Surface passivation of silicon solar cells using industrially relevant Al2O3 deposition techniques

Citation for published version (APA):

Document status and date:
Published: 01/01/2010

Document Version:
Publisher’s PDF, also known as Version of Record (includes final page, issue and volume numbers)

Please check the document version of this publication:

• A submitted manuscript is the version of the article upon submission and before peer-review. There can be important differences between the submitted version and the official published version of record. People interested in the research are advised to contact the author for the final version of the publication, or visit the DOI to the publisher’s website.
• The final author version and the galley proof are versions of the publication after peer review.
• The final published version features the final layout of the paper including the volume, issue and page numbers.

Link to publication

General rights
Copyright and moral rights for the publications made accessible in the public portal are retained by the authors and/or other copyright owners and it is a condition of accessing publications that users recognise and abide by the legal requirements associated with these rights.

• Users may download and print one copy of any publication from the public portal for the purpose of private study or research.
• You may not further distribute the material or use it for any profit-making activity or commercial gain
• You may freely distribute the URL identifying the publication in the public portal.

If the publication is distributed under the terms of Article 25fa of the Dutch Copyright Act, indicated by the “Taverne” license above, please follow below link for the End User Agreement:
www.tue.nl/taverne

Take down policy
If you believe that this document breaches copyright please contact us at:
openaccess@tue.nl
providing details and we will investigate your claim.

Download date: 16. Oct. 2020
Surface passivation of silicon solar cells using industrially relevant Al$_2$O$_3$ deposition techniques

Jan Schmidt, Florian Werner, Boris Veith, Dimitri Ziekel, Robert Bock & Rolf Brendel, Institute for Solar Energy Research Hamelin (ISFH), Emmerthal, Germany; Veronica Tiba, SoLayTec, Eindhoven, The Netherlands; Paul Poodt & Fred Roozeboom, TNO Science & Industry, Eindhoven, The Netherlands; Andrew Li & Andres Cuevas, The Australian National University (ANU), Canberra, Australia

ABSTRACT
The next generation of industrial silicon solar cells aims at efficiencies of 20% and above. To achieve this goal using ever-thinner silicon wafers, a highly effective surface passivation of the cell front and rear is required. In the past, finding a suitable dielectric layer providing a high-quality rear passivation has been a major challenge. Aluminium oxide (Al$_2$O$_3$) grown by atomic layer deposition (ALD) has only recently turned out to be a nearly perfect candidate for such a dielectric. However, conventional ALD is limited to deposition rates well below 2nm/min, which is incompatible with industrial solar cell production. This paper assesses the passivation quality provided by three different industrially relevant techniques for the deposition of Al$_2$O$_3$ layers, namely high-rate spatial ALD, plasma-enhanced chemical vapour deposition (PECVD) and reactive sputtering.

Introduction
In high-efficiency laboratory silicon solar cells, surface recombination is very effectively suppressed by means of silicon dioxide (SiO$_2$) grown in a high-temperature (≥900°C) oxidation process [1]. Very low surface recombination velocities (SRVs) are in particular realized at the lightly doped rear surface, where the combination of a thermally grown SiO$_2$ layer with an evaporated film of Al gives – after an additional annealing treatment at ~400°C (the so-called ‘alneal’) – SRVs below 20cm/s on low-resistivity (~1Ωcm) p-type silicon wafers [2]. In addition, the SiO$_2$/Al stack at the cell rear acts as an excellent reflector for near-bandgap photons, significantly improving the light-trapping properties and, hence, the short-circuit current of the cell. One of the main reasons why high-temperature oxidation has not been implemented into the majority of industrial cell processes so far is the high sensitivity of the silicon bulk lifetime to high-temperature processes. Particularly in the case of multicrystalline silicon wafers, thermal processes above 900°C typically lead to a significant degradation of the bulk lifetime [3]. Hence, low-temperature surface passivation alternatives are required for future industrial high-efficiency silicon solar cells.

