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High mobility titanium-doped indium oxide for use in tandem solar cells deposited via pulsed DC magnetron sputtering

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Abstract

The effects of pulsed DC (PDC) magnetron sputtering on the crystalline structure of the high mobility transparent conducting oxide (TCO), titanium-doped indium oxide (ITiO), are investigated. High mobility (μ >100 $V^{-1}s^{-1}cm^2$) ITiO films are deposited by PDC magnetron sputtering and compared to RF deposited films using optimized conditions. These high mobility ITiO films have shown to extend the transmission in the NIR region compared to typical TCOs, such as ITO, exhibiting their potential in a tandem or multiple junction solar cell application. ITiO films deposited by PDC magnetron sputtering offer an increased deposition rate without a significant reduction in mobility when compared to RF sputtering, thus potentially offering PDC as a preferred industrial choice over RF sputtering. Structural characterization of the ITiO films prepared by PDC show a change in crystalline orientation and crystallite shape when compared to RF films, measured by XRD and SEM, which have been linked with the electrical parameters of the TCO.

Peer-review under responsibility of The European Materials Research Society (E-MRS)

Keywords: High mobility transparent conducting oxide (HMTCO); pulsed DC (PDC) magnetron sputtering; RF magnetron sputtering; tandem solar cells; multi-junction solar cells;

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1. Introduction

The approach of a multi-junction architecture is currently responsible for the most efficient photovoltaic device reported to date [1]. This approach takes two or more different absorbing materials and combines them either in a physical stack of two devices or a monolithic cell as either a two or four wired configuration. This architecture is designed to absorb and convert as much of the solar spectrum received at the Earth's surface into electrical energy. This is different to a single-junction device, which typically has a more limited absorption profile, dependent on the materials band gap. Regardless of the choice of absorber material, the photovoltaic device requires a window layer, which will serve as the top electrical contact. The role of the window layer is performed by a thin film transparent conducting oxide (TCO). The TCO must first have an excellent optical transmission to ensure efficient light harvesting in the finished solar cell and secondly it must have excellent conductivity to enhance charge collection. Potential emerging multi-junction solar cells targeting the low cost area, such as the DSC/CIGS tandem [2], require the TCO to have excellent chemical and thermal stability due to the processing steps used to fabricate these devices.

Titanium-doped indium oxide (ITiO) has been demonstrated as a suitable TCO for use in multi-junction solar cells [3,4]. ITiO is able to demonstrate a high transmission in the near infra-red (NIR) due to a relatively lower carrier concentration when compared to other TCOs such as fluorine-doped tin oxide (FTO) or tin-doped indium oxide (ITO) [5]. This lower carrier concentration results in fewer photons lost due to excess carrier absorption in the NIR, leading to a better transparency. A comparison between these TCOs is shown in Figure 1. which showcases the excellent NIR transmission of ITiO as compared to its counterparts. To deliver a resistivity needed for use in a solar cell, typically in the range of $\rho \approx 1\text{-}5 \times 10^{-4}\ \Omega.cm$, ITiO thin films require a higher mobility to account for the reduced carrier concentration, given by the relationship

$$\sigma = \frac{1}{\rho} = \mu N q \tag{1}$$

Where σ is the conductivity, ρ is the resistivity, μ the mobility, N the charge carrier concentration and q the electrical charge due to electrons or holes in the material. Typically these films are deposited using RF magnetron sputtering, or similar vacuum deposition equipment. RF magnetron sputtering is often used to deposit materials from ceramic targets that are not conductive enough to be deposited using a standard DC power supply. As a result of this reduced conductivity the deposition rates of materials using a RF power supply can be significantly reduced when compared to DC power supplies. An alternate PDC power supply was designed to deposit less conductive materials whilst offering an excellent deposition rate. In addition RF power supplies need additional network matching equipment, which is often an expensive addition. Material ejected from the target surface in sputtering equipment using a PDC power supply will leave the target with more energy compared to a RF supply. As a result it has been shown that high energy deposition processes, such as PDC, could damage the film as it is deposited due to this increased amount of energy [6].

