Presented at the 35th PVSC, June 20-25, 2010, Honolulu, Hawaii

Effect of a post-deposition anneal on Al_2O_3/Si interface properties

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ABSTRACT

While Al_2O_3 has been proven to provide an excellent level of surface passivation on all sorts of p-type doped silicon surfaces, the passivation mechanism of this layer and especially the influence of the post-deposition anneal on the Al_2O_3/Si interface properties is not yet completely understood. A great increase in the surface passivation is observed after a post-deposition anneal, i.e. a post-deposition anneal is mandatory to activate the surface passivation. Thus, the influence of this anneal on the interface properties, density of negative fixed charges Q_f and density of interface traps D_{it}, will be investigated and correlated to the measured minority carrier lifetime. In the case of plasma enhanced ALD, Q_f is already high in the as-deposited state and the annealing process only has a minor effect on Q_f (Q_f increases by 20-50 %, depending on the annealing temperature). The D_{it} however is strongly reduced by the post-deposition anneal, decreasing by two orders of magnitude. This large reduction in D_{it} is a prerequisite for benefiting from the strong field effect induced by the high density of negative charges of the Al_2O_3.

INTRODUCTION

In recent years Al_2O_3 has been proven to be capable of providing an excellent passivation on all sorts of p-type doped surfaces [1, 2]. Especially in photovoltaics this closes a gap, as an effective low-temperature passivation on *p*-type surfaces was missing in the past. A first application is the reduction of the surface recombination at the rear side of *p*-type silicon solar cells. For this purpose Al_2O_3 is a promising alternative to thermally grown SiO_2. On p-type PERC solar cells several authors showed that Al_2O_3 is at least as effective for the rear side passivation as thermally grown, alnealed SiO_2 [3, 4]. Furthermore the realization of alternative solar cell concepts, e.g. on *n*-type silicon, might be enabled by the application of Al_2O_3 as well. Due to the effective passivation of the front side boron emitter by Al_2O_3, we were able to realize conversion efficiencies of 23.5% on *n*-type PERL solar cells. Thus, the properties of the Al_2O_3 passivation using different deposition techniques (ALD, PECVD, rf sputtering) are being investigated by various authors [5-10]. However, the passivation mechanism of Al_2O_3 is not yet completely understood. In general, two different strategies for the passivation of surfaces, i.e. the reduction of the surface recombination, exist: (i) reduction of the interface trap density (D_{it}) and (ii) field effect passivation due to fixed charges (Q_f) within the dielectric passivation layer. Particularly a very high density of fixed negative charges, Q_f, (up to -10^{13} cm^{-3}) is one of the special characteristics of the Al_2O_3. However, to be able to reach a high level of surface passivation as is reported for Al_2O_3, in addition to an effective field effect passivation, the density of interface traps has to be greatly reduced as well. Indeed, low densities of interface traps, D_{it}, in the range of ~8×10^{10} to 2×10^{11} cm^{-2} eV^{-1} are reported [6, 11]. However, in the as-deposited state, no passivation is provided by the Al_2O_3 at all, regardless of the deposition method. An additional post-deposition anneal is required to activate the surface passivation. In practice the initial carrier lifetime of 1 µs increases to >2 ms after annealing at 425°C (1 Ω cm p-type FZ-Si). Thus, substantial changes in the Al_2O_3 layer itself or at the silicon interface occur during the post deposition anneal. The influence of this post-deposition anneal on the Al_2O_3/Si interface properties (density of negative fixed charges Q_f as well as on the density of interface traps D_{it}) is investigated within this work and will be correlated to the measured minority carrier lifetime. A thin (~1–2 nm) layer of SiO_x is often observed to be present at the silicon interface or to develop during the anneal process [1, 12], i.e. an Al_2O_3/SiO_x-Si interface. In the following, however, the interface will be referred to as Al_2O_3/Si.

