

High-Efficiency Polycrystalline CdTe Thin-Film Solar Cells with an Oxygenated Amorphous CdS (a-CdS:O) Window Layer

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HIGH-EFFICIENCY POLYCRYSTALLINE CdTe THIN-FILM SOLAR CELLS WITH AN OXYGENATED AMORPHOUS CdS (a-CdS:O) WINDOW LAYER

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ABSTRACT

In the conventional CdS/CdTe device structure, the poly-CdS window layer has a bandgap of ~ 2.4 eV, which causes absorption in the short-wavelength region. Higher short-circuit current densities (J_{sc}) can be achieved by reducing the CdS thickness, but this can adversely impact device open-circuit voltage (V_{oc}) and fill factor (FF). Also, poly-CdS film has about 10% lattice mismatch related to the CdTe film, which limits the improvement of device V_{oc} and FF. In this paper, we report a novel window material: oxygenated amorphous CdS film (a-CdS:O) prepared at room temperature by rf sputtering. The a-CdS:O film has a higher optical bandgap (2.5-3.1 eV) than the poly-CdS film and an amorphous structure. The preliminary device results have demonstrated that J_{sc} of the CdTe device can be greatly improved while maintaining higher V_{oc} and FF. We have fabricated a CdTe cell demonstrating an NREL-confirmed J_{sc} of 25.85 mA/cm² and a total-area efficiency of 15.4%.

INTRODUCTION

Cadmium telluride (CdTe) has been recognized as a promising photovoltaic material for thin-film solar cells because of its near-optimum bandgap of ~ 1.5 eV and its high absorption coefficient. Small-area CdTe cells with efficiencies of more than 16% and commercial-scale modules with efficiencies of 11% have been demonstrated [1, 2]. However, the performance of CdTe cells has been limited by the conventional polycrystalline CdS/CdTe device structure. In the CdTe device, the poly-CdS film has been most commonly used as a window material. But it has two main issues that limit device performance. First, poly-CdS film has a bandgap of ~ 2.42 eV, which causes considerable absorption in the short-wavelength region. Higher J_{sc} can be achieved by reducing the CdS thickness to improve the blue spectral response. However, reducing the CdS thickness can adversely impact device V_{oc} and FF. We have previously reported that by integrating a high-resistivity zinc stannate (ZTO) buffer layer between the poly-CdS and poly-CdTe films, we can minimize these detrimental effects [3, 4]. The best way to solve this issue should be to find a new window material with a higher optical bandgap than the poly-CdS film. Second, there is a nearly 10% lattice mismatch between the poly-CdTe film and the poly-CdS film, which causes the high defect density at the junction region. To reduce the lattice mismatch between the CdS and CdTe films, high-

temperature device fabrication processes must be used to enhance the interdiffusion of the CdS and CdTe films and form an intermixed layer (CdTe_{1-x}S_x). But during the high-temperature processes, new defects and impurities are introduced that limit the improvement of device V_{oc} and FF. Therefore, a new window material that has both the higher optical bandgap and a better lattice match with the CdTe absorber is an important project for further improving CdTe cell performance.

Several groups have developed new window materials with higher optical bandgaps than poly-CdS film, such as: ZnSe (2.69 eV), ZnS (3.70 eV), and Zn_xCd_{1-x}S (2.42-3.70 eV) prepared by metal-organic chemical vapor deposition, spray pyrolysis, chemical bath deposition, sputtering, and screen-printing [5-10]. When using these window materials to replace the poly-CdS film, most device results show that V_{oc} and FF are reduced while J_{sc} is improved. An explanation for this could be that these new poly window materials not only have higher bandgaps, but also have larger lattice mismatches to CdTe film than the poly-CdS film.

In this paper, we report a novel window material: oxygenated amorphous CdS film (a-CdS:O) prepared at room temperature by rf sputtering. The a-CdS:O film has a higher optical bandgap than the poly-CdS film and an amorphous structure. The preliminary device results demonstrated that J_{sc} of the CdTe device can be greatly improved while maintaining higher V_{oc} and FF.

