermal expansion coefficient with CdTe. But the difference in work functions of p-CdTe and Mo necessitates the need of an interlayer between CdTe and Mo substrate which can give a non-rectifying tunneling contact. The materials used to obtain ohmic contact in superstrate CdTe devices are; graphite paste, Te/Au, Sb/Au, Ni, PbTe, SnTe, HgTe and ZnTe (Bube Richard, 1988; Mitchell et al., 1988).

2.1. Electro deposition of CdTe on Mo substrate

ED is a simple technique which can be used for the deposition of CdTe on various substrates; the material utilization in ED is very high since the electroplating occurs only on the substrate. The purity of the films can be controlled by electro purifying the plating electrolyte. The cathodic ED of CdTe for photovoltaic applications was initiated by the Monosolar Inc. in 1976 and their subcontractor University of Southern California (USC) (Kroger and Rod, 1979; Panicker et al., 1978). By mid-1978 they had developed an ITO/CdTe/Te device with efficiency 1.25%. The first Schottky barrier CdTe device Au/n-CdTe/ITO-glass was reported in 1980, and later the efficiency of this Schottky structure was improved to 6% by incorporating a CdS ohmic contact layer between the n-CdTe and the ITO (Basol, 1988). The electrodeposited CdTe Schottky devices were further improved by the Amtek group by introducing a cadmium contact. The first electrodeposited heterojunction CdTe/CdS solar cell was developed in the early 1980s (Basol, 1984). Later on BP Solar took over a leading position to scale up and improve the technology for industrial production. Despite the successful development of large area high efficiency modules, BP Solar closed down all thin film activities, including CdTe cell development for business reasons to focus on Si wafer technology.

The ED of CdTe on metallic substrates is easier and faster than that on the ITO or ITO/CdS substrates. Uniform CdTe films of about 2 μm thickness can be easily

deposited in a few hours, and the composition of the deposit can be controlled by varying the deposition potential (Panicker et al., 1978; German et al., 2001). This method can be utilized in developing a thin Te rich layer on the metallic substrate which can serve as a low resistive contact between the p-CdTe and the substrate. There is a recent publication of the development of CdTe thin films on flexible metallic substrates (Mathew et al., 2003).

The electrodeposited films are micro-crystalline with strong preferred orientation along the (111) plane, but after the annealing treatment grain size increases significantly and the orientation of the crystallites becomes random. The as deposited n-type films has resistivities in the range 10^4 – $10^6 \Omega\text{-cm}$, and the composition is uniform throughout the thickness of the film. However ellipsometric analysis of the CdTe/substrate interface revealed that the interface region has more Te than Cd (Paulson and Mathew, 2004). For device applications the Te concentration in the interface can be increased by depositing the film at a potential more positive than that required for the stoichiometric CdTe.

2.2. CdTe films on Mo substrates by CSS

CSS is an efficient technique for the preparation of larger grain films. The typical experimental parameters used 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 of 3–4 min. The devices presented in Section 2.4 have an Au/Pd interlayer deposited by sputtering. Under these conditions uniform films of about 6–8 μm thickness were obtained. For comparison, the SEM pictures of CdTe films prepared by CSS and ED are shown in Fig. 2. It is clear that the CSS prepared films are more closely packed than the ED films.

Even though CSS has many advantages from the point of view of process time and the photovoltaic performance of the devices, it imposes restrictions on the choice and applicability of interlayer because at high temperatures the interlayer may diffuse or decompose and may not remain suitable for back contacting purpose. We have studied different interlayer materials and a comparative study of ZnTe and Au/Pd interlayer showed that the Au/Pd interlayer gives low resistive contacts and is suitable for the CSS process. The I – V measurements of the Mo/interlayer/CdTe structure proved that the contact resistance decreases significantly with the interlayer. Vijay et al. have used thin films of Cu and Te as interlayer between Mo and thermally evaporated CdTe and found that the contact resistance has significantly reduced due to the introduction of the interlayer (Vijay et al., 1999). Matulionis et al. (2001) have used nitrogen doped ZnTe as an interlayer between Mo and CdTe, where CdTe was deposited by sputtering.

