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Effect of rapid thermal annealing on the properties of PECVD SiN_x thin films

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Abstract

Silicon nitride (SiN_x:H) thin films were grown on silicon by the plasma-enhanced chemical vapor deposition (PECVD) method at low temperature in order to study their optical, electrical properties and correlate these properties to the chemical composition of the layers, so that films with desired properties may be achieved for silicon solar cells. By varying the silane (SiH_4) to ammonia (NH_3) ratio in the plasma gas we have been able to modify the index of refraction (from 1.9 to 2.3) and also the silicon surface state passivation properties of the films. Our results indicate that the mid-gap surface state density in silicon can be reduced down to $1.1 \times 10^{10}\,cm^{-2}\,eV^{-1}$ for the SiN_x:H layer deposited under optimized silane to ammonia ratio. Also, an extensive study has been carried out on the effect of rapid thermal annealing (RTA) on the carrier lifetime, reflectance, chemical composition, refractive index and interface states which decides the final output of the solar cell.

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Keywords: SiN; RTA; PECVD; Solar cell; Optical properties

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1. Introduction

In recent years, the low-temperature surface passivation of crystalline silicon solar cells by means of PECVD silicon nitride films has attracted an increasing attention of the photovoltaic (PV) community. These films have proven to be capable of combining an outstanding surface passivation quality with excellent anti-reflection properties; in addition to these properties this is cost effective due to the gain of cell efficiency [1–5]. However, a great deal of research work has to be devoted in order to understand the real passivation effect; in particular, the effect of hydrogen contained in the SiN_x:H films on both the silicon surface and bulk has to be determined. Because of a lack of information on this question, many misleading interpretations and false conclusions are drawn by many researchers [6]. For example, sometimes it has been concluded that SiN_x:H requires an additional thin layer of SiO_2 in order to achieve similar low surface recombination velocities as those for thick thermal SiO_2 layers on silicon [6]. On typical p-type silicon solar cell substrates with the (1 0 0) crystal orientation and resistivity of 8–10 Ω cm, it has been shown that, provided the ion bombardment of the silicon surface during the plasma deposition is avoided, the surface passivation quality of very silicon-rich SiN films is superior to that of state-of-the-art high-temperature silicon dioxide [7–10]. However, the fact that these SiN films are extremely silicon-rich brings about several problems: (i) the films show a considerable absorption in the UV range, leading to a reduction of the short-circuit current, (ii) the films are very poor insulators and cannot be used at the point-contacted rears of solar cells, and (iii) etching rates of the films are extremely low. These problems strongly limit the applicability of silicon-rich SiN films, whereas stoichiometric SiN_x films do not absorb UV photons with wavelengths above 320 nm, act as perfect insulators and easily etchable.

In the present work, we have varied the SiH_4 to NH_3 ratio in the plasma and studied the variation of electrical, optical and chemical properties of the SiN_x:H layers obtained. It is well known that, the solar cell fabrication process involves high thermal treatment, which in turn changes the SiN_x properties. This paper mainly investigates the SiN_x deposition and the effect of rapid thermal annealing on the surface passivation and also on the anti-reflection properties. A thorough investigation has been carried out on the effect of rapid thermal processing on the carrier lifetime, reflectance, chemical composition, refractive index, interface states which are the deciding fac-

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tors of the final output and ultimately the efficiency of the solar cells.

2. Experimental

In the present work, SiN_x deposition was performed using a home made horizontal PECVD reactor system consisting of a long horizontal cylindrical quartz tube that was radiantly heated. Special and long rectangular graphite plates served as both the electrodes to establish the plasma and holders of the wafers. The electrode configuration was designed to provide a uniform plasma environment for each wafer and to ensure the film uniformity. These horizontally oriented graphite electrodes were stacked parallel to one another, side by side, with alternating plates serving as power and ground electrodes for the RF power supply. The plasma was formed in the space between each pair of plates. The electrode designed is capable of holding 20 wafers of maximum size 125 mm × 125 mm in a single deposition. The parameters which are kept constant during the SiN_x:H depositions are, the chamber pressure 0.6 Torr, deposition temperature 300 °C, power 0.08 W cm^{-2} and a plasma frequency of 13.56 MHz. We established these parameters after a preliminary study, so that we could make a systematic variation of the silane to ammonia (SiH_4/NH_3) ratio in the chamber.

The thickness and refractive index of the SiN films prepared by PECVD under different gas flow ratios was characterized by spectroscopic ellipsometry (SE). To study the electrical properties, films were deposited on p-type Si with (1 0 0) orientation with 10 Ω cm resistivity. Aluminum top electrodes (of area 2.8×10^{-3} cm^2) were deposited on silicon nitride using a thermal evaporation method and also aluminum was deposited on the back of silicon substrate to provide ohmic contact for MIS configuration. The high frequency *C–V* measurements were carried out using a HP4912 impedance analyzer.

