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Annealing optimization of silicon nitride film for solar cell application

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Abstract

Hydrogenated films of silicon nitride (SiN*x*:H) is commonly used as an antireflection coating as well as passivation layer in crystalline silicon solar cell. SiN*x*:H films deposited at different conditions in Plasma Enhanced Chemical Vapor Deposition (PECVD) reactor were investigated by varying annealing condition in infrared (IR) heated belt furnace to find the optimized condition for the application in silicon solar cells. By varying the gases ratio ($R = NH_3/SiH_4 + NH_3$) during deposition, the SiN*x*:H films of refractive indices 1.85–2.45 were obtained. Despite the poor deposition rate, the silicon wafer with SiN*x*:H film deposited at 450 °C showed the best effective minority carrier lifetime. The film deposited with the gases ratio of 0.57 shows the best peak of carrier lifetime at the annealing temperature of 800 °C. The single crystalline silicon solar cells fabricated in conventional industrial production line applying the optimized film deposition and annealing conditions on large area substrates (125 mm × 125 mm) were found to have the conversion efficiencies as high as 17.05 %. Low cost and high efficiency single crystalline silicon solar cells fabrication sequence employed in this study has also been reported in this paper.

Keywords: Silicon nitride; Annealing; Solar cell; Silicon

1. Introduction

Hydrogenated silicon nitride films (SiN*x*:H) prepared by PECVD for low-temperature surface passivation in silicon solar cells is a topic of increasing importance. Silicon nitride films have been widely used in the semiconductor device industry because they are mechanically strong, have good dielectric properties, and provide an excellent barrier against moisture corrosion and mobile ions [1–3]. These films have proven to be capable of combining an outstanding surface passivation quality with excellent anti-reflection properties [4,5]. The higher refractive index, which can be easily varied between 1.9 and 2.3, makes SiN*x*:H a much more efficient AR-coating than a thermal oxide, which has a refractive index between 1.4 and 1.5 only [6]. Large amount of atomic hydrogen is produced in the plasma during the deposition of SiN*x*:H, which is believed to provide additional bulk defect passivation in silicon material and consequently improve the efficiency of solar cells [7]. Not only the plasma, but also the nitride film itself contains high concentration of hydrogen, up to 20 at.% [8]. Therefore, the SiN*x*:H film also acts as a source of hydrogen in subsequent post-deposition anneals and provides additional bulk defect passivation [9,10]. It is well known that the cell fabrication process involves high thermal treatment, which in turn changes the properties of SiN*x*:H. In the present work, firstly, we have varied the silane to ammonia ratio (*R*) in the plasma and observed the variation of electrical, optical and chemical properties of the SiN*x*:H films thus deposited. This paper mainly investigates the effects of rapid thermal annealing (RTA) on the surface passivation as well as antireflection properties of the SiN*x* films deposited in various conditions. The investigation covers the measurements such as carrier lifetime, reflectance, chemical composition, refractive index, and interface trap density and their analysis relating them to the final output of the solar cell thus fabricated.

2. Experimental

The PECVD reactor with a plasma frequency of 13.56 MHz used for the SiN*x*:H film deposition for this study consists of a long horizontal cylindrical quartz tube and vertically placed graphite electrodes inside it that is radiantly heated. Five rectangular graphite plates each of dimensions 760 mm × 162 mm with the spacing of 15 mm between two consecutive plates serve as electrodes to establish the plasma and also act as holders for 40 wafers.

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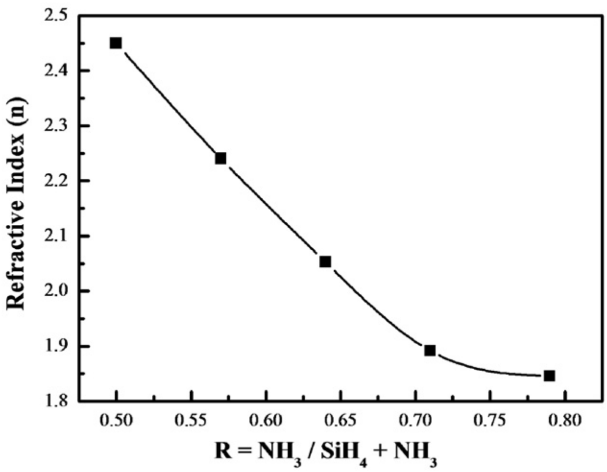

Fig. 1. Variation of refractive index as the function of gas ratio R (R=NH_3/SiH_4+NH_3).

