INFLUENCE OF THE SiN_X DEPOSITION TEMPERATURE ON THE PASSIVATION QUALITY OF AL_2O_3/SiN_X STACKS AND THE EFFECT OF BLISTERING

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ABSTRACT: In this study we investigate the influence of the hydrogen-rich silicon nitride (SiN_x:H) deposition temperature by a direct PECVD (plasma-enhanced chemical vapour deposition) on the passivation quality of Al_2O_3/SiN_x:H stacks and the effect of blister formation on FZ Si material. It is shown that the damage produced by the plasma during deposition of the SiN_x coating can be reduced by decreasing the SiN_x:H deposition temperature for a thin SiN_x:H layer of ~30 nm. Furthermore, the optical analysis shows that the blistering of the Al_2O_3/SiN_x:H stacks after SiN_x:H deposition depends on the deposition temperature and the thickness of the SiN_x:H layer in the case of a direct PECVD. Moreover, the density of blisters seems to be decreased by increasing the Al_2O_3 deposition temperature. An annealing step of 370°C for 40 min under atomic hydrogen atmosphere or under nitrogen atmosphere after SiN_x:H deposition seems to be beneficial for the samples not showing severe blister formation (Al_2O_3/SiN_x:H stack with a SiN_x:H layer deposited by direct PECVD at 300°C or by indirect PECVD at 400°C).
Keywords: annealing, lifetime, passivation, silicon nitride

1 INTRODUCTION

A good passivation of the backside of solar cells gains today in importance with the ever growing industrial onset of PERC (passivated emitter and rear cell) solar cells. Al_2O_3 is an appropriate candidate for the passivation of p-type silicon material due to its good chemical surface passivation and its negative fixed charges which yield to a field effect passivation [1]. However, the Al_2O_3 layer is not very stable for many solar cells process flows, especially for the high temperature processes, and needs generally to be capped [2]. In this regard the SiN_x:H, which is usually used in the solar cell industry to passivate the front side emitter, seems to be a good candidate. An advantage of SiN_x:H in addition to its chemical stability is its optical contribution to light trapping [3]. Furthermore, SiN_x:H can improve the passivation quality of the Al_2O_3 after firing [4]. The most often used method to deposit the SiN_x:H layer is PECVD. However, the use of a direct PECVD causes blistering of the Al_2O_3/SiN_x:H stack most probably because of the usual deposition temperature of ~400°C. Therefore, in this study, we shed light on the influence of SiN_x:H deposition temperatures below 400°C in case of a direct PECVD on the blistering and the passivation quality of the Al_2O_3/SiN_x:H stack on p-type FZ Si wafers.

2 EXPERIMENTS

2.1 1st experiment

5×5 cm^2 symmetrical lifetime samples were processed on <100> oriented ~250 µm thick p-type FZ silicon wafers of ~1 Ωcm resistivity as described in Fig. 1. After etching in a chemical polishing (CP) solution to remove the laser damage at the edges, they were RCA-cleaned. During the last step of the RCA cleaning the chemical oxide was not removed. A thin Al_2O_3 layer of ~7.5 nm was then deposited on both sides of the wafer at three different substrate set temperatures (170°C, 200°C, and 300°C) using a plasma-assisted atomic layer deposition (ALD) reactor from Oxford Instruments. Subsequently, an Al_2O_3 post deposition annealing at 420°C for 30 min followed to activate the passivation. The effective minority carrier lifetime τ_{eff} was measured using the photoconductance decay (PCD) method at an injection level of 1×10^{15} cm^{-3}. The deposition of a ~30 nm SiN_x:H capping layer on both sides of the wafer was then performed using a direct PECVD (Centrotherm) at three different temperatures (300°C, 350°C, and 400°C) and using a remote PECVD (Roth&Rau) at 400°C. The effective minority carrier lifetime τ_{eff} was once more measured, followed by an annealing at 370°C for 40 min in atomic hydrogen atmosphere. Finally, another lifetime measurement was performed.

