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Light Induced Curing (LIC) of Passivation Layers deposited on Native Silicon Oxide

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Abstract

This work presents a novel insight to the aspects of silicon surface passivation and the influence of thin intermediate layers generated by chemically grown silicon oxides. Strong light induced effects on passivation properties are investigated. After exposure to light (0.25 suns) for about 60 s, samples based on a PECVD layer system consisting of SiN_x and SiO_2 deposited on crystalline silicon with native silicon oxides show an improvement of more than 100% in minority carrier lifetime. These improvements are stable over months and lead to effective surface recombination velocities as low as 10 cm/s on chemically polished p-type FZ wafers. With the use of different light sources, corona charging and annealing experiments the effect is investigated in detail. Finally, the effect is proposed to be a photo induced curing process of defects in the Si / SiO_2 interface with the incorporation of hydrogen.

Keywords: Passivation; silicon nitride; silicon oxide; semiconductor-insulator boundaries

1. Introduction

A thin intermediate layer of silicon oxide is reported to have a significant influence on the surface passivation performance of dielectric layers grown by plasma-enhanced chemical vapor deposition (PECVD) and atomic layer deposition (ALD) [1], [2] . On the one hand this layer can shield fixed charges from the interface and lead to a decrease in passivation performance because of the fact that less minority charge carriers are repelled from the recombinative surface. On the other hand, the interface itself and thereby the chemical passivation quality can be improved by a reduction of recombinative interface states.

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Apart from dangling bond generation in a-Si, published work about the influence of exposure to light on passivation performance is limited. Some hints are given by Aberle [3], where a UV induced reduction of fixed charges in the SiN_x layer close to the silicon is reported. An increase of measured minority carrier lifetime by bias light exposure of SiN_x coated float zone (FZ) wafers is observed by Schuurmans [4]. As high quality material is used, the increase is suggested to be due to a reduction in surface recombination, although specific details are not investigated.

In this work characteristics of light induced changes to the passivation quality for wafers covered with chemically grown native oxides (Zhang [5]) are discussed. Symmetric lifetime samples passivated with a SiN_x/SiO_2 stack system are compared with respect to their reaction to broadband light exposure. The stack system is chosen because it is also used as an anti-reflection (AR) coating for solar cell production in other experiments were it shows a good optical performance.

2. Experimental Details

For the experiments mainly p-type FZ wafers are used (thickness: 250 µm, 1.7 Ωcm, (100)). For comparison some n-type FZ wafers are processed (thickness: 500 µm, 1.0 Ωcm, (100)) as well. After laser cutting in 5 x 5 cm² pieces all samples receive a chemical polishing damage etch (removal ~5 µm per side) followed by a standard RCA cleaning [6]. After the removal of the chemical native oxide which grows during the second RCA cleaning step in diluted HF, two different chemical native oxides with different exposure times to the oxidant are grown on the wafers.

SiN_x/SiO_2 ($n_{SiNx\ at\ 600\ nm} = 2.0$, d = 75 nm and $n_{SiO2\ at\ 600\ nm} = 1.5$, d = 100 nm) layers are deposited on both sides of the wafers in a lab-type PECVD setup (Oxford Instruments Plasmalab System 100, direct plasma, 13.56 MHz) at 400°C. As there is no evidence for cross contamination, the complete stack can be deposited within one deposition at a constant set-temperature of 400°C.

After deposition, the samples are fired at 855°C peak temperature (2 s) in an industrial belt furnace. Fig. 1 shows an overview of the process steps.

