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Real-Time Spectroscopic Ellipsometry of Sputtered CdTe Thin Films: Effect of Ar Pressure on Structural Evolution and Photovoltaic Performance

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ABSTRACT

In this study, 1 μm thick polycrystalline CdTe films were deposited by magnetron sputtering using a variable argon pressure, $2.5 \leq p_{Ar} \leq 50$ mTorr, and a fixed substrate temperature, $T_s = 230°C$. Real time spectroscopic ellipsometry (RTSE) was performed during each deposition in order to analyze the nucleation and coalescence. The evolution of the surface roughness layer thickness d_s with bulk layer thickness d_b and the depth profile in the void volume fraction f_v were also extracted from each RTSE data set. A linear correlation was found between the final d_s value measured by RTSE at the end of deposition and the root-mean-square (rms) surface roughness measured ex situ by atomic force microscopy (AFM) after deposition. A monotonic decrease in RTSE-determined roughness thickness is observed with decreasing Ar pressure from 18 to 2.5 mTorr. The lowest pressure also leads to the greatest bulk layer structural uniformity; in this case, f_v increases by 0.02 with increasing CdTe thickness to 1 μm. The photovoltaic performance of ~1.25 μm thick CdTe films prepared at the lowest pressure of $p_{Ar} = 2.5$ mTorr is compared with that of previously optimized solar cells with $p_{Ar} = 10$ mTorr.

INTRODUCTION

Sputtering is advantageous for CdTe thin film fabrication first because it provides the capability of control over the film microstructure [1], and second because it yields efficient solar cells in a low temperature process [2]. The power applied to the target provides a means for controlling the thickness rate, and hence the kinetics of the deposition, whereas the substrate temperature provides a means for controlling the surface diffusion length of the deposited species. Finally, the Ar pressure provides a means for controlling the momentum per incident species as well as the directionality of these species. By varying the sputtering parameters, films of different microstructures can be deposited, including films with different void volume fraction profiles, and films having a wide range of surface roughness thicknesses.

In previous research, real time spectroscopic ellipsometry (RTSE) has been demonstrated for the characterization of a variety of thin films used in photovoltaics technology [3]. Structural information of interest has been obtained from RTSE, including the characteristics of thin film nucleation and coalescence, as well as the evolution of the bulk and surface roughness layer thicknesses d_b and d_s, respectively, along with variously defined deposition rates. The dielectric function of the growing film, also obtained by RTSE, can provide additional information, for example, the depth profile of the void volume fraction f_v, based on the relationship of the dielectric function to the dipole moment per unit volume [4]. In a previous study [5], these capabilities have been applied to CdTe films deposited on native oxide covered silicon wafers to a thickness of 0.33 μm using T_s as a variable, $188 < T_s < 304°C$, at a fixed argon pressure, p_{Ar} = 18 mTorr. Such studies revealed a monotonic decrease in roughness layer thickness with increasing T_s; a minimum of 60 Å was observed at the end of deposition for the maximum T_s

value of 304°C. A minimum in void volume fraction of $f_v = 0.08$ for the bulk layer near its surface, adjacent to the roughness layer, was observed for an intermediate $T_s \sim 230°$ C.

In the present study, the effects of varying deposition pressure on the growth and microstructure of magnetron sputtered CdTe thin films have been examined using RTSE. Based on these results, solar cells have been fabricated using two different pressures for the CdTe layer, while also varying the post-deposition $CdCl_2$ treatment time, in order to obtain insights into the effects of microstructure of the initial CdTe (i.e., prior to post-deposition treatment) on the performance of solar cells made by magnetron sputtering.

EXPERIMENTAL DETAILS

In this study, CdTe thin films were magnetron sputtered to thicknesses of 1 μm onto native oxide covered silicon wafers at eight different Ar pressures over the range $2.5 \leq p_{Ar} \leq 50$ mTorr. Such substrates were used in order to ensure that the deposition started from a smooth surface. In this way, the roughness evolution is not controlled by the substrate in the early stages of growth, but rather by the deposition conditions. For all depositions, the substrate temperature and rf power were kept constant at 230°C and 60 W, respectively. The films were measured in real time throughout the thickness using a rotating compensator spectroscopic ellipsometer with a spectral range from 0.75 to 6.5 eV [6,7].