EXPERIMENTAL

For the investigation of the Al_2O_3/Si interface properties MIS (metal/insulator/semiconductor) capacitor structures were prepared on shiny etched 1 Ω cm p-type FZ Si(100) substrates with a thickness of 250 µm. D_{it} and Q_f of the MIS samples were determined by high-frequency and quasistatic capacitance-voltage (C-V) measurements [13]. To measure the effective minority carrier lifetime (τ_{eff}), symmetrically coated lifetime samples have been processed on the same substrate material. These samples were characterized by the Quasi Steady State PhotoConductance (QSSPC) method [14]. From these lifetime measurements the maximum effective surface recombination velocity S_{eff} was determined by [15]

$$\frac{1}{\tau_{eff}} = \frac{1}{\tau_{bulk}} + \frac{1}{W/(2S_{eff}) + W^2/(D\pi^2)} \quad (1)$$

with W the wafer thickness and D the minority charge carrier diffusion constant. Assuming an infinite bulk lifetime τ_{bulk}, we therefore determine an upper limit to S_{eff}. To get some information of a possible change in the layer composition by the annealing process FTIR

measurements have been performed on the symmetrically coated lifetime samples as well.
The dielectric passivation layer Al_2O_3 (30 nm) was deposited by PE-ALD (OpAL™, Oxford instruments) at a temperature of 180°C. Prior to the Al_2O_3 deposition the samples were cleaned by a HNO_3 etch followed by a short HF (1%) dip. The samples then underwent a 25 min post-deposition anneal on a hotplate in ambient atmosphere at a temperature ranging from 300°C to 550°C. For the MIS structure aluminium dots (700 µm) were thermally evaporated through a shadow mask. Eutectic gallium-indium was used to ensure a good rear side contact of the MIS structure.

RESULTS AND DISCUSSION

The measured injection-level-dependent minority carrier lifetime of the lifetime samples which were coated on both sides with Al_2O_3 in Figure 1 shows an extreme influence of the post deposition anneal on the Al_2O_3 surface passivation. Whereas in the as-deposited state with a measured lifetime of ~1 µs no passivation at all is provided by the Al_2O_3, the measured lifetime increases with increasing annealing temperature up to ~2.3 ms, a value close to the Auger-limit [16], at a temperature of ~425°C. For higher annealing temperatures above 425°C the lifetime decreases again. However, this decrease is only small, after annealing at 550°C the lifetime is still well above 1 ms (1.2 ms @ $\Delta n = 10^{15}$ cm^{-3}).

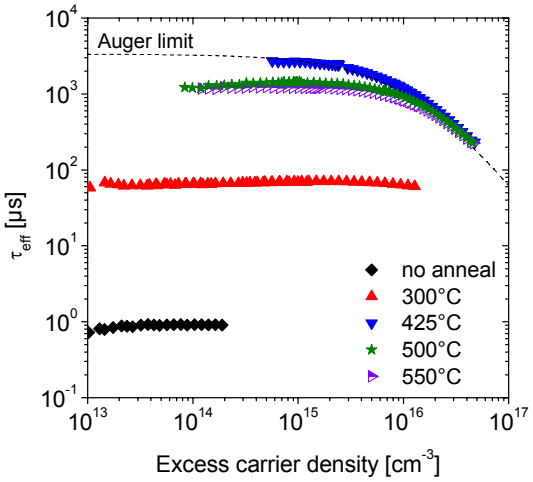

Figure 1 Injection-dependent minority carrier lifetime of the PE-ALD Al_2O_3 passivated lifetime samples in the as-deposited state as well as after annealing (hotplate) at different temperatures.

To relate this strong dependence of the passivation quality of the Al_2O_3 passivation on the post deposition anneal to the interface properties, MIS structures were measured with C-V techniques. Figure 2 shows the high-frequency and quasistatic C-V curves of the PE-ALD Al_2O_3 passivated MIS samples for different post deposition annealing temperatures.

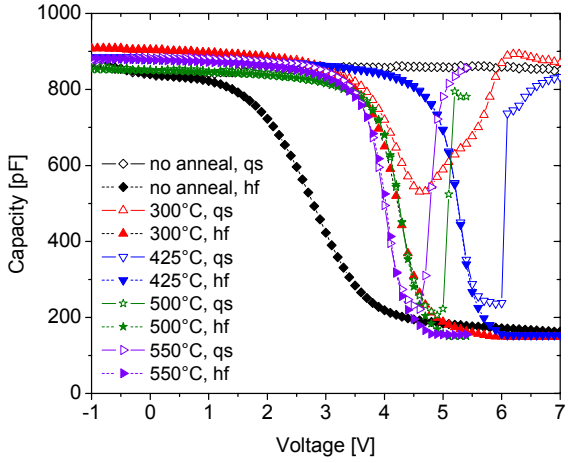

Figure 2 High-frequency (hf) and quasistatic (qs) capacitance-voltage measurements of PE-ALD Al_2O_3 passivated MIS samples (1 Ω cm *p*-type FZ) after post-deposition anneal (hotplate) at different temperatures.

