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A Study on High Frequency-Plasma Enhanced Chemical Vapor Deposition Silicon Nitride Films for Crystalline Silicon Solar Cells

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SiNx:H films have been widely used for anti-reflection coatings and passivation for crystalline silicon solar cells. In this study, SiNx:H films were deposited using high frequency (13.56 MHz) direct plasma enhanced chemical vapor deposition, and the optical and passivation properties were investigated. The radio frequency power, the spacing between the showerhead and wafer, the NH_3/SiH_4 ratio, the total gas flow, and the N_2 gas flow were changed over certain ranges for the film deposition. The thickness uniformity, the refractive index, and the minority carrier lifetime were then measured in order to study the properties of the film. The optimal deposition conditions for application to crystalline Si solar cells are determined from the results of this study.

Keywords: High frequency-plasma enhanced chemical vapor deposition, Silicon nitride, Refractive index, Thickness uniformity, Minority carrier lifetime

1. INTRODUCTION

The solar cells industry has been developing quickly and steadily, with a strong momentum in the entire photovoltaic market. There are different methods used to achieve high efficiency solar cells; anti-reflection coating technology is one of them.

Plasma enhanced chemical vapor deposition (PECVD) SiNx:H films which act as anti-reflection coatings have recently been widely used in the industrial fabrication of crystalline silicon solar cells. The SiNx:H films not only reduce optical losses but also provide a reasonable degree of surface passivation [1]. Regarding the optical properties, the refractive index is often chosen to be about 2.0 [2] and the thickness varies from 70~80 nm. These films passivate the surface dangling bonds. During firing, a part of the hydrogen in the SiNx:H films is released to the air and the other part diffuses into the SiNx:H/Si interface and combines with the defects, such as the dangling bonds, so that the defects become inactive.

There are two different PECVD methods: direct PECVD and remote PECVD. In direct PECVD reactors, all of the processing gases are excited by an electromagnetic field; the samples are located within the plasma. The electromagnetic field has a frequency of either 13.56 MHz ('high frequency') or in the 10~500 KHz range ('low frequency'). In remote PECVD reactors, the excitation of the plasma is spatially separated from the samples and one type of these different plasma excitations, such as microwaves, hollow cathode, arc jet, etc. is used [1].

There are not many studies regarding high frequency direct PECVD (HF-PECVD) SiNx:H films. Regarding the use of different PECVD systems, there has been no consensus on deposition conditions so far. Also In addition, different parameters play different roles in the PECVD processes [3].

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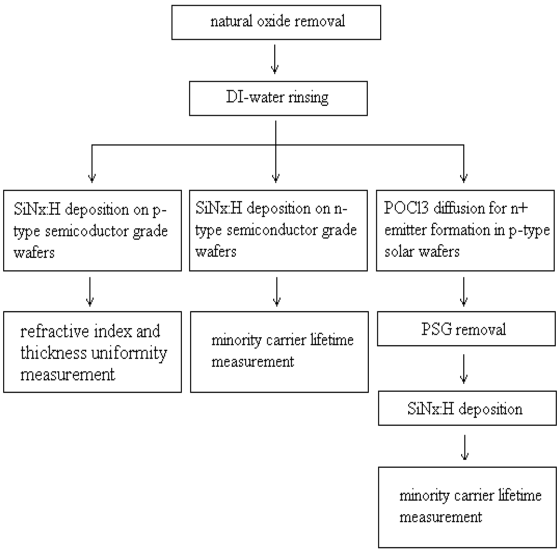

Fig. 1. The process sequences used in this study. PSG: phosphorus glass layer.

In this study SiNx:H films were deposited by HF-PECVD, using NH_3 and SiH_4 as the reaction gases in the N_2 ambient gas. In order to obtain the optimal deposition conditions, some parameters need to be taken into account, such as deposition temperature, pressure, radio frequency (RF) power, the spacing between the showerhead and wafer, the NH_3/SiH_4 ratio, total reaction gas flow, and N_2 gas flow. In this study, the deposition process was fixed at 400°C and 1 Torr, which has been discussed in former works [3]. The remaining parameters were varied over certain ranges. The optical and passivation properties of the films for crystalline solar cells were evaluated by investigating the refractive index, thickness uniformity and minority carrier lifetime.

