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Silicon Surface and Bulk Defect Passivation by Low Temperature PECVD Oxides and Nitrides

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ABSTRACT

The effectiveness of PECVD passivation of surface and bulk defects in Si, as well as phosphorous diffused emitters, is investigated and quantified. Significant hydrogen incorporation coupled with high positive charge density in the PECVD SiN layer is found to play an important role in bulk and surface passivation. It is shown that photo-assisted anneal in a forming gas ambient after PECVD depositions significantly improves the passivation of emitter and bulk defects. PECVD passivation of phosphorous doped emitters and boron doped bare Si surfaces is found to be a strong function of doping concentration. Surface recombination velocity of less than 200 cm/s for 0.2 Ohm-cm and less than 1 cm/s for high resistivity substrates (~500 Ohm-cm) were achieved. PECVD passivation improved bulk lifetime in the range of 30% to 70% in multicrystalline Si materials. However, the degree of the passivation was found to be highly material specific. Depending upon the passivation scheme, emitter saturation current density (J_{01}) can be reduced by a factor of 3 to 9. Finally, the stability of PECVD oxide/nitride passivation under prolonged UV exposure is established.

INTRODUCTION

Both surface and bulk defect passivation are critical for improving Si solar cell performance. Recently PECVD passivation has drawn considerable attention because of low-cost, low-temperature, and effective defect passivation[1-5]. Moreover, it is compatible with the formation of antireflection coating for Si solar cells[6]. Even though it is known that PECVD SiN improves the Si solar cell performance, it is still not fully understood and quantified how much improvement comes from surface and bulk defect passivation, what passivation scheme should be used, how important is post deposition anneal, and how effective is PECVD in passivating emitters.

This paper demonstrates and quantifies the effectiveness of PECVD passivation of bare Si surfaces, bulk defects, and phosphorous diffused emitters. The objective of this paper is four-fold: (a) investigate the role of post-deposition anneal on PECVD passivation of emitters and bulk defects in multicrystalline materials, (b) evaluate

different promising PECVD passivation schemes using various combinations of oxides and nitrides, (c) study the effect of doping concentration on PECVD passivation of phosphorous doped emitters and boron doped Si surfaces, and (d) investigate the stability of PECVD passivation under prolonged UV exposure.

EXPERIMENTS

A commercial Plasma-Therm reactor with 13.56 MHz rf power source was used for the PECVD deposition of oxides and nitrides. The top electrode was maintained at 80 °C while substrate temperature was kept at 250 - 300 °C. A low power level of 20 - 30 W (about 0.02 W/cm²) was used to prevent surface damage by ion bombardment. The PECVD coatings were deposited on both sides of the wafers and then the samples were subjected to photo-assisted anneal at 350 °C in a forming gas ambient for 20 min. The detailed wafer cleaning and deposition conditions have been published elsewhere[5]. For the two layer SiO₂/SiN passivation, 100 Å SiO₂ was deposited first on Si followed by 600 Å SiN deposition with refractive index of 2.3. The index of 2.3 was selected because it has a better match with glass and it is also suitable for double layer SiN(60nm)/SiO₂(95nm) AR coating[6].

The effective recombination lifetime, τ_{eff} , and emitter recombination current density, J_{01} , were measured by the photo-conductivity decay (PCD) technique at 25 degree C. The PCD setup and analysis are described in detail elsewhere[7,8]. The positive oxide charge density Q_{ox} was determined by high frequency C-V measurements on MOS capacitors fabricated on 0.2 Ω-cm Si wafers. In selected instances, the hydrogen content in SiN films was monitored by FTIR.

RESULTS AND DISCUSSIONS**1. PECVD Passivation of Si surfaces**

Three different passivation schemes were investigated for Si surface passivation: a) 100 Å SiO₂; b) 600 Å SiN; and c) 100 Å SiO₂/ 600 Å SiN. In order to determine the best passivation scheme, experiments were conducted on high resistivity (~500 ohm-cm) FZ Si with very high bulk lifetime ($\tau_b > 15$ ms). PCD measurements were performed after the PECVD passivation. It can be seen

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from Fig.1 that the 100Å SiO₂ / 600Å SiN double layer passivation gave the highest effective lifetime (~10ms) and the lowest surface recombination velocity ($S < 1\text{ cm/s}$). Such low S value results from the combination of large amount of hydrogen and high positive charge density in the PECVD SiN films.

Fig.1 The effect of three passivation schemes on τ_{eff}

Fig.2 shows a typical C-V curve for a MOS capacitor with SiN thickness of 66nm and positive charge density of $3.1 \times 10^{12} \text{ cm}^{-2}$. The high positive charge density in SiN leads to strong inversion, and increases the difference in electron and hole density near Si/SiN interface to reduce the surface recombination velocity.

Fig.2 A typical C-V curve for PECVD SiN MOS.

2. PECVD passivation of bulk defects in Si

A significant amount of hydrogen in PECVD SiN films was detected by FTIR, as shown in Fig.3. Two strong peaks at 2170 and 3358 wavenumbers are related to Si-H, and N-H bonds, respectively. Therefore, PECVD SiN layer

could provide a source of hydrogen for both surface

Fig.3 A FTIR absorption spectrum of PECVD SiN film.

and bulk defect passivation. The bulk defect passivation was studied in multicrystalline Si materials. The double layer passivation scheme was used on five different multicrystalline materials, namely EFG sheet Si, cast Osaka and Osaka EM Si, and cast Si from Solarex and Wacker. Minority carrier lifetime was measured on each sample by PCD before and after the passivation. In order to decouple the bulk and surface passivation, each sample was measured in concentrated HF solution before and after the PECVD passivation. HF solution is known to provide a near perfect surface passivation ($S < 1 \text{ cm/s}$) for silicon, via H-Si bond formation. Therefore, the PCD lifetime in HF (τ_{HF}) primarily represents true bulk recombination, and the change in τ_{HF} before and after the PECVD passivation gives a good indication of the degree of bulk defect passivation. Fig.4 shows the improvement in normalized bulk lifetime due to the PECVD passivation of all five multicrystalline Si materials.

