PV Asia Pacific Conference 2012

Characterisation and Optimisation of Indium Tin Oxide Films Deposited by Pulsed DC Magnetron Sputtering for Heterojunction Silicon Wafer Solar Cell Applications

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Abstract

Amorphous/crystalline heterojunction silicon wafer solar cells are attracting attention in recent years due to their potential to achieve high conversion efficiencies at low fabrication temperatures. However, to date, only SANYO (Japan) has brought this technology to commercial mass production, mainly due to the high sensitivity of the solar cell parameters to the growth conditions. One significant difference between a heterojunction and a standard screen-printed silicon wafer solar cell is the current collection scheme. As a heterojunction silicon wafer solar cell is limited by its low emitter lateral conductivity, a transparent conductive oxide (TCO) is employed to improve the carrier transport, whilst also acting as an antireflective coating (ARC) for the front side. From the variety of TCOs, indium tin oxide (ITO) is one of the most promising candidates due to its high electrical conductivity and excellent optical transmittance. For deposition of very thin ITO films (in the 70-90 nm range, in order to function as ARC), the restrictions and requirements for both high electrical and optical properties are rather challenging. In this study we focus on TCO deposition using an industrial pulsed direct current (DC) magnetron sputtering system (FHR, Germany). The effects of the applied DC power, the oxygen partial pressure, the deposition temperature, and the annealing conditions are investigated. Encouraging results demonstrate a resistivity in the range of $(4.6-5) \times 10^{-4}$ Ωcm and a transmission of above 90% in the visible range.

Keywords: DC sputtering, ITO, antireflective coating, heterojunction, silicon solar cells

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1. Introduction

Amorphous/crystalline heterojunction silicon wafer solar cells use crystalline silicon wafers for carrier collection and plasma-deposited amorphous thin silicon layers for surface passivation and junction formation [1]. The deposition temperature of the amorphous layers is typically below 200°C. This decreases the thermal budget in production of the solar cell and at the same time allows for high throughput production machinery [2]. SANYO (Japan) demonstrated efficiencies of up to 23.7% (open circuit voltage $V_{oc}$ 0.745 V, short circuit current density $J_{sc}$ 39.38 mA/cm², fill factor $FF$ 80.9%, cell area 100.7 cm²) for a 98 µm thick heterojunction solar cell in the R&D stage [3].

Transparent conductive oxides (TCOs) are required on top of the amorphous silicon layers to enhance carrier transport to the contacts and to function as an anti-reflection coating (ARC). Among all the TCO materials, indium tin oxide (ITO) is widely used for heterojunction silicon wafer solar cells, due to its high conductivity and transmission properties. TCOs can be prepared by various deposition techniques, and new techniques continue to be developed [4]. Magnetron sputtering, either direct current (DC) sputtering or radio frequency (RF) sputtering, appears to be the most common technique for large-area thin-film deposition, owing to its cost effectiveness and capability to grow films on large substrate areas [5].

The aim of this study is the optimisation of the sputtering parameters and annealing methods, using a pulsed DC sputtering system, in order to achieve very conductive and transparent thin ITO films for heterojunction silicon wafer solar cells. The importance of post-deposition annealing for further improvement of film qualities are demonstrated as well.

2. Experimental methods

2.1. System and material

Our inline pulsed DC magnetron sputtering system (FHR, Germany) enables high productivity deposition and coating of substrate on large surface area (30×40 cm²), capable of co-deposition onto six 125×125 mm² wafers in a single run. In addition to the advantage of fast deposition, pulsed power can be used to prevent the formation of arcs. When arcing occurs on or near the target surface, it will cause local melting [6]. Therefore a pulsed power system is suitable for high-throughput inline production. The system contains two chambers, one for deposition of metals and one for deposition of TCOs. Currently, in our setup, two types of TCO materials are available: Aluminum doped zinc oxide (AZO, dual magnetron rotatable target) and tin-doped indium oxide In$_2$O$_3$:Sn (ITO, planar target). The ITO planar target (In$_2$O$_3$:Sn 90:10 Wt.%, 99.99%) used in this work has dimensions of 54×9 cm², and it is about 80 mm away from the substrate. The upper limit of the discharge power of the used FHR system is 10 kW. The chamber contains a group of heaters, which can reach up to 500°C, resulting in a maximum substrate temperature of around 350°C. Individual gas sensors are used to control gas flow rate of pure oxygen (O$_2$), argon (Ar) and nitrogen (N$_2$).