2. EXPERIMENTS

The basic process sequences are shown in Fig. 1. The experiments consisted of two groups for the study of the optical properties and the passivation properties, respectively. For both groups, the deposition temperature was fixed at 400°C and the pressure was fixed at 1 Torr. Before deposition, all of the wafers were treated with an HF solution to remove the natural oxides and rinsed using deionized (DI)-water. A high frequency PECVD system (P-5000; Applied Materials, Santa Clara, CA, USA) was then used for the deposition process.

In the first group, for the optical properties study, 4 inch semiconductor grade polished p-type CZ <100> crystalline Si wafers were used in the deposition process. The RF power, the spacing between the showerhead and wafer, the total gas flow, and the N_2 gas flow were varied over certain ranges. Finally the thickness was measured at five different points on the films by thickness measurement equipment in order to obtain the thickness uniformity values. The refractive index was measured at about a 630 nm wavelength using an ellipsometry.

The second group, used to study the passivation properties, both semiconductor grade n-type CZ <100> Si wafers and solar grade p-type CZ <100> Si wafers were used in the deposition process. In the case of the solar grade p-type wafers, before the deposition of the SiNx:H films, an n+ emitter was formed by $POCl_3$ diffusion leading to a 60 Ω/sq emitter sheet resistance. After the deposition, firing was executed at 850°C for 30 seconds. Finally

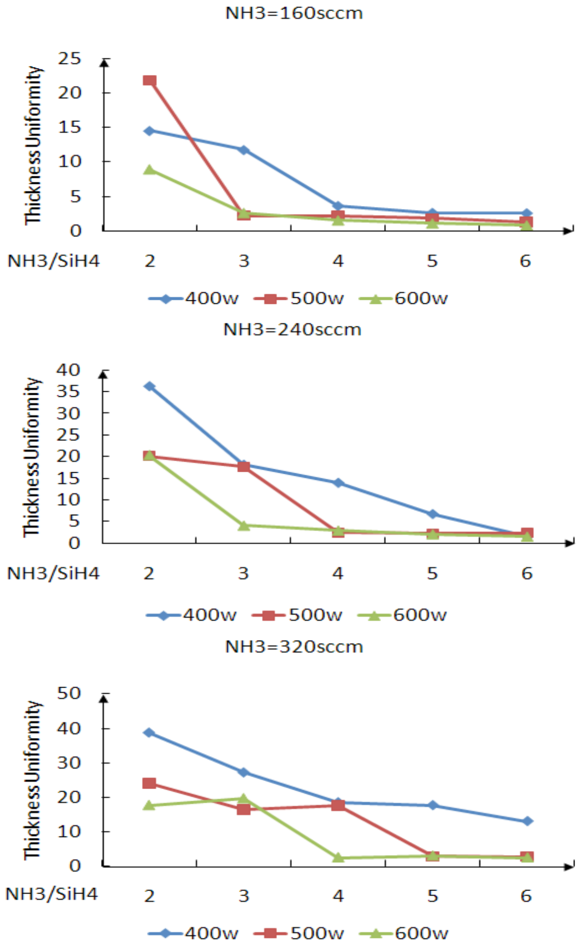

Fig. 2. (a) The thickness uniformity as a function of the NH_3/SiH_4 ratio at 400, 500, and 600 W.

the minority carrier lifetime was obtained through the microwave-detected photoconductance decay (μ-PCD) method [4].

3. RESULTS AND DISCUSSION

3.1 Thickness uniformity and the refractive index

For the experiments, the NH_3 gas flow was set to either 160, 240 and 320 sccm. The NH_3/SiH_4 ratio varied over the range of 2, 3, 4, 5 and 6. The N_2 gas flow was fixed at 240 sccm. The spacing between the showerhead and wafer was fixed at 320 mil. The RF power was varied over 400, 500 and 600 W; the changes in the thickness uniformity and refractive index of the films are shown in Figs. 2(a) and (b), respectively.

