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Status and prospects of Al₂O₃-based surface passivation schemes for silicon solar cells

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The reduction in electronic recombination losses by the passivation of silicon surfaces is a critical enabler for high-efficiency solar cells. In 2006, aluminum oxide (Al₂O₃) nanolayers synthesized by atomic layer deposition (ALD) emerged as a novel solution for the passivation of p- and n-type crystalline Si (c-Si) surfaces. Today, high efficiencies have been realized by the implementation of ultrathin Al₂O₃ films in laboratory-type and industrial solar cells. This article reviews and summarizes recent work concerning Al₂O₃ thin films in the context of Si photovoltaics. Topics range from fundamental aspects related to material, interface, and passivation properties to synthesis methods and the implementation of the films in solar cells. Al₂O₃ uniquely features a combination of field-effect passivation by negative fixed charges, a low interface defect density, an adequate stability during processing, and the ability to use ultrathin films down to a few nanometers in thickness. Although various methods can be used to synthesize Al_2O_3 , this review focuses on ALD—a new technology in the field of c-Si photovoltaics. The authors discuss how the unique features of ALD can be exploited for interface engineering and tailoring the properties of nanolayer surface passivation schemes while also addressing its compatibility with high-throughput manufacturing. The recent progress achieved in the field of surface passivation allows for higher efficiencies of industrial solar cells, which is critical for realizing lower-cost solar electricity in the near future. © 2012 American Vacuum Society. [http://dx.doi.org/10.1116/1.4728205]

I. INTRODUCTION

Over 85% of the solar cells currently produced are based on crystalline silicon wafers. The lion's share of these industrially manufactured cells have energy conversion efficiencies of typically $\eta = 16\%-18\%$, while the record of $\eta = 25.0\%$ for laboratory-type Si solar cells^{1,2} is already fairly close to the theoretical maximum of $\eta = \sim 29\%$.^{3–8} The efficiency of solar cells is significantly affected by electronic recombination losses at the wafer surfaces—primarily through a suboptimal open-circuit voltage. A reduction in surface recombination is called surface passivation. At present, only a fraction of industrial solar cells has effective passivation schemes implemented, which explains a significant part of the efficiency gap between industrial cells and high-efficiency laboratory cells.⁹

Over the years, various materials and material stacks have been investigated for surface passivation purposes of the cell's front and rear side.¹⁰ The suitability of a passivation scheme depends on doping type and Si resistivity and on aspects such as the thermal-, UV-, and long-term stability, the optical properties (i.e., parasitic absorption, refractive index), and the processing requirements (e.g., surface cleaning, available synthesis methods). Silicon nitride (a-SiN_x:H) is an important material in Si photovoltaics as it is used in virtually all (laboratory and industrial) solar cells as antireflective coating. a-SiN_x:H also provides (some) surface passivation and passivation of bulk defects for multicrystalline Si. Traditionally, thermally grown SiO₂ has been used as effective passivation scheme in high-efficiency laboratory cells, for instance in the record passivated emitter rear locally diffused (PERL) cell.^{1,2} Another widely investigated material is amorphous Si (*a*-Si:H). The combination of intrinsic and doped *a*-Si:H nanolayers (<10 nm) has been successfully applied in (commercial) heterojunction solar cells.¹¹

Aluminum oxide (Al₂O₃) has recently emerged as an alternative passivation material. Although not outstanding at that time, the passivation properties of Al₂O₃ were already reported in 1989 by Hezel and Jaeger.¹² Nonetheless, their publication was written for posterity. Al₂O₃ technology gained momentum only after its reintroduction—this time synthesized by atomic layer deposition (ALD).^{13–15} The level of passivation that was demonstrated by Hoex *et al.* in 2006 for Al₂O₃ on lowly doped Si and p^+ emitters was at least as good as obtained by thermally grown SiO₂.^{14,16} Compared to other investigated materials, a distinguishing property of Al₂O₃ appeared to be the field-effect passivation induced by *negative* fixed charges.^{14,17}

The popularity of Al_2O_3 can be explained by two important trends. First, the photovoltaics (PV) industry has

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recently been looking to improve the rear side of conventional screen-printed *p*-type Si solar cells by replacing the Al-backsurface field (Al-BSF) by a dielectrically passivated rear. The latter leads to lower surface recombination losses, better internal reflection, and reduced wafer bow for thin wafers. The adoption of a passivated rear side is inevitable concerning the demand for higher efficiencies and the use of thinner Si wafers. While the availability of (laser) processes to produce local rear contacts was not a (prominent) bottleneck anymore, the availability of suitable passivation schemes was. Due to inversion layer shunting, a-SiN_y:H was not a suitable candidate for the *p*-type Si rear. Due to reasons of costs, complexity, and a possible adverse impact of high temperatures on the bulk quality, thermal oxidation was also not a first choice. Although plasma deposited SiO_x/SiN_x stacks were considered as alternatives,¹⁸ the focus shifted to Al_2O_3 (and Al_2O_3/SiN_x stacks) as a solution for the *p*-type Si rear side. Second, for *n*-type Si solar cells a suitable passivation solution of the p^+ emitter was required. The negative charges of Al₂O₃ are an ideal match for the passivation of such emitters. To date, the application of Al₂O₃ on p^+ emitters and on the p-type Si rear has resulted in enhanced solar cell efficiencies up to 23.9%.^{9,19}

Along with the introduction of Al_2O_3 came the introduction of ALD in the field of Si PV. ALD differs from conventional (plasma-enhanced) chemical vapor deposition methods by the strict separation of the precursor gases in two half-cycles during deposition leading to self-limiting layer-by-layer growth. The hallmark of ALD is precise thickness control and very uniform and conformal deposition over large area surfaces. For these reasons, the technique has recently been adopted for the synthesis of high-*k* nanolayers (such as Hf-based oxides) in the semiconductor industry. For the PV industry, high-throughput spatial and batch ALD equipment have been designed in the last few years and are already commercially available.^{20,21}

In this review article, we aim to discuss the progress in the development and understanding of the properties of Al₂O₃-based surface passivation schemes over the last few years. In doing so, relevant literature will be referenced, but also some previously unpublished experimental results have been included. The focus will be on Al₂O₃ deposited by atomic layer deposition. The further development, adoption, and integration of Al₂O₃-based passivation schemes will rely on an understanding of the properties underlying the synthesis and key properties of the films. This article aims to contribute to the latter. After a general introduction about the basics of surface passivation (Sec. II), the synthesis methods and Al₂O₃ material properties will be discussed (Sec. III). Subsequently, atomic layer deposition of Al₂O₃ will be addressed in detail in Sec. IV. Section V covers the surface passivation properties and underlying mechanisms. Section VI reports on technological aspects that are relevant for the application of Al₂O₃-based surface passivation schemes in (industrial) solar cells. Finally, in Sec. VII, recent progress on the high-efficiency solar cells featuring Al₂O₃ films is reviewed.

II. SURFACE PASSIVATION: BASICS AND APPLICATIONS

A. Surface passivation mechanisms

It is insightful to discuss the rate of surface recombination, U_s (expressed in cm⁻² s⁻¹), by its description in the Shockley–Read-Hall (SRH) formalism.^{22,23} U_s can be expressed as a function of the interface defect density (N_{it} , expressed in cm⁻²), the hole and electron capture cross sections ($\sigma_{p/n}$), and the hole and electron densities at the surface (p_s and n_s , respectively),^{24–27}

$$U_{s} = \frac{(n_{s}p_{s} - n_{i}^{2})v_{th}N_{it}}{\frac{n_{s} + n_{1}}{\sigma_{p}} + \frac{p_{s} + p_{1}}{\sigma_{n}}} = \frac{n_{s}p_{s} - n_{i}^{2}}{\frac{n_{s} + n_{1}}{S_{p}} + \frac{p_{s} + p_{1}}{S_{n}}} \approx \frac{n_{s}p_{s}}{\frac{n_{s}}{S_{p}} + \frac{p_{s}}{S_{n}}}.$$
(1a)

The parameter $v_{\rm th}$ represents the thermal velocity of the electrons, n_1 and p_1 statistical factors, n_i the intrinsic carrier concentration, and $S_{n/p} = \sigma_{n/p} v_{\text{th}} N_{\text{it}}$. For sake of the discussion here, the energy dependence of the parameters ($\sigma_{n/p}$, n_1 , p_1 , and $N_{\rm it}$) is neglected by assuming a single defect at midgap. In the latter case, and for relevant illumination and doping levels, n_1 , p_1 and $n_i \ll n_s$ and p_s , and can therefore be neglected in Eq. (1a). In reality, the energy levels associated with surface defects (e.g., dangling bonds) are distributed throughout the bandgap due to slight variations in structure and bond angle. Therefore, formally, U_s should be expressed by the extended SRH formalism with an integral over the bandgap energies while replacing N_{it} by D_{it} (in units of eV^{-1} cm⁻²).^{24,26} As follows from the simple expression in Eq. (1a), the driving force in surface recombination processes is the term $(n_s p_s - n_i^2)$, which describes the deviation of the system from thermal equilibrium under illumination. Equation (1a) shows that U_s can be decreased by a reduction in $N_{\rm it}$ (or $D_{\rm it}$), which is referred to as *chemical passivation*. In a recombination event both electrons and holes are involved. It is notable that the highest recombination rate is achieved when $p_s/n_s \approx \sigma_n/\sigma_p^{27}$ with the ratio of the cross sections being dependent on the details of the passivation scheme. Consequently, another way to reduce the recombination is by a significant reduction in the density of one type of charge carrier at the surface by an electric field. This is called *field-effect passivation*.^{27,28} We note that, apart from the SRH model, also the amphoteric nature of dangling bonds can be used to describe chemical and field-effect passivation, as reported by Olibet et al.²⁹

Figure 1 shows the influence of a negative fixed interface charge, Q_f , of 2×10^{12} cm⁻² (in units of the elementary charge) on the simulated electron and hole density near the surface for *p*-type and *n*-type Si. The surface charge gives rise to band bending [Fig. 1(c)]. For *p*-type Si, the increased majority carrier density leads to accumulation conditions, whereas the *n*-type Si surface is inverted. In both cases, a decrease in recombination can be expected as n_s is strongly reduced. However, for the inversion conditions, the electron and hole density become equal a distance away from the



FIG. 1. (Color online) Electron and hole density below the Si surface for (a) *p*-type and (b) *n*-type Si under influence of a negative fixed surface charge of $Q_f = 2 \times 10^{12} \text{ cm}^{-2}$; (c) band bending under influence of Q_f . Data simulated by PCID for 2 Ω cm wafers under illumination.

interface. This phenomenon can be expected to enhance recombination in the subsurface when bulk defects are present.

A measure that reflects the level of surface passivation is the surface recombination velocity *S*:

$$S \equiv \frac{U_s}{\Delta n},\tag{1b}$$

with Δn the injection level. It is possible to deduce an effective surface recombination velocity, $S_{\rm eff}$, from the effective lifetime of the minority carriers in the Si substrate, $\tau_{\rm eff}$. The effective lifetime is often measured by the photoconductance decay technique and is controlled by bulk- and surface recombination processes,^{30–33}

$$\frac{1}{\tau_{\rm eff}} = \left(\frac{1}{\tau_{\rm SRH}} + \frac{1}{\tau_{\rm Auger}} + \frac{1}{\tau_{\rm rad}}\right)_{\rm bulk} + \frac{1}{\tau_{\rm surf}}.$$
 (2a)

Equation (2a) illustrates that both intrinsic (Auger and radiative recombination) and extrinsic recombination processes determine bulk recombination. Extrinsic recombination via bulk defects is also known as SRH recombination. Impurities, such as Fe,³⁴ lattice faults, and dangling bonds at grain boundaries (multicrystalline Si) can all represent bulk defect states. In addition, boron–oxygen complexes, formed during illumination, can be prominent recombination centers, especially for monocrystalline *p*-type Si grown by the Czochralski method (Cz-Si).^{35–38} These defects limit the maximum bulk lifetime. On the other hand, for high quality float-zone (FZ) Si, Auger recombination and, to a lesser extent, radiative recombination are generally more important processes than recombination through bulk defects, especially at high injection levels.

For a symmetrically passivated wafer with sufficiently low S_{eff} values, Eq. (2a) can be expressed as

$$\frac{1}{\tau_{\rm eff}} = \frac{1}{\tau_{\rm bulk}} + \frac{2S_{\rm eff}}{W},\tag{2b}$$

with *W* the wafer thickness. The relative error in $S_{\rm eff}$ is typically below 4% for *S* values <250 cm/s.^{24,30} For poorly passivated surfaces, a term accounting for the diffusion of minority carriers toward the surface is required to improve the accuracy as described by

$$\frac{1}{\tau_{\rm eff}} = \frac{1}{\tau_{\rm bulk}} + \left(\frac{W}{2S_{\rm eff}} + \frac{1}{D_n} \left(\frac{W}{\pi}\right)^2\right)^{-1},\tag{2c}$$

with D_n the diffusion coefficient (with a typical value of $30 \text{ cm}^2/\text{s}$).²⁴ To calculate the exact value for S_{eff} by Eq. (2b), the bulk lifetime-which is generally not known-is required as an input parameter. Some authors use the general parameterization of the Auger recombination by Kerr and Cuevas for wafers with various resistivities to obtain a measure for the bulk lifetime.³⁹ However, it should be noted that these values represent an approximation (derived under the assumption that S_{eff} was 0 cm/s). In fact, Benick *et al.* have reported τ_{eff} values above the "intrinsic Auger limit" as derived by Kerr and Cuevas, suggesting that the intrinsic lifetime can be higher in reality.⁴⁰ In addition, τ_{bulk} may vary significantly from wafer to wafer due to the presence of SRH recombination. Alternatively, an upper level of S_{eff} can be calculated by assuming that recombination only occurs at the wafer surfaces (i.e., $\tau_{\text{bulk}} = \infty$),

$$S_{\rm eff,max} = S_{\rm eff} < \frac{W}{2\tau_{\rm eff}}.$$
 (2d)

 $S_{\rm eff,max}$ is a good approximation for the actual value of $S_{\rm eff}$ (for injection levels for which Auger recombination is not dominant) when the passivation properties are evaluated on Si wafers with high bulk lifetimes (> 1 ms). On the other hand, for an excellent surface passivation quality, with the surface recombination approaching 0 cm/s, the effective lifetime becomes dominated by intrinsic recombination processes which will limit the minimal value of $S_{\rm eff}$ that can be experimentally determined.

The influence of the chemical and field-effect passivation on the surface recombination velocity is illustrated by the simulations in Fig. 2. The trend of S_{eff} was derived by using Eq. (1a) in conjunction with a Poisson solver (PCID) to obtain values for n_s and p_s under illumination. S_{eff} is observed to decrease linearly with a reduction in N_{it} , which directly follows from Eq. (1a) and (1b). In addition, it is observed that the reduction in S_{eff} by field-effect passivation is especially prominent for Q_f values $>10^{11}$ cm⁻². The simulations show that for moderately doped Si a twofold increase in Q_f produces a fourfold decrease in S_{eff} (i.e., $S_{\text{eff}} \sim 1/Q_f^2$, for sufficiently high Q_f values).¹⁷ For significantly higher doping concentrations at the surface (e.g., emitters), a given fixed





FIG. 2. (Color online) Simulated $S_{\rm eff}$ and $S_{\rm eff,max}$ values using Eq. (1a) and (1b) and the relation between negative Q_f and p_s and n_s using PCID. The values used for the defect cross sections ($\sigma_n = \sigma_p = 10^{-16} \, {\rm cm}^{-2}$) are somewhat arbitrary but of a typical order of magnitude. Note that these values affect the scaling between $S_{\rm eff}$ and $N_{\rm it}$ (vertical axis) and not the qualitative picture. For ratio of $\sigma_n/\sigma_p = 10^2$, values of $\sigma_n = 10^{-15} \, {\rm cm}^{-2}$; $\sigma_p = 10^{-17} \, {\rm cm}^{-2}$ were used. Other values included a bulk resistivity of 2 Ω cm *p*-type Si (doping of $7.2 \times 10^{15} \, {\rm cm}^{-3}$) and an injection level of $\Delta n = 5 \times 10^{14} \, {\rm cm}^{-3}$. To calculate $S_{\rm eff,max}$, a value of $\tau_{\rm bulk} = 10$ ms was used. The simulation is an approximation to illustrate general trends.

charge density has a relatively smaller influence on band bending and the charge carrier densities (not shown). Consequently, the influence of the (additional) field-effect passivation induced by the passivation scheme becomes smaller for higher doping densities.

Figure 2 also shows that the trend between S_{eff} and Q_f changes significantly when the value of σ_n/σ_p is increased from 1 to 10². In the latter case, a maximum appears in S_{eff} at $Q_f = \sim 2 \times 10^{11} \text{ cm}^{-2}$, which coincides with the condition for maximum recombination $(p_s/n_s = \sigma_n/\sigma_p = 10^2)$. In addition, higher Q_f values >4 × 10¹¹ cm⁻² appear to be required to *activate* the field-effect passivation. It is notable that, for the case of Al₂O₃, a value of $\sigma_n/\sigma_p \gg 1$ is probably more realistic than $\sigma_n/\sigma_p = 1$. As will be discussed later, the Si/Al₂O₃ interface is essentially "Si/SiO₂"-like.⁴¹ The value of $\sigma_n/\sigma_p = \sim 10^2$ reported for thermally grown SiO₂ interfaces may therefore be a better assumption for the Si/Al₂O₃ interface.^{28,42}

The experimentally accessible parameter, $S_{\rm eff,max}$, is also given in Fig. 2. $S_{\rm eff,max}$ was derived by combining Eqs. (2b) and (2d) and substituting a bulk lifetime of 10 ms. Figure 2 shows that for a very high level of surface passivation, $S_{\rm eff,max}$ becomes limited by the bulk lifetime. In that case, $S_{\rm eff,max}$ does not reflect the actual (extremely low) $S_{\rm eff}$ values anymore. This implies, for instance, that significant variations of $Q_f > 1 \times 10^{12}$ cm⁻² are not expected to lead to drastic changes in the measured $S_{\rm eff,max}$ values.

B. Surface passivation materials

The most important surface passivation materials used in photovoltaics include SiO_2 , a-SiN_x:H, and a-Si:H. Considering the recent progress, Al_2O_3 can now be added to this list.

