Blistering of magnetron sputtered thin film CdTe devices

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Abstract –**Magnetron sputtering is an industrially scalable technique for thin film deposition. It provides excellent coating uniformity and the deposition can be conducted at relatively low substrate temperatures. It is widely used in the manufacture of solar modules. However, its use for the deposition of thin film CdTe devices results in unusual problems. Blisters appear on the surface of the device and voids occur in the CdTe absorber. These problems appear after the cadmium chloride activation treatment. The voids often occur at the CdS/CdTe interface causing catastrophic delamination. This problem has been known for more than 25 years, but the mechanisms leading to blistering have not been understood. Using High Resolution Transmission Electron Microscopy we have discovered that during the activation process, argon trapped during the sputtering process diffuses in the lattice to form gas bubbles. The gas bubbles grow by agglomeration particularly at grain boundaries and at interfaces. The growth of the bubbles eventually leads to void formation and blistering.**

Index Terms — **CdTe, thin film, solar cell, magnetron sputtering, photovoltaics, electron microscopy, working gas.**

I. Introduction

The market for solar modules is currently dominated by crystalline silicon based technologies, which account for ~90% of the market [1]. Thin film CdTe photovoltaic (PV) modules are an attractive alternative. The technology is less complex and has lower manufacturing costs. The temperature coefficient of CdTe is also highly favourable. The record efficiency for thin film CdTe technology is 22.1% as reported by First Solar Inc. [2].

The use of magnetron sputtering for the deposition of PV devices has many potential advantages. The technique deposits thin films with excellent uniformity which allows the absorber thickness to be reduced to ~1 µm resulting in a useful reduction in materials cost [3], [4]. Also the coating uniformity enables the technology to be applied to new applications such as semi-transparent window products. The lower temperature of deposition also reduces manufacturing costs. Until recently, magnetron sputtering was exclusively carried out using Radio-Frequency (RF) power supplies. The drawback of using RF power is the low deposition rate due to the low duty cycle [5]. The use of RF power is not viable for a manufacturing process. We recently reported the successful use of pulsed DC magnetron sputtering for the deposition of thin film CdTe [3], [6]. The advantage of pulsed DC power is that sufficiently high deposition rates can be achieved to make the process viable as a production tool. This was a surprising development since compound targets are used that are highly resistive.

As deposited CdTe devices show poor electrical performance and require a cadmium chloride ($CdCl_2$) activation treatment [7], [8]. Surface blisters and void formation in RF magnetron sputtered films have been observed following the treatment for more than 25 years [9], [10]. An SEM image of a heavily blistered CdTe surface is shown in Fig. 1. The blisters are typically 10µm to 200µm in diameter and are often perforated causing spallation of the material. Fig 2 shows an SEM image of a cross-section of a blister prepared using a focused ion beam. Delamination of the CdTe layer has occurred at the CdS/CdTe junction. Even if blistering has not occurred, void formation at the junction would limit overall efficiency. Often, complete delamination of the absorber occurs along the CdS/CdTe junction. The mechanisms leading to the formation of blisters and voids in sputtered CdTe has remained unclear.

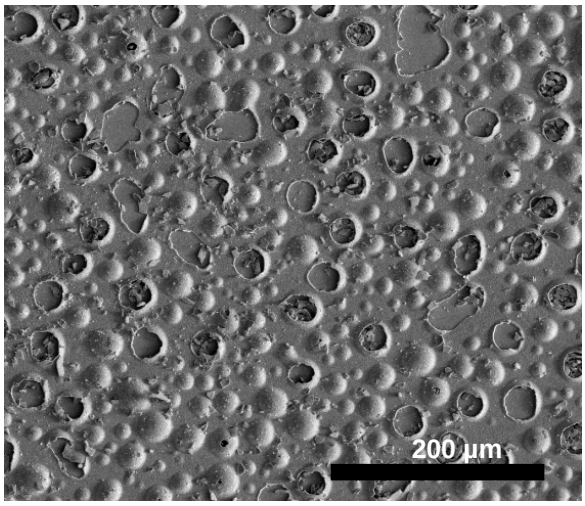

Fig. 1 SEM image of a CdTe device sputter deposited using argon and then activated using $CdCl_2$. Blisters appear on the surface and delamination often occurs at the junction.

