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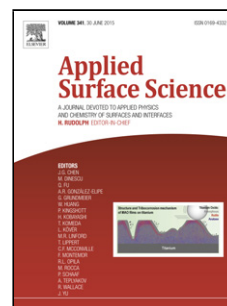
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## Stability study: Transparent conducting oxides in chemically reactive plasmas

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### Highlights

- *In-Situ* optical emission spectroscopy to diagnose the stability of ITO, FTO and AZO thin films.
- Improvement in the electrical and optical properties of AZO when exposed to Hydrogen plasma.
- Unexpected growth of silicon nanowires over chemically unstable ITO and FTO coated substrates.
- Extreme stability of AZO films towards higher temperatures and plasma conditions.
- AZO as an ideal transparent conductor for the fabrication on silicon nanowire solar cells.

### Abstract

Effect of plasma treatment on transparent conductive oxides (TCOs) including indium-doped tin oxide (ITO), fluorine-doped tin oxide (FTO) and aluminium-doped zinc oxide (AZO) are discussed. Stability of electrical and optical properties of TCOs, when exposed to plasma species generated from gases such as hydrogen and silane, are studied extensively. ITO and FTO thin films are unstable and reduce to their counterparts such as Indium and Tin when subjected to plasma. On the other hand, AZO is not only stable but also shows superior electrical and optical properties. The stability of AZO makes it suitable for electronic applications, such as solar cells and transistors that are fabricated under plasma environment. TCOs exposed to plasma with different fabrication parameters are used in the fabrication of silicon nanowire solar cells. The performance of solar cells, which is mired by the plasma, fabricated on ITO and FTO is discussed with respect to plasma exposure parameters while showing the advantages of using chemically stable AZO as an ideal TCO for solar cells. Additionally, *in-situ* diagnostic tool (optical emission spectroscopy) is used to monitor the deposition process and damage caused to TCOs.

**Keywords:** Transparent conducting metal oxides; optical emission spectroscopy; silicon nanowires; solar cells; Stability of TCOs; reactive plasma.

## 1. Introduction

Transparent conductive oxides (TCOs) are widely used as electrodes, hole and/or electron transport or blocking layer, sensors and scattering of light in electronic applications [1]-[3]. These electronic applications include; solar cells, displays, gas sensors, diodes, transistors, electrochromic smart windows and light emitting diodes [1], [4]. TCOs are generally expected to be fully transparent in certain characteristic wavelengths for a suitable application while maintaining metal-like conductivity. However, there is a trade-off between resistivity and transparency of TCOs, which demands attention to achieve properties suitable for appropriate applications. In particular, use of TCOs as electrodes in silicon-based thin film and nanowire solar cells often require exposure of TCOs to reactive plasmas, especially, hydrogen ( $H_2$ ), silane ( $SiH_4$ ), phosphine and trimethylborane. This is performed to both deposit doped and un-doped amorphous and polycrystalline silicon or to grow crystalline silicon nanowires (SiNWs) by DC and/or RF discharge plasma. A few studies have shown that exposure of TCOs to plasma hinders its stability in electrical and optical properties [5], [6]. Plasma containing hydrogen radicals results in reducing metal oxides to corresponding elemental metal and metal hydrides deteriorating performance of TCO films. However, a stable TCO is required for fabrication of active layers using plasma-based deposition techniques.

The impact of plasma and its chemical reactions to underlying films deposited on the chosen substrates (e.g. antireflection coating and TCO thin film) is often neglected but it is vital for understanding the performance of electronic devices. In this report, we discuss the performance of silicon nano-wires based solar cells fabricated by Plasma Enhanced Chemical Vapour Deposition (PECVD) process. Hydrogen atoms often bind to impurities and defects within a material and alter the electrical activity. These atoms modify the electrochemical properties of the host material (structure, electrical conductivity and grain boundaries) by occupying at a certain position in the lattice points [7]. Sometimes this can be disadvantageous as it can also break bonds between host atoms. Position of energy levels introduced by a hydrogen atom alters conductivity due to shift in Fermi level by either acting as donor ( $H^+$ ) and/or acceptor ( $H^-$ ).

This work provides insights about the stability of commonly used TCOs (ITO, FTO, AZO) and demonstrates AZO as a most suitable candidate among them due to better chemical stability and enhanced properties favourable for electronic applications despite being subjected to hydrogen containing plasma (HCP). With the use of optical emission spectroscopy (OEM), better analysis and evidence are provided regarding chemical instability and energy associated within the plasma that has a direct impact on the damaging of TCOs thin films. Diagnostic tools such as OEM discussed here, directly reveal characteristic parameters associated with plasma (density of ions and electrons, plasma temperature, composition, energy distribution) that influences the properties of the resulting films or nano-structures. Interpretation of data obtained is challenging, as it requires understanding of direct and indirect properties associated with emissions obtained from plasma [8]. For example, the measured light intensity of a particular emission line within a spectrum might usually be due to transitions from upper state to lower electronic state. Therefore, it can be assumed that upper electronic state is populated from excitations occurring from the ground state. But this can also be a consequence of de-excitation from even higher energy states or dissociation of molecules having similar energy. Hydrogen plasma provides an advantage by passivation of grain boundaries in the silicon thin films [9]. Additionally, it helps to deactivate impurities within a material and reduce the number of defects. However, the same property that might be advantageous for certain materials to improve their property can also cause severe damage if a material is chemically reactive. This study explains these problems in greater depth with an aid of several characterisation techniques used in this work.