1. SiO₂

The high quality interface between thermally grown SiO₂ and Si contributed significantly to the dominance of Si in the microelectronics industry⁴³ and is also responsible for high solar cell efficiencies.^{44,45} Thermal SiO_2 leads to very low surface recombination velocities ($S_{\rm eff} < 10 \, {\rm cm/s}$) after forming gas annealing or alnealing (using a sacrificial Al layer).^{45–49} The hydrogen that is introduced during the annealing process passivates the electronically active defects such as the prominent P_b -type defect which constitutes an Si dangling bond (=Sio). This leads to typical defect densities of the order of 10^{10} cm⁻² eV⁻¹.^{46,50} Field-effect passivation is not prominent with comparatively low values of Q_f in the range of 10¹⁰-10¹¹ cm⁻². Hence, an important benefit of thermal SiO₂ is the high level of chemical passivation that can be achieved for both *n*- and *p*-type Si surfaces over a wide range of relevant doping levels. Moreover, it can be used to engineer diffusion profiles. Thermal oxidation can be carried out in H₂O-vapor ($T \sim 850-900$ °C) or O₂ atmosphere $(T \sim 950-1000 \,^{\circ}\text{C})$.^{44,45,49} The growth rate for the former "wet" thermal process is significantly higher than for the "dry" process. Various other methods have been explored for developing SiO₂ surface passivation films at low temperatures. Low-temperature processing can be technologically interesting as it opens up the possibility for using materials that are less thermally stable and avoids the risk of bulk lifetime degradation. The most widely investigated low-temperature method is plasma-enhanced chemical vapor deposition (PECVD), which allows for high-throughput processing.^{18,51,52} Another option for the synthesis of SiO_x is a chemical oxidation of the Si surface, for example using HNO₃.^{53,54} A drawback of this method is that it can only produce SiO_x with a thickness of a few nanometers. In general, the level of passivation induced by single layer SiO₂ synthesized at low temperatures is seriously lower than obtained by thermal oxidation processes. However, these properties can be improved drastically by the application of a-SiN_x:H or Al₂O₃ capping layers (see Sec. VI B).

2. a-SiN_x:H

The working horse thin film dielectric in c-Si photovoltaics is a-SiN_x:H (for brevity, SiN_x) synthesized by PECVD.^{55–61} Owing to the fact that the optical properties of the material can be varied in a wide range, SiN_{y} is the standard for antireflection coatings in solar cells. Figure 3 shows the material composition in terms of the atomic H, Si, and N density as a function of the refractive index. Films with comparatively high nitrogen content exhibit refractive indices of approximately 2, which results in optimal antireflection properties when applied on the front side of a solar cell. The films also contain a relatively large amount of hydrogen of \sim 10–15 at. %. The hydrogen released during firing plays an important role in the bulk passivation of multicrystalline Si.^{61–63} Depending on film composition, the films provide a reasonable to high level of passivation. Optimal surface passivation is generally achieved for relatively Si-rich films. However, the nitrogen-rich films exhibit a superior thermal

and chemical stability and can be useful as a capping layer on Al₂O₃. The passivation mechanisms of the a-SiN_x:H films strongly depend on the nitrogen content. When the nitrogen content is relatively low, the films exhibit amorphous Si-like properties. In this case, the high level of passivation is mainly governed by chemical passivation. On the other hand, for high [N], the films induce a significant amount of fieldeffect passivation with fixed charge densities of the order of 10^{12} cm⁻², as shown in the following. This is related to the so-called K-center (an Si atom backbonded with three N atoms) that can be charged positively [see Fig. 3 (inset)].^{64–67} A significant positive charge density leads to inversion conditions for *p*-type Si surfaces. Strong inversion can give rise to transport properties parallel to the interface. $a-SiN_x$ applied on the rear side of a *p*-type Si solar cell can therefore compromise solar cell performance by the so-called parasitic or inversion layer shunting effect.⁶⁷ SiO_2/SiN_x stacks are expected to reduce or nullify this detrimental effect.^{68,69}

3. a-Si:H

Hydrogenated amorphous Si (*a*-Si:H) is a semiconductor; in contrast to the dielectrics discussed so far. a-Si:H leads to excellent passivation properties with $S_{\rm eff}$ as low as 2 cm/s.⁷⁰⁻⁷⁵ The growth related material properties of PECVD a-Si:H have been studied in depth for applications such as thin film Si solar cells.^{76–80} This knowledge is also useful for the optimization and understanding of the a-Si:H properties for crystalline Si technology. In particular, heterojunction solar cells have attracted considerable attention in recent years.^{11,81–83} For such cells, high-temperature dopant diffusion processes are replaced by the deposition of doped a-Si:H films at low temperature. The surface passivation and unique contacting approach contribute to high open-circuit voltages (>700 mV). Efficiencies of 23.7% have been achieved using industrial processes.⁸⁴ Limitations of the application of a-Si:H surface passivation films are parasitic absorption effects and the lack of thermal stability during



FIG. 3. (Color online) Composition of *a*-SiN_x:H films in terms of H, Si, and N density plotted over the resulting refractive index. The films were deposited in a Roth & Rau MW-PECVD reactor. The atomic densities were obtained by Rutherford backscattering spectroscopy and elastic recoil detection. The inset shows some possible bonding configurations of Si (with dangling bonds) where $N_3 \equiv Si$ - represents the amphoteric *K*-center, which is typically positively charged for *a*-SiN_x:H films on Si substrates.

high-temperature processes (such as contact firing). The latter is an impediment to the use of *a*-Si:H in standard screen-printed solar cells.

Significant differences exist between the level of chemical and field-effect passivation afforded by the various passivation schemes. Thermal SiO₂ and intrinsic a-Si:H do not provide a high level of field-effect passivation, whereas this mechanism is quite significant for N-rich SiN_x and Al_2O_3 . To illustrate the differences in the passivation mechanisms of the materials, corona charging experiments are insightful. In Fig. 4, $S_{\rm eff,max}$ is plotted as a function of the corona charge density, ranging from negative to positive, deposited on ALD Al_2O_3 , N-rich SiN_x and SiO_x films synthesized by PECVD. The maximum in $S_{\text{eff,max}}$ is a measure for the chemical passivation because at this point the effect of intrinsic charge in the passivation scheme is nullified by the deposited corona charges. It is observed that the chemical passivation induced by Al₂O₃ is better than obtained by the SiN_x or PECVD SiO_x films. In addition, Fig. 4 illustrates that the SiO_x and SiN_x films exhibit a positive fixed charge density, whereas Al₂O₃ leads to a significantly higher and negative Q_{f} .

C. Surface passivation in high-efficiency solar cells

From the previous discussion, the question arises how the solar cell efficiency is affected by the implementation of a surface passivation scheme. Here, we consider a conventional *p*-type Si solar cell as an example to illustrate the effect of rear surface passivation. By using an Al₂O₃ film as dielectric in combination with local contacts [PERC-type cell (passivated emitter and rear cell)], the solar cell efficiency can be significantly higher than obtained with a full Al-BSF. This is related to (1) lower S_{eff} values and (2) the enhanced absorption in photon energy range of 1–1.2 μ m by an enhanced reflection from the solar cell's rear side. For the latter, a thickness of the passivation scheme of approximately 100–150 nm is beneficial.

The optical properties for a PERC cell with Al_2O_3 on the rear surface were simulated⁸⁵ and used as an input for the PCID program to simulate solar cell performance. The enhanced photon absorption for the PERC solar cell relative



FIG. 4. (Color online) $S_{\text{eff,max}}$ vs deposited corona charge density for *a*-SiN_x:H (~80 nm, after firing) and PECVD SiO_x (~50 nm) and Al₂O₃ films (~30 nm) after annealing at 400 °C in H₂/N₂ and N₂, respectively.

to the Al-BSF cell is demonstrated by an increase in the energy conversion efficiency in Fig. 5 (i.e., a vertical shift from the dashed to the solid line), which can be attributed to improved short-circuit current J_{sc} . The relative increase in $J_{\rm sc}$ is approximately 0.6–1.1 mA/cm², depending on the level of reflection R = 80%–65% of the Al-BSF reference. On the other hand, the open-circuit voltage V_{oc} is mainly sensitive to (surface) recombination processes. A decrease of S_{rear} from 500 to 50 cm/s, for instance, gives rise to an increase in both $V_{\rm oc}$ (by ~12.5 mV) and $J_{\rm sc}$ and results in an estimated efficiency improvement of approximately 1% absolute (Fig. 5). Due to synergistic effects, the influence of S_{rear} can be even more pronounced for cells with an improved front side. For increasingly low $S_{\rm eff} < 100 \, {\rm cm/s}$, the solar cell efficiency levels off. Note here that the minimum effective S_{rear} values associated with a typical Al-BSF are considerably higher than those corresponding to Al₂O₃ films. (Although also values as low as $S_{\rm eff} \sim 300 \, {\rm cm/s}$ have been reached for an optimized Al-BSF.^{86,87}) For PERC cells with Al_2O_3 , the effective S_{rear} is not only determined by the Al₂O₃ covered surface, which is typically $\sim 95\%$ of the area of the rear. It is also determined by recombination under the metal point or line contacts, i.e., local Al-BSF. In other words, the quality of the rear side also depends on the quality of the local Al-BSF. The S_{rear} values in actual solar cells will therefore be intrinsically somewhat higher compared to the Seff values obtained for lifetime samples. For increasingly good surface passivation, recombination losses associated with the local contacts will become of increasing importance.88 Therefore, innovative ways to mitigate such losses, e.g., by developing "passivated contacts"⁸ (as employed in heterojunction solar cells) will become an increasingly relevant research topic. It is also illustrated in Fig. 5 that, apart from surface recombination, the bulk lifetime of the minority carriers in the Si plays an important role in the overall efficiency. A discus-



FIG. 5. (Color online) Simulated solar cell efficiency as a function of the surface recombination velocity at the rear, S_{rear} , for a *p*-type silicon solar cell with 100 nm Al₂O₃/Al rear (PERC-type) or a rear Al-BSF. An Si bulk lifetime of 500 and 50 μ s was used. Simulations were performed with PCID using the following parameters: n^+ emitter sheet resistance of 60 Ω /sq; $S_{\text{front}} = 10^5$ cm/s; *p*-type Si bulk resistivity of 1 Ω cm; wafer thickness of 200 μ m, and the absorption characteristics as determined by Opticalculate (Ref. 85). The (small) effect of the local contacts on the rear reflection was neglected. The simulations serve to show general trends only.

sion of recent experimental results for solar cells with Al_2O_3 passivation schemes implemented is provided in Sec. VII.

III. AI₂O₃ PROPERTIES AND SYNTHESIS TECHNIQUES

A. Synthesis methods

1. Atomic layer deposition

The virtue of ALD is the control of the deposition process at the atomic level by self-limiting surface reactions during the alternate exposure of the substrate surface to gas-phase precursors.^{89–91} Each surface chemical reaction occurs between a gas-phase reactant and a surface functional group. These reactions automatically stop when all available surface groups have reacted, which makes the reactions self-limiting. A standard ALD process uses two precursors (A and B), and growth proceeds by alternating the precursors in an ABAB... fashion. After reaction of precursor A with the surface groups, the remaining precursor and the volatile reaction products are pumped away, and precursor B is introduced. This leads to the deposition of a second element through reaction with the new surface functional group. Also, the initial surface groups are restored. This reaction sequence forms one ALD cycle and results in one or less than one atomic layer of film growth, typically 0.5–1.5 Å/cycle. The ALD cycle can be repeated until the desired film thickness is reached. Unlike chemical vapor deposition, the deposition rate of ALD is not proportional to the "precursor" flux on the surface. Therefore, the same amount of material is deposited everywhere on the surface, even on nonplanar surfaces, provided that the precursor exposure times are sufficient.

Al₂O₃ deposited by ALD most commonly uses trimethylaluminum (Al(CH₃)₃ or TMA) as the aluminum source.^{92–105} Water, ozone, or oxygen radicals from a plasma can serve as the oxidants. Processes with water (illustrated in Fig. 6) and ozone are referred to as thermal ALD, while the process employing a plasma is referred to as plasma (-assisted) ALD. Each ALD cycle consists of Al(CH₃)₃ dosing followed by a purge, then oxidant exposure followed by a purge. The choice of oxidant depends on the application. In general, oxygen radicals generated by a plasma source are more reactive than H₂O. The increased reactivity of plasma ALD can give improved film quality with lower impurity levels, in particular for low substrate temperatures.⁹¹ However, plasma ALD equipment is more complex as a plasma source needs to be incorporated. In batch ALD processes, O₃ is often used as it exhibits good reactivity and is relatively easy to purge.^{103,106,107}

ALD is suitable for depositing a whole range of different materials, including (noble) metals, oxides, and nitrides.^{89,91,93} Also mixed and doped oxides can be readily synthesized by ALD.¹⁰⁸ Various ALD processes and materials have been investigated for virtually all types of solar cells.^{109,110} This includes CI(G)S, CdTe, organic-, and dye-synthesized cells. For instance, ALD ZnSe and ZnO films have been tested as buffer layers for CI(G)S thin film solar cells.^{111–114} Another example is Al-doped ZnO as a transparent conductive oxide.¹⁰⁸ Moreover, ALD Al₂O₃ has also



FIG. 6. (Color online) Schematic of ALD cycle comprising two precursor dosing steps and two purge steps.

been used; for example, as encapsulation layer in CI(G)S and organic cells. $^{115-118}$

Benefits of ALD over PECVD and PVD are the excellent uniformity that can be achieved on large substrates, the relatively low substrate temperatures used in the process (temperature window typically 100–350 °C), and the fact that ALD can readily produce multilayer structures. On the other hand, due to the purge steps, the ALD cycle times are typically of the order of a few seconds (single-wafer reactor), which leads to low deposition rates for temporal ALD. However, the throughput can be significantly enhanced using ALD batch reactors or a novel approach based on the spatial separation of the ALD precursors. These options for highvolume manufacturing are discussed in detail in Sec. VI C.

2. PECVD

Plasma-enhanced chemical vapor deposition is not a traditional synthesis method for Al₂O₃ and the amount of technologically relevant literature available on this topic is limited. Nevertheless, before Al₂O₃ became of interest for solar cell applications, some PECVD processes were reported using Al precursors such as Al(CH₃)₃ and AlCl₃.^{119–121} In the last few years, additional PECVD processes have been developed with the incentive to mitigate the drawbacks of temporal ALD. Miyajima et al. were the first to report on PECVD Al₂O₃ for surface passivation applications.^{122,123} They used a capacitively coupled plasma in combination with Al(CH₃)₃, H₂, and CO₂ process gasses. Furthermore, a PECVD process was developed in an industrial inline reactor that is already widely used for a-SiN_x:H deposition (Roth & Rau).¹²⁴ The plasma is created via a linear antenna by 2.45 GHz microwave pulses. N₂O, Al(CH₃)₃, and argon were used as process gasses. Deposition rates of 100 nm/min could be achieved. Roth & Rau now offers a tool that enables the deposition of Al_2O_3 and a-SiNx:H without vacuum break. In addition to the continuous flow processes, an alternative PECVD process has been reported in which the Al(CH₃)₃ precursor was pulsed.^{98,125} This pulsed process leads to additional control over the material properties. Collectively, the various reports have shown that for optimized PECVD processes the passivation quality of the deposited aluminum oxide films can be quite comparable to that achieved by ALD.

3. Other synthesis methods

In the first report on Al₂O₃ for surface passivation, atmospheric pressure chemical vapor deposition (APCVD) of aluminum-triisopropoxide was used.¹² Very recently, good results were reported using a large-scale deposition tool based on the APCVD method.¹²⁶ Physical vapor deposition, i.e., sputtering, has also been applied for the synthesis of Al₂O₃ passivation layers. RF magnetron sputtering of an aluminum target in an O₂/Ar mixture led to deposition rates of \sim 4 nm/min in a laboratory system.¹²⁷ Although only preliminary data are available, sputtering appears to produce Al₂O₃ with a lower level of passivation compared to ALD or PECVD.

B. Material and interface properties of Al₂O₃ on Si

The material properties of amorphous Al_2O_3 vary with deposition method.⁹⁸ A prominent factor influencing the Al_2O_3 composition is the incorporation of other elements than O and Al, such as carbon and most notably hydrogen. For ALD processes, the Al_2O_3 properties and the hydrogen content are primarily controlled by the substrate temperature during deposition T_{dep} .^{97,98} Fourier-transform infrared absorption (FTIR) measurements have indicated that hydrogen is incorporated as OH-groups, and that also some CH_x may be present.¹²⁸ In addition, the presence of carbonates was observed for Al_2O_3 films deposited by plasma ALD. Both the hydrogen and carbon content were observed to decrease with increasing deposition temperature.

Table I lists the important material properties of ALD Al₂O₃. For the relevant range of $T_{dep} = 150-250$ °C, both thermal and plasma ALD Al₂O₃ exhibited a comparable mass density and refractive index. However, the hydrogen content for thermal ALD Al₂O₃ (~3.6 at. %) was higher than for plasma ALD (~2.7 at. %) at $T_{dep} = 200$ °C. We verified with Rutherford backscattering spectroscopy (RBS) and x-ray photoelectron spectroscopy (XPS) that the carbon content in the films deposited at a temperature of ~200 °C was negligible with [C] < 1 at. %. In Fig. 7 data are shown for the refractive index, *n*, and extinction coefficient, *k*, as determined for plasma ALD Al₂O₃ films from spectroscopic ellipsometry measurements. Annealing at 400 °C did not change the optical

TABLE I.	Properties	of Al_2O_3 .
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Physical property	ALD Al ₂ O ₃ ($T_{dep} = \sim 200 ^{\circ}\text{C}$)		
Phase	Amorphous up to \sim 850 °C (Refs. 129 and 130)		
Resistivity	$\sim 10^{16} \Omega \mathrm{cm} (\mathrm{Ref.} 108)$		
Dielectric constant	7–9 (Refs. 94 and 97)		
Mass density	\sim 3.0 g/cm ³		
Hydrogen content	\sim 2–4 at. %		
Optical bandgap	6.4 eV		
Refractive index	1.64 (at 2 eV)		
RMS roughness	≤ 2 Å on polished Si(100) ^a		

^aVerified with atomic force microscopy for 15 nm films, using O_2 plasma, O_3 or H_2O as oxidants.

properties of the film significantly and thermal ALD with H₂O gave similar results. From the dielectric function ε_2 , an optical bandgap of $E_{opt} = 6.4 \pm 0.1$ eV was determined for both the as-deposited and annealed films. This experimentally determined value for (amorphous) Al₂O₃ films is lower than the value of ~8.8 eV representative for crystalline Al₂O₃. The Al₂O₃ films crystallize at temperatures above ~850 °C.^{129,130} Given the optical bandgap, parasitic absorption in the amorphous Al₂O₃ films will not occur in the range relevant for photovoltaics as only light with $\lambda < \sim 200$ nm is absorbed by the Al₂O₃ films. This is in contrast to, e.g., *a*-SiN_x:H films, with typical $E_{opt} = 3-3.5$ eV.

Apart from the bulk properties, the properties of the interface between Al₂O₃ and Si are obviously also of crucial importance for surface passivation. It was found that a thin $(\sim 1-2 \text{ nm}) \text{ SiO}_x$ layer is present at this interface. ^{14,131,132} This interfacial SiO_x is formed even on H-terminated Si (e.g., after HF treatment). Figure 8 shows a high-resolution transmission electron microscopy (TEM) image of the interfacial region of Al₂O₃ on Si(100). The presence of SiO_x was corroborated by FTIR by the detection of the Si-O stretching vibration around $\sim 1000 \text{ cm}^{-1}$.^{17,128} In addition, XPS revealed that the SiO_x layer is formed during the first few cycles of the deposition process (Sec. V D). Hoex *et al.* reported a (very small) increase of the SiO_x thickness during annealing at ~ 425 °C of $\sim 0.3 \text{ nm}$, which is close to the resolution of TEM. ¹⁴ Our XPS measurements confirmed that the SiO_x thickness was not



FIG. 7. (Color online) Refractive index, n, and extinction coefficient, k, as a function of the photon energy. Data obtained by spectroscopic ellipsometry.