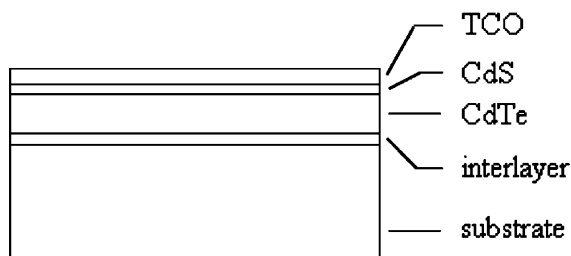


Fig. 1. Schematic of a CdTe/CdS device in the substrate configuration.

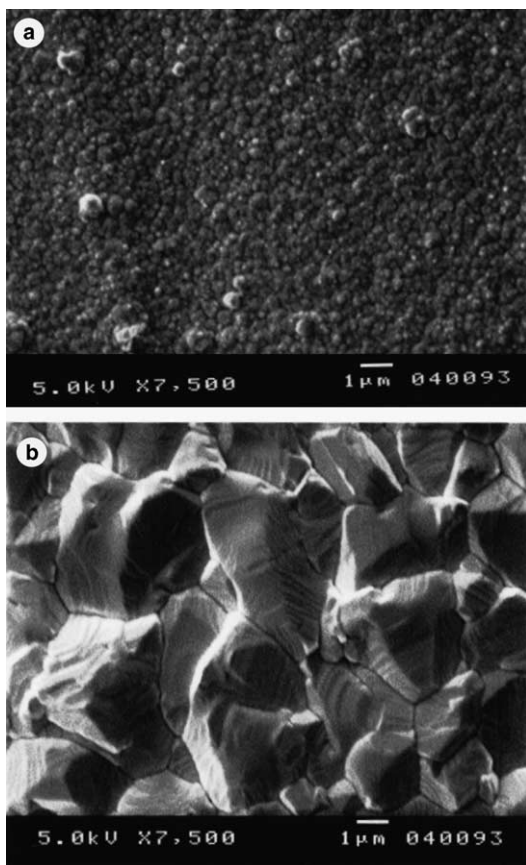


Fig. 2. (a) SEM picture of a CdTe film developed on flexible molybdenum substrate by ED. (b) SEM picture of a CdTe film developed on flexible molybdenum substrate by CSS.

It was reported that the Mo/CdTe junction improved significantly with the ZnTe interlayer, but rectifying effects were still observed. The development of conducting interlayer between the CdTe and the metallic substrate is an area which requires most attention in the development of CdTe based photovoltaic devices on metallic substrates.

2.3. Formation of the CdTe/CdS hetero junction

The well known hetero junction partner to the CdTe absorber layer is the CdS. The CdS can be deposited on top of the CdTe in a variety of methods such as ED, chemical bath deposition, thermal evaporation, spray pyrolysis and sputtering etc. In the conventional glass based superstrate devices, the formation of the CdS layer is much easier since it is deposited prior to the deposition of CdTe. But in the substrate configuration, the CdS has to be deposited on the rough CdTe surface and the properties of the CdTe have an influence on the formation of the CdS film. Among the various CdS deposi-

tion methods, thermal evaporation is found to be more suitable for depositing CdS on top of CdTe in the substrate configuration devices. But in glass based superstrate devices, the best cells are prepared with the chemical bath deposited CdS film.

2.4. Effect of annealing temperature on the photovoltaic parameters

Attempts were made to investigate the effect of post-formation annealing of the CdTe/CdS device on the junction parameters of the substrate configuration CdTe/CdS solar cell. The devices were treated with a saturated solution of CdCl₂ in methanol and annealed at various temperatures prior to the deposition of the ITO. Fig. 3 demonstrates the variation of the open circuit voltage V_{oc} and the short circuit current density J_{sc} of the devices due to annealing at different temperatures. It is clear that the annealing temperature of the CdTe/CdS device has an influence on both V_{oc} and J_{sc} . The value of V_{oc} and J_{sc} are significantly higher for the device annealed at 400°C. The spectral response of the different devices is shown in Fig. 4, as expected, the spectral response improves with annealing and shows a dependence on the temperature. The behavior of the devices with respect to the annealing temperature can be understood by analyzing the compositional changes of the CdTe/CdS interface by the AUGER technique. The substrate configuration is convenient for analyzing the interface using AUGER since the junction is more accessible than in superstrate configuration.