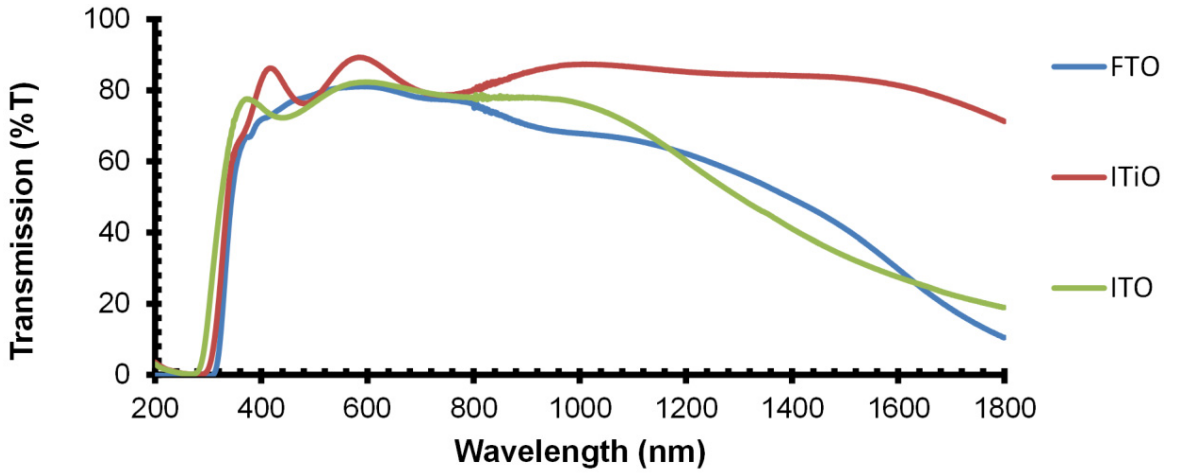

Figure 1. A comparison of transmission data from two commonly used TCOs, ITO and FTO against titanium-doped indium oxide.

It is therefore possible that by attempting to increase the deposition rate through the use of a PDC power supply that the film may be damaged during deposition, leading to reduced electron mobility. For ITiO to be considered useful for low cost photovoltaics, the cost must be reduced. Keeping these limitations in mind and achieving comparable performance of high mobility ITiO, PDC sputtering parameters have been optimized, which are discussed in the following section and compared with RF sputtered films of ITiO. As a result this paper focuses on the comparison between films deposited by both RF and PDC.

2. Experimental

A set of ITiO films were deposited with a variation in working pressure for both RF and PDC power supplies. The working pressure variation provides a useful basis for comparison of the structure of the films, as depositions at a higher working pressure typically lead to a poor performing TCO. All ITiO films were deposited to a thickness of 200 nm, with deposition rates calculated for each pressure from samples deposited previously.

The ITiO films were deposited onto 0.1 cm thick 5 cm x 5 cm soda-lime glass substrates. These substrates were cleaned prior to deposition using the RCA cleaning method. The glass substrates are cleaned thoroughly with soapy de-ionised water and placed in a PTFE sample holder, which is then immersed into a soap water solution and left in a sonic bath for 30 minutes at 70 °C. This sample holder is then placed into the first of two cleaning solutions, 'RCA 1' which consists of 50 ml ammonia, 50 ml hydrogen peroxide (40 % v/v) and 250 ml DI water. The substrates are left to soak in this solution for 10 minutes at 70 °C. The sample holder is then removed and washed with DI before being placed in the second solution, 'RCA 2', which consists of 50 ml conc HCl, 50 ml hydrogen peroxide and 250 ml DI water. The substrates are left to soak again for 10 minutes at 70 °C. When finished the sample holder is removed, rinsed and placed in a beaker with fresh DI water. The samples are removed and dried using nitrogen prior to loading into the magnetron sputtering equipment.

ITiO films were deposited from a ceramic titanium-doped indium oxide target (3" diameter, 2% wt TiO_2:98 % In_2O_3) using an AJA International (USA) ATC Orion 8 magnetron sputtering system. Prior to deposition the chamber was evacuated to a minimum base pressure of 1 x 10^{-7} mTorr. Films were deposited separately by reactive sputtering using both an RF and PDC power supply and at working pressures of 1, 5 and 10 mTorr. The oxygen content during the deposition was kept at a ratio of 99:1 argon to oxygen to ensure excellent transmission and adhesion to the substrate. The power density used was for depositing all ITiO films was 3.28 $W.cm^{-2}$ for both the RF and PDC power supply; in addition the PDC supply was kept at a frequency of 150 kHz and a reverse time of 3 µs. Substrates were heated to 450 °C and rotated at 50 rpm during the deposition.

