Silicon surface passivation by transparent conductive zinc oxide

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ABSTRACT
Surface passivation is essential for high-efficiency crystalline silicon (c-Si) solar cells. Despite the common use of transparent conductive oxides (TCOs) in the field of solar cells, obtaining surface passivation by TCOs has thus far proven to be particularly challenging. In this work, we demonstrate outstanding passivation of c-Si surfaces by highly transparent conductive ZnO films prepared by atomic layer deposition. Effective surface recombination velocities as low as 4.8 cm/s and 11 cm/s are obtained on 3 Ω cm n- and p-type (100) c-Si, respectively. The high levels of surface passivation are achieved by a novel approach by using (i) an ultrathin SiO2 interface layer between ZnO and c-Si, (ii) a sacrificial Al2O3 capping layer on top of the ZnO film during forming gas annealing, and (iii) the extrinsic doping of the ZnO film by Al, B, or H. A combination of isotope labeling, secondary-ion mass spectrometry, and thermal effusion measurements showed that the sacrificial Al2O3 capping layer prevents the effusion of hydrogen from the crystalline ZnO and the underlying Si/SiO2 interface during annealing, which is critical in achieving surface passivation. After annealing, the Al2O3 capping layer can be removed from the ZnO film without impairing the high levels of surface passivation. The surface passivation levels increase with increased doping levels in ZnO, which can be attributed to field-effect passivation by a reduction in the surface hole concentration. The ZnO films of this work are suitable as a transparent conductor, an anti-reflection coating, and a surface passivation layer, which makes them particularly promising for simplifications in future solar cell manufacturing.

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I. INTRODUCTION
The passivation of electronic defect states at the crystalline silicon (c-Si) surface has been a topic of research already for decades, due to its large impact on the performance of silicon-based devices. For c-Si solar cells specifically, surface defect states induce the Shockley-Read-Hall recombination of light-generated charge carriers, a process in which their free energy is lost for further power conversion. Therefore, in high-efficiency solar cells, the Si surface is typically being passivated by a thin film. Such surface passivation generally relies on the reduction of the interface defect density, referred to as chemical passivation, and the reduction of either the electron or hole concentration at the surface, referred to as field-effect passivation. While to date numerous materials are being used for surface passivation in c-Si solar cells, they are typically either electrically insulating (e.g., Al2O3, SiNx, and SiO2), or not transparent to the solar spectrum [e.g., hydrogenated amorphous silicon (a-Si:H) and polycrystalline silicon (poly-Si)], which restricts their applicability in solar cells. A highly transparent and conductive passivation layer would be ideal for the application at the front surface of solar cells, as it can, besides providing passivation, also assist in the current collection. Although in the last few years several new passivation materials have been discovered, including AlN, TiOx, GaOx, TaOx, HfOx, POx, NbOx, and ZrOx, sufficient passivation by a transparent conductive oxide (TCO) has not yet been achieved. In this work, we report on outstanding passivation of the c-Si surface by ZnO, a material that is widely used in the field of photovoltaics as TCO.
ZnO is an abundant n-type semiconductor with a wide and direct optical bandgap ($E_g > 3.2$ eV), making it transparent for most of the solar spectrum. The refractive index of $n \approx 2$ at $2$ eV makes the ZnO films of 60–80 nm in thickness well-suited as an anti-reflection coating for c-Si solar cells. The carrier density and hence the work function of ZnO can accurately be controlled by the incorporation of extrinsic n-type dopants in the ZnO films, such as Al, B, Ga, or H.\textsuperscript{12–16} Due to the above-mentioned properties and the relatively low work function of $\sim 4.4$ eV, ZnO is customarily being used as a transparent window layer to collect the current from (non-transparent) carrier-selective contact materials, such as doped c-Si, a-Si:H, or poly-Si.\textsuperscript{17} Interestingly, TCOs could also in principle be used as a carrier-selective contact with Si. Already in the late 1960s, TCOs had been explored as electron-selective contact materials in rudimentary Si solar cells.\textsuperscript{18} Also, ZnO specifically has recently been explored as electron-selective material for c-Si solar cells\textsuperscript{19–21} or as an integral part of a hole-selective tunneling contact.\textsuperscript{22} Most notably, Ding et al. have recently achieved a solar cell efficiency of 17% using the ZnO films as electron-selective contact for lowly-doped c-Si.\textsuperscript{21} Nevertheless, it was found that the insertion of an intrinsic a-Si:H layer between the c-Si and the ZnO strongly improved the open-circuit voltage of the solar cell from 645 to 672 mV,\textsuperscript{23} as the a-Si:H layer substantially improved the level of surface passivation.