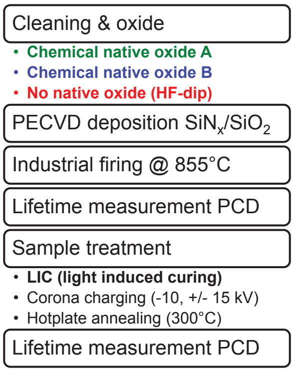

Fig. 1. Lifetime samples process flow

Effective minority charge carrier lifetimes (τ_{eff}) are measured using the PCD (photo-conductance decay) technique with a WCT-120 tool [7]. For comparison, lifetimes are measured at an excess minority carrier injection level of 1×10^{15} cm^{-3}. In a PCD measurement a flash is used to generate excess charge carriers. To minimize the influence of this flash on the wafer properties, the shortest possible flash timings and an IR passfilter (> 700 nm) are used. Light induced curing (LIC) is performed by a thermal light source emitting approximately blackbody radiation of 3000 K with up to 4 suns (1 sun equals

2.7×10^{17} photons $cm^{-2}\ s^{-1}$) intensity, and by LEDs with a wavelength of 630 nm with intensities up to 3.3×10^{17} photons $cm^{-2}\ s^{-1}$.

The influence of heat is investigated by different annealing times on a hotplate at 300°C. To reduce the risk of contamination, the samples are annealed on a cleaned multicrystalline silicon carrier wafer.

For the corona charging measurements the setup of the charger is comparable to Weinbergs setup [8] and voltages of -10 kV and ±15 kV (50 / 65 nA charging current) are used. The distance between the sample and the charging needle is about 7 cm. To remove the charges the wafers are rinsed in isopropyl alcohol (IPA).

3. Results

Fig. 2 a) and b) show the lifetime change during the curing process for exposure to thermal light with approximately 0.25 suns intensity. After a sharp increase lifetimes saturate at a high level after about 30 s.

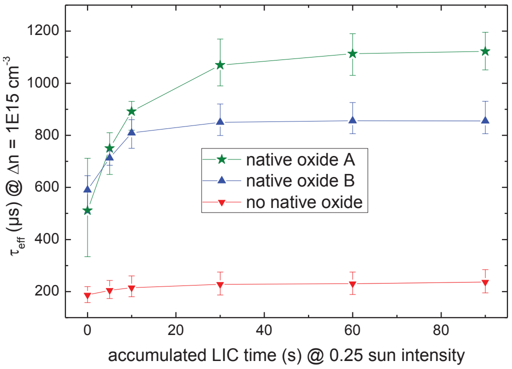

Fig. 2. Effect of LIC on fired SiN_x/SiO_2 stacks deposited on chemical native oxide A, B and on samples without native oxide (HF dip before deposition). The lines are just a guide to the eye

An effective lifetime of 1200 µs (as reached for the best samples) can be translated into an effective maximum surface recombination velocity [9] of only 10 cm s^{-1} (assuming infinite bulk lifetime) which is an excellent passivation quality for a low refractive index SiN_x/SiO_2 coating.

For comparison some samples are exposed to direct sunlight at noon in August. These samples show a comparable improvement in lifetime. Tests with an IR pass filter (> 700 nm) in combination with the thermal light source show the improvements as well. To be sure that the lifetime measurement itself does not lead to LIC many consecutive measurements at different LIC times are performed. This leads to lifetime values within the expected spread and does not show an increase over the number of measurements.

The stability of the improvement is checked on a regular basis. After three months of storage in the dark a decrease in surface passivation below 10% is measured which could be recovered by 5 s of LIC. To exclude surface charge effects samples are rinsed in isopropanol alcohol; also with no measurable effect.

Using a photoluminescence setup with tuneable red excitation LEDs (630 nm, spectral range FWHM: 16 nm) a threshold value for lifetime improvements can be found. Below an intensity of 1.3×10^{16} photons $cm^{-2}\ s^{-1}$ and 1 s exposure time there is no measurable increase in lifetime or intensity counts. As Cuevas [10] states, a transient lifetime measurement gives easy access to the maximum lifetime within the measured area, but it lacks information about the average values. For spatially resolved information about passivation quality, photoluminescence (PL) measurements are performed. PL intensity maps are a good indicator to show the homogeneity of the surface passivation and it is possible to record them at low enough LED excitation to minimise the influence on the sample properties. Fig. 3 shows one p-type wafer (native oxide A) processed as described in the experimental details. After the firing step the right half of the wafer is covered by an aluminium plate and exposed to light of about 0.25 suns intensity for 20 s before the first measurement (a).

