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# Electronic Passivation of Crystalline Silicon Surfaces Using Spatial-Atomic-Layer-Deposited HfO<sub>2</sub> Films and HfO<sub>2</sub>/SiN<sub>x</sub> Stacks

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Spatial atomic layer deposition (SALD) is applied to the electronic passivation of moderately doped ( $\approx 10^{16}$  cm<sup>-3</sup>) p-type crystalline silicon surfaces by thin layers of hafnium oxide (HfO2). For 10 nm thick HfO2 layers annealed at 400 °C, an effective surface recombination velocity  $S_{eff}$  of 4 cm s<sup>-1</sup> is achieved, which is below what has been reported before on moderately doped p-type silicon. The one-sun implied open-circuit voltage amounts to  $iV_{oc} = 727$  mV. After firing at 700 °C peak temperature in a conveyor-belt furnace, as applied in the production of solar cells, still a good level of surface passivation with an  $S_{\rm eff}$  of 21 cm s<sup>-1</sup> is attained. Reducing the HfO2 thickness to 1 nm, the passivation virtually vanishes after firing (i.e.,  $S_{\rm eff} > 1000 \,\rm cm \, s^{-1}$ ). However, by adding a capping layer of plasma-enhanced-chemical-vapor-deposited hydrogen-rich silicon nitride (SiNx) onto the 1 nm HfO2, a substantially improved firing stability is attained, as demonstrated by  $S_{\text{eff}}$  values as low as 30 cm s<sup>-1</sup> after firing, which is attributed to the hydrogenation of interface states. The presented study demonstrates that SALD-deposited HfO<sub>2</sub> layers and HfO<sub>2</sub>/SiN<sub>y</sub> stacks have the potential to evolve into an attractive surface passivation scheme for future solar cells.

## 1. Introduction

Recombination losses are still one major loss mechanism in today's state-of-the-art industrial-type silicon solar cells.<sup>[1]</sup> One

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recombination losses in such solar cells, besides bulk recombination, is surface recombination, which has to be minimized through suitable and firing-stable surface passivation schemes. Today, for the nonmetallized solar cell surfaces, electronic passivation of industrial-type solar cells is typically realized via the deposition of dielectric layers such as silicon dioxide (SiO<sub>2</sub>), silicon nitride (SiNx), amorphous silicon (a-Si), aluminium oxide (Al<sub>2</sub>O<sub>3</sub>), and stacks thereof.<sup>[2]</sup> In particular, a large fraction of today's industrially produced high-efficiency silicon solar cells applies  $Al_2O_3/SiN_x$  stacks, where the interface passivation is provided by the ultrathin (typically only a few nm) Al<sub>2</sub>O<sub>3</sub> layer and the hydrogen-rich SiN<sub>x</sub> layer protects the vulnerable Al<sub>2</sub>O<sub>3</sub> layer and serves as hydrogen donor, improving the firing stability of the Al2O3/c-Si interface passivation.[3]

important contribution to the overall

Although Al<sub>2</sub>O<sub>3</sub> has proven to be an outstanding dielectric layer for the surface passivation of silicon, single Al<sub>2</sub>O<sub>3</sub> layers are not perfectly suitable in all application cases. One reason is that Al<sub>2</sub>O<sub>3</sub> easily reacts/dissolves with metal pastes used for the solar cell metallization during firing as well as in contact with chemicals such as hydrofluoric acid. Both are usually avoided by adding the  $SiN_x$  protection/capping layer. Another problem, which also applies to Al<sub>2</sub>O<sub>3</sub>/SiN<sub>x</sub> stacks, is related to the fundamental passivation mechanism. The predominant passivation mechanism of Al<sub>2</sub>O<sub>3</sub> on silicon is based on the very large negative fixed charge density within the Al<sub>2</sub>O<sub>3</sub> layer ("field-effect passivation").<sup>[4]</sup> This passivation mechanism leads to, for example, problems on phosphorus-diffused n<sup>+</sup>-type silicon surfaces<sup>[5]</sup> and leads to shunt-causing inversion layers on n-type silicon surfaces, a problem for the rear passivation of interdigitated backcontact (IBC) solar cells.<sup>[6]</sup>