Fig. 5 is the AUGER profile of the untreated CdTe/CdS device, the intermixing of the CdTe and CdS occurs in a region of approximately 0.2 μm which

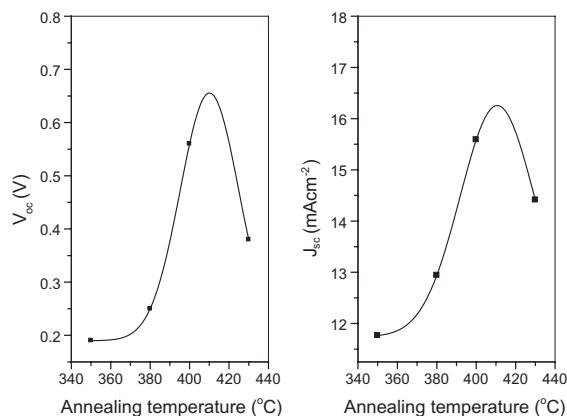


Fig. 3. Dependence of the open circuit voltage (V_{oc}) and short circuit current density (J_{sc}) on the annealing temperature of the CdTe/CdS device. The markers are experimental data and the line is guide to the eye.

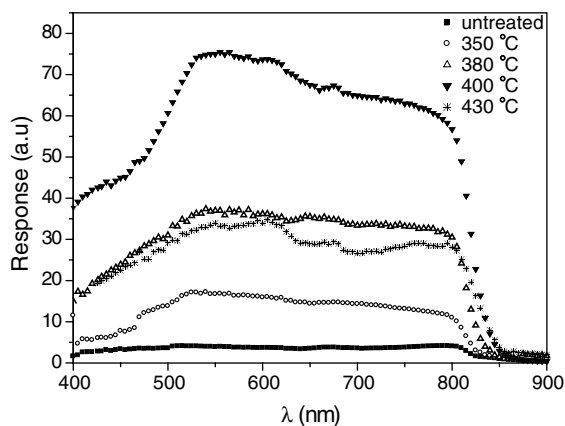


Fig. 4. Relative spectral response of a CdTe/CdS photovoltaic device developed on molybdenum substrate. The different curves correspond to the responses of the device after annealing at different temperatures.

can be considered as the width of the interface. Beyond $0.4\mu\text{m}$ depth there is presence of sulfur (S) which has diffused during the deposition of CdS from the chemical bath at 90°C . The AUGER spectrum of the device annealed at 400°C is shown in Fig. 6. One can observe that the annealing at 400°C causes inter-diffusion of both Te and S as well as sublimation of S from the CdS film reducing the effective thickness of the CdS layer. The width of the interface is more than that of the untreated device. In the case of devices annealed above 450°C , the width of the interface region increases further and the thickness of the window layer decreases and finally disappears leaving a Cd rich $\text{CdTe}_{1-x}\text{S}_x$ surface. This explains the observation in Fig. 3 where the photovoltaic parameters decrease beyond 400°C indicating degradation of the device.

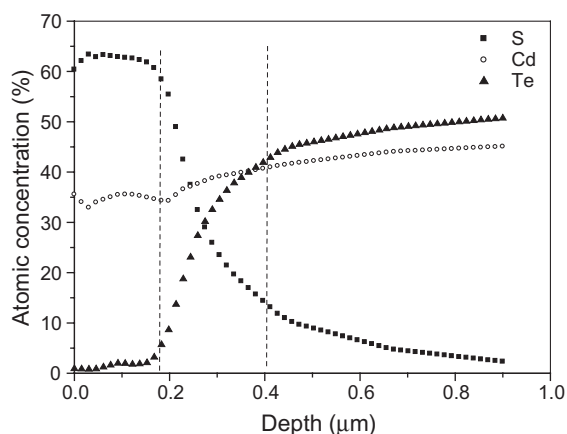


Fig. 5. AUGER profile of the as deposited CdTe/CdS device.

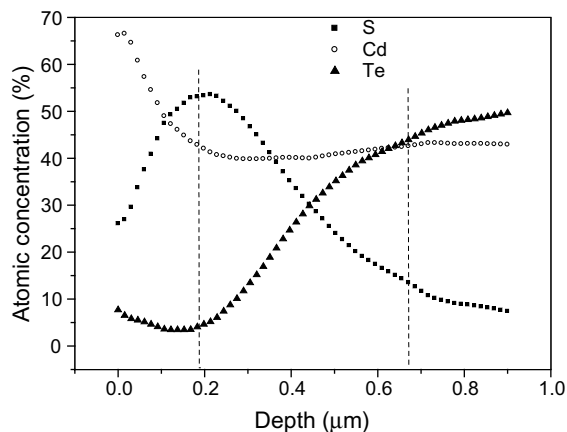


Fig. 6. AUGER profile of the CdTe/CdS device after annealing at 400°C .