The RTSE analysis results motivated additional studies of a series of thin film CdTe solar cells. The devices consist of ~ 1000 Å thickness of CdS and ~ 1.25 μm thickness of CdTe, both layers deposited by magnetron sputtering. For this series, the CdTe layer was deposited under standard conditions [2] with the exception of the pressure, which was adjusted in order to evaluate the role of CdTe microstructure in cell performance. For the performance data reported here, the Ar pressure was set either at the lowest value of 2.5 mTorr, the minimum value for a stable plasma, or at the standard optimized value of 10 mTorr. The devices were fabricated on 3 x 3 in^2 Pilkington TEC-15 glass substrates which were over-deposited in turn with an ~ 1000 Å thick high-resistivity transparent layer (HRT) by the manufacturer in a proprietary process under development. The use of the HRT layer between the CdS and a low sheet resistance transparent conducting oxide layer, such as the top-most SnO_2:F of TEC-15, is known to result in improved overall solar cell efficiency and yield [8,9]. Once deposited, the device structures were cut into four 1.5 x 1.5 in^2 pieces, and each piece was subjected to a post-deposition $CdCl_2$ treatment at 387°C with treatment times ranging from 10 to 35 minutes. The motivation for the different times was to assess whether the solar cells incorporating CdTe films deposited at low pressure required re-optimization of the $CdCl_2$ treatment due to their higher density depth profiles with bulk layer thickness. After standard Cu/Au back-contact formation and annealing [2], the devices were measured under a solar simulator and tested for J_{sc}, V_{oc}, fill factor, and efficiency.

Finally, deposition system geometry necessitated different sputtering configurations for RTSE and for cell fabrication. As a result, detailed correlations between the two studies cannot be drawn; however, we expect that qualitative conclusions are transferrable between the studies.

RESULTS AND DISCUSSION

Figure 1 shows the Ar pressure dependence of the deposition rate, expressed in terms of the increase in CdTe bulk layer thickness per unit time determined by RTSE. As the Ar pressure decreases, the deposition rate increases due to a reduction in scattering of the sputtered species incident on the substrate. In Fig. 2, the nucleating film and surface roughness thickness d_s is

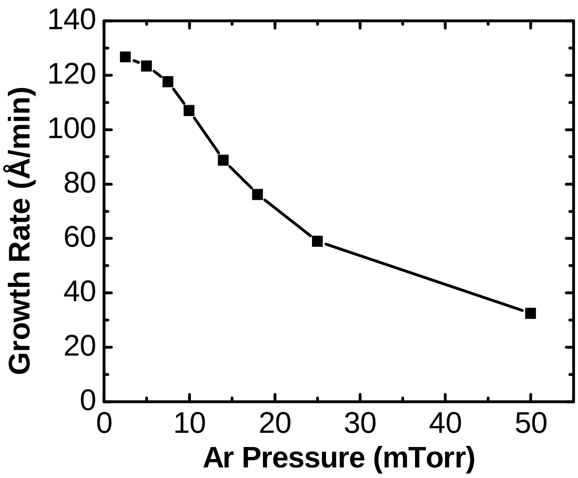
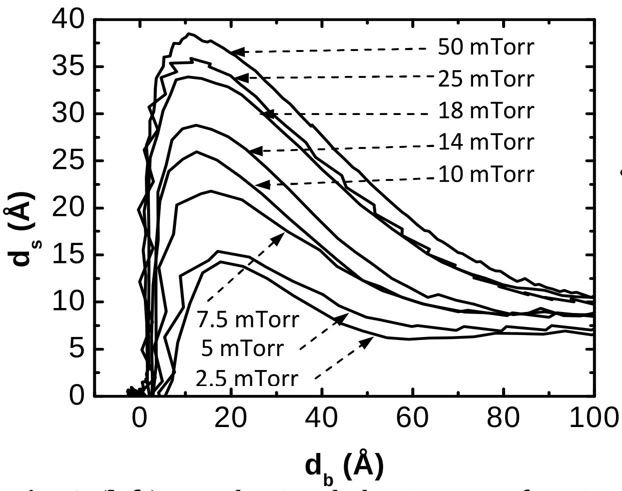


Fig. 1: *Growth rate versus deposition pressure for eight different CdTe depositions.*

shown versus bulk layer thickness d_b in the first ~100 Å for CdTe films of different Ar pressures. A clear monotonic decrease in nucleating cluster height is observed as the pressure decreases, demonstrating the sub-monolayer sensitivity of RTSE in this application. The physical effect is attributed to enhanced ion bombardment, which may compact the film by re-sputtering asperities and filling in the atomic scale voids between the growing clusters. Figure 3 also shows a clear trend in the final surface roughness thickness deduced by RTSE plotted as a function of Ar pressure. For an ~ 1 μm thick film, the surface roughness increases rapidly over the range from 2.5 to 20 mTorr, above which it decreases more gradually as the pressure increases to 50 mTorr.