The accumulation and inversion capacitance of all four MIS structures is consistent with the values expected of such samples. The accumulation capacitance assumed equal to the insulator capacitance, is measured to be $C_{insulator}$ = 880 ± 30 pF, which amounts to the Al_2O_3 having a dielectric constant of 8.1 ± 0.3, as calculated from the area of the metal (A = 0.0038 cm^2) and the thickness of the Al_2O_3 ($t_{insulator}$ = 30 nm), from

$$\varepsilon_i = \frac{C_{insulator}\, t_{insulator}}{A} . \qquad (2)$$

While the accumulation and inversion capacitance are similar for all four MIS structures, the C-V curves also exhibit pronounced differences in relation to (i) translation on the X-axis due to charge in the dielectric; (ii) the difference between quasistatic and high frequency curves due to the interface states; and (iii) "stretch-out", also due to interface states [13].
The fixed charge in the dielectric layer, Q_f, can be determined from the flatband voltage, V_{fb}, (neglecting the influence of Q_{it}) from the high-frequency C-V curve by

$$Q_f = (\Phi_{ms} - V_{fb})\, C_{insulator} \qquad (3)$$

with Φ_{ms} being the difference between the metal and silicon work functions, and where Q_f is assumed to reside at the Al_2O_3/Si interface. The flatband voltage increases from 2.8 V in the as-deposited state up to 4.9 V at an annealing temperature of 425°C, the charge densities are -6.0×10^{12} cm^{-2} and -9.9×10^{12} cm^{-2} respectively. For higher

post-deposition annealing temperatures the shift in the flatband voltage is smaller, and thus Q_f is comparatively smaller in magnitude as well (see Fig. 3a).

A number of methods are available for extracting the density of interface states D_{it}. One of the more accurate and very common methods for the extraction of D_{it} is based on the comparison of the high-frequency and quasistatic C-V curve (Castagne and Vapaille [17]). The smaller the difference between the two C-V curves, the lower is the density of interface traps. Thus, by regarding the original curves it can be qualitatively stated that the D_{it} decreases with increasing temperature of the post-deposition anneal. We have used three different methods to determine D_{it}: (i) from the high-frequency [18], (ii) from the quasistatic [19] and (iii) from the comparison of high-frequency and quasistatic C-V curves [17]. An overview over the data extracted from the C-V curves (Q_f, D_{it} at midgap) as well as the respective minority carrier lifetimes (at $\Delta n = 10^{15}$ cm^{-3}) is shown in Figure 3. As mentioned earlier, up to ~425°C the density of negative charges increases with increasing temperature of the post-deposition anneal and decreases again for higher temperatures. In general, with a value of -6.0×10^{12} cm^{-2} already in the as-deposited state the density of negative charges is relatively high. The increase of the charge density, due to the post deposition anneal, therefore only corresponds to a factor of 1.6. D_{it} at midgap however decreases with increasing post deposition annealing temperature by two orders of magnitude. In the as-deposited state, due to the flat progression of the quasistatic C-V curve, the D_{it} could only be extracted from the high-frequency C-V curve. With a value of $\sim3\times10^{13}$ cm^{-2} eV^{-1} at midgap, the D_{it} in the as-deposited state is very high. However, by the post deposition annealing this high D_{it} can be lowered by approximately two orders of magnitude, to $\sim1.3\times10^{11}$ cm^{-2} eV^{-1} at midgap, by annealing at a temperature of 500°C. The different methods for the extraction of D_{it} here result in comparable D_{it} values, suggesting a reliable D_{it} measurements. Regarding the measured minority carrier lifetime, shown in Fig. 3c, it can be seen that the lifetime varies by orders of magnitude as well. The increase of the minority carrier lifetime with increasing annealing temperature (up to 425°C) thus can be related to the improvement of the interface, i.e. the reduction of the density of interface traps. This becomes particularly obvious by the comparison of the samples annealed at 300°C and 500°C. Those samples having a comparable density of negative interface charges ($Q_{f,300} = -8.2\times10^{12}$ cm^{-2} and $Q_{f,500} = -8.3\times10^{12}$ cm^{-2} respectively, $Q_{f,500}/Q_{f,300} = 1.02$), show a pronounced difference in the density of interface traps of more than one order of magnitude ($D_{it,300}/D_{it,500} = 26.0$). Thus, as the density of fixed charges of these samples is nearly the same and the effective surface recombination velocity is proportional to D_{it}, the ratio $S_{eff,300}/S_{eff,500}$ should be the same as $D_{it,300}/D_{it,500}$. In fact, taking the quotient $S_{eff,300}/S_{eff,500}$ this results in a value of 22.1, which is close to the value that has been calculated for $D_{it,300}/D_{it,500}$ (26.0). Thus, it can be stated, that the great improvement of the surface passivation of the Al_2O_3 by a post-deposition anneal is mainly related to the reduction of D_{it}. A sufficiently low level of D_{it} therefore is necessary to benefit from the field effect induced by the negative interface charges.

