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Effect of Double Layer (SiO_2/TiO_2) Anti-reflective Coating on Silicon Solar Cells

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Silicon based solar cells have been fabricated for single layer SiO_2 and double layer SiO_2/TiO_2 antireflective coatings (ARC) using rf sputtering technique. The results were obtained with non-texturized surface of *p*-type mono-crystalline silicon (100) substrate and compared with the as-grown Si solar cell. Effect of single layer (SLAR) and double layer (DLAR) AR coatings on the performance of solar cell were characterized through electrical (AM 1.5G, 100 mW/cm^2), optical and morphological measurements. The addition of the DLAR initiated 37% improvement in the efficiency of the mono-crystalline Si solar cells, compared with 4.5% of the SLAR Si solar cell. Morphological and optical measurements were carried out by atomic force microscopy (AFM), field emission scanning electron microscopy (FESEM), Raman spectra and reflectance spectra. A reflection spectrum of DLAR was also measured which shows the minimum reflection of 2.3% at 630 nm with an average reflection of 7% (within the 400-1000 nm range). The results indicated that the DLAR SiO_2/TiO_2 coatings could be valuable in achieving highly absorbent surfaces in optoelectronic devices as well as in the production of high efficiency low cost silicon solar cells.

Keywords: double layer anti reflection coating; silicon solar cell, sputtering, SiO_2/TiO_2

1. INTRODUCTION

The importance of ARC cannot be denied in solar cell fabrication process as it gives significant improvement in solar cell efficiency [1, 2]. According to Fresnel relation, reflectance (R) varies from 31% to 51% at 1.1 pm to 0.40 pm respectively. So, without ARC, the silicon would only transmit about 70% of IR and 50% of UV portions of the sunlight into the cell [3]. Although other factors such as recombinations, poor contacts etc. [4] influence the solar cell efficiency but overall performance of an actual Si solar cell is limited by light trapping conditions [5]. Thus ARCs are of great importance to get low solar cell reflectance. To achieve lowest reflection of a single wavelength of incident radiation, the ARC may consist of a SLAR, which must retain (a) square root of the refractive indices of the materials constrained the coating equal to the refractive index of the ARC and (b) thickness of ARC equal to one quarter of the wavelength [6]. The SLAR coating can be non-reflective only at single wavelength, normally at the middle of the visible spectrum. DLAR coatings are more effective over the whole visible spectrum. Various materials have been used to date as ARC's in silicon solar cells, e.g. SiO, SiO_2, Si_3N_4, TiO_2, Al_2O_3, SiO_2–TiO_2 and ZnS [7-11].

In the present research work SiO_2 and TiO_2 have chosen to prepare SLAR and DLAR coatings. The SiO_2 has good passivation and scratch resistant properties and chemically stable at elevated temperatures [12]. Another material is TiO_2 which has suitable refractive index and a low absorption throughout the visible region. In addition TiO_2 is known for its chemical stability mechanical hardness, less moisture absorption, and comparatively smooth fabrication process [13]. Different techniques have been used to deposit SiO_2/TiO_2 films, including sputtering, sol-gel [14], chemical vapor deposition (CVD) [8], atomic layer deposition (ALD) [9], chemical spray pyrolysis (CSP) [15], screen printing [16], pulsed laser deposition (PLD) [13], sputtering [17], and hydrolysis [18].

Substrates heating (during or after the deposition) are required in most of these techniques [8, 19]. Whereas in some cases, the samples are annealed up to a temperature of 1050 $^{\circ}$C for a long period of time (1–6 h) [20]. Though sol-gel is cost effective efficient method for Si solar cell layering but thickness is not precisely controlled by this technique[21]. In the same time, necessity of high vacuum in CVD makes this technique inadequate for mass production of Si solar cells [8]. Heat treatments applied in the solar cell processing may introduce defects that act as recombination centres for charge carriers in the solar cell device. In addition these heat treatments may alter the intended compositional distribution in the solar cell [22, 23]. Whereas sputtering method employs an efficient and sophisticated process. In the present work, the SiO_2 SLAR and SiO_2/TiO_2 DLAR coatings on monocrystalline Si solar cells were prepared by sputtering technique. In this paper, we present the structural and optical results of SLAR and DLAR coatings on polished silicon substrates.

