ABSTRACT: Dc magnetron sputter deposited indium tin oxide (ITO) films for silicon based hetero-junction solar cell application are studied. The films show suitable properties with transmittance as high as ~94% and resistivity as low as $2.2 \times 10^{-4} \ \Omega \ \text{cm}$. Oxygen is used as reactive gas and the sputtering gas is argon. The depositions are done at room temperature, and subsequent annealing is carried out on a hot-plate at different temperatures (250 °C, 300°C and 350°C) in air atmosphere. The $O_2/(Ar+O_2)$ flow vol% into the sputtering chamber is varied from 0 to 25. An improvement in optical and electrical properties is demonstrated when the films are annealed. The structure of the as-deposited films is shown to be dependent on the oxygen present during sputtering. When no oxygen is added, the films exhibit an amorphous structure. When oxygen flow is introduced, the XRD patterns indicate crystalline films. Besides, high flows of oxygen results in higher resistivity of the films. The resistivity can be considerably reduced by a post-deposition heat treatment.

Keywords: ITO, annealing, sputtering

1 INTRODUCTION

Transparent conducting oxides (TCO) are materials which have the property of transmitting light in the visible and infrared range of the electromagnetic spectrum, even though they are highly conducting. This is due to a wide band gap and a high doping level. Among the TCOs, indium tin oxide (ITO) is one of the most promising material due to its low resistivity ($\sim 10^{-5} \ \Omega \ \text{cm}$) and high transparency ($\sim 90\%$) [1]. Due to these excellent material properties, the application areas of ITO are several. Some of these are gas sensors [2], light emitting diodes [3], flat panel displays [4] and photovoltaic cells [5].

Production of such devices demands different kinds of deposition techniques. It is known that ITO is deposited by methods such as the sol-gel process [6], reactive thermal deposition technique [7] pulsed laser deposition [8], electron beam evaporation [9, 10], r.f. magnetron sputtering [11] and DC magnetron sputtering [12]. Due to its capability of large scale production and high throughput of uniform films of sufficient quality, dc magnetron sputtering is one of the most efficient deposition methods.

In order to produce films with sufficient properties, the processing parameters are of importance. Parameters such as substrate temperature, present gases and the partial pressure of these during deposition, and post-deposition treatment are vital for determining whether the film will obtain the properties requested or not [11, 12].

In order to lower the cost of photovoltaic cells, the production demands high throughput and low cost processes. One main parameter for these requirements is low temperature production. The motivation for our experiments was to optimize parameters for room temperature deposition of ITO thin films by an industrial designed dc magnetron sputter. The present study shows the effect of various flow ratios of oxygen and argon ($O_2/(Ar + O_2)$). In addition, the impact of annealing treatment at different temperature on the films is studied in terms of electrical, optical and structural properties. This is done with the aim to make high quality ITO thin films for silicon based hetero-junction solar cell application.

2 EXPERIMENTAL

2.1 Sample preparation

Thin films of indium tin oxide were deposited at room temperature by an industrial designed dc magnetron sputter on glass substrates of size 72 mm x 26 mm x 1 mm. Prior deposition, all samples were cleaned 30 min in sonicator in de-ionized water and subsequently dried with compressed air. A pre-heating of the samples before deposition was done in load lock at 100 °C for 30 min, in order to evaporate water residuals. Temperature measurements showed that the substrate temperature during deposition was lower than 45 °C. The base pressure in the sputtering chamber was in the order of $10^{-7}$ mbar and the working pressure was kept at $3.1 \times 10^{-3}$ mbar for all experiments. The flow of argon was constant at 180 sccm and the flow of oxygen was varied from 0 to 60 sccm. The different flow rates, in percentage oxygen of total flow, were 0, 0.3, 1.6, 3.2, 6.3, 9.1, 14.3 and 25.0. This will later be denoted as $O_2$ flow with percentage as unity. The weight ratio of the target (In$_2$O$_3$/SnO$_2$) was 90/10%. The power density was held constant at 5.3 W/cm$^2$ and the target to sample distance was 80 mm. The sample holder was oscillated once in front of the target. The oscillation velocity of the sample holder was kept at 0.7 m/min. Subsequent heat treatment was performed in air on a hot-plate. The temperatures examined were 250 °C, 300 °C and 350 °C and the duration of the annealing was 15 min.

