Optimization of experimental study of PECVD SiN_x to improve antireflection and passivation coating multicristalline silicon solar cells.

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Abstract*— Plasma Enhanced Chemical Vapor Deposition (PECVD) silicon nitride (SiN_x:H, simply called SiN_x) has been widely used in photovoltaic silicon solar cells as dielectric, because of low deposited temperature and compatibility with other process. SiN_x gradually becomes the first choice in industry silicon solar cells production. Nowadays, in photovoltaic silicon solar cells, the excellent antireflection and passivation quality of PECVD SiN_x have obvious effect on efficiency of solar cells. In this paper, we analysis several critical parameters for PECVD SiN_x deposition, such as temperature of substrate, plasma power, ratio of NH_3/SiH_4 and deposition time, and to investigate optical properties such as weighted reflectance (R_w), ellipsometry measurement for SiN_x thin film refractive indices and thickness, then we investigate the correlation between the ratio R=[NH_3/SiH_4] and plasma power with refractive indices and deposition rate. At last, we propose a set of optimized parameters for PECVD-SiN_x deposition in silicon solar cells application.

Keywords- SiN_x; PECVD; passivation; antireflection coating.

I. INTRODUCTION

The stoichiometry of the silicon nitride (SiNx) layer can be varied from Si to N rich by varying the silane SiH4 to ammonia NH3 gas ratio in the PECVD (Plasma Enhanced Chemical Vapor Deposition) deposition technique [1,2]. It has been reported that SiNx films would be applicable for use as an antireflection coating (ARC)/passivation on multicristalline silicon solar cells [3]. In this case of solar cells with high efficiency, the passivation of emitter is an important aspect. Usually not only must the passivation layer reduce the surface recombination velocity, it also require that it must compatible with antireflection coating to minimize the photo-generated current within the solar cell device. Relatively higher refractive index that can be easily varied between 1.9 and 2.6 makes SiN_x a much more efficient ARC than any thermal oxide with refractive index varying between 1.4 and 1.5 only [4,5]. In the present work, firstly the SiH_4 to NH_3 ratio (R) was varied in the plasma and observed the variation of optical properties, minority carrier effective lifetime and the thickness of layers. Hence, we have committed ourselves to show that there are optimum conditions for making PECVD SiN_x layers.

II. EXPERIMENTAL

Hydrogen amorphous silicon nitride films were grown by using a pulsed low frequency (LF) batch reactor direct-PECVD [6]. The SiN_x films were deposited on 4inch HEM multicristalline silicon. These wafers of area 10x10cm^2 were manufactured by CRTSE. The schematic diagram is shown in Fig. 1 which consists of a long radiantly heated horizontal cylindrical quartz tube containing 102 graphite plate electrodes. Using this electrode assembly, we were able to simultaneously deposit SiN_x for 100 wafers in a single run. All the mc-Si (and Cz-Si mono-cristalline) samples were first etched in NaOH to remove saw damage material 10 µm thick from each side of wafers and after that rinsed in HF (10%). All the chemical processes were completed by rinsing in deionized water and drying in N_2. The thickness and the refractive index of the SiNx films prepared by PECVD under different parameters were measured with an ELX 02C ellipsometer employing a He–Ne laser beam (wavelength of 632.8 nm), at an angle of 70°. The measurements were performed on CZ-silicon like-mirror polished wafers. The reflectance was measured using a Varian Cary spectrophotometer (UV-VIS-IR) equipped with an integrated sphere. Although minimizing the reflectivity is highly desirable. For reflectance measurement, the spectral aspect of incident sunlight has to be taken into account. The weighted average reflectance R_w between λ_1 and λ_2 is defined as [7]:

$$R_w = \int_{\lambda 1}^{\lambda 2} R(\lambda)\, \phi(\lambda)\, d\lambda \,/ \phi(\lambda) d\lambda \qquad (1)$$

Where $\phi(\lambda)$ is the spectral irradiance of sunlight, and $R(\lambda)$ is the reflectance of the solar cell.

In this work, the general parameters for deposition are substrate temperature 380°C, pressure 1700 mTorr through varying the deposition parameters, such as ratio NH_3/SiH_4, deposition time and power.