In this study, we examine the surface passivation performance of thin layers of hafnium oxide (HfO<sub>2</sub>) and HfO<sub>2</sub>/SiN<sub>x</sub> stacks on moderately doped 1.4  $\Omega$  cm p-type silicon surfaces. In the past, atomic-layer-deposited HfO<sub>2</sub> layers were applied as high- $\kappa$  dielectrics in microelectronics<sup>[7]</sup> and are well known to show a much better resistance against acidic etching compared to Al<sub>2</sub>O<sub>3</sub>.<sup>[8]</sup> In addition, there have been several studies published in recent years demonstrating a promising potential of HfO<sub>2</sub> for the electronic passivation of crystalline silicon surfaces.<sup>[9–14]</sup> Most of these studies found that the fixed charge density in the HfO<sub>2</sub>



lavers deposited on silicon is smaller compared to that in  $Al_2O_3$ layers.<sup>[15]</sup> Hence, the surface passivation mechanism of HfO<sub>2</sub> is assumed to be less field-effect passivation and a larger fraction of "chemical" interface passivation, that is, a reduction of the interface state density. One might hence expect that HfO<sub>2</sub> provides a comparable passivation level on p- and on n-type silicon surfaces. However, the majority of studies published so far have examined n-type silicon surfaces, resulting in much lower surface recombination velocities compared to the very few results on p-type silicon wafers. In this contribution, we try to fill this gap and examine HfO<sub>2</sub> passivation of p-type silicon surfaces. For the first time, we also examine the firing stability of HfO<sub>2</sub> layers and of HfO<sub>2</sub>/SiN<sub>x</sub> stacks in an industrial conveyor-belt firing furnace, as used for the metal contact formation in the production of commercial silicon solar cells. The technique applied for the HfO<sub>2</sub> deposition is spatial atomic layer deposition (SALD)<sup>[16]</sup> with a movable substrate table, which is a sufficiently fast deposition technique ready for the industrial scale-up.

### 2. Experimental Section

We use 6 inch diameter shiny-etched  $1.4 \Omega$  cm boron-doped float-zone (FZ) silicon wafers for our experiments. The 300 µm thick (100)-oriented wafers are all RCA-cleaned with hydrofluoric acid dip as last step. Subsequently, HfO<sub>2</sub> layers are symmetrically deposited on both wafers sides using SALD. A schematic of the deposition technique is shown in **Figure 1**. **Figure 2** shows a photograph of the deposition head, as developed by SALD B.V. In contrast to the conventional sequential atomic layer deposition (ALD) process, as mostly used, the two half-reactions in the SALD process are spatially separated, eliminating the need for intermediate pumping steps, which accelerates the deposition significantly.<sup>[16,17]</sup> In the SALD system shown in Figure 1 and 2, the wafer is positioned on a substrate table that moves forward and back below the deposition head. For each pass of the wafer, one atomic layer of HfO<sub>2</sub> is grown.

Tetrakis(dimethylamido)hafnium (TDMAHf) is used as precursor and oxidation is performed using water vapor (H<sub>2</sub>O). H<sub>2</sub>O and TDMAHf inlets are separated by N<sub>2</sub>, which acts as a gas curtain between H<sub>2</sub>O and TDMAHf, preventing any reaction of both components before they react on the Si wafer surface. One pass of the wafer through the three zones corresponds to one ALD cycle, resulting in one monolayer of HfO<sub>2</sub>. The thickness of ALD HfO<sub>2</sub> is proportional to the number of ALD cycles. We have determined a growth per cycle for the SALD of HfO<sub>2</sub> of 0.12 nm/cycle. The deposition rate is scalable to several





**Figure 2.** Photograph of the SALD head. The wafer is positioned on a substrate table (heated to  $\approx 200$  °C), which moves forward and back below the deposition head. For each pass of the wafer one atomic layer of HfO<sub>2</sub> is grown.

nanometers per second, depending on the hardware configuration, compared to typically much less than an nm per minute for the conventional sequential ALD processes usually used in the laboratory. The movable substrate table is kept at a constant temperature of 200 °C during our depositions.