Transmission data was acquired using a UV-VIS-NIR spectrophotometer with an integrating sphere accessory (Cary 3000). Electrical properties of the ITiO films were calculated from four point probe (Jandel) and Hall

measurements (Ecopia HMS 3000). Structural characterization was performed using power X-Ray diffraction (D2 Bruker), Scanning Electron Microscopy and cross-section Transmission Electron Microscopy. STEM imaging was carried out using a FEI Tecnai F20 (S)TEM, collected using a Bright Field detector at 200 kV. The TEM samples were prepared by Focused Ion Beam (FIB) milling using a dual beam FEI Nova 600 Nanolab. A standard in situ lift out method was used to prepare cross-sectional samples through the coating into the glass substrate. A Pt over-layer was deposited to define the surface of the samples and homogenise the final thinning of the samples, down to 75 nm.

3. Results

A summary of the electrical and Hall measurements for the ITiO films deposited can be seen in Table 1. Changes are observed between the RF and PDC samples for the varying pressures. The RF film deposited at a working pressure of 1 mTorr exhibited the highest mobility of all films in this study, although the PDC grown film demonstrates the next highest mobility and resistivity values. The PDC 1 mTorr film exhibits a desirable mobility of ≥ 100 $V^{-1}s^{-1}cm^2$, demonstrating that a PDC power supply does slightly decrease the mobility when compared to a RF film deposited under the same conditions. Despite this slight reduction in mobility the PDC 1m Torr film demonstrates desired electronic properties for use in a multi-junction solar cell. For both power supplies an increased working pressure during deposition leads to an increased resistivity whilst the carrier concentration decreases. Although a reduction in free charge carriers is a primary objective during the optimization of TCOs for multi-junction devices, the mobility must also increase proportionally.

The mobility decreases for both RF and PDC films as the working pressure increases. As a result this identifies that for both RF and PDC films, sputtering at lower working pressures deposits an ITiO film with superior electronic properties relative to films deposited at higher working pressures. It is interesting though, to note the extent of the reduced electrical performance when comparing films deposited with both the RF and PDC power supplies. Although both sets of films follow the same trend in terms of decreasing performance, the PDC films appear to be more resilient to a decrease in Hall parameters as the working pressure is increased during deposition. This could be attributed to the higher kinetic energy that ejected target material possesses when a PDC power supply is used, relative to RF, leading to fewer collisions with Ar^+ ions and more preserved energy before being deposited onto the substrate.

Table 1. Hall measurement data of ITiO films deposited for this study under RF and PDC conditions.

Sample	Power Supply	Pressure Deposited (Pa)	Mobility ($V^{-1}s^{-1}cm^2$)	Carrier Concentration (cm^3)	Resistivity (Ωcm)	Deposition Rate ($nm.min^{-1}$)
13A0314	RF	1	108	1.7×10^{20}	3.4×10^{-4}	4.7
13A0316	RF	5	35	3.3×10^{19}	5.4×10^{-3}	4.1
13A0318	RF	10	10	2.7×10^{19}	2.3×10^{-2}	2.3
13A0337	PDC	1	101	1.9×10^{20}	3.2×10^{-4}	5.2
13A0339	PDC	5	64	7.1×10^{19}	1.4×10^{-3}	4.5
13A0341	PDC	10	39	2.8×10^{19}	5.7×10^{-3}	3.3

The difference in the deposition rate decrease between the 1 mTorr and 10 mTorr samples in the RF films is interesting when compared to the PDC, as the sputtering rate decrease is much sharper. This again could be attributed to the energy in which the PDC power supply grants the ejected material, giving it a greater likelihood of reaching the substrate following a collision. For a 200 nm ITiO film, a sheet resistance of 16.4 Ω/□ is obtained from the 1 mTorr RF deposited film. For use in a solar cell this value would preferably be closer to 10 Ω/□. We can roughly estimate the thickness of the film needed to supply this sheet resistance, from $R_{sheet}=\rho/t$ where t is the film thickness. This would mean that an RF deposited film would need to be approximately 330 nm thick, taking 70 minutes to deposit. By comparison a PDC film deposited at 1 mTorr, which demonstrates a similar mobility, would

take approximately 63 minutes to deposit an equivalent film. Although this difference in time appears to be minimal with respect to deposition rate, it would result as a much greater loss of time in an industrial environment.

The transmission data for both RF and PDC ITiO 1 mTorr films can be seen in Figure 2. Both films demonstrate a superior transparency in the NIR when compared to FTO, fulfilling the ≥ 80 % transmission criteria between 800 - 1800 nm.