Throughout this research, microscope glass slides (Menzel Gläser, Germany, 2.5×7.6 cm²) were used as a substrate for characterisation purposes. The glass samples were cleaned in isopropanol (IPA) and acetone, and then blown dry with nitrogen. All glass samples were taped at the same area by Kapton tape (DuPont, USA) for film thickness measurement. Prior to sputtering, the samples were attached to a stainless-steel carrier and then transferred in the vertical position to the sputtering chamber through the
load-lock chamber. During the deposition, the carrier travels between the predefined positions back and forth to realise desired film thickness, as shown in Fig. 1.

Fig. 1. Schematic illustration of the inline pulsed DC sputtering chamber.

2.2. Experiment description and characterisation methods

Single variable control methodology was conducted throughout the optimisation, and optimised parameter settings were used in the sequential optimisation. Four main sputtering parameters were investigated: discharge power, deposition pressure, oxygen partial pressure and deposition temperature. For the requirement of heterojunction solar cells, the sputtering power should be relatively low to ensure minimum ion bombardment damage to the amorphous layer. The power density for ITO to be used in heterojunction silicon wafer solar cells by DC sputtering can be as low as 1 W/cm² [7] or as high as 5 W/cm² [8] depending on the target-to-substrate distance and sputtering chamber conditions. A sputtering power from 250 W to 2500 W (power density from 0.5 to 5 W/cm²) was used in this work.

The deposition chamber pressure can be controlled by changing the gas flow rate (low pressure is achieved at low gas flow rate). An Ar flow rate below 115 sccm cannot be detected by the Ar sensors in our current system, whilst the lower limit for the oxygen gas line is 3.5 sccm. Due to the gap between the heater and the substrate in the high vacuum chamber, the heating mechanism is dominated by radiative heating. The difference between the heater-temperature and the substrate-temperature is maximal 150 ºC.

Other parameters, such as pulse frequency, carrier transport speed, and number of deposition cycles have an impact on the film property and quality; nevertheless, in this work, they were fixed to 50 kHz (pulse frequency), 12 mm/s (carrier transport speed) and three deposition cycles at each condition. The absolute distance of the oscillations was set to 600 mm (i.e., 300 mm to each side of the target center). For each sputtering condition, two glass samples were used, one acted as a reference sample, whilst the other sample was annealed for three hours at 160 ºC in air after the deposition.

The sheet resistance of the ITO samples was measured with a four-point probe (4PP, CRESBOX, NAPSON, Japan), while the thickness of the film was estimated by measuring the step height of the taped
area using a stylus profiler (DEKTAK 150, VEECO, USA). A UV/VIS/NIR spectrophotometer (PerkinElmer, Lambda 950, USA) was used for transmittance measurements, while the average transmission in the visible range (390-750 nm) was obtained by a haze meter (Haze-gard plus, BYK-Gardner, Germany). The optical and electrical properties were characterised and recorded at the end of the deposition after a post-annealing step.

3. Results and discussions

3.1. Sputtering parameter optimisation

The discharge power was found to be one the most influential parameters. Figure 2 shows that the discharge power determines the resistivity and the growth rate of the ITO film. As indicated in Fig. 2(a), an increase in DC sputtering power results with a reduced resistivity of the ITO film; furthermore, annealing reduces the film resistivity and minimises the difference among different power levels. Figure 2(b) shows the average growth rate (nm/s) at each power condition, which increases approximately linearly with increasing power.

As the TCO layer is intended to be deposited onto the amorphous silicon layers of heterojunction silicon wafer solar cells, its deposition condition influences not only its quality, but also the quality of the layers beneath it as it can possibly damage their electrical performance. A medium power of 1500 W (power density of 3 W/cm²) was chosen for sequential parameter optimisations.

![Figure 2](image)

Fig. 2. (a) ITO resistivity as a function of deposition power; (b) ITO growth rate as a function of deposition power.

Figure 3 shows the film resistivity as a function of the Ar flow rate at deposition power of 1500 W. These initial results demonstrate that low chamber pressure is beneficent for ITO conductivity and transmission. After annealing the sample for 3 hours at 160°C in air, the resistivity of all samples was reduced by a further 20%. Guillén and Herero [9] associated changes in the optical and electrical properties of the material with changes in the local ordering of material during crystallisation and also with the creation of the oxygen-vacancy and/or the annihilation which is depend on the annealing temperature. Since the annealing temperature in our case is relatively low, the improved quality of ITO film is assumed to be due to the increased formation of oxygen-vacancies [10]. In the tested range, the chamber pressure has only a little influence on the growth rate (within the range of measurement error) and the average growth rate was found to be 0.92 nm/s. Reduced transmission is observed with increased...
Ar flow rate (for the range below 200 sccm). The above results indicate that a low gas flow rate is beneficial for both conductivity and transparency. A gas flow rate of 125 sccm (corresponding chamber pressure of $1.7 \times 10^{-6}$ bar) was used for the next optimisation step.