Figure 1. Schematic of one cycle of a thermal and a plasma-assisted ALD process. Each cycle consists of two half-steps: first, the trimethyl aluminium (TMA) molecules attach to the hydroxyl groups bound to the silicon surface; second, the molecules are oxidized by H$_2$O (thermal ALD) or an O$_2$ plasma (plasma ALD).

One intensively investigated low-temperature surface passivation alternative to thermal oxide is silicon nitride (SiN$_x$) grown by PECVD at ~400°C, which has proven to give comparably low SRVs as thermal SiO$_2$ on low-resistivity p-type silicon [4,5]. However, when applied to the rear of PERC (passivated emitter and rear cell)-type solar cells on a p-type substrate, the short-circuit current density is strongly reduced compared to the SiO$_2$-passivated cell rear [6]. This effect has been attributed to the large density of fixed positive charges within the SiN$_x$ layer, inducing an inversion layer in the p-type silicon underneath the SiN$_x$. The coupling of this inversion layer to the base metal contact leads to a significant loss in the short-circuit current density and the fill factor, a detrimental effect that is known as ‘parasitic shunting’ [7].

“Aluminium oxide (Al$_2$O$_3$) has proven capable of providing an excellent level of surface passivation.”

Fortunately, the negative-charge-dielectric aluminium oxide (Al$_2$O$_3$) has proven capable of providing an excellent level of surface passivation on low-resistivity p-type and n-type silicon wafers as well as on boron- and aluminium-doped p+-emitters [8–21]. Al$_2$O$_3$ can be deposited by various techniques, such as ALD, PECVD and reactive sputtering. In particular, it was demonstrated that it is ideally suited to the rear passivation of...
PERC solar cells, as parasitic shunting is completely absent thanks to the fixed negative charges [11]. In this contribution, we systematically compare the passivation quality of Al\(\text{2O}_3\) films deposited by various deposition techniques. Atomic layer deposition performed in lab reactors (plasma-assisted as well as thermal ALD) provides an outstanding surface passivation quality; however, it is limited to very low deposition rates (<2nm/min), making conventional, temporal ALD reactors unsuitable for industrial solar cell production. On the other hand, we will demonstrate that high-rate spatial ALD, PECVD, and reactive sputtering have an enormous potential for a transfer of Al\(\text{2O}_3\) into industrial cell production in the near future.

**Atomic layer deposition**

In the ALD process, one monolayer of Al\(\text{2O}_3\) is grown per cycle, with each cycle consisting of two half-reactions, as depicted in Fig. 1. In the first half-reaction, trimethyl aluminium (TMA) molecules react with hydroxyl (OH) groups attached to the surface. At the end of the first half-reaction, Al atoms and methyl groups cover the surface and the remaining TMA molecules in the deposition chamber are no longer able to react with the surface. After purging the deposition chamber with inert or oxygen gas, the second half-reaction of the ALD cycle starts. One can apply two different realization forms for the second half-reaction: in the thermal ALD process, water vapour is injected into the deposition chamber. The H\(\text{2O}\) molecules react very fast with the Al-CH\(_3\) complex attached to the surface. In between both precursor doses, however, the reactor chamber is purged by an inert gas and subsequently pumped to remove the residual process gas and reaction products. In order to prevent parasitic CVD processes and ensure a true ALD process, pumping times of a few seconds are required, severely limiting the growth rate to approximately 2nm/min. This renders conventional ALD unsuitable for high-throughput industrial solar cell production.