Some of the 6" wafers received silicon nitride (SiN<sub>x</sub>) capping layers on top of the SALD-HfO<sub>2</sub> films, resulting in HfO<sub>2</sub>/SiN<sub>x</sub> stacks. 90 nm thick SiN<sub>x</sub> layers were deposited at ≈400 °C onto the HfO<sub>2</sub> layers on both wafer sides using microwave-remote plasma-enhanced chemical vapor deposition (PECVD) using silane (SiH<sub>4</sub>) and ammonia (NH<sub>3</sub>) and hydrogen (H<sub>2</sub>) as process gases. We apply an industrial deposition system (Meyer Burger, SiNA).<sup>[18]</sup> The resulting SiN<sub>x</sub> capping layers have a refractive index of 2.05 (at a wavelength of 633 nm) and are very rich in hydrogen (>10 at.%).

After HfO<sub>2</sub> or HfO<sub>2</sub>/SiN<sub>x</sub> depositions on both wafer sides, the 6" wafers were laser-cut into quarters to increase the number of samples. Sample annealing was performed on the HfO<sub>2</sub>-passivated samples in the temperature range between 350 and 550 °C in air on a temperature-controlled hot-plate with cover. Some HfO<sub>2</sub>- and all HfO<sub>2</sub>/SiN<sub>x</sub>-passivated samples were fired in an industrial conveyor-belt furnace (centrotherm, DO-FF-8.600-300) at a belt speed of 7.2 m min<sup>-1</sup>, as typically applied for the contact firing in solar cell production. The actual temperature profiles on the wafer surface were measured using a temperature tracker (Datapaq DQ1860A) and a type-K thermocouple (Omega, KMQXL-IM050G-300) attached to the wafer surface.



Figure 1. Schematic of the SALD deposition head, where  $H_2O$  inlet, Tetrakis(dimethylamido)hafnium (TDMAHf) and  $H_2O$  inlet are separated by  $N_2$  curtains.



The reported peak temperatures are all measured temperatures, the set-peak temperatures are significantly higher.

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The effective carrier lifetime  $\tau_{\rm eff}$  of the processed samples was measured as a function of the excess carrier concentration  $\Delta n$  at a temperature of 30 °C using a WCT-120 lifetime tester from Sinton Instruments. For effective lifetimes larger than 200 µs, the transient photoconductance decay (PCD) mode was applied, whereas for lifetimes lower than 200 µs, the quasi-steady-state photoconductance (QSSPC) mode was used.<sup>[19]</sup> The one-sun implied open-circuit voltages  $iV_{\rm oc}$  were calculated from the  $\Delta n$ values measured at one-sun illumination intensity as well as the known doping concentration  $N_{\rm dop} = 1.05 \times 10^{16} \, {\rm cm}^{-3}$  of the 1.4  $\Omega$  cm p-type silicon material used from the equation<sup>[19]</sup>

$$iV_{\rm oc} = \frac{kT}{e} \ln\left(\frac{\Delta n(\Delta n + N_{\rm dop})}{n_{\rm i}^2}\right) \tag{1}$$

where  $n_i$  is the intrinsic carrier concentration of silicon, k is the Boltzmann constant, e is the elementary charge, and T is the absolute temperature. Note that the  $iV_{oc}$  value calculated through Equation (1) includes recombination in the bulk as well as at the surfaces of the FZ-Si wafers examined.

In order to separate the surface from the bulk recombination, we calculate the effective surface recombination velocity  $S_{\text{eff}}$  from the measured effective lifetime  $\tau_{\text{eff}}$ , the intrinsic carrier lifetime  $\tau_{\text{intr}}$  of the silicon bulk, the wafer thickness *W*, and the minority-carrier diffusion coefficient *D* (relevant only for large  $S_{\text{eff}}$  values >230 cm s<sup>-1</sup>) using the equation<sup>[20]</sup>

$$S_{\rm eff} = \frac{W}{2} \left[ \left( \frac{1}{\tau_{\rm eff}} - \frac{1}{\tau_{\rm intr}} \right)^{-1} - \frac{W^2}{D\pi^2} \right]^{-1}$$
(2)

To calculate  $\tau_{intr}$ , the most recent parameterization of Niewelt et al.<sup>[21]</sup> is used. For the bulk material we hence assume that recombination only takes place via Auger and radiative recombination and no additional defect-related recombination is present. The calculated *S*<sub>eff</sub> values are therefore upper limits, as we cannot completely exclude defect-related bulk recombination.