## 2. Experimental details

Glass substrates coated with ITO and FTO thin films used in this work were purchased from Sigma-Aldrich and AZO was purchased from Kaivo. All TCOs mentioned above are sequentially cleaned in an ultrasonic bath in organic solvents such as Hellmanex, IPA and de-ionised water. Substrates are dried with nitrogen gas and baked for 30 minutes in the oven at 110 °C. Then substrates are transferred to a capacitively coupled plasma enhanced chemical vapour deposition (PECVD) chamber and evacuated to base pressure of 10 mTorr. All TCOs are exposed to hydrogen and/or silane plasma and their properties are studied by varying RF-power, pressure deposition time while the deposition temperature maintained at 400 °C in all the experiments.

Time resolved optical emission spectroscopy (OES) technique was used to understand plasma dynamics from the emissions. Spectrometer (AVANTES – AvaSpec-2048) was coupled with a PECVD system and electromagnetic emissions at 60mm height above substrate holder from the plasma are guided through optic fibre connected through a quartz viewport without UV filter. Spectrometer (grating - 600 lines/mm, 100um slit, UV coating to enhance the response in the lower wavelengths) used in this work is equipped with 2048 pixel Sony detector and a cylindrical collimation lens to focus more light onto the 56um height of the pixels. Fabrication of SiNW solar cells involved thermal evaporation of Ga for 10 seconds at the rate of 0.1nm/s at 5e-7 mBar pressure over cleaned ITO, FTO and, AZO coated substrates. Deposited Ga is used a catalyst for the growth of SiNWs. Schottky junction SiNWs solar cell is fabricated by loading substrates into a PECVD system and pumped down to 10mTorr base pressure. The temperature of substrates is raised to 400 °C and exposed to H-plasma (hydrogen gas flow at 100 sccm, 550 mTorr chamber pressure and, 33mW/cm<sup>2</sup> RF power density) for 3 minutes. This is immediately followed by addition of SiH<sub>4</sub> gas at 20 sccm into the chamber maintaining all other deposition parameters same as H-plasma for 15 minutes. 500nm thick circular (1mm and 2mm diameter) silver top contacts are evaporated over SiNWs surface to complete the fabrication of solar cells.

Transmittance of all the substrates is studied with an aid of Thermoscientific UV-Vis- near-IR spectrometer (Evolution-300). Resistivity of TCOs is measured from in-house measurement setup comprised of programmable Keithley 220 current source, Keithley 195A multimeter and ECOPIA gold coated four probes (SPCB- 01C15) system. LEICA –S430 scanning electron microscope is used in this work to study morphology of TCOs and nanowires.

### **3. Results and discussion**

#### **3.1 Stability study of TCOs**

##### **3.1.1 Optical Emission Spectroscopy**

The plasma process adopted for the deposition of a material involves optimisation of several parameters including pressure, RF-power, temperature, gas flow and many more. Reactions occurring within the plasma and its species show direct correlation with the quality of a deposited film and underlying layers. This demands controlled technique to study and optimise plasma process compatible for a particular application. Simple and effective technique is an optical emission spectroscopy (OES). Such a technique is used for measuring density of species/radicals from the intensity of emitted wavelength and electron distribution function. Changes in the intensity of emitted wavelengths are a consequence of the concentration of ions, plasma species, electrons and energy associated with them. Additionally, this technique has been widely investigated for detection of contamination, vacuum leak, predicting crystallinity of the deposited material and, change in the bandgap of the silicon thin films [10], [11].

Plasma is comprised of neutral atoms, ions, electrons and molecules. Their population over many energy levels are described by means of Boltzmann distribution that refers to the temperature of the plasma, which is also termed as excitation temperature. During all the experiments performed in this work, emissions for spectral lines corresponding to Balmer series ( $n \geq 3 \rightarrow n = 2$ ) of Hydrogen is identified in the spectra with a broad peak in UV region. Considering the composition of TCOs used in

this work expected emissions from the plasma from 200 to 700 nm wavelengths are summarised in Table 2. All possible emissions occurring from the plasma species are listed in the Table 2. Few prominent peaks corresponding to the emissions from oxygen (dissociated from unstable TCO) in the region  $> 700\text{nm}$  is not shown due to spectrometer used in this work is limited to the detection limit of 700nm maximum. Hence, the use of spectrometer that can detect emissions corresponding to wavelengths up to 1000 nm is most preferable for accurate analyses of excited oxygen (O) atoms.

### 3.1.2 RF-power density

Fig 1. depicts instability of ITO and FTO films due to variation in transmittance of untreated and H-plasma treated samples. Decrease in transmittance of FTO is a consequence of reduction into metal and discontinuity in the film that leads to the increased value of sheet resistance ( $R_{sh}$ ) as shown in Fig 1 (b-e). However, the behaviour of the ITO transparency is different when compared with FTO due to increased transmittance. Melting point of Indium is lower ( $157\text{ }^\circ\text{C}$ ) compared with Tin ( $232\text{ }^\circ\text{C}$ ) that leads to increased instability when exposed to H-plasma at temperatures above the melting point of metals. Increase in  $R_{sh}$  is ascribed to the increased scattering centres for the carriers in deteriorated thin film [5].

H-plasma treated ITO loses its conductivity when subjected to a plasma generated at an RF power density greater than  $33\text{mW}/\text{cm}^2$ . In contrast to ITO and FTO, H-plasma treated AZO thin films are stable and exhibits increased transmittance and conductivity. This is the key requirement for an ideal TCO.  $\text{H}^+$  ions impinging over the surface of the AZO thin film emerging out from the plasma passivates various defects by electron transfer within the material leading to the growth of grain size [20], [21]. Along with optical and electrical analyses, instability of FTO and ITO are further understood with an aid of OES spectra.