The electrode configuration was designed to provide a uniform plasma environment for each wafer and to ensure the uniformity in the properties of the SiNx:H deposited on each wafer. The vertically oriented graphite electrodes are parallel to one another with alternating plates serving as power and ground electrodes for the RF power supply. The film deposition temperature of 450 °C was used as the optimized parameter for this study. The CZ silicon wafers of resistivity 10 Ω cm were cut into the pieces of size 2 cm × 2 cm to use as a starting material. Experimental conditions were set up only after a preliminary study so that a systematic variation of the gases ratio (R) could be done. The thickness and refractive index of the SiNx:H films grown on silicon substrate by PECVD under different gases ratio and annealed at various temperatures were measured with Spectroscopic Ellipsometer. The effective minority carrier lifetimes (τ_{eff}) of the silicon substrate coated with the films were measured with microwave photo conductance decay (MWPCD) technique. The variation of hydrogen bonding with the gases ratio (R) and annealing temperature were studied with Fourier Transform Infrared (FTIR) spectroscopy (Bruker IFS66V/S) and also the hydrogen content was calculated from this measurement. Electrical characteristics of SiNx:H films were obtained by measuring capacitance–voltage (C–V) curves at high frequency (1 MHz) of Metal-Insulator-Semiconductor (MIS) structures.

For the solar cell fabrication, we first started with the bare Cz–Si wafers of size 125 mm × 125 mm (pseudo square). Surface of the wafer was first cleaned and saw damage marks were removed by alkali etching, which was followed by alkali texturing. The wafers were doped with a conventional thermal diffusion process using liquid $POCl_3$ as the dopant source. The sheet resistance of the doped wafers was maintained in the range of 40–45 Ω/□. The doped wafers were then oxide passivated and edge isolated after which the films of SiNx:H with refractive index ~2.24 and thickness ~720 Å were deposited by PECVD technique. The deposited films of SiNx: H acted as antireflection and passivation layer in the fabricated solar cells. Screen printing metallization technique was used for high throughput metal contact formation using aluminum (Al) paste for the back surface and silver (Ag) paste on the front surface, followed by co-firing in rapid thermal processing (RTP) unit. The Illuminated Current–Voltage characteristics and the performance parameters of the solar cell fabricated by using the SiNx:H film of optimized properties were determined under one sun global solar spectrum of Air Mass (AM) 1.5 at 25 °C.

3. Results and discussion

As can be seen from Fig. 1, hydrogenated silicon nitride (SiNx:H) films deposited as the function of gases ratio R have the refractive indices varying from 2.45 to 1.85 for which the deposition rate varied from 142 Å/min to 98 Å/min. This is due to the probability of dissociation of NH_3 being superior to SiH_4 in the gases ratio R. Therefore, the nitrogen-rich SiNx:H films had lower refractive index due to increased N–H bond concentration

