

Dependence of SiN_x Properties on Deposition Time Prepared by PECVD

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ABSTRACT: This study aims to overcome the efficiency limitations of monocrystalline silicon solar cells due to the optical losses, charge recombination, and trap in the material. Plasma-enhanced chemical vapour deposition (PECVD) SiN_x is the typical choice as an anti-reflection coating (ARC) for silicon solar cells. SiN_x films were prepared using a gas mixture of high-purity silane (SiH₄) and ammonia (NH₃) at 380 °C in the time range of 5 min. - 13 min. The optical properties of SiN_x films based on deposition time have been investigated, and a correlation between these properties and solar cell characteristics are demonstrated. The highest conversion efficiency of silicon solar cells is 18.84%.

KEYWORDS—Silicon solar cells, Silicon nitride, PECVD, Antireflection coatings

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I. INTRODUCTION

World's energy demand increasing significantly to meet the requirements of growing population in the world and industrial evolution. However, conventional energy sources are failing to meet with this heavy requirement in the power sector as well as the serious global environmental problems [1]. Therefore, there is a pressing need to accelerate the development of advanced clean energy technologies [2]. It is therefore vital to go for eco-friendly energy sources for the betterment of the future world. Considering renewable energy sources such as solar energy, wind energy, hydropower and geothermal, is critically important in this sense as they are ecofriendly [1]. With a global market share of about 90%, crystalline silicon is by far the most important photovoltaic technology today [3]. The conversion efficiency of crystalline solar cells is generally limited by the reflection of light at the surface, charge recombination and trapping in the material [4]. A significant portion of a solar radiation (reflectance value may be >35 %) is reflected from the surface of the silicon solar cells, and, as a consequence, this does not contribute to the electron-hole pair photogeneration. Obviously, the huge optical loss heavily influences light harvesting, this leads to a solar cell efficiency limitation and reduction. Therefore, light trapping is a very important technique for increasing solar cell efficiency [5][6].

Two practical techniques minimize the optical loss of surface reflection. The first technique is surface texturization that increases light absorption in silicon. Another widespread approach to minimize the reflectance is to deposit a suitable anti-reflection layer on the surface of the silicon solar cells [7]. The SiO₂, TiO₂, silicon nitride (SiN_x) and boron nitride (BN_x) films are good anti-reflective coatings for solar cells. Silicon nitride films can be prepared by various methods such as low pressure chemical vapour deposition (LPCVD), plasma enhanced chemical vapour deposition (PECVD) and sputtering technique [8]. The most common technique is plasma enhanced chemical vapor deposition (PECVD), in which silane (SiH₄) and ammonia (NH₃) are normally used as reactive gases. Moreover, PECVD provides such advantages as high throughput, good uniformity and excellent reproducibility [3]. PECVD process is suitable for depositing an ARC layer of SiN_x which not only reduces the reflection but also passivates the front-side n-type emitter and the bulk thus improving the solar cell efficiency [9][10].

In this paper, silicon nitride (SiN_x) thin films were prepared from ammonia and silane by (PECVD) at different deposition times. Film thickness, refractive index and reflectivity of the SiN_x samples were evaluated as functions of deposition time using a multiple angle laser ellipsometer and spectrophotometer. Also, this work demonstrates the best SiN_x deposition time which enhances the performance and efficiency of the monocrystalline silicon solar cell. Monocrystalline silicon solar cells passivated with SiN_x antireflection

coatings are fabricated, and their characteristics are analyzed using current-voltage (I-V) and power voltage (P-V) measurements.

