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## Anti-reflection porous  $SiO<sub>2</sub>$  thin film deposited using reactive high-power impulse magnetron sputtering at high working pressure for use in a-Si:H solar cells



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#### 1. Introduction

Commercially produced a-Si:H solar cells use transparent conductive oxide (TCO) coated glass substrates. It is feasible to produce cost-effective a-Si:H solar cells with thicknesses of  $\sim$  400 nm through vapor deposition processes, minimizing material consumption. However, a-Si:H thin films have limited light absorption as a solar cell material due to their high band gap energy of  $\sim$  1.7 eV. Therefore, it is necessary to reduce the light reflection from the outer-most layer of the glass substrate to improve the light absorption [\[1](#page--1-0)–3].

Recently, various attempts have been made to improve the efficiency of a-Si:H thin film solar cells. An anti-reflection coating enables more efficient use of the incoming light by reducing reflections. Typically,  $\sim$  10% of the incident light on the glass substrate of an a-Si:H solar cell is reflected at the interface between the air and glass due to their differences in refractive index, with air at  $n = \sim 1$  and glass at  $n = \sim 1.5$ . Currently, an anti-reflection coating is achieved by one of two techniques, with the first being the destructive interference method, where alternating layers of high and low refractive-index materials are deposited  $[4-7]$  $[4-7]$ . However, this method is expensive and works for only a single wavelength. The other method uses the

#### **ABSTRACT**

Porous SiO<sub>2</sub> thin films with low reflectance and high transmittance were obtained using reactive high power impulse magnetron sputtering (HIPIMS) at a high working pressure of 6.67 Pa (50 mTorr). The average transmittance (450–600 nm) of the SiO<sub>2</sub> thin films was 94.45%. In comparison, SiO<sub>2</sub> thin films deposited at a low working pressure of 0.27 Pa (2 mTorr) showed an average transmittance of 91.26%. The improvement in the transmittance was attributed to the lower refractive index resulting from the porous structure of the SiO<sub>2</sub> thin films. To examine the effect of the anti-reflection SiO<sub>2</sub> coating, an a-Si:H solar cell was produced on fluorine-doped tin oxide (FTO) glass. The initial energy conversion efficiency for cells using the anti-reflection,  $SiO<sub>2</sub>$ -coated FTO glass was 11.75%, higher than the 10.75% for the sample using the bare FTO glass. The increase in the short-circuit current density  $(J_{\rm sc})$  due to the decreased light reflectance was the largest contributor to the increase in the a-Si:H solar cell efficiency.  $\odot$  2014 Elsevier B.V. All rights reserved.

> deposition of an intermediate refractive index material such as  $MgF_2$  $(n = \sim 1.38$  at 500 nm) on the glass substrate [\[8,9\].](#page--1-0) Porous SiO<sub>2</sub> is a low-cost alternative to  $MgF<sub>2</sub>$  for achieving a lower refractive index. Glancing angle deposition (GLAD) is a typical method used to obtain porous  $SiO<sub>2</sub>$  thin films with a low refractive index [\[10](#page--1-0)–12]. However, the low deposition rate and the inability to use it for large-area depositions make it difficult to transfer to commercial applications. According to Thornton's thin film deposition model, the structure of the deposited thin film becomes more porous with increasing working pressure [\[13](#page--1-0)–15]. This is due to the frequent collisions between the deposition atoms with the surrounding gas atoms during their flight to the substrate, resulting in a loss of directionality, and it is this randomness of the incoming atomic flux that results in the deposited film having a porous structure [\[16](#page--1-0)–18].

> The high power impulse magnetron sputtering (HIPIMS) technique, adopting an extremely high sputtering power density on the order of kW/cm<sup> $-2$ </sup> with a low duty cycle below 10%, enables a high deposition rate during pulse-on time [19–[21\].](#page--1-0) The high deposition rate of the HIPIMS technique can achieve a coarser structure of the deposited thin films, along with the high-pressure sputtering effect. In this work, we studied the thin film deposition of porous  $SiO<sub>2</sub>$  using the HiPIMS technique at a high working pressure to attain a low refractive index film for use as the anti-reflection coating in a-Si:H thin film solar cells.

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#### 2. Experimental

To determine the optimum anti-reflection  $SiO<sub>2</sub>$  thin film deposition conditions using reactive magnetron sputtering of a Si target,  $SiO<sub>2</sub>$  thin films were deposited on Corning Eagle 2000™ glass substrates for analysis. Before the  $SiO<sub>2</sub>$  deposition, the vacuum chamber was evacuated to a base pressure of  $1.47 \times 10^{-3}$  Pa ( $1.1 \times 10^{-5}$  Torr). In order to prevent arcing at the Si sputter target, a pulsed-DC power at a 25 kHz frequency and a 60% duty cycle was used instead of continuous DC power. The working gas was a mixture of Ar and  $O<sub>2</sub>$  at total pressures of 6.67, 10.0, and 13.3 Pa (50, 75, and 100 mTorr), with an Ar flow rate of 10 sccm and an  $O<sub>2</sub>$  flow rate of 0.5 sccm. The distance between the Si sputter target and the substrate was 10 cm; an average power of 200 W was applied to the 3-inch-diameter Si target, and the SiO<sub>2</sub> deposition rate at 6.67 Pa (50 mTorr) was  $\sim$  20 nm/min. The SiO<sub>2</sub> film thickness was varied between 50–200 nm and the deposition conditions are summarized in Table 1.

