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Ultralow surface recombination of *c*-Si substrates passivated by plasma-assisted atomic layer deposited Al_2O_3

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Excellent surface passivation of *c*-Si has been achieved by Al_2O_3 films prepared by plasma-assisted atomic layer deposition, yielding effective surface recombination velocities of 2 and 13 cm/s on low resistivity *n*- and *p*-type *c*-Si, respectively. These results obtained for ~30 nm thick Al_2O_3 films are comparable to state-of-the-art results when employing thermal oxide as used in record-efficiency *c*-Si solar cells. A 7 nm thin Al_2O_3 film still yields an effective surface recombination velocity of 5 cm/s on *n*-type silicon. © *2006 American Institute of Physics*. [DOI: 10.1063/1.2240736]

Surface passivation of crystalline silicon (*c*-Si) is of key importance for the performance of high efficiency industrial solar cells. The surface to volume ratio is increasing due to the cost-driven reduction of the solar cell thickness, which makes surface passivation a decisive factor for the final solar cell efficiency. Hydrogenated amorphous silicon nitride (a-SiN_x:H) is routinely applied in solar cell production as an antireflection coating on the front side and provides good surface passivation of low resistivity *n*- and *p*-type *c*-Si. However, the surface passivation of a-SiN_x:H on highly doped *p*-type silicon (e.g., *p*-type emitters) is rather poor. When a-SiN_x:H is applied on the back of a *p*-type solar cell the high positive built-in charge induces a parasitic junction, limiting the solar cell efficiency.[1] Thermally grown oxide is the state-of-the-art surface passivation layer for *n*- and *p*-type *c*-Si of arbitrary doping level and is used in the record-efficiency passivated emitter and rear localy-diffused (PERL) *c*-Si solar cell.[2] The surface passivation of the as-grown thermal oxide is moderate, but is significantly improved by a subsequent annealing in a forming gas (H_2 in N_2). The best results are obtained by the so-called *alneal* scheme, where a sacrificial layer of Al is evaporated on the film prior to annealing. The oxidation of the Al film during the annealing releases atomic hydrogen that strongly reduces the number of interface defect states. However, the high processing temperatures (~950–1100 °C) and elaborate processing necessary to obtain such a high quality thermal oxide are not always desirable. Therefore considerable effort is put in the development of low temperature surface passivation schemes that do not show the limitations of thermal oxide and a-SiN_x:H. Materials such as amorphous silicon carbide (a-SiC_x:H) and hydrogenated amorphous silicon (*a*-Si:H) have recently demonstrated a good level of surface passivation on both *n*- and *p*-type *c*-Si.[3–5] However, both materials have significant absorption in the visible part of the solar spectrum. These films are also thermally unstable; hence, only steps with a low thermal budget can be used after deposition of these films.

Another interesting option is the use of the high bandgap dielectric Al_2O_3 as a surface passivation layer. With a refractive index of ~1.65 and no significant absorption in the visible part of the solar spectrum, Al_2O_3 is well suited to improve the optical quality at the front or the back of the solar cell. Hezel and Jaeger already demonstrated that Al_2O_3 grown by the pyrolysis of aluminium-tri-isopropoxide can show a reasonable level of surface passivation.[6] More recently, Agostinelli *et al.* have shown that Al_2O_3 films grown by thermal atomic layer deposition provide a good level of surface passivation on *p*-type *c*-Si.[7]

In this letter we will show that ultrathin films of Al_2O_3 exhibit a similar level of surface passivation as alnealed thermal silicon oxide on both *n*- and *p*-type silicon. These films were prepared by plasma-assisted atomic layer deposition (PA-ALD) allowing monolayer growth control of high quality thin films, while the plasma step enables the use of relatively short purging times and low deposition temperatures.

Al_2O_3 films with a thickness of 7–30 nm were grown in a homebuilt PA-ALD reactor at a substrate temperature of 200 °C.[8] The films were prepared by alternating trimethylaluminium exposure and a remote O_2 plasma with a total cycle time of ~30 s. The film growth was monitored by means of *in situ* spectroscopic ellipsometry (250–1000 nm range) and revealed a growth rate in the 1.2 Å range per cycle. The atomic composition of the films was determined by means of Rutherford backscattering (RBS) and elastic recoil detection (ERD). The films were oxygen rich (Al:O =2:3.14), and a small amount of hydrogen (~3 at. %) was detected in the films. The carbon content was below the detection limit of RBS (<2 at. %). The surface passivation was tested by depositing identical Al_2O_3 films on both sides of low resistivity *p*-type (300 μm, ⟨111⟩, 2.0 Ω cm) and *n*-type (275 μm, ⟨100⟩, 1.9 Ω cm) float zone *c*-Si substrates. The substrates received a standard RCA clean with a final HF dip prior to deposition to remove the native oxide. After deposition, the lifetime samples were annealed in a N_2 environment for 30 min at 425 °C in a rapid thermal annealing furnace. The effective lifetime τ_{eff} was measured using a lifetime tester (Sinton WCT-100) in both the quasi-steady-state and transient mode.[9] The level of surface passivation is quantified by the effective surface recombination velocity. Assuming an infinite bulk lifetime, the upper limit of the effective surface recombination velocity S_{eff} can be calculated by