It has already been reported that a density of negative charges in the range of -5×10^{12} cm^{-2} is sufficient for an effective field effect passivation [20, 21]. Higher charge densities therefore only lead to modest improvements of the passivation. This is also confirmed by the samples annealed at 425°C and 500°C, which have almost identical values for D_{it}. The effect of the different charge densities (-9.9×10^{12} cm^{-2} and -8.3×10^{12} cm^{-2}) of these samples is only moderate (2660 µs and 1460 µs respectively).

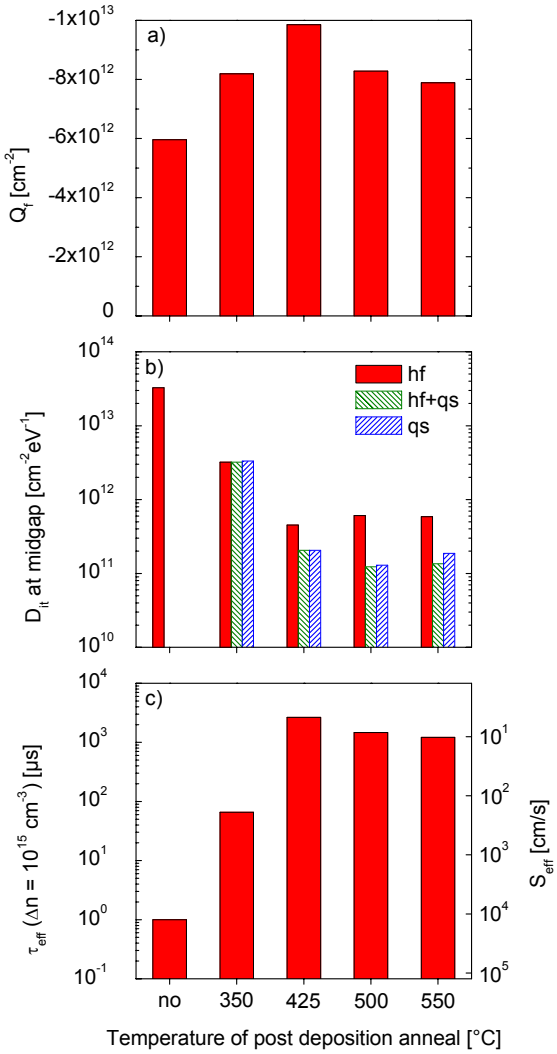

Figure 3 Charge density (Q_f), interface defect density (D_{it}) at midgap and effective lifetime (τ_{eff}) of the annealed samples passivated by PE-ALD Al_2O_3. Q_f and D_{it} were extracted from the C-V data, τ_{eff} was measured on identically processed lifetime samples (1 Ω cm *p*-type FZ Si).