Recently, Poodt et al. proposed a high-rate ALD concept based on spatially separated ALD (‘spatial ALD’) [22], enabling deposition rates of 70nm/min. In contrast to the conventional sequential separation, both half-reactions are spatially separated (see Fig. 2), thus eliminating the need for intermediate pumping steps. In a first proof-of-principle lab tool developed at TNO, the spatial separation was achieved by rotating the wafer underneath a round reactor head incorporating gas inlets for TMA and water vapour, separated by gas bearings formed by a flow of pressurized nitrogen. Since both reaction zones are sealed off by nitrogen flow, any unintentional interaction of the process gases is prevented and the deposition can be performed under atmospheric conditions, an additional advantage concerning the industrial applicability. The spatial ALD concept has recently led to excellent surface passivation results on p- and n-type silicon wafers [23]. Note that high-throughput (up to 3,000 wafers per hour) reactors based on the spatial ALD approach are currently under development at two different companies, namely SolayTec and Levitech, and will be commercially available in the near future.

In a conventional ALD process, the separation of the half-reactions is implemented by alternate dosing of the process gases. Exposure times of only a few milliseconds are sufficient to ensure complete saturation of the growth surface. In between both precursor doses, however, the reactor chamber is purged by an inert gas and subsequently pumped to remove the residual process gas and reaction products. In order to prevent parasitic CVD processes and ensure a true ALD process, pumping times of a few seconds are required, severely limiting the growth rate to approximately 2nm/min. This renders conventional ALD unsuitable for high-throughput industrial solar cell production.

Recently, Poodt et al. proposed a high-rate ALD concept based on spatially separated ALD (‘spatial ALD’) [22], enabling deposition rates of 70nm/min. In contrast to the conventional sequential separation, both half-reactions are spatially separated (see Fig. 2), thus eliminating the need for intermediate pumping steps. In a first proof-of-principle lab tool developed at TNO, the spatial separation was achieved by rotating the wafer underneath a round reactor head incorporating gas inlets for TMA and water vapour, separated by gas bearings formed by a flow of pressurized nitrogen. Since both reaction zones are sealed off by nitrogen flow, any unintentional interaction of the process gases is prevented and the deposition can be performed under atmospheric conditions, an additional advantage concerning the industrial applicability. The spatial ALD concept has recently led to excellent surface passivation results on p- and n-type silicon wafers [23]. Note that high-throughput (up to 3,000 wafers per hour) reactors based on the spatial ALD approach are currently under development at two different companies, namely SolayTec and Levitech, and will be commercially available in the near future.

**Figure 2. Schematic of the spatial ALD concept [22]. The TMA and water half-reaction zones are separated by N\(_2\) gas bearings.**

**Figure 3. Effective lifetime \(\tau_{\text{eff}}\) as a function of the injection density \(\Delta n\) measured on 1.3Ωcm p-type FZ-Si passivated by Al\(\text{2O}_3\) deposited by plasma, thermal and spatial ALD.**
near future with the extra option of an additional gas bearing at the wafer back side, thus enabling double-floating wafer transport in a reciprocating manner or in a single direction.

Fig. 3 shows the effective lifetimes $\tau_{\text{eff}}$ measured as a function of the injection density $\Delta n$ for 1.3 $\Omega\text{cm}$ p-type float-zone silicon (FZ-Si) wafers passivated using $\text{Al}_2\text{O}_3$ deposited by plasma-assisted, thermal and spatial ALD. Lifetimes were measured by the photoconductance decay (PCD) method using a Sinton lifetime tester. All $\text{Al}_2\text{O}_3$ films received a post-deposition anneal at $(400\pm50)°C$ for ~15 min to activate the surface passivation [19]. As can be seen from Fig. 3, all three ALD techniques result in $\text{Al}_2\text{O}_3$ films of outstanding surface passivation quality, which shows an extremely weak injection dependence over the complete relevant injection range between $10^{13}$ and $10^{15}$ $\text{cm}^{-3}$. $\text{Al}_2\text{O}_3$ deposited by plasma ALD provides effective lifetimes between 3 and 4.8 ms in the relevant injection range. The measured lifetime of 4.8 ms at $\Delta n = 10^{15}$ $\text{cm}^{-3}$ lies well above the commonly used empirical expression for the intrinsic lifetime limit for crystalline silicon [24], indicating a nearly perfect surface passivation, even better than that previously achieved with ‘alnealed’ thermally-grown $\text{SiO}_2$. Assuming an infinite bulk lifetime, we can calculate an upper limit to the SRV $S_{\text{max}}$ using the simple relation $S_{\text{max}} = W/2\tau_{\text{eff}}$, where $W = 290\mu\text{m}$ is the measured wafer thickness. Using this relation, $\tau_{\text{eff}} = 4.8$ ms, corresponds to an upper SRV limit of $S_{\text{max}} = 3$ cm/s. Given that the measured lifetime is above the previous intrinsic limit for silicon, the lower limit is $S_{\text{max}} = 0$ cm/s, and the real SRV is in between those two values – too low to be noticed by a normal solar cell. In this work, all SRVs reported are $S_{\text{max}}$ values.