The numerical values of the thickness uniformity show the quality of the thickness homogeneity in the SiNx:H films. The higher numerical values mean a bad homogeneity and the low ones represent a good homogeneity. As seen in Fig. 2(a), all three cases have the same tendency in that the thickness uniformity improves as the RF power increases. It also improves as the NH_3/SiH_4 ratio increases. So, when the RF power equals 600 W and the NH_3/SiH_4 ratio is greater than 4, a good thickness homogeneity of SiNx:H films will be obtained.

In the same way, shown in Fig. 2(b), all three cases have the same tendency in that the refractive index obviously decreases as the NH_3/SiH_4 ratio increases. But it only slightly decreases as the RF power increases. Notably, when the NH_3/SiH_4 ratio equaled 2,

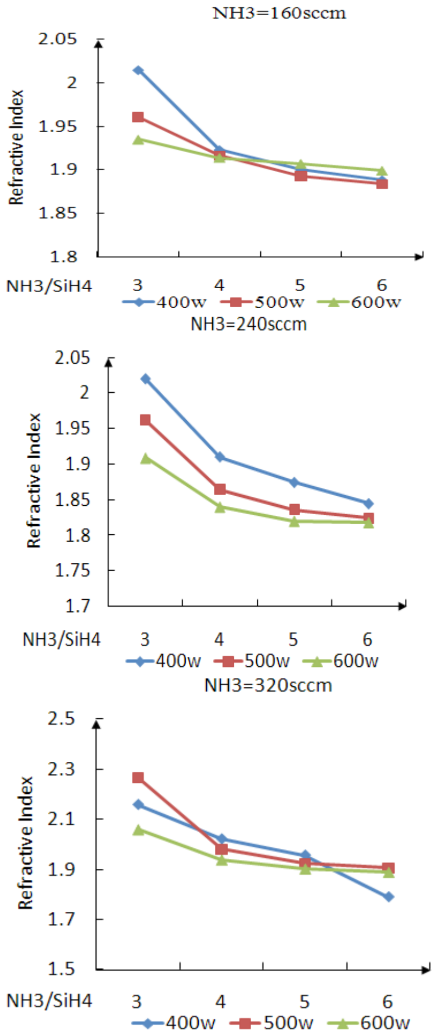

Fig. 2. (b) The refractive index as a function of the NH_3/SiH_4 ratio at 400, 500 and 600 W.

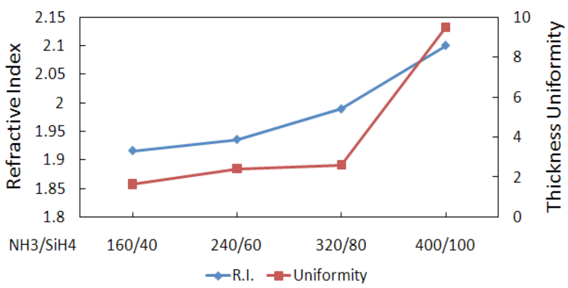

Fig. 3. The variation of the refractive index and thickness uniformity as both the NH_3 and SiH_4 gas flow increased proportionally.

the thickness homogeneity was so terrible that the refractive index could not be measured. The refractive index decreases as the NH_3/SiH_4 ratio increases, due to the fact that the films become less Si-rich as the amount of SiH_4 decreases leading to N-rich films [5,6].

With the thickness uniformity taken into account, the optimal RF power was determined to be 600 W and the NH_3/SiH_4 ratio as 4, which has the closest refractive index to 2.0 among the three cases. Therefore, in the following experiments, the RF power was fixed at 600 W and the NH_3/SiH_4 ratio was fixed at 4.