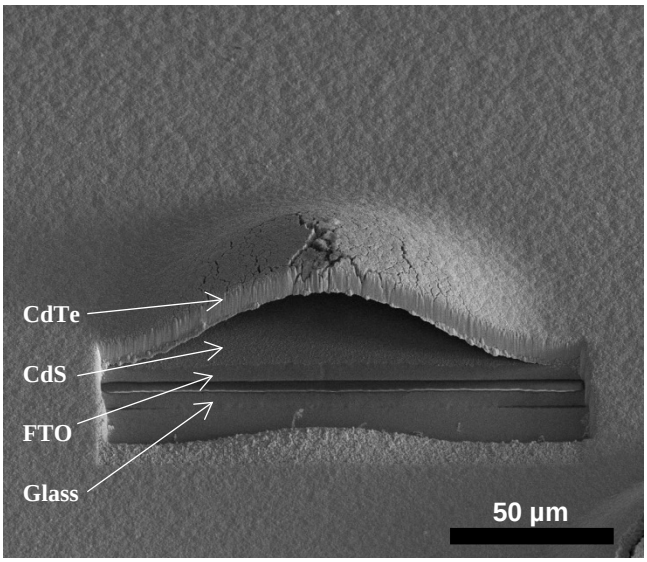

Fig 2 An SEM image cross-section of a large blister |100 um in diameter) prepared using a Focused ion beam. Delamination has occurred at the CdS/CdTe interface.

II. EXPERIMENTAL

a. Magnetron sputtering

A PV Solar (PowerVision Ltd.) magnetron sputtering system was used to deposit the CdS/CdTe devices using compound CdS and CdTe targets. The magnetrons are powered by a pulsed DC power supply (Advanced Energy Inc. Pinnacle plus 5kW). The 50mm x 50mm substrates are mounted vertically on a substrate carrier which rotates at 120rpm during the deposition process. The vacuum chamber is load locked and is fitted with three 150mm diameter, circular unbalanced magnetrons targets. The deposition chamber is pumped using a turbomolecular pump (Edwards nEXT300D) mounted vertically above the chamber. Internal radiant heaters are available to raise the substrate temperature to 250^0C during rotation. The operation of each magnetron and all process parameters are under computer control.

The films were deposited onto NSG Pilkington Fluorine doped tin oxide coated Soda Lime glass (TEC 100) substrates. Prior to deposition, the substrates were cleaned in an ultrasonic bath in a 10% Isopropyl alcohol (IPA) solution in DI water at 60°C for 60min followed by the RCA cleaning process [11]. The surface was activated prior to deposition by a low pressure plasma treatment with 100W Ar/O_2 plasma (Glen 1000P series) for 5 minutes

b. Cadmium Chloride Activation Process

The activation process was performed using a $CdCl_2$ vapour treatment in a tube furnace. Samples were placed in a graphite substrate holder above a crucible with $CdCl_2$ powder. The tube was evacuated to 50 mbar and heated with Infra-Red lamps to a temperature of 400°C and the devices were treated for 6 min.

c. Device Characterisation

Transmission Electron Microscopy (TEM) was used to investigate the microstructure of the CdTe thin films deposited. TEM images were obtained using a Jeol JEM 2000FX operating at 200kV. Samples for TEM were prepared by Focused Ion Beam (FIB) milling using a dual beam FEI Nova 600 Nanolab. Cross-sections of samples were prepared through the coating and into the glass superstrate. A standard in situ lift out method was used. A platinum over-layer was deposited to determine the surface and homogenize the thinning of the samples. High resolution TEM images were obtained using a FEI Tecnai F20.