### 3. Results

Figure 3 shows the one-sun implied open-circuit voltages  $iV_{oc}$  as obtained from Equation (1) using the  $\Delta n$  values measured at onesun using the Sinton WCT-120 system. The examined samples are 300  $\mu$ m thick 1.4  $\Omega$  cm p-type silicon wafers passivated (on both sides) with HfO2 layers of 10 nm (blue circles), 5 nm (red triangles), 3 nm (green squares), and 1 nm (pink diamonds) thickness. Directly after the SALD process, which is carried out at  $\approx$ 200 °C, very low *iV*<sub>oc</sub> values of 600 mV and below indicate that there is no significant level of surface passivation achieved without additional thermal post-deposition annealing. However, subsequent annealing on a hot-plate in air drastically increases  $iV_{oc}$ with maximum values of  $iV_{oc} = 727 \text{ mV}$  for the 10 nm HfO<sub>2</sub> annealed at 400 °C, demonstrating an excellent level of surface passivation. For the 5 nm HfO<sub>2</sub> layer, still a very good passivation with  $iV_{oc} = 713 \text{ mV}$  is achieved after annealing at an increased annealing temperature of 450 °C. However, reducing the HfO<sub>2</sub> film thickness further to 3 nm does not provide any sufficient level of surface passivation anymore, as indicated by a maximum



**Figure 3.** Measured one-sun implied open-circuit voltages  $iV_{oc}$  of  $1.4 \Omega$  cm p-type silicon wafers passivated (on both sides) with HfO<sub>2</sub> layers of 10 nm (blue circles), 5 nm (red triangles), 3 nm (green squares), and 1 nm (pink diamonds) thickness as a function of hot-plate annealing temperature.

 $iV_{\rm oc}$  of 645 mV after annealing at 500 °C. For even thinner HfO<sub>2</sub> films, the level of surface passivation further deteriorates, as indicated by a maximum  $iV_{\rm oc}$  of only 623 mV for the 1 nm thick HfO<sub>2</sub> layer after annealing at 350 °C. The optimum annealing temperature shows a pronounced dependence on the film thickness. For the 10 nm HfO<sub>2</sub> layer, a very broad  $iV_{\rm oc}$  plateau between 350 and 450 °C annealing temperature is observed, whereas the 5 and 3 nm thick HfO<sub>2</sub> layers cannot be fully activated in the low-temperature range 350–400 °C, but require temperatures of 450 and 500 °C, respectively. For the very thin 1 nm thick HfO<sub>2</sub> layer, this trend is obviously reversed, giving the best passivation at 350 °C annealing temperature, however, at an extremely poor passivation level.

The injection-dependent lifetime measurements of the bestpassivating  $HfO_2$  layers of Figure 3 are shown as open symbols in **Figure 4**. The maximum effective lifetime of  $\tau_{\text{eff}} = 2.14 \text{ ms}$  is measured in the injection range  $\Delta n = 2$  to  $3 \times 10^{15}$  cm<sup>-3</sup> on the silicon sample passivated with 10 nm HfO2 and annealed at 400 °C. Note that the  $\tau_{\rm eff}(\Delta n)$  dependence is not very pronounced and that in the entire injection range relevant to silicon solar cells, effective lifetimes exceeding 1 ms are measured for the 10 nm HfO<sub>2</sub> thickness. Using Equation (2), the corresponding injection-dependent effective surface recombination velocity  $S_{\text{eff}}(\Delta n)$  is calculated from the measured  $\tau_{\text{eff}}$  (closed symbols). Due to the decreasing intrinsic lifetime with increasing injection level given by the Niewelt parameterization,<sup>[21]</sup> S<sub>eff</sub> of the wafer passivated with 10 nm HfO<sub>2</sub> is continuously decreasing with increasing  $\Delta n$ . The decrease of  $\tau_{\text{eff}}$  with increasing  $\Delta n$  for  $\Delta n > 3 \times 10^{15} \,\mathrm{cm}^{-3}$  is obviously caused be the increasing intrinsic recombination alone. For  $\Delta n > 5 \times 10^{15} \text{ cm}^{-3}$  the surface recombination velocity approaches a constant value of  $S_{\rm eff} = 4 \, {\rm cm \, s^{-1}}$ , which is comparable to what has been reported for Al<sub>2</sub>O<sub>3</sub> on p-type silicon with comparable doping concentration.<sup>[16]</sup> For HfO<sub>2</sub>, this is the lowest S<sub>eff</sub> reported so far for surface passivation on moderately doped p-type silicon.<sup>[12]</sup> For the 5 nm