II. EXPERIMENTAL

This study was carried out in the Joint National Egyptian-Chinese Renewable Energy laboratory, Sohag, Egypt. SiN_x films were deposited by PECVD furnace (M82200-9/UM PECVD computer technology automatic control system V9.1) using high purity SiH₄ and NH₃ of (99.9999%) and (99.9995%) respectively as precursor's gases. Deposition times were varied from 5 min. to 13 min to study the effect of time, with the fixed deposition parameters as deposition temperature was an of 380 °C, deposition pressure of 195 Pa, flow rate (NH₃/ SiH₄) of 9, and plasma power was set at 3100 W. The PECVD equipment is shown in Fig.1 and the reaction takes place in Electrothermal furnace as following [11]:



The display panel of the SiN_x thin film deposition parameters setting in the PECVD equipment during operation is shown in Fig.2. The SiN_x films' deposition conditions are listed in Table 1. Mono-crystalline Czochralski silicon (Cz-Si), p-type (100) wafers (doped boron) of a resistivity (ρ) 0.8–2.6 Ω.cm and thickness of about 180 μm were used as the starting material. Saw damage marks were removed by an aqueous alkali solution containing 0.1675 M KOH at 70 °C followed by surface texturing with an alkali solution of potassium hydroxide, deionized water, and additive material (IPA) at 85 °C for 16 min. and subsequently subjected to etching in an aqueous acid solution of 10 % HF (2.26 M) and then in 10 % of HCl (1.2 M) to remove the oxides and organic contaminations. The textured wafers were washed and dried by a dryer machine at 50 °C for 5 min. then the phosphorous diffusion process in the high-temperature diffusion furnace using POCl₃ as the phosphorus source to form an n-type layer on the textured wafers, The sheet resistance of the phosphorous doped silicon wafers was in the range of 40–45 Ω/sq. after that edges isolation by etching through plasma etching equipment with CF₄ (150 sccm/min.) and O₂ (15 sccm/min.) for 15 min to remove short circuit in the cell. Phosphosilicate glass (PSG) layer which was formed during the diffusion process was removed manually with a diluted aqueous solution containing 12 % HF (2.71M). Next step, all cells were washed and dried by a dryer machine at 50 °C for 5 min., after which the films of silicon nitride (SiN_x) for ARC and passivation were deposited in PECVD furnace using a pure silane and ammonia. The deposition times were changed (5 min.-13 min.), then screen printing metallization technique was used for metal contact formation using silver (Ag) and Ag/Al (aluminum) paste on the front and back surface for the cell respectively. SiN_x film-coated samples and silver (Ag) paste in the front surface were followed by drying and annealing in a sintering furnace to form ohmic contacts between metal and semiconductor. Finally, the cells were tested for electrical parameters determination.



Fig.1. PECVD equipment.

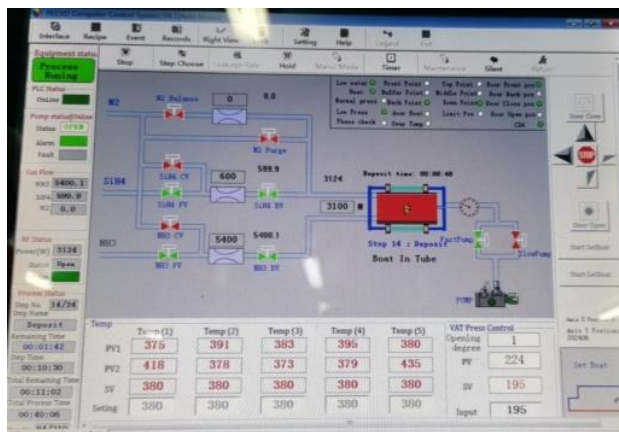


Fig.2. SiN_x film deposition parameters setting in PECVD equipment.

Table 1 Deposition conditions of SiN_x films at various times

PECVD	
Substrate	P-type Silicon wafer [$\rho=0.8-2.6 \Omega \cdot \text{cm}$]
RF Power	3100 W
Pressure	195 pa
Temperature	380 °C
SiH ₄	600 sccm/ min
NH ₃	5400 sccm/ min
NH ₃ / SiH ₄	9
SiN _x Films Deposition Time	
	5 min.
	7 min.
	9 min.
	11 min.
	13 min.