2. EXPERIMENTAL

2.1 Solar Cell Fabrication

Table 1 and 2 represents the sputtering conditions and deposition results of the SLAR and DLAR coatings. Solar cells were prepared using a 3–5 Ωcm boron-doped mono-crystalline Si wafer with one side polished. Surface contamination of the Si substrates was initially removed by standard Radio Corporation of America (RCA) method. Then after de-ionized water rinse ($\rho >$ 18.2 MΩcm) and N_2 blow the emitter region was fabricated by thermal diffusion of phosphorous atoms in a quartz tube furnace at 1000°C. The samples were then thermally evaporated at a pressure of 3×10^{-5} Torr in oil vacuum pump system. A thick layer of aluminum was made with high purity (99.999%) on the whole back side and then sintered at 850 $^{\circ}$C in order to form effective back surface field (BSF). Thickness measurement of the aluminium layer was calculated using "gravimetrical technique" and the weight of the samples were measured before and after evaporation process.

Table 1. Parameters and deposition results of the SiO_2 and TiO_2 films.

Antireflection Coating	Layer	Time (min)	Temperature (°C)	Thickness (nm)	Refractive index (λ = 500 nm)
SiO_2	Single	45	30	81	1.5
TiO_2	Double	8	25	18	2.5
SiO_2	Double	23	35	40	1.5

After BSF formation, the p^+ regions were delineated by etching the silicon wafer in an acid solution. The SLAR SiO_2 and DLAR SiO_2/TiO_2 coatings were deposited on the front side of solar cells using sputtering technique. For that purpose pure SiO_2 and TiO_2 targets (99.9995%) were used in sputtering system (Auto HHV500 Sputter Coater). Both SiO_2 and TiO_2 depositions were carried out under constant vacuum pressures with different oxygen flow rate. The refractive index, thickness and reflectance of the ARCs were measured using an optical reflectometer, (Filmetrics F20). For that purpose white light, having the frequency range 3×10^{14}-7.5×10^{14}Hz was used.

Table 2. The growth conditions of the TiO_2/SiO_2 film depositions on the Si substrate.

Target	TiO_2 99.99%	SiO_2 99.99%
Target diameter	7.6 cm	7.6 cm
Target to substrate distance	10 cm	10 cm
Substrate	Si	Si
Substrate temperature	31 °C	33°C
Ultimate pressure	2.82×10^{-5} mbar	3.16×10^{-5} mbar
Vacuum (Plasma) pressure	6.75×10^{-3} mbar	2.51×10^{-3} mbar
Gases	$Ar+O_2$ (99.99%)	$Ar+O_2$ (99.99%)
RF sputtering power	150 W	200 W
Deposition rate	0.4 A° sec	0.3 A° sec
Deposition time	8 min	45/23 min
The required thickness	18 nm	81/40 nm

It was a combination of different wavelengths ranging from 400-1000nm having different colours. While the morphology of the structure was characterized using a field emission scanning electron microscope (Nova NanoSEM 450). The FESEM, surface reflectivity and optical measurements were also performed on a reference *p*-type (100) monocrystalline Si substrate (as-grown) for comparison purpose. EDX spectroscope is often coupled with the FESEM and was applied to study the elemental composition. The AFM model (Dimension edge, Bruker) with non-contact operation mode was used to obtain 3D images of the samples. Raman spectra measurements were performed using Jobin Yvon HR 800 UV spectroscopic system. After fabrication the device, current density versus voltage measurements were taken using a simulator (Leios IV SolarCT) under the air mass 1.5 (100mW/cm^2) white light illumination conditions.

2.2 Design of SLAR and DLAR Coatings

The optimum thickness and refractive index with a minimum reflectance for a single-layer ARC can be deduced through the following equation:

$$\lambda_o = 4n_1 \times d_1 \qquad (1)$$

where, λ_o represents the mid-range wavelength of 500 nm, n_1 and d_1 represents the refractive index and layer thickness, respectively. A design diagram of SLAR coating is shown in Fig. 1(a).