This degradation can be due to the change in junction characteristics as well as due to the loss of CdS material from the surface. The annealing and subsequent deposition of multiple CdS layers can permit higher annealing temperatures and better performance for the CdTe/CdS device. It can be seen that in the untreated device there is a small amount of Te in the CdS layer, which may have diffused during the CdS deposition. The Te concentration in the CdS layer increases with annealing temperature and it can be seen that in the interface region (beyond $0.2\mu\text{m}$) the Te concentration decreases as the temperature increases, indicating that more Te is diffused in to the CdS region. Annealing has two effects on the CdS layer; S diffuses into the bulk of the CdTe and also there is a loss of S from the CdS surface due to sublimation leaving a Cd rich surface. The observed improvement of the photovoltaic parameters with the CdCl_2 treatment and annealing can be due to the improvement of the CdS layer, passivation of defects as well as the improved junction properties and the reduction in lattice mismatch between CdTe and CdS due to inter-diffusion of S and T and the formation of $\text{CdTe}_{1-x}\text{S}_x$ (McCandless et al., 1999).

3. CdTe/CdS solar cells on flexible polymer substrates

3.1. Superstrate configuration

The choice of an appropriate substrate is a crucial factor for flexible solar cells in the superstrate configuration because the substrate should be optically transparent and should withstand the high processing temperature. Most of the CdTe/CdS cell fabrication techniques require temperatures in the range $450\text{--}500^\circ\text{C}$.

Commercially available transparent polymers are not stable at such high temperatures. The polyimide films such as Kapton and UpilexTM can withstand high temperatures ($\sim 450^\circ\text{C}$), but they are dark yellow and they strongly absorb visible radiation, and hence CdTe solar cells on such commercially available polyimide films will yield only low current due to large optical absorption loss. But the development of an in-house built polyimide film having transmission of about 75% helped to obtain CdTe/CdS devices in the superstrate configuration with efficiency of 11% (Romeo et al., 2002; Tiwari et al., 2001). Fig. 7 shows the scheme of the processing of a solar cell on flexible polyimide in the superstrate configuration. A thin buffer layer of NaCl was evaporated on a glass substrate and later a polyimide layer was spin coated and cured at 430°C . The TCO layer was deposited on the polyimide by RF sputtering. The CdS window layer as well as the CdTe absorber was prepared by evaporation. The completed device was detached from the glass base by dissolving the NaCl buffer in water. The most interesting advantage of this configuration is that similar to the glass based devices the ohmic contact formation is the last step in the device fabrication. The solar cells grown on this polyimide exhibit efficiency of 8.6% with ZnO:Al and 11% with ITO as the front contact under AM1.5 illumination (Fig. 8). The lower efficiency of the devices with ZnO:Al as the front contact was explained as due to instability of the ZnO:Al during fabrication process. In the case of devices with ITO as front contact, high values of V_{oc} and (842 mV) and fill factor (70.9%) are obtained, however the J_{sc} was only about 18.5 mA cm^{-2} (Romeo et al., 2002). Recently CdTe/CdS solar cells of 11.3% efficiency were directly grown on commercially available foils (UpilexTM) which suggests that roll-to-roll manufacturing can be applied (Romeo et al., 2004).

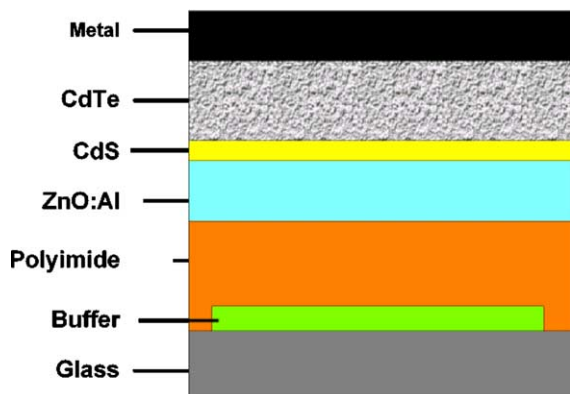


Fig. 7. Scheme of the processing of a solar cell on flexible polyimide sheet in the superstrate configuration with a lift off approach.