The refractive index and the thickness of the SiN_x films on the textured monocrystalline Si solar cells after rpsg process were measured with a multiple angle laser ellipsometer SE 400 adv and the reflectance of the SiN_x films was measured using a computer programmable double beam spectrophotometer model JASCO V-570 with reflectivity attachment model ISN-470, (Japan). Surface morphology of the SiN_x films on the textured monocrystalline Si solar cells was examined using scanning electron microscopy (SEM), model Philips XL30, with accelerating voltage 30 kV, magnification up to 400 000 x and resolution for W. 3.5 nm. Current-voltage (I-V), power-voltage (P-V) characteristics, and the parameters of the solar cells were determined using Solar Cell Tester (SCMT) with a pulsed xenon lamp.

III. RESULTS AND DISCUSSION

3.1 SiN_x films Characteristics

Fig.3. shows the SiN_x film thickness in nm as a function of deposition time (5 min. – 13 min.). The thickness increases with increasing deposition time, film thickness increases from 78.4 nm at 5 min. to 91.9 nm at 13 min.

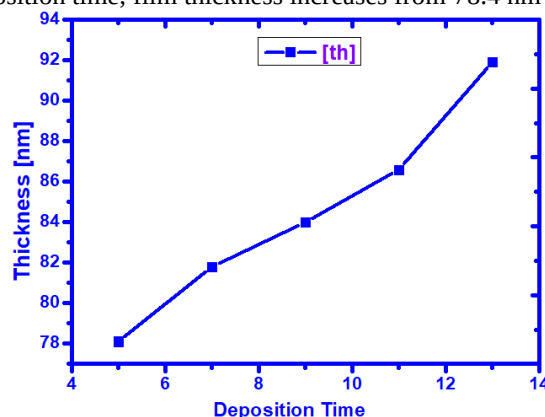


Fig. 3 Effect of deposition times on the deposited SiN_x films thickness.

Fig.4. shows the refractive index (n) at 633 nm of SiN_x thin films as a function in the deposition time. No obvious changes in refractive index can be observed for SiN_x samples prepared at different deposition time, the obtained values of $n \sim 2$ suitable as antireflection coating for mono crystalline Si solar cell (optimal values 1.9- 2.2). Table 2 illustrates the properties of SiN_x films prepared at different times.

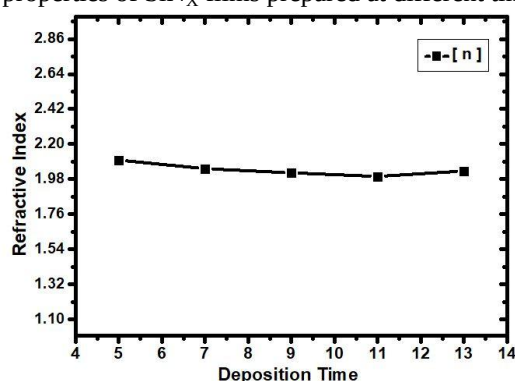


Fig.4. Effect of the deposition times of the SiN_x film on refractive index.

Table 2: The properties of the SiN_x films deposited at different deposition time.

Deposition Time (min.)	Thickness th (nm)	Refractive Index (n) @ 633 nm
5	78.4	2.1003
7	81.8	2.0463
9	84	2.0199
11	86.6	2.0040
13	91.9	2.0317

Fig.5. shows the variation of SiN_x reflection (R) with wavelength for different SiN_x deposition time. It is observed that, SiN_x reflectance in the visible range is decreased with increase in time.

At wavelength of 632 nm, the SiN_x reflectance was 3.672%, 1.724%, 1.589%, 0.934% and 4.315% for 5min, 7min, 9min, 11 min and 13 min respectively. At wavelength range 530 nm-650nm that required for solar cell, the lowest reflection (R) is about 0.934% at the deposition time of 11 min.

