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Achieving a pinhole-free CdS layer is necessary to produce high performance thin film CdTe solar cells. Pinholes in the CdS layer can compromise the efficiency of a CdTe solar cell by causing shunts. We have investigated the use of a plasma treatment of a fluorine doped tin oxide coated glass substrate (NSG TEC 15) and its effect on pinhole reduction in thin film CdS layers grown by Chemical Bath Deposition. CdS films, $<100\,nm$ thickness, were deposited on both O_2/Ar plasma cleaned and conventionally cleaned substrates. We show that the O_2/Ar plasma treatment of the TEC 15 substrate reduced the water contact angle from $\sim 55°$ to less than $12°$ indicating a substantial increase in the surface energy. The CdS deposited on the plasma treated TEC 15 was pinhole free, very smooth and homogenous in morphology and composition. Scanning electron microscopy images show that the O_2/Ar plasma treatment is effective in increasing film density and grain size. Corresponding spectroscopic ellipsometry measurements show an increase in the refractive index from 2.18 to 2.43 at $550\,nm$ wavelength. © *2013 AIP Publishing LLC*. [http://dx.doi.org/10.1063/1.4828362]

I. INTRODUCTION

Surface treatment by plasma cleaning has been reported to be a useful process tool for more than 30 yr in a broad range of applications spanning from microelectronics and photovoltaics (PVs) to automotive, textiles, medical, plastics, etc.[1,2]

Plasma cleaning is an effective and environmentally safe method for surface preparation. Activation of the surface of a material is important for the growth of thin films since surface contaminants and the native oxide can alter the growth mode and thin film adhesion. It can also affect the properties of the deposited films and therefore the performance of the PV devices.[3,4]

The surface properties of transparent conducting oxides (TCOs) have an influence on the quality of the other films comprising the cell. In particular, sputter treatments have been shown to reduce carbon contamination and modify the resulting interface between the SnO_2 and the CdS layers.[5] Poor growth regions, appearing as pinholes, can form in the n-type CdS layer, allowing a shunt path to develop between the front contact and the p-type CdTe film.[6] Pinholes are particularly troublesome when a thin CdS layer is deposited on TCO-coated glass that has been cleaned using industry-standard techniques.[7]

Plasma treatments have previously been applied to TCOs such as indium tin oxide (ITO),[1] aluminium-doped zinc oxide (AZO),[8] and zinc oxide (ZnO)[9] with different gas combinations such as argon, hydrogen, or oxygen. These treatments have been shown to change the properties of the TCO surfaces.

In this paper, we discuss the plasma treatment of a commercially available fluorine doped tin oxide (FTO) transparent conducting oxide NSG TEC 15, which is used as superstrate in CdTe solar cell devices.
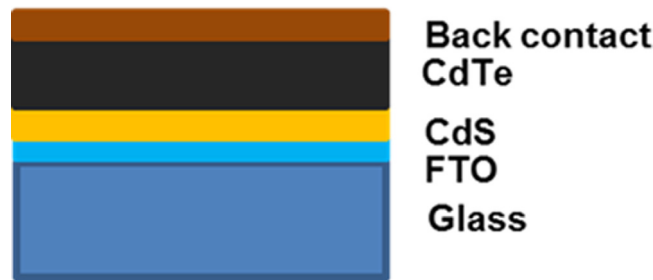
FIG. 1. Schematic of a thin film CdTe solar cell in superstrate configuration.

A thin film CdTe solar cell consists of a multi-layer stack material system, with layers having specifically defined properties. Thin film CdTe solar cells are grown in a superstrate configuration as shown in Figure 1 on a FTO coated glass substrate.[10] The light transmits through the TCO coated glass before reaching the p-n heterojunction, consisting of the n-type CdS layer and a p-type CdTe layer.

The plasma pre-treatment of the TEC 15 glass was performed to activate the surface prior to the chemical bath deposition (CBD) of the thin CdS film.

Good surface wettability of the TCO coated substrate is required to avoid the presence of the pinholes and ensure continuity in the deposited CdS thin films. Fluorine doped tin oxide is deposited on an industrial scale using an atmospheric pressure CVD process that results in a relatively rough surface. This roughness can increase the probability of pinhole formation. Here we report on the use of a plasma treatment process to grow pinhole-free CdS thin films on TEC 15 glass.