As a plasma density increases with increase in RF power from  $5$  to  $55\text{ mW}/\text{cm}^2$ , intensity of  $\text{H}_\alpha$ ,  $\text{H}_\beta$  and  $\text{H}_\delta$  increases proportionally (Fig 1a) indicating an increase in excitation temperature of a plasma. This is a clear indication of increased monoatomic hydrogen. The intensity of the high energy radicals such as  $\text{H}_\beta$  and  $\text{H}_\delta$  directly relates to the increase in the damage caused to the TCO. Emissions from excited species of Sn, In and, O (fig 1a) from the plasma sheath indicates presence of these ions that are etched from the substrate indicating that ITO and FTO are chemically unstable for plasma treatment involving RF power density greater than  $5\text{mW}/\text{cm}^2$ . Further evidence is observed from increased  $R_{sh}$  and decreased transmittance in ITO and FTO coated substrates. With increase in the RF power, wider continuous and increased intensity in the UV region of the spectra is observed in Fig 1a. Such high-energy photons (UV) and hyperthermal ions pose severe damage to the underlying layers over the substrate (e.g. TCO layer used in this work). Light (UV) induced degradation of amorphous silicon is often improved by minimising shoulder of UV spectra obtained from in situ OES measurements during the deposition process [11]. Recombination at the surface of substrates is high at elevated temperatures in the presence of H-plasma. Due to recombination and surface reactions, metal aggregations are observed initially and they tend to vaporise with time, this is significant at temperatures higher than melting point of metals present in a TCO film.

### 3.1.3 Pressure

An emission intensity corresponding to the Balmer series mentioned in Table 1. indicates influence of the pressure on the density of excited species and temperature. Drastic decrease in the intensity of  $\text{H}_\alpha$  and  $\text{H}_\beta$  with increase in pressure from 250 to 900 mTorr is observed. This is due to reduced mean free path at high pressures and less energy (increased collisions) associated with electrons that are insufficient for excitation of H atoms. At low pressures, the energy associated with the electrons is high for exciting atoms that leads to increased monoatomic H species. During such a process, it is reported that the excitation temperature is also increased [11]. At higher pressures, sheath is mainly collisional;

hence, ions originated at the sheath possess less energy and do not cause detrimental damage to the surface of TCO coated substrates as ions arriving at the surface has less energy either to break the bond or to passivate defects. At low pressure, collisions occurring due to exchange of charges generate enormous hyperthermal hydrogen atoms at the plasma sheath [8], [11] and these can penetrate deep inside the material causing damage to the material. These observations are evident from the results obtained in this work. Damage caused to an ITO and FTO thin film is detrimental at low pressures that reduces transmittance and increases  $R_{sh}$  (Fig 2 b-e). Increase in the intensity of emission peaks (Fig 2a) corresponding to the molecular and atomic transitions of In, Sn, O and H at low pressures indicates severe damage caused to TCO.

This paper discusses about H-plasma treatment of TCOs, which is performed at elevated temperatures in the presence of ionised atoms and molecules that is a consequence of applied RF-power. Few experiments involving heat treatment of TCOs were performed to understand their stability. Heat treatments of ITO and FTO above 300 and 350 °C respectively indicate the start of instability with an indication of little decrease in the transmittance and the increase in the  $R_{sh}$ . However, this is negligible when heated and significant when treated under the H-plasma at the same temperature. TCOs stability concerning heat treatment is not discussed in detail here since that is not within the scope of this study. XPS studies have shown that during H-plasma treatment chemically unstable films which are deficient of oxygen atoms create additional energy levels between the Fermi level and valence band edge [5], [22]. In a n-type TCO energy/localised levels increasing closer to valance band edge act as a sink for electrons [23] that increases  $R_{sh}$  of a material as seen in Fig 2. In particular, FTO, it is shown that the concentration of deuterium within plasma plays significant role in reducing  $SnO_2$  into metallic Sn [9].

Decrease in  $R_{sh}$  of AZO (Fig 2c) thin films is attributed to hydrogen ions ( $H^+$ ) that take part in the doping and the reduction in electron traps/defects at the grain boundaries. Increase in carrier concentration is due to interstitial Zn atoms generated by loss of oxygen atoms [7], [24]. In this study, blue shift in the absorption edge from transmission spectra for AZO thin films is noticed when exposed to H-plasma. This suggests an increase in bandgap allowing more light to pass through, and decrease in the  $R_{sh}$  is witnessed, which is of a key importance and beneficial when such a TCO film is used in the fabrication of a solar cell. Formation of Zn-H or Zn-OH surface over AZO film during H-plasma might lead to a stable and chemically strong passivation surface that inhibits incoming H atoms that demonstrates good stability over H-plasma [9], [25].

#### ***3.1.4 Duration of Plasma Exposure***

ITO and FTO films showed changes in the colour (Fig 3f) with increased duration of H-plasma exposure. Additionally, decrease in transmittance and increase in  $R_{sh}$  is evident from Fig 3 (b-e). This is ascribed to the formation of oxygen-depleted surface that is a consequence of chemical reduction of metal oxide into a metal. Auger electron microscopy measurements show changes in stoichiometry of the film, which strongly alters  $R_{sh}$  [6]. The sheet resistance of AZO decreases with an increase in the duration of H-plasma as shown in the Fig 3(d). A possible reason would be H-passivation and formation of Zn-H surface compared to Zn-O surface that increases surface free carriers. Stability of AZO films are studied using XPS and EDX; which show no significant change in Zn and O concentrations before and after H-plasma exposure [6]. Blue shift in the transmittance spectra of AZO films is ascribed to shift in the fermi level closer to conduction band leading to band broadening with increasing concentration of the carriers. This is often termed as Burstein-Moss effect [20]. Instability of ITO and FTO are discussed earlier with several mechanisms occurring during H-Plasma. It is worth to indicate that when the temperature of the electrode during H-plasma treatment is maintained at 400 °C, diffusion process is significant at such temperatures. Therefore, thermally activated hydrogen atoms that have high energies diffuse deep inside the thin films of a chemically unstable TCO and cause tremendous damage.