EXPERIMENTAL

CdS films were prepared by rf magnetron sputtering at room temperature. The sputtering was carried out in a modified CVC SC-3000 system, evacuated to a base pressure of $\sim 2\text{--}3 \times 10^{-6}$ torr and then backfilled with an oxygen/Argon gas mixture at different ratios. Here, we refer to the O₂/Ar ratio as the ratio of its flow rates. A Corning 7059 glass substrate or glass/CTO (Cd₂SnO₄)/ZTO stack was placed on a sample holder parallel to the target surface. The distance between the substrate and the target was varied from 6 to 9 cm. In this study, we used a commercial hot-pressed CdS target with 99.99% purity. Depositions were performed at an O₂/Ar partial pressure of $10\text{--}20 \times 10^{-3}$ torr with rf power between 50–70 watts, providing a deposition rate of 5–10 Å/sec.

Five sputtered CdS samples (marked as sample #1–#5) were deposited at O₂/Ar ratios of 0, 1%, 2%, 3% and 5%, respectively, on Corning 7059 glass substrates

and used for material property characterizations. The electrical, optical, compositional, structural, and morphological properties of the a-CdS:O film were characterized using a Keithley 6517A electrometer, Cary 5 spectrophotometer, X-ray photoemission spectroscopy (XPS), X-ray diffraction (XRD), Raman spectra, and atomic force microscopy (AFM).

MATERIAL PROPERTIES

Compositional analysis (XPS data)

Table 1 lists oxygen atomic concentrations of sputtered films deposited at different O_2/Ar ratios. We observe that the oxygen atomic concentration in CdS films increases with increasing O_2/Ar ratio. Higher oxygen atomic concentration in CdS film can help to reduce Te diffusion from the CdTe to CdS film, thereby improving device J_{sc} and efficiency [11, 12].

Table 1. The oxygen atomic concentration of sputtered CdS films deposited at different O_2/Ar ratios.

Sample	O_2/Ar (%)	O (at.%)
1	0	4.35
2	1	8.66
3	2	11.08
4	3	13.88
5	5	22.73

Structural property

Figure 1 shows XRD patterns of sputtered-CdS films deposited at different O_2/Ar ratios. It can be seen that sample #1, deposited in pure Ar, exhibits a polycrystalline structure with the preferential orientation along the (002) axis. The intensity of the (002) peak is reduced with the increase of the O_2/Ar ratio (see sample #2), then it disappears when the O_2/Ar ratio increase to 2% or more. The CdS films, deposited at 2% or higher O_2/Ar ratio, have an amorphous structure.

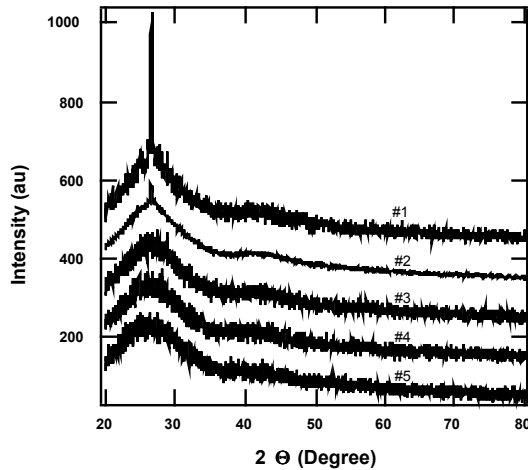


Figure 1. X-ray diffraction patterns of sputtered CdS films deposited at different O_2/Ar gas ratios.

The results of Raman spectra measurements provide more detailed information on the structural property of these sputtered CdS films (see Figure 2). Figure 2(a)

shows that with the increase of oxygen atomic concentration: (1) Raman peak intensity decreases, (2) Raman peak width broadens, and (3) Raman peak shifts to higher frequency, revealed in different orders of Raman transitions. Figure 2(b) also shows that on increasing oxygen atomic concentration: (1) CdS LO phonon frequency increases due to the incorporation of oxygen into the CdS films, and (2) Raman intensity decreases due to the reduction in volume of the crystalline CdS.