The NH_3/SiH_4 ratio was fixed to 4 and the NH_3/SiH_4 gas flow increased proportionally, at 160/40, 240/60, 320/80 and 400/100

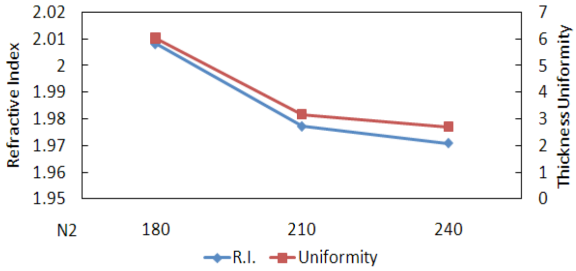

Fig. 4. The variation of the refractive index and thickness uniformity as the N_2 gas flow increased over the range of 180, 210 and 240 sccm.

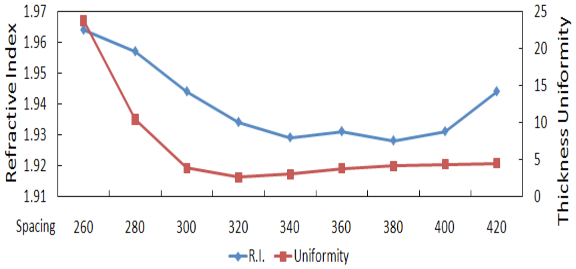

Fig. 5. The variation of the refractive index and thickness uniformity as the spacing between the showerhead and wafer increased over the range of 260, 280, 300, 320, 340, 360, 380, 400 and 420 mil.

sccm; the resulting variations of the refractive index and thickness uniformity are shown in Fig. 3. The N_2 gas flow was fixed at 240 sccm. Obviously, as the gas flow increased, both the refractive index and the numerical values of the thickness uniformity increased. The increment in the refractive index is considered to be due to the fact that the high gas flow causes the films to become more Si-rich [7]. In addition, the increment of the NH_3/SiH_4 gas flow results in a bad thickness homogeneity. Notably, when the NH_3/SiH_4 gas flow equaled 400/100 sccm, the thickness homogeneity was the worst one recorded for the four films. However, when the NH_3/SiH_4 gas flow equaled 320/80 sccm, the refractive index was closest to 2.0 and the thickness homogeneity was also good. So the optimal NH_3/SiH_4 gas flow was determined to be 320/80 sccm.

The NH_3/SiH_4 gas flow was fixed to 320 sccm and 80 sccm, respectively, and the N_2 gas flow was addressed in the next experiments. As seen in Fig. 4, the N_2 gas flow was varied over the range of 180, 210 and 240 sccm.

As N_2 gas flow increased, the refractive index decreased, but the thickness homogeneity was improved. The decrease of refractive index is due to the increment of the N_2 gas flow resulting in making the films more N-rich. Therefore, in order to maintain a good thickness homogeneity, 240 sccm was chosen as the optimal N_2 gas flow.

Figure 5 shows the effects of the showerhead and wafer spacing on the refractive index and thickness uniformity. The RF power, NH_3/SiH_4 gas ratio and N_2 gas flow were se to 600 W, 320/80, 240 sccm, respectively. As the spacing between the showerhead and wafer increased, the refractive index changes over a certain range, but the thickness homogeneity becomes better. Consequently, with the thickness uniformity taken into account first, 320 mil was chosen for the spacing between the showerhead and wafer.

3.2 Minority carrier lifetime

In the previous sub-section, some optimal parameters were determined. The RF power = 600 W, NH_3 gas flow = 320 sccm, N_2

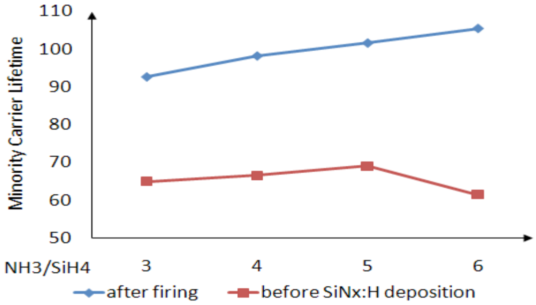

Fig. 6. The minority carrier lifetime as a function of the NH_3/SiH_4 ratio on the n-type semiconductor grade wafers.