2.2 Characterization

The transmittance of the films was measured as a function of wavelength in the range 400-1000 nm by the use of a spectral response. Film thickness was measured using an alpha-step 200 profilometer (TENCOR Instruments). Resistivity measurements were done by the use of a four-point-probe set-up (ai-alessi). Structural characterization was done by X-ray diffraction (XRD) with Cu $K\alpha$ ($\lambda = 1.5418$ Å) radiation using a Bruker-Siemens D5000 diffractometer. Electronic properties were examined by X-ray photoelectron spectroscopy (XPS). The instrument used was a KRATOS AXIS ULTRADLD. A monochromatic Al $K\alpha$ radiation with
3.2 Electrical properties

Figure 2 shows the measured resistivity as a function of oxygen flow. The figure shows that increasing oxygen flow raises the resistivity of the films. It is also observed in the figure that annealing has a large impact on the ITO films, especially on films deposited with high O₂ flows. In the cases of annealed ITO deposited with oxygen flows higher than about 3.2%, the figure illustrate that the resistivity decreases to about 10⁻² Ω cm, regardless of the annealing temperatures studied. This is a five orders of magnitude decrement in resistivity for the films deposited with 25% O₂ flow. For films deposited with lower than 3.2% oxygen, there are only small changes in the resistivity due to annealing and the annealing temperature is not significant. The lowest resistivity of the as-deposited samples was 3.4 x 10⁻⁵ Ω cm. This was the resistivity of the film deposited with 1.6% oxygen. When this sample was annealed at 250 °C the resistivity decreased to 2.2 x 10⁻⁵ Ω cm. This resistivity was also measured on the sample deposited with 0.3% oxygen flow and annealed at 300 °C.

3.3 Structural properties

The growth rate of the ITO film is shown to be linearly dependent on the O₂ flow (figure 3). This implies that the thicknesses of the deposited films decrease with increasing oxygen flow as the oscillation velocity of the sample holder was kept constant. Hence, the thickness may have an impact on the transmittance shown in figure 1. The thickness varied between 30 and 90 nm.

Figure 4 shows the XRD pattern of as-deposited films and films annealed at 300 °C. The figure shows the pattern for films deposited with 0%, 3.2% and 25 % oxygen flow. The film deposited without oxygen present during sputtering shows only a small indication of a peak at 2θ=30°, suggesting that the film has a dominating amorphous structure. For reactive sputtering with oxygen, the as-deposited films show a single oriented crystalline structure, independent on oxygen flow. The peak shown at 2θ=30° corresponds to the (222) diffraction plane of In₂O₃, as reported in the literature [13, 14]. In case of 3.2 % oxygen, small indications of other peaks are seen at 2θ about 21°, 41° and 51°.

When the films are annealed, the film deposited without supply of oxygen shows a randomly oriented crystalline structure. The films sputter deposited with oxygen show an increased intensity of the (222) intensity peak after annealing (clearly shown in preliminary study, not presented).
3.4 Electronic properties

The valence band spectra of the as-deposited films and annealed films at 300 °C, are illustrated in figure 5. The figure shows that the slope of the valence band decreases and the valence band maxima shift towards lower binding energies, as the oxygen flow increases. After annealing, the difference between the valence band spectra is absent.

![Figure 4. XRD pattern of as-deposited (a) and annealed (at 300 °C) (b) ITO.](image1)

![Figure 5. Valence band spectra of as-deposited (a) and annealed (at 300 °C) (b) ITO films versus oxygen flow.](image2)

4 DISCUSSION

4.1 Optical properties

The transmittance of the as-deposited samples shows a dependency of the O₂ flow. When the transmittance is analysed taking film thickness into account, it is obvious that transmittance of films deposited with small flows, i.e. lower than 3.2% O₂, is not dependent on thickness as there are small variations in thickness of these films. The difference in transmittance between these films must be related to other properties like film structure. This is indicated by the XRD patterns. The XRD results show that the structure of the film deposited with 25% O₂ flow is similar to the structure of the film deposited with 3.2%. Hence, the measured transmittance of films deposited with higher O₂ flows is more likely influenced by the film thickness as the thickness is shown to be dependent of O₂ flow.

Heat treatment improves the transmittance of the films. In our study, the as-deposited film sputtered with pure argon is shown to be amorphous. From the XRD results shown in figure 4, it is obvious that annealing in air at 300 °C crystallizes this film. We therefore assume that the improvement in transmittance of this film is a consequence of incorporation of oxygen and crystallization during annealing [9, 15].

Other films which showed crystallinity when as-deposited, also exhibit a higher transmittance after annealing. We suggest that this improvement can be addressed to increased grain size and a lower degree of defects after annealing. Increase in grain size is indicated by preliminary examination of XRD peak width before and after annealing (results not presented). Increased transmittance due to annealing is previously attributed to enlargement of crystallite size [16].