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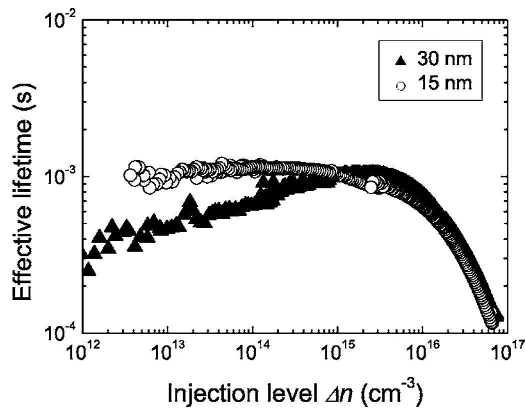

FIG. 1. Effective lifetime as a function of the excess carrier density for low resistivity *p*-type (300 μm, ⟨111⟩, 2.0 Ω cm) float zone *c*-Si substrate passivated with 30 and 15 nm thick Al_2O_3 films.

$$S_{\mathrm{eff}} \leqslant \frac{W}{2 \cdot \tau_{\mathrm{eff}}}, \quad (1)$$

with W the substrate thickness.

In Fig. 1 the effective lifetime as a function of the injection level is shown for the low resistivity *p*-type substrates passivated by 15 and 30 nm thin Al_2O_3 films. The postdeposition annealing was necessary to obtain the reported effective lifetimes, as the effective lifetime of the samples with the *as-deposited* Al_2O_3 films was only in the range of 2–8 μs. Effective lifetimes up to 1.2 ms were measured for a *p*-type substrate passivated by 30 nm Al_2O_3 film corresponding to a $S_{\mathrm{eff}} \leqslant 13$ cm/s. No difference in effective lifetime is observed when a 15 nm Al_2O_3 film is used instead of a 30 nm Al_2O_3 film, except for the behavior for lower injection levels.

The surface passivation of Al_2O_3 was also tested on *n*-type *c*-Si. In Fig. 2 the effective lifetime for 1.9 Ω cm *n*-type silicon passivated by 7, 14, and 26 nm Al_2O_3 is shown. A maximum lifetime of 6.6 ms was measured for an *n*-type substrate passivated by a 26 nm Al_2O_3 film corresponding to a $S_{\mathrm{eff}} \leqslant 2$ cm/s. For Al_2O_3 film thicknesses of 7 and 15 nm comparable results were obtained and effective lifetimes up to 3.0 ms were measured, corresponding to a $S_{\mathrm{eff}} \leqslant 5$ cm/s.

The postdeposition annealing was essential for a good level of surface passivation; however, from RBS/ERD no

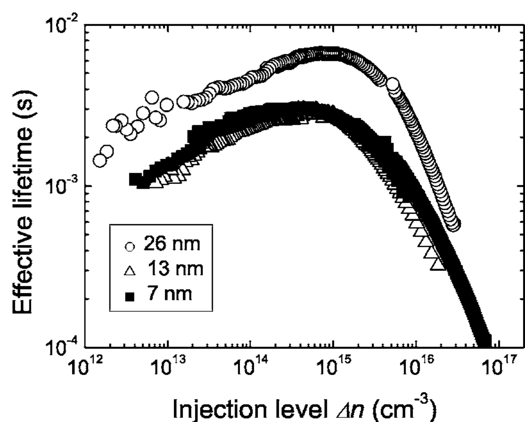

FIG. 2. Effective lifetime as a function of the excess carrier density for low resistivity *n*-type (275 μm, ⟨100⟩, 1.9 Ω cm) float zone *c*-Si substrate passivated with 30, 15, and 7 nm thick Al_2O_3 films.

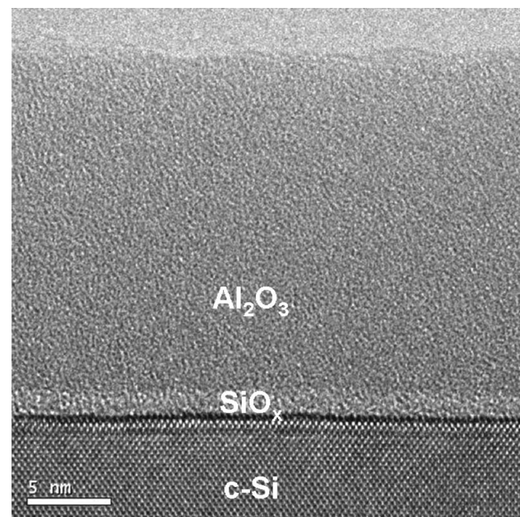

FIG. 3. High resolution TEM image showing a 20 nm thick Al_2O_3 film on *c*-Si after a 30 min annealing at 425 °C in a N_2 environment.