For the DLAR coating design, the high-low refractive index on the Si substrate (i.e., the upper film has the high refractive index and lower layer has low refractive index) was used. Schematic design of SiO_2/TiO_2 DLAR coating is shown in Fig. 1(b), where d_1 and d_2 represents the thickness of the outer and inner layers, respectively. Moreover, n_0, n_1, n_2 and n_s denote the refractive index of air, outer, inner films and substrate respectively. In order to achieve a zero reflectance each film must meet Eqs. (2) and (3) [24],

$$\frac{n_2 d_2}{\lambda_o} = \frac{1}{2\pi}\tan^{-1}\left\{\pm\left[\frac{(n_s - n_o)(n_o n_s - n_1^2)n_2^2}{(n_1^2 n_s - n_o n_2^2)(n_2^2 - n_o n_s)}\right]^{1/2}\right\} \qquad (2)$$

$$\frac{n_1 d_1}{\lambda_o} = \frac{1}{2\pi}\tan^{-1}\left\{\pm\left[\frac{(n_s - n_o)(n_o n_s - n_2^2)n_1^2}{(n_1^2 n_s - n_o n_2^2)(n_1^2 - n_o n_s)}\right]^{1/2}\right\} \qquad (3)$$

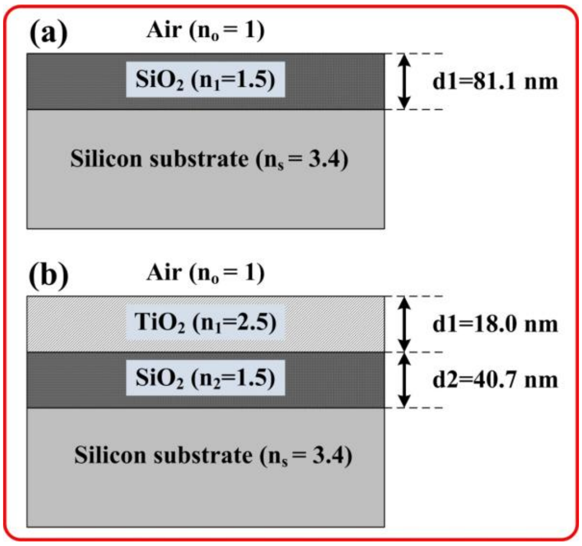

Figure 1. Schematic diagram of antireflection coatings (a) SLAR (SiO_2) (b) DLAR (SiO_2/TiO_2).

3. RESULTS AND DISCUSSION

The film elemental analysis of SiO_2 and SiO_2/TiO_2 ARC's was investigated through energy dispersive x-ray spectroscopy (EDX) and surface morphology image was taken by FESEM (Fig. 2). The Fig. 2(a) shows the energy dispersive x-ray spectra of the different elements in SiO_2 SLAR coating deposited on c-Si p-type (100). The elemental composition of the SiO_2 layered silicon wafer was found to be dominated by Si (58.12 wt. %) followed by oxygen (41.68 wt. %).

