Surface passivation by Al₂O₃ and a-SiN_x: H films deposited on wet-chemically conditioned Si surfaces

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Surface Passivation by Al₂O₃ and *a*-SiN_x:H Films Deposited on Wet-Chemically Conditioned Si Surfaces

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The surface passivation of *p*- and *n*-type silicon by different chemically grown SiO₂ films (prepared by HNO₃, H₂SO₄/H₂O₂ and HCl/H₂O₂ treatments) was investigated after PECVD of *a*-SiN_x:H and ALD of Al₂O₃ capping films. The wet chemically grown SiO₂ films were compared to thermally grown SiO₂ and the surface passivation was benchmarked against single-layer *a*-SiN_x:H and Al₂O₃ films deposited on HF-last Si surfaces. Directly after PECVD and ALD the surface passivation was found to be similar for all chemically grown SiO₂ stacks and higher than for the single-layer films. After annealing at 400°C the level of surface passivation improved but remained similar for the chemically grown SiO₂ stacks. Corona charging experiments on the annealed chemically grown SiO₂/Al₂O₃ stacks revealed that the fixed charge density, i.e. the field-effect passivation, was lower compared to single-layer Al₂O₃ films whereas the chemical passivation was found to be higher. The surface passivation was also investigated as a function of the annealing time. Chemically grown SiO₂ stacks achieved the maximum level of surface passivation after annealing for half a minute which is different from the stacks with *a*-SiN_x:H and Al₂O₃ films deposited on thermally grown SiO₂ or HF-last Si surfaces which required considerably longer annealing times.

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Within Si photovoltaics, manufacturing of solar cells requires surface conditioning and/or cleaning steps of the Si wafers prior to passivation processes to assure high energy conversion efficiencies. The most common conditioning process is H-termination of Si surfaces realized by hydrofluoric acid treatments (HF-dip). The surface passivation can be subsequently realized by depositing dielectric layers such as single-layer SiO₂,¹⁻³ *a*-SiN_x:H⁴⁻¹¹ and Al₂O₃ films¹²⁻²⁰ as well as by stacks consisting of these films, e.g. SiO₂/*a*-SiN_x:H,²¹⁻²⁷ SiO₂/Al₂O₃^{19,28-34} and Al₂O₃/*a*-SiN_x:H.^{19,35-39} In contrast to exposing the Si wafers to HF yielding an H-terminated Si surface other wet chemical treatments can oxidize the Si resulting in an OH-terminated ultrathin SiO₂ film. This happens, for example, when treating the Si by HNO₃,⁴⁰⁻⁴³ NH₄/H₂O₂,⁴⁴⁻⁴⁷ HCl/H₂O₂,^{40,43,45-47} or H₂SO₄/H₂O₂.^{40,43,48} It should be noted that such an ultrathin SiO₂ film can also be present when passivating an H-terminated Si surface as a native and/or interfacial SiO₂ film can grow unintentionally when H-terminated Si surfaces are exposed to the ambient (for a significant amount of time)^{2,49} or when oxides (such as Al₂O₃) are deposited on the Si.^{14,19,50,51}

From recent studies it is known that an interfacial SiO₂ layer between the passivation material and the Si has a significant effect on the surface passivation of Al₂O₃ and *a*-SiN_x:H films as shown for thin ALD, PECVD and thermally grown SiO₂ interlayers.^{25,29-31,33} More specifically, from the studies of Dingemans et al. it has been clearly observed that the level of field-effect passivation caused by fixed charges in the passivation material depends heavily on the SiO₂ interlayer thickness while the level of chemical passivation remains high.^{25,32} This is of interest for solar cells as it might provide identical passivation schemes for *n*⁺- and *p*⁺-type Si surfaces (so-called symmetrical passivation) which are relevant when passivating both emitter and surface field surfaces at once (e.g., for passivating both sides of conventional cells or the back side of interdigitated back contact cells).^{52,53} The interest in such symmetrical passivation schemes has motivated recent studies on the passivation of Si by stacks of chemically grown SiO₂ films and *a*-SiN_x:H and Al₂O₃ films. This would provide a means to combine a relatively straightforward and economically viable method of surface cleaning/conditioning with the formation of a very thin SiO₂ film and the passivation of the surface.^{43,46-48}