III. RESULTS

a. As-deposited CdS/CdTe devices

Fig. 3 shows a TEM image of a cross-section of a CdS/CdTe photovoltaic device sputter deposited using argon as the working gas. The CdS layer and the CdTe absorber were deposited sequentially without breaking vacuum. The argon flow rate was set to 20 sccm and the substrate temperature was maintained at ~200°C during the deposition. The structure of the films is dense and columnar. The film is uniform and no voids or pinholes were observed in the films after deposition. The average grain diameter was ~200nm. The open circuit voltage of the as-deposited sample was ~50mV. The elemental composition of the CdTe absorber was analysed using Energy Dispersive Spectroscopy (EDS). A spectrum obtained from the as-deposited film is shown in Fig. 4. The spectrum confirms the stoichiometry of the CdTe, but also reveals the presence of argon with a concentration of 4 At%. The argon appears to be distributed uniformly. The argon has been trapped in the growing CdTe layer during the deposition process. Argon ions are accelerated to the film by the potential difference between the target and the substrate. Magnetrons are deliberately unbalanced to encourage argon ion bombardment of the growing film to aid its densification.

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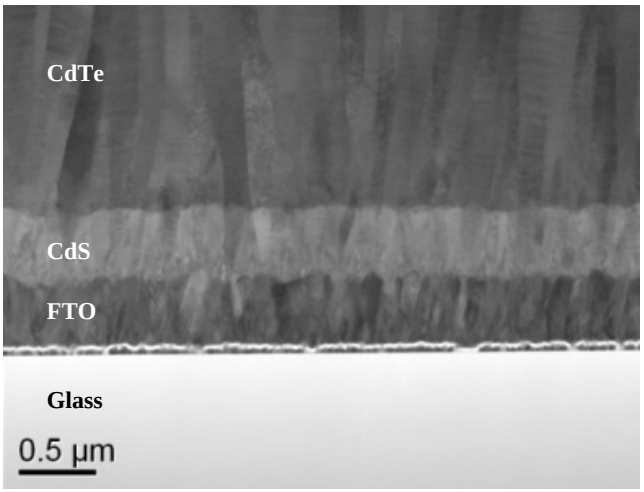

Fig. 2 TEM image of a cross-section of an as deposited CdS/CdTe film using argon working gas. The microstructure of the CdTe is dense and columnar.

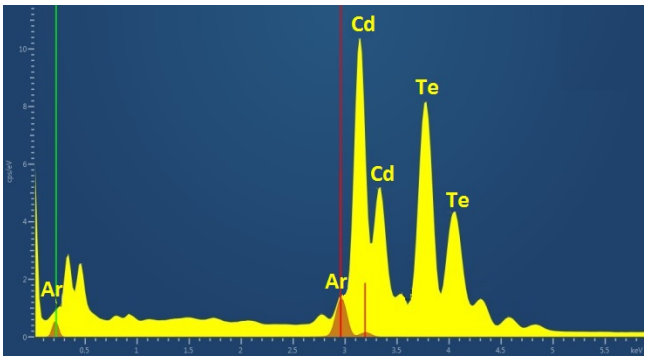

Fig. 4 An Energy Dispersive spectrum obtained from the CdTe absorber in an as-deposited CdS/CdTe device revealing the presence of 4At% of argon trapped in the film.

b. Cadmium chloride activation

The devices were activated using the $CdCl_2$ treatment at 400°C for 6min. The Voc of the device increased to ~700mV. Blistering of the CdTe surface was observed following the $CdCl_2$ treatment similar to that shown in the SEM image in Fig. 1. Fig. 5 is a TEM image of a device cross-section following the $CdCl_2$ activation process. A high density of large voids is observed in the CdTe layer. Voids are often located at grain boundaries and are also observed at the CdS/CdTe junction. The CdS layer and the fluorine doped tin oxide layers are largely unaffected by the treatment.