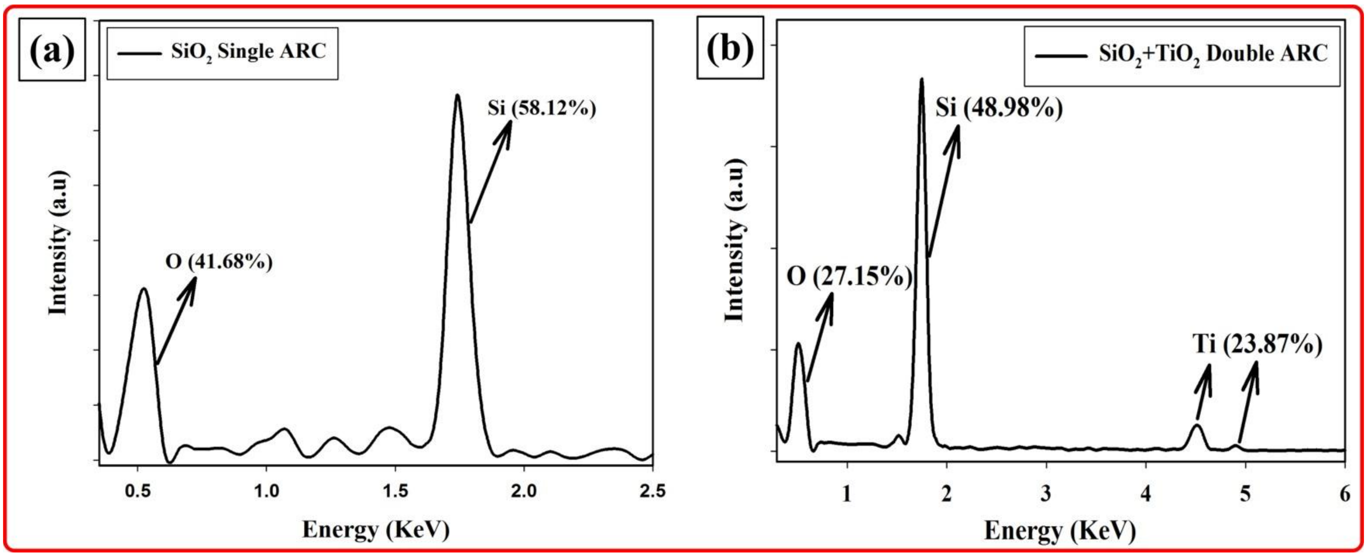

Figure 2. EDX spectra (a) SiO_2 film, (b) SiO_2/TiO_2 film.

It can be seen from spectra (fig. 2(b)) of SiO_2/TiO_2 layered silicon wafer, the dominance of silicon (48.98 wt. %) and titanium (27.15%) with oxygen (23.87%). Fig. 3(a) shows FESEM cross-section of Al-alloyed p^+ layer formed at 850 $^{\circ}$C in ambient nitrogen condition.

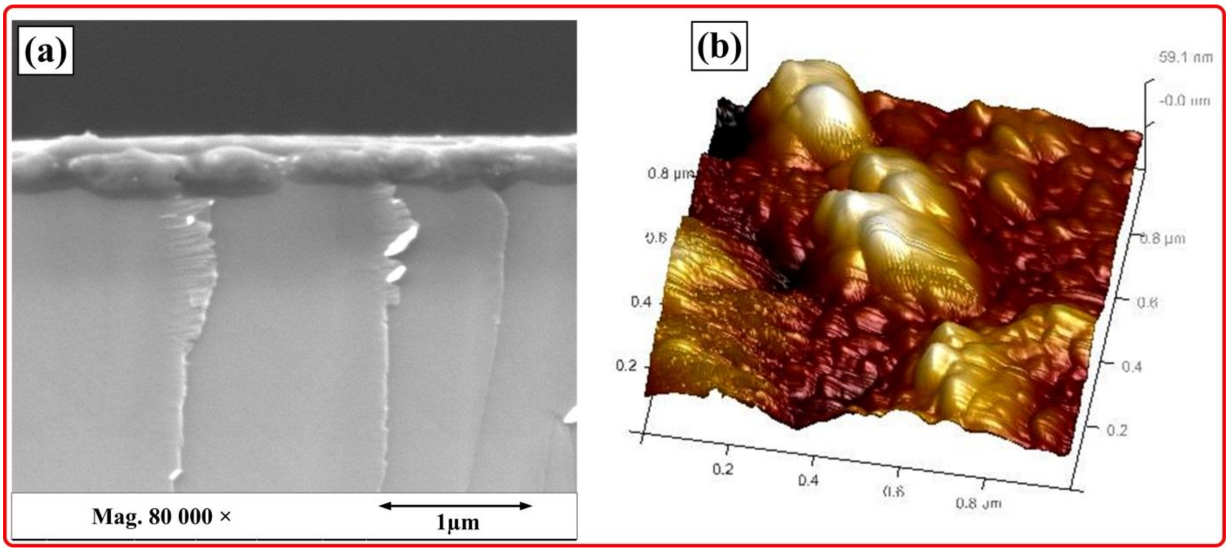

Figure 3. Al-alloyed p^+ layer (a) FESEM cross sectional view (b) AFM back side view.

FESEM Fig. 3(b) represents the AFM back view of Al-BSF layer on the Si substrate. Cross-section view shows the uniformity of Al-BSF layer along the Si substrate while little spikes of p^+ layer can be seen in the back view of AFM micrograph.

Fig. 4 shows the Raman spectra of the as-grown Si sample, SLAR SiO_2 and DLAR SiO_2/TiO_2 coatings deposited on the c-Si p-type (100) using an Argon ion excitation laser source (514.5 nm) at room temperature. The as-grown Si sample produced a sharp solid line with a FWHM of 0.08 cm^{-1} located at 528.72 cm^{-1} because of the scattering of first-order phonons.