In this article we extend previous work by carrying out a systematic investigation of the surface passivation induced by stacks of chemically grown SiO₂ films and PECVD *a*-SiN_x:H and ALD Al₂O₃

capping films. This is done for three different wet chemically grown SiO₂ films such that the passivation performance induced by the *a*-SiN_x:H and Al₂O₃ films can be directly compared for differently prepared surfaces and for the two dielectric films. A main difference between these passivation films is that they contain fixed charges with opposite polarity, i.e., positive for *a*-SiN_x:H negative for Al₂O₃. Moreover, the surface passivation of *a*-SiN_x:H and Al₂O₃ stacks containing chemically grown SiO₂ films is compared to one of stacks with thermally grown SiO₂ and with the passivation induced by the films when directly deposited on HF-last Si. In these aspects, the results described in this article distinguish themselves from those in our previous publication.⁴³ Additionally, the Al₂O₃ stacks were investigated by corona charging experiments to reveal the role of chemical passivation and field-effect passivation. This study was complemented by second harmonic generation analysis which also yields insight into the field-effect passivation. Another aspect addressed in this work is the improvement of surface passivation performance after annealing for different durations. This motivated by the fact that annealing times <10 min are desired from a technological and economical perspective. In this work we show that wet chemically grown SiO₂ stacks yield the advantage that maximum surface passivation levels can be reached well within 2 min of annealing.

Experimental

The surface passivation was evaluated on phosphorous doped 2-3 Ω · cm *n*-type float zone (FZ) wafers with a thickness of 200 μm and on boron doped 10-12 Ω · cm *p*-type Czochralski (Cz) Si(100) wafers with a thickness of 160 μm. The saw-damage of the Cz wafers was removed in KOH. Afterwards the *p*- and *n*-type wafers received a standard RCA cleaning procedure. The wafers passivated by the direct deposition of single-layer films on the H-terminated Si surfaces resulting from the RCA cleaning are referred to as “HF-last” for brevity. The rest of the wafers were exposed to a wet chemical or thermal oxidation process. For the wet chemical oxidation process three different solutions were used: 65% nitric acid (HNO₃), hydrochloric acid with hydrogen peroxide (HCl/H₂O₂) with 1:1:10 at 80°C and a sulphuric acid mixture with hydrogen peroxide (H₂SO₄/H₂O₂) with 1:5 at 140°C. The samples were treated for 10 min with the wet chemical solutions. The thermal oxidation took place at 900°C in wet ambient and resulted in a film thickness of 200 nm as measured by spectroscopic ellipsometry. All wafers were covered by PECVD *a*-SiN_x:H films or ALD Al₂O₃ films. The *a*-SiN_x:H films were prepared at 350°C by a linear microwave plasma source. The *a*-SiN_x:H film thickness was 70 nm and the refractive index was *n* = 2.05 (at 2 eV) as

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determined by spectroscopic ellipsometry. By Rutherford backscattering spectroscopy the ratio of $[N]/[Si]$ was found to be 1.14. By elastic recoil detection the atomic hydrogen concentration was found to be 9 at.%. The Al_2O_3 films were deposited by an ALD process at 220°C using $Al(CH_3)_3$ and O_3 as reactants. The process consisted of 330 ALD cycles that resulted in a film thickness of about 30 nm. One set of wafers was annealed at 400°C in N_2 atmosphere for 10 min. In addition, an experiment was carried out in which the annealing time was varied between 30 s and 20 min.

The level of surface passivation was expressed by the injection dependent effective minority carrier lifetime τ_{eff} that was measured with the photoconductance decay method using a Sinton instrument WCT 120 system.⁵⁵ The surface recombination velocity S_{eff} was calculated from the effective lifetime at an injection level of $\Delta n = 10^{14} \text{ cm}^{-3}$. The S_{eff} -values were evaluated as an upper limit, i.e. as $S_{eff,max} = W/2 \cdot (\tau_{eff}^{-1} - \tau_{Auger}^{-1})$, with W representing the wafer thickness and by considering the Auger lifetime τ_{Auger} as proposed by Kerr.⁵⁶