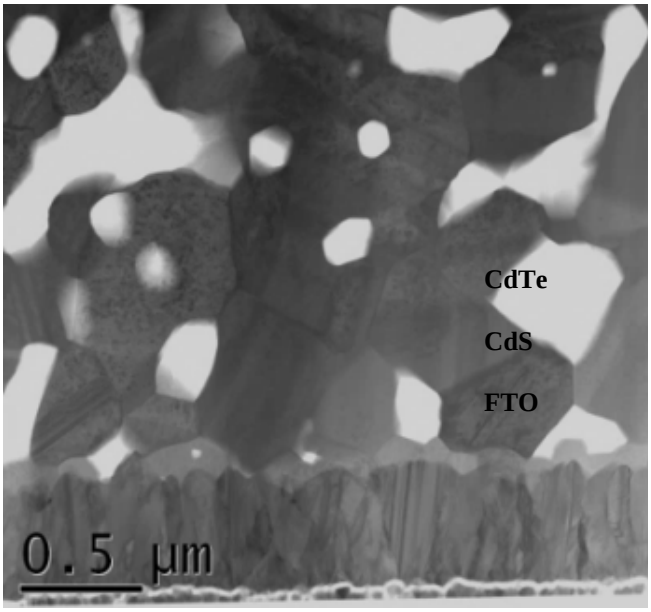

Fig. 5 A TEM cross-section image of a CdS/CdTe device following the $CdCl_2$ treatment. Large voids are observed in the CdTe layer. Although voids are observed at the CdTe interface, the CdS layer is unaffected.

c. Rapid thermal annealing

It is not clear if the voids and blisters in the CdTe absorber are caused by the annealing at 400°C or by the presence of cadmium chloride. This question was addressed by simply annealing sputtered CdTe using a Rapid Thermal Annealing process. Devices were annealed at 350^0C for 12 hours without $CdCl_2$. The device cross-sections were inspected using High Resolution Transmission Electron Microscopy (HR-TEM).

Fig. 6 shows a HR-TEM image of a cross-section of a thin film CdTe device annealed in a Rapid Thermal Processing system The atomic resolution HR-TEM image reveals a number of spherical features about 5nm in diameter through the thin CdTe laminar film prepared using a Focused Ion beam.. Use of EDS elemental mapping confirmed the presence of argon in the absorber material which is trapped during the sputtering process. During annealing the trapped argon atoms diffuses in the lattice to form gas bubbles. In in situ annealing experiments in the TEM we have observed movement of the small bubbles to grain boundaries where they coalesce and dramatically increase in size. The presence of cadmium chloride appears to accelerate this process through recrystallization to cause the formation of large voids and surface blistering in the CdTe layer. Although the CdS layer is unaffected void formation at the CdS/CdTe interface junction damages the junction and reduces the device efficiency.

d. Krypton working gas

Argon is the conventional working gas used in magnetron sputtering. However, it is useful to explore the use of alternatives for the magnetron working gas. Here we compare argon with the use of alternative inert gases. The sputter yield of helium is too low to be useful and is known to cause bubble formation in a number of materials. This study explores the use of neon and krypton. These inert gas atoms both have lower atomic mass than cadmium and tellurium. However, krypton is heavier than argon while neon is lighter.

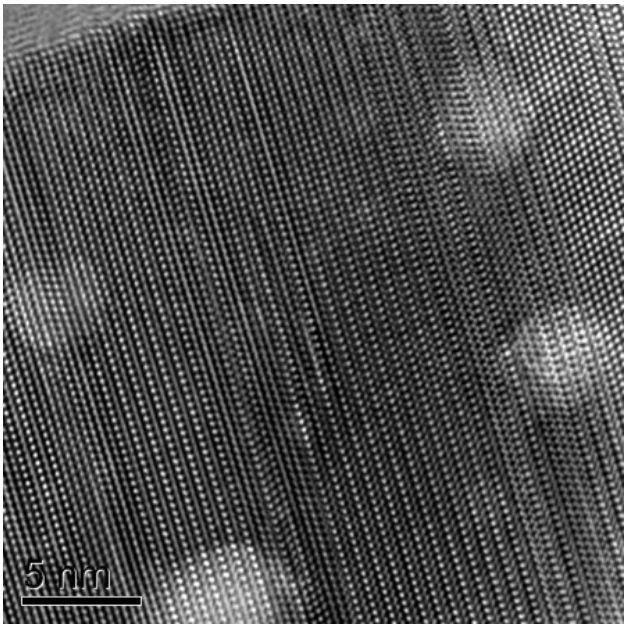

Fig. 6 A HR-TEM atomic scale image of a cross-section of a CdTe thin film annealed at 350^0C in a Rapid Thermal Processing system. The image reveals the presence of argon gas bubbles. The argon is trapped during the magnetron sputtering process and diffuses in the lattice to form bubbles during annealing.

