**Effect of hydrogen on passivation quality of SiN_x/Si-rich SiN_x stacked layers
deposited by catalytic chemical vapor deposition on c-Si wafers**

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Abstract

We investigate the role of hydrogen content and fixed charges of catalytic chemical vapor deposited (Cat-CVD) SiN_x/Si-rich SiN_x stacked layers on the quality of crystalline silicon (c-Si) surface passivation. Calculated density of fixed charges is on the order of 10¹² cm⁻², which is high enough for effective field effect passivation. Hydrogen content in the films is also found to contribute significantly to improvement in passivation quality of the stacked layers. Furthermore, Si-rich SiN_x films deposited with H₂ dilution show better passivation quality of SiN_x/Si-rich SiN_x stacked layers than those prepared without H₂ dilution. Effective minority carrier lifetime (τ_{eff}) in c-Si passivated by SiN_x/Si-rich SiN_x stacked layers is as high as 5.1 ms when H₂ is added during Si-rich SiN_x deposition, which is much higher than the case of using Si-rich SiN_x films prepared without H₂ dilution showing τ_{eff} of 3.3 ms.

Keywords: Si-rich SiN_x, silicon nitride, passivation quality, Catalytic CVD, fixed charges, hydrogen content, surface recombination velocity.

1. Introduction

It is very important to provide an excellent coating layer for high-efficiency crystalline silicon (c-Si) solar cells. The important roles of the coating layers are to decrease optical and electrical losses at c-Si surface which cause reduction in c-Si solar cell efficiency. Recently, Koyama *et al.* have reported that SiN_x/a-Si stacked layers prepared by catalytic chemical vapor deposition (Cat-CVD) method show excellent passivation quality with extremely low surface recombination velocity (SRV) [1]. However, a-Si film absorbs sun-light, causing reduction in c-Si solar cell efficiency. In order to solve this problem, in a previous study, we have attempted to use Si-rich SiN_x films instead of a-Si films. Here, Si-rich SiN_x is defined as SiN_x whose composition ratio [Si]/[N] is larger than 1 (in other word, its refractive index (n) at wavelength of 630 nm is larger than that of stoichiometric SiN ($n \sim 2$)). We have found that SiN_x/Si-rich SiN_x stacked layers prepared by Cat-CVD are good candidates for coating layers on c-Si wafers with a low SRV of 3 cm/s and higher transparency than a-Si [2]. In this study, we focus on the effect of fixed charges and H concentration in Si-rich SiN_x film on the passivation quality of the stacked films. The obtained results suggest that the amount of H atoms formed in a Cat-CVD chamber during film deposition can be an important factor to enhance the passivation quality of the stacked layers. Si-rich SiN_x films are thus deposited using SiH₄, NH₃ and H₂ as gas sources. It is demonstrated that SiN_x/Si-rich SiN_x stacked layers with Si-rich SiN_x films prepared with H₂ dilution shows better passivation quality than the stacked films with Si-rich SiN_x films deposited without H₂ dilution. At a same n of a Si-rich SiN_x film of 2.92, minority carrier lifetime (τ_{eff}) in c-Si passivated by SiN_x/Si-rich SiN_x stacked layers improves from 3.3 ms to 5.1 ms by adding H₂ dilution during the deposition of Si-rich SiN_x films.

2. Experimental Procedure

2.1. Sample Preparation

After cleaning c-Si wafers by diluted (5%) hydro-fluoric acid (HF) solution to remove native oxide on c-Si surface, 10-nm-thick Si-rich SiN_x films and 100-nm-thick SiN_x films were deposited by Cat-CVD method in this order. The films were formed also on glass substrates for optical transmission measurement. Si-rich SiN_x films and SiN_x film were deposited in a same chambers. Source gases introduced to the chambers were decomposed on a heated tungsten catalyzer, which has a length of 210 cm and a diameter of 0.5 mm. The distance between substrate and catalyzer was 8 cm. The deposition conditions and composition ratios ([Si]/[N]) of the films, which are evaluated by X-ray photoelectron spectroscopy, are summarized in Table 1. For Fourier-transform infrared (FTIR) spectroscopy, Si-rich SiN_x films with a thickness of about 150 nm were deposited on n-type (100) c-Si substrates with a resistivity of 3460 Ωcm.

