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Very low surface recombination velocity on *p*-type *c*-Si by high-rate plasma-deposited aluminum oxide

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Aluminum oxide layers can provide excellent passivation for lowly and highly doped *p*-type silicon surfaces. Fixed negative charges induce an accumulation layer at the *p*-type silicon interface, resulting in very effective field-effect passivation. This paper presents highly negatively charged ($Q_{\text{ox}} = -2.1 \times 10^{12} \text{ cm}^{-2}$) aluminum oxide layers produced using an inline plasma-enhanced chemical vapor deposition system, leading to very low effective recombination velocities ($\sim 10 \text{ cm s}^{-1}$) on low-resistivity *p*-type substrates. A minimum static deposition rate (100 nm min^{-1}) at least one order of magnitude higher than atomic layer deposition was achieved on a large carrier surfaces ($\sim 1 \text{ m}^2$) without significantly reducing the resultant passivation quality. © 2009 American Institute of Physics. [doi:10.1063/1.3250157]

Crystalline silicon solar cell technology currently holds the main share of the photovoltaic (PV) market. Industrially manufactured crystalline silicon solar cells typically have a front surface antireflection coating (ARC) of plasma-enhanced chemical vapor deposited (PECVD) hydrogenated amorphous silicon nitride (*a*-SiN_x:H), a local metal front contact grid and a full-area aluminum rear contact. The latter provides an Al-back-surface field (Al-BSF) responsible for limited electrical rear surface passivation. In order to reduce the amount of expensive silicon material used, the industry is continually moving toward thinner solar cells. However, the thinner solar cells become, the more overall efficiency is limited by surface recombination.¹

P-type silicon substrates are typically used in the Si PV industry in preference over *n*-type substrates. One reason for this choice is the lack of high-quality passivation for *p*-type emitters. However, *n*-type solar cells show interesting benefits when compared to *p*-type, such as a higher tolerance to impurities present in low-grade silicon (for example Fe),² and not suffering from oxygen–boron–complex degradation.³

Positively charged dielectric layers such as *a*-SiN_x:H (Ref. 4) provide good passivation for lowly and highly doped *n*-type silicon, as well as for lowly doped *p*-type silicon substrates. The built-in positive charges present in *a*-SiN_x:H (typically in the range of $Q_f \sim 10^{12} \text{ cm}^{-2}$) (Ref. 5) induce an accumulation or inversion layer on *n*-type and *p*-type silicon surfaces, respectively. This holds the Fermi level at the interface far from the intrinsic level, where the recombination centers are more efficient. This kind of passivation is referred as field-effect passivation.

When used for the passivation of the rear surface of *p*-type solar cells, the application of *a*-SiN_x:H leads to an inversion channel, and in most cases causes shunting at the *p*-contacts, inducing local current losses.⁶ Thermally grown silicon dioxide (SiO₂), used in the high-efficiency solar cells,^{7,8} provides very good passivation on lowly doped *p*-type silicon. However, the high thermal budget during oxidation limits the application of this passivation process on

different materials. An alternative approach uses a stack of thin SiO₂ and PECVD dielectrics instead of a thick SiO₂.⁹ Amorphous silicon (*a*-Si:H) obtained by PECVD has also shown good passivation quality demonstrated on solar cells.¹⁰ However, *a*-Si:H layers show significant light absorption and poor stability at higher temperatures, strongly limiting the range in which thermal processing can be carried out after the deposition of such a layer.

In addition, *a*-SiN_x:H neither thermal SiO₂ afford the same level of surface passivation for *p*-type emitters as observed for phosphorus-doped emitters.^{11,12}

Conversely, Al₂O₃ layers can provide excellent passivation on lowly and highly-doped *p*-type silicon. Various deposition techniques are appropriate for surface passivation, including chemical vapor deposition,^{4,13} sol-gel,¹⁴ atomic layer deposition (ALD)^{15,16} and sputtering.¹⁷ The highest reported passivation quality to date has been obtained using plasma-assisted ALD (PA-ALD).¹⁸ Such layers have been applied to high-efficiency *n*-type⁸ and *p*-type¹⁹ solar cells. The ALD technique²⁰ cycles reactant gas insertions and purges in order to achieve a precisely controlled deposition, atomic layer by atomic layer. Therefore typical deposition rates of PA-ALD limit its application in a commercial production line. One approach to circumvent this problem is to decrease the total deposition time using only thin PA-ALD Al₂O₃ layers¹⁸ ($\sim 7 \text{ nm}$). Although the ALD deposition rate is low, the technique provides the advantage of very uniform and conformal deposition over large area with a low pinhole density.