4.2 Electrical properties

It was shown that the resistivity of the ITO thin films was affected by the content of oxygen present during deposition and presumably during post-deposition heat treatment as well. The film deposited with 0% O₂ flow experienced a small improvement in resistivity after annealing. We attribute this to the transformation of the amorphous film to a polycrystalline film. The films deposited with 1.6% and 3.2% O₂ flow exhibit low resistivity as as-deposited and heat treatment does not affect this resistivity significantly.

Films deposited with higher O₂ flows, i.e. >3.2%, show increased resistivity with increased O₂ flow. A
Amorphous films are usually achieved when deposition was done with oxygen the XRD patterns showed that the film we achieved was amorphous. When the deposition without oxygen added during sputtering the as-deposited oxygen present during sputtering at room temperature. The XRD results show that the structural properties exhibit higher transmittance. Thus, the decrease in resistivity due to annealing of our films deposited with high flows of oxygen is therefore attributed to the dissociation of such interstitial defects and outdiffusion of the non-stoichiometric extra oxygen.

4.3 Structural properties

As shown in figure 3, the thickness of the samples decreases as the O₂ flow increases. The most significant changes in thickness are observed for flows higher than 3.2%. It is known from the literature that above a certain percentage of oxygen present during sputtering, the deposited film will not be able to absorb significant amounts of oxygen as a fully stoichiometric structure is formed. At this critical point the excess oxygen will start to create an insulating surface on the sputtering target, and hence, the sputtering yield is significantly reduced [19]. The lower sputtering yield causes thinner ITO films as the flow increases. The thickness variations can explain variations in optical properties, as thinner films exhibit higher transmittance.

The XRD results show that the structural properties of the as-deposited films are dependent on the content of oxygen present during sputtering at room temperature. Without oxygen added during sputtering the as-deposited film we achieved was amorphous. When the deposition was done with oxygen the XRD patterns showed that the films were crystalline.

Amorphous films are usually achieved when deposition is performed at low substrate temperatures. Sun et al. [8] reported amorphous films deposited by excimer pulsed laser deposition at substrate temperatures below 150 °C. This was found to be due to initial 3D growth with nucleation separation distance dependent on substrate temperature. Ma et al. [20] achieved crystalline films at deposition temperature as low as 50 °C with a facing target sputtering system. Nevertheless, other deposition parameters than substrate temperature may also affect the film structure. Song et al. [21] reported that the morphology of ITO films deposited by DC magnetron sputtering at room temperature was dependent on the total pressure of the sputtering gas. They assigned this dependency to the number of collisions the sputtered particles were exposed to. The higher pressure the more collisions and the lower kinetic energy of the sputtered particles reaching the sample surface. Other deposition parameters such as target to substrate distance may also affect the surface mobility of the deposited particles and hence, the structure of the sputter deposited films [22, 23]. We assume that the deposition parameters used in our system are optimal for achieving deposition particles with sufficient surface mobility and hence, crystalline films.

In the case of the amorphous as-deposited film we assume that the lack of oxygen present during deposition induce an amorphous structure as the film becomes non-stoichiometric without the required amount of oxygen for forming a crystalline film [21]. We also assume that when the amorphous film is annealed, enough energy is supplied for incorporation of the oxygen present in the annealing ambient and a crystalline structure is formed.

4.4 Electronic properties

It is evident from figure 5 that the oxygen content during deposition affects the valence band maxima. Higher oxygen content induces lower binding energy of the valence bands, i.e. the Fermi energy level lies closer to the valence band edge. A lower Fermi level is assumed to be a consequence of lower doping. This coincides with the resistivity measurements, which showed that increased oxygen flow led to increased resistivity. The lower doping level is presumably an effect of the formation of interstitial defects previously discussed [24]. As the films are annealed, the shift in binding energy disappears and the resistivity drops. This can be attributed to the dissociation of the defects caused by the excess oxygen.

5 CONCLUSION

Both amorphous and crystalline ITO films were deposited at room temperature by dc magnetron sputtering. The film structure was affected by the oxygen present during deposition. Adding oxygen to the sputtering gas induced crystalline films. By adding a small amount of oxygen, the films obtained high transparency and conductivity. Large oxygen flows increased the resistivity, which is attributed to formation of oxygen-related interstitial defects. Annealing of these films caused a decrease in resistivity, presumably due to dissociation of the defects.

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REFERENCES