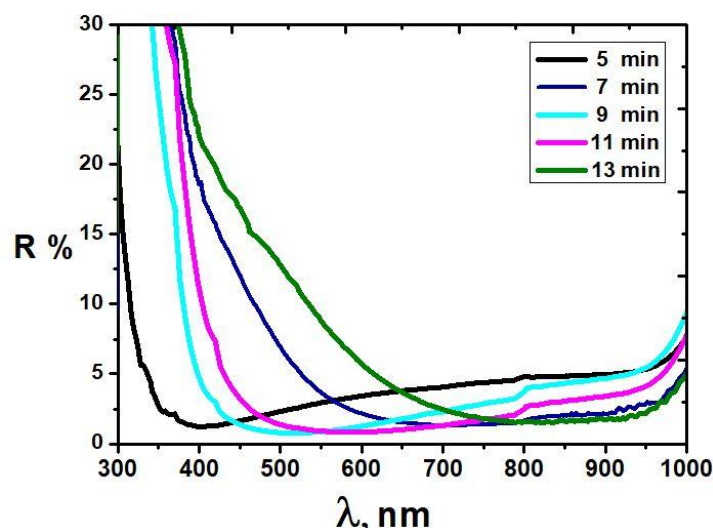


Fig.5. Reflectance of SiN_x films at deposition times 5min., 7min., 9min., 11min., 13min.

Fig.6. shows the images of SiN_x thin films on textured monocrystalline Si solar cells at various deposition times. The film's colour changes with changing time, it is seen that sample prepared at 5 min. appear a yellowish (actually appears to be light creamy grey or metallic) colour. While blue-violet, dark blue, blue and light blue colours were corresponding to 7, 9, 11 and 13 min. respectively. The change in film colors is attributed to the change in films thickness. Also, the film homogeneity and uniformity enhanced with increasing deposition time up to 11 min.

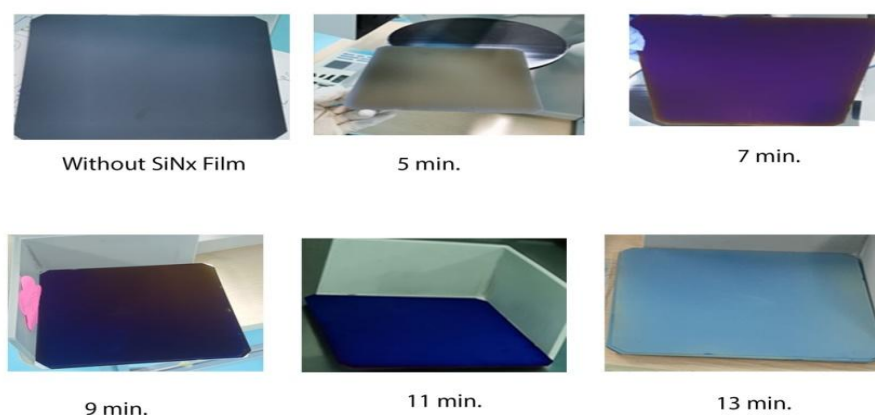


Fig. 6. Effect of the deposition time on the homogeneity of the SiN_x films deposited on monocrystalline silicon solar cells.

Fig.7.(a)–(d) shows the surface morphology of the textured monocrystalline Si solar cells passivated by SiN_xfilm deposited at 5 min, 7 min,11 min and 13 min, respectively. According to the results, at 5 min appreciable voids between the pyramids. A more homogeneous and dense structure with increasing the deposition time. When the deposition time is 11 min.,the SiN_x film appears to get denser, more homogeneous, and has a better coverage on textured monocrystalline Si solar cells .