Intensity of emission peaks (Fig 3a) corresponding to In, Sn and, O increases until three minutes indicating presence of large amounts of etched species from the substrate in the plasma sheath. The intensity drops after from 5-minute H-plasma treatment due to decrease in the concentration of etched metal atoms/ions that are no more available over the substrate and continuous removal of vaporised species within the chamber. Similar observation is evident from transmittance of FTO (Fig. 3c) coated substrates that decrease until 5-minute treatment and begin to increase for plasma treatment durations exceeding 5 minutes.

### ***3.2 Constituent metals of TCOs prone to the growth of SiNWs***

Transmission and  $R_{sh}$  values corresponding to AZO discussed earlier corroborates with the stability of AZO. H-plasma treated FTO films are inhomogeneous and reduce to tin and tin-oxide particles. Unstable metal oxides that are reduced to corresponding metals are often reduced in the form of nano and/or micro-sized particles. This is due to essential modification of surface and change in surface energy. Often surface reduction within a film is observed due to reaction of hydrogen with oxygen over top surface of thin film; such a phenomenon has less impact on the stability of TCOs compared to reduction of bulk material into constituent metal particles over the surface. However, this has significant impact on the properties of a SiNW solar cell. Reduced metal particles over the surface of a TCO under favourable conditions act as a nucleation centres for Si atoms and potentially grow unexpected SiNWs.

TCOs available today include oxides of zinc, indium, and, tin that are extensively used for several applications as mentioned earlier. These metal oxides are doped with metals and non-metals such as tin, fluorine, aluminium, indium, and, gallium. Fabrication parameters play significant role in the growth of SiNWs without the need of a metal catalyst or precursor from a chosen TCO. Hence, the choice of TCO used for the fabrication of a solar cell should show good chemical stability towards  $\text{SiH}_4$ -plasma along with the H-plasma as discussed earlier. Most importantly, Eutectic temperature (ET) of silicon and metal (metals present in a TCO) alloy with the silicon has to be considered and appropriate temperature must be chosen for the growth of SiNWs used in solar cells [26], [27]. If the chosen temperature for the growth of SiNWs is higher than ET and glass substrates coated with a TCO is chemically unstable; would potentially grow SiNWs that would affect the properties of a TCO. This is evident from Fig 4g and 4h with the growth of SiNWs from In and Sn that are reduced due to chemical instability of ITO and FTO respectively. Fig 4d and 4e indicate reduction of ITO and FTO thin films into metal and metal-oxide particles. Moreover, AZO demonstrates extreme chemical stability over reactive plasmas used in this work. Considering the instability of TCOs discussed here and ET of metals with silicon used for the growth of SiNWs, we recommended avoiding TCOs that contain metals such as gallium, tin, indium and, bismuth for fabrication temperatures exceeding 300 °C. In contrast, metals in AZO, namely aluminium and zinc have ET > 400 °C with silicon and is ideal for fabrication of silicon-based thin film/nanowire solar cells at 400 °C.

### ***3.3 SiNW solar cells***

Owing to the instability of ITO and FTO compared to better stability shown by AZO thin films, SiNWs were grown on these substrates with gallium as a catalyst to fabricate solar cells. ITO and FTO films damaged due to chemical instability and thereby conductivity and transmittance is reduced that does not facilitate fabrication of a good solar cell. Contrary to ITO and FTO, AZO films are stable in reactive plasma comprised of gases that are used for the fabrication of SiNW solar cells and facilitates fabrication of a SiNW solar cell.

Current-voltage (IV) measurements in fig 5c shows clear indication of a successful solar cell fabricated on AZO with 0.3V ( $V_{oc}$ ) and 4.8mA ( $I_{sc}$ ) under illumination. However, fabrication of solar cells on ITO and FTO coated substrates was unsuccessful due to their chemical instability that loses its conductivity when exposed to H-plasma and reduced metal particles contributing towards the growth of SiNWs. The small value of current ( in the range of nano Ampere) measured (Fig 5a and 5b) in ITO

and FTO based solar cells is due to leakage and defects within the material. TCO films are discontinuous due to formation of particles (Fig. d- e). Interestingly, solar cells fabricated over FTO coated substrates shows double Schottky IV characteristics; this is ascribed to reduced tin and tin oxide establishing abrupt junctions or heterojunction with Si and Ag. It is worth to mention that use of H-plasma treated AZO as a transparent conductor in solar cells further improves efficiency due to increased transparency in the visible region allowing more light to pass and decreased  $R_{sh}$  that minimises parasitic Resistances losses. Many interesting properties shown by SiNWs such as reduced reflection, light trapping, broadband optical absorption beyond visible spectrum and guided resonance for better absorption of light, and short carrier collection lengths has shown potential towards next generation solar cells with an aim to achieve higher efficiency and reduction in the fabrications costs thus minimising carbon footprints [26]-[28]. Owing to several advantages of SiNWs, solar cells are fabricated by utilisation of SiNWs including both radial and axial junction architectures. Different combinations of semiconductor and metal junctions including PiN, NiP, PN, NP, and, schottky SiNW solar cell [28]-[31] are demonstrated until now. However, research concerning SiNWs solar cells is at exploration stage and demonstrates conversion efficiencies below 10% for those fabricated on glass substrates.