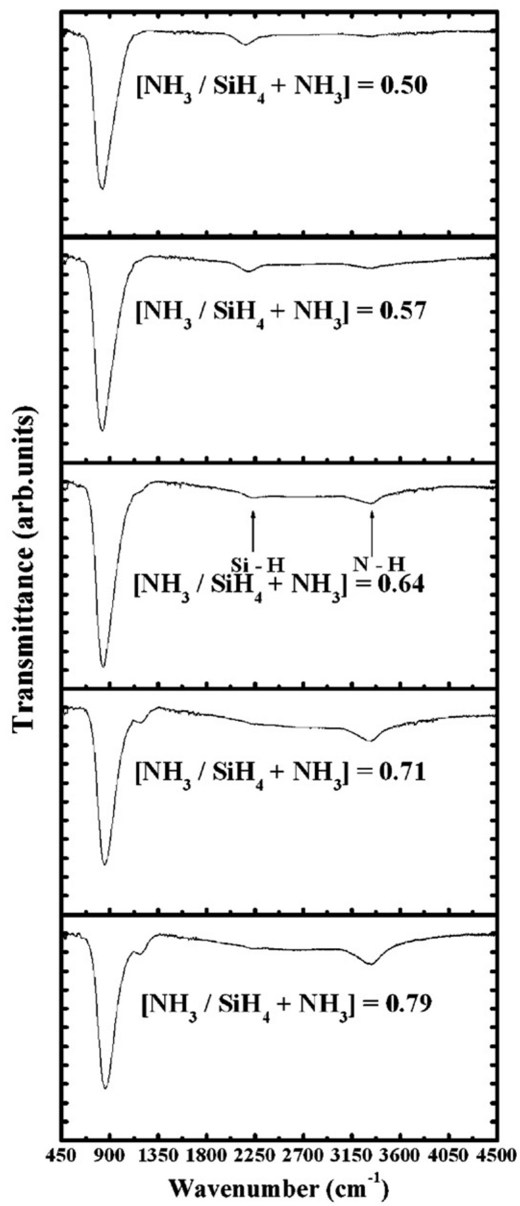

Fig. 2. Variation in the concentration of Si–H and N–H bonds concentration with the gases ratio R (R=NH_3/SiH_4+NH_3) seen in the form of FT-IR peaks.

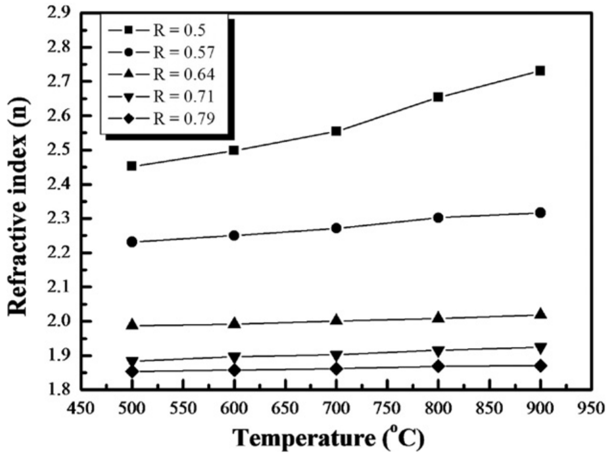

Fig. 3. Effect of annealing temperature on the refractive index of the SiN*x*:H films.

and higher deposition rate due to decreased Si–H bond concentration. In silicon nitride film, it is well known that the main vibrational mode in the FTIR peak appears at around 850 cm^{-1} for Si–N and at 1200 cm^{-1} in bending mode, at 3360–3460 in stretching modes for N–H bonds; 650 cm^{-1} (wagging mode) and 2100–2150 cm^{-1} (stretching mode) for Si–H bonds, respectively [11]. In the present work, different absorption bands associated to N–H bonds at 3340 and 1170 cm^{-1}, and those caused by the Si–H bonds at 2170 and 630 cm^{-1}, together with the fundamental bands at 850 and 465 cm^{-1} associated to the Si–N bonds are observed. With the help of Beer's Law [12] and data published by Lanford and Rand [13], we could determine the relative concentration of these bonds in the films as a function of the gas ratio R in the PECVD chamber during the film deposition. The hydrogen content in the SiN*x*:H film was evaluated by integrating the peak in the FTIR spectrum of Si–H and N–H bonds, respectively. The FTIR peaks in the Fig. 2 show the variation of the concentration of Si–H and N–H bonds as a function of the gases ratio, R. To evaluate the amount of Si–H and N–H bonds, we took the absorption bands at 2170 and 3340 cm^{-1} respectively. It is observed from the figure that the Si–H bond

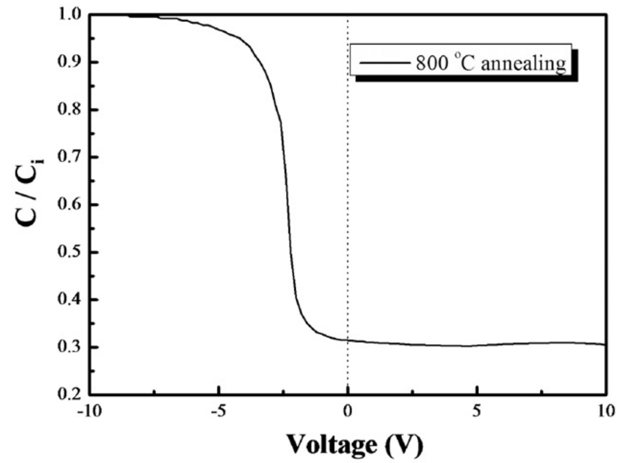

Fig. 5. High frequency (1 MHz) C–V characteristics of MIS device formed by using PECVED SiN*x*:H films annealed at 800 °C.

concentration decreases as the gas ratio R increases and it is reverse in the case of N–H bond concentration. Hydrogen content in the form of Si–H bond is found to decrease from 1.4×10^{22} cm^{-3} to 2.92×10^{21} cm^{-3} and that in the form of N–H bond increases from 4.84×10^{21} cm^{-3} to 4.07×10^{22} cm^{-3} as the gases ratio (*R*) increases from 0.5 to 0.79.