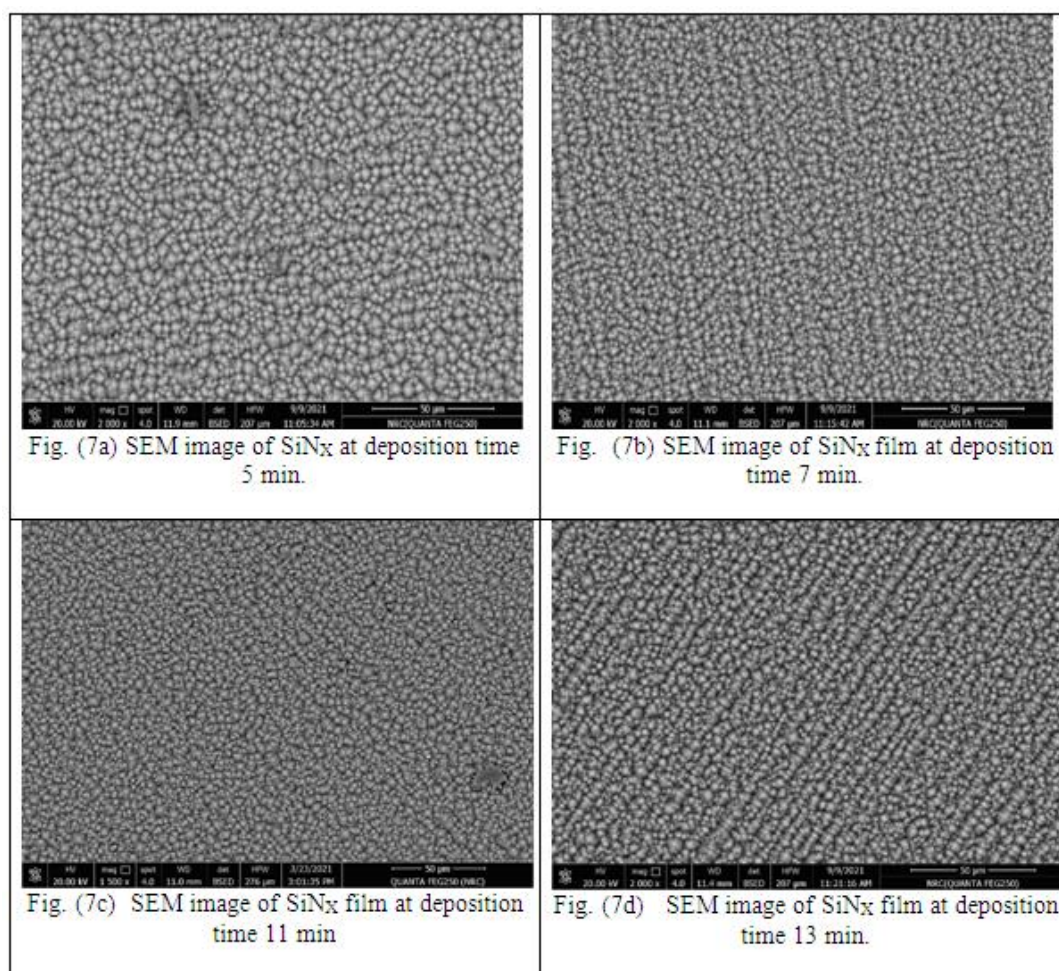


Fig.7. SEM images of solar cells for different SiN_xfilm deposition times; (a) 5min., (b)7min., (c)11min.,(d)13min.

3.2 Solar cells characteristics

Deposition time of PECVD SiN_x film is a conclusive parameter to determine the passivation effect for silicon properties and the shape of the SiN_x films. The electrical characteristics of the developed solar cells were studied under standard conditions (100mW/cm², AM1.5G, and 25 °C).

Fig.8 shows that the all photovoltaic parameters; short circuit current (I_{sc}), open circuit voltage (V_{oc}), fill-factor (FF), and efficiency (Eff), enhanced with increasing SiN_x film deposition time up to 11min.