Most importantly, it can be concluded from Fig. 3 that both traditional thermal ALD as well as spatial ALD provide $\text{Al}_2\text{O}_3$ films with an extremely high level of surface passivation, as indicated by lifetimes of 2 ms, corresponding to an upper SRV limit of $S_{\text{max}} = 7$ cm/s, for both techniques and a practically negligible injection dependence over the relevant injection range. It is quite remarkable that the high-rate (in our example 14nm/min) spatial ALD produces exactly the same excellent level of surface passivation as the slow (< 2nm/min) conventional thermal ALD [23].

Spatial ALD, PECVD and sputtering

In addition to spatial ALD, two other techniques have recently been demonstrated to be suitable for depositing surface-passivating $\text{Al}_2\text{O}_3$ layers. PECVD [14,15,21] has been shown to provide SRVs of only 10 cm/s on 1 $\Omega\text{cm}$ p-type FZ-Si, whereas reactive sputtering [16] on comparable material has resulted in SRVs down to 55 cm/s. In addition to the $\text{Al}_2\text{O}_3$ films deposited by spatial ALD, we have examined the passivation quality of $\text{Al}_2\text{O}_3$ films deposited in an in-line microwave-remote PECVD (Roth&Rau, SiNA) system and in an RF magnetron sputtering lab system [19]. The sputtering uses an aluminium target, which is reactively sputtered in an $\text{O}_2/\text{Ar}$ atmosphere, while the PECVD uses TMA and nitrous oxide as process gases.

Fig. 4 compares the effective lifetimes measured on 1.3 $\Omega\text{cm}$ p-type FZ-Si wafers passivated by $\text{Al}_2\text{O}_3$ films deposited using spatial ALD, PECVD, and reactive sputtering.
values < 10cm/s, clearly outperforming the sputtered Al2O3. Nevertheless, the sputtered Al2O3 passivation layer results in a surface recombination velocity between 35 and 70cm/s in the relevant injection range, which would still be acceptable for the next generation of industrial high-efficiency solar cells.

“The PERC solar cells with sputtered Al2O3 as rear passivation achieve an independently confirmed efficiency of 20.1%.”

Another very important property is the stability of the surface passivation during a firing step as it is typically applied in the screen-printing metallization of solar cell production lines. We annealed lifetime samples in an industrial infrared conveyor-belt furnace (Centrotherm Contact Firing Furnace DO 8.600-300-FF) at a set temperature of 920°C (measured peak temperature ~800°C). Fig. 5 shows the injection-dependent lifetimes and corresponding surface recombination velocities measured after firing. The Al2O3 deposited by spatial ALD shows clearly the best firing stability, providing SRVs of ~20cm/s after firing over the entire relevant injection range. The Al2O3 layer deposited by inline PECVD also results in a good passivation quality after firing, providing $S_{max}$ values between 30 and 80cm/s in the injection range of relevance. The sputtered Al2O3 shows the strongest increase in the surface recombination after firing, leading to SRVs between 300 and 800cm/s. Obviously, the sputtered Al2O3 needs further optimization, while the PECVD-Al2O3 and in particular the spatial ALD-Al2O3 layers can be directly implemented in a screen-printing solar cell process.