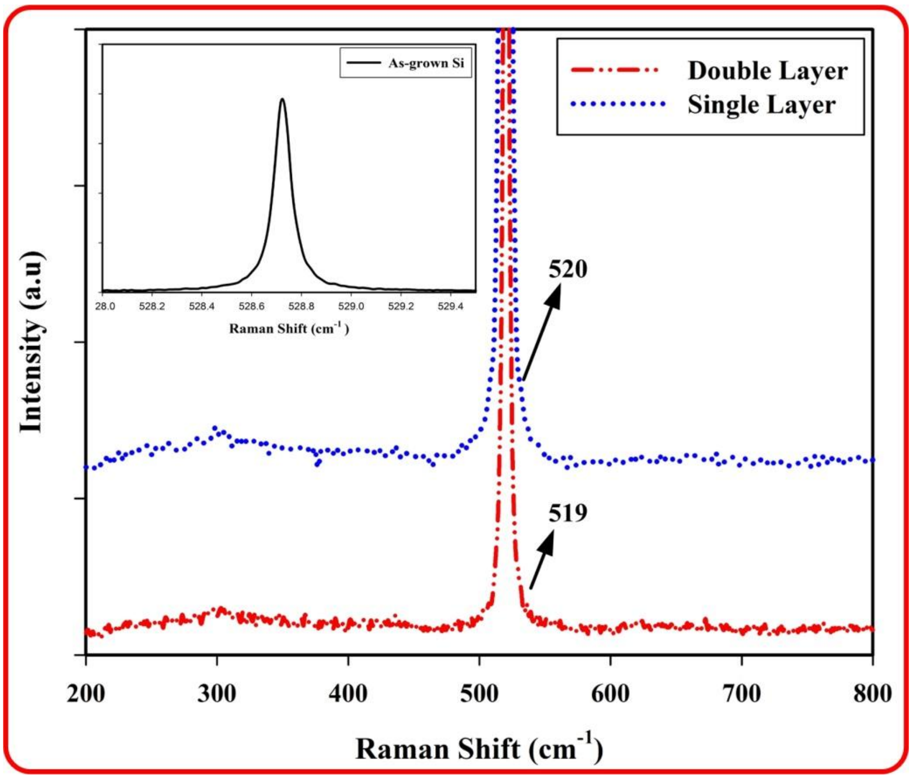

Figure 4. Raman spectra of the SiO_2 and SiO_2/TiO_2 coatings deposited on the c-Si *p*-type (100).

Raman spectra of SiO_2 SLAR layer deposited at room temperature shows one strong sharp peak at 520 cm^{-1} having FWHM of 9.3 cm^{-1}. The absence of other features in the Raman spectra of SiO_2 and SiO_2/TiO_2 films indicates the absence of other phases, such as amorphous Si phase**.** Raman spectra of SiO_2/TiO_2 DLAR layer shows one strong sharp peak at 519 cm^{-1} having FWHM of 9.9 cm^{-1}. The Raman spectra of SiO_2/TiO_2 DLAR films do not contradict from that of the as-grown Si nor from the SiO_2/Si one, that is in accordance with an amorphous state [25].

Fig. 5 represents the measured reflectance spectra of the SiO_2 and SiO_2/TiO_2 coatings deposited on the c-Si *p*-type (100) non-textured substrates. The reflection loss can be reduced significantly via a suitable ARC as the bare silicon has a high-refractive index and averaged solar reflectance of about 35%. The average reflectance of approximately 7% and 15% between 400 and 1000nm was achieved by the DLAR SiO_2/TiO_2 and SLAR SiO_2 coatings on the non-textured Si substrates, respectively.