The short circuit current strongly increases with deposition time from 5 min. to 11min as the surface reflectance decreases. Then it reduces at a higher deposition time (13 min) as the surface reflectance increases, as shown in Fig.5. The open-circuit voltage rises steadily with deposition time, from 0.621mV at 5min. to 0.633 mV at 11min. The increase of V_{oc} can be imputed to the improvement of passivation. As deposition time increases, more hydrogen atoms penetrate into the silicon bulk to passivate defects and dislocations, reducing the recombination. At 13 min. V_{oc} reduced to 0.628 mV. The increase of time at 13 min leads to a decrease of the solar cell efficiency from 18.84% to 17.76 % and affects all solar cell parameters (I_{sc} , (V_{oc}) and (FF)). Reducing the fill factor is likely due to increased film thickness at 13 min., as the silver (Ag) paste is difficult to fire through thick SiN_x film as the thickness of the film increases [12]. Table 3 clarifies detailed monocrystalline Si solar cells characteristics deposited by SiN_x films at different times.

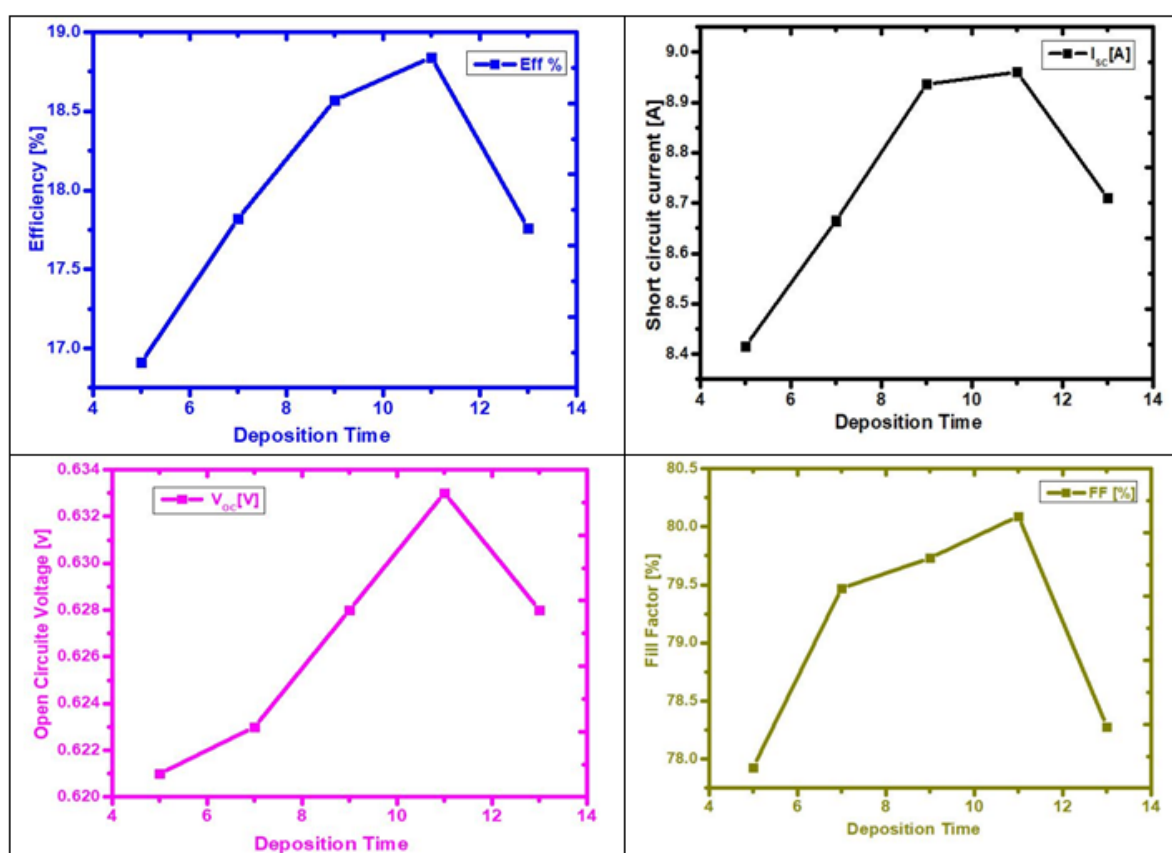


Fig. 8. Dependence of the solar cells parameters on the SiN_x film deposition time.