II. EXPERIMENTAL

TEC 15 glass supplied by NSG-Pilkington was used as the substrate material. TEC 15 is a multilayer stack of materials deposited on a 3.2 mm thick glass. The stack consists of a 25 nm SnO_2 layer, a 25 nm SiO_2 layer, and a 280 nm thick conducting layer of fluorine doped tin oxide (SnO_2:F). TEC 15 has a sheet resistance of 15 $\Omega/\square$ and a relatively good transparency, ~82% light transmittance. These properties are a good compromise between the electrical and the optical requirements of a PV device substrate. The substrate was treated using 20 sccm O_2/30 sccm Ar plasma for 5 min prior to the CdS film growth. The plasma power was set at 100 W and at a pressure of between 335 and 273 mTorr. Electrodes and sample trays are 406.4 mm × 406.4 mm in area using perforated aluminium of thickness 3.175 mm. The parallel electrodes are used to provide uniform plasma across the sample area. All substrate surfaces are treated to the same degree, irrespective of their position on the sample tray. The plasma treatment reactor, Glen100-P AE Advanced Energy, was a parallel plate system using AC plasma power source with potential for three gas admittance lines. The system was pumped to a pre-process pressure of 332 mTorr using a rotary pump.

A 50 nm CdS thin film was deposited by CBD, the reaction occurs in a beaker immersed in a water jacket to ensure constant temperature (70 °C). The bath solution was made of 200 ml of de-ionized water, 15 ml of $Cd(CH_3COO)_2$ 0.01 M, 25 ml of NH_4OH 25%, and 10 ml of $CS(NH_2)_2$. A magnetic bar was used to stir the solution to accelerate the reaction kinetics.

III. RESULTS AND DISCUSSION

A. Substrate surface modification

Plasma treatment activates the substrate surface by increasing the surface energy. The surface energy of the material was tested by measuring the water contact angle before and immediately after the treatment. Figure 2 shows the effect of the plasma treatment on the FTO coated glass surface. The equilibrium contact angle that the drop makes with the surface is 54.3°
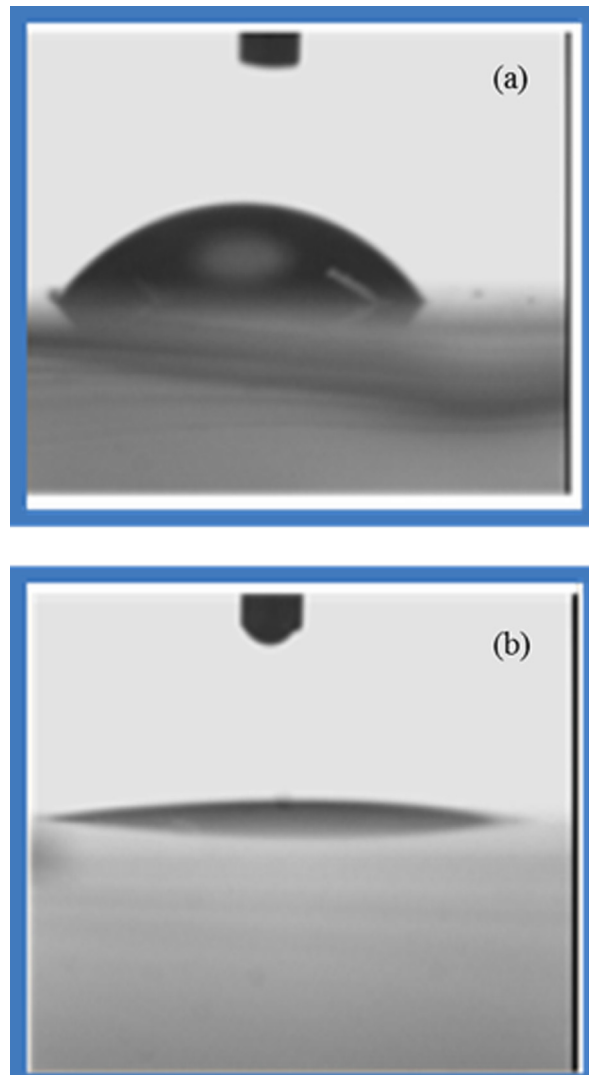
FIG. 2. Water contact angle images (a) prior and (b) post plasma treatment.