FIG. 8. High resolution transmission electron microscopy (TEM) image of Al_2O_3 deposited on Si(100). The presence of an interfacial SiO_x layer is clearly visible (Ref. 14).

strongly affected by annealing at moderate temperatures (\sim 400 °C).

IV. ATOMIC LAYER DEPOSITION OF Al₂O₃

A. Surface chemistry

The growth mechanism of Al_2O_3 is well understood,^{89,93,104,133} and often used to exemplify the working principle of ALD in general. A schematic representation of a thermal and plasma ALD cycle is given in Fig. 9. In the first ALD half-cycle, the Al(CH₃)₃ precursor reacts through ligand exchange with the surface hydroxyls under formation of methane and O–Al bonds. This reaction is very efficient due to the formation of the strong O–Al bond.⁸⁹ The reaction between Al(CH₃)₃ and the surface can be monofunctional, but also bifunctional in which case two methyl groups react with two (neighboring) OH groups. The latter becomes more important at low substrate temperatures because of the higher density of surface OH groups. The surface chemistry during the first half-cycle is similar for plasma and thermal ALD, and can be described by

$$Al - OH^* + Al(CH_3)_3(g) \to AlO - Al(CH_3)_2^* + CH_4(g).$$

(3)

During the second half-cycle step, the surface changes from methyl-terminated to hydroxyl-terminated. For thermal ALD, methane is produced during the second half-cycle,

$$AlO - AlCH_3^* + H_2O(g) \rightarrow AlOAl - OH^* + CH_4(g).$$
 (4)

For plasma ALD, the reactions can be summarized by^{96,105}



Fig. 9. (Color online) Schematic representation of typical plasma and thermal ALD cycles for Al_2O_3 .

$$AlO - AlCH_3^* + 4O(g) \rightarrow AlOAl - OH^* + H_2O(g) + CO_x(g).$$
(5)

Note that the formation of the H_2O by-product during the plasma step can give rise to a secondary reaction pathway.⁹⁶

In addition to H_2O and an O_2 plasma, O_3 also can be used as coreactant. The reaction chemistry during O_3 -based ALD appeared to be more complex than the H_2O and O_2 -plasmabased process (see, for example, Refs. 103–105).

Depending on the length of each of the steps in the ALD cycle (Fig. 9), subsaturated growth, true ALD growth, or ALD growth with a parasitic CVD component takes place. The latter refers to a growth process that is not fully selflimiting. A true, saturated ALD process is obtained when an increase in the duration of the precursor and oxidant exposure times, in conjunction with sufficiently long purge steps, does not produce a higher growth per cycle (GPC). Under such circumstances, the deposition is highly uniform and conformal. Figure 10 shows that the thickness increases linearly with the number of cycles without apparent growth delay for deposition on Si(100). The associated growth rates were 1.0 A/cycle (thermal ALD) and 1.1 A/cycle (plasma ALD) for $T_{dep} = \sim 250 \,^{\circ}$ C. Note that these values are below the approximate thickness of a monolayer (~ 0.3 nm), which can be attributed to incomplete surface OH coverage and steric hindrance effects of the precursor molecules.

B. ALD process parameters

The influence of the relevant ALD parameters on the GPC of Al₂O₃ is shown in Fig. 11, comparing thermal ALD and plasma ALD. The TMA dosing time had virtually no effect on the growth process in our reactor configuration (Oxford Instruments OpAL). For dosing times of 10 ms and above, saturated ALD growth was observed for both methods. However, the purge time after the Al(CH₃)₃ dosing strongly influenced the growth process. Figure 11 shows that purge times $<\sim3$ s gave rise to higher GPC values for plasma and thermal ALD. In addition, short purge times led to a decrease in refractive index ($n = \sim1.61$ vs 1.64 for a true ALD process) and corresponding decrease in mass density of the Al₂O₃ films. A parasitic CVD growth component also produces film nonuniformity and is expected to impair



Fig. 10. (Color online) Al₂O₃ film thickness as a function of the number of ALD cycles ($T_{dep} = 250 \text{ °C}$).

the conformality of ALD. The minimum purge times required after the $Al(CH_3)_3$ precursor injection are closely related to the gas residence time. For short purge times, a fraction of $Al(CH_3)_3$ precursor remains in the reactor and can react with the oxidant introduced in the subsequent oxidation half-cycle.

Whether parasitic CVD reactions occur can be detected by optical emission spectroscopy measurements during plasma ALD. Figure 12 shows the presence of CO^{*}, H^{*}, and OH^{*} emission in the plasma.¹³⁴ When the spectrum is recorded after a sufficiently long purge time, the emission associated with C and H fragments can only originate from a monolayer of $-CH_3$ ligands at the growth interface. However, when reducing the purge time below 3.5 s, we observe an increase in the emission of CO^{*}, H^{*}, and OH^{*} as shown in Fig. 12(b). This is indicative of the dissociation of residual Al(CH₃)₃ in the plasma and corresponds well with the observed higher GPC values.

Regarding the second half-cycle, a saturated ALD process was obtained already for short H₂O dosing times (\sim 10–20 ms), which also led to high refractive index values of \sim 1.64. A slight increase of the GPC was, however, observed for longer H₂O dosing times. This is typically observed for thermal ALD at relatively low substrate temperatures and is referred to as "soft saturation."94 The plasma time had a more pronounced effect on the growth process. Plasma times <2 s clearly led to subsaturated growth. Under these circumstances the total flux of oxygen radicals during the oxidation half-cycle is insufficient to remove all the precursor ligands and restore the surface with OH groups. The plasma time can therefore be associated with the rate of the surface chemical reactions. The refractive index was also observed to drop for short plasma times, which is indicative of the incorporation of impurities into the material. Moreover, it was observed that subsaturated growth led to a significant deterioration of the thickness uniformity, especially at the edges of the substrate holder. The final purge step in the ALD cycle serves to remove the traces of the oxidant and reaction products left in the reactor. Figure 11 demonstrates that significant purging after plasma exposure was not required, while after H2O dosing, purge times ≥ 1 s were important to avoid parasitic CVD reactions. This implies that the very small amount of H₂O produced during the O₂ plasma step did not lead to significant reactions with the Al(CH₃)₃ precursor introduced in the subsequent step. This may change at lower deposition temperatures, for which generally longer plasma purge times are required.

For the optimized ALD processes in the single-wafer reactor (Oxford Instruments OpAL), nonuniformities of 1.5% and 4.3% were obtained for thermal and plasma ALD for wafers 200 mm in diameter. For similar wafer sizes, values of <2% have been reported for thermal and plasma ALD before.⁹⁷ The slight nonuniformity of plasma ALD can be attributed to a radial nonuniformity of the plasma species and can be decreased when using smaller wafers.

C. Substrate temperature

The substrate temperature is the most important parameter affecting the growth rate and, as discussed in Sec. III B,



FIG. 11. (Color online) Growth per cycle (GPC) as a function of the length of successive ALD steps for (a) thermal ALD and (b) plasma ALD. The films were deposited in an Oxford Instruments OpAL reactor ($T_{dep} = 250$ °C). The nonvaried parameters (purge and dose times) were sufficiently long to be compatible with saturated ALD growth and did not affect the influence of the varied parameter on the GPC.

the material properties of ALD Al₂O₃ films. Figure 13 shows that the influence of T_{dep} on film growth is markedly different for plasma and thermal ALD.^{97–99} For plasma ALD, the GPC and the number of Al atoms deposited per cycle decreases with increasing T_{dep} . This trend can be attributed to a lower OH surface coverage at higher T_{dep} , due to thermally activated dehydroxylation reactions under formation of H₂O.⁹² For thermal ALD, an *increase* in the growth rate was observed for increasing T_{dep} up to ~250 °C, whereas for $T_{dep} > 250$ °C the trend was similar to plasma ALD. This difference between thermal and plasma ALD at low T_{dep} can be explained by a lower reactivity of H₂O at low substrate temperatures. In contrast, the reactivity of the O₂ plasma is not controlled by the temperature. From a technological point of view, it is important to note that the purge times to remove H₂O from the reactor increase drastically with decreasing



FIG. 12. (Color online) (a) Optical emission spectroscopy spectrum recorded during plasma ALD. (b) Emission intensity of OH, H*, and CO* as a function of the preceding $Al(CH_3)_3$ purge length. Every data point represents a separate measurement during the initial stages of plasma operation. Note that for the purge time of 0 s, the plasma was switched on directly after the precursor dose.



FIG. 13. (Color online) Influence of the substrate temperature on the growth per cycle in terms of (a) film thickness and (b) Al atoms deposited (Refs. 98 and 99). The latter was determined by RBS measurements.

 T_{dep} . Plasma ALD is therefore generally preferred over thermal ALD for low-temperature applications (<150 °C).

V. SURFACE PASSIVATION BY Al₂O₃

A. Passivation performance

Very low surface recombination velocities $S_{\rm eff} < 5 \, {\rm cm/s}$ have been reported for Al₂O₃ on low-resistivity *p*-type and *n*-type Si (typically, 1–4 Ω cm) after annealing at moderate temperatures.^{14,15,40,98,135,136} In addition, for boron-doped emitters ALD Al₂O₃ resulted in very low emitter saturation current densities of $J_{0,e} \sim 10$ and 30 fA/cm² for >100 and 54 Ω /sq sheet resistances, respectively.¹³⁷ In other studies, Al₂O₃ passivation has shown to be compatible with implied $V_{\rm oc}$ values up to 700 mV (90 Ω /sq emitter).^{40,138} Also for screen-printed Al- p^+ -emitters comparatively low $J_{0,e}$ values $(\sim 160 \text{ fA/cm}^2)$ have been obtained.¹³⁹ The level of passivation achieved by Al₂O₃ for p^+ surfaces was higher than obtained by thermal SiO2 and a-Si:H and significantly higher than by SiN_x .^{16,137} This can be explained by the differences in strength and polarity of the fixed charges present in the passivation schemes. Possibly, differences in the capture cross section ratios—a relatively lower σ_n/σ_p is beneficial for p^+ passivation—may contribute as well (see Sec. II A). For n^+ emitters, it is expected that the negative Q_f of Al₂O₃ will not contribute to optimal passivation properties when compared to SiN_x containing positive charges. Preliminary measurements have indeed revealed significantly higher $J_{0,e}$ values for Al₂O₃ (~170 fA/cm²) than for SiN_x (~62 fA/cm²) on 62 $\Omega/sq n^+$ emitters.¹⁴⁰ Another report has shown that implied $V_{\rm oc}$ values between ~640 and ~680 mV can be achieved for sheet resistances between 20 and $\sim 100 \Omega/sq$ using plasma ALD Al₂O₃.¹⁴¹ It was argued that the low interface defect density induced by Al₂O₃ is primarily responsible for the passivation of n^+ emitters with low sheet resistances ($< \sim 100 \Omega/sq$).

Prior to deposition of the Al₂O₃ films on lifetime samples, the native oxide is generally removed from the wafers by treat-

ment in diluted HF (e.g., 1%) followed by rinsing in de-ionized-H₂O and drying (e.g., in an N₂ flow). The time between this cleaning step and film deposition is not a critical parameter. In addition, even surface chemical treatments (e.g., treatment in HNO₃) that result in a chemical oxide on the wafer surface can be applied prior to Al₂O₃ deposition.⁵⁴ To activate the passivation, annealing temperatures in the range of 350–450 °C were found to be optimal.¹³⁵ Annealing can be simply carried out in N₂ environment, as a gas mixture containing H₂ (i.e., forming gas annealing) led to similar results. Annealing times between 10 and 30 min are generally applied. However, we verified that annealing times of ~1–2 min can already be sufficient to fully activate the passivation performance of the films.

Figure 14 shows the injection-level-dependent effective lifetime for Al₂O₃ films deposited on *p*-type and *n*-type Si, comparing plasma and thermal ALD. The films were deposited in a saturated ALD regime at $T_{dep} = 200$ °C, which falls in the range of 150–250 °C for optimal passivation.⁹³ In the as-deposited state, thermal ALD affords a reasonable level of surface passivation with $S_{eff} < \sim 30$ cm/s ($\Delta n = 10^{15}$ cm⁻³) in marked contrast with plasma ALD Al₂O₃ ($S_{eff} \sim 10^3$ cm/s). After annealing at ~400 °C, very high levels of surface passivation with $S_{eff} < 5$ cm/s (*p*-type Si) and $S_{eff} < 2$ cm/s (*n*-type Si) were obtained for both ALD methods. Nevertheless, the plasma ALD process led to a slightly higher level of passivation than the thermal ALD process, which can be related to small differences in the level of chemical and field-effect passivation obtained by both methods (Sec. V B).

Regarding the injection level dependence, the effective lifetime is observed to decrease at high injection levels >10¹⁵ cm⁻³, which mainly reflects the Auger recombination. At low injection levels, the effective lifetime remains approximately constant for *p*-type Si. This is important for solar cells, as they often operate under relatively low illumination levels (e.g., $\Delta n = 10^{12}-10^{14}$ cm⁻³). In contrast, for *n*-type *c*-Si, the effective lifetime is observed to decrease significantly below injection levels of 5×10^{14} cm⁻³. The decrease in lifetime has been explained by enhanced (bulk)



FIG. 14. (Color online) Injection-level-dependent effective lifetime for plasma and thermal ALD Al₂O₃ before and after annealing (N₂, 400 °C, 10 min) on (a) $\sim 2 \Omega$ cm *p*-type *c*-Si and (b) $\sim 3.5 \Omega$ cm *n*-type *c*-Si (Refs. 107 and 135). The wafers received a treatment in diluted HF prior to deposition. Films with a thickness of ~ 30 nm were deposited using a substrate temperature of ~ 200 °C.

recombination in the inversion layer induced by the negative Q_{f} .^{17,28,142} Further evidence for this hypothesis is provided by the observation that the effective lifetime under low illumination conditions could be improved by a significant reduction in Q_{f} .¹⁴³

The influence of the ALD process parameters (i.e., dose and purge times, see Fig. 11) on the passivation quality of asdeposited and annealed Al₂O₃ films was also assessed. The passivation performance appeared to be insensitive to variations in the process parameters (not shown), with the exception of the plasma time. Interestingly, a reduction in plasma time led to a significant decrease in the Seff values for asdeposited plasma ALD Al₂O₃ ($T_{dep} = 250 \,^{\circ}\text{C}$). This can be attributed to a detrimental impact of vacuum ultraviolet (VUV) radiation from the plasma which is reduced for shorter plasma times.¹⁰⁷ Furthermore, it is important to note that a pure ALD growth mode was not necessary for obtaining optimal passivation. For example, a reduction in the $Al(CH_3)_3$ purge times from 3.5 to 0.5 s led to significantly higher growth rates (GPC values of ~ 1.8 Å, see Fig. 11) without compromising the passivation performance ($S_{eff} < 2 \text{ cm/s}$). Nonetheless, conditions outside the ALD growth window are expected to lead to an increase in thickness nonuniformity.

B. Effect of annealing on chemical and field-effect passivation

Figure 15 shows the influence of annealing on the surface passivation mechanisms of Al_2O_3 films synthesized by plasma ALD and thermal ALD (using H_2O). For thermal ALD Al_2O_3 , the key effect of annealing is the increase of Q_f , whereas for plasma ALD the chemical passivation improves dramatically. The relatively low D_{it} value of $\sim 3 \times 10^{11}$ eV⁻¹ cm⁻² for as-deposited thermal ALD Al_2O_3 is consistent with the moderate level of surface passivation obtained prior to annealing (compare Fig. 14).¹⁰⁷ This is in sharp contrast with plasma ALD, which did not provide passivation in the as-deposited state despite the high value of Q_f . It has been shown that the high D_{it} values for as-deposited plasma ALD Al_2O_3 are, at least partially, related to the exposure of



FIG. 15. (Color online) Influence of annealing on the negative fixed charge density, Q_f , and interface defect density at midgap, D_{it} , for plasma and thermal ALD Al₂O₃ films. In the various studies annealing took place at temperatures of ~400 °C.

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the surface to VUV radiation that is present in the plasma.^{107,144} After annealing, both ALD processes resulted in low $D_{it} \leq 1 \times 10^{11} \text{ eV}^{-1} \text{ cm}^{-2}$.^{107,146,147} Also for films deposited by PECVD, similar low defect densities were reported.¹⁴⁵

Regarding the field-effect passivation, it is notable that the thermal ALD Al₂O₃ films exhibited very low Q_f values of the order of 10^{11} cm⁻² prior to annealing; in contrast to plasma ALD with Q_f of the order of 10^{12} cm⁻². Also after annealing, the highest Q_f values have been reported for Al₂O₃ synthesized by plasma ALD. Furthermore, it was verified that Q_f was not critically dependent on the annealing temperature (T = 300-600 °C), see Fig. 16. While an initial increase is observed between T = 300 and 400 °C, Q_f appeared to be relatively independent of the annealing temperature for $T \ge 400$ °C. Similar observations were reported by Benick *et al.*¹⁴⁶

In general, the Q_f values that are reported for Al₂O₃ in various studies fall in the range of $(2-13) \times 10^{12}$ cm⁻² after annealing at moderate temperatures. ^{12,16,98,107,123,124,127,146,147} Note that these films all afforded low S_{eff} values < ~10 cm/s. Although the relevant material or processing parameters responsible for the variations in Q_f have not been fully identified, it was reported that the deposition temperature during ALD can affect the passivation mechanisms of the films. It was found that a variation in T_{dep} between 150 and 300 °C also gave rise to a variation in Q_f between 6 and 3.5×10^{12} cm⁻². ¹⁴⁸

C. Effect of film thickness

A key benefit of ALD is the ability to deposit ultrathin films. For thermal ALD, a correlation between film thickness and as-deposited surface passivation performance was found.¹³⁵ This effect may be attributed to a small "*in situ* annealing effect" taking place in the ALD reactor (at a deposition temperature of 200 °C) during prolonged processing time. More interesting is the thickness dependence after annealing. A constant high level of surface passivation could be maintained down to approximately 5 and 10 nm, for plasma and thermal ALD, respectively.^{135,147} It has been established that the cause of the deterioration is a decrease in



FIG. 16. (Color online) Negative fixed charge density Q_f vs annealing temperature (N₂, 10 min) for plasma and thermal ALD Al₂O₃ films. Q_f was determined from C-V measurements. Film thickness was ~ 30 nm.

the chemical passivation.^{145,149,150} Measurements by the noncontacting technique of secondary-harmonic spectroscopy have shown that the field-effect passivation remained constant while decreasing the film thickness to 2 nm.¹⁵⁰ This is consistent with the fixed negative charges being located near the SiO_x/Al₂O₃ interface. Similar conclusions have been drawn from C–V measurements.^{151,152}

Also, corona charging experiments are insightful when studying the effect of film thickness on the level of chemical passivation. Figure 17 shows results for the thickness dependence (5-30 nm) of the chemical and field-effect passivation for films deposited by thermal ALD. As discussed previously, the S_{eff} value measured at the point where Q_f is nullified by the deposited corona charges $(Q_{\text{total}} = Q_{\text{corona}} + Q_f = 0)$ can be used as an approximate measure for the chemical passivation (note, however, that some degradation may occur during charging). At this compensation point, the field-effect passivation is rendered inactive. While Q_f remained constant in the thickness range investigated [Fig. 17(c)], the results indicate that the level of chemical passivation strongly deteriorated for films of 5 nm [Fig. 17(b)]. This suggests that a minimum film thickness is required for effective interface hydrogenation during annealing (see Sec. V D).