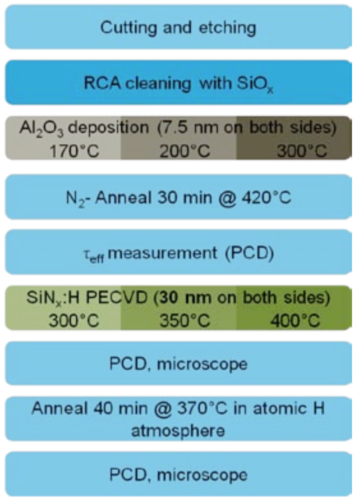

Figure 1: Process flow of 1 Ωcm p-type FZ lifetime samples. The chemical oxide was not removed after the last step of the RCA cleaning. Passivation was performed by Al_2O_3 deposited at three different temperatures (170°C, 200°C and 300°C). The SiN_x:H capping layer of ~30 nm was deposited using a direct PECVD at three different temperatures (300°C, 350°C and 400°C) or a remote PECVD at 400°C.

2.2 2nd experiment

To investigate the influence of the thickness of the SiN_x:H layer, a second set of lifetime samples was processed as illustrated in Fig. 2. In addition, the influence of the chemical oxide and the Al_2O_3 post deposition annealing on τ_{eff} and on the blistering phenomenon was examined.

The sample preparation is the same as in the first experiment, except for some process steps and the additional firing step at the end. After the last step of the RCA cleaning the chemical oxide was removed for some samples. Prior to the deposition of the SiN_x:H capping layer, some samples were annealed at 420°C for 30 min in N_2 environment, followed by the first τ_{eff} measurement. Thereafter, a thick SiN_x:H capping layer of ~120 nm was deposited using a direct PECVD at 300°C or a remote PECVD at 400°C. After a second τ_{eff} measurement, an annealing step was carried out not in atomic hydrogen atmosphere, but in nitrogen environment. The third lifetime measurement was performed before a firing step in a belt furnace at ~850°C preceding another lifetime measurement.

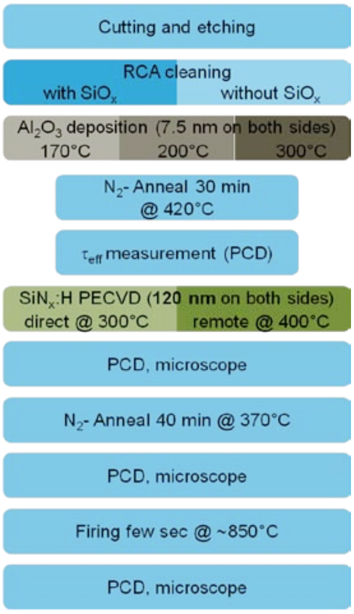

Figure 2: Process flow of 1 Ωcm p-type FZ lifetime samples. For some samples the chemical oxide was removed after the RCA cleaning. Passivation was carried out by Al_2O_3 deposited at three different temperatures (170°C, 200°C and 300°C), subsequently, some samples were annealed before the first τ_{eff} measurement. The SiN_x:H capping layer of ~120 nm was deposited using a direct PECVD at 300°C or a remote PECVD at 400°C.

3 LIFETIME MEASUREMENTS

3.1 1st experiment: thin SiN_x:H capping layer

The τ_{eff} measurements after the Al_2O_3 post-deposition anneal (blue and red squares shown in Fig. 3) reveal that the passivation quality of Al_2O_3 depends on the deposition temperature in accordance with previous results [5].

As can be seen in Fig. 3, τ_{eff} is decreased after the SiN_x:H deposition (round symbols) independently of the deposition method and the Al_2O_3 deposition temperature. This is probably due to the plasma damage on the Al_2O_3 layer or the Al_2O_3/Si interface, respectively. This was also observed in a similar study [6]. For the direct PECVD (blue symbols), the plasma damage during SiN_x:H deposition depends strongly on the SiN_x:H deposition temperature and there is a tendency of augmentation with increasing temperature. This can be explained by the fact that during SiN_x:H deposition the velocity of the particles on the substrate surface increases with increasing temperature [9].