For the optimized condition of the SiN*x*:H film deposition, the effect of change in gas ratio (*R*) from 0.5 to 0.79 and annealing temperature from 500 to 900 °C for the applications in Silicon Solar cells were also investigated. SiN*x*:H films with as-deposited refractive index values of 2.45, 2.23, 1.98, 1.88 and 1.85 were grown by varying the gases ratio (*R*). Rapid thermal annealing using incoherent light from the tungsten halogen lamps has been reported to be more effective than furnace annealing [14]. Fig. 3 shows the effect of annealing temperature on the refractive index of the film. With the increase in temperature, the SiN*x*:H films with high as-deposited refractive index show more increase in refractive index than those with low refractive indices. The variation of refractive index and film thickness by increasing the annealing temperature is caused by the densification of the thin film [15].

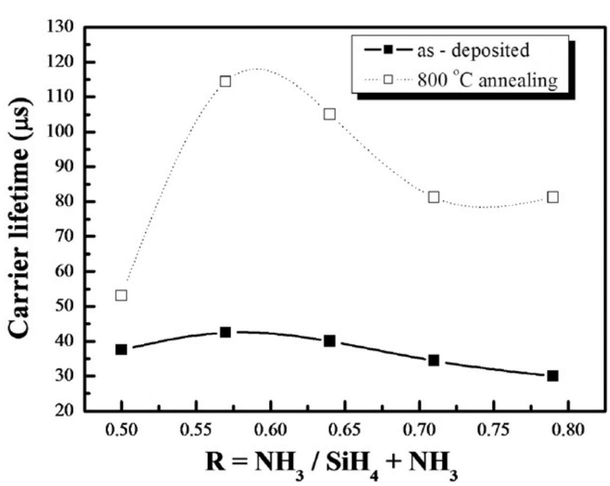

Fig. 4. Effective carrier lifetime of the samples with as-deposited SiN*x*:H films as well as that with SiN*x*:H films annealed at 800 °C with different gases ratio *R*.

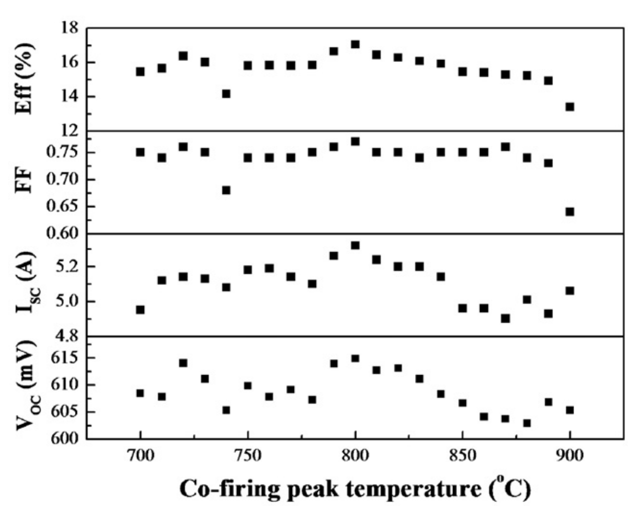

Fig. 6. Comparison of performance parameters of cells by varying the co-firing peak temperature.

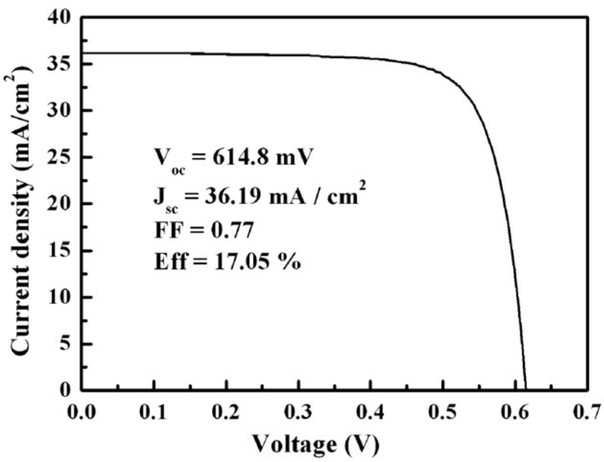

Fig. 7. Illuminated Current–Voltage characteristics of the single crystalline silicon solar cell fabricated on large area (125 mm × 125 mm) pseudo squared substrate applying the SiN*x*:H film of the best deposition and annealing condition.