Table 3: Parameters of silicon solar cells with varying SiN_x thin films deposition time.

Deposition Time(min.)	I_{sc} [A]	V_{oc} [V]	I_{pm} [A]	V_{pm} [V]	P_m [W]	FF %	Eff %
5	8.416	0.621	7.655	0.532	4.072	77.93	16.91
7	8.665	0.623	8.056	0.533	4.292	79.47	17.82
9	8.725	0.628	8.310	0.538	4.363	79.65	18.11
11	8.96	0.633	8.329	0.545	4.539	80.09	18.84
13	8.710	0.628	8.030	0.533	4.279	78.28	17.76

3.3 Solar cell without and with SiN_x film

Fig.9. shows the bare (planer) mono C-Si wafer reflected around 34.248 % of the light. After texturing, the reflectance falls to around 12.278 %. The reflectance of the wafer after deposition SiN_x film as an ARC is observed to be about 1 % (0.934 %) (down to less than 1 % for the silicon cell coated with SiN_x), As we can observe that the reflectance of SiN_x film reduces to <10% over a wide range of spectra (i.e. for wavelengths of

404–1014 nm) and becomes less than 2% for wavelengths of (476–780) nm, becomes less than 1% for wavelengths of (536–648) nm. These results show that the performance of the solar cell is improved considerably with the use of SiN_x film on the front surface of the cell this significant decrease in reflectance also illustrates the improved SiN_x film's effectiveness, and the efficiency of the cell become 18.84 %.

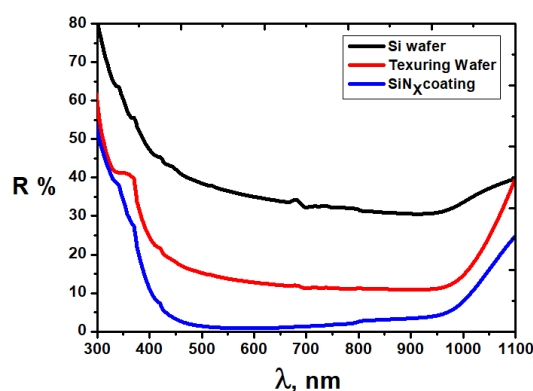


Fig.9. Reflectance of a planar monocrystalline Si wafer, a textured monocrystalline Si wafer, and a textured Si wafer coated with a SiN_x film.

The image of monocrystalline Si solar cells without and with SiN_x film showed in Fig.10. Table 4. shows the characteristics of monocrystalline Si solar cells without and with SiN_x film, the efficiency of the silicon solar cell without SiN_x film is 11.95%, whereas it becomes 18.84% with SiN_x film. The electrical characteristics of the solar cell are predicted to improve significantly as a result of improvements in the optical properties as it has been established that by using SiN_x film, low reflectance may be attained, a significant improvement in the short circuit current due to the SiN_x film, increasing I_{SC} from 7.896 to 8.96 while also increasing efficiency to around 18.84 %. The I-V and P-V curves of the solar cell without SiN_x film and with SiN_x film are shown in Fig.11.

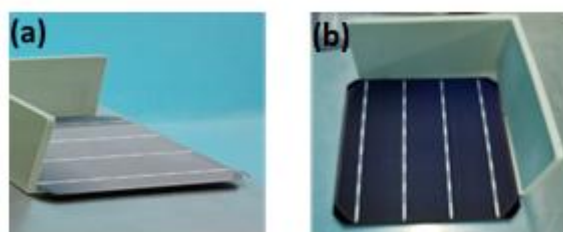


Fig.10. The image of monocrystalline Si solar cells (a) without SiN_x film (b) with SiN_x film.