These observed significant changes in the interface properties indicate that substantial changes in the physical Al_2O_3/Si interface occur. For non-annealed Al_2O_3 layers, i.e. in the as-deposited state, different observations have been reported. An abrupt interface between Al_2O_3 and Si is reported for Al_2O_3 layers deposited by low pressure MOCVD and thermal ALD [12, 22]. For plasma assisted ALD deposited Al_2O_3 layers however a thin (1.2 nm) interfacial SiO_x is reported [1], that has been attributed to the exposure of the substrate to the O_2 plasma during the first ALD cycles. An annealing process however leads to the formation of a thin interfacial SiO_x, independent of the initial interface [1, 12]. The interfacial SiO_2 layer is supposed to play a central role with respect to the Al_2O_3 surface passivation. Johnson *et al.* [23] and Kimoto *et al.* [24] have already shown that an interfacial SiO_2 is crucial for the formation of the negative interface charges. Further, SiO_2 is known to effectively reduce the D_{it} at the SiO_2/Si interface [25]. Thus, such a thin interfacial SiO_2 might be responsible for the low D_{it} of the Al_2O_3 passivation after the post-deposition anneal.

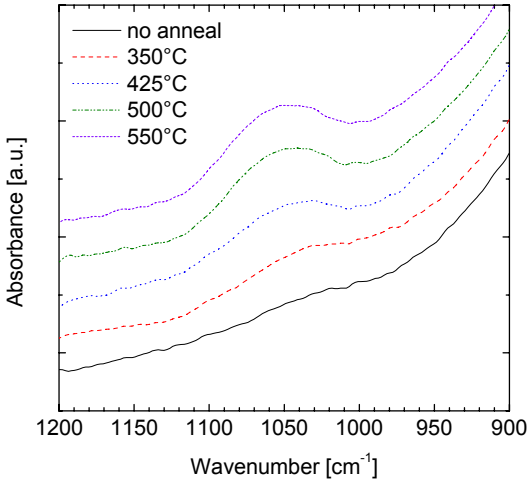

Figure 4 FTIR spectra of the ALD Al_2O_3 passivated samples annealed at different temperatures. After annealing the peak related to the asymmetric stretch of the O in Si-O-Si bridging bonds can be observed and increases with increasing annealing temperature.

The FTIR measurements that were performed on the Al_2O_3 passivated lifetime samples with increasing annealing temperature show the evolution of an absorption band at 1060 cm^{-1}. This absorption band is known to originate from the TO mode arising from the asymmetric stretching of O in Si-O-Si in thermally grown amorphous silicon dioxide (a-SiO_2) [26, 27]. Thus, this indicates that for the annealed samples an interfacial SiO_2 layer exists between the Al_2O_3 and the silicon substrate. However for the as-deposited sample this absorption band cannot be observed, indicating a different chemical configuration or even a non-existence of an intermediate SiO_2 layer. Thus, by the correlation to the measured effective lifetime as well as the D_{it} it can be stated that the interfacial SiO_x plays a central role in the passivation of silicon surfaces by Al_2O_3.

SUMMARY

In summary, the Al_2O_3/Si interface properties, D_{it} and Q_f have been measured as a function of the temperature of the post-deposition annealing and have been correlated to the minority carrier lifetime. Both, Q_f and D_{it} are affected by the post deposition anneal. However, even in the as-deposited state the PE-ALD deposited Al_2O_3 shows a sufficiently high density of negative charges and the impact of the annealing on the charge density is only moderate. From C-V measurements, Q_f increases from -6.0×10^{12} cm^{-2} in the as-deposited state to -9.9×10^{12} cm^{-2} after annealing at a temperature of 425°C ($Q_{f,425}/Q_{f,as\text{-}dep}$ = 1.6). The initially high D_{it} at midgap, however is strongly reduced (two orders of magnitude) with increasing temperature of the post deposition annealing up to 550°C. The minority carrier lifetime at the same time increases from 1 µs in the as deposited state to >2 ms after annealing at 425°C. Thus the great improvement of the Al_2O_3 surface passivation by the post deposition annealing is mainly related to the strong improvement of the D_{it} at the Al_2O_3/Si interface. A sufficiently low D_{it} therefore is a prerequisite to benefit from the strong field effect induced by the high density of negative charges of the Al_2O_3. FTIR measurements indicate that a thin interfacial layer of SiO_2 is formed during the annealing process. This interfacial SiO_2 layer is supposed to play a central role with respect to the Al_2O_3 surface passivation and further investigations have to be performed to examine the function of this layer on a microscopic scale.

ACKNOWLEDGEMENT

J. B. acknowledges the DAAD for financial support. The work was supported by the German Federal Ministry for the Environment, Nature Conservation and Nuclear Safety under contract number 0329849A “Th-ETA”.

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