Although not optimal, the level of passivation induced by Al_2O_3 films with a thickness <5 nm may still prove adequate for solar cells (Sec. II C), especially when combined with a capping layer.

D. Fundamental mechanisms

1. Defect passivation

To detect the physical and chemical nature of the interfacial defects, electron spin resonance (ESR) has proven to be a powerful technique. Stesmans and Afanas'ev have reported that Si/Al₂O₃ interface exhibits P_b -type defects (P_{b0} and P_{b1}).⁴¹ This is also the case for the Si interface with other "high-k" dielectrics such as HfO₂ and ZrO₂. The P_b -type defect is a trivalently bonded Si atom (Si₃=Si^o), which represents the prominent electronically active defects characteristic of the Si/SiO₂ interface.^{153,154} Electronically, the Si/Al₂O₃ interface can therefore be regarded as Si/SiO₂-like with the P_b -center density being a criterion for the interface quality. The similarity between Si/Al₂O₃ and Si/thermally grown SiO₂ was recently also corroborated by a deep-level transient spectroscopy study.¹⁵⁵ The observations are in line with the formation of an interfacial SiO_x layer (Sec. III B).

To investigate the nature of the defects in plasma ALD Al₂O₃ in the as-deposited state and after annealing, contactless electrically detected magnetic resonance (EDMR) measurements were performed.^{156–158} Compared to ESR, EDMR measurements are more sensitive to small defect densities, although they lack the quantitative information. From the determined g-factors in the EDMR spectra (Fig. 18), it was possible to identify the P_{b0} center (g = 2.0087 and 2.0036) as the main trapping center for the as-deposited plasma ALD Al₂O₃. This was similar for thermal ALD (not shown). In addition, an isotropic center with g = 2.0055, and an E'-like defect with g = 1.999 were observed. The former relates to a dangling bond at the Si surface, which was also observed for amorphous Si.^{159,160} The E'-like defects are associated with the SiO_x interface (O \equiv Si^o). After a standard annealing step (400 °C), EDMR did not reveal the presence of remaining defect states. This is in good agreement with the low D_{it} values $\leq 10^{11}$ cm⁻² eV⁻¹ obtained after annealing (Fig. 15).

It is well known that the trivalent Si interface trap is chemically active and can be passivated by hydrogen. For SiO₂, the P_b -type defect density is typically $\sim 1 \times 10^{12}$ cm⁻² after oxidation and can be reduced $<10^{10}$ cm⁻² after annealing in H₂ ambient.^{46,50,153} The passivation of P_b-type defects in H_2 exhibits an activation energy of ~1.5 eV, which is significantly lower than the energy for dissociation of Si-H (~2.8 eV) in the range of optimal annealing temperatures.¹⁵³ With isotope labeling using deuterated Al₂O₃, it has been shown experimentally that hydrogenation of the interface plays an important role in the chemical passivation of the Al₂O₃ films.¹⁶¹ Moreover, the diffusion of hydrogen in Al₂O₃ was found to critically depend on the annealing temperature and the Al_2O_3 structural



FIG. 17. (Color online) Effect of film thickness on the chemical and field-effect passivation. (a) $S_{eff,max}$ as a function of the deposited corona charge density Q_{corona} . (b) Chemical passivation in terms of the value of $S_{eff,max}$ for which Q_f is exactly balanced by positive corona charges (i.e., $Q_{total} = Q_f + Q_{corona} \approx 0)$ for film thicknesses in the range of 5–30 nm. (c) Negative Q_f values for the thickness range investigated. Films were deposited by thermal ALD and were annealed at 400 °C (N₂, 10 min). Lines serve as a guide to the eye.



Fig. 18. (Color online) Electrically detected magnetic resonance (EDMR) spectra obtained for plasma ALD Al_2O_3 films deposited on Si(100). As-deposited and annealed samples were compared.

properties.¹⁶² For films that exhibited either a low mass density (and high hydrogen content) or a very low initial hydrogen content (and a high mass density), the passivation was less thermally stable at temperatures of $\sim 600 \,^{\circ}\text{C}$ compared to films with intermediate properties. Finally it is speculated that, apart from the interface hydrogenation, the chemical passivation may also be influenced by film relaxation, Si–O bond rearrangements, and some additional interfacial oxide growth during annealing.

2. Negative charge formation

The microscopic origin of the defect states in the Si–Al₂O₃ system that lead to negative Q_f has not been clearly established (see the discussion in Ref. 17). Moreover, dedicated theoretical or experimental work on this topic has not yet been carried out in the *context* of field-effect passivation. However, in a broader context, defects in Al₂O₃, and especially in other (high-*k*) metal oxides, have been studied for their important role in metal–oxide–semiconductor applications. It is well known that the origin of the charge traps are (ionized) point defects, ^{163–166} with candidates such as (oxygen or metal atom) vacancies and interstitials. The latter may also include extrinsic defects, such as interstitial hydrogen. ¹⁶⁷ The defects in these ionic metal-oxides are different from those in thermally-grown SiO₂.

Various simulation studies have identified the point defects in Al₂O₃, i.e., the O vacancy, the O interstitial, the Al vacancy, and the Al interstitial, and their energetic positions in the bandgap.^{164,168–170} Liu *et al.* have provided evidence that the O vacancy is responsible for transport and trapping properties.¹⁶⁴ However, it is not likely responsible for negative charge. In a simulation study, Matsunaga *et al.* have reported that the Al vacancy (V_{Al}) and the O interstitial (O_i) can be charged negatively.¹⁶⁸ V_{Al} was found to be stable in the -3state, and O_i in the -2 state.^{168,169} Using more advanced simulations, Weber *et al.* have recently analyzed the defects in Al₂O₃ in the context of III–V electronics.¹⁶⁹ They found that V_{Al} and O_i produce levels in the Al₂O₃ bandgap *below* midgap. Both defects are therefore likely candidates to trap negative fixed charge in, e.g., the InGaAs/Al₂O₃ system which has a valence band offset of $E_v \sim 3$ eV compared to the Al₂O₃ valence band maximum. As $E_v \ge 3$ eV for Si,^{164,171,172} we may expect that the negative fixed charge in the Si/Al₂O₃ system has a similar origin.

Experimentally, however, it is difficult to determine unambiguously the presence and type of point defects in the bulk of ultrathin films. Moreover, the concentration and type of defects that form near the Si/Al₂O₃ interface may differ from the bulk. When the negative charge is related to the presence of V_{Al} and O_i defects, a slightly oxygen-rich structure in proximity of the Si interface would be expected. In agreement with this, Shin *et al.* have demonstrated that negative fixed charges were indeed correlated with the presence of an O-rich region near the interface for InGaAs/Al₂O₃ MOS structures.¹⁷⁰ Also for the Si/Al₂O₃ system, depthdependent structural properties have been reported by Kimoto *et al.*¹⁷³ Both tetrahedrally and octahedrally coordinated Al atoms exist in Al₂O₃, but the former appeared to be more dominant near the surface.

Regarding the stoichiometry of the ALD films, an O/Al ratio very close to ~ 1.5 was determined by RBS for a film deposited using 250 ALD cycles $(T_{dep} \ge 200 \text{ °C}).^{98}$ However, due to the presence of a small amount of OH groups $(\sim 1-3 \text{ at. }\%)$ it is expected that the films are slightly O-rich. To investigate whether the stoichiometry of Al₂O₃ is thickness dependent, XPS spectra were recorded for films grown using 10 cycles (\sim 1.2 nm) and 100 cycles (\sim 12 nm). The Al 2p peak is sensitive to structural variations in the Al₂O₃ films, and it was found to consist of multiple contributions for the ultrathin 1.2 nm film. The most prominent contributions can be assigned to an Al₂O₃ structure (\sim 74.4 eV) and the presence of Al–OH bonds (\sim 75.6 eV),¹⁷⁴ see Fig. 19(b). At the surface, carbon was detected [Fig. 19(c)], which also appears in the Al 2p spectrum. To obtain a semiquantitative analysis of the atomic Al and O density for ultrathin Al₂O₃ films, the O contribution originating from the carbonates on the surface and from the interfacial oxide is significant and has to be corrected for. Moreover, an adsorbed H₂O layer on the surface can also contribute.¹⁷⁵ This leads to an inherent uncertainty in the O/Al ratio for very thin films. Also for thicker films, a sensitivity factor is required to calibrate the O/Al ratio as determined by XPS to the more precise value determined by RBS. Figure 19(d) shows that small variations in the stoichiometry near the interface, most likely a higher oxygen concentration, may exist. In contrast, a more dramatic change in stoichiometry near the interface was recently suggested by Werner et al., with the O/Al ratio reaching a value as high as \sim 8, as was inferred from XPS measurements.147

However, in this context, it is relevant to consider that the number of defect states near the interface that is required to account for Q_f is relatively small. Using atomic densities obtained by RBS, we can estimate the number density of "Al₂O₃ units" to be approximately 7×10^{14} units/cm² at the SiO_x/Al₂O₃ interface. Therefore, for a fixed charge density of



FIG. 19. (Color online) (a)–(c) X-ray photoelectron spectroscopy (XPS) applied to an ultrathin Al_2O_3 film synthesized using 10 plasma ALD cycles on HF-last Si(100). Data are obtained before and after annealing (400 °C, 10 min, N₂). (d) Estimate of the O/Al ratio for films deposited using 10 and 100 cycles (XPS measurement) and 250 cycles (Rutherford backscattering spectroscopy measurement).

 7×10^{12} charges/cm², we find that only one "surface charge" is present for every 10^2 Al₂O₃ units. Thus, a very large deviation from stoichiometry appears not to be a prerequisite to account for the typical negative fixed charge densities of Al₂O₃.

Another important issue is the role of charging of defect states. The charge state of an (ionized) defect can be changed by electron (or hole) injection into the conduction (or valence) band of the dielectric and by tunneling from the dielectric into the substrate or from the dielectric surface into the metal (gate).^{176,177} For the Si/Al₂O₃ system, there are some indications that charge injection from Si into Al₂O₃ may play a role in the formation of the negative Q_{f} . Secondharmonic generation experiments have demonstrated that Q_f can increase under influence of laser irradiation.¹⁷² This is consistent with (multi-) photon-induced charge injection from Si into preexistent defect states at the SiO_x/Al₂O₃ interface. In addition, we have observed a hysteresis during corona charging experiments that is consistent with a charge injection phenomenon. For annealed Al₂O₃ samples, the fixed charge density was observed to increase by (1-2) $\times 10^{12}$ cm⁻² after deposition of positive corona charges $(\sim 10^{13} \text{ cm}^{-2})$ on the Al₂O₃ surface (not shown). The net positive charge may attract electrons from the Si wafer into defect states at the SiO_x/Al₂O₃ interface. In addition, it has been demonstrated that an increase in the SiO₂ interlayer thickness over the range of 1-30 nm gave rise to a decrease in negative Q_{f} .^{69,143} For instance, flatband conditions were observed for an ALD SiO₂ interlayer thickness of \sim 5 nm.¹⁴³ The simplest explanation is that the SiO₂ acts as a barrier, reducing charge injection from the Si substrate into defect states at the SiO₂/Al₂O₃ interface.

In conclusion, simulations and experiments have provided evidence that the negative charge at the SiO₂/Al₂O₃ interface may be related to V_{Al} and O_i defects. Charge injection phenomenon across the interface may play a role in the formation of the negative charge associated with these defects. It is important to point out that also other mechanisms can contribute to negative charges, and that more research is required to draw final conclusions.

VI. IMPLEMENTATION IN SOLAR CELLS

A. Stability

1. UV stability

The ultraviolet (UV) stability of a passivation layer is important when applied at the front side of a solar cell. With an optical bandgap of ~6.4 eV, amorphous Al₂O₃ is transparent for the UV radiation in the solar spectrum. The surface passivation induced by Al₂O₃ was not found to degrade during the UV exposure of an Hg lamp (~254 nm). In fact, in some cases the effective lifetime of an Al₂O₃-passivated wafer exposed to UV light was even observed to increase by ~40%.¹⁷⁸ This was tentatively explained by an increase in Q_f by photon-induced charge injection from the Si substrate. Other reports have shown that during light soaking the passivation performance remained stable.¹⁷⁹

2. Firing stability

When Al_2O_3 surface passivation films are implemented in screen-printed solar cells, the thermal stability of the films during high-temperature firing processes (>800 °C) is crucial. The impact of direct firing and firing after a preceding lowtemperature annealing step on the passivation properties of Al_2O_3 has been evaluated.^{40,136,178} The reports show that the level of passivation by Al_2O_3 decreases, but that its thermal stability is generally sufficient for application in screenprinted solar cells. On the other hand, the exact level of passivation that can be expected after firing is strongly dependent on the peak temperature and the duration of the firing step.

For low resistivity *n*- and *p*-type *c*-Si, $S_{\text{eff}} < 14$ and 25 cm/s have been reported after annealing (400 °C) and subsequent firing (800 °C).^{178,180} After direct firing at 750 °C, an S_{eff} value of ~20 cm/s could be achieved for *p*-type Si.⁴⁰ Moreover, a good thermal stability was obtained for the passivation of p^+ emitters.^{40,138,181} The latter also appeared to be less sensitive to the peak temperature than the passivation of low resistivity Si wafers. For instance, the level of passivation of a 90 Ω /sq. p^+ emitter was compatible with

open-circuit voltages > ~695 mV after firing at 825 °C.⁴⁰ Also, for Al₂O₃ synthesized by PECVD and spatial ALD good thermal stabilities have been reported.^{180,182,183} Furthermore, when ultrathin films <20 nm were considered, the firing stability for Al₂O₃/SiN_x stacks was found to be better than for single layer Al₂O₃. For uncapped 3.6 nm thick Al₂O₃, very high *S*_{eff} values of ~300 cm/s were obtained after firing (830 °C), while a corresponding stack comprising a 75 nm thick SiN_x capping film resulted in a significantly lower value of *S*_{eff} < 44 cm/s.¹³⁶

The results on lifetime samples have recently been corroborated by a good thermal stability for Al₂O₃ films implemented in screen-printed solar cells. For example, Gatz *et al.* have extracted an S_{eff} value of 70 ± 30 cm/s (contact pitch 1 mm) for an Al₂O₃/SiN_x stack at the rear side of a screen-printed *p*-type PERC solar cell leading to an efficiency of 19%.¹⁸⁴

The relative deterioration in passivation quality during firing can be attributed mainly to an increase in D_{it} at high annealing temperatures, while the value of Q_f was found to be less affected.¹³⁸ The increase in D_{it} can be ascribed to the dissociation of interfacial Si–H bonds at elevated temperatures. Thermal effusion measurements revealed that hydrogen is released from the film at such high annealing temperatures.¹⁷⁸ Furthermore, it was found that the firing induced degradation could not be improved significantly by subsequent annealing in forming gas.¹⁷⁸ This contrasts the behavior of fired thermally grown SiO₂, and can likely be explained by the fact that Al₂O₃ film acts as a barrier for the diffusion of H₂ from the annealing atmosphere at moderate temperatures (~400 °C).

Apart from the stability of the passivation, the physical and optical properties of the Al₂O₃ (bulk) material should, preferably, not deteriorate at high temperatures. While cracking of the Al₂O₃ films did not occur, small blisters have in several cases been observed after high-temperature processing.^{185,186} The key parameters (e.g., synthesis method, film thickness, structural properties, firing recipe, capping layer) that affect blister formation have not yet been conclusively identified, and it should be noted that in some cases (e.g., when using ultrathin films) no blistering was observed after firing. Figure 20 shows an SEM image of thin Al₂O₃ film that exhibited round blisters with a typical diameter of \sim 50 μ m. Figure 20 clearly illustrates that blistering is associated with local film delamination. The formation of blisters can likely be attributed to the local accumulation and subsequent release of gaseous hydrogen and/or H₂O from the films. It should be noted that the passivation performance was not (strongly) affected by film blistering, which may be expected on the basis of the typically low surface coverage of blisters (5%–10%). More research is required for a better understanding of the conditions that lead to film blistering.

B. Surface passivation stacks

1. Al₂O₃/a-SiN_x stacks

a-SiN_{*x*}:H capping layers, synthesized by PECVD, have been applied on top of thin Al₂O₃ films at the rear and front side of solar cells.^{184,187,188} The thermal budget during *a*-SiN_{*x*}:H deposition (~350–450 °C) can activate the surface passivation induced by Al₂O₃.¹⁷⁸ As discussed before, the application of an SiN_{*x*} capping layer can extend the process window for screen-printed solar cells in terms of Al₂O₃ film thickness and firing temperature.^{136,138} Richter *et al.* have recently reported that five ALD cycles of Al₂O₃ in combination with an SiN_{*x*} capping layer already produces good passivation properties for *p*⁺ emitters.¹³⁷

An important reason for the use of Al_2O_3/SiN_x stacks at the rear side of screen-printed solar cells is the improved *chemical* stability. It has been observed that the application of metal pastes directly on Al_2O_3 can disintegrate the material during firing. N-rich SiN_x layers appear to be robust and to remain chemically stable. These capping films can therefore protect the Al_2O_3 films from damage caused by metal paste. Moreover, when ultrathin Al_2O_3 films are considered at the rear side, an SiN_x capping layer can be useful to increase the physical thickness to improve the rear reflection properties of the solar cell.

The stacks exhibit a negative fixed charge density.^{69,138} This is consistent with the expectation that the positive fixed charge density in SiN_x films applied on Si is related to the



Fig. 20. Example of an Al_2O_3 film with "blisters" formed after high-temperature annealing. The images were obtained by scanning electron microscopy (SEM).

2. SiO₂/AI₂O₃ stacks

A different approach is to use Al_2O_3 as a capping layer on SiO₂. These SiO₂/Al₂O₃ stacks have significant technological potential for the passivation of both *n*- and *p*-type Si. They lead to a considerable improvement in the passivation properties and stability of SiO₂, regardless of the synthesis method.^{52,69,143,161,162} Results on stacks comprising thermally grown SiO₂ and SiO₂ synthesized at low temperatures by PECVD and ALD have been reported.