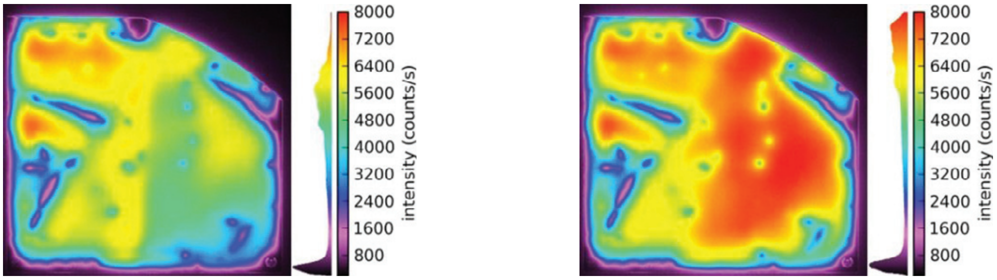

Fig. 3. PL measurement after a) 20 s LIC with 50% (right side) covered by an aluminium plate and b) additional 60 s LIC by 630 nm LEDs. A high PL intensity indicates a high τ_{eff}

Apart from scratches one can see that the part exposed to LIC before the measurement shows a higher maximum signal and is clearly separated from the right part that is not exposed to LIC. For further LIC the excitation LEDs are used at high intensities for 60 s without covering parts of the wafer (Fig. 3 b). Thereby the signal rises in the not yet exposed part. Apart from areas with very low signal the improvement is largely homogeneous over the wafer.

Another interesting aspect of the PL measurements is the possibility for single sided exposure to light. 633 nm light is absorbed in silicon within the first 10 µm. Thereby no photons should reach the interface on the not exposed side of the sample. The increase in lifetime, however, is almost completely reached with single sided exposure (before: 350 µs, single side LIC: 603 µs, double side LIC: 610 µs). This leads to the assumption that the LIC effect is mainly due to generated charge carriers and not photon based.

A very strong effect on the improvement potential has the native oxide. HF-dipped samples showed improvements around 25%, whereas native oxide B showed up to 60% and native oxide A topping above 200%. Very promising is the fact that equally processed samples even in different batches show comparable results for lifetime measurements after LIC. Table 1 shows the characteristic findings.

Table 1. Exemplary results of wafers before / after LIC treatment

Sample preparation	τ_{eff} as processed [µs]	τ_{eff} after 60 s LIC [µs]	Δ [%]
SiN_x/SiO_2 stack on HF-dipped FZ p-type	175	217	+ 24
SiN_x/SiO_2 stack on native oxide on FZ p-type	334	1147	+ 243
SiN_x/SiO_2 stack on native oxide on FZ n-type	2820	2770	- 1.8

The same layer system deposited on n-type material shows a minor reduction in lifetime when exposed to the LIC treatment. This effect will be discussed later in combination with the results obtained by corona charging. With high quality FZ material used, there should be no change in the bulk material. The reduced effect on the HF dipped sample leads to the suggestion that the dielectric is also not responsible for the change. The silicon / dielectric interface with the presence of a native oxide seems to be the critical point. For further insight into the processes in n- and p-type material corona charging experiments are performed.

With corona charging one can influence the amount of charges on the surface and thereby the passivation quality of lifetime samples. If charges with the same polarity as the fixed charges of the dielectric are used, in principle the passivation could be improved as more minority carriers are repelled from the recombinative surface and vice versa. Table 2 shows the impact of corona charging on measured lifetime.