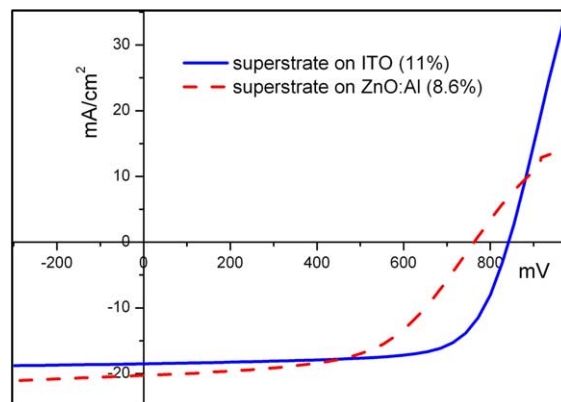


Fig. 8. I - V curves of the CdTe/CdS solar cell developed on flexible polyimide sheet in the superstrate configuration.

3.2. Substrate configuration

The advantage of the substrate configuration is that the polymer substrate does not need to be transparent. The reported CdTe/CdS solar cell on polymer foil in the substrate configuration is made by a novel preparation method which permits the use of ordinary polymers. The production of the device was similar to the procedure mentioned in the previous section, starting by depositing a thin layer of NaCl on glass. The ITO was deposited directly onto the NaCl layer. The CdS and CdTe layers are grown by HVE over the ITO. After processing the cell, a thin polyimide layer (or a metal foil) was laminated on the back of the device and the front glass can be removed by dissolving the NaCl in water. In this way the presence of polyimide layer was avoided during processing and the result is a solar cell in substrate configuration. The major attraction of such a process is that glass is the substrate during all the fabrication steps, avoiding temperature issues as in the case of polyimide or diffusion issues like in the case of metal sheets. The solar cells in this configuration have efficiencies of 7.3% with fluorine doped tin oxide front contact and 6% with aluminum doped zinc oxide front contact under AM1.5 illumination (Romeo et al., 2002). Low values (49% and 40%) of fill factor are related to the low stability of the TCO on NaCl layer, which means that the electrical properties of the front contact tend to degrade after processing. Despite lower values of the open circuit voltage (692 mV and 743 mV, respectively for FTO and ZnO:Al as front contact) and fill factor the current density is higher than in the superstrate case (21.6 mA cm^{-2} and 20.3 mA cm^{-2} , respectively for FTO and ZnO:Al as front contact) because of the absence of polyimide on the front of the cell.

4. Conclusions

We have reviewed CdTe/CdS solar cells on flexible light weight metallic and polymer substrates. Development of CdTe solar cells on flexible substrates started only recently, despite that encouraging results have been achieved. The devices on metallic substrates showed only 7.8% efficiency and the major issues to be solved in the development of the CdTe/CdS devices on metallic substrate are (1) ohmic contact between CdTe and the substrate, (2) development of the hetero junction partner CdS on the CdTe surface, (3) the effect of post-formation heat treatments on the CdS layer and (4) deposition of the TCO layer. The ohmic contact issue can be addressed by depositing a p+ inter-layer on the metallic substrate prior to the deposition of CdTe which can act as a tunneling contact. The development of CdS layer by different methods needs a systematic investigation and careful evaluation of the results. In the conventional glass based devices, the CdS layer is made more resistant to the Te diffusion by a post-deposition annealing in CdCl₂. But in the substrate configuration there is always diffusion of Te into the CdS layer and any post-formation annealing of the junction further promotes this diffusion. In superstrate devices TCO development is the first step, but in substrate configuration, it is the last step. The TCO deposition method has an influence on the characteristics of the CdTe/CdS junction.

Development of superstrate solar cells on polymer substrates is interesting, but the current densities are low due to the light absorption in the polymer. The lack of a transparent polymer which is stable at the high processing temperature of CdTe is a hurdle in this direction. The highest reported efficiency of a flexible CdTe/CdS solar cell on polymer substrate is 11.3%. This efficiency compares well with the efficiency of CIGS or a-Si solar cells developed on polymer foils. The use of very thin polyimide films and a low temperature (<450 °C) process can reduce the absorption of light in the polymer and the stability problems of the substrate.

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