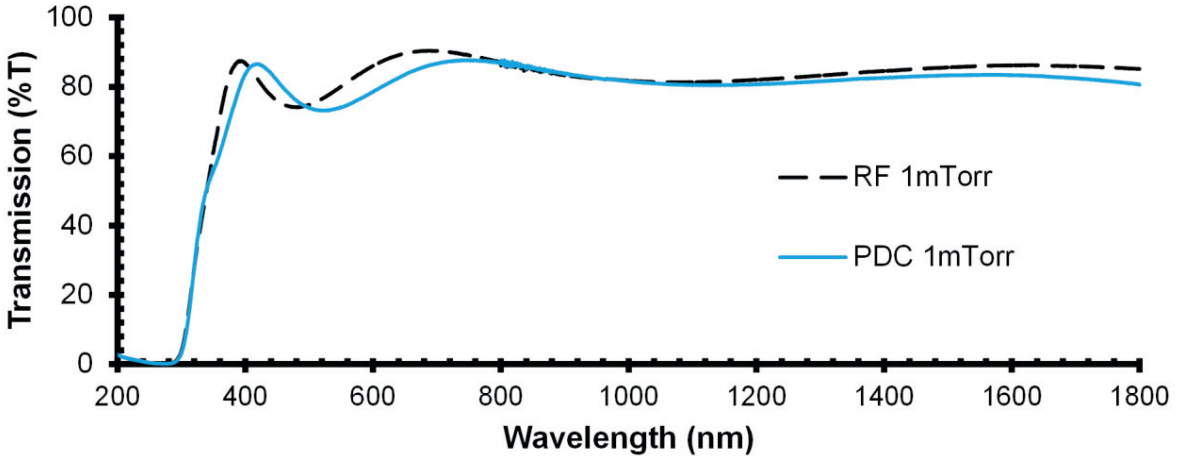

Figure 2. Comparison of the transmission between ITiO 200nm films deposited by RF and PDC magnetron sputtering.

Investigation into the crystal structure can potentially identify the cause of the electrical trends seen. Powder X-ray diffraction is a particularly useful characterization tool to assist in analyzing the crystalline structure of both the RF and PDC ITiO films. Differences in the structure between the films can be seen in Figure 3, where it becomes apparent between the pressure variations and the change in power supply. All ITiO films have a strong peak at 30.5°, which corresponds to the (222) In_2O_3 peak, but with the RF films having a much greater intensity relative to the other peaks. This would suggest a preferred orientation towards the (222) plane in the RF films when compared to PDC films. The PDC sample set have a much stronger correlation to the (211), (222) and (440) peaks seen in a reference In_2O_3 diffractogram (PDF 00-006-0416).

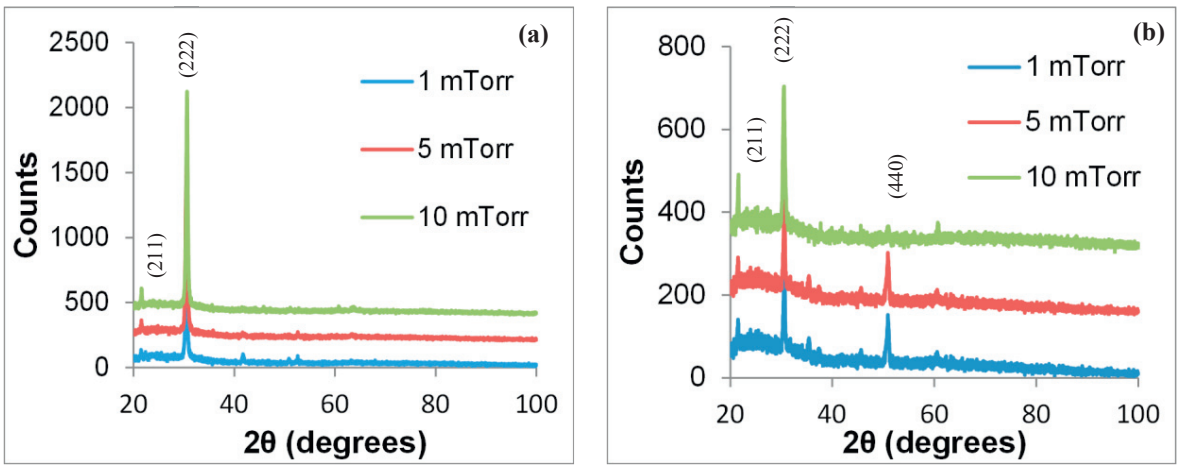

Figure 3. Powder X-Ray diffractograms of (a) RF deposited ITiO and (b) PDC deposited ITiO at various pressures.