Stacks comprising thermally grown SiO₂ exhibited $S_{\rm eff}$ values <5 cm/s after annealing in N₂, which was slightly better than obtained by single layer SiO₂ after forming gas annealing.^{162,180} An Al₂O₃ thickness of 10 nm and above was found to be sufficient to fully activate the passivation performance of the stacks (Fig. 21). Moreover, the poor passivation properties of SiO₂ synthesized at low temperatures could be improved dramatically by application of an ultrathin Al₂O₃ capping layer.⁵² S_{eff} values < 5 cm/s (*n*-type Si) were obtained for SiO₂ films (10–85 nm) synthesized by PECVD and ALD.^{52,143} Moreover, the stacks exhibited an excellent firing stability,^{52,69,161} and did not suffer from a poor long-term stability as is sometimes observed for single layer SiO₂.¹⁸⁹

The low S_{eff} values obtained for the SiO₂/Al₂O₃ stacks can be attributed to (very) low interface defect densities $D_{it} < 10^{11}$ cm⁻² eV⁻¹.^{52,69,189} This is illustrated for PECVD SiO₂/Al₂O₃ stacks by the capacitance–voltage measurement in Fig. 22. The *C*–*V* characteristics reveal an almost negligible frequency dispersion (i.e., insignificant time-dependent response of interface defects) indicative of an excellent interface quality. In turn, the low defect densities can be attributed to the effective hydrogenation of the Si/SiO₂ interface during annealing under influence of the Al₂O₃ capping layer. Evidence has been provided that atomic hydrogen could play a role for Al₂O₃ films.¹⁶² These observations are reminiscent



FIG. 21. (Color online) Surface passivation quality in terms of $S_{\rm eff,max}$ of SiO₂/Al₂O₃ stacks as a function of Al₂O₃ capping layer thickness. The SiO₂ was synthesized by wet thermal oxidation and had a thickness of ~200 nm. Annealing was performed at 400 °C (N₂, 10 min). Al₂O₃ was synthesized by thermal ALD.

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FIG. 22. (Color online) Low- and high-frequency capacitance–voltage (C-V) measurements for a PECVD SiO₂/Al₂O₃ stack and single layer Al₂O₃. Evaporated Al was used for the contacts and these were applied after annealing the samples at 400 °C (N₂, 10 min). As substrates, 2 Ω cm *p*-type *c*-Si wafers were used.

of the "*alnealing*" process for which a sacrificial aluminum capping layer is used during annealing of the SiO₂ layer. It has been hypothesized that the *alnealing* effect is related to an oxidation reaction of Al (e.g., reaction with H₂O) under formation of (atomic) hydrogen and AlO_x .^{10,46} Also the Al_2O_3 layer could be removed after annealing (by etching in diluted HF) without compromising the passivation properties.¹⁶¹

The field-effect passivation induced by the stacks was found to decrease strongly for increasing SiO2 thickness.^{69,143} This is illustrated by the reduced flatband voltage shift in Fig. 22 for the PECVD SiO₂/Al₂O₃ stacks. For stacks comprising ALD SiO₂, a strong decrease in field-effect passivation was observed for a thickness range of 1-5 nm.¹⁴³ For increasing SiO₂ thickness, the negative Q_f at the SiO₂/ Al_2O_3 decreases and, consequently, the positive charges associated with SiO₂ start to play a more prominent role. The latter also depends on the synthesis method of the SiO_2 as thermally grown SiO₂ generally contains less positive charges than SiO₂ deposited at low temperatures. Therefore, depending on the SiO₂ film thickness and synthesis method, the net fixed charge density of the stacks can vary from negative to positive. The results for SiO₂/Al₂O₃ stacks appear to be more general as a decrease in field-effect passivation was also observed for SiO₂/SiN_x stacks.^{68,69} Therefore, material stacks are not only useful to optimize the optical and physical properties but also to tailor the underlying surface passivation mechanisms.

C. Industrial-scale ALD

The traditionally low deposition rate of ALD has been regarded as the main obstacle for the use of ALD in photovoltaics where the throughput requirements are significantly higher than in the microelectronics industry. For single-wafer reactors, the deposition rate is typically $\sim 1-2$ nm/min for cycle times of a few seconds in length. However, while the growth per cycle for Al₂O₃ is fixed at roughly ~ 1 Å for

all ALD equipment, the duration of the cycle and the number of wafers that can be deposited simultaneously, and therewith the deposition rate (i.e., thickness per unit of time per wafer), can vary substantially. With the incentive to overcome the throughput limitations of existing ALD Al_2O_3 methods, equipment manufacturers such as Beneq and ASM have redesigned or adapted their ALD batch tools, which were originally designed for the semiconductor industry, to meet the throughput requirements of typically >3000 solar cells/h. Moreover, *spatial* ALD equipment has recently been developed specifically for the deposition of Al_2O_3 for PV applications.²¹

The concept of spatial ALD was already described in the original ALD patent of Suntola.¹⁹⁰ More recently, technology to enable atmospheric spatial ALD has been explored by Levy et al.¹⁹¹ The difference between spatial and temporal ALD pertains to the separation of the precursor and oxidant steps (Fig. 23). In conventional temporal ALD processes, such as used in batch reactors, the precursor and oxidants are injected sequentially into the same reactor volume. In spatial ALD, the precursor and oxidants are separated spatially in different zones of the reactor. Two spatial ALD concepts have been commercialized-by SoLayTec and by Levitech.^{192,193} Both concepts are quite similar with the main difference being the transport of the wafers (Fig. 23). The Levitech approach is based on an inline reactor (the Levitrack) where transport is controlled by an atmospheric gas bearing on which the wafer floats. While the wafer moves through the reactor, it is sequentially exposed to Al(CH₃)₃, N₂, H₂O, and again N₂. The precursor zones are repeated over the length of the track, which also has a heating and cooling zone in the initial and final part of the reactor. The system yields $\sim 1 \text{ nm}$ Al_2O_3 per 1 m system length in its current configuration. In the SoLayTec reactor, the wafer moves back and forth underneath TMA and H₂O injection zones. Therefore, film thickness is independent of system length. As is the case in the Levitrack, wafer movement is fully controlled by gas flows. In the SoLayTec concept, the deposition rate depends on the number of injection slots integrated in the injector head and the number of passages of the wafer per second.

In spatial ALD, the cycle time is ultimately dictated by the speed of the precursor reactions at the growth surface and not by the purge steps that avoid parasitic CVD reactions between precursors. Both spatial ALD reactors lead to significantly higher deposition rates (e.g., 30–70 nm/min) than generally obtained by temporal ALD (a few nm/min at most). Other benefits of these reactors are that no vacuum pumps are required as the reactors are operated under atmospheric pressure conditions, and that, in the ideal case, only the wafer is coated (either single-side or double-side depending on the reactor design) and not the reactor walls. In addition, there are no moving equipment parts apart from the wafers. More details on spatial ALD and the systems can be found in Refs. 20 and 21 and 194–198.

An important question to address is whether the scale-up of the ALD processes compromises the passivation properties of Al_2O_3 films in comparison with single-wafer laboratory systems. Here, we focus on the passivation properties of Al_2O_3 films that were deposited in an ASM ALD batch reactor and in the inline ALD reactor from Levitech.

1. Batch ALD

The surface passivation properties of Al_2O_3 deposited in the ASM ALD batch reactor were optimized for substrate temperature and precursor dosing times. O_3 was used as the oxidant and the lifetime wafers were deposited at both sides simultaneously. The wafers can also be placed back-to-back, which results in single-side deposition of twice the amount of wafers and, therefore, a higher wafer throughput. The Al_2O_3 films afforded a low level of surface passivation in the as-deposited state. This is similar to the results for plasma



FIG. 23. (Color online) (a) Schematic representation of atomic layer deposition processes for oxides where the precursor dose step and the oxidant are (i) separated in time or (ii/iii) separated spatially. The precursor and oxidant are prevented from reacting with each other, either by purging the reactor or by their spatial separation involving purge flows in between the precursor inlets. (b) Schematic of an ALD batch reactor. (c) Spatial ALD setup as commercialized by the company Levitech, where the wafer moves through an inline reactor, see also (ii). Note that (iii) is the approach commercialized by the company SolayTec, where the substrate moves back and forth between two reactor zones.

ALD. The surface passivation was activated by annealing, resulting in low $S_{\rm eff}$ values < 6 cm/s for Al₂O₃ films with a thickness of ~15 nm for 2 Ω cm *p*-type Si wafers.¹⁰⁷ This high level of passivation after annealing can be explained by a high fixed negative charge density of 3.4×10^{12} cm⁻² and a low interface defect density $D_{\rm it}$ of ~1 × 10¹¹ eV⁻¹ cm⁻² as determined by *C*–*V* measurements.¹⁰⁷

2. Spatial ALD

The Al₂O₃ films deposited in the Levitrack afforded some surface passivation in the as-deposited state with $S_{\rm eff} < 50 \, {\rm cm/s}$ for a film thickness of $\sim 15 \, {\rm nm}$. This is in agreement with results for thermal ALD with H₂O in a lab scale reactor (Fig. 14). After a standard anneal, the effective lifetime increased significantly to $\tau_{eff} = 2.5$ ms, resulting in very low $S_{\rm eff} < 6$ cm/s [Fig. 24(a)].¹⁸⁰ Reference samples deposited with plasma ALD Al2O3 in a single-wafer reactor showed similar low Seff values. For annealed films, Seff decreased with increasing film thickness and saturated for thicknesses $> \sim 10$ nm. Interestingly, after a subsequent firing process in an industrial belt line furnace $(T > 800 \,^{\circ}\text{C})$, the thickness dependence of the passivation disappeared. Ultrathin films of $\sim 5 \text{ nm}$ yielded relatively low S_{eff} values <25 cm/s after firing. Regarding the field-effect passivation, it was verified by corona charging experiments that the spatial ALD Al₂O₃ films exhibited a high negative Q_f of $(4 \pm 0.5) \times 10^{12} \text{ cm}^{-2}$ after annealing [Fig. 24(b)].

The excellent passivation results for the spatial and batch ALD Al₂O₃ processes are comparable to those obtained for single-wafer reactors. This is also true for the Al₂O₃ films deposited in the spatial ALD tools of SoLayTec, which led to low S_{eff} values of <8 cm/s on low-resistivity *p*- and *n*-type Si.^{197,198} Therefore, no apparent compromised performance in terms of resulting passivation quality was observed when going to scaled-up ALD processes. To date, spatial and batch ALD equipment has already been installed in pilot production lines at a number of solar cell manufacturers and research institutes.



FIG. 24. (Color online) Results obtained for the inline thermal ALD reactor of Levitech. (a) Thickness dependence of the passivation performance of Al₂O₃, for as-deposited films, after annealing (10 min) and after subsequent firing at ~850 °C. The results are compared with plasma ALD reference samples. (b) Corona charging graph for an 18 nm Al₂O₃ film after annealing. A negative Q_f of ~4 × 10¹² cm⁻² was obtained. Wafers with a resistivity of ~2 Ω cm (*p*-type) were used as substrates.

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3. ALD or PECVD?

PECVD is a serious contender for the deposition of Al₂O₃ in the PV industry. Good surface passivation properties $(S_{eff} < 10 \text{ cm/s}, 1 \Omega \text{ cm } p$ -type Si), on par with ALD, have been reported for Al₂O₃ synthesized by PECVD in an industrial Roth & Rau reactor.¹²⁴ A difference may be the refractive index of the PECVD deposited films, which is generally somewhat lower (~1.60) than for ALD (~1.64).^{124,125} This is indicative of a slightly lower film density.

The PECVD and the ALD processes both have strengths and weaknesses. Hence, it is likely that there are opportunities for both—and perhaps also other—deposition technologies depending on specific demands and applications. When ultrathin Al_2O_3 films are required (<10 nm), the thickness control and uniformity of ALD may provide key benefits over PECVD. This will also be the case for concepts in which Al_2O_3 films are required on both sides of the solar cell, and for more advanced passivation schemes comprising stacks of ALD materials, nanolaminates, or perhaps doped and mixed oxides. However, when thick Al_2O_3 films are required, PECVD may be the preferred option. In the end, cost-of-ownership considerations (such as operational costs, footprint, equipment down-time, precursor consumption, etc.) may be at least as important as the purely technological specifications of the system.

D. Alternative precursors

1. Solar grade TMA

Cost-of-ownership for Al₂O₃ deposition technology could be reduced when, instead of highly purified "semiconductor grade" Al(CH₃)₃, a lower cost precursor can be used. The precursor costs are directly related to the number of purification steps required during precursor synthesis. Possible impurities that can be present in lower grade TMA include Ga, Zn, Cl atoms. To assess the possible influence of the purity level on the passivation properties of the Al₂O₃ films, Al(CH₃)₃ with two different purities, i.e., semiconductor grade and solar grade, were compared.¹⁸⁰ For both thermal and plasma ALD, no significant difference was observed between the two precursors in terms of resulting passivation performance. This holds for both p- and n-type silicon. It can therefore be concluded that the surface passivation is not compromised by the higher impurity level of solar grade Al(CH₃)₃. This compatibility is crucial for large-scale production.

2. DMAI

As an alternative to $Al(CH_3)_3$, dimethylaluminium isopropoxide [AlMe2(OⁱPr)] can be used as Al precursor during ALD. This novel precursor (in brief DMAI), commercialized by Air Liquide, is not pyrophoric. DMAI is therefore safer to handle and store than TMA. In the DMAI molecule, the Al atom is bonded to an isopropoxide group and to two methyl groups [Fig. 25(inset)]. DMAI can be used in combination with O₃, H₂O, or an O₂ plasma as coreactants. A saturated process was developed for plasma and thermal ALD in our OpAL reactor.¹⁹⁹ Slightly longer dosing times (~100 ms) were required for DMAI than for TMA, which can be



FIG. 25. (Color online) Injection-level-dependent effective lifetime for Al₂O₃ films synthesized by plasma ALD using DMAI as precursor for Al. Annealing was performed at 400 °C (10 min, N₂). Data for *n*- (3.5 Ω cm) and *p*-type (2 Ω cm) Si is shown (Ref. 199). Inset shows precursor drawings, comparing TMA and DMAI.

attributed to a lower vapor pressure for DMAI (9 Torr at 66.5 °C) than for TMA (9 Torr at 16.8 °C). The plasma ALD process yielded a growth rate of 0.9 Å/cycle for $T_{dep} = 200$ °C, which is lower than the 1.2 Å obtained when using TMA in plasma ALD. In addition, the DMAI-Al₂O₃ films exhibited a higher hydrogen content of ~7 at. % and, consequently, a lower mass density of ~2.6 g/cm³ ($T_{dep} = 200$ °C) compared to Al₂O₃ deposited from TMA. These differences illustrate that a relatively small change to the precursor molecule can give rise to different growth and material properties.

The surface passivation performance of the DMAI-Al₂O₃ films is displayed in Fig. 25, comparing results for *n*- and *p*-type *c*-Si. Before annealing, the passivation performance was very poor with S_{eff} values of the order of 10^3 cm/s, as expected for plasma ALD. After annealing, the effective life-time is observed to improve significantly. S_{eff} values <6 and

<3 cm/s were obtained for *p*- and *n*-type Si, respectively. These values are quite comparable to those reported for plasma ALD Al₂O₃ using Al(CH₃)₃.

VII. SOLAR CELLS FEATURING AI₂O₃

One key aspect of all high-efficiency solar cells is the incorporation of effective surface passivation schemes on the front and/or rear side. Figure 26 illustrates a selection of solar cell structures based on *p*-type and *n*-type Si base material. It is evident that the number of process steps required for the fabrication of the different cells varies widely. The industrial standard screen-printed p-type Si solar cell, which can be manufactured in only eight process steps, exemplifies the simplest device structure [Fig. 26(i)]. The energy conversion efficiency of this type of solar cell can be increased by improving the front side, e.g., by using a selective emitter and higher aspect ratio front contacts. However, to achieve a significant increase in efficiency, it is necessary to also improve the rear side by the implementation of a passivated rear with local backsurface field (PERC-type solar cell). The PERC-type design is compatible with high cell efficiencies,47,200 and is currently being introduced in mass production. The adaptation from the standard Al-BSF cell to a PERC cell requires the deposition of a rear passivation film, local contact formation by, for example, laser processing,^{201,202} but it also changes, for example, the requirements for the optimal Si bulk resistivity^{9,203} and the composition of the metal pastes. Another route to realize high efficiencies is the use of *n*-type Si base material. The effective passivation of p^+ emitters by Al₂O₃ has been an important step forward for various types of n-type Si solar cells. An advantage of using *n*-type Si is the high bulk lifetime, which does not suffer from light-induced degradation by the formation of boron-oxygen complexes as is the case for Czochralski (Cz) p-type Si. This is one of the reasons why cells based on *n*-type Cz Si have a higher efficiency potential than those using Cz p-type Si.⁹ However, for n-type cells, an n^+ BSF [or front surface field (n^+ FSF)] cannot be simply formed



Fig. 26. (Color online) Various solar cell concepts based on p- and n-type Si wafers. (i) Full Al-BSF; (ii) passivated emitter and rear (PERC) cell; (iii) backcontacted emitter wrap through (BC EWT) cell; (iv), (v) passivated emitter and rear totally diffused (PERT) cell; (vi) passivated emitter and rear locally diffused (PERL) cell; (vii) backjunction Al alloyed rear emitter ("BJ-Alp+") cell; (viii) backjunction PERT cell; (ix) bifacial cell; (x) interdigitated backcontacted backjunction (IBC BJ) cell; (xi) backcontacted emitter wrap through (BC EWT) cell; (xii) heterojunction (HJ) cell.

during the metallization process similar to the formation of the Al-BSF for *p*-type cells and therefore requires additional process steps. On the other hand, screen printing can be employed to create an $Al-p^+$ emitter at the rear side[Fig. 26 (vii)]. It is important to note, however, that elaborate cleaning steps are required to remove the Al and passivate the emitter. Obviously passivation of the emitter is more straightforward when using boron diffusion or ion implementation processes.²⁰⁴

 Al_2O_3 -based passivation schemes have been employed for various types of solar cells listed in Fig. 26. An overview of important results is presented in Table II. Note that not all efforts could be included, given the accelerating activity in the field.