The density of the fixed charges Q_f incorporated in the dielectric passivation films was measured by corona charging experiments.^{10,57} This method combines the deposition of corona charges^{58,59} with Kelvin probe measurements of the surface voltage⁶⁰ and photoconductance decay measurements to extract the corona charge density Q_C and the corresponding surface passivation, respectively. The accuracy of the measurement is related to the uniformity of the deposited corona charges which was fairly good, i.e., 10–15% within a circle area with a diameter of 12 cm. The position of the peak value of $S_{eff,max}$ in the $S_{eff,max}(Q_C)$ -plot reflects the point where Q_f is compensated by the deposited corona charges. From this value of Q_C , the number density of Q_f incorporated in the passivation films can be extracted. The $S_{eff,max}$ -values obtained in the corona charging experiments were calculated from the effective lifetime at an injection level of $\Delta n = 3 \cdot 10^{14} \text{ cm}^{-3}$ to assure accurate photoconductance decay measurements also at low lifetime values.

The field-effect passivation was also studied with the method of optical second harmonic generation (SHG) that is sensitive to electric fields.⁶¹ Electric fields are present in the space charge region at the Si surface, e.g. created by the Q_f of passivation films.⁶² The amplitude of the SHG intensity of the peak centered at the SHG photon energy of 3.4 eV is a measure for the electric-field at the Si surface when probing Si surfaces covered by dielectric films such as Al_2O_3 .⁶³

Results and Discussion

Surface passivation quality of Al_2O_3 and $a\text{-SiN}_x\text{:H}$ stacks.— The surface recombination velocity as a measure for the surface passivation quality was determined for Al_2O_3 and $a\text{-SiN}_x\text{:H}$ stacks with chemically and thermally grown SiO_2 films and for single-layer Al_2O_3 and $a\text{-SiN}_x\text{:H}$ films deposited on HF-last Si surfaces. In Table I the $S_{eff,max}$ -values are listed as obtained directly after deposition of the Al_2O_3 and $a\text{-SiN}_x\text{:H}$ films and after annealing at 400°C. The measurement uncertainty of the $S_{eff,max}$ -values was about 15%. The thermally grown SiO_2/Al_2O_3 stacks resulted in low $S_{eff,max}$ -values of 84 cm/s and the chemically grown SiO_2/Al_2O_3 stacks in $S_{eff,max}$ -values between 22 and 324 cm/s directly after ALD process. No clear correlation between the used wet chemical treatments and the level of surface passivation was

observed. The $S_{eff,max}$ -values directly after Al_2O_3 deposition on HF-last Si surfaces were significantly higher, up to 610 cm/s, than those for the chemically grown SiO_2/Al_2O_3 stacks. For the Al_2O_3 coated, HF-last p -type Cz samples a larger spread in the $S_{eff,max}$ -values was observed than for the HF-last n -type Fz samples. Some values for this p -type Si were similar to those obtained for the chemically grown SiO_2/Al_2O_3 stacks. This can possibly be attributed to a longer time delay between the HF dip and deposition of the Al_2O_3 films for these samples causing a growth of native oxide films that have a thickness similar to those of the chemically grown SiO_2 films of this work.^{44,44} Apparently a thin chemically grown or natively grown SiO_2 film underneath the Al_2O_3 layers can result in similar $S_{eff,max}$ -values.

Annealing of the chemically grown SiO_2/Al_2O_3 stacks decreased the $S_{eff,max}$ -values and resulted in quite similar values ranging between 2 and 14 cm/s. The thermally grown SiO_2/Al_2O_3 stacks showed a similar level of $S_{eff,max}$ of 14 cm/s. The uniformity of the surface passivation of the chemically grown SiO_2/Al_2O_3 stacks was about 10 to 15% as obtained by photoluminescence imaging using the 6 inch p -type Cz samples. Single-layer Al_2O_3 films deposited on HF-last Si surfaces showed low surface recombination velocities of $S_{eff,max} = 2\text{--}6$ cm/s after anneal. These surface recombination values are in the same range as those obtained in earlier studies, e.g. reported by Hoex et al. with $S_{eff,max} = 2$ cm/s.¹⁴

For the samples with $a\text{-SiN}_x\text{:H}$ films the highest recombination velocity was obtained for single-layer films deposited on HF-last Si surfaces with approx. 400–460 cm/s achieved directly after deposition. The chemically grown $SiO_2/a\text{-SiN}_x\text{:H}$ stacks gave $S_{eff,max}$ -values below 47 cm/s and the thermally grown $SiO_2/a\text{-SiN}_x\text{:H}$ stacks yielded a slightly higher value of 67 cm/s. The annealing improved the level of surface passivation of all $a\text{-SiN}_x\text{:H}$ stacks. The best surface passivation was observed for the chemically grown $SiO_2/a\text{-SiN}_x\text{:H}$ stacks with $S_{eff,max}$ -values down to 4 cm/s.