Table 2. Corona charging results on n- and p-type FZ

Sample treatment	τ_{eff} as processed [µs]	τ_{eff} charged [µs]	τ_{eff} IPA rinsed [µs]	τ_{eff} 60 s LIC [µs]
SiN_x/SiO_2 on p-type - 10 kV for 40 s	903	313	1280	
SiN_x/SiO_2 on p-type - 15 kV for 40 s	841	333	218	
SiN_x/SiO_2 on p-type + 15 kV for 40 s	852	1050	100	830
SiN_x/SiO_2 on n-type - 15 kV for 40 s	2892	2380	3062	
SiN_x/SiO_2 on n-type + 15 kV for 40 s	3004	3185	1891	2905

For voltages up to - 10 kV for p-type and - 15 kV for n-type the samples could be recovered to, or even be enhanced above their initial value after rinsing the wafers in IPA. With higher voltages a degradation after rinsing can be seen. The lifetime of the degraded samples recovers more or less to the initial value after about 4 h in the dark. In the case of negative charges the recovery within the first minutes seems not to be influenced by LIC whereas in the case of positive charges the recovery can be speeded up dramatically. Within 60 s the initial value is reached.

As shown by Jin et al. [11] corona charging generates atomic or protonic hydrogen that degrades a Si / SiO_2 interface. They further show that this degradation can be removed with a combination of RTA (rapid thermal annealing) or FGA (forming gas anneal). RTA uses high intensity lamps or lasers to achieve the desired process temperatures so it might be comparable with the light sources used in this work. To separate the effect of heat from the effect generated by photons, annealing tests on a hot plate were carried out. Up to 300°C these tests show no measurable increase or decrease in lifetime leading to the suggestion that mainly photons are responsible for the observed improvement.

Cartier [12] showed that atomic hydrogen can passivate and depassivate silicon dangling bonds in a Si / SiO_2 interface and that hydrogen generates additional interface states. This could explain the observed behavior of the samples as corona charging can push or pull charged hydrogen atoms to or from the interface. In the case of the improvement of the p-type and n-type sample after moderate negative charging and an IPA rinse there might be a reduction of defect generating hydrogen at the interface. All positive charged samples which suffered from lifetime degradation after charging could almost completely be recovered by a short LIC treatment (60 s). This leads to the assumption that in this case the charging induced hydrogen which is responsible for the lifetime degradation is compensated by LIC.

The behavior of the n-type sample can be attributed to the asymmetric positions of the donor and acceptor levels of hydrogen in the band gap [13]. This leads to significant differences in ease of passivation. As seen in Table 1 the measured lifetime is higher for the n-type sample although the doping is higher. In n-type material hydrogen is usually not found as H^+ whereas in p-type material it is. Initially n-type showed a slightly negative effect on LIC. After positive charging it also shows an improvement (1891 µs to 2905 µs). As Jin [11] stated that corona charging induces protonic hydrogen at the interface, the assumption is that this protonic hydrogen which creates interface states is compensated by LIC. In the case of positive charging of the n-type and p-type sample there might be protonic hydrogen from the passivation layer induced to the interface. It seems like this hydrogen can be pushed to the bulk by LIC because in the case of negative charging where H^+ is induced to the interface from the bulk LIC shows no positive effect as it cannot diffuse back into the bulk.

4. Conclusion

Reproducible and long-time stable light induced curing of lifetime samples is observed for SiN_x/SiO_2 stacks. A homogeneous improvement of 100% and more in minority charge carrier lifetime could be measured which leads to surface recombination velocities as low as 10 cm/s on chemically polished p-type FZ wafers. Native silicon oxides below PECVD layers are found to be the main influencing factor for the strength of the observed effect and in this respect the investigated native silicon oxides show a behaviour comparable to a thermally grown SiO_2. The combination of lifetime and PL measurements, corona charging and annealing leads to the suggestion that the underlying effect of LIC takes place at the Si / SiO_2 interface and is a photo-induced curing process of defects with the incorporation of protonic hydrogen.

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