#### 4. Conclusion

*In situ* OEM measurements performed during fabrication of a SiNW solar cell provides direct evidence of TCOs that are damaged during the fabrication process. This is evident from the emission lines obtained from the plasma sheath corresponding to the etched metal atoms from a chemically unstable TCO that are ionised. Degradation threshold is summarised as ITO < FTO < AZO when exposed to hydrogen containing reactive plasma at 400 °C. Change in the electrical and optical properties of a TCO provides additional evidence to understand their stability. Metals within a TCO under favourable conditions contribute to the growth of unexpected SiNWs that not only affects the properties of SiNW solar cells but also degrades the properties of a TCO. Hence, proper attention is required during the selection process of a TCO used in the fabrication of a SiNW solar cell. Here, we report AZO as a good candidate for use in the fabrication of SiNW solar cell considering theoretical ET of Al and Zn higher than the fabrication temperature (>400 °C) and better chemically stability in hydrogen containing plasma. Experimental results not only determines extreme stability of AZO but also indicates improvement in AZO properties, such as reduced  $R_{sh}$  and increased transmittance in visible region when exposed to H-plasma. This is ideal for further improving electric current within a fabricated SiNW solar cell.

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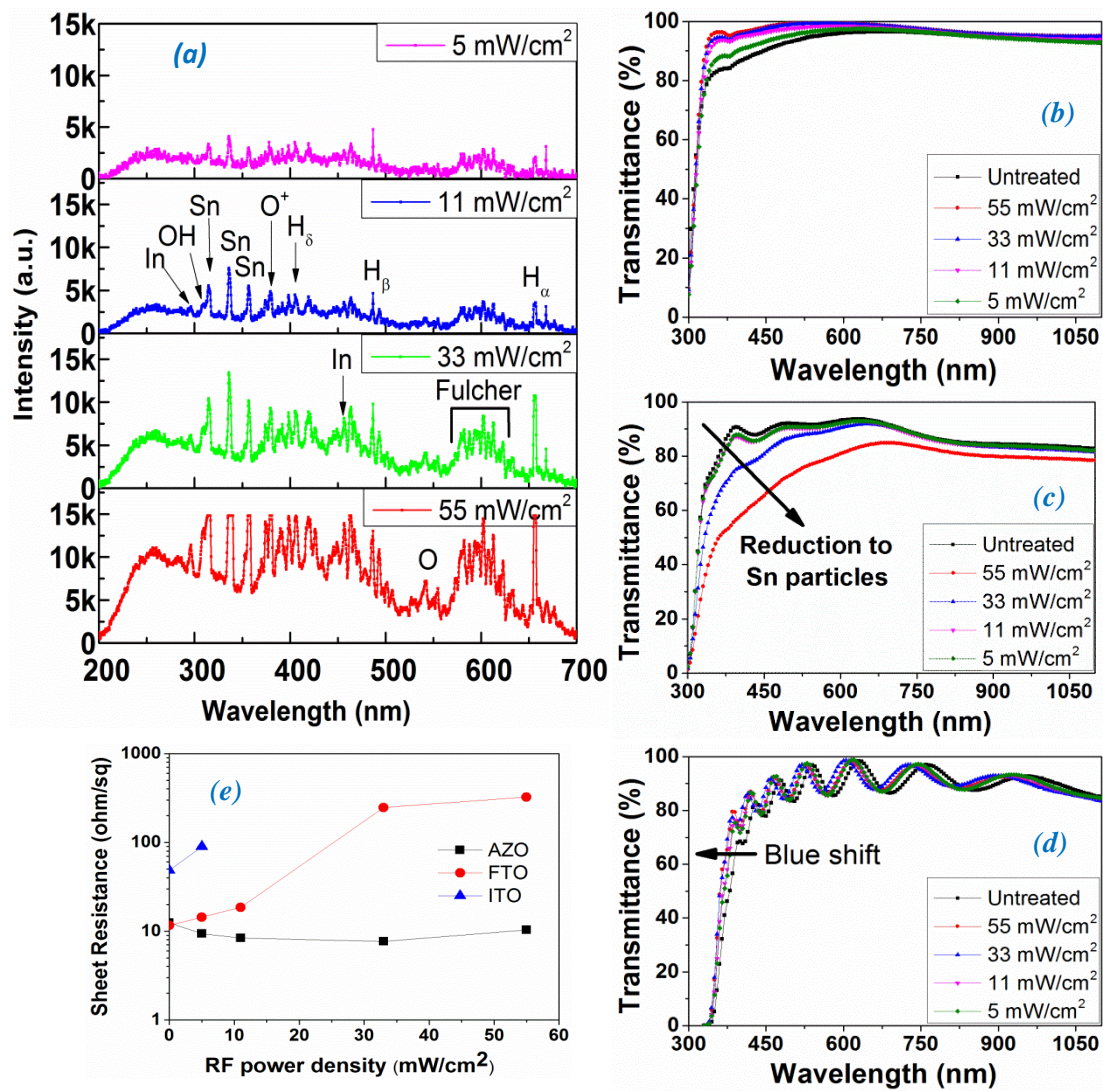


Fig. 1. Measured optical emission spectra (a) during H-plasma treatment of TCOs by varying applied RF power. Transmittance spectra of ITO (b), FTO (c), and AZO (d) coated glass substrates exposed to H-plasma at different RF-power. Measured  $R_{sh}$  (e) of above mentioned TCOs. Prominent peaks are labelled in OES spectra (a). Sheet resistance at  $0\text{mW/cm}^2$  refers to untreated samples. Missing data corresponding to  $R_{sh}$  of ITO is due to high resistance comparable to insulators that cannot be measured with available instrument.