The comparison of the different $a\text{-SiN}_x\text{:H}$ and Al_2O_3 stacks revealed that before annealing the $a\text{-SiN}_x\text{:H}$ -based stacks resulted in lower recombination velocities compared to the Al_2O_3 based stacks. Among other things, this experimental finding can probably be attributed to the different deposition temperatures for PECVD and ALD. PECVD was carried out at 350°C, i.e. at only 50°C lower than the annealing temperature, whereas ALD was carried out at 200°C. Higher deposition temperatures enable a more effective hydrogenation process of the Si surface and consequently enhance the deactivation of Si dangling bonds that otherwise act as recombination active centers.^{64,67}

When comparing the surface passivation results of the chemically grown SiO_2/Al_2O_3 stacks with the $a\text{-SiN}_x\text{:H}$ based stacks after annealing a quite equal level of surface passivation can be observed. No correlation between wet chemical solution used for the growth of the SiO_2 films and the surface passivation quality can be distinguished.

In the case of HF-last Si surfaces the annealed Al_2O_3 films showed higher passivation qualities than the $a\text{-SiN}_x\text{:H}$ films. The chemical passivation after annealing was reported to be similar for Al_2O_3 and $a\text{-SiN}_x\text{:H}$ films with mid-gap defect densities of about $10^{11} \text{ eV}^{-1} \text{ cm}^{-2}$.^{3,65} In contrast to the chemical passivation, the field-effect passivation was found to be different as evident from the measured

Table I. Maximum surface recombination velocity $S_{eff,max}$ (cm/s) extracted from the effective lifetime τ_{eff} at $\Delta n = 10^{14} \text{ cm}^{-3}$ for wet chemically grown and thermally grown SiO_2 as well as HF-last Si substrates. The $S_{eff,max}$ -values are obtained directly after ALD of Al_2O_3 and PECVD of $a\text{-SiN}_x\text{:H}$ (referred to “As-dep.”) and after an additional anneal step at 400°C for 10 min in N_2 . The measurement uncertainty of the $S_{eff,max}$ -values was ~15%.

		HNO ₃ SiO ₂		HCl/H ₂ O ₂ SiO ₂		H ₂ SO ₄ /H ₂ O ₂ SiO ₂		HF-last Si		Thermal SiO ₂
		<i>p</i> -Cz Si	<i>n</i> -FZ Si	<i>p</i> -Cz Si	<i>n</i> -FZ Si	<i>p</i> -Cz Si	<i>n</i> -FZ Si	<i>p</i> -Cz Si	<i>n</i> -FZ Si	<i>n</i> -FZ Si
Al_2O_3	As-dep.	22	143	114	47	324	91	164–400	609	84
	Annealed	3	14	2	4	5	8	2	6	14
$a\text{-SiN}_x\text{:H}$	As-dep.	15	18	47	17	27	22	461	393	67
	Annealed	4	14	5	11	4	25	31	23	22

fixed charge densities of $Q_f = 2 \pm 0.5 \cdot 10^{12} \text{ cm}^{-2}$ for $a\text{-SiN}_x\text{:H}$ films and $Q_f = -6.5 \pm 0.5 \cdot 10^{12} \text{ cm}^{-2}$ for Al_2O_3 films. These values were obtained by corona charging experiments on the films considered in this work (see below). Consequently the difference in surface passivation of single-layer $a\text{-SiN}_x\text{:H}$ and Al_2O_3 films can be attributed mainly to differences in field-effect passivation.