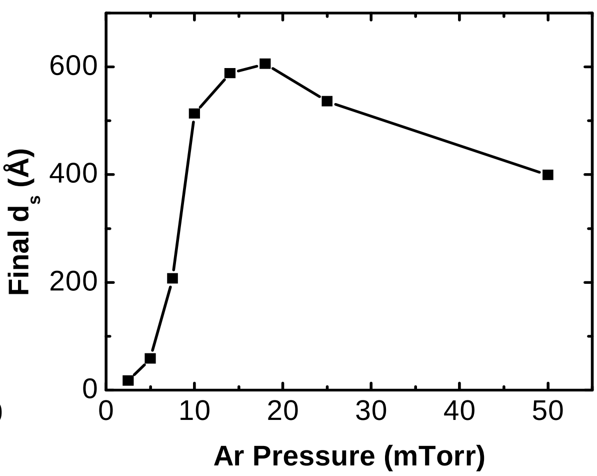


Fig. 2 (left): *Nucleation behavior as a function of bulk layer thickness for different pressures.* **Fig. 3 (right):** *Final surface roughness (at 1 μm CdTe thickness) as a function of Ar pressure.*

After deposition, atomic force microscopy (AFM) images were acquired for the CdTe films deposited at different Ar pressures. Figure 4 shows 5 x 5 μm^2 AFM images for the films deposited at 2.5 mTorr, 10 mTorr, and 50 mTorr. The image of the film deposited at 10 mTorr shows the most clearly defined crystalline grain structure, whereas the 2.5 mTorr film shows the smoothest surface. Figure 5 shows the correlation between surface roughness given by RTSE and the rms surface roughness obtained from the AFM images. The linear correlation between these two is given by the following equation: d_s(RTSE) = 2.0 d_{rms}(AFM) – 120 Å. The fit does not include the three films with the largest surface roughness since they do not closely follow the linear trend. This may be due to an increase in the presence of roughness components of large in-plane scale that may not be detectable by RTSE due to the breakdown of the effective medium theory (EMT) used in the analysis. The EMT loses sensitivity for in-plane roughness scales greater than 0.1λ, where λ is the probe wavelength [10]. In fact, the negative intercept is attributed to the fact that such roughness components exist for all films.

Using layer-by-layer analyses, RTSE data can provide the void volume fractions as depth profiles in the bulk layer thickness [5]. In these analyses, each reference dielectric function is determined simultaneously from data collected in the first 500 Å (closest to the substrate). Figure 6 shows the top-most void fraction in the profile as a function of the Ar pressure. The depth range from which this information is extracted varies with the gradient of the void fraction, but in all cases covers at least the top ~500 Å (closest to the surface roughness layer). A monotonic increase in void fraction occurs in the top-most layer for pressures ranging from 2.5 to 25 mTorr, with a decrease above 25 mTorr. The void fractions > 0.25 in Fig. 6 are attributed to the surface-connected void structures between grains and grain clusters in the AFM images of Fig. 4. For such large bulk layer void fractions, there is not a clear distinction between the bulk and surface roughness layers, the latter defined by a region with average void fraction of 0.5.