2.2. Characterization of Prepared Samples

The thickness and n of SiN_x and Si-rich SiN_x films was measured on J. A. Woollam Co., HS-190TM spectroscopic ellipsometer, using the Cauchy model for data analysis [3]. Optical transmission spectra were observed on an Ultraviolet-visible-near infrared spectrophotometer, SHIMAZU Co. Ltd., UV-3150. The film density was measured by X-ray reflectivity. In order to investigate the passivation quality of the stacked layers on c-Si, microwave photo-conductivity decay (μ -PCD) measurement was carried out on KOBELCO LTA-1510EP using a pulse laser with a wavelength of 904 nm and a photon density of $5 \times 10^{13} \text{ cm}^{-2}$. For this measurement, SiN_x/Si-rich-SiN_x stacked layers were deposited on both sides of 290- μ m-thick n-type (100) floating-zone (FZ)-grown Si wafers with a resistivity of 2.5 Ωcm. The method to determine τ_{eff} was described in the previous paper [2].

For C-V measurement, a 100-nm-thick Aluminum (Al) layer was deposited on one side of 2 Ωcm p-type (100) FZ c-Si wafers by evaporation method. To obtain ohmic contact, the Al/c-Si structure was annealed at 400 °C for 15 minutes in N₂ atmosphere.

Then, Si-rich SiN_x films and SiN_x films were deposited on the other surface of the c-Si wafer. Finally, 2-mm-diameter Al electrodes were evaporated on SiN_x layers through a hard mask. C-V characteristics were obtained in the dark at a high frequency of 1 MHz using Keithley 6517A. Fixed positive charges density Q_f was calculated by:

$$Q_f = Q_{total} - Q_m.$$

Here, Q_{total} and Q_m are determined by:

$$Q_{total} = \frac{C_i}{A} (\Delta\phi_{ms} - V_{FB1}),$$

$$Q_m = \frac{C_i}{2A} (V_{FB1} - V_{FB2}),$$

where C_i is an insulator capacitance, A is the area of electrodes, $\Delta\phi_{ms}$ is work function difference between the metal and the silicon, and V_{FB1} and V_{FB2} are flat band voltages for forward and reverse C-V curves, respectively. They are determined through flat band capacitance, which is calculated to be 6×10^{-9} F [4].

The concentration of bonded H (C_H) in Si-rich SiN_x films is determined from the integrated areas of a Si-H stretching mode peak (A_{Si-H}) and a N-H stretching peak (A_{N-H}) in FTIR spectra using the following equation:

$$C_H = 1.36 \times 10^{17} \times (1.4 \times A_{N-H} + A_{Si-H}) \times \frac{1}{d} \text{ (cm}^{-3}\text{)},$$

where d is a thickness of the film [5].

3. Results and discussion

3.1. The role of fixed charges

It is reported that both H atoms included during deposition process and fixed charges contribute to improvement in the passivation quality of SiN_x layer on c-Si [6]. Fixed charges in SiN_x layers can prevent recombination of photo-generated carriers by field effect, while H atoms can decrease recombination centers by passivating dangling bonds on the surface of c-Si. In order to investigate clearly which factor is more significant in the passivation quality of the stacked layers, we evaluated fixed charge density and H content in the films. For this study, the composition of Si-rich SiN_x films

was varied by adjusting the ratio of the silane (SiH_4)-to-ammonia (NH_3) gas flow rates ($R = [\text{SiH}_4]/[\text{NH}_3]$) from 0.04-0.08. R was varied by changing the SiH_4 flow rate from 10 sccm to 20 sccm at a fixed NH_3 flow rate of 250 sccm.