From the above, it is clear that the transparent ZnO films thus potentially can be used as an electrical conductor, anti-reflection coating, passivation layer, and carrier-selective contact in c-Si solar cells. Yet, achieving surface passivation by TCOs, including ZnO, has thus far proven to be particularly challenging. Only recently, passivation by highly doped ZnO was demonstrated with an implied open-circuit voltage of 650 mV by Panigrahi et al.\textsuperscript{24} Such a level of passivation may, however, be insufficient for most high-efficiency c-Si solar cells. Note also that other transparent materials that are currently of high interest as, e.g., electron- or hole-selective contact, such as MoO$_x$, WO$_x$, and V$_2$O$_5$,\textsuperscript{25} are commonly being restricted by a lack of surface passivation and are therefore typically used in combination with passivating a-Si:H interlayers. Understanding how Si surface passivation can be reached therefore remains a highly relevant research question.

In attempting to find a new route to enable excellent surface passivation by ZnO (which is a polycrystalline material), it is instructive to look at poly-Si passivating contacts that are well-known for their ability to provide excellent passivation to c-Si surfaces. In poly-Si passivating contacts, highly n- or p-type doped poly-Si layers are typically prepared on top of an ultra-thin SiO$_2$ interfacial oxide layer of 1–2 nm thickness (commonly termed “tunnel oxide”). The preparation method of this interfacial oxide layer is key in achieving high levels of surface passivation.\textsuperscript{25} Additionally, after preparation, the SiO$_2$/poly-Si stack is typically being hydrogenated to further enhance the surface passivation levels. Such hydrogenation can be realized by exposing the poly-Si films to a remote hydrogen plasma,\textsuperscript{26} or alternatively, by capping the poly-Si by thin films of Al$_2$O$_3$ or SiNx followed by thermal annealing.\textsuperscript{27–29}

In this work, we adopted a similar approach as the poly-Si case to investigate surface passivation by highly transparent and conductive ZnO films. Specifically, we explore the use of an ultra-thin interface oxide and an Al$_2$O$_3$ capping layer to achieve surface passivation by highly-doped ZnO films that are prepared by atomic layer deposition (ALD). In this way, we show that the ZnO films can provide excellent passivation to both n- and p-type c-Si surfaces. In addition, we scrutinize the passivation mechanisms using a combination of isotopic labeling, secondary-ion mass spectrometry (SIMS), and thermal effusion measurements. Finally, the influence of the ZnO doping level on the passivation is demonstrated.

II. EXPERIMENTAL DETAILS

As substrates for lifetime measurements, 280-μm thick n- and p-type polished floatzone c-Si (100) wafers with a base resistivity of 3 Ω cm were used. Before the deposition of ZnO, the wafers received various pre-treatments, which were either:

(i) Radio Corporation of America (RCA) standard cleans 1 and 2\textsuperscript{16} (which leave a thin SiO$_2$ layer at the c-Si surface),
(ii) the RCA cleans followed by a dip in diluted hydrofluoric acid (HF, 1%).
(iii) the RCA cleans, an HF dip and a subsequent nitric acid oxidation step (NAOS) for 15 min at room temperature.

After these various surface treatments, the lifetime samples were exposed to an inductively-coupled plasma with oxygen (4 s at a plasma power of 200 W). This plasma treatment was required to initiate the ALD of ZnO on surfaces which received the NAOS treatment. Immediately afterwards, the doped ZnO films were prepared by ALD. More specifically, Al-doped ZnO (ZnO:Al), B-doped ZnO (ZnO:B), or hydrogen-doped ZnO (ZnO:H) films were prepared on both sides of the lifetime samples in an Oxford Instruments OpAL\textsuperscript{16} reactor at 200 °C. The thickness of the ZnO films was $\sim 75$ nm, unless stated otherwise. The deposition of ZnO was carried out using diethylzinc (DEZ) and H$_2$O as precursors. Aluminum dopants were incorporated in the ZnO:Al films by using “supercycles” with dopant cycle ratio $m=15$, meaning that every 15 ALD cycles of ZnO were followed by 1 ALD cycle of “Al$_2$O$_3$” using trimethylaluminum (TMA) and H$_2$O.\textsuperscript{22} The ZnO:B films were prepared in a similar way with varying m, using triisopropyl borate (TIB) and H$_2$O as precursors during the dopant cycle.\textsuperscript{23} Hydrogen was incorporated in the ZnO:H films by remote plasma treatments.\textsuperscript{24} Note that the highly doped ZnO films already have been prepared in high-throughput spatial ALD reactors that are designed for high volume manufacturing in photovoltaic industries.\textsuperscript{25} As a reference to the ALD ZnO films, 70 nm ZnO:Al films were also prepared by sputter deposition in a Kurt J. Lesker reactor at 155 °C, using ZnO:Al targets with 2 wt. % Al, and a plasma power density of 0.56 W/cm$^2$. For selected samples, the ZnO films...
were capped by 30 nm of Al2O3, prepared by ALD at 200 °C using TMA and H2O as precursors. Post-deposition annealing was carried out in a step-wise fashion at various temperatures (250, 300, 350, 400, 450 °C) in either forming gas (FGA) or nitrogen ambient in a Jipelec rapid thermal anneal furnace. The thickness and optical properties of the films were determined by spectroscopic ellipsometry (SE). The SE data of the ZnO films were modelled using Tauc-Lorentz and Drude oscillators, following the approach of Knoops et al. Hall measurements were carried out in the van der Pauw configuration to derive the resistivity \( \rho \), the electron density \( N_e \), and electron mobility \( \mu_e \) of the as-deposited ZnO films on wafers with a thick thermal SiO2 layer. The effective minority carrier lifetime \( \tau \) and the \( iV_{oc} \) were determined by generalized photocurrent decay measurements using a Sinton Instruments WCT120. Thermal effusion measurements were carried out by heating samples at a constant rate of 20 °C/min in a quartz tube. The effused species were detected by a quadrupole-mass spectrometer. SIMS measurements were carried out at Philips Innovation Services.