Recently, Miyajima *et al.*¹³ reported a value of $S_{\text{eff}} \sim 10 \text{ cm s}^{-1}$ obtained at a deposition rate of $\sim 5 \text{ nm min}^{-1}$ using PECVD AlO_x. The experiments were conducted on *p*-type $10 \Omega \text{ cm}$ Czochralski (Cz) Si wafers assuming 1.36 ms bulk lifetime. In our case highly doped *p*-type float-zone (FZ) material was used assuming infinite bulk lifetime. However highly doped substrates are mostly used in crystalline silicon solar cell technology due to their higher efficiency potential.

In this work, an aluminum oxide (AlO_x) layer has been developed using an inline industrial-type PECVD system (Roth&Rau SiNA). This system is currently in extensive use in the crystalline Si PV industry, typically used to deposit

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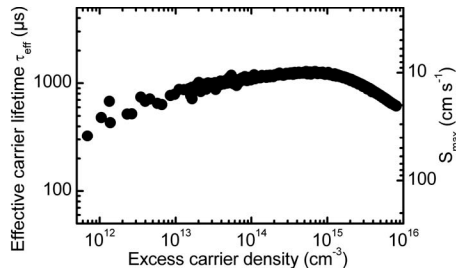


FIG. 1. Effective carrier lifetime τ_{eff} and the corresponding S_{max} of *c*-Si (FZ (100), *p*-type, 1 Ω cm, 250 μm thick), with symmetrically passivated front and back surfaces using industrial inline PECVD AlO_x layers as a function of the excess carrier density Δn (AlO_x thickness: 50 nm).

a- $\text{SiN}_x\text{:H}$ ARC layers. Inline systems of this type reach production throughputs of more than 1000 wafers per hour²¹ and are not a limiting step in production. The plasma is created by 2.45 GHz microwave (MW) pulses, which are introduced to the reaction chamber via a linear antenna. A chamber pressure of approximately 0.15 mbar and a temperature 300 °C were used. A mix of nitrous oxide (N_2O), trimethylaluminum [TMA, $\text{Al}(\text{CH}_3)_3$], and argon (Ar) was used as reactant gas.

Layer characterization was performed on *p*-type (boron-doped) shiny-etched FZ wafers with a crystal orientation of (100), 1 Ω cm resistivity and 250 μm thickness. Prior to the deposition, a wet chemical surface cleaning was carried out, consisting of a hot HNO_3 treatment, a short HF dip and a water rinse. Layers were deposited on both sides of the wafers by two successive PECVD processes, each deposition exclusively to one side of the wafer. We obtain a symmetric test structure, which has the advantage that the effective surface recombination velocity (S_{eff}) can be directly extracted from the effective excess carrier lifetime (τ_{eff}). The maximum effective surface recombination velocity (S_{max}) can then be calculated using²²

$$S_{\text{max}} = \frac{W}{2 \times \tau_{\text{eff}}}, \quad (1)$$

where W is the wafer thickness. This equation assumes an infinite bulk lifetime. The τ_{eff} of the sample was determined using a Sinton Consulting WCT-120 lifetime tester,²³ operated in transient mode.