A. p-type Si cells

The first *p*-type PERC solar cell featuring Al₂O₃ surface passivation was reported in 2008 by Schmidt *et al.*²⁰⁵ It was demonstrated on cell level that the passivation performance of Al₂O₃ can be on par or superior to *alnealed* thermally grown SiO₂. An effective surface recombination velocity of ~70 cm/s was deduced from the internal quantum efficiency measurements for Al₂O₃ with a PECVD SiO_x capping layer and local rear contacts. The SiO_x capping films can be applied on top of the thin Al₂O₃ films to improve the rear reflection properties. Efficiencies of 20%–20.6% were reported, which were later increased up to 21.4% (Jsc=40.7 mA/cm², Voc=664 mV, FF=79.4%) in a follow-up experiment.¹⁸² As expected, the Al₂O₃-passivated PERC cells did not suffer from parasitic shunting (by the formation of an inversion layer), as can be the case when SiN_x is applied on the rear. By direct comparison, it was furthermore concluded that Al₂O₃ synthesized by sputtering led to a lower V_{oc} and η compared to ALD Al₂O₃ films, which is consistent with the differences in passivation quality as deduced from effective lifetime measurements.¹⁸² Very similar efficiencies of up to 21.5% have been reported for PERC cells by Saint-Cast et al.¹⁸⁸ The passivation by PECVD or plasma ALD Al₂O₃ led to similar solar cell performance. Moreover, the rear reflection properties for single layer Al₂O₃ with a thickness of $\sim 100 \,\mathrm{nm}$ were equivalent to those of SiO₂ or Al₂O₃/SiO_x stacks. The high open-circuit voltages >675 mV clearly demonstrate the excellent rear surface passivation properties of the Al₂O₃ films.¹⁸⁸ The front side of the PERC cells in Refs. 188 and 205 exhibited high-efficiency n^+ emitters of 100 and 120 Ω /sq, respectively. In Ref. 205, the emitter surface was very lightly oxidized ("tunnel oxidation," leading to $\sim 1.5 \text{ nm SiO}_x$) to improve the front side contact resistance and therewith the fill-factor (FF) of the cells. Zielke et al. have recently demonstrated that a few ALD cycles of Al₂O₃ on top the n^+ emitter also had a positive impact on the cell efficiency and reproducibility.²⁰⁶ However, when more than two ALD cycles were employed, a decrease in FF and η was observed, which the authors ascribed to a decrease in tunneling probability. A similar front and rear passivation scheme was used by Petermann et al. for thin 43 μ m epitaxial Si layer solar cells in combination with the porous Si layer transfer process.²⁰⁷ Partially due to the improved surface passivation, they were able to improve the efficiency of this type of solar cells from 16.9% to 19.1%. It is important to note that the laboratory-type PERC cells discussed before were based on high-quality FZ Si (B-doped, $0.5 \ \Omega \ \text{cm}, \sim 4 \ \text{cm}^2$) with an evaporated Al backcontact. Either

TABLE II. Selection of solar cell results with implemented Al_2O_3 -based surface passivation schemes. The "solar cell types" in the first column refer to Fig. 26.

Solar cell type	Passivation layer(s)	Cell efficiency (%)	Additional details	References
p-PERC (ii)	(Rear) ALD $Al_2O_3 + SiO_x$ (Rear) sputtered $Al_2O_3 + SiO_x$	21.4 20.1	Al evaporated contacts, 0.5 Ω cm FZ, 4 cm 2	182, 205 182
<i>p</i> -PERC (ii)	(Rear) ALD $Al_2O_3 + SiO_x$ (Rear) PECVD $Al_2O_3 + SiO_x$	21.3 21.5	Al rear, plated front contacts, $0.5 \ \Omega \ cm \ FZ, 4 \ cm^2$	188
p-PERC (ii)	(Front) few ALD cycles $Al_2O_3 + SiN_x ARC$; (rear) Al_2O_3/SiN_x stack	21.7	Al evaporated contacts, 0.5 Ω cm FZ, 4 cm^2	206
		19.1	43 μ m thick, B-doped epitaxial Si, 0.5 Ω cm FZ, 4 cm ²	207
p-PERC (ii)	(Rear) Al_2O_3/SiN_x stack	18.6	Screen-printed, 3 Ω cm Cz, 125 \times 125 mm	208
p-PERC (ii)	(Rear) Al_2O_3/SiN_x stack	19.0	Screen-printed, 2–3 Ω cm Cz, 125 \times 125 mm	184
p-PERC (ii)	(Rear) $Al_2O_3/SiO_x/SiN_x$ stack	19.1	Screen-printed, 1 Ω cm Cz, 148.25 cm ²	209
<i>n</i> -PERT (iv)	(Front) Al_2O_3/SiN_x	20.8 (FZ)	Full metallization of n^+ diffused rear side,	213
<i>n</i> -PERL (vi)	(Front) Al ₂ O ₃ /SiN _x stack (Rear) thermal SiO ₂	19.4 (Cz) 23.9	90 $\Omega/\text{sq} p^+$, 1 Ω cm FZ, 4 cm ² Local diffused n^+ BSF, 140 $\Omega/\text{sq} p^+$, 1 Ω cm FZ, 4 cm ²	9, 19
n-PERL (vi)	(Front) Al ₂ O ₃ /SiN _x stack (Rear) <i>a</i> -Si:C	22.4	Local n^+ BSF (<i>PassDop</i> , Laser doping), 1 Ω cm FZ, 4 cm ²	212
<i>n</i> -IBC (x)	(Rear) Al_2O_3 (Front) SiN_x	19.0	Al- p^+/n^+ (rear side), 2 Ω cm Cz, 4 cm ²	220
EWT (xi)	(Front/rear p^+) Al ₂ O ₃ /SiN _x (Rear n^+ BSF) thermal SiO ₂ + Al ₂ O ₃ /SiN _x	21.6	$1.5 \Omega \mathrm{cm} \mathrm{Cz}, 4 \mathrm{cm}^2$	221

photolithography-based processes were used to create openings in the rear surface passivation scheme,²⁰⁵ or laser-fired-contacts (LFCs) were implemented.¹⁸⁸

Results on industrially feasible PERC cells, based on Cz-Si and screen-printed metallization, have also been reported (Table II). For these type of cells, a stack of Al_2O_3/a -SiN_x:H is used on the rear, instead of single layer Al₂O₃. This is chiefly related to the high chemical stability of N-rich SiN_x when covered by metal paste. Lauermann et al. reported a $\sim 0.7\%$ higher (absolute) efficiency for PERC cells (18.6%) than for Al-BSF reference cells.²⁰⁸ The combination of increased surface passivation performance and enhanced rear reflection led to an increase of J_{sc} by 1.5 mA/cm² compared to the references. These results demonstrate on a device level that the Al_2O_3/SiN_x passivation scheme is sufficiently firing stable. Gatz et al. reported an energy conversion efficiency of 19.0% for large area Cz Si solar cells passivated by an Al₂O₃/ SiN_x stack.¹⁸⁴ As expected, the J_{sc} (38.9 mA/cm²) and V_{oc} (652 mV) were significantly higher than for the Al-BSF reference ($\eta = 18.6\%$, $J_{sc} = 37 \text{ mA/cm}^2$, $V_{oc} = 636 \text{ mV}$). Very recently, Vermang et al. reported an efficiency of 19.1% for a PERC cell with a triple-layer $Al_2O_3/SiO_x/SiN_x$ stack on the rear.²⁰⁹ Taken together, the PERC cells exhibited significantly lower FF values [e.g., 77.2% (Ref. 208) and 75.1% (Ref. 184)] than were obtained for the Al-BSF references (79.5%) and 78.7%, respectively). An enhanced series resistance associated with the local (line or point) contacts is responsible for this difference. For PERC cells, the pitch and local contact size are critical parameters for optimizing the rear side, which involves a trade-off between a low contact resistance (narrow pitch and large contacts) and low surface recombination velocities (wide pitch and small contacts). Ongoing optimization of metal pastes for local contacts will contribute to further reductions in contact resistance. Apart from laser ablation (or etching) of the dielectric prior to metallization, another industrially feasible option is to use LFCs at the rear side where structuring is done after the application of the metal paste.²⁰¹ An alternative rear side metallization process based on an open grid is used for the so-called PASHA cell (Passivated on all sides H-pattern), compare Fig. 26 (ix).²¹⁰ Although the efficiency potential for these cells is somewhat lower than for PERC cells, the fabrication is simpler as the contacts are fired through the dielectric layer forming an effective BSF. A capping layer on Al₂O₃ is not necessary.

Apart from PERC cells based on Cz-Si, excellent results were reported recently by Q-Cells for industrially manufactured multicrystalline Si (mc-Si) cells with improved front and rear side. Using a rear surface passivation stack (materials undisclosed) and LFCs, Engelhart and co-workers demonstrated record efficiencies of up to 19.5% (mc-Si) and 20.2% (Cz-Si).^{203,211} The authors estimated that the improvement in J_{sc} due to enhanced rear reflection ($\Delta J_{sc} \sim 1$ mA/cm²) was almost as important as the reduction in electronic rear side recombination ($\Delta J_{sc} \sim 1.2$ mA/cm²) for the mc-Si cells ($J_{sc} = 38.9$ mA/cm², $V_{oc} = 652$ mV, FF = 76.7%). These solar cell results demonstrate clearly that rear side surface passivation is not only useful for monocrystalline Si cells but has also significant potential for cells based on lower quality Si substrates, which was previously unexpected. Moreover, these developments suggest that the performance gap between industrially produced Cz-Si cells and cheaper mc-Si cells can be reduced by the implementation of new technologies. Finally, it is important to point out that a fair comparison between various surface passivation schemes should also address the solar cell performance under low-illumination conditions.²¹¹

B. n-type Si cells

 Al_2O_3 -based passivation was first tested for *n*-type Si solar cells in a PERL cell design. An Al₂O₃/SiN_x stack was used on the front side boron emitter ($\sim 140 \Omega/sq$).¹⁹ Hoex *et al.* demonstrated that Al₂O₃-passivated boron emitters with comparable sheet resistance lead to ultralow J_0 of ~10 fA/cm².¹³⁷ For the PERL cell, Benick et al. reported record efficiencies of, at that time, 23.2% (or 23.4% after adjustment of the AM1.5 spectrum).¹⁹ In subsequent work, the efficiency was even improved further to 23.9%.9 Internal quantum efficiencies of approximately 100% were obtained for the front side, in combination with $V_{\rm oc}$ values >700 mV. These results underline the passivation properties of Al_2O_3 for highly doped *p*-type surfaces on a device level. The PERL cell, featuring local n^+ BSFs fabricated using photolithography processes, presents a complex cell concept involving many different process steps. To simplify the formation of the n^+ BSF, a novel process was developed at Fraunhofer ISE where a phosphorous containing passivation layer (called PassDop) is locally opened by a laser under the simultaneous diffusion of P atoms into Si. Using this process, promising efficiencies of 22.4% have already been demonstrated.²¹² A next step toward industrial feasibility is the use of screen-printed metallization.

Another approach, which is compatible with industrial processing, consists of a full-area n^+ diffusion. [Fig. 26 (iv)] . Richter et al. demonstrated efficiencies of 20.8% for this concept using an Al₂O₃/SiN_x stack on the front side p^+ emitter (90 Ω /sq) in combination with screenprinting technology.²¹³ The p-n junction can also be formed at the rear side by the formation of an $Al-p^+$ emitter and efficiencies up to 19.8% have been reported.²¹⁴ It is evident that both cells are limited by the properties of the rear side, which does not comprise dielectric passivation. Therefore, to further improve the energy conversion efficiency, a passivated rear with local contacts can be implemented similar to p-type PERC cells. In a preliminary study, SiN_x and $SiON_x/SiN_x$ stacks have been evaluated for the passivation of the rear n^+ BSF.²¹⁵ In combination with a stack comprising 0.5 nm Al₂O₃ and 70 nm SiN_x on the front side, a significantly enhanced V_{oc} of 671 mV was obtained, which represented an increase of ~ 15 mV compared to the cell with fully metalized BSF. At Q-Cells, the potential of concept (viii) was evaluated (Fig. 26). As the p-n junction is moved to the rear side, the front side can be manufactured similarly to conventional industrial p-type cells. First results already demonstrated a promising efficiency of 20.2% for large area Cz cells using industrially feasible techniques (passivation materials not disclosed).²¹⁶

In addition to the PERL and PERT cells, various other *n*-type cell designs have the potential of high efficiencies and can

therewith exploit the benefits of *n*-type Si over *p*-type Si base material. Bifacial cells [Fig. 26 (ix)] have attracted considerable attention due to the simplicity of the rear side, which does not require any structuring or local opening of the passivation layer. Efficiencies of 19.5% have been reported for industrially produced cells by Yingli in collaboration with Energy Center Netherlands.²¹⁷ Although promising, to our knowledge no results have been reported for *n*-type bifacial cells with Al₂O₃ passivation as yet. Another concept compatible with very high efficiencies is the so-called interdigitated backcontacted (IBC) cell design, which has been commercialized by Sunpower. Exceptionally high efficiencies up to 24.2% have been realized.⁸⁴ Low recombination on the front side—obtained by effective surface passivation and/or the implementation of an FSF—and in the Si bulk are crucial as the minority carriers generated near the front side have to diffuse to the rear p-njunction. At the rear side, a passivation scheme compatible with both n^+ - and p^+ -type Si is required. Moreover, depending on cell design, the passivation scheme needs to ensure excellent electrical insulation as the oversized metal contacts (of the n^+ BSF) need to be isolated from the emitter underneath. Gong et al. reported that higher implied V_{oc} values were obtained when using Al₂O₃ instead of SiO_x/SiN_x on the Al- p^+ emitters, but this was not yet corroborated on the solar cell level.²¹⁸ Reichel et al. have reported efficiencies up to 23% for IBC cells, but no details were given concerning the rear side passivation.²¹⁹ IBC cells with a screen-printed Al- p^+ emitter have been reported by Bock et al. For these cells with Al₂O₃ passivation on the rear side, efficiencies of 19% were obtained with significant room for improvement up to 21.3%, as suggested by device simulations.²²⁰ Another backcontacted cell concept is the so-called emitter wrap through (EWT) cell. In this cell concept, the requirements on the bulk lifetime and front side recombination are less strict than in the IBC concept. Therefore, a separate diffusion for the front side is not necessary for the EWT cells. Kiefer *et al.* reported a cell efficiency of 21.6% for EWT cells using Al_2O_3/SiN_x passivation on the front and rear side p^+ emitter.²²¹ Low $J_{0,e}$ of 60 and 35 fA/cm² were reported for the textured and planar p^+ emitter (~50 Ω/sq) surfaces. For the n^+ BSF, the Al₂O₃/SiN_x layers were deposited on top of a thermally grown SiO₂ layer. Note that Sun et al. employed such an SiO₂/Al₂O₃ stack at the rear of *p*-type PERC cells and reported excellent passivation properties and $\eta = 20.1\%$ ²²² The SiO₂/Al₂O₃ stack system leads to a high level of chemical passivation (Sec. VI B). Moreover, the absence of significant negative fixed charge density in the SiO_2/Al_2O_3 is expected to be beneficial for the passivation of n^+ surfaces.

Finally, heterojunction (HJ) cells critically rely on an excellent level of surface passivation, typically realized by using undoped *a*-Si:H thin films below the *p*- and *n*-doped *a*-Si:H films [Fig. 26 (xii)]. The latter concept is used in the successful Heterojunction with Intrinsic Thin layer cells commercialized by Sanyo.^{11,84} Note that HJ technology can also be combined with the IBC concept for realizing high $V_{\rm oc}$ and $J_{\rm sc}$.⁸¹ It is expected that the passivation properties of Al₂O₃ films can be exploited for HJ cells using innovative approaches and cell designs. For example, Al₂O₃ could be

applied on a front side (diffused) p^+ emitter for cells with an n^+ heterojunction at the rear side.⁹

VIII. CONCLUDING REMARKS

In this article the fast-growing activities relating to Al₂O₃ thin films applied for the passivation of Si surfaces since 2006 have been reviewed. The appearance of Al_2O_3 as a very effective passivation material was not anticipated in the field, where surface passivation schemes had primarily been based on Si-containing films (e.g., SiO₂, a-SiN_x, and a-Si:H). Compared to these other materials, a distinguishing characteristic of the Al₂O₃ films is field-effect passivation induced by negative fixed charges. Nonetheless, the very low defect densities $(D_{it} \le 10^{11} \text{ eV}^{-1} \text{ cm}^{-2})$ induced by the films are also essential for the low surface recombination velocities that have been reported for p, p^+ , and *n*-type Si. Depending on sheet resistance, Al₂O₃ may even contribute to sufficiently low emitter saturation current densities for n^+ Si, although SiO₂/Al₂O₃ stacks without negative charges are likely preferable.

Atomic layer deposition is also novel in the field of *c*-Si photovoltaics. Because of its precise thickness control, ALD is ideally suited for engineering the Si surface and tailoring the properties of nanolayer surface passivation schemes. For example, ultrathin SiO₂ interlayers have been used to control the fixed charge density associated with Al₂O₃. In addition, the application of just a few ALD Al₂O₃ cycles, prior to *a*-SiN_x deposition, was demonstrated to be already sufficient to improve the passivation properties of p^+ emitters. Other enticing possibilities for the future may include the use of ALD for ultrathin pinhole-free inversion, barrier and tunneling layers, selectively doped films, and stacks in combination with transparent conductive oxides. This may contribute to developments regarding novel low-recombination contact and metallization schemes.

The use of ALD is no longer limited to ultrathin films of only a few nanometers. With the availability-and further development-of spatial ALD and large-scale batch reactors, ALD may soon be a technologically and cost-effective deposition process for the PV industry. The industry at large has been relying on the successful screen-printed Al-BSF technology for the last few decades, but it is expected that the PERC-type solar cells featuring dielectric rear side passivation will become a prominent technology in the next few years. Subsequently, and partially concurrently, higher efficiency *n*-type Si cells featuring passivation on the front and rear sides will play an increasingly important role. It has been demonstrated that Al₂O₃, deposited either by ALD or PECVD, and in combination with an a-SiN_x:H capping layer, provides a metallization-stable solution for both pand *n*-type Si cells. Nonetheless, the integration of the (novel) technologies (i.e., cleaning, deposition, contacting methods) in industrial process flows can still pose challenges. In addition, methods to monitor the passivation quality during manufacturing have to be developed. Appropriate tests (e.g., accelerated aging) to determine the long-term field performance of surface passivation films are also not available yet.

In the broader field of photovoltaics, surface passivation schemes based on ALD Al_2O_3 may be a natural choice for future developments regarding nano- and microwire solar cells^{223–225} and other next-generation concepts that require ultrathin conformal films.²²⁶ However, given the urgency for the large-scale adoption of sustainable energy sources, we hope that the technology described in this paper will contribute significantly to improving the conversion efficiency of industrial solar cells and further reducing the price of solar electricity on the short term.