Figure 4. Injection-dependent measurements of a) the effective lifetime  $\tau_{eff}(\Delta n)$  and b) the corresponding effective surface recombination velocity  $S_{eff}(\Delta n)$  of the best-passivating HfO<sub>2</sub> layers of Figure 3.

thick HfO<sub>2</sub> layer, an even weaker injection dependence of the effective lifetime and the corresponding surface recombination velocity is observed. From  $\Delta n = 10^{14}$  to  $10^{15}$  cm<sup>-3</sup>,  $S_{\rm eff}$  is slightly decreasing from 16 to 10 cm s<sup>-1</sup> and for  $\Delta n > 10^{15}$  cm<sup>-3</sup>,  $S_{\rm eff}$  is constant at 10 cm s<sup>-1</sup>. Note that such a weak  $S_{\rm eff}(\Delta n)$  dependence is beneficial for optimal solar cell operation. For layer thicknesses below 5 nm, the measured lifetimes strongly decrease and the corresponding  $S_{\rm eff}$  values increase. For the 3 nm thick HfO<sub>2</sub> layer, over the measured injection range,  $S_{\rm eff}$  varies between 145 and 170 cm s<sup>-1</sup> and for the 1 nm thick HfO<sub>2</sub>,  $S_{\rm eff}$  is even in the range 320–420 cm s<sup>-1</sup>, not providing any sufficient level of surface passivation.

We conclude that a minimum thickness of  $5 \text{ nm HfO}_2$  is required to allow for a high level of surface passivation and for excellent passivation, the HfO<sub>2</sub> layers should be 10 nm thick. HfO<sub>2</sub> layers thinner than 5 nm do not provide a sufficient level of passivation on p-type silicon surfaces after low-temperature annealing.

Note that recently, a decreasing  $S_{\rm eff}$  with increasing HfO<sub>2</sub> film thickness has also been reported by Tomer et al.<sup>[22]</sup> for n-type as well as p-type silicon surfaces, where the HfO<sub>2</sub> layers were deposited via traditional sequential thermal ALD. On the contrary, in another study, Pain et al.<sup>[23]</sup> reported an increasing  $S_{\rm eff}$  with increasing film thickness. This discrepancy might be due to the fact that they used an O<sub>2</sub> plasma (i.e., plasma-enhanced ALD) rather than a thermal oxidation by H<sub>2</sub>O, as in our SALD process and also the sequential thermal ALD processes applied by Tomer et al. Obviously, depending on the deposition conditions, very different thickness dependences of the HfO<sub>2</sub> passivation quality can be achieved.

A rapid thermal annealing step, usually called "firing step", is applied as final process step in the production of silicon solar cells for the contact formation. Any surface passivation layer has to keep a stable level of surface passivation during such a firing step. The firing is thereby performed in an infrared conveyor-belt furnace heating up the solar cell to a peak temperature of 650–800 °C for a few seconds. It is well known that such high temperatures can be detrimental to some passivation layers, such as ultrathin (i.e., a few nm thick)  $Al_2O_3$  layers.<sup>[3]</sup> For ultrathin  $Al_2O_3$  layers, hydrogen-rich  $SiN_x$  capping layers were added, which led to a significant improvement of the thermal stability of the surface passivation during firing.<sup>[3]</sup>