3. Results and discussions

The main PECVD parameters varied in this study is the gas flow and the silane/ammonia gas flow ratio $[SiH_4]/[NH_3]$. The NH_3 flow was fixed at 60 sccm, the pressure at 0.6 Torr and the plasma power at 200 W during this experiment. The important SiN_x deposition parameter is indeed the ratio of the gas flows and not the actual gas flows. In Figs. 1 and 2, we show the variation of refractive index (*n*) and deposition rate as a function of the NH_3/SiH_4 ratio respectively. Five different gas ratios (0.8, 0.89, 1, 1.33, 2 and 3.14) of NH_3/SiH_4 have been studied in the present study. From Fig. 1 we can clearly observe the decrease in the refractive index from 2.3 to 1.8 with the increase in the NH_3/SiH_4 ratio from 0.8 to 3.14. From Fig. 2, we can observe a fall in deposition rate of the SiN_x films from 4.26 Å s^{-1} to 2.33 Å s^{-1} with the increase in the NH_3/SiH_4 from 0.8 to 3.14. The low refractive index (1.8) and lower deposition rate (2.33 Å s^{-1}) was observed for sampled where nitrogen is rich, but as the silane quantity increases the refractive index and deposition rate was found to increase, because the samples are Si-rich.

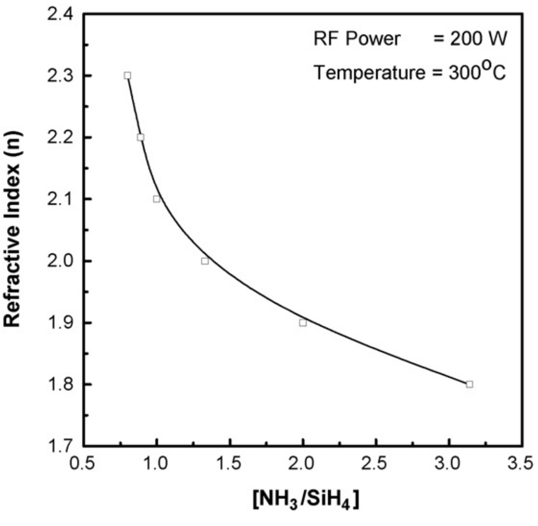

Fig. 1. Dependence of refractive index on the NH_3/SiH_4 ratio.

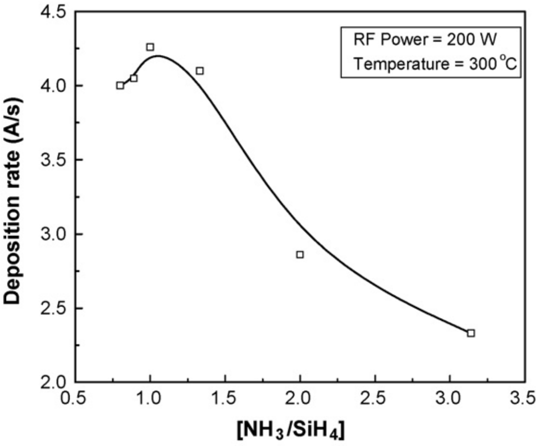

Fig. 2. Variation of deposition rate as a function of NH_3/SiH_4 ratio.

The FT-IR spectra (not shown) exhibited typical peaks of SiN:H thin films grown with our PECVD system. In silicon nitride film it is well known that the main vibrational mode will appear at around 850 cm^{-1} for Si–N and 1200 cm^{-1} (bending mode), 3360–3460 cm^{-1} stretching modes for N–H bonds, 650 cm^{-1} (wagging mode) and 2100–2150 cm^{-1} (stretching mode) for Si–H bonds, respectively [11]. Here in the current work, we noted some more absorption bands associated to N–H bonds at 3340 cm^{-1} and 1170 cm^{-1}, and those caused by the Si–H bonds at 2170 cm^{-1} and 630 cm^{-1}, together with the fundamental bands at 850 cm^{-1} and 465 cm^{-1} associated to the SiN bonds. With the help of Beer's Law and data published by Lanford and Rand [12] we could determine the relative concentration of these bonds in the films as a function of the NH_3/SiH_4 ratio in the PECVD chamber. Here in this work, with the increase in the gas ratio, the Si–H bond concentration was found to decrease, while the N–H bond concentration found to increase, which agrees well with the details observed for SiN_x films deposited using RPCVD [13].