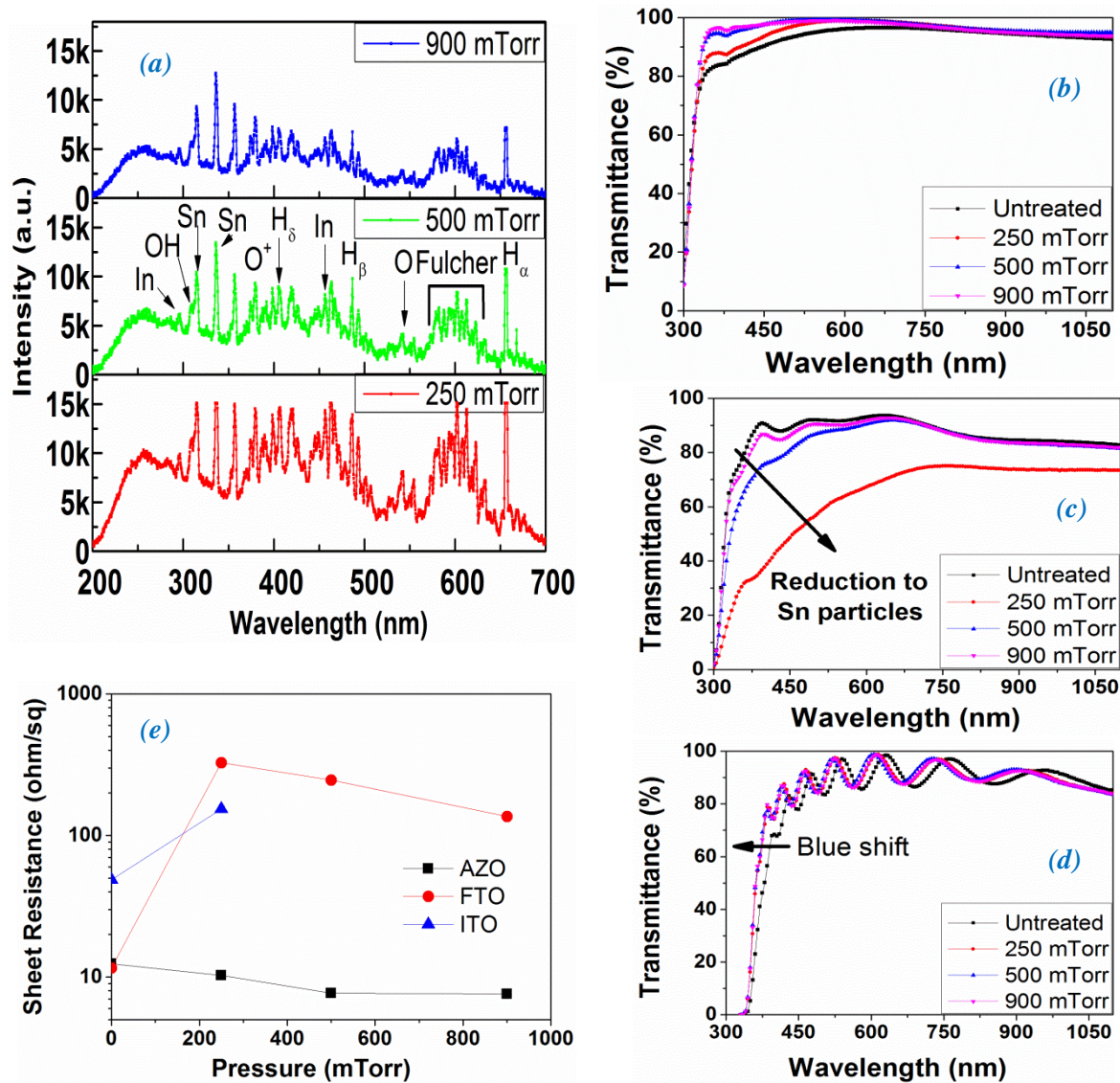


Fig. 2. Measured optical emission spectra (a) during H-plasma treatment of TCOs by varying pressure in the PECVD system. Transmittance spectra of ITO (b), FTO (c), and AZO (d) coated glass substrates exposed to H-plasma at different pressures. Measured  $R_{sh}$  (e) of above mentioned TCOs. Prominent peaks are labelled in OES spectra (a). Sheet resistance at 0 mW/cm $^2$  refers to untreated samples. Missing data corresponding to  $R_{sh}$  of ITO is due to high resistance comparable to insulators that cannot be measured with available instrument.