A CdS/CdTe device was deposited using Krypton as the magnetron working gas. The gas flow was maintained at 20sccm and the substrate temperature was 200ºC during the deposition, conditions the same as those used with argon. Fig. 7 shows a TEM image of a cross-section of the device after 6min $CdCl_2$ treatment at 400ºC. The use of krypton also leads to the formation of gas bubbles which coalesce during the cadmium chloride treatment. Extensive void formation is again observed within the CdTe film after activation. The voids are smaller than those observed in the films deposited using Argon as the working gas. Although voids are present at the CdS/CdTe junction, the CdS layer is again largely unaffected.

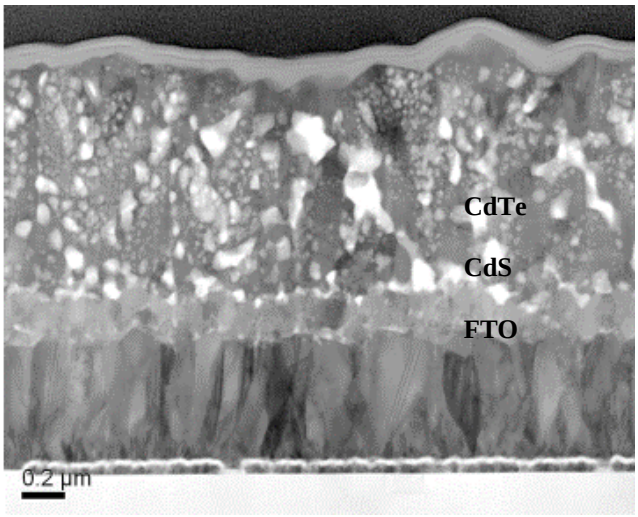

Fig. 7 A TEM cross section image through a CdS/CdTe device deposited using Kr as the magnetron working gas following the $CdCl_2$ activation treatment. A high density of smaller voids is observed.

Fig 8 shows a composite EDS elemental map of the device deposited using Kr as the working gas following the $CdCl_2$ treatment. The image is focused on the region surrounding the CdS/CdTe junction. The image shows that the Kr gas is trapped in the film can be detected (red in the image) and forms small bubbles similar in size to the void features in the electron image. Krypton is not observed in the CdS layer and the CdS layer is undamaged.

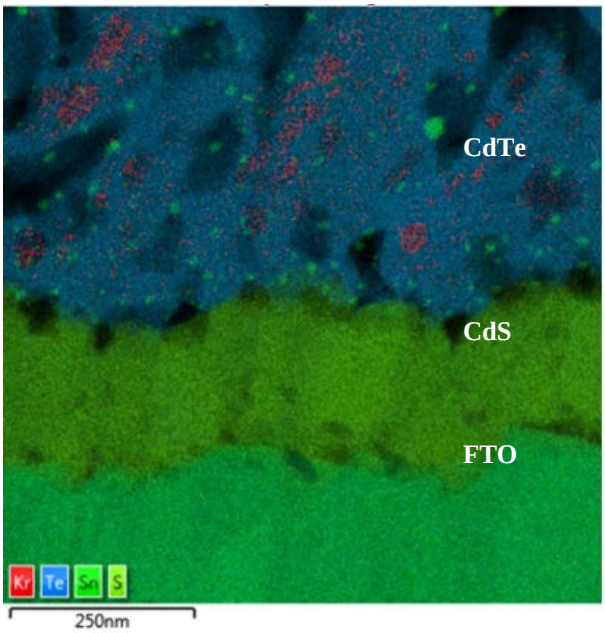

Fig. 8 An EDS composite elemental map of a CdS/CdTe device deposited using Kr as working gas following the $CdCl_2$ treatment. Regions containing high densities of Krypton (red) are observed.