In order to have a typical RTA firing condition for the bulk and surface passivation, we treated the samples under different firing conditions (600 °C, 700 °C, 800 °C and 900 °C). At first, we studied the variation of refractive index of the samples at different firing conditions and the typical results observed are presented in Fig. 3. No significant change in the value of refractive index was observed for the samples fired at different temperatures. Fig. 4 shows the dependence of carrier lifetime on the RTA firing temperature, it can be seen from the figure that the carrier lifetime of all the films of different refractive index (ranging from 1.9 to 2.3) was found to show a maximum carrier lifetime at around 600 °C. For instance we can see that the carrier lifetime of the sample with refractive index 2.3 showed

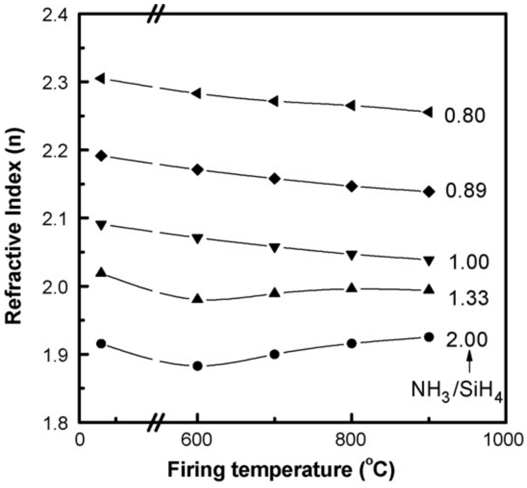

Fig. 3. Refractive index *vs.* RTA firing temperature for the films prepared at different NH_3/SiH_4 ratios.

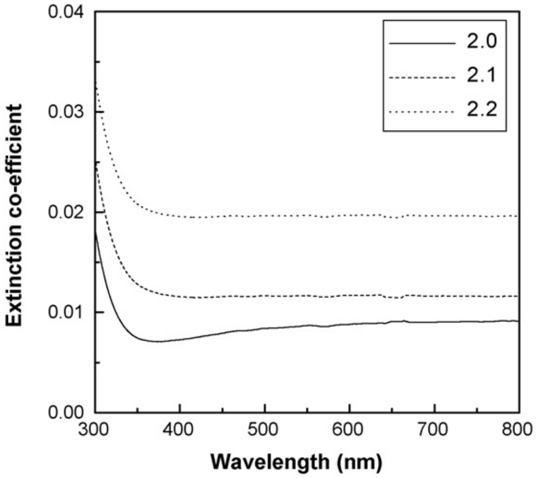

Fig. 5. Extinction coefficient *vs.* wavelength for different refractive index.

maximum carrier lifetime of 21 μs when it was fired at 600 °C. A drastic decrease in carrier lifetime was observed for the sample fired at temperatures above 600 °C that is; a decrease of carrier lifetime from 21 μs to 8 μs was observed for the sample fired at 600 °C and 700 °C, respectively. From the reflectance measurements, the average reflectance of the samples were evaluated and the minimum reflectance was observed for the samples fired at 600 °C and the reflectance was found to increase with the further increase of RTA temperature. Similar trend was observed for samples with different refractive index. Reflectance of the film was found to decrease with the increase in refractive index which is resulting from the richness of Si in the deposited SiN_x film.

Ideally the refractive index is around 1.9 for the Air/SiN_x/Si structure and around 2.3 under the encapsulated condition. Since all cells are finally put into a module, the value of 2.3 is the one that is most important. However, this observation makes abstraction from another feature, light absorption. When the extinction coefficient of the deposited layer rises more light will be absorbed in the layer itself. These photons will therefore not contribute to the cell current. Characterizations based on SE have indicated that this effect becomes especially important for short-wavelength light. This effect is directly influenced by the NH_3/SiH_4 ratio during deposition. With more silicon incorporation into the layers, the extinction coefficient (as well as the absorption losses) and the refractive index are found to increase. At higher refractive indices, the reflection losses will be lower but this will be compensated by the absorption loss (higher extinction coefficient) in the layer itself. This is clearly predicted in Fig. 5 where the variation of extinction coefficient for different gas ratio is given. Higher extinction coefficient is observed for higher refractive index (i.e. silicon-rich film), hence it is favorable to limit the refractive index to values around 2.0.

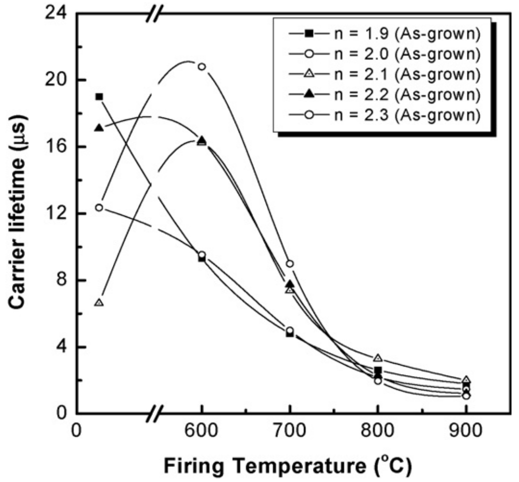

Fig. 4. Variation of carrier lifetime with RTA firing temperature at different refractive indexes.