As-deposited τ_{eff} values were measured in the range of 1 μs . To achieve the full surface-passivation potential, a forming gas anneal (FGA) was applied for 25 min with temperatures ranging from 350 to 500 °C. Figure 1 presents τ_{eff} as a function of the excess carrier density inside the wafer which is passivated with 50 nm PECVD AlO_x . For solar cells under standard irradiation (~ 1 sun), the excess carrier density typically varies from 10^{13} to 10^{15} cm^{-3} . In this range, PECVD AlO_x leads to an almost constant τ_{eff} peaking at 1.2 ms. Unlike *a*- $\text{SiN}_x\text{:H}$ and SiO_2 the lifetime achieved with PECVD AlO_x is not observed to decrease significantly at lower injection levels ($\sim 10^{13} \text{ cm}^{-3}$). Hoex *et al.*¹⁸ interpreted this phenomenon as an effect of the accumulation layer induced by negative-charge passivation. A high dynamic deposition rate²⁴ of 25 nm cm/min was achieved in our inline system, which corresponds to a minimum static deposition rate of 100 nm min⁻¹. The static deposition rate for laboratory PA-ALD (Ref. 18) and laboratory PECVD (Ref. 13) are reported to be 2 and 5 nm min⁻¹, respectively.

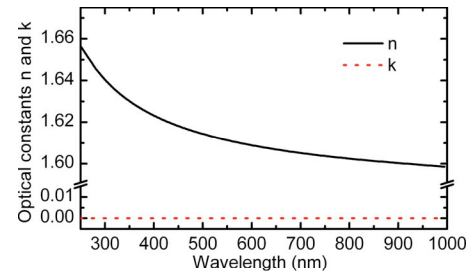


FIG. 2. (Color online) Optical constants n and k of PECVD AlO_x as a function of the wavelength, obtained fitting a Cauchy model with ellipsometry measurement.

Therefore, the inline PECVD presented here is at least one order of magnitude faster than PA-ALD, without significantly sacrificing resulting passivation quality.

Figure 2 presents the refractive index and the extinction coefficient measured by spectroscopic ellipsometry in the wavelength range of 250–1000 nm. In this range, the refractive index is measured to be between 1.60 and 1.65, while the photon absorption was below the detection limit. This is comparable to PA-ALD Al_2O_3 values¹⁵ also reported to be between 1.60 and 1.65. Benick *et al.*⁸ showed that thin Al_2O_3 layers can be used in combination with *a*- $\text{SiN}_x\text{:H}$ for ARCs, while Schmidt *et al.*¹⁹ showed that Al_2O_3 exhibits similar behavior to SiO_2 for internal back reflection at the rear of *c*-Si solar cell. The same characteristics are also expected for PECVD AlO_x layers presented in this letter.

The exact composition of the layers has been determined by x-ray photoelectron spectroscopy. The measurement was performed on the surface of the deposited layer after 15 s of Ar sputtering. The layer is found to be approximately stoichiometric with 60% oxygen (O), 36% aluminum (Al), and 4% carbon (C), while nitrogen (N) and silicon (Si) were not detected. A similar ratio has been previously observed.²⁵ The small carbon content is attributed to the methyl groups of TMA.

High-frequency and quasistatic capacitance-voltage (CV) measurements using a mercury probe were performed in order to extract the charge density (Q_{ox}) and the interface defect density (D_{it}) of the PECVD AlO_x layers (Fig. 3). The D_{it} was calculated using the method of Castagné and Vapaille.²⁶ Values of $Q_{\text{ox}} = -2.1 \times 10^{12} \text{ cm}^{-2}$ and $D_{\text{it}} = 1.7 \times 10^{11} \text{ eV}^{-1} \text{ cm}^{-2}$ were measured for a 30 nm thick PECVD AlO_x layer after FGA. A stack composed of the same 30 nm PECVD AlO_x layer (which was deposited first) with a 100 nm PECVD silicon oxide was measured. In this case a D_{it} value of $(2-5) \times 10^{10} \text{ eV}^{-1} \text{ cm}^{-2}$ was calculated. The high

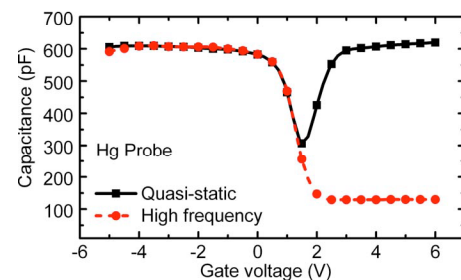


FIG. 3. (Color online) High-frequency and quasistatic capacitance-voltage measurements of a 30 nm thin PECVD AlO_x layer deposited on a *p*-doped substrate (1 Ω cm). A negative charge density of $Q_{\text{ox}} = -2.1 \times 10^{12} \text{ cm}^{-2}$ was calculated from this curve.