Electron microscopy may be used to analyze changes in the film surface structure. (S)TEM and SEM images of all deposited ITiO samples can be seen in Figure 4 and Figure 5 respectively. The PDC films deposited at all pressures have triangular crystallites, with the size of these decreasing as the working pressure increases. The 5 mTorr and 10 mTorr samples appear to show pin holes between the crystallites, with the amount increasing in the 10 mTorr sample. This appears to be in agreement with the electrical properties measured previously, as smaller crystallites lead to a greater concentration of grain boundaries, serving as an area of high resistivity for electrons thus reducing electrical performance. A trend is hard to observe between the RF samples, as the crystallite shape appears to change in the 1 mTorr sample. The 5 and 10 mTorr samples show similarities to their PDC counterparts, albeit with a slight increase in crystallite size and reduced pinhole density. This contradicts what would be expected from the electrical properties of the films. This could be caused by the change in the crystal orientation, as this is known to alter the properties of a TCO. The most intriguing property of the RF sample set however is the 1 mTorr sample. The crystallites in this film hold no similarity to either the other RF or PDC samples. The RF 1 mTorr sample crystalizes with smaller crystalline grains, but appears to be more laterally oriented.

A cross section of the film allows further analysis of the bulk structure, particularly the growth pattern of the grains. Unfortunately the thickness was a limitation when attempting a fracture cross section with the FEGSEM equipment. As a result a higher resolution (S)TEM technique was used. The images of the 1 mTorr RF and PDC films can be seen in Figure 4. As these samples have been measured using a bright field detector the glass substrate appears white in the image, which is not easily distinguished on a white background. These images are all positioned such that the glass substrate is always at the bottom of the image, with the scale bar overlaid. The black coating on top of the ITiO film is a sputtered layer of platinum, required for the imaging. The grains between both samples appear to have formed differently, with the RF sample having more ordered grains. This combined with the XRD data confirms the orientation change between the RF and PDC films. The RF film appears to be more constantly compact throughout the film, suggesting a more epitaxial orientation compared to the PDC film, which has a much more random grain orientation. This also assists in explaining the superior charge transport and thus mobility in the RF ITiO film.

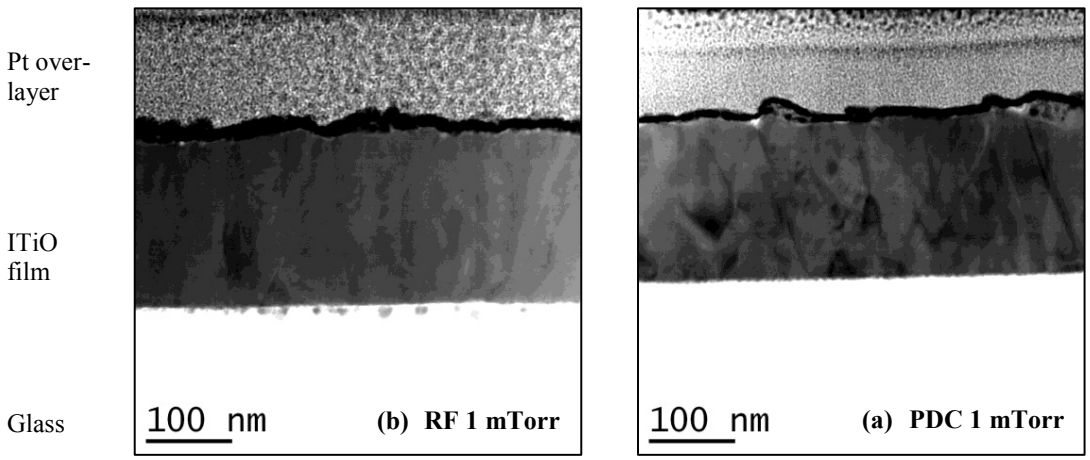

Figure 4. Cross section BF-STEM images of the (a) 1 mTorr RF and (b) 1 mTorr PDC ITiO films.