The capacitance–voltage (*C*–*V*) characteristics of the samples in Al/SiN_x:H/p-type Si configuration is given in Fig. 6. The figure shows the accumulation, depletion and inversion regions of MIS capacitors. The *C*–*V* characteristics of the samples exhibit considerable change in terms of flat band voltage. The dielectric constant of the films has been calculated in the accumulation region. The forward and reverse trace of the *C*–*V* curve showed anti-clockwise hysterisis, which indicates the hole

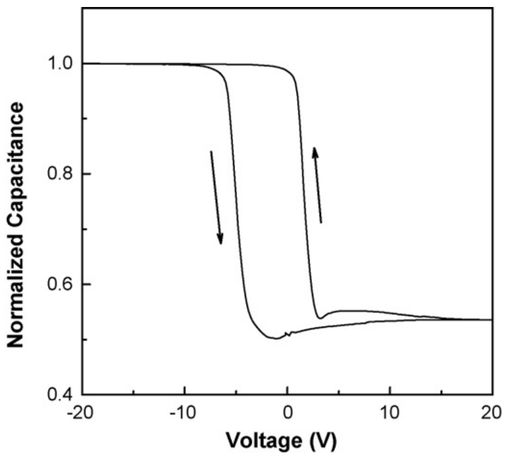

Fig. 6. *C*–*V* plot of the Al/SiN_x/Si sandwich structure.

Table 1
Variation of D_{it} with firing temperature (for samples with $n = 2$)

Silicon nitride ($t = 70$ nm)	Refractive index	D_{it} ($cm^2 eV^{-1}$)
As-deposited	2.0	8.0×10^{11}
RTP fired at 600 °C		1.4×10^{11}
RTP fired at 700 °C		5.0×10^{10}
RTP fired at 800 °C		1.1×10^{10}

Table 2
D_{it} values of the samples fired at the optimized temperature of 600 °C

Silicon nitride refractive index	Temperature	D_{it} ($cm^2 eV^{-1}$)
1.9	600 °C	8.16×10^{10}
2.0		1.40×10^{11}
2.1		3.36×10^{11}
2.2		5.00×10^{11}
2.3		8.60×10^{11}

injection into the silicon nitride film [14,15] and can also be associated with silicon dangling bonds (Si–N_3) [16]. The interface state density has been calculated using Terman's analysis [17] from the high frequency C–V measurements. The flat band offset voltage V_{fb} shows a shift towards the negative value which indicates that there are positive fixed-charges present [18] at the SiN_x/Si interface. The other noticeable feature is that the interface state density (D_{it}) decreases as the firing temperature increased as shown in Table 1. The interface state density D_{it} is related to structural defects at insulator/semiconductor surface, the value of D_{it} is expected to be higher for silicon-rich films [19]. Therefore the films having more nitrogen content will show less interface state density. The interface trap density of the films of various refractive indexes after fired at the optimized firing condition of 600 °C is shown in Table 2. It is well known that the interface trap density estimated from Terman's analysis is always underestimated, the interface trap minimum values given in Tables 1 and 2, may not be exactly true, but the values obtained clearly shows the degree of Si surface passivation obtained in different films prepared at different conditions.

A thermal treatment after the deposition of silicon nitride can release hydrogen from the Si–H and N–H bonds present in the nitride layer into the cell, passivating the silicon surface and the bulk. Based on the extensive study carried out in the above section it was identified that the SiN_x with a refractive index 2 and fired in RTP at 600 °C was found to give the best results in all aspects, these results can be utilized for the fabrication of high efficiency Si solar cells.

4. Conclusions

SiN_x:H films have been deposited using silane/ammonia mixture in a PECVD system. High quality silicon nitride is obtained with a RF power of 200 W with the substrates maintained at a temperature of 300 °C. Variation of refractive index and deposition rate were studied as a function of ammonia and silane gas ratio. With this process we were able to fix the refractive index between 1.8 and 2.3. The low refractive index and lower deposition rate was observed for nitrogen-rich samples and a reverse case was observed for Si-rich films. At higher refractive indices, the reflection losses will be lower but this will be over compensated by the absorption loss in the layer itself. For this reason, it is favorable to limit the refractive index to values around 2.0. RTA firing optimization is also carried out and it is found that, typical firing temperature of 600 °C yield high carrier lifetime, low reflectance for all the samples of different refractive index. The application of this typical silicon nitride layer along with the optimized firing temperature might be very useful for the fabrication of high efficiency Si solar cells.

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