As large-area in-line PECVD systems are already available on the market, PECVD seems to be the preferred short-term deposition technique for Al2O3. The preferred medium-term and long-term deposition technique might be ultrafast spatial ALD due to its reduced TMA gas consumption compared to PECVD, the absence of parasitic deposition at the reactor wall and a smaller footprint of the deposition systems currently under development. Also, ALD provides highest-quality pinhole-free Al2O3 films and allows conformal film deposition, which might prove useful for advanced solar cell concepts.

**PERC solar cells**

We have implemented our Al2O3 rear passivation layers deposited by plasma ALD, thermal ALD and sputtering into passivated emitter and rear cells using the process sequence described in [11]. Fig. 6 shows the cell structure featuring a PECVD-SiNx-passivated 100Ω/sq phosphorus-diffused $n^+$ front emitter and a rear surface passivated by the dielectric layer systems shown in the first column of Table 1. The front grid is made by shadow-mask evaporation of aluminium and the rear is fully metallized by aluminium evaporation (~4% rear metal contact fraction) after point contact openings have been generated. Table 1 summarizes the one-sun parameters of the best PERC solar cells, as measured under standard testing conditions (25°C, 100mW/cm², AM 1.5 G). The measured open-circuit voltages ($V_{oc}$) and short-circuit current densities ($J_{sc}$) of the ALD-passivated cells are clearly superior to the $V_{oc}$ and $J_{sc}$ values of the cell with sputtered Al2O3. $V_{oc}$ values of ALD-passivated cells are all > 660mV and $J_{sc}$ values are > 40mA/cm², demonstrating the huge potential of ALD for the rear surface passivation of PERC-type cells. We deposited thicker PECVD-SiOx or SiNx layers on top of the very thin ALD-Al2O3 layers, mainly to improve the internal rear reflection of the cell. The independently confirmed conversion efficiencies are 21.4% for the plasma ALD-Al2O3 rear passivation and 20.7% for the thermal ALD-Al2O3 passivation. The passivation quality of the sputtered Al2O3 is clearly inferior to that of the ALD-Al2O3 films, as indicated by an ~10mV lower $V_{oc}$ and an ~1.5mA/cm² reduced $J_{sc}$. Nevertheless, the PERC cells with sputtered Al2O3 as rear passivation achieve an independently confirmed efficiency of 20.1% – the first 20%-efficient solar cell made using a sputtered Al2O3 passivation layer.

**Conclusions**

Despite their lower passivation quality compared to Al2O3 films deposited by ALD and by PECVD, we have demonstrated that sputtered Al2O3 layers are suitable for the fabrication of 20% efficient PERC cells, while Al2O3 deposited by ALD resulted on the same cell structure in efficiencies up to 21.4%. After firing in a conveyor-belt furnace, the SRV provided by Al2O3 films deposited by high-rate spatial ALD was found to be below 20cm/s and that of PECVD-Al2O3 was in the range 30–80cm/s, indicating a very good firing stability of the layers deposited by spatial ALD as well as PECVD. On the other hand, sputtered Al2O3 passivation layers degraded to SRVs larger than 300cm/s after firing. We conclude that spatial ALD and PECVD are already compatible with screen-printing, while the firing stability of sputtered Al2O3 needs further optimization, e.g. by deposition of hydrogen-rich SiNx on top of the sputtered Al2O3. As high-throughput PECVD systems are already well introduced in the market, PECVD will, in our opinion,
be the preferred short-term deposition technique for Al$_2$O$_3$ passivation layers. If the firing stability of sputtered Al$_2$O$_3$ layers can be further improved (e.g. by using SiN$_x$ capping layers), this could become another option for the short term. Spatial ALD might be the most interesting medium- to long-term option due to the superior overall precursor use and material properties of atomic-layer-deposited Al$_2$O$_3$.