Surface passivation mechanism of Al_2O_3 stacks.— For the chemically grown and thermally grown SiO_2 films in stacks with Al_2O_3 the layer structure is $\text{Si}/\text{SiO}_2/\text{Al}_2\text{O}_3$. This is basically also the case for single-layer Al_2O_3 films deposited on HF-last Si surfaces because the deposition of the Al_2O_3 leads to a thin interfacial SiO_2 film with a typical thickness of about 1.2 nm.^{14,19,50,51} The thickness of this interfacial SiO_2 film is in the same range as those of the chemically grown SiO_2 films which have thickness values of 0.5–2 nm as found by spectroscopic ellipsometry. Recently it was reported that even very thin interfacial SiO_2 films in the range of a few nanometers have a significant effect on the field-effect passivation of Al_2O_3 films.^{29–31} Consequently it was decided to investigate the surface passivation mechanisms of the Al_2O_3 stacks reported in this work by corona charging experiments in order to distinguish between the role of chemical and field-effect passivation. Corona charging could not be employed successfully to the samples coated with $a\text{-SiN}_x\text{:H}$ films due to the too low electrical resistivity of the $a\text{-SiN}_x\text{:H}$ films which preclude the surface charging of these films by corona charges.¹⁰ Corona charging experiments were carried out on the n -type Fz samples directly after the ALD process as well as after annealing. However directly after ALD the corona charging experiments turned out not to be feasible on single-layer Al_2O_3 films and stacks with SiO_2 synthesized in HNO_3 because the τ_{eff} -values were too low for an accurate measurement with the photoconductance decay method that is part of the corona charging experiments. The corona charging results of the chemically grown $\text{SiO}_2/\text{Al}_2\text{O}_3$ stacks are shown in Fig. 1 as a plot of $S_{\text{eff,max}}$ as a function of Q_C . The change of $S_{\text{eff,max}}$ with Q_C reflects the transition of the surface carrier concentration from inversion conditions via flatband conditions to accumulation conditions. This transition is caused by the Q_C that compensates the Q_f of the passivation layers. In the case of flatband conditions the surface recombination is at maximum leading to a peak value of $S_{\text{eff,max}}$ in the $S_{\text{eff,max}}(Q_C)$ -plot. At this point the peak value of $S_{\text{eff,max}}$ can be regarded as a measure for the chemical passivation due to absence of the field-effect passivation. Furthermore the nullification of the field-effect passivation with $Q_C = -Q_f$ allows the extraction of the number density of the fixed charges in the passivation material. The $\text{H}_2\text{SO}_4/\text{H}_2\text{O}_2$ -based $\text{SiO}_2/\text{Al}_2\text{O}_3$ stacks resulted in a peak value of $S_{\text{eff,max}}$ of about 1670 cm/s and a Q_f of $-2.6 \pm 0.2 \cdot 10^{12} \text{ cm}^{-2}$ as shown in Fig. 1. The $\text{HCl}/\text{H}_2\text{O}_2$ -based $\text{SiO}_2/\text{Al}_2\text{O}_3$ stacks showed a

Figure 1. Corona charging experiments of chemically grown $\text{SiO}_2/\text{Al}_2\text{O}_3$ stacks on n -type Fz Si to determine the fixed charge density Q_f of the films. The Q_f -values can be extracted from the value of Q_C yielding the maximum value of the $S_{\text{eff,max}}$. The level of chemical passivation is represented by the maximum value of $S_{\text{eff,max}}$ reached. The experiments were done directly after ALD of Al_2O_3 films and after an anneal step at 400°C for 10 min in N_2 .

Figure 2. Second harmonic generation (SHG) intensity as a function of the second harmonic photon energy for chemically grown $\text{SiO}_2/\text{Al}_2\text{O}_3$ stacks to evaluate the field-effect passivation directly after ALD process and after annealing at 400°C for 10 min in N_2 .

peak value of $S_{\text{eff,max}}$ of about 1200 cm/s and a Q_f -value of $-2.4 \pm 0.2 \cdot 10^{12} \text{ cm}^{-2}$. Therefore the level of field-effect passivation and chemical passivation were found to be quite equal for both as-deposited chemically grown $\text{SiO}_2/\text{Al}_2\text{O}_3$ stacks.