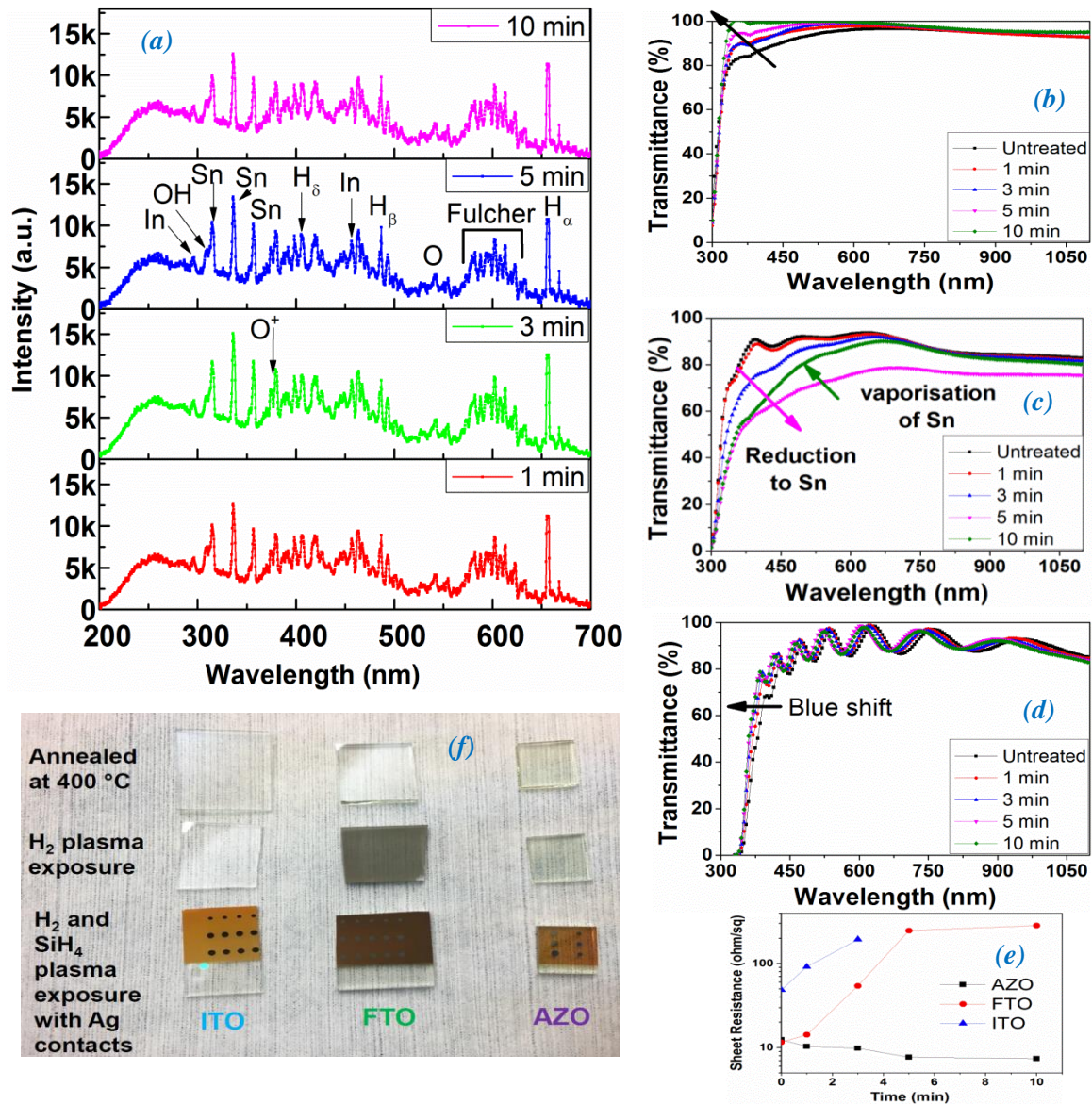


Fig. 3. Measured optical emission spectra (a) during H-plasma treatment of TCOs by varying plasma exposure durations. Transmittance spectra of ITO (b), FTO (c), and AZO (d) coated glass substrates exposed to H-plasma at different durations. Measured  $R_{sh}$  (e) of above mentioned TCOs. Optical image of TCOs that are treated with temperature and combination of H<sub>2</sub> and/or SiH<sub>4</sub> plasmas (f). Prominent peaks are labelled in OES spectra (a). Sheet resistance at 0mW/cm<sup>2</sup> refers to untreated samples. Missing data corresponding to  $R_{sh}$  of ITO is due to high resistance comparable to insulators that cannot be measured with available instruments.