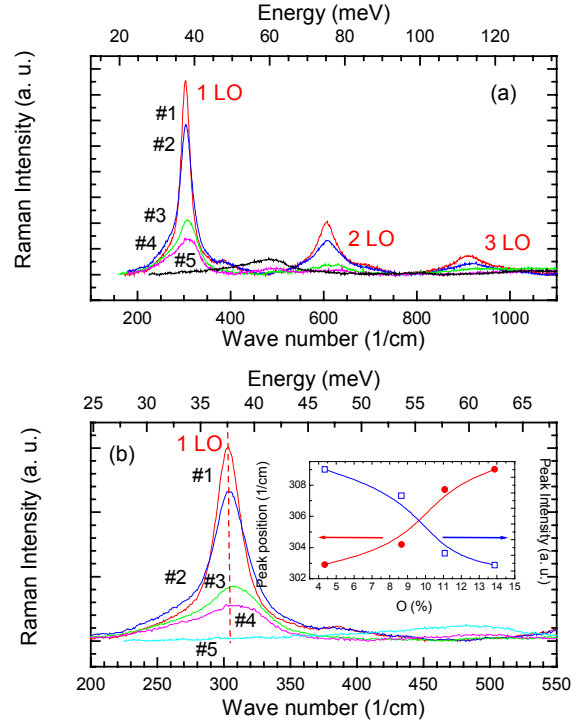


Figure 2. Raman spectra of sputtered CdS films deposited at different O_2/Ar gas ratios.

Grain size and surface roughness (AFM data)

The grain size and average surface roughness of two samples have been measured by AFM. The results demonstrate that sample #1, deposited in pure Ar, has a polycrystalline structure with grain size of about a few hundred Å and average surface roughness of ~15 Å. In contrast, sample #3, deposited in 2% O_2/Ar ambient, demonstrates an amorphous structure and has an extremely smooth surface with average surface roughness of ~3 Å.

Electrical properties

Table 2 lists light conductivities (σ_L), dark conductivities (σ_D), and photoconductivity ratios (σ_L / σ_D) of sputtered CdS films deposited at different O_2/Ar gas ratios. We can see from Table 2 that the maximum photoconductivity ratio of about 1000 is observed in sample #3 and #4, deposited at 2% and 3% O_2/Ar gas ratios, respectively. The amorphous CdS films (sample #3 and #4) with high photoconductivity ratios are suitable as a window layer in polycrystalline CdTe devices.

Table 2. Electrical properties of sputtered CdS films deposited in different O₂/Ar gas mixtures.

Sample #	O ₂ /Ar (%)	σ_D (1/ Ω cm)	σ_L (1/ Ω cm)	σ_L / σ_D (%)
1	0	8.2×10^{-7}	2.8×10^{-5}	34
2	1	2.2×10^{-8}	8.3×10^{-6}	377
3	2	2.7×10^{-9}	2.6×10^{-6}	963
4	3	6.3×10^{-10}	6.3×10^{-7}	1000
5	5	4.3×10^{-9}	1.2×10^{-7}	30

Optical properties

The optical measurement results demonstrate that the optical bandgaps of sputtered film increase with the increase of O₂/Ar ratio (see Table 3). The amorphous CdS films (such as sample #3, #4, and #5) have higher bandgap than poly-CdS (such as sample #1), which can greatly help to improve device J_{sc} and efficiency.

Table 3. Optical bandgaps of sputtered CdS films deposited at different O₂/Ar gas mixtures.

Sample #	O ₂ /Ar (%)	Optical bandgap (eV)
1	0	2.42
2	1	2.52
3	2	2.65
4	3	2.80
5	5	3.17

DEVICE RESULTS AND ANALYSIS

A limited number of CdTe cells, with a modified CTO/ZTO/a-CdS:O/CdTe device structure were prepared for demonstrating the application of a-CdS:O films. CTO transparent conductive oxide (TCO) films and ZTO buffer layers were deposited in pure oxygen at room temperature, as previously described [1,4]. The CdS films were deposited in a 2% O₂/Ar gas mixture. The CdTe films were prepared by the close-spaced sublimation (CSS) technique and were deposited at 570°–630°C for 3–5 min. After CSS deposition of the CdTe, the substrates were treated in CdCl₂ vapor at 400°–430°C for 15 min. HgTe:CuTe-doped graphite paste, followed by a layer of Ag paste, was then applied to the devices as the back-contact layer.