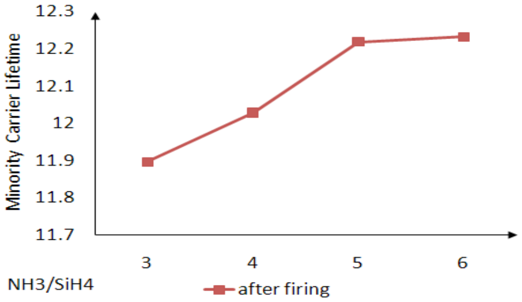

Fig. 7. The minority carrier lifetime as a function of the NH_3/SiH_4 ratio on the p-type solar grade wafers.

gas flow = 240 sccm, and the spacing between showerhead and wafer = 320 mil were fixed.

In order to study the passivation properties of the films, two kinds of experiments were performed. One was that the SiNx:H films were deposited on n-type semiconductor grade wafers and fired at 850°C. The resulting variations in the minority carrier lifetime are shown in Fig. 6.

The other experiment had the SiNx:H films deposited after a $POCl_3$ diffusion, which led to a 60 Ω/sq emitter sheet resistance. The firing was executed at 850°C in the same manner as the first passivation experiment. The resulting variations in the minority carrier lifetime are shown in Fig. 7.

Both of the experiments showed the same tendency regarding the minority carrier lifetime. As the NH_3/SiH_4 ratio increased, minority carrier lifetime improved. The NH_3/SiH_4 ratio plays a very important role in influencing the refractive index and passivation. This is because the different NH_3/SiH_4 ratios cause different chemical compositions in the SiNx:H films. A high NH_3/SiH_4 ratio leads to a more N-rich SiNx:H film. Contrarily, a low NH_3/SiH_4 ratio leads to a more Si-rich SiNx:H film. In addition, Fig.6 shows that the minority carrier lifetime increases greatly after firing, compared to that before the SiNx:H deposition.

The results shown in Figs. 6 and 7 can be explained by the following: During the firing process, the Si-H and N-H bonds in the films are broken due to the high temperature. A part of hydrogen becomes the molecular form H_2, which is released into the air. The other part of the hydrogen still keeps its atomic form and diffuses into the SiNx:H/Si interface, passivating the defects, such as dangling bonds. In the Si-rich films, there are a great many Si-H bonds, which are easier to break in the high temperature process than N-H bonds. Because the films become less dense, more hydrogen is released in the molecular form and less hydrogen diffuses into the SiNx:H/Si interface in the atomic form. Otherwise, in the N-rich films, there are a great many N-H

Parameters	Conditions
Temperature (°C)	400
Pressure (Torr)	1
RF power (W)	600
Gas flow (sccm)	NH3 = 320, SiH4 = 80, N2 = 240
Spacing between showerhead and wafer (mil)	320

bonds, which are more difficult to break in the high temperature process compared to the Si-H bonds. Meanwhile, because the films become denser, less hydrogen is released in the molecular form and more hydrogen diffuses into the substrates in the atomic form. So the N-rich films provide a better passivation than the Si-rich ones. In addition, after firing, the films with the high NH_3/SiH_4 ratio also provided high values for the minority carrier lifetime [7,8].

4. CONCLUSIONS

In this study, SiNx:H films were deposited using high frequency (13.56 MHz) direct PECVD for application to crystalline Si solar cells, and the optical and passivation properties were investigated. The RF power, the spacing between the showerhead and wafer, the NH_3/SiH_4 ratio, the total gas flow, and the N_2 gas flow were varied over certain ranges for the experiments. The thickness uniformity, refractive index and minority carrier lifetime were then measured in order to study the properties of the film.

A NH_3/SiH_4 ratio of 4 was determined to be the optimal NH_3/SiH_4 ratio, because it can provide a relatively good passivation and good thickness homogeneity, obtaining a refractive index closest to 2.0 among the NH_3/SiH_4 ratios greater than 4. The final optimal conditions are given in Table 1.

When the NH_3/SiH_4 ratio increased, better passivation effects were obtained. So for some cases that the passivation properties need to be taken into account first, an NH_3/SiH_4 ratio greater than 4 can be selected for the film deposition.

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