before the treatment and 12.3° after the plasma treatment. This indicates that the treatment increases the hydrophilic nature of the surface. The increased surface energy is beneficial for adhesion and the continuity of the thin film. It is possible that the increase in surface energy may change the thin film growth kinetics. However, there was only a marginal difference in thin film thickness (∼50 nm) for films deposited on the treated and untreated surfaces as measured by spectroscopic ellipsometry. Hence a valid comparison was possible between their properties.

This hydrophilic behaviour corresponds to the removal of contaminates from the surface, as confirmed by X-ray photoelectron spectroscopy (XPS) analysis. Table I reports the atomic

TABLE I. Atomic % composition as determined by XPS.

	Untreated	Plasma treated
C1s %	24.5	11.9
O1s %	46.3	55.2
Sn3d %	27.3	31.4

percentage of Carbon (C1s), Oxygen (O1s), and Tin (Sn3d) for the untreated and the plasma treated substrates, indicating carbon contamination reduction without altering the Sn/O ratio.

B. Impact of substrate plasma treatment on the CdS films

Scanning white light interferometry (SWLI) is a powerful tool for the metrology of surfaces. We use a variant of SWLI called Coherence Correlation Interferometry (*CCI*) developed by Taylor Hobson, Ltd. The CCI technique was used to analyse the surface morphology of the CdS films and detect pinholes in the CdS. Pinholes appear as spikes in the CCI surface image as shown in Figure 3(a). In this case the CdS was deposited on the untreated substrate; pinholes were detected with a mean depth of 55 nm and a width of 0.65 μm as shown in Figure 4. The spatial resolution of the CCI is determined by the wavelength of light and the numerical aperture of the lens used and is typically $\sim$0.3 μm. The vertical resolution is typically <1 nm.

The CCI analysis shows that the pinhole density was dramatically decreased and virtually eliminated for the film grown on the plasma treated substrate (Fig. 3(b)); the thin film also has a smoother surface.

Scanning Electron Microscopy (SEM) images were obtained to study the surface morphology of the grown CdS films. Figure 5 shows the comparison between the surface of the untreated (a) and the plasma treated (b) samples. The CdS films exhibit a crystalline structure with grain size increasing from $\sim$108 nm to $\sim$175 nm following plasma treatment of substrate.
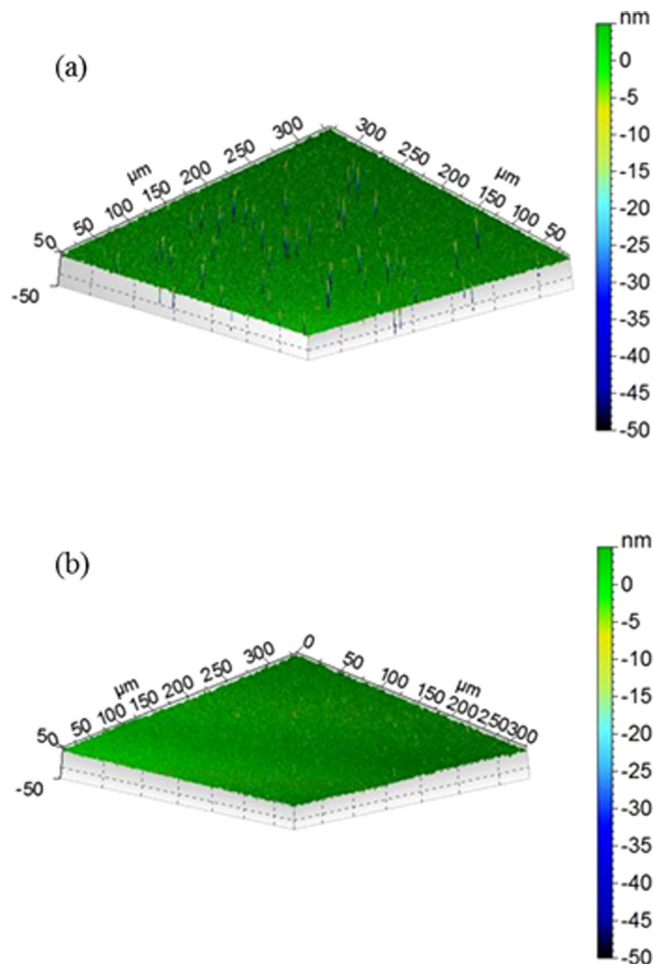