Annealing of the three chemically grown SiO_2 stacks resulted also in quite similar values of Q_f and peak values of $S_{\text{eff,max}}$. The Q_f -values were in the range of $-4.4 \cdot 10^{12}$ to $-4.6 \cdot 10^{12} \text{ cm}^{-2}$ and the peak values of $S_{\text{eff,max}}$ between 230 and 260 cm/s, as shown in Fig. 1. Both the chemical passivation and field-effect passivation of the chemically grown $\text{SiO}_2/\text{Al}_2\text{O}_3$ stacks improved with annealing. To verify the increase in field-effect passivation SHG measurements were carried out. The SHG intensity at a photon energy $E_{\text{ph}} = 3.4 \text{ eV}$ is dominated by field-induced second harmonic generation and is therefore a reasonable measure of the field-effect passivation.⁶² As shown by Terlinden et al. differences in the field-effect passivation of Al_2O_3 films can be analyzed with SHG measurements.⁶⁶ In Fig. 2 the SHG intensity is depicted as a function of the SHG photon energy for as-deposited and annealed chemically grown $\text{SiO}_2/\text{Al}_2\text{O}_3$ stacks. The SHG intensity at $E_{\text{ph}} = 3.4 \text{ eV}$ was found to be similar for the three different chemically grown $\text{SiO}_2/\text{Al}_2\text{O}_3$ stacks measured directly after the ALD process as well as measured after annealing. Furthermore an increase in SHG intensity, and therefore in field-effect passivation, was observed after annealing. Consequently both corona charging and SHG experiments revealed that the field-effect passivation obtained by the wet chemically grown SiO_2 films was similar directly after the ALD process and after annealing and that the field-effect passivation improved by the annealing process.

In Fig. 3 the results of the corona charging experiments of the chemically grown $\text{SiO}_2/\text{Al}_2\text{O}_3$ stacks are compared to the results

Figure 3. The maximum surface recombination velocity $S_{\text{eff,max}}$ as a function of deposited corona charge density Q_C . Corona charging experiments were done after annealing at 400°C (10 min, N_2) for Al_2O_3 films deposited on chemically, thermally oxidized, and HF-last Si surfaces. The thermally grown $\text{SiO}_2/\text{Al}_2\text{O}_3$ stacks were also measured directly after ALD of Al_2O_3 films (Labeled: "As-dep.").

obtained for the thermally grown $\text{SiO}_2/\text{Al}_2\text{O}_3$ stacks and Al_2O_3 films deposited on HF-last Si surfaces. All samples shown were annealed at 400°C . The $S_{\text{eff,max}}(Q_C)$ -plot obtained for Al_2O_3 films deposited on HF-last Si surfaces resulted in Q_F -values of $-6.5 \pm 0.5 \cdot 10^{12} \text{ cm}^{-2}$ which was about 1.5 times higher than the Q_F -value of the chemically grown $\text{SiO}_2/\text{Al}_2\text{O}_3$ stacks. However the maximum value of $S_{\text{eff,max}}$ of 290 cm/s was about a factor of 1.6 higher than for the chemically grown SiO_2 stacks. Consequently the chemically grown $\text{SiO}_2/\text{Al}_2\text{O}_3$ stacks showed a lower level of field-effect passivation but a higher level of chemical passivation than the Al_2O_3 films deposited on HF-last Si surfaces. Nevertheless both passivation materials resulted in a similar overall level of passivation as shown in the previous section. Stacks with thermally grown SiO_2 films yield a significantly better chemical passivation after annealing with peak values of $S_{\text{eff,max}} = 76 \text{ cm/s}$. The field-effect passivation of the thermally grown $\text{SiO}_2/\text{Al}_2\text{O}_3$ stacks is of minor importance as this stack has the lowest fixed charge density, i.e. $Q_F = 4.6 \cdot 10^{11} \text{ cm}^{-2}$. Moreover the polarity of the thermally grown $\text{SiO}_2/\text{Al}_2\text{O}_3$ stacks was found to be positive in contrast to the results with the chemically grown SiO_2 stacks. A similar Q_F and a similar high level of chemical passivation has also been reported for single-layer thermally grown SiO_2 films, e.g. in Ref. 3. The positive polarity of Q_F for the stacks with thick (200 nm) thermally grown SiO_2 is in agreement with recently published results of ALD $\text{SiO}_2/\text{Al}_2\text{O}_3$ stacks.³⁰ In that work the authors showed that with increasing SiO_2 thicknesses the polarity of Q_F changed from negative to positive. The reason is that for SiO_2 thicknesses larger than approximately 10 nm the positive fixed charge density of the SiO_2 bulk starts dominating the field-effect passivation. The data presented here are perfectly in line with this observation because the $\text{SiO}_2/\text{Al}_2\text{O}_3$ stack with thin (<5 nm) SiO_2 films also resulted in a negative fixed charge density whereas for thick (200 nm) SiO_2 films a positive fixed charge density was obtained. Moreover the results clearly demonstrate that in all cases a similar overall level of surface passivation quality was obtained for the different films and stacks but that nevertheless the surface passivation mechanism in terms of chemical and field-effect passivation were significantly different.