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- ¹J. H. Zhao, A. H. Wang, and M. A. Green, Prog. Photovoltaics 7, 471 (1999).
- ²M. A. Green, Prog. Photovoltaics **17**, 183 (2009).
- ³T. Tiedje, E. Yablonovitch, G. D. Cody, and B. G. Brooks, IEEE Trans. Electron Devices **31**, 711 (1984).
- ⁴M. A. Green, IEEE Trans. Electron Devices **31**, 671 (1984).
- ⁵M. J. Kerr, A. Cuevas, and P. Campbell, Prog. Photovoltaics 11, 97 (2003).
- ⁶M. A. Green, *Silicon Solar Cells: Advanced Principles and Practice* (Bridge Printery, Sydney, Australia, 1995).
- ⁷W. Shockley and H. J. Queisser, J. Appl. Phys. **32**, 510 (1961).
- ⁸R. M. Swanson, *Proceedings of the 31st IEEE Photovoltaic Specialists Conference*, Lake Buena Vista, FL, 3–7 January 2005 (IEEE, New York, 2005).
- ⁹S. W. Glunz *et al.*, *Proceedings of the 35th IEEE Photovoltaic Specialists Conference*, Honolulu, HI, 20–25 June 2010 (IEEE, New York, 2010).
- ¹⁰A. G. Aberle, Prog. Photovoltaics **8**, 473 (2000).
- ¹¹Y. Tsunomura, T. Yoshimine, M. Taguchi, T. Baba, T. Kinoshita, H. Kanno, H. Sakata, E. Maruyama, and M. Tanaka, Sol. Energy Mater. Sol. Cells **93**, 670 (2009).
- ¹²R. Hezel and K. Jaeger, J. Electrochem. Soc. **136**, 518 (1989).
- ¹³G. Agostinelli, P. Vitanov, Z. Alexieva, A. Harizanova, H. F. W. Dekkers, S. De Wolf, and G. Beaucarne, *Proceedings of the 19th European Photovoltaic Solar Energy Conference*, Paris, 7–11 June 2004 (unpublished).
- ¹⁴B. Hoex, S. B. S. Heil, E. Langereis, M. C. M. van de Sanden, and W. M. M. Kessels, Appl. Phys. Lett. 89, 042112 (2006).
- ¹⁵G. Agostinelli, A. Delabie, P. Vitanov, Z. Alexieva, H. F. W. Dekkers, S. De Wolf, and G. Beaucarne, Sol. Energy Mater. Sol. Cells **90**, 3438 (2006).
- ¹⁶B. Hoex, J. Schmidt, P. Pohl, M. C. M. van de Sanden, and W. M. M. Kessels, J. Appl. Phys **104**, 044903 (2008).
- ¹⁷B. Hoex, J. J. H. Gielis, M. C. M. van de Sanden, and W. M. M. Kessels, J. Appl. Phys. **104**, 113703 (2008).
- ¹⁸M. Hofmann, S. Janz, C. Schmidt, S. Kambor, D. Suwito, N. Kohn, J. Rentsch, R. Preu, and S. W. Glunz, Sol. Energy Mater. Sol. Cells 93, 1074 (2009).
- ¹⁹J. Benick, B. Hoex, M. C. M. van de Sanden, W. M. M. Kessels, O. Schultz, and S. W. Glunz, Appl. Phys. Lett. **92**, 253504 (2008).
- ²⁰W. M. M. Kessels and M. Putkonen, MRS Bull. **36**, 907 (2011).
- ²¹P. Poodt, D. C. Cameron, E. Dickey, S. M. George, V. Kuznetsov, G. N. Parsons, F. Roozeboom, G. Sundaram, and A. Vermeer, J. Vac. Sci. Technol. A **30**, 010802 (2012).

- ²²W. Shockley and W. T. J. Read, Phys. Rev. 87, 835 (1952).
- ²³R. N. Hall, Phys. Rev. 87, 387 (1952).
- ²⁴S. Rein, *Lifetime Spectroscopy* (Springer, Berlin, 2004).
- ²⁵A. G. Aberle, Crystalline Silicon Solar Cells: Advanced Surface Passivation and Analysis (University of New South Wales, Sydney, Australia, 1999).
- ²⁶R. B. M. Girisch, R. P. Mertens, and R. F. de Keersmaecker, IEEE Trans. Electron Devices 25, 203 (1988).
- ²⁷A. G. Aberle, S. Glunz, and W. Warta, Sol. Energy Mater. Sol. Cells 29, 175 (1993).
- ²⁸S. W. Glunz, D. Biro, S. Rein, and W. Warta, J. Appl. Phys. **86**, 683 (1999).
- ²⁹S. Olibet, E. Vallat-Sauvain, and C. Ballif, Phys. Rev. B 76, 035326 (2007).
- ³⁰A. B. Sproul, M. A. Green, A. W. Stephens, J. Appl. Phys. **72**, 4161 (1992).
- ³¹D. Macdonald and A. Cuevas, Sol. Energy 76, 255 (2004).
- ³²R. A. Sinton and A. Cuevas, Appl. Phys. Lett. **69**, 2510 (1996).
- ³³H. Nagel, C. Berge, and A. G. Aberle, J. Appl. Phys. 86, 6218 (1999).
- ³⁴G. Coletti, R. Kvande, V. D. Mihailetchi, L. J. Geerlings, L. Arnberg, and E. J. Vrelid, J. Appl. Phys. **104**, 104913 (2008).
- ³⁵S. W. Glunz, S. Rein, J. Y. Lee, and W. Warta, J. Appl. Phys. **90**, 2397 (2001).
- ³⁶J. Schmidt and K. Bothe, Phys. Rev. B 69, 024107 (2004).
- ³⁷D. Macdonald, F. Rougieux, A. Cuevas, B. Lim, J. Schmidt, M. Di Sabatino, and L. Geerlings, J. Appl. Phys. **105**, 093704 (2009).
- ³⁸B. Lim, V. V. Voronkov, R. Falster, K. Bothe, and J. Schmidt, Appl. Phys. Lett. 98, 162104 (2011).
- ³⁹M. J. Kerr and A. Cuevas, J. Appl. Phys. **91**, 2473 (2002).
- ⁴⁰J. Benick, A. Richter, M. Hermle, and S. W. Glunz, Phys. Status Solidi (RRL) 3, 233 (2009).
- ⁴¹A. Stesmans and V. V. Afanas'ev, Appl. Phys. Lett. **80**, 1957 (2002).
- ⁴²A. G. Aberle, S. Glunz, and W. Warta, J. Appl. Phys. 71, 4422 (1992).
- ⁴³M. L. Green, E. P. Gusev, R. Degraeve, and E. L. Garfunkel, J. Appl. Phys. **90**, 2057 (2001).
- ⁴⁴O. Schultz, A. Mette, M. Hermle, and S. W. Glunz, Prog. Photovoltaics 16, 317 (2008).
- ⁴⁵J. Benick, K. Zimmermann, J. Spiegelman, M. Hermle, and S. W. Glunz, Prog. Photovoltaics **19**, 361 (2011).
- ⁴⁶M. L. Reed and J. D. Plummer, J. Appl. Phys. 63, 5776 (1988).
- ⁴⁷A. W. Blakers, A. Wang, A. M. Milne, J. Zhao, and M. A. Green, Appl. Phys. Lett. 55, 1363 (1989).
- ⁴⁸M. J. Kerr and A. Cuevas, Semicond. Sci. Technol. 17, 35 (2002).
- ⁴⁹S. Mack, A. Wolf, A. Walczak, B. Thaidigsmann, E. Allan Wotke, J. J. Spiegelman, R. Preu, and D. Biro, Sol. Energy Mater. Sol. Cells **95**, 2570 (2011).
- ⁵⁰W. D. Eades and R. M. Swanson, J. Appl. Phys. **58**, 4267 (1985).
- ⁵¹B. Hoex, F. J. J. Peeters, M. Creatore, M. A. Blauw, W. M. M. Kessels, and M. C. M. van de Sanden, J. Vac. Sci. Technol. A 24, 1823 (2006).
- ⁵²G. Dingemans, M. C. M. van de Sanden, and W. M. M. Kessels, Phys. Status Solidi (RRL) 5, 22 (2011).
- ⁵³V. D. Mihailetchi, Y. Komatsu, and L. J. Geerligs, Appl. Phys. Lett. 92, 063510 (2008).
- ⁵⁴S. Bordihn, P. Engelhart, V. Mertens, G. Kesser, D. Köhn, G. Dingemans, M. M. Mandoc, J. W. Müller, and W. M. M. Kessels, Energy Procedia 8, 654 (2011).
- ⁵⁵C. Leguijt *et al.*, Sol. Energy Mater. Sol. Cells **40**, 297 (1996).
- ⁵⁶J. Schmidt and A. Cuevas, J. Appl. Phys. 85, 3626 (1999).
- ⁵⁷M. J. Kerr and A. Cuevas, Semicond. Sci. Technol. **17**, 166 (2002).
- ⁵⁸S. de Wolf, G. Agostinelli, G. Beaucarne, and P. Vitanov, J. Appl. Phys. 97, 063303 (2005).
- ⁵⁹A. G. Aberle and R. Hezel, Prog. Photovoltaics 5, 29 (1997).
- ⁶⁰B. Hoex, A. J. M. van Erven, R. C. M. Bosch, W. T. M. Stals, M. D. Bijker, P. J. van den Oever, W. M. M. Kessels, and M. C. M. van de Sanden, Prog. Photovoltaics 13, 705 (2005).
- ⁶¹J. Hong, W. M. M. Kessels, W. J. Soppe, W. W. Weeber, W. M. Arnoldbik, and M. C. M. van de Sanden, J. Vac. Sci. Technol. B 21, 2123 (2003).
- ⁶²F. Duerinckx and J. Szlufcik, Sol. Energy Mater. Sol. Cells **72**, 231 (2002).
- ⁶³M. I. Bertoni et al., Prog. Photovoltaics 19, 187 (2010).
- ⁶⁴W. L. Warren, J. Kanicki, J. Robertson, E. H. Poindexter, and P. J. McWhorter, J. Appl. Phys. 74, 4034 (1993).
- ⁶⁵S. E. Curry, P. M. Lenahan, D. T. Krick, J. Kanicki, and C. T. Kirk, Appl. Phys. Lett. 56, 1359 (1990).
- ⁶⁶H. Mäckel and R. Lüdemann, J. Appl. Phys. **92**, 2602 (2002).

- ⁶⁷S. Dauwe, L. Mittelstädt, A. Metz, and R. Hezel, Prog. Photovoltaics 10, 271 (2002).
- ⁶⁸G. Dingemans, M. M. Mandoc, S. Bordihn, M. C. M. van de Sanden, and W. M. M. Kessels, Appl. Phys. Lett. 98, 222102 (2011).
- ⁶⁹S. Mack, A. Wolf, C. Brosinsky, S. Schmeisser, A. Kimmerle, P. Saint-Cast, M. Hofmann, and D. Biro, IEEE J. Photovoltaics 1, 135 (2011).
- ⁷⁰M. Schaper, J. Schmidt, H. Plagwitz, and R. Brendel, Prog. Photovoltaics 13, 381 (2005).
- ⁷¹S. Gatz, H. Plagwitz, P. P. Altermatt, B. Terheiden, and R. Brendel, Appl. Phys. Lett. **93**, 173502 (2008).
- ⁷²C. Leendertz, N. Mingirulli, T. F. Schulze, J. P. Kleider, B. Rech, and L. Korte, Appl. Phys. Lett. 98, 202108 (2011).
- ⁷³T. F. Schulze, H. N. Beushausen, C. Leendertz, A. Dobrich, B. Rech, and L. Korte, Appl. Phys. Lett. 96, 25102 (2010).
- ⁷⁴S. de Wolf, B. Demaurex, A. Descoeudres, and C. Ballif, Phys. Rev. B **83**, 233301 (2011).
- ⁷⁵A. Illiberi, M. Creatore, W. M. M. Kessels, and M. C. M. van de Sanden, Phys. Status Solidi (RRL) 4, 206 (2010).
- ⁷⁶A. Shah, P. Torres, R. Tscharner, N. Wyrsch, and H. Keppner, Science **285**, 692 (1999).
- ⁷⁷R. W. Collins, A. S. Ferlauto, G. M. Ferreira, C. Chen, J. Koh, R. J. Koval, Y. Lee, J. M. Pearce, and C. R. Wronski, Sol. Energy Mater. Sol. Cells 78, 143 (2003).
- ⁷⁸A. H. M. Smets, W. M. M. Kessels, and M. C. M. van de Sanden, Appl. Phys. Lett. 82, 1547 (2003).
- ⁷⁹M. N. van den Donker, B. Rech, W. M. M. Kessels, and M. C. M. van de Sanden, New J. Phys. 9, 280 (2006).
- ⁸⁰G. Dingemans, M. N. van den Donker, D. Hrunski, A. Gordijn, W. M. M. Kessels, and M. C. M. van de Sanden, Appl. Phys. Lett. **93**, 111914 (2008).
- ⁸¹N. Mingirulli et al., Status Solidi (RRL) 5, 159 (2011).
- ⁸²S. Martín de Nicolá, D. Muñoz, A. S. Ozanne, N. Nguyen, and P. J. Ribeyron, Energy Procedia 8, 226 (2011).
- ⁸³D. L. Bätzner et al., Energy Procedia 8, 153 (2011).
- ⁸⁴M. A. Green, K. Emery, Y. Hishikawa, W. Warta, and E. D. Dunlop, Prog. Photovoltaics 20, 12 (2012).
- ⁸⁵R. Santbergen and R. J. C. van Zolingen, Sol. Energy Mater. Sol. Cells 92, 432 (2008).
- ⁸⁶T. Fellmeth, S. Mack, J. Bartsch, D. Erath, U. Jäger, R. Preu, F. Clement, and D. Biro, IEEE Electron Device Lett. 32, 1101 (2011).
- ⁸⁷J.-H. Lai, A. Upadhyaya, R. Ramanathan, A. Das, K. Tate, V. Upadhyaya, A. Kapoor, C.-W. Chen, and A. Rohatgi, IEEE J. Photovoltaics 1, 16 (2011).
- ⁸⁸A. Wolf, D. Biro, J. Nekarda, S. Stumpp, A. Kimmerle, S. Mack, and R. Preu, J. Appl. Phys. **108**, 124510 (2010).
- ⁸⁹S. M. George, Chem. Rev. **110**, 111 (2010).
- ⁹⁰M. Leskelä and M. Ritala, Angew. Chem., Int. Ed. 42, 5548 (2003).
- ⁹¹H. B. Profijt, S. E. Potts, M. C. M. van de Sanden, and W. M. M. Kessels, J. Vac. Sci. Technol. A **29**, 050801 (2011).
- ⁹²R. L. Puurunen, Appl. Surf. Sci. 245, 6 (2005).
- ⁹³R. L. Puurunen, J. Appl. Phys. **97**, 121301 (2005).
- ⁹⁴M. D. Groner, F. H. Fabreguette, J. W. Elam, and S. M. George, Chem. Mater. 16, 639 (2004).
- ⁹⁵M. D. Groner, F. H. Fabreguette, J. W. Elam, and S. M. George, Thin Solid Films 413, 186 (2002).
- ⁹⁶S. B. S. Heil, J. L. van Hemmen, M. C. M. van de Sanden, and W. M. M. Kessels, J. Appl. Phys. **103**, 103302 (2008).
- ⁹⁷J. L. van Hemmen, S. B. S. Heil, J. H. Klootwijk, F. Roozeboom, C. J. Hodson, M. C. M. van de Sanden, and W. M. M. Kessels, J. Electrochem. Soc. 154, G165 (2007).
- ⁹⁸G. Dingemans, M. C. M. van de Sanden, and W. M. M. Kessels, Electrochem. Solid-State Lett. **13**, H76 (2010).
- ⁹⁹S. E. Potts, W. Keuning, E. Langereis, G. Dingemans, M. C. M. van de Sanden, and W. M. M. Kessels, J. Electrochem. Soc. 157, P66 (2010).
- ¹⁰⁰J. W. Lim and S. J. Yun, Electrochem. Solid-State. Lett. 7, F45 (2004).
- ¹⁰¹S.-C. Ha, E. Choi, S.-H. Kim, and J. S. Roh, Thin Solid Films **476**, 252 (2005).
- ¹⁰²S. K. Kim and C. S. Hwang, J. Appl. Phys. **96**, 2323 (2004).
- ¹⁰³S. D. Elliott, G. Scarel, C. Wiemer, M. Fanciulli, and G. Pavia, Chem. Mater. 18, 3764 (2006).
- ¹⁰⁴D. N. Goldstein, J. A. McCormick, and S. M. George, J. Phys. Chem. C 112, 19530 (2008).
- ¹⁰⁵E. Langereis, J. Keijmel, M. C. M. van de Sanden, and W. M. M. Kessels, Appl. Phys. Lett. **92**, 231904 (2008).

- ¹⁰⁶E. Granneman, P. Fischer, D. Pierreux, H. Terhorst, and P. Zagwijn, Surf. Coat. Technol. 201, 8899 (2007).
- ¹⁰⁷G. Dingemans, N. M. Terlinden, D. Pierreux, H. B. Profijt, M. C. M. van de Sanden, and W. M. M. Kessels, Electrochem. Solid-State Lett. 14, H1 (2011).
- ¹⁰⁸J. W. Elam, D. Routkevitch, and S. M. George, J. Electrochem. Soc. **150**, G339 (2003).
- ¹⁰⁹J. R. Bakke, K. L. Pickrahn, T. P. Brennan, and S. F. Bent, Nanoscale 3, 3482 (2011).
- ¹¹⁰J. A. van Delft, D. Garcia-Alonso, and W. M. M. Kessels, "Atomic layer deposition for photovoltaics: application and prospects for solar cell manufacturing," Semicond. Sci. Technol. (to be published).
- ¹¹¹E. B. Yousfi, T. Asikainen, V. Pietu, P. Cowache, M. Powalla, and D. Lincot, Thin Solid Films **361**, 183 (2000).
- ¹¹²P. Genevée, F. Donsanti, G. Renou, and D. Lincot, *Proceedings of the* 25th European Photovoltaic Solar Energy Conference, Valencia, Spain, 6–10 September 2010 (unpublished).
- ¹¹³Y. Ohtake, K. Kushiya, M. Ichikawa, A. Yamada, and M. Konagai, Jpn. J. Appl. Phys., Part 1 34, 5949 (1995).
- ¹¹⁴C. Platzer-Bjorkman, J. Lu, J. Kessler, and L. Stolt, Thin Solid Films 431, 321 (2003).
- ¹¹⁵W. J. Potscavage, S. Yoo, B. Domercq, and B. Kippelen, Appl. Phys. Lett. **90**, 253511 (2007).
- ¹¹⁶S. Sarkar, J. H. Culp, J. T. Whyland, M. Garvan, and V. Misra, Org. Electron. **11**, 1896 (2010).
- ¹¹⁷P. F. Carcia, R. S. McLean, and S. Hegedus, Sol. Energy Mater. Sol. Cells 94, 2375 (2010).
- ¹¹⁸S. Hegedus, P. F. Carcia, R. S. McLean, and B. Culver, *Proceedings of the 35th IEEE Photovoltaic Specialists Conference*, Honolulu, HI, 20–25 June 2010 (IEEE, New York, 2010).
- ¹¹⁹C. Cibert, H. Hidalgo, C. Champeaux, P. Tristant, C. Tixier, J. Desmaison, and A. Catherinot, Thin Solid Films **516**, 1290 (2008).
- ¹²⁰M. T. Seman, D. N. Richards, P. Rowlette, and C. A. Wolden, Chem. Vap. Deposition 14, 296 (2008).
- ¹²¹C. E. Chryssou and C. W. Pitt, IEEE J. Quantum Electron. 34, 282 (1998).
- ¹²²S. Miyajima, J. Irikawa, A. Yamada, and M. Konogai, *Proceedings of the 23rd European Photovoltaic Solar Energy Conference*, Valencia, Spain, 1–5 September 2008 (unpublished).
- ¹²³S. Miyajima, J. Irikawa, A. Yamada, and M. Konagai, Appl. Phys. Express **3**, 012301 (2010).
- ¹²⁴P. Saint-Cast, D. Kania, M. Hofmann, J. Benick, J. Rentsch, and R. Preu, Appl. Phys. Lett. 95, 151502 (2009).
- ¹²⁵G. Dingemans, M. C. M. van de Sanden, and W. M. M. Kessels, "Plasma-enhanced Chemical Vapor Deposition of Aluminum Oxide Using Ultrashort Precursor Injection Pulses," Plasma Processes Polym. (in press).
- ¹²⁶L. Black, K. M. Provancha, and K. R. McIntosh, *Proceedings of the 26th European Photovoltaic Solar Energy Conference*, Hamburg, Germany, 5–9 September 2011 (unpublished).
- ¹²⁷T.-T. Li and A. Cuevas, Phys. Status Solidi (RRL) 3, 160 (2009).
- ¹²⁸V. Verlaan, L. R. J. G. van den Elzen, G. Dingemans, M. C. M. van de Sanden, and W. M. M. Kessels, Phys. Status Solidi C 7, 976 (2010).
- ¹²⁹G. Dingemans, A. Clark, J. A. van Delft, M. C. M. van de Sanden, and W. M. M. Kessels, J. Appl. Phys. **109**, 113107 (2011).
- ¹³⁰V. V. Afanas'ev, M. Houssa, A. Stesmans, C. Merckling, T. Schram, and J. A. Kittl, Appl. Phys. Lett. 99, 072103 (2011).
- ¹³¹A. Roy Chowdhuri, C. G. Takoudis, R. F. Klie, and N. D. Browning, Appl. Phys. Lett. 80, 4241 (2002).
- ¹³²R. Kuse, M. Kundu, T. Yasuda, N. Miyata, and A. Toriumi, J. Appl. Phys. **94**, 6411 (2003).
- ¹³³S. D. Elliott and J. C. Greer, J. Mater. Chem. 14, 3246 (2004).
- ¹³⁴A. J. M. Mackus, S. B. S. Heil, E. Langereis, H. C. M. Knoops, M. C. M. van de Sanden, and W. M. M. Kessels, J. Vac. Sci. Technol. A 28, 77 (2010).
- ¹³⁵G. Dingemans, R. Seguin, P. Engelhart, M. C. M. van de Sanden, and W. M. M. Kessels, Phys. Status Solidi (RRL) 4, 10 (2010).
- ¹³⁶J. Schmidt, B. Veith, and R. Brendel, Phys. Status Solidi (RRL) **3**, 287 (2009).
- ¹³⁷B. Hoex, J. Schmidt, R. Bock, P. P. Altermatt, and M. C. M. van de Sanden, Appl. Phys. Lett. **91**, 112107 (2007).
- ¹³⁸A. Richter, J. Benick, M. Hermle, and S. W. Glunz, Phys. Status Solidi (RRL) 5, 202 (2011).