FIG. 3. Three dimensional CCI images of CdS deposited on (a) untreated and (b) plasma treated substrates (20 sccm O$_2$/30 sccm Ar).
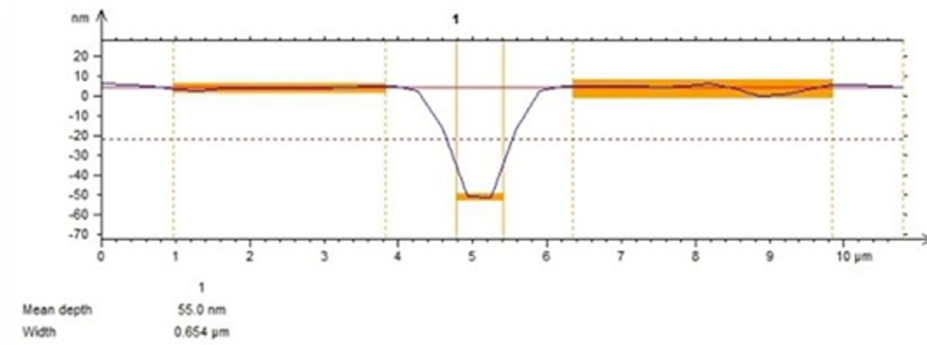
FIG. 4. Mean depth and width of pinholes in CdS observed on the surface of the untreated samples. The thickness of the CdS layer was 50 nm.

The treated samples generally showed more uniform coverage of the surface with a more compact deposited film.

XPS analysis was also performed on the CdS films to analyse their stoichiometry. Figure 6(a) shows the XPS spectra of Cd3d and S2p photoelectron core levels for the untreated
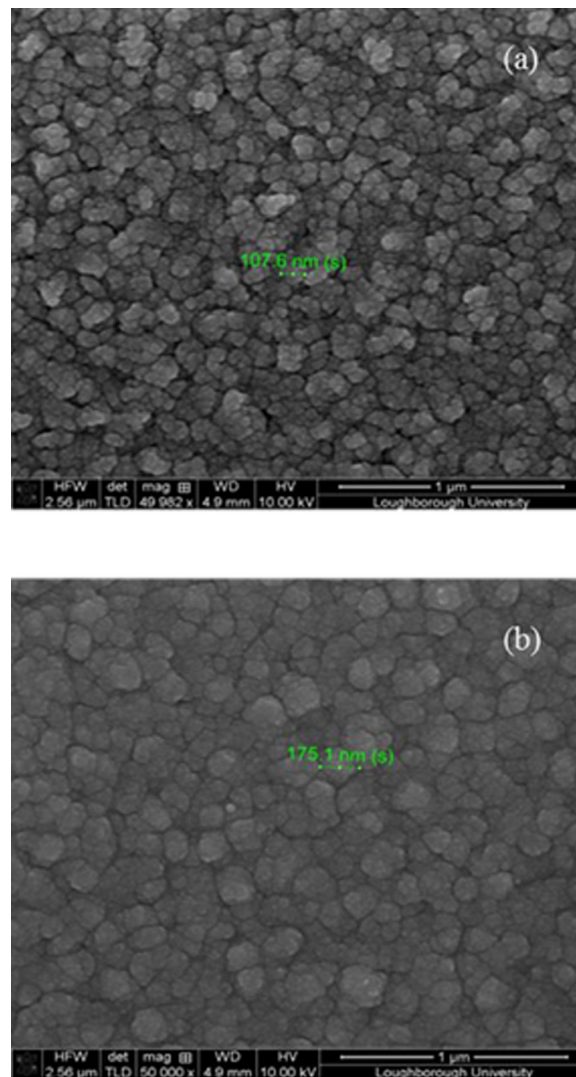