Improvement of surface passivation with annealing time.— Commonly lifetime samples including Al_2O_3 films are exposed to $\sim 400^\circ\text{C}$ at annealing times between 10 and 30 min to activate the surface passivation.^{67,68} In this work successive anneal steps were applied at $T = 400^\circ\text{C}$ to investigate the improvement of surface passivation during annealing at shorter times, in particular for annealing times less than 10 min for both the Al_2O_3 and $a\text{-SiN}_x\text{:H}$ stacks. For comparison purposes, the $S_{\text{eff,max}}$ -values at different annealing times t_{ann} were normalized to the $S_{\text{eff,max}}$ -values obtained after depositing the Al_2O_3 or $a\text{-SiN}_x\text{:H}$ films. The normalized $S_{\text{eff,max}}(t_{\text{ann}})$ -plots are shown in Fig. 4 for the Al_2O_3 stacks and in Fig. 5 for the $a\text{-SiN}_x\text{:H}$ stacks.

Figure 4. The change of the surface passivation performance, expressed in terms of normalized maximum surface recombination velocity $S_{\text{eff,max}}$, with annealing time t_{ann} for Al_2O_3 stacks. The $S_{\text{eff,max}}$ -values were normalized to the values obtained directly after the ALD process ($t_{\text{ann}} = 0 \text{ min}$). Annealing took place at 400°C in N_2 .

Figure 5. The change of the surface passivation performance, expressed in terms of normalized maximum surface recombination velocity $S_{\text{eff,max}}$, with annealing time t_{ann} for $a\text{-SiN}_x\text{:H}$ stacks. The $S_{\text{eff,max}}$ -values were normalized to the values obtained directly after the PECVD process ($t_{\text{ann}} = 0 \text{ min}$). Annealing took place at 400°C in N_2 .

Annealing of Al_2O_3 stacks.—The chemically grown $\text{SiO}_2/\text{Al}_2\text{O}_3$ stacks showed the fastest improvement of the surface passivation with t_{ann} and the lowest $S_{\text{eff,max}}$ -values were already obtained after annealing for 30 s. Annealing of single-layer Al_2O_3 films deposited on HF-last Si surfaces resulted in a relatively slow improvement of the passivation level. After annealing for 2 min the lowest $S_{\text{eff,max}}$ -values were reached. Moreover, in contrast to the chemically grown SiO_2 stacks first an increase in the normalized $S_{\text{eff,max}}$ -values was observed after 30 s annealing time. Thermally grown SiO_2 stacks showed an even slower reduction of the normalized $S_{\text{eff,max}}$ -values compared to the single-layer Al_2O_3 films and chemically grown SiO_2 stacks. This slower reduction of the normalized $S_{\text{eff,max}}$ -values could be attributed to a small improvement of the chemical passivation as revealed by corona charging experiments. The improvement of the chemical passivation with t_{ann} is illustrated by the reduction of the peak values of the $S_{\text{eff,max}}$ in Fig. 6.

An initial increase in surface recombination was only observed for single-layer Al_2O_3 films. The origin of that effect could not be determined by corona charging experiments. Therefore C-V measurements and infrared spectroscopy were used to investigate the field-effect passivation and the chemical passivation, respectively. With C-V measurements a flatband voltage shift was observed that indicated that the fixed charge density, i.e. the field-effect passivation, steadily improved with increasing annealing time. The infrared spectroscopy data revealed that the density of Si-H stretching bonds initially decreased after annealing for 30 s and afterwards increased with annealing times leading to the highest absorption values after 10 min. The density of Si-H bonds can be only present at the Si interface and is consequently taken as a measure for the chemical passivation. The change in infrared absorption is seen as an indirect evidence for

Figure 6. The surface recombination velocity $S_{\text{eff,max}}$ for thermally grown $\text{SiO}_2/\text{Al}_2\text{O}_3$ stacks as a function of deposited corona charge density Q_C after annealing at 400°C for various annealing times.