Figure 1(a) shows the C-V curves of an Al/ SiN_x /Si-rich SiN_x /c-Si structure before and after annealing at an annealing temperature (T_a) of 350 °C and 500 °C for 30 minutes. We can see large hysteresis for all samples. We consider that the hysteresis originates from mobile positive charges. The mobile charges are ionic impurities such as Na^+ , K^+ , Li^+ and H^+ [7], and we believe that the main mobile charges are H^+ ions because a large amount of H atoms must be captured in the films during deposition process due to the dissociation of SiH_4 and NH_3 . Hysteresis becomes smaller after annealing, which may be because the hydrogen atoms can bond with Si dangling bonds or bond together to form H_2 molecules. Figure 1(b) shows the fixed charge density of the films before and after annealing at 350 °C for 30 min as a function of SiH_4/NH_3 gas flow rate ratio (R). The highest value of Q_f is $2.29 \times 10^{12} \text{ cm}^{-2}$ for only stoichiometric SiN_x film. With Si-rich SiN_x film insertion, Q_f tends to decrease with increase in R and reaches $1.54 \times 10^{12} \text{ cm}^{-2}$ when Si-rich SiN_x films with $R=0.08$ ($n=2.92$) is used. The positive fixed charges are probably Si dangling bond defects with a configuration of $\text{N}_3\equiv\text{Si}^+$ in SiN_x films, generally referred to as K^+ centers [8, 9]. Although Q_f decreases after annealing process, the values of Q_f are still sufficiently high for effective field effect passivation [8], and can partially contribute to suppression in surface recombination. However, τ_{eff} rather increases with increase in R , that is, with decrease in Q_f , as shown in Fig. 1(b). This means that there is a more significant factor to reduce SRV other than field effect induced by fixed charge.

3.2. The role of hydrogen

H atoms formed during deposition process can contribute greatly to improvement in the passivation quality of the SiN_x /Si-rich SiN_x stacked films. For more

detailed understanding of this effect, H content in Si-rich SiN_x films is investigated. Figure 2 shows H concentration in Si-rich SiN_x films before and after annealing at 350 °C for 30 min as function of R . The film density of Si-rich SiN_x films is also plotted in the same figure. H concentration increases with R due to increase in Si-H bondings. Increase in H concentration in Si-rich SiN_x films after annealing at a T_a of 350 °C may be because Si-rich SiN_x films have low density (also shown in Figure 2), and H atoms existing in the voids of the films can diffuse and bond with Si dangling bonds, forming Si-H bondings. However, Si-H peak around 2100 cm⁻¹ disappears after annealing at a T_a of 500 °C, as shown in Fig. 3, which means that Si-H bonds are broken and hydrogen atoms are released to environment. We have previously reported that τ_{eff} drastically decreases to 300 μ s after annealing at a T_a of 500 °C [2], the reason of which is probably the desorption of H atoms from the films observed in this study.

The above results show the important role of H content in the passivation quality of the SiN_x/Si-rich SiN_x stacked layers on c-Si wafers. The H atoms may passivate dangling bonds on c-Si surface not only during the deposition of Si-rich SiN_x films but also during SiN_x film deposition and annealing. Therefore, rich H content is an important factor to realize the good passivation quality of SiN_x/Si-rich SiN_x stacked films.

3.3. Addition of H₂ during Si-rich SiN_x deposition

As mentioned above, H atoms formed during deposition process are key point for improvement in the passivation quality of the SiN_x/Si-rich SiN_x stacked films. Therefore, in this study, H₂ gas was added during the deposition of Si-rich SiN_x films. We adjusted R to from various Si-rich films with different n . Figure 4 shows τ_{eff} of c-Si wafers passivated by SiN_x/Si-rich SiN_x stacked layers as a function of n when Si-rich SiN_x films were deposited with and without H₂. One can see improvement in τ_{eff} when Si-rich SiN_x films are deposited with H₂ addition. In particular, we obtained a τ_{eff} of 5.1