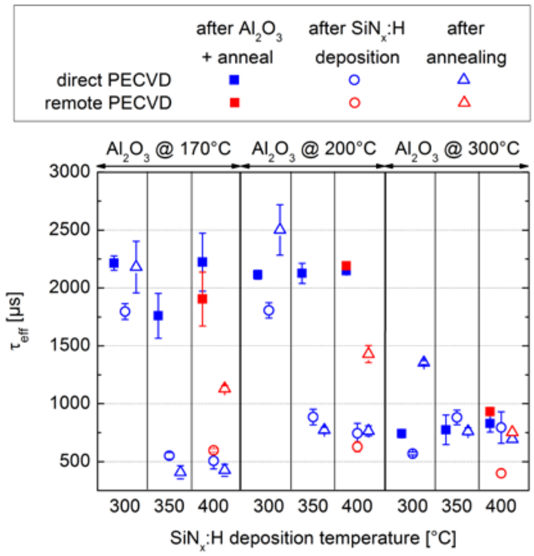

Figure 3: Effective minority carrier lifetime τ_{eff} dependant on Al_2O_3 and SiN_x:H (direct and remote PECVD) deposition temperature. The SiN_x:H layer thickness is ~30 nm. Measurements were carried out after the Al_2O_3 post deposition anneal at ~420°C for 30 min (square), after SiN_x:H deposition (dot) and after an annealing step at 370°C for 40 min (triangle).

An annealing step at 370°C for 40 min under 1 mbar atomic hydrogen atmosphere after the SiN_x:H deposition increases τ_{eff} again for the samples which did not show blister formation after the SiN_x:H deposition. This healing of plasma damage by a post-deposition anneal was also found in the aforementioned study [6]. The annealing step was performed in [6] under 10 mbar nitrogen atmosphere. Therefore, the improvement of τ_{eff} after the annealing step is not due to the presence of atomic hydrogen, but seems to be temperature-dependent.

3.2 2nd experiment: thick SiN_x:H capping layer

Fig. 4 shows τ_{eff} of samples with a chemical oxide after the RCA cleaning (solid symbols) and samples without chemical oxide (empty symbols). The thickness of the SiN_x:H layer is ~120 nm. As can be seen in Fig. 4, τ_{eff} is much higher for the samples with a chemical oxide than for the samples without it after the Al_2O_3 post deposition anneal (black squares). The plasma damage during the SiN_x:H deposition at 300°C (direct PECVD) is more pronounced for a thicker SiN_x:H layer (~120 nm) than for a thinner one (~30 nm) (compare red solid circles in Fig. 4 and empty blue circles in Fig. 3 for a SiN_x:H deposition temperature of 300°C). The absolute decrease of τ_{eff} after the SiN_x:H deposition is stronger for samples with a chemical oxide in comparison to samples without it, but absolute τ_{eff} values for samples with chemical oxide are mostly higher than values without chemical oxide. On the contrary, τ_{eff} increases (direct PECVD) or is constant (remote PECVD) after the silicon nitride deposition for the samples without chemical oxide for an Al_2O_3 deposition temperature of 300°C.