FIG. 5. SEM images of CdS films grown on (a) untreated and (b) plasma treated (20% O_2/30% Ar) FTO coated glass.
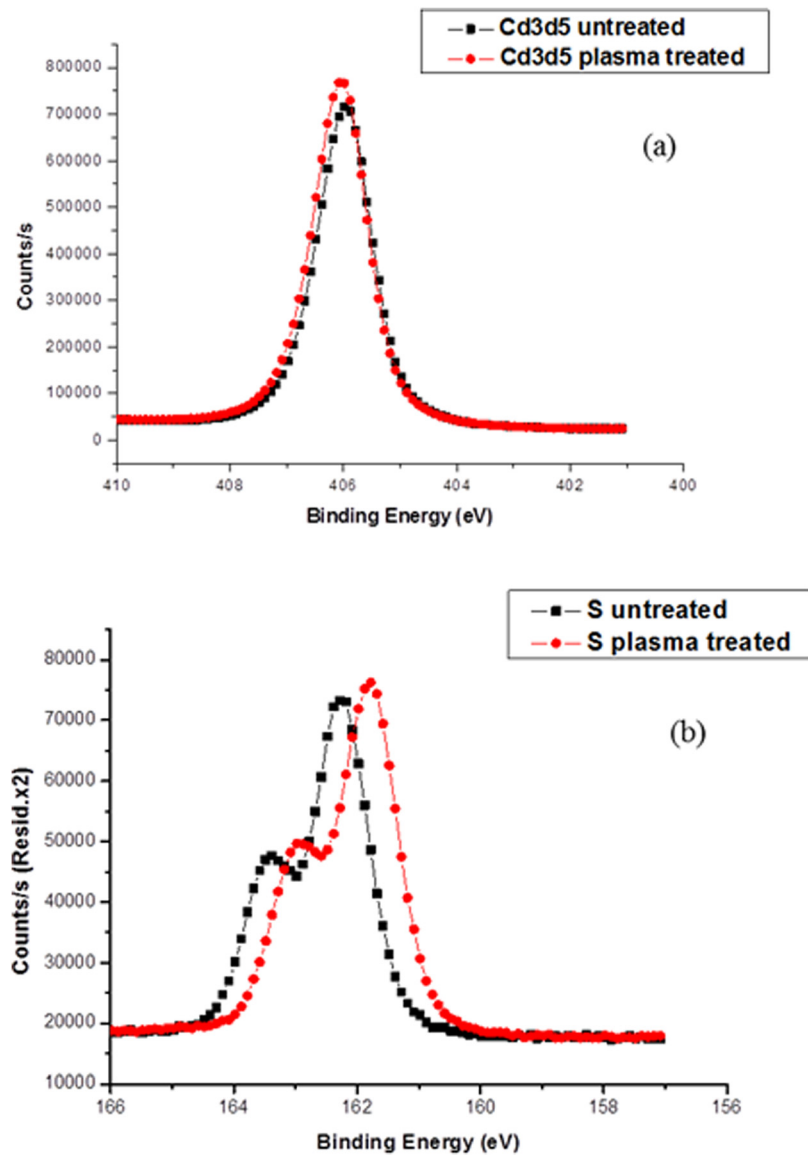
FIG. 6. XPS measurements of samples untreated and plasma treated (20 sccm O_2) for Cd 3d5/2 (a) and S2p peak (b).

and the plasma treated samples. The position of the peak at 405.8 eV for Cd orbital $3d_{5/2}$ and the shape and binding energy of 161.6 and 162.8 eV for $S2p_{3/2}$ and $S2p_{1/2}$, match the theoretical CdS values,[11] indicating that CdS was not incorporating oxygen into the films.

The optical properties of the CdS films were measured using spectroscopic ellipsometry. Transmission and reflection measurements were obtained using a spectrophotometer. The Tauc-Lorentz model[12] was used to parameterise the spectral dependence of the CdS refractive index, n, and extinction coefficient, k. The derived optical properties are shown in Figure 7. The CdS film deposited on the plasma treated substrate showed increased refractive index (Figure 7(a)). The film also showed increased absorption and a red-shift of the absorption edge (Figure 7(b)). This is consistent with the increased grain size, increased compactness, and reduced pinhole density observed for the film deposited on the plasma treated substrate.