significant changes could be detected in the atomic composition of the annealed Al_2O_3 films. From high resolution transmission electron microscopy (HR-TEM) it was found that both the as-deposited and annealed Al_2O_3 films are amorphous in composition, as shown in Fig. 3 for the annealed film. An interfacial oxide layer of ~1.5 nm (~1.2 nm prior to anneal) is present between the *c*-Si and Al_2O_3 as a result of the deposition process, possibly from the exposure of the substrate to the O_2 plasma in the first ALD cycles. In a separate experiment it was verified that the oxide layer formed during the O_2 plasma exposure in itself does not yield any surface passivation, also not after annealing.

The effective lifetimes measured for a *p*-type *c*-Si substrate passivated by a 15 nm Al_2O_3 film in this study are significantly higher compared to the results reported for substrates passivated by a-SiC_x:H films or Al_2O_3 films grown by thermal ALD.[4,7] The results are comparable to the best results obtained for alnealed thermal SiO_2 and nearly stoichiometeric a-SiN_x:H and approach the results obtained for *a*-Si:H.[3,10–12] It should be noted that the reported literature values were obtained for films with thicknesses in the range of 20–100 nm and that the level of surface passivation of a-SiC_x:H and a-SiN_x:H is reported to deteriorate for films with thicknesses below 40 and 20 nm, respectively.[13,14] On the other hand, the effective lifetimes for *n*-type *c*-Si passivated with a 26 nm Al_2O_3 film are comparable to the best results obtained for alnealed thermal SiO_2, a-SiN_x:H, and *a*-Si:H films and significantly higher than reported for a-SiC_x:H films.[3,5,10,11]

All lifetime curves in Figs. 1 and 2 show the expected decrease in effective lifetime at higher injection levels due to Auger recombination. For the *p*-type wafer in Fig. 1 passivated with a 30 nm Al_2O_3, the effective lifetime shows the typical injection level dependence also reported for *p*-type wafers passivated by a-SiN_x:H, a-SiC_x:H, or thermal oxide,[4,10,11] probably caused by Shockley-Read-Hall (SRH) recombination in the bulk or at the surface through a midgap defect.[15,16] Remarkably, the lifetime curve for the *p*-type wafer passivated by a 15 nm film is constant for lower injection level. For the *n*-type wafers passivated by 7–26 nm Al_2O_3, the effective lifetime slightly decreases for lower injection level comparable to results obtained for *n*-type wafers passi-

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vated by a-SiC$_x$:H and a-Si:H.[3,5] This decrease can again be attributed to SRH recombination in the bulk or at the surface.

The excellent surface passivation by the Al_2O_3 film is mainly determined by the field effect passivation due to a large ($\sim 10^{13}$ cm^{-2}) built-in *negative* charge as indicated by *C-V* measurements. This negative built-in charge for Al_2O_3 was also reported by Hezel and Jaeger[6] and Agostinelli *et al.*[7] The negative charge in Al_2O_3 is suggested to be present at the unique tetrahedrally coordinated Al site present at the interface that has a net negative charge, in contrast to the octahedrally coordination site where Al has a charge of 3+.[17] For the commonly used thermal oxide and a-SiN:H *positive* built-in charges in the range of $10^{10}-10^{12}$ cm^{-2} are reported,[6,18] and for a-SiC:H the sign of the built-in charge is reported to depend on the wafer doping type.[4,5] A negative built-in charge is especially beneficial for passivation of highly doped p-type silicon.

The fact that the high level of surface passivation could only be obtained by a postdeposition annealing of the Al_2O_3 films (deposited at 200 °C) could be caused by a local reconstruction of the Al_2O_3 at the interface, consequently increasing the negative built-in charge.[19] In addition, hydrogen from the Al_2O_3 bulk could diffuse and provide chemical passivation at the c-Si/Al_2O_3 interface, thereby reducing defect related recombination. A factor of 10 reduction of the interface defect density was reported for a metal-insulator-semiconductor structure with Al_2O_3 as the insulator after a 15 min annealing at 500 °C.[6]

In conclusion, we have shown that excellent surface passivation, similar to alnealed thermal oxide, can be obtained on n- and p-type c-Si by thin Al_2O_3 films prepared by the PA-ALD technique. An ultrathin film of 7 nm thick Al_2O_3 yields a $S_{\mathrm{eff}} \leq 5$ cm/s on n-type c-Si. By optimization process, cycle times could be reduced to a (sub) second level and the total process, growth, and annealing would be significantly faster compared to the state-of-the-art passivation schemes applied presently.

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