We fabricated a number of CTO/ZTO/a-CdS:O/CdTe cells with NREL-confirmed efficiencies of more than 15% (see Table 4). It can be seen that when using an a-CdS:O film as the window layer, J_{sc} of the CdTe device can be greatly improved while maintaining higher V_{oc} and FF, due to its high bandgap and amorphous structure.

Table 4. High-efficiency CTO/ZTO/a-CdS:O/CdTe cells.

Cell #	V _{oc} (mV)	J _{sc} (mA/cm ²)	FF (%)	η (%)	Area (cm ²)
1	828.9	25.49	71.47	15.0	1.119
2	828.5	24.58	73.97	15.1	1.011
3	830.8	24.55	73.79	15.1	1.225
4	832.2	24.68	74.03	15.2	1.083
5	821.1	25.71	72.55	15.3	1.166
6	832.4	25.85	71.77	15.4	1.056
7	837.1	24.36	75.30	15.4	1.137

In Fig. 3, we have demonstrated the relative internal quantum efficiency of a CTO/ZTO/a-CdS:O/CdTe cell with an NREL-confirmed total-area efficiency of 15.4% (V_{oc}=832.4 mV, J_{sc}=25.85 mA/cm², FF=71.77%, and Area=1.056 cm²).

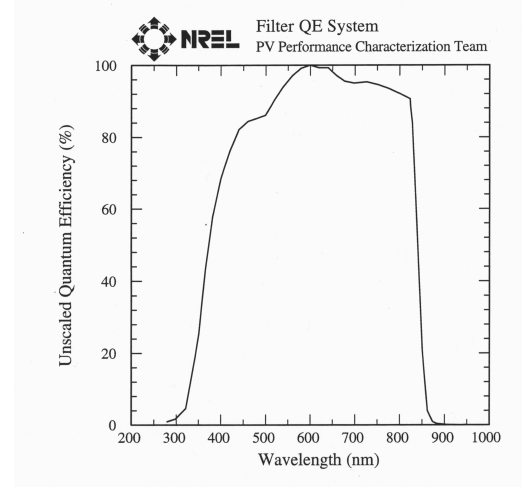


Figure 3. Relative internal quantum efficiency of a CTO/ZTO/a-CdS:O/CdTe thin-film solar cell.

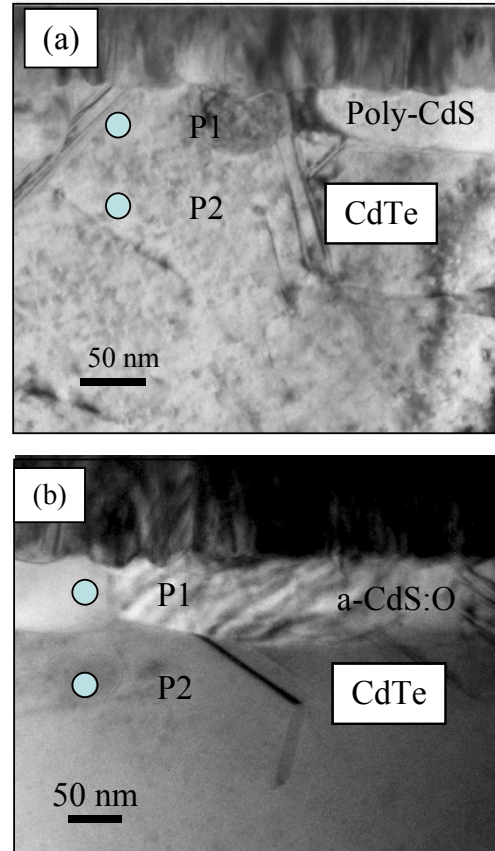


Figure 4. Cross-sectional TEM images of a poly-CdS/CdTe cell (a) and an a-CdS:O/CdTe cell (b).