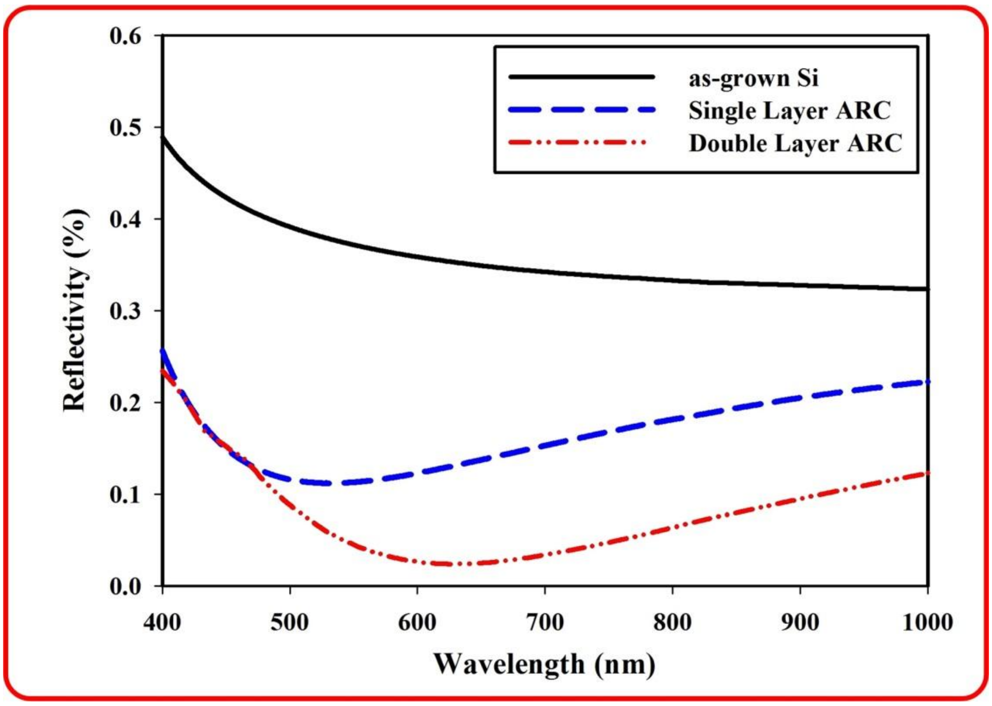

Figure 5. Shows the reflectance spectra for SLAR and DLAR coatings with the as-grown Si sample.

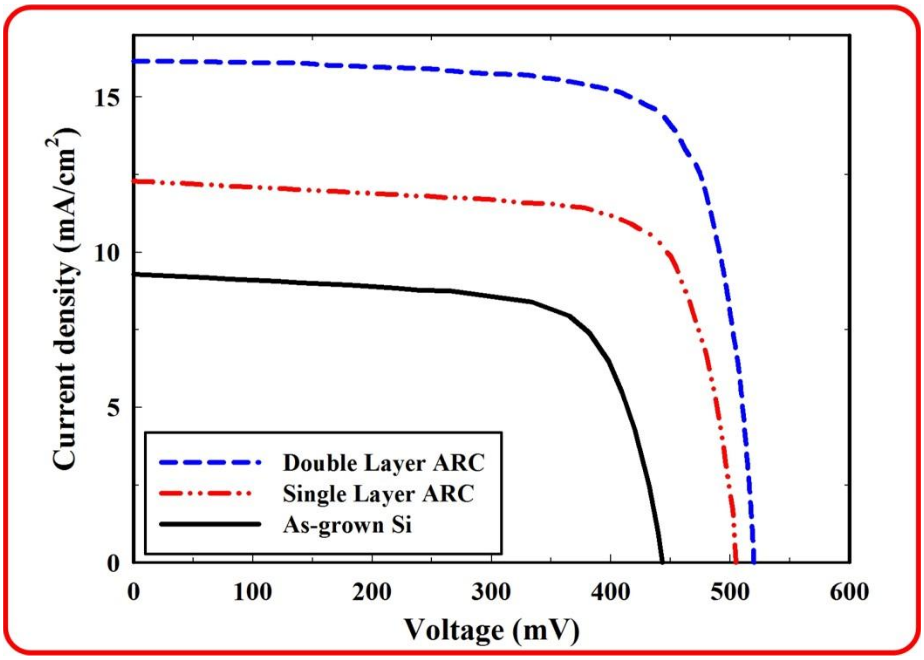

Figure 6. Shows the *I-V* graphs formed with SLAR (SiO_2) and DLAR (SiO_2/TiO_2) coatings with the as-grown Si solar cell.