ms for a Si-rich SiN_x film with a n of 2.92 deposited with H_2 dilution, corresponding to a SRV of as low as 2.9 cm/s, which is much better than for a Si-rich SiN_x films deposited without H_2 dilution showing τ_{eff} of 3.3 ms. One possible reason for this tendency is that higher amount of H atoms are formed in the Cat-CVD chamber during deposition process with H_2 dilution, and therefore, more H atoms passivate dangling bonds at the surface of c-Si. In order to support this assumption, Si-rich SiN_x films were deposited at various H_2 gas flow rate with keeping n of the films. Figure 5 shows τ_{eff} of c-Si wafers passivated by SiN_x /Si-rich SiN_x stacked layers ($n=2.82$) and H concentration in Si-rich SiN_x films at various H_2 flow rate. One can see that H concentration in the films increases monotonically with increase in H_2 gas flow rate. τ_{eff} also tends to increase with H_2 flow rate up to a H_2 flow rate of 100 sccm, while starts to decrease after reaching the highest τ_{eff} . Increase in τ_{eff} is probably due to higher H content during film deposition which acts to terminate dangling bonds on c-Si surface. At H_2 gas flow rate of 200 sccm, τ_{eff} becomes lower compared to τ_{eff} in case of without H_2 dilution even higher H contents. One possible reason for decreased τ_{eff} is that very large amount of H atoms come onto the surface of c-Si wafers, and cause damage by the etching of Si leading to decrease in τ_{eff} .

4. Conclusion

We investigated the role of fixed charges and hydrogen in Cat-CVD Si-rich SiN_x films for the passivation of c-Si surface. Fixed charge density in the stacked layers is sufficiently high and can contribute to field passivation effect. H content is found to be more important in the passivation quality of the SiN_x /Si-rich SiN_x stacked layers on c-Si wafers. The addition of H_2 during the deposition process of Si-rich SiN_x films improves significantly the passivation quality of the stacked layers. The best τ_{eff} obtained for Si-rich SiN_x film ($n=2.92$) deposited with H_2 dilution is 5.1 ms, corresponding to a SRV of 2.9 cm/s, which is much larger than the case of using a Si-rich SiN_x film with a same

n deposited without H₂ dilution showing τ_{eff} of 3.3 ms.

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Table 1. Deposition conditions of Si-rich SiN_x and SiN_x films.

Fig. 1. (a) C-V curves of Al/SiN_x/Si-rich SiN_x/c-Si structure before and after annealing at a T_a of 350 °C and 500 °C for 30 minutes, and (b) Q_f and τ_{eff} before and after annealing at 350 °C for 30 min as a function of R .

Fig. 2. H concentration in Si-rich SiN_x films as function of R before and after annealing at T_a of 350 °C and the film density of Si-rich SiN_x films as function of R .

Fig. 3. FTIR spectra of Si-rich SiN_x films before and after annealing at a T_a of 350 °C and 500 °C for 30 minutes.

Fig. 4. τ_{eff} of c-Si wafers passivated by SiN_x/Si-rich SiN_x stacked layers as a function of n when Si-rich SiN_x films were deposited with and without H₂.

Fig. 5. τ_{eff} of c-Si wafers passivated by SiN_x/Si-rich SiN_x stacked layers ($n=2.82$) and H concentration in Si-rich SiN_x films at various H₂ flow rate.

Table 1.

Films	SiH ₄ (sccm)	NH ₃ (sccm)	H ₂ (sccm)	Gas pressure (Pa)	Substrate- catalyzer distance (cm)	T _s (°C)	T _{cat} (°C)	[Si]/[N]
Si-rich SiN _x (without H ₂)	10	250	0	10	8	250	1800	1.4
	12.5	250	0	10	8	250	1800	1.8
	15	250	0	10	8	250	1800	2.0
	17.5	250	0	10	8	250	1800	2.7
	20	250	0	10	8	250	1800	3.5
SiN _x	6.9	200	0	10	8	250	1800	0.8
Si-rich SiN _x (with H ₂)	15	20-50	50-200	10	8	250	1800	

Fig. 1.

Fig.2.

Fig. 3.

Fig. 4.

Fig. 5.