III. RESULTS AND DISCUSSION

A. Surface passivation by ALD ZnO

Figure 1 shows the effective minority carrier lifetime for various lifetime samples passivated by 70 nm ALD ZnO:B. In the as-deposited state, ZnO:B did not provide any surface passivation to n-type Si, as is evident from the very low effective lifetime values (sample 1). Moreover, the effective lifetime improved only marginally by a subsequent 30-min FGA at 450 °C (sample 2). However, in the case that the as-deposited ZnO:B films were capped by Al2O3 films, excellent passivation could be achieved after such FGA, with \( \tau = 1.53 \) ms (at \( \Delta n = 5 \times 10^{18} \text{cm}^{-3} \)) for n-type Si and \( iV_{oc} = 657 \text{mV} \) (sample 3). This lifetime corresponds to effective surface recombination velocities as low as \( S_{eff} = 4.8 \text{cm/s} \) when accounting for the intrinsic recombination parameterization of Richter et al. The same conditions resulted also for p-type Si in outstanding levels of surface passivation, with \( iV_{oc} = 709 \text{mV}, \tau = 760 \mu\text{s}, \) and \( S_{eff} = 11 \text{cm/s} \) (sample 4).

It was found that an appropriate surface treatment prior to the deposition of ZnO was essential to achieve the high levels of surface passivation. For example, for n-type Si wafers which received an HF dip prior to the ZnO deposition, a significantly lower level of surface passivation was obtained, with \( \tau = 312 \mu\text{s} \) and \( iV_{oc} = 725 \text{mV} \) (not shown). Furthermore, the thickness of the ZnO film was not critical in achieving surface passivation either (see, e.g., Fig. S1 in the supplementary material). For example, a passivation test with 13 nm instead of 75 nm thick ZnO:Al films (both having the same doping level) resulted in a similar high lifetime value of \( \tau = 1.2 \) ms.

Figure 2 shows a high-resolution cross-sectional transmission electron microscopy (TEM) image of the passivating stack. It can be observed that the ZnO:B film is ~73 nm thick and polycrystalline and forms a sharp interface with a uniform SiO2 interface oxide of 1.5 ± 0.1 nm in thickness. On top of the ZnO:B, part of the amorphous ALD Al2O3 capping layer is visible. The optical and electrical properties corresponding to the ZnO:B film of Fig. 2 are summarized in Table I. To evaluate the case that the ~73 nm thick ZnO:B passivation layer serves as an anti-reflection coating on random-pyramid textured silicon, the maximum short-circuit current density \( J_{sc,max} \) of a solar cell under AM1.5G illumination was simulated by OPAL2. In this simulation, no encapsulation (e.g., by EVA or glass) or any rear contacting materials were taken into account. The optical properties of the ZnO:B film derived from SE measurements were used as input for the simulation (see Table S1 in the supplementary material). The resulting \( J_{sc} \) of 41.6 mA/cm² for ZnO is comparable to \( J_{sc} \) values obtained when simulating optimized SiN\(_x\) layers as anti-reflection coating in OPAL2. This underlines that the conductive and passivating ZnO:B films of this work are also very suitable as an anti-reflection coating for c-Si solar cells.