**Acknowledgments**

Parts of this work have been funded by the German Ministry for the Environment, Nature Conservation and Nuclear Safety (BMU) under contract number 0325050 ("ALD").

**References**


**About the Authors**

Jan Schmidt is head of the PV Department at ISFH and professor of physics at the Leibniz University of Hanover, Germany. He received his Ph.D. degree in 1998 from the Leibniz University of Hanover. His current research interests include the development of novel characterization techniques, as well as the development and evaluation of novel surface passivation methods for silicon solar cells.

Boris Veith studied physics at the Leibniz University of Hanover, Germany, and received his diploma degree in 2010. He is now employed as a researcher at ISFH, working on the aluminium oxide surface passivation of silicon solar cells.

Dimitri Zielke is a physics student at the Leibniz University of Hanover, Germany, and is currently working towards his diploma degree in physics at ISFH. The main topic of his diploma thesis is the surface passivation of silicon solar cells using aluminium oxide.

Robert Bock studied materials science at the Christian Albrechts University Kiel, Germany, and received his diploma degree in 2006. He is currently doing Ph.D. research at ISFH with focus on n-type silicon solar cells with screen-printed aluminium-alloyed emitters.

Rolf Brendel, Director of the ISFH, completed his studies in physics and mathematics, and joined the Max Planck Institute for Solid State Research in Stuttgart following his Ph.D. work. He was appointed head of the Division for Thermosensors and Photovoltaics at the Bavarian Center for Applied Energy Research in Erlangen. Since 2004 he has been a professor at the Institute of Solid State Physics at the Leibniz University of Hanover.

Veronica Tiba is a process development engineer, responsible for the knowledge transfer of (atmospheric) ultrafast spatial ALD of Al$_2$O$_3$ from research to industrialization at SoLayTec in Eindhoven, The Netherlands. She received her Ph.D. degree in 2005 from the Eindhoven University of Technology.

Paul Poodt is a researcher at the Materials Technology business unit at TNO Science & Industry. He received his Ph.D. degree in 2008 from the Radboud University Nijmegen, The Netherlands. His current research interests include the development of novel gas-phase deposition techniques as well as the physics and chemistry of thin-film deposition for photovoltaics and other (compound) semiconductor devices.

Fred Roozeboom is a senior technical advisor at TNO Science & Industry, and part-time professor at the University of Technology, both in Eindhoven, The Netherlands. He received his Ph.D. degree in chemical engineering in 1980 from Twente University, after which he worked on zeolite catalysis with Exxon (USA and The Netherlands) and Philips Research (The Netherlands). His topics of interest include ultrathin-film technology, plasma processing, microsystem technology, sensors and 3D integration.

Andrew Li has recently submitted his Ph.D. thesis for examination at The Australian National University, Canberra, Australia, which investigated the sputtering method for the deposition of aluminium oxide for the surface passivation of silicon solar cells. His research interests include cell design and characterization, particularly of high efficiency solar cells. He is now working for REC, Singapore.

Andres Cuevas has contributed to the development of silicon solar cell technology since 1976, first at the Universidad Politecnica de Madrid, Spain, where he obtained his Ph.D. degree in 1980 and then at ANU, where he now is Professor of Engineering. His current research interests include the characterisation and understanding of the fundamental properties of silicon, the passivation of silicon surfaces using dielectric coatings, and the development of new technologies for n-type silicon solar cells.

**Enquiries**

Prof. Jan Schmidt
Institute for Solar Energy Research
Hamelin (ISFH)
Am Ohrberg 1
31860 Emmerthal
Germany
Tel: +49 5151 999 100
Fax: +49 5151 999 400
Email: jschmidt@isfh.de
Web: www.isfh.de