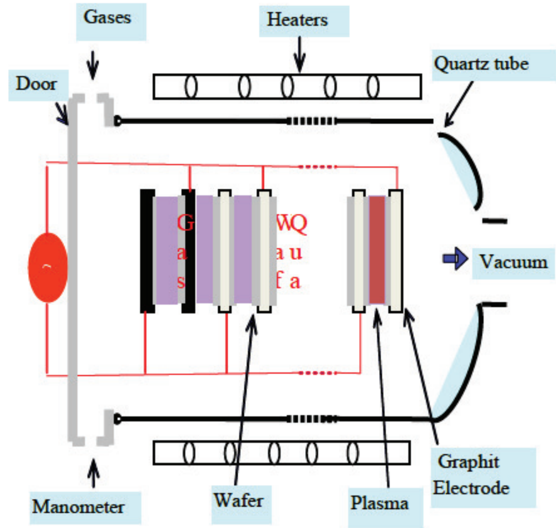

Figure 1. Schematic diagram of the PECVD system.

III. RESULTS AND DISCUSSION

The thickness and refractive indices of SiNx thin film deposited in different R=[NH_3/SiH_4] were determined by ellipsometry. Under the optimum antireflection condition: $d_{optim} = \lambda_{optim}/4n$ [8,9], the thickness of SiN_x film should be 75-80nm, refractive index should be 2.0. Through empirical knowledge, SiN_x takes on blue color. From this experience, ARC quality of deposited SiN_x thin film should be good.

In our study, the R is varied in the range of 2.4-33.7 while keeping the total flow rate (NH_3/SiH_4) constant. The temperature, power and pressure were set constant to 380°C, 3.5 kW and 1700 mTorr, respectively.

From the above Fig. 2 we can see that, as R increases from 2.4 to 33.7, refractive index of SiNx film decreases from 2.6 to 1.88 in the contradictory direction. Indeed, the decreases of refractive index with the increases of R means that they are a strong amount of nitrogen and they leads to a porous structure while higher refractive indices results a densified SiN_x films. The more percentage of silicon in the SiN_x thin film, the more density the SiN_x thin film [10].

At the part of relationship between R and X=N/Si, we use a model [11, 12] to analysis the ratio of N/Si in SiNx thin film, and then we make some comparison. The ratio of N/Si is a critical parameter, which indicate both optical and passivation quality of SiN_x [13]. According to the model, ratio N/Si in a specially selected parameter could be demonstrated as formula (2):

$$X = \frac{N}{Si} = \frac{4(3.3-n)}{3(n-0.5)} \qquad (2)$$

In formula (2), n is the refractive indices of the deposited SiN_x thin film.

In this case, as the R increases, we can see the ratio of N/Si in the deposited thin film is between 0.4 and 1.4, which indicates that the deposited film is Nitrogen-rich SiN_x ($x \approx 1.33$), and also we could adjust the refractivity of deposited SiN_x thin film to get the optimum antireflection quality through altering the ratio N/Si with a minimum interface state density (D_{it}). Furthermore, the minimum D_{it} is observed to decrease with the increase in N/Si, the concentration of both electron and hole traps are much lower for nitrogen-rich SiN_x. Because D_{it} is directly associates with the passivation of SiN_x film on emitter of solar cells.

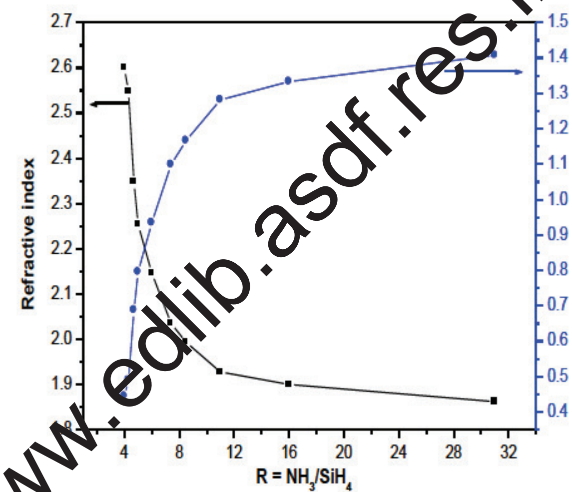

Figure 2. The relationship of R=NH_3/SiH_4 with SiN_x refractive index and X=N/Si.