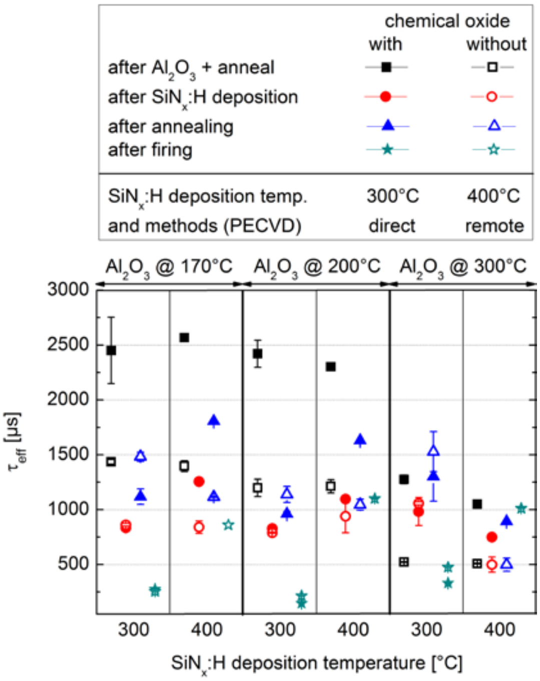

Figure 4: Effective minority carrier lifetime τ_{eff} dependant on Al_2O_3 deposition temperature and SiN_x:H deposition method (direct PECVD at 300°C and indirect PECVD at 400°C). The thickness of the SiN_x:H layer is ~120 nm. The solid symbols represent samples with a chemical oxide after RCA cleaning whereas the empty ones represent the samples without chemical oxide. Measurements were carried out after the Al_2O_3 post deposition anneal at ~420°C for 30 min (black squares), after SiN_x:H deposition (red circles), after an annealing step at 370°C for 40 min (blue triangles) and after firing at ~850°C in a belt furnace (cyan dark stars). There is no data for the remote PECVD (at 400°C) after firing.

There is an improvement of τ_{eff} after an annealing step at 370°C under 10 mbar in nitrogen atmosphere in agreement with the aforementioned study [6]. After a firing step at ~850°C in a belt furnace, τ_{eff} decreases for almost all the samples except the sample without a chemical oxide at Al_2O_3 deposition temperature of 300°C for the remote plasma, where τ_{eff} increases.

Fig. 5 compares τ_{eff} for samples with an Al_2O_3 post deposition annealing step (solid symbols) with samples without it (empty symbols). These samples have a chemical oxide after the RCA cleaning. For the direct PECVD, the Al_2O_3 post deposition anneal seems to be detrimental (red circles and blue triangles for a SiN_x:H deposition temperature of 300°C). It is the opposite for the remote PECVD (for the SiN_x:H deposition temperature of 400°C). For it, τ_{eff} of the samples that have seen an Al_2O_3 post deposition anneal is better than that for the samples without it.

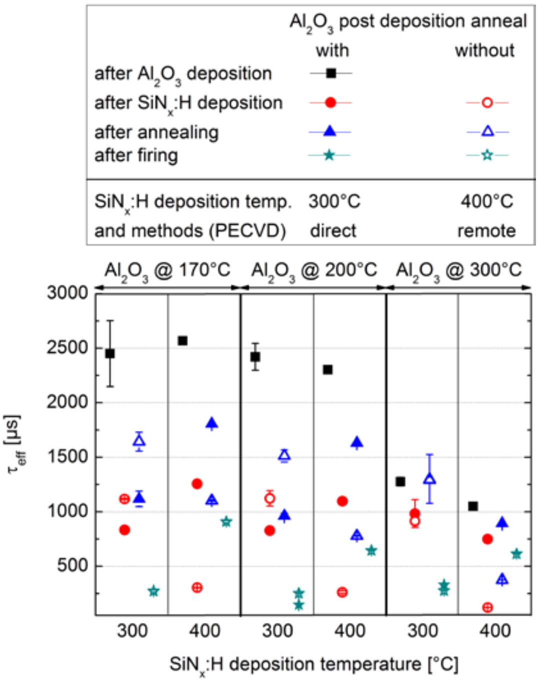

Figure 5: Effective minority carrier lifetime τ_{eff} dependant on Al_2O_3 deposition temperature and SiN_x:H deposition method (direct PECVD at 300°C and indirect PECVD at 400°C). The thickness of the SiN_x:H layer is ~120 nm. The samples were either annealed after the Al_2O_3 deposition (solid symbols) or not (empty symbols). Measurements were carried out after the Al_2O_3 post deposition anneal at ~420°C for 30 min (black squares), after SiN_x:H deposition (red circles), after an annealing step at 370°C for 40 min (blue triangles) and after firing at ~850°C in a belt furnace (cyan dark stars). There is no data for the remote PECVD (at 400°C) after firing.