Fig. 4 shows the τ_{eff} of the samples with as-deposited SiN*x*:H films along with the film annealed at 800 °C with different gases ratio *R*. All the samples with SiN*x*:H films deposited on their surfaces at various gases ratio (*R*) during PECVD were found to have the peak τ_{eff} at 800 °C but the value sharply decreased above 800 °C. The reduction in the τ_{eff} of the samples annealed above 800 °C might have taken place due to decrease in the retention of hydrogen at defect sites in Si at high temperature. The samples with SiN*x*:H film deposited with the gases ratio (*R*) of ~0.57 are found to have highest value of effective minority carrier lifetime of 114 µs. It was also found that the silicon-rich SiN*x*:H films with $R \leq 0.5$ shows relatively lower carrier lifetime after annealing as shown in Fig. 4. The film deposited keeping $R = 0.79$ shows the least carrier lifetime. It means that the extreme cases of silicon or nitrogen rich films are not suitable to generate high carrier lifetime of silicon substrate. The comparative study of the minority carrier effective lifetime clearly indicates that there is an optimized condition of the gases ratio and annealing temperature to be maintained during SiN*x*:H deposition and annealing during solar cell fabrication, which are found to be 0.57 and 800 °C, respectively in our study.

The high frequency (1MHz) C–V characteristics of MIS structure made using SiN*x*:H films deposited with the gases ratio 0.57 and annealing temperature 800 °C is shown in Fig. 5. The Flatband voltage (V_{fb}) and Surface state density (N_{ss}) calculated from C–V characteristics were −2.57 V and 4.96×10^{11}/cm^2, respectively. The midgap D_{it} in the Si–SiN*x*:H interface was as low as 1.67×10^{11} cm^{-2} eV^{-1}. This indicates the high potentiality of the film of SiN*x*:H for the silicon surface passivation when applied for the solar cell fabrication.

Based on the extensive study carried out, it is identified that the SiN*x*:H film deposited at 450 °C keeping gases ratio $R = 0.57$, which has a refractive index of 2.24, and annealed at 800 °C is suitable for the solar cell application. The comparison of the performance parameters of the cells fabricated with SiN*x*:H films deposited in the optimized condition and co-fired at different peak temperatures are shown in Fig. 6. Almost all the parameters have their maximum values at ~800 °C peak temperature of co-firing in a belt furnace. This is the temperature around which the maximum carrier lifetime was recorded after annealing the silicon nitride film as shown in Fig. 4. The current-voltage characteristic curve along with the performance parameters of the best single crystalline silicon solar cell fabricated with the SiN*x*:H films deposited and co-fired at the optimized conditions are shown in Fig. 7. It shows the values of conversion efficiency (Eff), Fill Factor (FF), short circuit current density (Jsc) and open circuit voltage (Voc) of the cell as 17.05 %, 0.77, 36.19 mA/cm^2, and 0.614 V, respectively. Such performance parameters of the cell fabricated in a conventional industrial production line indicate the good surface as well as bulk passivation achieved with the optimized SiN*x*:H deposition and annealing conditions.

4. Conclusion

A comprehensive study on the SiN*x*:H film deposition and annealing conditions was carried out to optimize the film for the application in crystalline silicon solar cells. The silicon substrate coated with SiN*x*:H film, deposited by keeping gases ratio ($R = NH_3/SiH_4 + NH_3$) 0.57 and annealed at 800 °C was found to have effective minority carrier lifetime as high as 114 µs. Using the optimized SiN*x*:H film deposition and annealing condition, single crystalline silicon solar cells of conversion efficiency as high as high as 17.05 % was fabricated in a conventional industrial production line for which the co-firing was carried out at the peak temperature of 800 °C. The peak co-firing temperature was found to be the same as the annealing temperature optimized for very effective minority carrier lifetime and very low D_{it}.

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