This was the motivation in the present study, to also examine  $HfO_2/SiN_x$  stacks during firing at different peak temperatures and compare the firing stability with that of  $HfO_2$  single layers. Figure 5 shows measured 1-sun  $iV_{oc}$  values of p-type silicon wafers passivated on both sides with  $HfO_2/SiN_x$  stacks (open symbols). The  $HfO_2$  thickness was varied, whereas the  $SiN_x$  thickness was kept constant at 90 nm. Directly after the deposition of the  $SiN_x$  layers on both  $HfO_2$ -coated sides of each sample, the measured  $iV_{oc}$  values depend strongly on the  $HfO_2$  layer



**Figure 5.** Measured one-sun implied open-circuit voltages  $iV_{oc}$  of 1.4  $\Omega$  cm p-type silicon wafers passivated on both sides with HfO<sub>2</sub>/SiN<sub>x</sub> stacks (open symbols) directly after SiN<sub>x</sub> deposition on top of the HfO<sub>2</sub> layers and after firing at measured peak temperatures from 640 to 710 °C. For comparison,  $iV_{oc}$  values measured on silicon wafers passivated with HfO<sub>2</sub> single-layers and fired at 700 °C are also shown (closed symbols).



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thickness and  $iV_{\rm oc}$  > 710 mV is only obtained for the 10 nm thick HfO<sub>2</sub> layer. The improvement compared to the status directly after HfO<sub>2</sub> deposition (see Figure 3) is probably just due to the annealing during the PECVD-SiN<sub>x</sub> deposition at  $\approx$ 400 °C, which is less effective for the thinner HfO<sub>2</sub> layers, in agreement with the results shown in Figure 3. Firing at measured peak temperatures in the range 640-710 °C does not show a significant impact on  $iV_{oc}$  for the 10 nm thick HfO<sub>2</sub> layer, but improves the passivation quality for all thinner HfO<sub>2</sub> layers. However, only the 5 nm thick HfO<sub>2</sub> layer with  $SiN_x$  capping exceeds the  $iV_{oc}$  of 700 mV (at 675 °C peak firing temperature). Also shown in Figure 5 are  $iV_{oc}$  values measured on samples passivated with  $HfO_2$  single-layers (without hydrogen-rich SiN<sub>x</sub> capping layers) and fired at 700 °C peak temperature (filled symbols). These samples show a slightly reduced  $iV_{oc}$  by 12 and 6 mV for the 10 nm and the 5 nm HfO<sub>2</sub>, respectively, compared to the respective HfO<sub>2</sub>/SiN<sub>x</sub> stacks, demonstrating only a small hydrogenation effect of the hydrogen-rich SiNx capping layers. However, the impact of the  $SiN_x$  capping, and probably of the hydrogenation of interface states, is much more pronounced for the ultrathin, only 1 nm thick HfO<sub>2</sub> layer, where we measure a drastic improvement by adding the SiN<sub>x</sub> capping layer. After firing at  $\approx$ 700 °C peak temperature, the 1 nm thick HfO2 single-layer provides practically no surface passibilities as shown by a measured  $iV_{oc}$  of only 580 mV. On the contrary, when capped by the hydrogen-rich  $SiN_{x}$ , the 1 nm HfO<sub>2</sub> provides a much higher  $iV_{oc}$  of 670 nm after firing at  $\approx$ 700 °C. These results demonstrate, for the first time, the benefit of hydrogen-rich capping layers concerning the firing stability of the surface passivation provided by HfO<sub>2</sub> films.

**Figure 6** shows the injection-dependent lifetime curves (open symbols, left scale) and the corresponding surface recombination velocities (closed symbols, right scale) measured on p-type silicon wafers passivated with 1 nm HfO<sub>2</sub> single-layers compared to



**Figure 6.** Injection-dependent measurements of the effective lifetime  $\tau_{\rm eff}(\Delta n)$  (open symbols, left scale) and the corresponding surface recombination velocity  $S_{\rm eff}(\Delta n)$  (closed symbols, right scale) of 1.4  $\Omega$  cm p-type silicon wafers passivated with 1 nm HfO<sub>2</sub> single-layers and stacks consisting of 1 nm HfO<sub>2</sub> plus 90 nm hydrogen-rich SiN<sub>x</sub> after firing at a peak temperature of 700 °C.