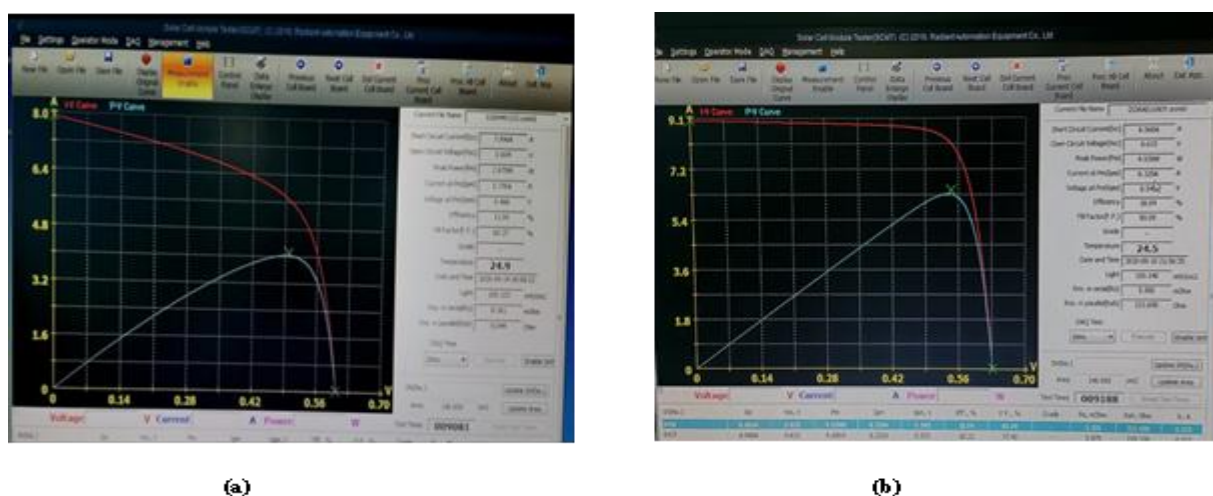


Fig.11. I-V and P-V curves of the solar cell (a) without SiN_x film and (b) with SiN_x film.

Table 4: The performance of silicon solar cell without and with SiN_x film.

	I _{sc} [A]	V _{oc} [V]	I _{pm} [A]	V _{pm} [V]	P _m [W]	FF %	Eff %
Without SiN_x film	7.896	0.604	5.776 A	0.498	2.879	60.37	11.95
With SiN_x film	8.96	0.633	8.329	0.545	4.539	80.09	18.84

IV. CONCLUSION

Silicon nitride (SiN_x) films were deposited by inline plasma-enhanced chemical vapor deposition (PECVD) using a gas mixture of ammonia NH₃ and silane SiH₄. We have studied the effect of SiN_x films deposition time (5 min.- 13 min.) on the optical properties, morphology of SiN_x films, and the efficiency of mono crystalline silicon solar cells. It has been verified that the growth of a high-quality SiN_x film can be recognized by adjusting the deposition time. A significant improvement of solar cell efficiency was obtained at a deposition time of 11 min. In addition, reducing an optical loss at this condition influences positively mono crystalline silicon solar cells' conversion efficiency. We also found that uniformity and homogeneity of the morphology of SiN_x films reduce the optical reflection and provides surface and bulk passivation. The Refractive index (n) ~2, SiN_x thickness (th) of 86.6 nm, and reflection (R) about 0.934 % gave the best solar cell parameters at 11 min. This cell has short-circuit current (I_{sc}) of 8.96 A, open-circuit voltage (V_{oc}) of 0.633 V, fill factor (FF) of 80.09% and conversion efficiency of 18.84 %. A comparison between two-silicon solar cells without and with SiN_xARC was performed. We found that the cell's reflectance with the SiN_x film reduced from 12.278 % to 0.934 %, and the cell efficiency was increased from 11.95 % to 18.84 %.

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