Figure 8 shows the transmittance and reflectance spectra of the CdS thin films deposited on the untreated and on the plasma treated substrates. The transmittance of the thin films reaches a maximum of $\sim$80% and it decreases near the absorption edge at 500 nm; this confirms that the CdS has good crystallinity.[13]
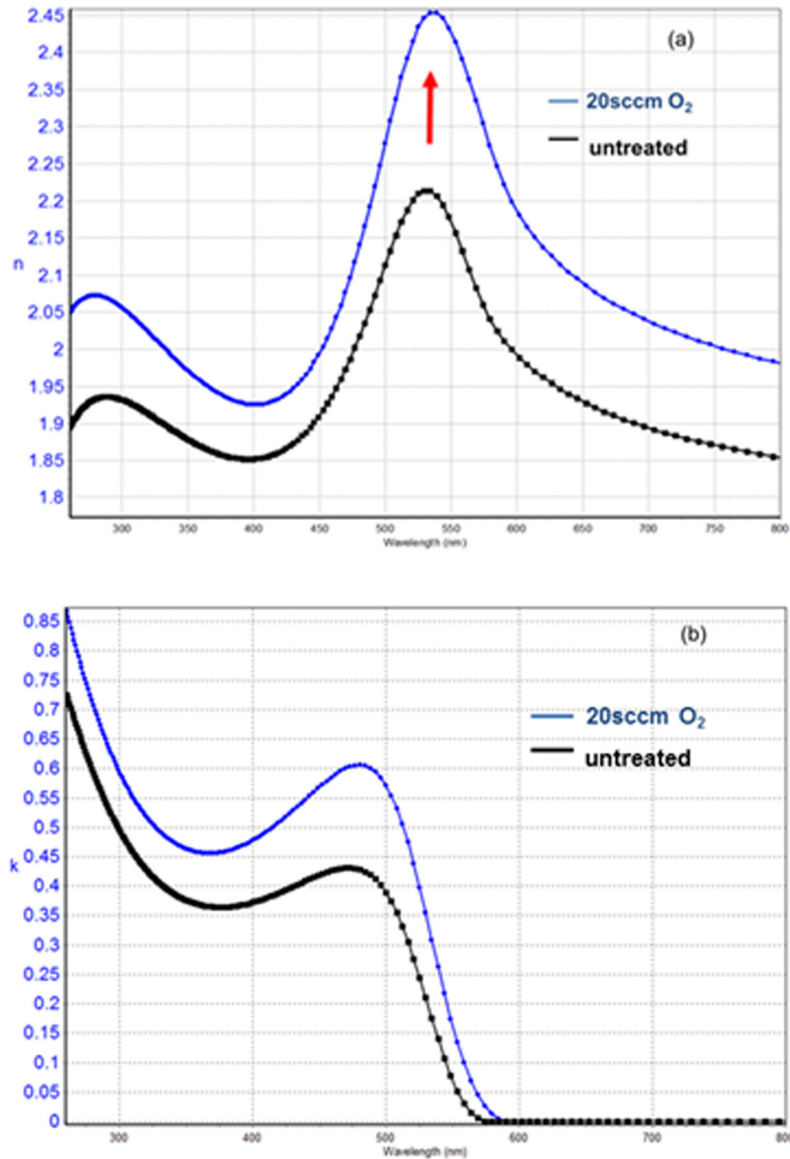
FIG. 7. n (a) and k (b) dispersions measured for CdS films deposited on the untreated substrate and the plasma treated substrate (20 sccm of O_2).