¹³⁹R. Bock, J. Schmidt, S. Mau, B. Hoex, and R. Brendel, IEEE Trans. Electron Devices 57, 1966 (2010).

- ¹⁴¹B. Hoex, M. C. M. van de Sanden, J. Schmidt, R. Brendel, and W. M. M. Kessels, Phys. Status Solidi (RRL) 6, 4 (2012).
- ¹⁴²S. Steingrube, P. P. Altermatt, D. S. Steingrube, J. Schmidt, and R. Brendel, J. Appl. Phys. **108**, 014506 (2010).
- ¹⁴³G. Dingemans, N. M. Terlinden, M. A. Verheijen, M. C. M. van de Sanden, and W. M. M. Kessels, J. Appl. Phys. **110**, 093715 (2011).
- ¹⁴⁴H. B. Profijt, P. Kudlacek, M. C. M. van de Sanden, and W. M. M. Kessels, J. Electrochem. Soc. 158, G88 (2011).
- ¹⁴⁵P. Saint-Cast, Y.-H. Heo, E. Billot, P. Olwal, M. Hofmann, J. Rentsch, S. W. Glunz, and R. Preu, Energy Procedia 8, 642 (2011).
- ¹⁴⁶J. Benick, A. Richter, T. -T. A.A. Li, N. E. Grant, K. R. Mc Intosh, Y. Ren, K. J. Weber, M. Hermle, and S. W. Glunz, *Proceedings of the* 35th IEEE Photovoltaic Specialists Conference, Honolulu, HI, 20–25 June 2010 (IEEE, New York, 2010).
- ¹⁴⁷F. Werner, B. Veith, D. Zielke, L. Kühnemund, C. Tegenkamp, M. Seibt, R. Brendel, and J. Schmidt, J. Appl. Phys. **109**, 113701 (2011).
- ¹⁴⁸G. Dingemans and W. M. M. Kessels, ECS Trans. 41, 293 (2011).
- ¹⁴⁹F. Werner, B. Veith, V. Tiba, P. Poodt, F. Roozeboom, R. Brendel, and J. Schmidt, Appl. Phys. Lett. 97, 162103 (2010).
- ¹⁵⁰N. M. Terlinden, G. Dingemans, M. C. M. van de Sanden, and W. M. M. Kessels, Appl. Phys. Lett. 96, 112101 (2010).
- ¹⁵¹R. S. Johnson, G. Luckovsky, and I. Baumvol, J. Vac. Sci. Technol. A 19, 1353 (2001).
- ¹⁵²D. Hoogeland, K. B. Jinesh, F. Roozeboom, W. F. A. Besling, M. C. M. van de Sanden, and W. M. M. Kessels, J. Appl. Phys. **106**, 114107 (2009).
- ¹⁵³A. Stesmans, J. Appl. Phys. 88, 489 (2000).
- ¹⁵⁴C. R. Helms and E. H. Poindexter, Rep. Prog. Phys. 57, 791 (1994).
- ¹⁵⁵E. Simoen, A. Rothschild, B. Vermang, J. Poortmans, and R. Mertens, Electrochem. Solid-State Lett. 14, H362 (2011).
- ¹⁵⁶M. Fanciulli, O. Costa, S. Baldovino, S. Cocco, G. Seguini, E. Prati, and G. Scarel, *Defects in High-k Gate Dielectric Stacks*, NATO Science Series Vol. 220 (Springer, Dordrecht, 2005), p. 263.
- ¹⁵⁷G. Kawachi, C. F. O. Graeff, M. S. Brandt, and M. Stutzmann, Phys. Rev. B 54, 7957 (1996).
- ¹⁵⁸S. Baldovino, S. Nokhrin, G. Scarel, M. Fanciulli, T. Graf, and M. S. Brandt, J. Non-Cryst. Solids **322**, 166 (2003).
- ¹⁵⁹D. Haneman, Phys. Rev. **170**, 705 (1968).
- ¹⁶⁰M. H. Brodsky and R. S. Title, Phys. Rev. Lett. 23, 581 (1969).
- ¹⁶¹G. Dingemans, W. Beyer, M. C. M. van de Sanden, and W. M. M. Kessels, Appl. Phys. Lett. 97, 152106 (2010).
- ¹⁶²G. Dingemans, F. Einsele, W. Beyer, M. C. M. van de Sanden, and W. M. M. Kessels, J. Appl. Phys. **111**, 093713 (2012).
- ¹⁶³A. Stesmans and V. V. Afanas'ev, J. Appl. Phys. **97**, 033510 (2004).
- ¹⁶⁴D. Liu, S. J. Clark, and J. Robertson, Appl. Phys. Lett. **96**, 032905 (2010).
- ¹⁶⁵P. C. McIntyre, ECS Trans. **11**, 235 (2007).
- ¹⁶⁶J. Robertson, Solid-State Electron. **49**, 283 (2005).
- ¹⁶⁷P. W. Peacock and J. Robertson, Appl. Phys. Lett. 83, 2025 (2003).
 ¹⁶⁸K. Matsunaga, T. Tanaka, T. Yamamoto, and Y. Ikuhara, Phys. Rev. B
- **68**, 085110 (2003).
- ¹⁶⁹J. R. Weber, A. Janotti, and C. G. van de Walle, J. Appl. Phys. **109**, 033715 (2011).
- ¹⁷⁰B. Shin, J. R. Weber, R. D. Long, P. K. Hurley, C. G. van de Walle, and P. C. McIntyre, Appl. Phys. Lett. **96**, 152908 (2010).
- ¹⁷¹V. V. Afanas'ev, A. Stesmans, B. J. Mrstik, and C. Zhao, Appl. Phys. Lett. 81, 1678 (2002).
- ¹⁷²J. J. H. Gielis, B. Hoex, M. C. M. van de Sanden, and W. M. M. Kessels, J. Appl. Phys. **104**, 073701 (2008).
- ¹⁷³K. Kimoto, Y. Matsui, T. Nabatame, T. Yasuda, T. Mizoguchi, I. Tanaka, and A. Toriumi, Appl. Phys. Lett. **83**, 4306 (2003).
- ¹⁷⁴T. Gougousi, D. Barua, E. D. Young, and G. N. Parsons, Chem. Mater. 17, 5093 (2005).
- ¹⁷⁵C. van der Marel, M. Yildirim, and H. R. Stapert, J. Vac. Sci. Technol. A 23, 1456 (2005).
- ¹⁷⁶S. Guha and V. Narayanan, Phys. Rev. Lett. 98, 196101 (2007).
- ¹⁷⁷A. S. Foster, F. Lopez Gejo, A. L. Shluger, and R. M. Nieminen, Phys. Rev. B 65, 174117 (2002).
- ¹⁷⁸G. Dingemans, R. Seguin, P. Engelhart, F. Einsele, B. Hoex, M. C. M. van de Sanden, and W. M. M. Kessels, J. Appl. Phys. **106**, 114907 (2009).

- ¹⁷⁹J. Schmidt et al., Proceedings of the 23rd European Photovoltaic Solar Energy Conference, Valencia, Spain, 1–5 September 2008 (unpublished).
- ¹⁸⁰G. Dingemans and W. M. M. Kessels, *Proceedings of the 25th European Photovoltaic Energy Conference*, Valencia, Spain, 6–10 September 2010 (unpublished).
- ¹⁸¹A. Richter, M. Horteis, J. Benick, S. Hennick, M. Hermle, and S. W. Glunz, *Proceedings of the 35th IEEE Photovoltaic Specialists Conference*, Honolulu, HI, 20–25 June 2010 (IEEE, New York, 2010).
- ¹⁸²J. Schmidt et al., Proceedings of the 25th European Photovoltaic Energy Conference, Valencia, Spain, 6–10 September 2010 (unpublished).
- ¹⁸³D. Kania, P. Saint-Cast, M. Hofmann, J. Rentsch, and R. Preu, Proceedings of the 25th European Photovoltaic Energy Conference, Valencia, Spain, 6–10 September 2010 (unpublished).
- ¹⁸⁴S. Gatz, H. Hannebauer, R. Hesse, F. Werner, A. Schmidt, Th. Dullweber, J. Schmidt, K. Bothe, and R. Brendel, Phys. Status Solidi (RRL) 5, 147 (2011).
- ¹⁸⁵A. Richter, S. Hennick, J. Benick, M. Hörteis, M. Hermle, and S. W. Glunz, *Proceedings of the 25th European Photovoltaic Energy Conference*, Valencia, Spain, 6–10 September 2010 (unpublished).
- ¹⁸⁶B. Vermang et al., Proceedings of the 37th IEEE Photovoltaic Specialists Conference, Seattle, WA, 19–24 June 2011 (IEEE, New York, 2011).
- ¹⁸⁷J. Benick, B. Hoex, G. Dingemans, A. Richter, M. Hermle, and S. W. Glunz, *Proceedings of the 24th European Photovoltaic Energy Conference*, Hamburg, Germany, 21–25 September 2009 (unpublished).
- ¹⁸⁸P. Saint-Cast, J. Benick, D. Kania, L. Weiss, M. Hofmann, J. Rentsch, R. Preu, and S. W. Glunz, IEEE Electron Device Lett. **31**, 695 (2010).
- ¹⁸⁹G. Dingemans, C. A. A. van Helvoirt, W. Keuning, and W. M. M. Kessels, J. Electrochem. Soc. **159**, 277 (2012).
- ¹⁹⁰T. Suntola and J. Antson, U.S. Patent 4,058,430 (15 November 1977).
- ¹⁹¹D. H. Levy, D. Freeman, S. F. Nelson, P. J. Cowdery-Corvan, and L. M. Irving, Appl. Phys. Lett. **92**, 192101 (2008).
- ¹⁹²See: http://www.levitech.nl
- ¹⁹³See: http://www.solaytec.com
- ¹⁹⁴E. H. A. Granneman, P. Vermont, V. Kuznetsov, M. Koolen, and K. Vanormelingen, *Proceedings of the 25th European Photovoltaic Energy Conference*, Valencia, Spain, 6–10 September 2010 (unpublished).
- ¹⁹⁵I. Cesar et al., Proceedings of the 35th IEEE Photovoltaic Specialists Conference, Honolulu, HI, 20–25 June 2010 (IEEE, New York, 2010).
- ¹⁹⁶P. Poodt, A. Lankhorst, F. Roozeboom, K. Spee, D. Maas, and A. Vermeer, Adv. Mater. 22, 3564 (2010).
- ¹⁹⁷B. Vermang, A. Rothschild, A. Racz, J. John, J. Poortmans, R. Mertens, P. Poodt, V. Tiba, and F. Roozeboom, Prog. Photovoltaics **19**, 733 (2011).
- ¹⁹⁸F. Werner, W. Stals, R. Görtzen, B. Veith, R. Brendel, and J. Schmidt, Energy Procedia 8, 301 (2011).
- ¹⁹⁹S. E. Potts, G. Dingemans, Ch. Lachaud, and W. M. M. Kessels, J. Vac. Sci. Technol. A 30, 021505 (2012).
- ²⁰⁰O. Schultz, S. W. Glunz, and G. P. Willeke, Prog. Photovoltaics **12**, 553 (2004).
- ²⁰¹E. Schneiderlöchner, R. Preu, R. Lüdemann, and S. W. Glunz, Prog. Photovoltaics 10, 29 (2002).
- ²⁰²P. Engelhart, S. Hermann, T. Neubert, H. Plagwitz, R. Grischke, R. Meyer, A. Schoonderbeek, U. Stute, and R. Brendel, Prog. Photovoltaics 15, 521 (2007).
- ²⁰³P. Engelhart *et al.*, Energy Procedia **8**, 313 (2011).
- ²⁰⁴N. Bateman, P. Sullivan, C. Reichel, J. Benick, and M. Hermle, Energy Proceedia 8, 509 (2011).
- ²⁰⁵J. Schmidt, A. Merkle, R. Brendel, B. Hoex, M. C. M. van de Sanden, and W. M. M. Kessels, Prog. Photovoltaics 16, 461 (2008).
- ²⁰⁶D. Zielke, J. H. Petermann, F. Werner, B. Veith, R. Brendel, and J. Schmidt, Phys. Status Solidi (RRL) 5, 298 (2011).
- ²⁰⁷J. H. Petermann, D. Zielke, J. Schmidt, F. Haase, E. Garralaga Rojas, and R. Brendel, Prog. Photovoltaics **20**, 1 (2012).
- ²⁰⁸T. Lauermann, T. Lüder, S. Scholz, G. Hahn, and B. Terheiden, *Proceedings of the 35th IEEE Photovoltaic Specialists Conference*, Honolulu, HI, 20–25 June 2010 (IEEE, New York, 2010).
- ²⁰⁹B. Vermang, H. Goverde, L. Tous, A. Lorenz, P. Choulat, J. Horzel, J. John, J. Poortmans, and R. Mertens, Prog. Photovoltaics **20**, 269 (2012).
- ²¹⁰I. Cesar *et al.*, 37th IEEE Photovoltaic Specialists Conference, Seattle, WA, 19–24 June 2011 (IEEE, New York, 2011).

¹⁴⁰S. Bordihn, *et al*. (to be published).

- ²¹¹P. Engelhart *et al.*, *Proceedings of the 26th European Photovoltaic Energy Conference*, Hamburg, Germany, 5–9 September 2011 (unpublished).
- ²¹²D. Suwito, U. Jäger, J. Benick, S. Janz, M. Hermle, and S. W. Glunz, IEEE Trans. Electron Devices **57**, 2032 (2010).
- ²¹³A. Richter, M. Hörteis, J. Benick, S. Henneck, M. Hermle, and S. W. Glunz, *Proceedings of the 35th IEEE Photovoltaic Specialists Conference*, Honolulu, HI, 20–25 June 2010 (IEEE, New York, 2010).
- ²¹⁴C. Schmiga, M. Hörteis, M. Rauer, K. Meyer, J. Lossen, H.-J. Krokoszinski, M. Hermle, and S. W. Glunz, *Proceedings of the 24th European Photovoltaic Energy Conference*, Hamburg, Germany, 21–25 September 2009 (unpublished).
- ²¹⁵A. Richter, J. Benick, A. Kalio, J. Seiffe, M. Hörteis, M. Hermle, and S. W. Glunz, Energy Proceedia 8, 479 (2011).
- ²¹⁶V. Mertens *et al.*, *Proceedings of the 26th EUPVSEC*, Hamburg, Germany, 5–9 September 2011 (unpublished).
- ²¹⁷A. R. Burgers *et al.*, *Proceedings of the 25th EUPVSEC*, Valencia, Spain, 6–10 September 2010 (unpublished).
- ²¹⁸C. Gong, S. Singh, J. Robbelein, N. Posthuma, E. Van Kerschaver, J. Poortmans, and R. Mertens, Prog. Photovoltaics **19**, 781 (2011).

- ²¹⁹C. Reichel, M. Reusch, F. Granek, M. Hermle, and S. W. Glunz, *Proceedings of the 35th IEEE Photovoltaic Specialists Conference*, Honolulu, HI, 20–25 June 2010 (IEEE, New York, 2010).
- ²²⁰R. Bock, S. Mau, J. Schmidt, and R. Brendel, Appl. Phys. Lett. 96, 263507 (2010).
- ²²¹F. Kiefer, C. Ullzhofer, T. Brendemühl, N.-P. Harder, R. Brendel, V. Mertens, S. Bordihn, C. Peters, and J. W. Müller, IEEE J. Photovoltaics 1, 49 (2011).
- ²²²W. C. Sun, W. L. Chang, C. H. Chen, C. H. Du, T. Y. Wang, T. Wang, and C. W. Lana, Electrochem. Solid-State Lett. **12**, H388 (2009).
- ²²³L. Tsakalakos, J. Balch, J. Fronheiser, B. A. Korevaar, O. Sulima, and J. Rand, Appl. Phys. Lett. **91**, 233117 (2007).
- ²²⁴M. D. Kelzenberg, D. B. Turner-Evans, M. C. Putnam, S. W. Boettcher, R. M. Briggs, J. Y. Baek, N. S. Lewis, and H. A. Atwater, Energy Environ. Sci. 4, 866 (2011).
- ²²⁵D. R. Kim, C. H. Lee, P. M. Rao, I. S. Cho, and X. Zheng, Nano Lett. 11, 2704(2011).
- ²²⁶A. Polman and H. A. Atwater, Nature Mater. 11, 174 (2012).