A similar result was obtained by Richards [18] with double layer TiO_2 ARC for Si solar cell. The results indicate the reduced reflectance losses when compared to Hocine and Richards [8, 26] for TiO_2 single layer ARC. A similar result was also obtained by Panek [27] for SiO_2 single layer ARC. This indicated that the bare Si absorbance increased by approximately 13% and 40% for SLAR and

DLAR coatings, respectively. Reflection spectrum of SLAR SiO_2 coating shows the minimum reflection of 11% at 530 nm while reflection spectrum of DLAR SiO_2/TiO_2 coating shows the minimum reflection of 2.3% at 630 nm within the 400-1000 nm range. Further, the DLAR reflectance is lower than 5% within the 540-760 nm wavelength range. It means the absorption of the incident photons was increased and hence the photo-generated current, which has significant effect in enhancing the solar cell efficiency.

The current–voltage characteristics of the solar cell devices with SLAR and DLAR coatings are shown in Fig. 6. The solar cells were characterized under 100 mW/cm^2 illumination condition. It is given in Table 3 that the solar cell with DLAR SiO_2/TiO_2 coating has shown the best photovoltaic achievement, in special, a short circuit current J_{sc} of 16.1 mA/ cm^2 which increases by ΔJ_{sc}=6.9 mA/cm^2 [8] related to the as-grown Si solar cell. On the other hand the results indicate the improved current density value as compared to Richards [18] for an optimized TiO_2 DLAR coating. This consequently results in the improvement of cell efficiency to 6.2% which is an increase of 3.4% absolute in comparison to the as-grown Si solar cell.

Further the solar cell with SLAR SiO_2 coating has demonstrated the short circuit current J_{sc} of 12.3 mA/ cm^2 which rises by ΔJ_{sc}=3.1 mA/cm^2 compared to the as grown Si cell. It enhances the cell efficiency by 4.5%, which is an improvement of 1.7% absolute in comparison to the as-grown Si cell. The addition of the TiO_2 layer initiated 37% improvement in the efficiency of the DLAR SiO_2/TiO_2 coated Si solar cells, compared to 4.5% of the SLAR SiO_2 coated Si solar cell. A similar photovoltaic efficiency result was obtained by Szlufcik and Majewski [16] for silicon solar cell. These indicate that the sputtering deposited SiO_2 and TiO_2 films can be used as DLAR ARCs for Si solar cells. The low temperature ARC depositions are also beneficial for the production of Si solar cells with minimum defects [28]. The Si solar cells with SLAR SiO_2 and DLAR SiO_2/TiO_2 coatings show an increase of efficiency of about 60% and 214%, respectively, as compared to as-grown Si solar cell.

Table 3. Current–Voltage measurements of back surface field solar cells with and without ARC layers with the as-grown Si solar cell.

Samples	V_{oc} (mV)	I_{sc} (mA)	V_m (mV)	I_m (mA)	F.F (%)	η (%)
As-grown Si	441.81	9.24	365.83	7.71	69	2.8
Single ARC	504.46	12.35	423.89	10.65	72	4.5
Double ARC	520.02	16.13	436.18	14.47	75	6.2

Analogous to these results, the gain in conversion efficiency of Si solar cells was principally attributed to the enhancement of the short circuit current due to the reduction of optical losses from the solar cell surface and the improvement of light transmission by TiO_2 and SiO_2 ARCs [29, 30].

4. CONCLUSION

In this paper a preparation and comparison of high quality SLAR (SiO_2) and DLAR (SiO_2/TiO_2) coatings on Si solar cells have been performed using sputtering technique at room temperature. Room temperature deposition of ARCs is feasible for making defects free solar cells. It is realized that the efficiency of solar cell with the DLAR (SiO_2/TiO_2) coating was better than that of SLAR (SiO_2) solar cell. The reflectance of SLAR (SiO_2) and DLAR (SiO_2/TiO_2) coatings were observed to be 15 and 7%, respectively. An enhancement of 214% and 60% in conversion efficiencies were obtained in the DLAR (SiO_2/TiO_2) and SLAR (SiO_2) coated monocrystalline Si solar cells, respectively; as compared to the as-grown Si solar cell. The addition of the DLAR initiated 37% improvement in the efficiency of the monocrystalline Si solar cells, compared with 4.5% of the SLAR Si solar cell. Current-voltage characteristics have shown that the antireflection coatings have significant effect over the short circuit current of the solar cells. This addition of DLAR SiO_2/TiO_2 coating at low temperature sputtering conditions could be a significant contribution to currently well-known antireflective films for optoelectronic nano-devices as well as in silicon solar cells.

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