The CdS deposited on the plasma treated substrate shows lower transmission compared to the film deposited on the untreated substrate. The transmittance is lower due to the higher optical density of the CdS film as shown by the SEM measurements and the removal of pinholes as shown by the CCI metrology measurements. The Urbach equation can be used to obtain the absorption coefficient,[14] it is defined by formula

$$\alpha = \frac{A(h\nu - E_g)^p}{h\nu},\tag{1}$$

where A is a constant, E_g is the band gap energy, ν is the frequency, h is the Plank's constant, p is the numerical coefficient. In Figure 9, $[\alpha h\nu]^2$ is shown as a function of the energy (eV), p in this case is 0.5. The single slope in the curve explains the direct transition of electrons between the valence band and the conduction band. Extrapolating the linear region of $[\alpha]^2$ up to the value $\alpha = 0$, the band gap energy (E_g) is determined to be 2.3 eV.
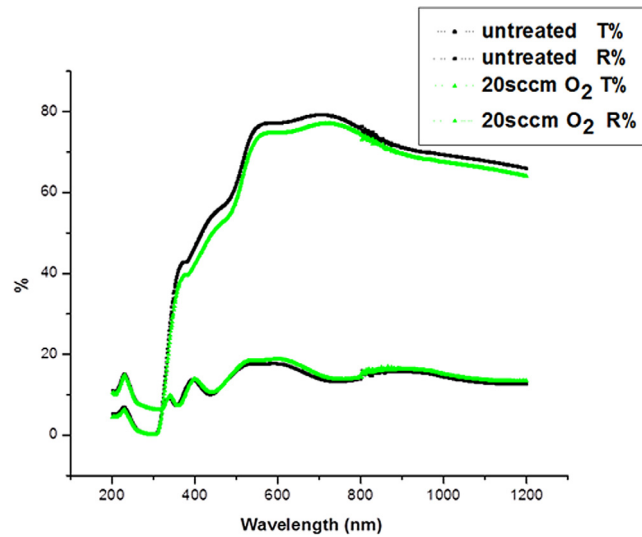
FIG. 8. Transmission and reflection spectra for CdS thin films deposited on TEC 15, comparing the untreated and the plasma treated surface, with 20 sccm of O_2.
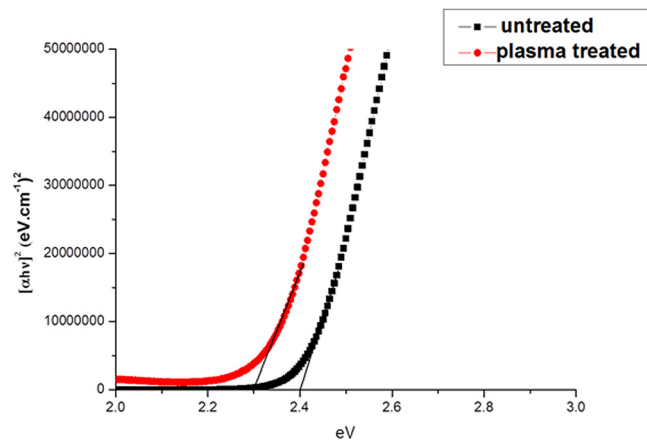

FIG. 9. Energy band gap (E_g) of the untreated and plasma treated sample, estimated from the $[\alpha h\nu]^2 = f(h\nu)$, by using the Urbach equation.

The band gap decreased from 2.4 eV to 2.3 eV as a result of the substrate plasma cleaning due to the increased density of the film or the small grain size.[15]

IV. CONCLUSIONS

Plasma cleaning of FTO-coated glass prior to the deposition of the CdS/CdTe solar cell strongly affects the TCO surface, and improves the quality of the subsequently deposited CdS thin film. Specifically, the plasma cleaned FTO exhibits increased hydrophilic behaviour, due to a reduction or elimination of surface contamination. This corresponds to a reduction in water contact angle and increased surface energy. When CdS thin films are deposited on to a plasma cleaned FTO surface we have shown that the pinhole density is greatly reduced and virtually eliminated compared with CdS films deposited on substrates treated using standard wet cleaning techniques.

The plasma treatment improves the wettability of the substrate as demonstrated using water contact measurements. This improves the optical and morphological properties of the deposited CdS thin films, resulting in a higher refractive index and a higher absorption coefficient related

to the increased film density and increased grain size of CdS film. The pinhole removal and the increased density allow the use of a much thinner CdS layer. Use of a thinner CdS layer actually reduces absorption of blue spectrum photons thereby increasing the efficiency of the thin film CdTe cell. Further experiments are now planned to incorporate the plasma cleaning process into a full cell deposition process to assess the improvement to device performance.

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