TABLE I. Summary of aluminum oxide deposition techniques used for passivation of *c*-Si *p*-type surfaces. A table presenting D_{it} and Q_{ox} for the different aluminum oxide deposition techniques that has been reported in literature is included in Ref. 29.

Deposition technique	Substrate	S_{eff} (cm s ⁻¹)	Q_{ox} (cm ⁻²)
APCVD ⁴	2 Ω cm	210	-3×10^{12}
sol-gel ¹⁴	Fz, 1 Ω cm	~ 100	-1.6×10^{12}
PA-ALD ¹⁸	Fz, 2 Ω cm	~ 6	-1×10^{13}
PECVD ¹³ (with CO ₂)	Cz, 10 Ω cm	~ 10	-1.6×10^{12}
rf sputter AlO _x ¹⁷	Fz, 0.8 Ω cm	~ 55	-3×10^{12}
PECVD (this work)	Fz, 1 Ω cm	~ 10	-2.1×10^{12}

density of negative charges induces an accumulation layer on *p*-type silicon, producing a field effect passivation. Low D_{it} associated with high negative surface charge density can explain the excellent passivation shown by PECVD AlO_x layers on *p*-type silicon. These measurements show also that D_{it} at the Si/AlO_x interface after annealing can be as low as at a Si/SiO₂ interface. A thin SiO₂ layer (thickness below 5 nm) is often observed at the interface between *c*-Si and Al₂O₃ after annealing.¹⁵ Johnson *et al.*²⁷ suggested that the negative charges in Al₂O₃ are situated close to the SiO₂/Al₂O₃ interface, which may also be occurring in our case. An interstitial SiO₂ layer between PECVD AlO_x and *c*-Si may provide a good interface quality with *c*-Si, and low D_{it} values.

Table I summarizes aluminum oxide deposition techniques used for passivation of *p*-type silicon surfaces. The highest passivation quality is obtained using PA-ALD, but the measured S_{eff} is not significantly lower than obtained using PECVD. The very conformal characteristic of the layer obtained using PA-ALD is apparently not required to obtain low S_{eff} . Nearly the same S_{eff} can be achieved on a large carrier surface (approximately a square of ~ 1 m²) using PECVD deposition under low vacuum conditions (0.15 mbar), obtaining the layer at a much higher deposition rate. For all deposition techniques cited a negative charge density between 10^{12} and 10^{13} cm⁻² is reported for aluminum oxide after annealing. Although the charge density achieved is higher using PA-ALD than using PECVD, this does not necessarily mean a lower potential in terms of passivation quality for PECVD AlO_x. For example, a saturation of field-effect passivation has been observed experimentally using corona charging on SiO₂.²⁸

In conclusion, AlO_x layers were deposited using a large carrier surface (~ 1 m²) PECVD system on FZ-Si wafers (*p*-type, 1 Ω cm, shiny-etched surfaces, 250 μ m thick) at an equivalent static deposition rate of 100 nm min⁻¹. Effective surface recombination velocities S_{eff} value ~ 10 cm/s were achieved after forming gas annealing, which is comparable to the record values reported using PA-ALD. High negative charge densities of $Q_{ox} = -2.1 \times 10^{12}$ cm⁻² and low defect densities of $D_{it} = 1.7 \times 10^{11}$ eV⁻¹ cm⁻² were detected using CV measurements. The PECVD AlO_x layers have a measured refractive index of $n = 1.61$ at a wavelength of 632

nm without detectable absorption, making them well suited for the passivation of *p*-type surfaces at both the front and the rear side of crystalline silicon solar cells.

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