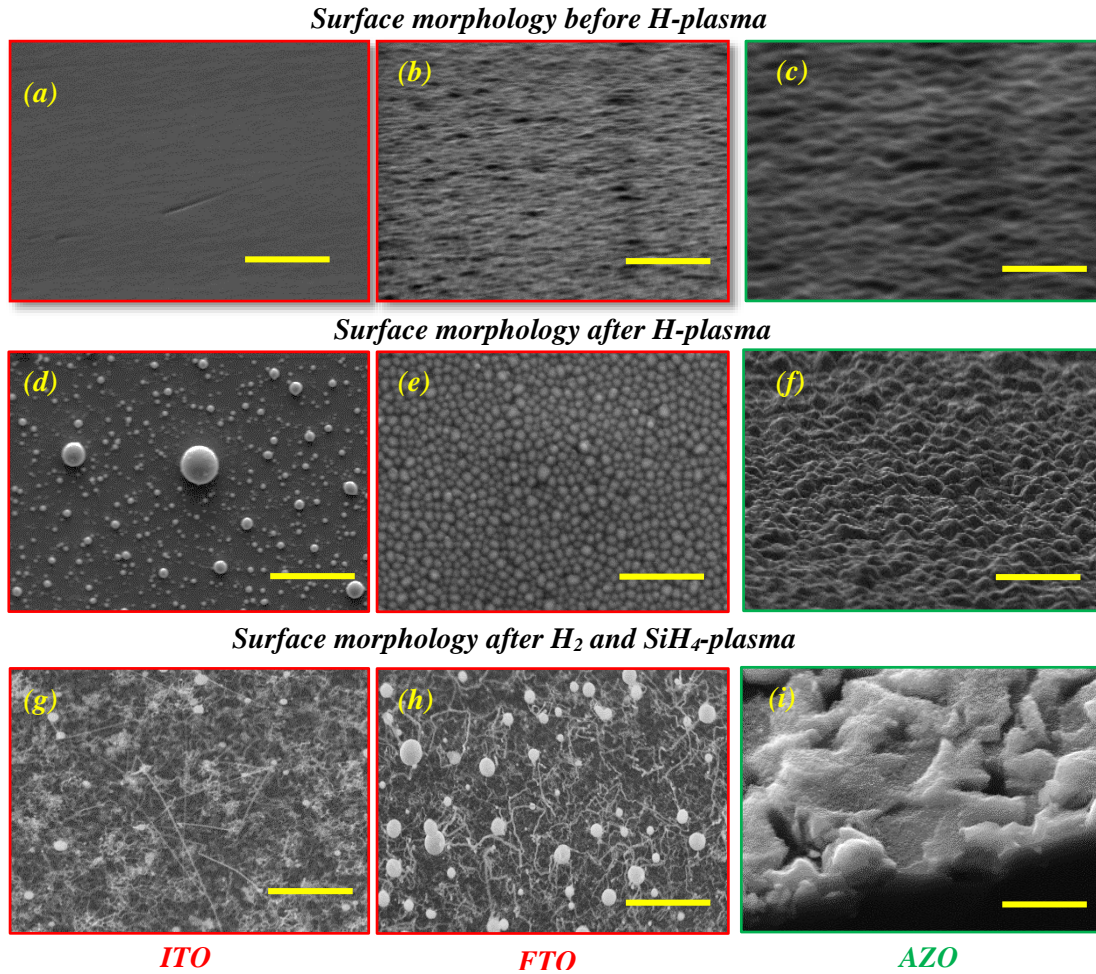


Fig 4. The surface morphology of untreated ITO, FTO and AZO thin films on glass substrates (a-c) and treated with H-plasma (d-e). ITO and FTO break down to In, Sn, InO and SnO particles when exposed to H-plasma at 400 °C. However, AZO film is stable up to 400 °C and exposure to plasma. Growth of SiNWs from ITO and FTO without the need for additional catalyst when exposed to H diluted SiH<sub>4</sub> plasma (g-h). No evidence of SiNW growth from AZO coated glass due to its extreme chemical stability towards reactive plasma from H<sub>2</sub> and SiH<sub>4</sub> gases. However, deposition of a-Si:H is observed over AZO coated glass. Scale bar in SEM images is 500nm.

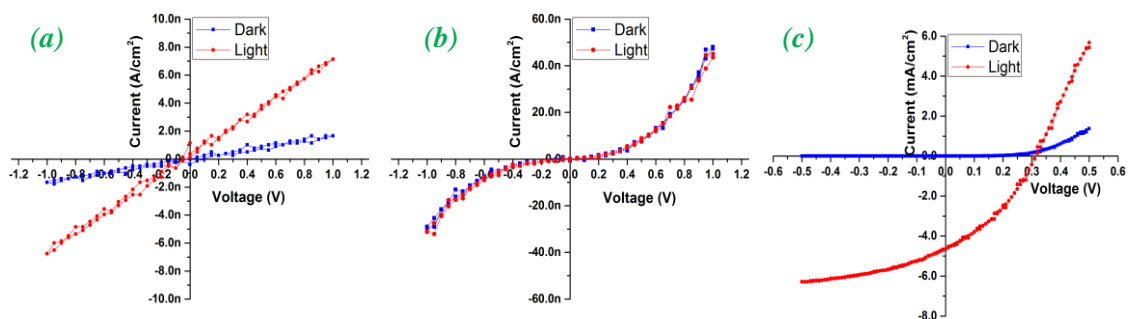


Fig 5. IV characteristics of SiNW solar cells fabricated on ITO (a), FTO (b) and, AZO (c) transparent conductors.

Table.1 H-plasma parameters (pressure, H gas flow rate, RF power density, temperature and duration) used in the study the stability of TCO thin films.

H-plasma parameters	Variable
33mW/cm <sup>2</sup> , 400 C, 100Sccm, 5min.	Pressure: 250, 500, 900 mTorr
400 C, 500 mtorr, 100Sccm, 5min.	RF power: 5, 11, 33,55 mW/cm <sup>2</sup>
33mW/cm <sup>2</sup> , 500 mtorr, 100Sccm,400 C.	Time: 1,3,5,10 minutes.

Table.2 Emissions/wavelengths emerging out from the plasma with possible transitions are summarised by obtaining data from the literature [12]-[19].

Species	Transition	$\lambda$ (nm)
H <sub><math>\alpha</math></sub>	3d $\rightarrow$ 2p	656.2
H <sub><math>\beta</math></sub>	4d $\rightarrow$ 2p	486.1
H <sub><math>\delta</math></sub>	6d $\rightarrow$ 2p	409.8
H <sub>2</sub>	Fulcher	486.1
Zn	3s1 $\rightarrow$ 3p0	468.0
Zn	3s1 $\rightarrow$ 3p1	472.2
Zn	3s1 $\rightarrow$ 3p2	481.0
Zn	1d2 $\rightarrow$ 1p1	636.2
Sn	5p 5d <sup>3</sup> d <sub>1</sub> $\rightarrow$ 5s <sup>2</sup> 5p <sup>2</sup> <sup>1</sup> s <sub>0</sub>	314.3
Sn	Sn-II ionised	335.3
Sn	Sn-II ionised	556.1
In	5 <sup>2</sup> P <sub>1/2</sub> $\rightarrow$ 5 <sup>2</sup> D <sub>3/2</sub>	303.9
In	5 <sup>2</sup> P <sub>3/2</sub> $\rightarrow$ 6 <sup>2</sup> S <sub>1/2</sub>	451.1
O <sup>+</sup>	Atomic ion	375
O	3p-6s	543.5
OH	Molecular ion	309.0