The anti-reflection  $SiO<sub>2</sub>$  thin films were also fabricated utilizing reactive high power impulse magnetron sputtering (HIPIMS) at a frequency of  $0.8-1.5$  kHz and pulse width of  $8-11$   $\mu$ s as shown in Table 2. A mixture of Ar and  $O<sub>2</sub>$  gases at a total pressure of 6.67 Pa (50 mTorr) was used as the working gas, with the Ar and  $O<sub>2</sub>$  flow rates at 10 sccm and 0.6 sccm, respectively. As shown in Fig. 1, the peak sputtering power applied to the Si target increased with increasing the pulse width at  $-1.2$  kV bias. For the peak power at 54, 72, and 84 kW, the peak deposition rates for the  $SiO<sub>2</sub>$  thin films were 2.1, 2.6, and 3.7  $\mu$ m/min, respectively. The peak deposition rate was calculated using the following equation.

#### Peak deposition rate  $=$  deposited film thickness  $/(deposition timeE frequencyE^{E}^{E}^{E})$  (1) (1)

To investigate the effect of the anti-reflection  $SiO<sub>2</sub>$  coating, a-Si: H solar cells were produced on fluorine-doped tin oxide (FTO) glass substrates using plasma enhanced chemical vapor deposition (PECVD). Fig. 2 illustrates the structure of an a-Si:H solar cell on FTO glass with a  $SiO<sub>2</sub>$  anti-reflection coating. The a-Si:H solar cell was fabricated after the  $SiO<sub>2</sub>$  thin film was deposited on the glass side of the FTO glass substrate. Anti-reflection  $SiO<sub>2</sub>$  thin films of 130 nm thickness were deposited at 6.67 Pa (50 mTorr) using the pulsed-DC and HIPIMS techniques. On the FTO side, the B-doped (p), intrinsic (i), and P-doped (n) layers were sequentially deposited with thicknesses of 5 nm, 400 nm, and 18 nm, respectively. An RF power of 20 W at 80 MHz was applied to deposit the p, i, and n layers; for i layer deposition, a gas mixture of Ar (10 sccm),  $SiH<sub>4</sub>$  (20 sccm), and H<sub>2</sub> (60 sccm) was used, while for the p and n layers, additional  $B_2H_6$  (1.2 sccm) gas and PH<sub>3</sub> (2 sccm) gas, respectively, were included for doping. The deposition pressure

Table 1 Deposition condition of  $SiO<sub>2</sub>$  thin film samples using reactive pulsed-DC sputtering. was 53.3 Pa (0.4 Torr) and the sample temperature of 250  $\degree$ C was maintained during deposition. Finally, a  $\sim$  200-nm-thick Ag layer was deposited as a back electrode.

The reflectance and transmittance of the  $SiO<sub>2</sub>$  thin films were measured using a UV/visible Spectrometer (Perkin Elmer, Lambda 20) and the refractive index was measured with an Ellipsometer (Ellipso Technology, Elli-SE). An Atomic Force Microscope (Park Systems, XE-100) was used to investigate the surface roughness of the  $SiO<sub>2</sub>$  thin films, and cross-sections were observed using a Field Emission Scanning Electron Microscope (Hitachi, S-4700). A Solar Simulator (San-Ei Electric, XES-40S1) along with a Source-Meter (Keithley, Model 2400) were used to measure the efficiency of the



Fig. 1. Peak sputter power of reactive HIPIMS deposition with varying pulse width.



Fig. 2. Schematic illustration of the structure of an a-Si:H solar cell on FTO glass with a  $SiO<sub>2</sub>$  anti-reflection coating.

|      |     |    |    |     | Working pressure (Pa) Power (W) Frequency (kHz) Duty (%) Film thickness (nm) Average transmittance (%) Deposition rate (nm/min) Surface roughness (nm) |    |      |
|------|-----|----|----|-----|--|----|------|
| 0.27 | 200 | 25 | 60 | 130 | 91.25  | 50 | 1.12 |
| 6.67 | 200 | 25 | 60 | 130 | 93.23  | 20 | 0.93 |
| 10.0 | 200 | 25 | 60 | 130 | 93.04  | 16 | 1.62 |
| 13.3 | 200 | 25 | 60 | 130 | 92.92  | 10 | 1.36 |

Table 2

Deposition condition of SiO<sub>2</sub> thin film samples using reactive HIPIMS technique at 6.67 Pa (50 mTorr).

| Bias $(-V)$          | Frequency (kHz)      |                        | Pulse width $(\mu s)$ Duty $(\%)$ Peak power $(kW)$ | Film thickness (nm) |                         | Average transmittance $(\%)$ Peak deposition rate ( $\mu$ m/min) |
|----------------------|----------------------|------------------------|---|---------------------|-------------------------|--|
| 1200<br>1200<br>1200 | 1.50<br>1.25<br>0.80 | .200<br>1.125<br>0.880 | 54<br>72<br>84                                      | 130<br>130<br>130   | 93.92<br>94.12<br>94.45 | 2.1<br>2.6   |

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