Fig.4 The effect of PECVD passivation on normalized τ_b .

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It can be seen that with the exception of Osaka EM, all others showed significant bulk defect passivation after the PECVD deposition of SiN/SiO₂. The τ_{HF} increased by 30% to 70% after the passivation, depending upon the multicrystalline material. It is noteworthy that the bulk defect passivation efficiency is materials specific, probably due to the difference in the nature of defects in each material, but seem to be less sensitive to the initial bulk lifetime value.

3. PECVD passivation of phosphorous diffused emitters

The effects of post PECVD deposition anneal and various passivation strategies on emitter surface passivation were investigated. A comparison between photo-assisted anneal in a tungsten halogen lamp-heated system and conventional furnace anneal was made. Fig.5 shows that PECVD deposition alone, without any anneal, reduces J_0 by a factor 2. Photo-assisted anneal at 350°C for 20 min in forming gas, after the PECVD deposition, reduces J_0 by an additional factor of 3.4, while a comparable furnace anneal decreases J_0 by a factor of 2.5. These results not only

Fig.5 Effect of post deposition anneal on J_0

demonstrate the effectiveness of PECVD coatings for emitter passivation but also show the importance of post-deposition anneal and the superiority of photo-anneal over the furnace anneal.

Five different schemes were investigated for passivating phosphorous diffused emitters; (a) 100nm thick PECVD SiO₂/Si; (b) 60nm thick PECVD SiN/Si; (c) PECVD SiN(60nm)/PECVD SiO₂(10nm)/Si; (d) 110nm thick thermal SiO₂/Si; and (e) PECVD SiN(60nm)/thin thermal SiO₂(10nm)/Si. The schemes (b) and (c) were used on the emitters diffused at 900°C with J_0 value of 1300 (tA/cm²) before the passivation, while schemes (a), (d), and (e) were performed on the emitters diffused at 875°C with a J_0 value of 900 (tA/cm²). The passivation layers were deposited on both surfaces of the wafers, and were subjected to photo-anneal at 350 °C in forming gas ambient for 20 min. J_0 measurements were performed by using PCD technique.

Fig.6 shows that J_0 decreases by a factor of 3.7, 5.7 and

Fig.6 Changing in J_0 with different passivation schemes.

6.3 due to PECVD passivation schemes a, b, and c, respectively. Scheme (d), which uses thick thermal oxide, lowers J_0 by a factor of 9, and scheme (e), which involves the combination of PECVD SiN and thin thermal SiO₂, decreases J_0 by a factor of 9.5. It should be recognized that even though thick thermal oxide provides better surface passivation, it has poor antireflection properties for planar cells. On the other hand, schemes (b) and (c) provide relatively inferior surface passivation but very effective antireflection coating. If a higher degree of emitter surface passivation is critical, scheme (e) can provide excellent emitter passivation without sacrificing antireflection properties.

It is important to recognize that the effectiveness of PECVD passivation is also a function of doping concentration. Bulk doping concentration was found to influence the degree of PECVD passivation of Si surfaces. Fig.7 shows that surface recombination velocity, S , of the

Fig.7 Effect of bulk doping on PECVD passivation.

PECVD oxide/nitride coated Si wafer increases from less than 1 to about 150 cm/s when the bulk resistivity decreases from 500 to 0.2 ohm-cm.

Similarly, it was found that the J_{sc} of phosphorus diffused emitter, coated with the PECVD oxide/nitride, increased from 200 to 650 $\mu\text{A}/\text{cm}^2$, Fig.8, with the increase in surface doping concentration, which was varied by changing the diffusion temperature from 820 to 900 °C. Thus, the absolute value of PECVD-induced S or J_s is also a strong function of surface doping concentration.

Fig.8 Effect of emitter diffusion temperature on PECVD passivation.

4. Stability of PECVD passivation

Finally, the UV stability of PECVD passivation was studied for both single layer SiN(60nm) and double layer SiN(60nm)/SiO₂(10nm) coated emitters by exposing the passivated emitters to a concentrated light source (40 suns). Preliminary results, in Fig.9, show that both SiN and SiN/SiO₂ passivation are stable over 1000 sun-hour UV exposure.

Fig.9 The stability of PECVD passivation under UV exposure.

In conclusion, we have shown that the proper choice of PECVD passivation scheme and photo-assisted anneal conditions can effectively passivate bulk and surface defects in silicon, as well as phosphorous diffused emitters. The surface recombination velocity of less than 200 cm/s for 0.2 Ohm-cm Si and less than 1 cm/s for high resistivity substrates (~500 Ohm-cm) were achieved by PECVD passivation. The bulk defect passivation was investigated in multicrystalline materials, and it was found that bulk lifetime improved in the range of 30% to 70% after PECVD oxide/nitride deposition and photo-anneal. However, the degree of the passivation is highly material specific. The PECVD passivation was able to reduce the phosphorus diffused emitter saturation current density J_{sc} by a factor of 3 to 6. The thick thermal oxide can reduce J_{sc} by a factor of 9, however it does not provide efficient AR coating for planar Si solar cells. On the other hand, the combination of thin thermal oxide capped with PECVD SiN layer not only reduces J_{sc} by a factor of 9.5, but also serves as a good antireflection coating, especially under the glass. The merit of photo-assisted anneal was demonstrated for PECVD bulk and surface passivation. Finally, stability of PECVD passivation of diffused emitters was established by prolonged UV exposure under concentrated light source.

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