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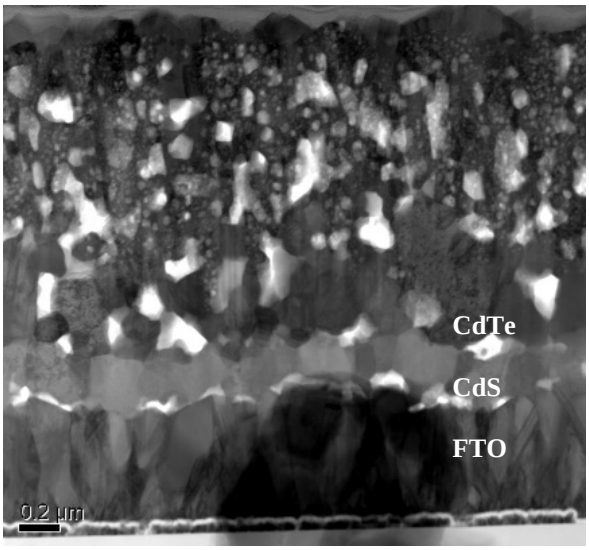

Fig. 9 A TEM cross-section of CdS/CdTe thin film stack deposited using Ne as working gas followed by the $CdCl_2$ activation treatment.

e. Neon working gas

Fig. 9 shows a TEM cross-section of the CdS/CdTe thin film stack deposited using Ne as the working gas. The gas flow was maintained at 20sccm and the substrate temperature was 200ºC during the deposition (identical to the argon conditions). After the $CdCl_2$ activation treatment severe void formation is again observed. The void are large and numerous. Corresponding EDS elemental maps of the cross-section obtained after the $CdCl_2$ treatment show that Ne is present in the CdTe film. The trapping of Neon in the CdTe leads to the formation of neon bubbles and void and surface blister formation.

IV SUMMARY

Thin film CdTe photovoltaic devices have been deposited by pulsed dc magnetron sputtering using Ne, Ar, and Kr as the magnetron working gas. The as-deposited thin film CdTe was in each case dense and columnar. The working gas was trapped in the CdTe lattice in each case. Using rapid thermal annealing without the presence of chlorine we have observed the formation of small spherical features in HR-TEM images typically 5nm in diameter when argon is used. These defects are caused by diffusion of the trapped gas atoms in the CdTe lattice during annealing to form small gas bubbles. In the cadmium chloride activation process at 400°C for 6 minutes, the gas bubbles move and agglomerate especially along grain boundaries and at the CdS/CdTe junction. The large bubbles then cause surface blistering and exfoliation. Large voids are formed in the CdTe layer and are often located at grain boundaries and at the junction. Voids at the CdS/CdTe interface leads to poor junction formation and often to catastrophic delamination. This is a major reason for the comparatively poor performance of magnetron sputtered devices. The problem becomes more acute with the lower mass of the inert gas used. The problem is also likely to occur with if gases such as nitrogen are trapped in the CdTe layer. The level of gas trapping can be controlled by lowering the energy of the argon ions in the magnetron plasma. This is largely controlled by the target Voltage.

Similar problems of surface blistering have been reported to occur in a number of materials if sputter deposition is followed by high temperature annealing. Blistering of Cu_2ZnSnS_4 (CZTS) photovoltaic devices deposited by magnetron sputtering has been reported recently. A correlation was drawn between blistering and the amount of trapped gas [12]. However, this paper provides the first direct observation for the formation of inert gas bubbles after annealing at the atomic scale using HR-TEM. The fabrication of thin film CdTe devices is further complicated by the presence of cadmium chloride.

Magnetron sputtering is a widely used and industrially capable technique for the deposition of thin films. The technique produces dense and uniform coatings. Its use for the deposition of thin film CdTe has been held back because the absorber suffers from a high density of voids and blistering occurs on the CdTe surface. This paper reports the discovery that the formation of gas bubbles is responsible for these problems. Mitigating the mechanism that causes blistering and voids should result in an industrially viable sputtering process for the deposition of uniform and stable thin film cadmium telluride solar cells.

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