The variation of deposition rate of the SiNx films according to the gas ratio R is shown in Fig. 3. The values of the deposited rate are scattered. This means that the deposition rate is independent of the gas flow ratio. However, it presents a maximum of 28.7 nm/min at R = 16. As the gas flow ratio increase the silane gas flow rate diminishes leading to the less deposition rate, then inducing the presence of more hydrogen radical and ions which are effective SiN_x etchants [14]. In work performed by A. El Amrani et.al [15], a regular variation of the deposition rate was found as the gas flow rate ratio increases with SiH_4 flow rate decrease and NH_3 flow rate kept constant. In the present work, the irregular behavior of the deposition rate is due to that the two gas flow rate of silane and ammonia vary simultaneously.

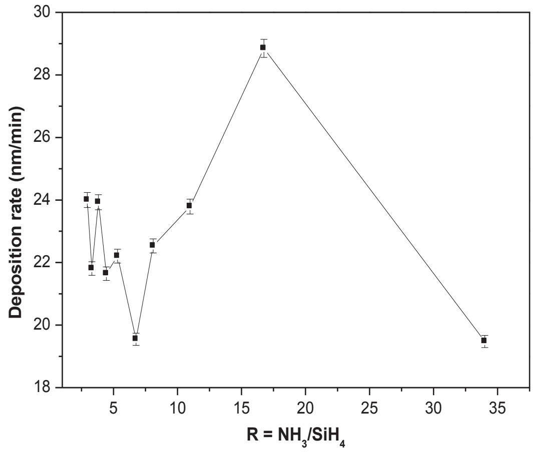

Figure 3. Variation of deposition rate with gas ratio R = [NH_3/SiH_4].

In the part of study the effect of power, the temperature, gas flow ratio and pressure were set constant to 380°C, R = 6 and 1700 mTorr, respectively. The LF power was varied within the range 3.5-5kW. Fig. 4, show the variation of the deposition rate and refractive index with the plasma power. The deposition rate strongly depends on the LF power in the range of 3.5-4.5 Kw. It is clear that the electrical power discharge provides energy to dissociate the gas precursors and induce chemical reaction. The increase of LF power speeds up the reactions and thus the deposition rate. The other variation presented in the Fig. 4 is the effect of power on the refractive index. This last as it has varied between 2.0 – 2.06 with the power. In the power range 3.5 – 4.5 kW, we observe a slight decrease on refractive index. This is probably due to that the NH_3 has higher dissociation energy than the SiH_4, so that the dissociated fraction of NH_3 compared to SiH_4 dissociation increases with increasing power leading to higher N bonding in SiN_x, thus as result a nitrogen-rich silicon nitride with lower refractive index.

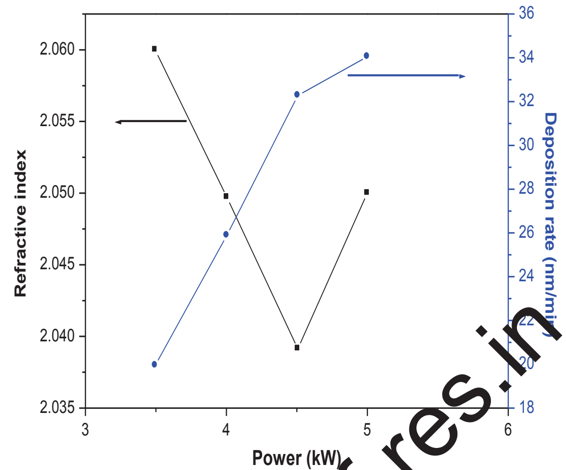

Figure 4. Variation of the deposition rate and the refractive index with the power.

Fig. 5 shows the variation of deposition rate and refractive index with the temperature deposition. The refractive index increases with the elevation of the temperature. From 1.78 at 50°C it reaches 2.04 at 380°C. The SiN_x film changes from N-rich to Si-rich. This indicated that the N/Si ratio decreases with the substrate temperature. The behavior which is contrary has been showed in Fig. 2, when the N/Si ratio increases with the R = [NH_3/SiH_4]. Indeed, high temperature leads to high energy electrons in the reaction chamber, which enhances the dissociation of the reactant gases. Otherwise, the increase of deposition temperature promotes the release of hydrogen [16]. As reported and explained by B. Kim et al. [17] and K. Byungwhan et al. [18], it is generally observed that increasing the temperature decreases the deposition rate. At other hand, as shown in Fig. 5, the deposition rate decreases from 37nm/min to 31nm/min at 200°C, and has a slight increase with further temperature beyond 200°C. In addition, an accurate temperature control is not very important in our PECVD process because the deposition rate decreases by less than 5% for every 50°C increase in temperature.