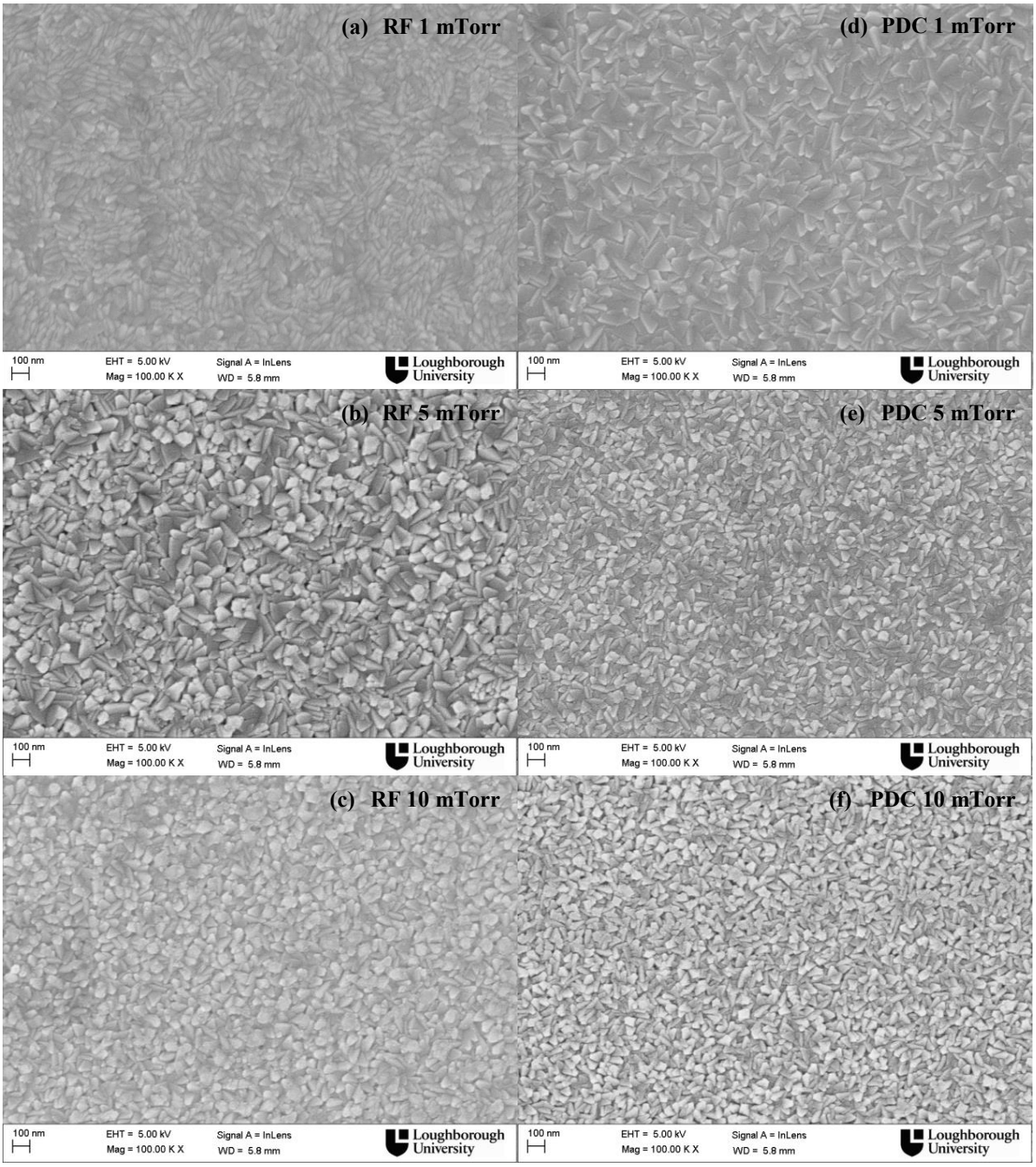

Figure 5. Scanning Electron Microscope images of RF deposited samples at (a) 1 mTorr (b) 5 mTorr (c) 10 mTorr and PDC deposited samples at (d) 1 mTorr (e) 5 mTorr and (f) 10 mTorr.

4. Conclusions

The materials characterization has revealed that PDC films are deposited with a comparable mobility relative to RF deposited ITiO films (101 and 108 $V^{-1}s^{-1}cm^2$ respectively). These films demonstrate similar electrical and optical performance and despite the slight decrease in mobility seen in this experiment, the PDC deposited film fits parameters required for use in a multi-junction solar cell. The PDC power supply in this experiment has delivered an increase in deposition rate, which would in theory lead to an increased throughput if used in an industrial environment. In addition it is interesting to observe that the reduction in mobility and resistivity as the working pressure is increased does not occur as rapidly with in the PDC deposited films. As these films will ideally be used in tandem DSC/CIGS devices (but not limited to these multi-junction devices) it would be prudent to study their suitability in the conditions used for the fabrication of such devices, given that a series of layers are deposited onto the film. The effect, if any, of the difference in crystal structure to the adhesion or performance of the layers successively deposited would be of interest.

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