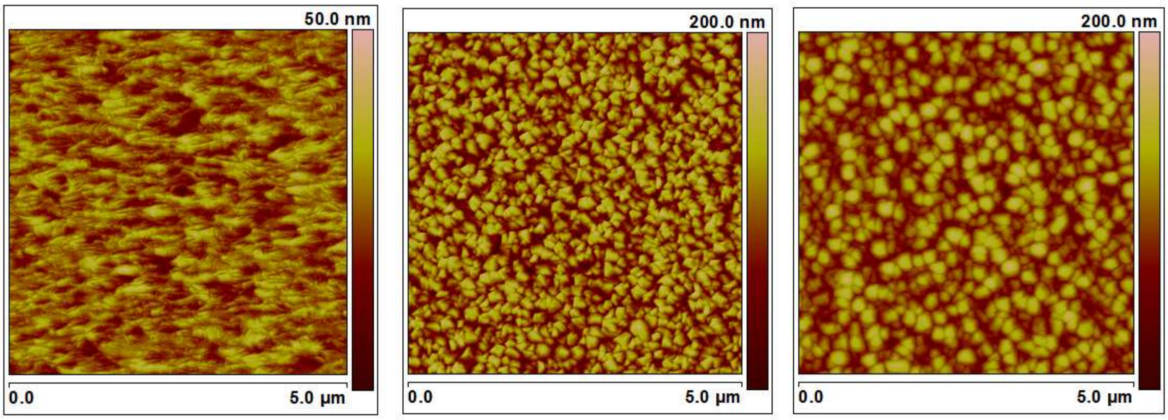
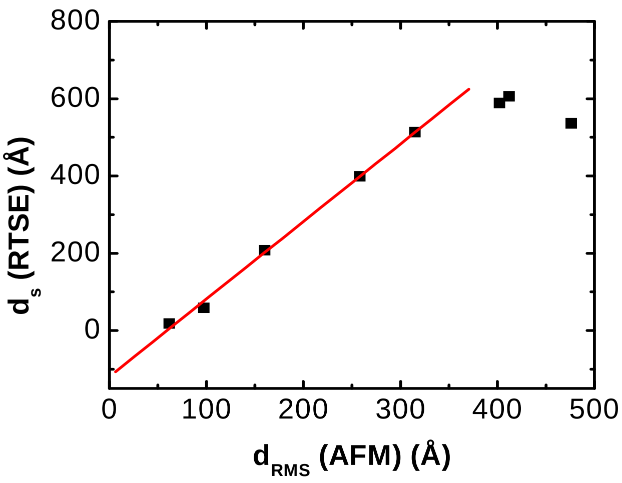


Fig. 4: *AFM images for the 2.5, 10 and 50 mTorr films (increasing order from left to right).*

Since the CdTe film deposited at 2.5 mTorr is the densest and smoothest member of the series studied, it is of interest to evaluate solar cells with the CdTe layers fabricated under the corresponding lowest pressure conditions, even though currently CdTe solar cells are empirically optimized using 10 mTorr Ar pressure [2]. Figure 7 shows J_{sc}, V_{oc}, FF, and efficiency measurements of cells incorporating CdTe films deposited at 2.5 and 10 mTorr. These cells were subjected to different $CdCl_2$ post-deposition treatment times, and the 10 mTorr results show better overall performance in all device metrics. Each data point represents an average of the best ten cells fabricated under the given set of conditions. For CdTe films deposited at 10 mTorr, a high V_{oc} (> 770 mV) and fill factor (> 0.65) are obtained over a range of treatment times from 10 to 35 minutes. For CdTe deposited at 2.5 mTorr, a high V_{oc} and FF require at least 30 and 20 minutes of treatment time respectively, possibly due to the high density of the film and the resulting slower diffusion processes. Because V_{oc} is most affected by the quality of the CdS/CdTe interface whereas FF is influenced by the overall bulk quality, the longer time required for improving the interface region would be consistent with diffusion occurring from



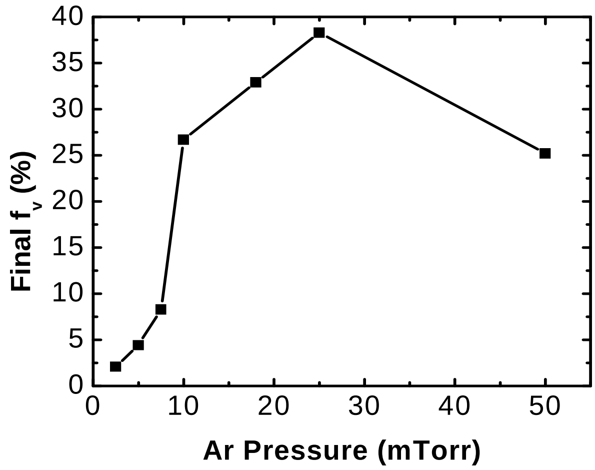


Fig. 5 (left): *Correlation of RTSE and AFM rms surface roughness thicknesses.*
Fig. 6 (right): *Void vol. % in the top ~500 Å of the bulk layer as a function of pressure***.**