4 OPTICAL SURFACE IMAGES – BLISTER FORMATION

4.1 1st experiment: thin SiN_x:H capping layer

For the remote PECVD, optical microscope images do not show the formation of blisters after SiN_x deposition independent of the Al_2O_3 deposition temperature. As shown in Fig. 6 for the direct PECVD, the formation of blisters directly after the deposition of a SiN_x:H layer of ~30 nm seems to depend only on the deposition temperature of the SiN_x:H (shown in the columns). The Al_2O_3 deposition temperature (displayed on the rows in Fig. 6) does not have a direct influence on the blistering phenomenon. The optical microscope images taken after the annealing step show no significant difference.

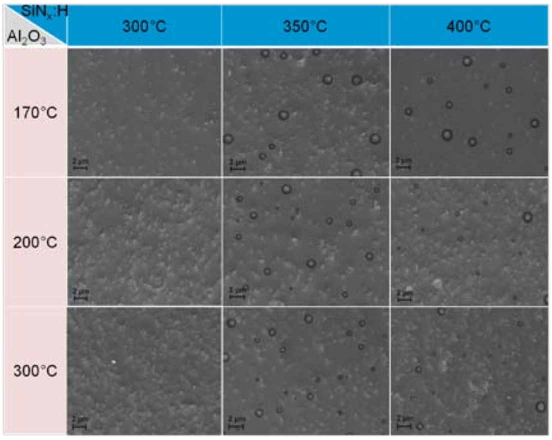

Figure 6: SEM images of the surface of Al_2O_3/SiN_x:H stacks after SiN_x:H deposition. The 7.5 nm thick Al_2O_3 layer was deposited by plasma-assisted ALD at three different temperatures 170°C, 200°C, and 300°C (displayed in the rows), and the ~30 nm thick SiN_x:H capping layer coated using direct PECVD also at three different temperatures 300°C, 350°C, and 400°C (shown in the columns).

4.2 2nd experiment: thick SiN_x:H capping layer

The optical images of Al_2O_3/SiN_x:H stacks with a thicker SiN_x:H layer of ~120 nm deposited using direct PECVD at 300°C show the formation of blisters directly after the silicon nitride deposition (shown in Fig. 7). Therefore, the formation of blisters in the direct PECVD seems to be strongly dependent on the thickness of the deposited SiN_x:H layer. For a thick silicon nitride layer of ~120 nm deposited using the indirect PECVD, there is not blister formation.

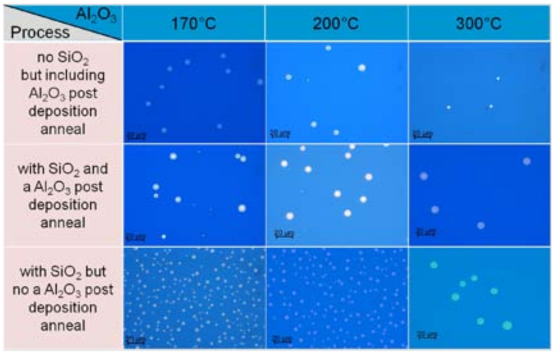

Figure 7: Optical microscope images of the surface of Al_2O_3/SiN_x:H stacks directly after the SiN_x:H deposition. The 7.5 nm thick Al_2O_3 layer was deposited by plasma-assisted ALD at three different temperatures (170°C, 200°C, and 300°C, shown in the columns), and the ~120 nm thick SiN_x:H capping layer coated using direct PECVD at 300°C. Some process sequences like with or without chemical oxide after the RCA cleaning and with or without Al_2O_3 post deposition anneal are displayed on the rows.

For the direct PECVD, the density of blisters after the deposition of a SiN_x:H layer of ~120 nm thick seems to be lessened by increasing the Al_2O_3 deposition temperature. This trend was also observed in a previous investigation for the case of a Al_2O_3/SiN_x stack for which the SiN_x layer was deposited using an indirect PECVD, after the firing step [5]. Furthermore, this tends to be depending on the process sequences. Accordingly, for the samples without an Al_2O_3 post deposition anneal (last row, Fig. 7), the density of the blisters is more pronounced. For the samples without chemical oxide (shown in the first row), the density of blisters is lower, particularly for an Al_2O_3 deposition temperature of 300°C.