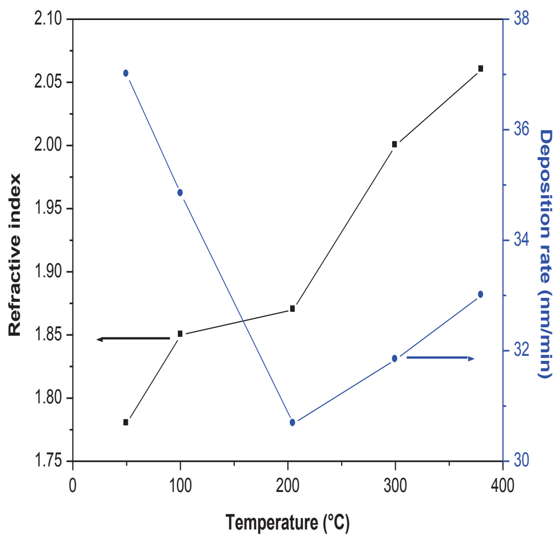

Figure 5. Effect of deposition temperature on the refractive index and deposition rate.

For optical properties, we studied the variation of reflectance which is shown in Fig. 6. This last gives a typical reflectance spectrum for SiN_x thin films with different refractive index in the range of usable portion of the solar spectrum AM1.5G (400-1100nm). The average weighted reflectance presented in figure inset show that the R_w increases with the refractive indices. Note that the optimum R_w is given with the value of refractive index equal to 2 with $NH_3/SiH_4 = 6$ and 4.5kW of the power.

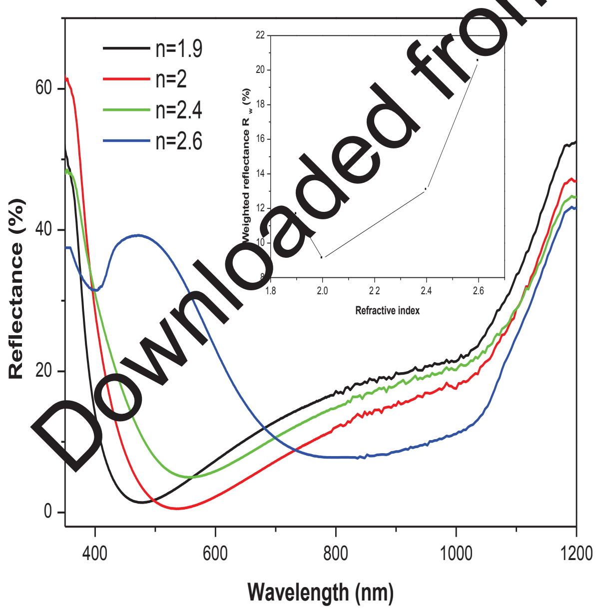

Figure 6. Reflection as function refractive index. Figure inset shows the weighted reflectance vs. refractive index.

IV. CONCLUSION

Silicon nitride films were deposited by a PECVD process using a mixture of ammonia-silane as reactant-gas. NH3/SiH4, power and temperature were investigated with the aim of determining the SiNx film optimum optical properties for photovoltaic application. The gas flow ratio R is a major process parameter. It was found that the refractive index varies (between 1.85 to 2.6) with R, thus the optimum weighted reflectance re given with the optimum R = 6. The power is another parameter process. The power is not a sensible process parameter for the refractive index contrary to the deposition rate witch increase with the power increase. The deposition temperature is also a critical process parameter. Its variation leads to a significant change in the refractive index and a moderate change in the deposition rate. Finally, the important and optimum parameters that can be used to deposit SiN_x films with PECVD process of CRTSE are: R = 6, 4.5kW of power, temperature = 380°C and pressure = 1700mTorr.

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