stacks consisting of 1 nm HfO<sub>2</sub> plus 90 nm hydrogen-rich SiN<sub>x</sub> after firing at a peak temperature of 700 °C. Whereas the 1 nm HfO<sub>2</sub> single-layer provide no sufficient level of surface passivation is reached after firing (as indicated by  $S_{\rm eff}$  values >1000 cm s<sup>-1</sup> over the entire relevant injection range), the addition of the SiN<sub>x</sub> capping layer improves the level of surface passivation drastically, as indicated by  $S_{\rm eff}$  values as low as 30 cm s<sup>-1</sup>. We conclude that in particular for ultrathin HfO<sub>2</sub> layer, a hydrogen-rich SiN<sub>x</sub> capping drastically improves the firing stability of the surface passivation quality, which might be attributed to the hydrogenation of interface states.

### 4. Conclusions

A surface recombination velocity  $S_{\rm eff}$  of 4 cm s<sup>-1</sup> was measured for SALD-deposited 10 nm thick HfO<sub>2</sub> layers on p-type silicon after low-temperature annealing at 400 °C, which is the lowest  $S_{\rm eff}$  reported so far for HfO<sub>2</sub> passivation of moderately doped ( $\approx 10^{16}$  cm<sup>-3</sup>) p-type silicon surfaces. The measured  $iV_{\rm oc}$  of the corresponding sample was 727 mV. For a reduced HfO<sub>2</sub> layer thickness of 5 nm,  $S_{\rm eff}$  increased to 10 cm s<sup>-1</sup> and  $iV_{\rm oc}$  dropped to 713 mV. For even thinner layers (3 and 1 nm),  $S_{\rm eff}$  drastically increased to values >100 cm s<sup>-1</sup>. We conclude that for lowtemperature annealed HfO<sub>2</sub> layers, a minimum thickness of 5 nm is required to allow for a good level of surface passivation and for excellent passivation, the layers should be 10 nm thick.

As any surface passivation layer used in a solar cell production process has to maintain a sufficiently stable level of surface passivation during a firing step in a conveyor-belt furnace, we have examined the passivation quality of the HfO<sub>2</sub> layers during firing and compared single HfO<sub>2</sub> layers with HfO<sub>2</sub>/SiN<sub>x</sub> stacks. The iVoc values measured on samples passivated with HfO2 singlelayers (i.e., without hydrogen-rich SiN<sub>x</sub> capping layers) showed a reduction in  $iV_{0c}$  by only 12 and 6 mV after firing at 700 °C for the 10 nm and the 5 nm HfO<sub>2</sub>, respectively, compared to the respective  $HfO_2/SiN_x$  stacks. However, the impact of the  $SiN_x$  capping was significantly more pronounced for the ultrathin, only 1 nm thick HfO<sub>2</sub> layer. Here, a drastic firing-induced degradation in  $iV_{\rm oc}$  to only 580 mV was observed without SiN<sub>x</sub> capping layer. The addition of the  $SiN_x$  capping layer improved  $iV_{oc}$  to 670 mV after firing, clearly demonstrating the benefit of hydrogen-rich capping layers on the firing stability of the surface passivation provided by HfO<sub>2</sub> films.

The presented results on p-type silicon surfaces clearly show that  $HfO_2$  and  $HfO_2/SiN_x$  stacks could evolve into an interesting alternative for the rear surface passivation of PERC or IBC cells as well as to the front passivation of POLO or TOPCon solar cells.

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# **Conflict of Interest**

The authors declare no conflict of interest.



### **Author Contributions**

Jan Schmidt: Conceptualization (lead); Data curation (lead); Formal analysis (lead); Investigation (lead); Methodology (lead); Validation (lead); Visualization (lead); Writing—original draft (lead); Writing—review & editing (lead). Michael Winter: Investigation (supporting); Methodology (supporting); Writing—review & editing (supporting). Floor Souren: Conceptualization (supporting); Investigation (supporting); Resources (supporting); Writing—review & editing (supporting); Resources (supporting); Writing—review & editing (supporting). Jons Bolding: Resources (supporting). Hindrik de Vries: Methodology (supporting).

## Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

## **Keywords**

carrier lifetimes, crystalline silicon, firing stability, hafnium oxide, silicon nitride capping layers, solar cells, surface passivation

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