The optical microscope images recorded after the annealing step at 370°C for 40 min do not reveal significant differences. After the firing step, the density of blisters seems to be increased for the samples where the SiN_x:H capping layer was deposited using the direct PECVD.

For stacks using the remote PECVD, no large blister formation occurred after the firing step. The density of blisters is lower for samples without a chemical oxide and including an Al_2O_3 post deposition anneal than for samples with oxide and without a post deposition anneal.

5 DISCUSSION

For the thin SiN_x:H capping layer (~30 nm) coated using the direct PECVD at 300°C, no blistering phenomenon occurs directly after its deposition. This is most likely the reason for the lower decrease of the lifetime. For the thick capping layer of ~120 nm deposited under the same conditions, blister formation happens and τ_{eff} decreases drastically. One possible explanation is that the thicker capping layer of ~120 nm represents a diffusion barrier for gaseous effusion of H_2 and H_2O. In fact, according to [7], the blistering phenomenon of the Al_2O_3 layer during high temperature steps occurs under an external load and the gaseous desorption of H_2 and H_2O from the Al_2O_3 layer and the Si/Al_2O_3 interface. In addition to the stress induced by rapid particles colliding with the substrate surface during the SiN_x:H deposition using a direct PECVD, a thick SiN_x:H layer in the range of 120 nm probably represents a diffusion barrier for the effusion of H_2 and H_2O (because a thin Al_2O_3 layer of ~7.5 nm is not a diffusion barrier for gases [8]), leading to blistering of the stack. For a thin Al_2O_3/SiN_x:H stack with a silicon nitride layer of ~30 nm deposited by direct PECVD at temperatures $\geq$350°C, blister formation may be explained by the fact, that for those deposition temperatures the SiN_x:H layers become more dense [9, 10] and then represent diffusion barriers for the desorption of H_2 and H_2O. The Al_2O_3/SiN_x:H stacks for which the silicon nitride capping layer was deposited using remote plasma do not show blister formation independent of the SiN_x thickness, most probably because the substrate surface is not subjected to big external load during the silicon nitride deposition.

For all samples not showing blister formation after SiN_x:H deposition and those for which the SiN_x:H deposition was carried out at 300°C, τ_{eff} increases after the subsequent annealing step at 370°C independently of the environment (N_2 or atomic H atmosphere). This effect is therefore more due to the temperature.

The drop of τ_{eff} after firing is probably due to the slight increase of the density of blisters.

6 CONCLUSION

Effective carrier lifetimes τ_{eff} from p-type FZ Si

(1 Ωcm) samples passivated with Al_2O_3/SiN_x:H stacks show a strong influence of the SiN_x:H deposition temperature and its thickness in the case of direct PECVD. A subsequent annealing step seems to be beneficial for samples for which blister formation does not occur and those for which the SiN_x:H capping layer was deposited at 300°C. Optical microscopy shows a dependence of the blistering effect on the deposition temperature and the thickness of the deposited SiN_x:H layer for a direct PECVD, affecting τ_{eff} considerably.

The Al_2O_3 pre-deposition treatment (RCA cleaning with or without chemical oxide) and the Al_2O_3 post deposition anneal seem to have a slight influence on the blistering phenomenon. For samples without a post deposition anneal the density of blisters is larger compared to the other ones.

The best Al_2O_3/SiN_x:H stack obtained after the firing step was processed without the chemical oxide, had seen the Al_2O_3 post deposition anneal and the SiN_x:H capping layer was deposited using the remote PECVD. The effective minority carrier lifetime τ_{eff} for this sample after firing is above 1 ms, leading to a maximal effective surface recombination velocity $S_{eff,\,max}$ below 10 cm/s.

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