Figure 7. The surface recombination velocity $S_{\text{eff,max}}$ for thermally grown $\text{SiO}_2/\text{a-SiN}_x\text{:H}$ stacks as a function of deposited corona charge density Q_c after annealing at 400°C for various annealing times.

an initial decrease in chemical passivation that improved again after longer annealing times. As the field-effect passivation was found to be constant it is suggested that the change in chemical passivation is the reason for the change in the overall surface passivation with annealing time.

Annealing of $\text{a-SiN}_x\text{:H}$ stacks.—The improvement of the surface passivation with annealing time of the $\text{a-SiN}_x\text{:H}$ stacks was found to be similar to the one achieved for the Al_2O_3 stacks. Again the stacks with chemically grown SiO_2 films showed the fastest improvement and the lowest values of $S_{\text{eff,max}}$ were already achieved after 30 s. In the case of single-layer $\text{a-SiN}_x\text{:H}$ films the normalized $S_{\text{eff,max}}$ -values increased first and started to decrease again after 1 min. annealing time. The thermally grown $\text{SiO}_2/\text{a-SiN}_x\text{:H}$ stacks showed a similar trend. By corona charging experiments it was found that this initial increase in recombination observed for thermally grown $\text{SiO}_2/\text{a-SiN}_x\text{:H}$ stacks was related to an initial loss of chemical passivation as the peak value of $S_{\text{eff,max}}$ after 30 s and 1 min annealing time was higher than for the as-deposited case as can be seen in Fig. 7.

The observation of an initial increase and subsequent decrease in $S_{\text{eff,max}}$ with annealing time for selected samples with both $\text{a-SiN}_x\text{:H}$ and Al_2O_3 films, suggests that (de)passivation of the Si surface happens with two timescales: a fast depassivation of Si interface bonds during annealing at short times and a longer-term passivation of the Si dangling bonds by hydrogen provided from the bulk of the $\text{a-SiN}_x\text{:H}$ and Al_2O_3 films. The latter largely compensates the initial depassivation such that the overall surface recombination decreases by annealing. More data is however necessary to further support this hypothesis.

Conclusions

The effect of three wet chemically grown SiO_2 films on the surface passivation of Al_2O_3 and $\text{a-SiN}_x\text{:H}$ films was studied after the deposition processes of the films as well as after annealing. Directly after ALD of Al_2O_3 and PECVD of $\text{a-SiN}_x\text{:H}$ the stacks with chemically grown SiO_2 films showed the lowest recombination values compared to single-layer Al_2O_3 and $\text{a-SiN}_x\text{:H}$ films deposited on HF-last Si surfaces. Moreover, for the stacks with wet chemically grown SiO_2 films the surface passivation was found to be rather independent of the used wet chemical solutions, both directly after the deposition processes and after annealing. For the annealed films the lowest recombination was found for single-layer Al_2O_3 films but the slightly higher level of surface recombination velocity obtained for the chemically grown SiO_2 stacks is still appropriate for the application of these stacks in solar cell devices. Moreover, although a similar overall level of surface passivation quality was achieved for chemically grown $\text{SiO}_2/\text{Al}_2\text{O}_3$ stacks and single-layer Al_2O_3 films, the level of chemical and field-effect passivation differed significantly as concluded from corona charging and second harmonic generation measurements. A better chemical passivation but lower field-effect passivation was found for

the chemically grown $\text{SiO}_2/\text{Al}_2\text{O}_3$ stacks compared to single-layer Al_2O_3 films. It was also shown that the commonly used relatively long annealing times can be replaced by annealing times in the range of one or a few minutes when stacks with chemically grown SiO_2 films are used.

The high level of surface passivation obtained for chemically grown SiO_2 based stacks with Al_2O_3 or $\text{a-SiN}_x\text{:H}$ films offers the possibility to straightforwardly establish stable surface conditions, i.e. the formation of ultrathin SiO_2 films, prior to the deposition of the passivation layers without significantly comprising the passivation quality. Therefore this kind of surface conditioning might be preferred under industrial circumstances when working with (unstable) H-terminated surface conditions is not preferred. Moreover, such stacks allow for the use of shorter annealing times to reach the maximum level of surface passivation. Also this is beneficial from an industrial point of view.

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