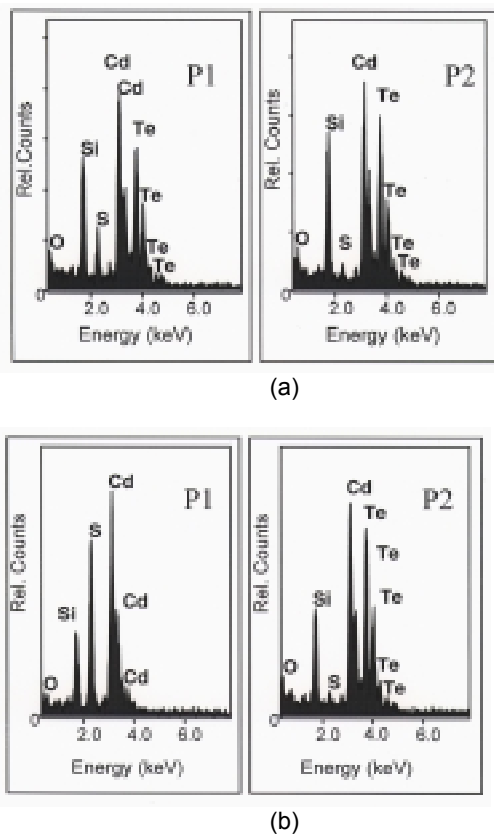


Figure 5. EDS (a) and (b) taken from points P1 and P2 marked on Fig. 4(a) and Fig. 4(b), respectively.

It can be seen from Fig. 3 that this cell with $\sim 1100\text{\AA}$ a-CdS:O film still has high blue quantum efficiency (QE) and high J_{sc} . We have done transmission electron microscopy (TEM) and energy-dispersive spectroscopy (EDS) measurements to explain why this cell with a thicker CdS film has high blue QE and J_{sc} .

Figures 4 (a) and 4(b) show cross-sectional TEM images of a poly-CdS/CdTe cell (a) and an a-CdS:O/CdTe cell (b). In the poly-CdTe cell, the CdS film with a polycrystalline structure was deposited in pure Ar by rf sputtering. In Fig. 4(a), the CdS layer is not visible in some regions, which indicates total consumption of the CdS film. In some areas, the CdS is seen, but with significantly decreased thickness, suggesting that the CdS consumption is spatially variable in the plane of the film. The EDS measurement results (see Fig 5(a)) also indicate Te diffusion into the CdS layer (point P1 in Fig. 5(a)). Optical bowing in the $\text{CdS}_x\text{Te}_{1-x}$ alloy system is such that small changes in the Te content of CdS can result in a large decrease in bandgap [13, 14]. The formation of $\text{CdS}_x\text{Te}_{1-x}$ alloy having a lower bandgap results in poor quantum efficiency in the short-wavelength region. In contrast, it can be seen that the a-CdS:O layer is still very visible (see Fig. 4(b)). The a-CdS:O film has much higher oxygen atomic concentration than poly-CdS film (see Table 1). Therefore, this strongly indicates that oxygen present in a-CdS:O films significantly suppresses the Te

interdiffusion from the CdTe to the CdS film and the formation of a $\text{CdS}_x\text{Te}_{1-x}$ alloy. The EDS results (see Fig. 5(b)) also confirm that Te cannot be found in the a-CdS:O layer (point P1 in Fig. 5(b)), which results in a high QE in the short-wavelength region (see Fig. 3) and a high J_{sc} .

CONCLUSIONS

We have developed a process for preparing the oxygenated amorphous CdS window material (a-CdS:O) at room temperature by rf sputtering. The a-CdS:O films have a higher optical bandgap (2.5-3.1 eV) than poly-CdS film and an amorphous structure, which result from its higher oxygen atomic concentration. The higher O content presented in the a-CdS:O films can significantly suppress the Te diffusion from the CdTe into the CdS film and the formation of a $\text{CdS}_x\text{Te}_{1-x}$ alloy. When integrating the a-CdS:O film into CdTe cell, the J_{sc} can be greatly improved while maintain higher V_{oc} and FF. A CdTe cell demonstrating an NREL-confirmed J_{sc} of 25.85 mA/cm^2 and a total-area efficiency of 15.4% has been achieved.

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