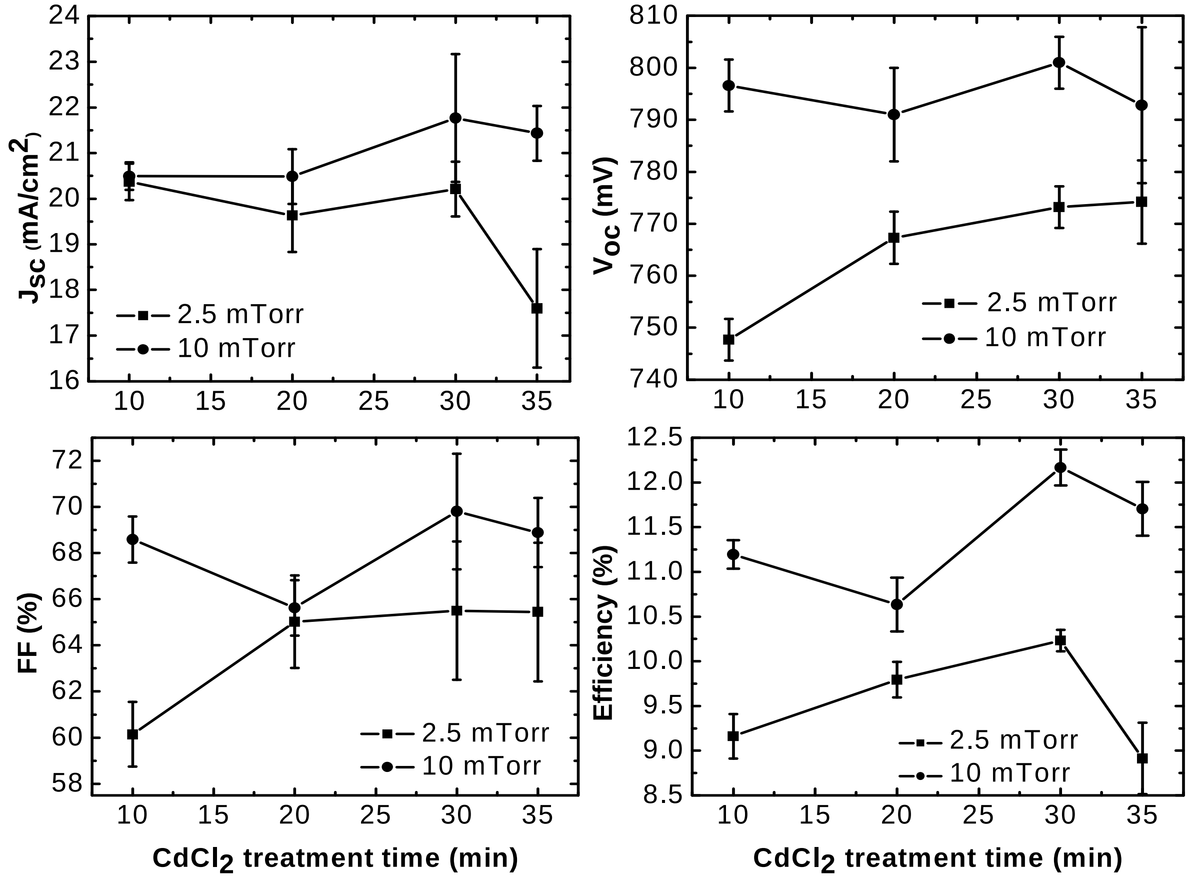


Fig. 7: *J_{sc}, V_{oc}, FF, and efficiency for solar cells fabricated with ~ 1000 Å of CdS and ~1.25 μm CdTe, the latter deposited at 2.5 and 10 mTorr.*

the CdTe near-surface to the interface. It is apparent that the best ten-cell average efficiency for low pressure is poorer than the best ten-cell average efficiency for 10 mTorr irrespective of the

$CdCl_2$ treatment time. This may be due to ion bombardment damage and the associated fine grain structure that makes post-deposition treatment less effective. In fact, the AFM morphology may indicate re-sputtering of the CdTe surface at the lowest pressure.

SUMMARY

Magnetron sputtering combined with RTSE is useful for CdTe solar cell fabrication because it allows analysis of the film bulk and surface microstructure with the potential for future control capabilities. One possible approach in the future is to vary the deposition conditions in a step-wise or graded fashion in order to separately tailor the near-interface, bulk, and near-surface properties, rather than relying on the natural film growth evolution that occurs under fixed deposition conditions. In the study reported here, significant differences in the surface roughness evolution and void volume fraction profiles can be seen for CdTe films deposited at different Ar pressures. The RTSE analysis is supported by a clear monotonic correlation between surface roughness thickness given by RTSE and the rms surface roughness determined from AFM images. Complete solar cells have been fabricated using CdTe deposited at the lowest pressure, which leads to the lowest average void fraction in the film bulk and the smoothest surface in the RTSE studies. In addition, the post-deposition $CdCl_2$ treatment time has been varied in an effort to re-optimize this low pressure process. Such results suggest that ion-bombardment may generate damage and/or structure that cannot be healed by treatment and that the CdTe sputtering pressure must be raised to moderate this bombardment for optimum devices.

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