![Graph](image1)

Fig. 3. (a) ITO resistivity as a function of gas flow rate; (b) ITO transmission as a function of gas flow rate.

Having determined the optimal chamber pressure, a fixed total gas flow rate of 125 sccm was applied during the oxygen influence investigation. Three oxygen flow rates were chosen (4, 6 and 9 sccm), which contribute 3.2, 4.8 and 7.2%, respectively, to the total gas flow rate of 125 sccm. As indicated in Fig. 4, 3.2% oxygen improves the sample's transmission in the visible range (390-750 nm) from 51 to 89%, whilst the resistivity drops from $2.5 \times 10^{-3}$ to $1 \times 10^{-3}$ Ω cm. ITO was found to be quite sensitive to the oxygen content, whereby the appropriate amount of oxygen will improve both the conductivity and the transmission. However, a high oxygen concentration will improve only the transmission, while increasing the resistivity.

![Graph](image2)

Fig. 4. (a) ITO resistivity as a function of oxygen percentage; (b) ITO transmission as a function of oxygen percentage.

Figure 5 presents the transmittance of glass samples for different oxygen concentrations, before and after annealing. As indicated, annealing improves the transmittance at short wavelengths (300-500 nm),
which contributes to the transmission improvement in the visible range as shown in Fig. 4(b). Besides, for an oxygen ratio of 3.2%, the transmittance also improves at wavelengths of about 1000 nm. The reduced transmittance in the range 2000-2500 nm may arise from free electron carrier absorption attributed to increased formation of oxygen vacancies [11].

Fig. 5. Transmittance as a function of the wavelength for oxygen concentrations of (a) 3.2%; (b) 4.8% and (c) 7.2%, before and after annealing.

Sputtering at room temperature in a pulsed DC sputtering system showed encouraging results. Increasing the deposition temperature further improves the ITO resistivity, as shown in Fig. 6. It seems that with the present system configuration, a deposition temperature of 180°C provides the best results in terms of resistivity and high visible light transmission of around 90%. The improvement at high sputtering temperature may result from partial recovery of degradation during the deposition [12]. Three hours of post-deposition annealing further improves the film quality.

Fig. 6. (a) ITO resistivity as a function of the deposition temperature; (b) ITO transmission as a function of the deposition temperature.
3.2. Post-deposition treatment

In this work, annealing at a fixed condition (three hours at 160°C in air) improves the ITO conductivity in most of the cases, except for ITO films sputtered with an excess of oxygen. Oxygen atoms improve the film’s quality only if the right amount of oxygen is incorporated; too much or too little oxygen will result in a high resistivity. When oxygen partial pressure is lower than the optimum concentration, the high resistivity is due to the formation of non-stoichiometric film; when oxygen partial pressure is above the optimum concentration, high resistivity might result from additional oxygen accumulated at grain boundaries which acting as scattering centres to electrons [10]. However, to date all the films experience increased visible transmission after annealing. The improved transmission will increase the current density of a solar cell, thus has a high potential to improve solar cell’s efficiency.

4. Conclusion

The quality of sputtered ITO films is greatly determined by the deposition conditions. It is rather challenging to achieve high conductivity and high transparency simultaneously for heterojunction solar cell applications. Thin films below 100 nm are a major challenge for the deposition technology, as films will often start to grow in a distributed manner with inferior properties until the film reaches bulk properties beyond a certain minimum film thickness [13]. At this stage, the lowest resistivity achieved by us is in the range of \((4.6-5) \times 10^{-4}\) Ωcm. The transmission in the visible range is around 90%. These encouraging results demonstrate the potential of the FHR inline pulsed DC sputtering system to deposit highly conductive and transparent TCO films for heterojunction silicon wafer solar cell applications at low temperature and low discharge power.

Acknowledgements

The Solar Energy Research Institute of Singapore is supported by the National University of Singapore (NUS) and Singapore’s National Research Foundation (NRF) through the Singapore Economic Development Board (EDB). Funding for this research under NRF grant NRF2010EWT-CERP001-022 is acknowledged.

References