B. Influence of interface pretreatments, annealing conditions, and deposition method on the surface passivation

In Sec. III A, it was found that the passivation quality provided by ZnO relies on the (chemical) pretreatment of the
c-Si surface. To investigate the influence of pretreatments in more detail, in Fig. 3, the passivation quality provided by 50-nm ZnO:Al is compared for different surface pretreatments as a function of the annealing temperature. As can be seen, the highest \(iV_{oc}\) was achieved for the RCA-cleaned samples after annealing up to 450 °C. Most likely, at higher annealing temperatures, hydrogen effuses from the film stacks and the passivation worsens. For the samples that received an HF-dip after the RCA cleans, lower overall passivation levels were obtained. Moreover, the passivation in this case only increases from \(\sim 425 °C\) onwards. This can potentially be attributed that at these temperatures, a (better) interface oxide is formed. In case a surface oxide layer was re-grown after the HF-dip by a NAOS treatment (which leaves a 1.1–1.3 nm thick interface oxide \(^{26}\)), a high \(iV_{oc}\) was again reached, comparable to the RCA-treated samples, with \(\tau = 1.02\) ms. Apparently, the presence of a high-quality interface oxide is helpful for achieving high levels of surface passivation by ZnO:Al, as has been found for several other passivating materials as well.\(^{26,36,37}\) Also, interface oxide layers grown by UV-ozone oxidation showed good surface passivation with ZnO, with lifetime values \(\gtrsim 1.5\) ms.

Note that also other materials than SiO\(_2\) may be used as interface oxide to achieve surface passivation. For instance, an ultra-thin layer of TiO\(_2\)—a material which is currently of high interest for Si solar cells due to its passivating contact properties\(^{38}\)—also resulted in excellent surface passivation. Specifically, a 2.5-nm thick TiO\(_2\) layer prepared by thermal ALD on an HF-dipped c-Si wafer capped by ZnO:Al and AlO\(_3\) showed a similar trend with annealing as the samples with the NAOS and RCA treated surfaces, reaching \(iV_{oc} = 689\) mV and \(\tau = 755\) us. Note that this is one of the few examples in the literature where surface passivation is reached when TiO\(_2\) is combined with a TCO.

When using interface oxides with a thickness in the \(~\)nm range, it is important that the tunnel oxide is not damaged during the subsequent deposition of ZnO in order to achieve surface passivation. To illustrate this, besides ALD also sputter deposition was explored as a preparation method for ZnO:Al films. In analogy to previous experiments, the sputtered ZnO:Al films were capped by 30-nm thick ALD Al\(_2\)O\(_3\) films and subjected to FGA in a stepwise fashion. Despite the same experimental procedure (except the ZnO deposition), only very low effective minority carrier lifetimes of \(\sim 30\) \(\mu s\) were achieved for RCA-treated lifetime samples with sputtered ZnO:Al films. The large differences in surface

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**TABLE I.** Summary of physical properties corresponding to the ALD ZnO:B film of Fig. 2. The \(iV_{oc}\) was obtained on \(n\)-type c-Si after capping the ZnO:B films by Al\(_2\)O\(_3\) and a subsequent FGA up to 450 °C.

<table>
<thead>
<tr>
<th>Physical property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Thickness</td>
<td>73 nm</td>
</tr>
<tr>
<td>Resistivity ((\Omega) cm(^{-1}))</td>
<td>(9.87 \times 10^{-4})</td>
</tr>
<tr>
<td>Carrier density (cm(^{-3}))</td>
<td>(4.05 \times 10^{20})</td>
</tr>
<tr>
<td>Electron mobility (cm(^2) V(^{-1}) s(^{-1}))</td>
<td>(15.6)</td>
</tr>
<tr>
<td>Tauc optical bandgap (eV)</td>
<td>(3.73)</td>
</tr>
<tr>
<td>Refractive index (at 2.0 eV)</td>
<td>(1.84)</td>
</tr>
<tr>
<td>(J_{sc, max}) (stimulated by OPAL2)</td>
<td>(41.5) mA/cm(^2)</td>
</tr>
<tr>
<td>Implied open-circuit voltage</td>
<td>(725) mV</td>
</tr>
</tbody>
</table>

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**FIG. 2.** High-resolution transmission electron microscopy image of a c-Si (100) wafer, passivated by \(\sim 73\) nm ZnO:B. The c-Si wafer received the RCA 1 and 2 cleans prior to ZnO:B deposition. On top of the ZnO:B film, an Al\(_2\)O\(_3\) capping film is present. The sample has received a 30-min forming gas anneal at 450 °C.

**FIG. 3.** The implied open-circuit voltage under 1-sun illumination for \(n\)-type c-Si lifetime samples passivated by 50 nm ZnO:Al and 30 nm Al\(_2\)O\(_3\). Data are shown for cumulative annealing steps of 5 min in forming gas. The wafers received prior to ALD either (i) the RCA standard cleans 1 and 2, (ii) the RCA cleans followed by a dip in 1% HF, or (iii) the RCA, HF, and NAOS treatments.
passivation quality between samples with ALD and sputtered ZnO films can be explained by the “soft deposition” nature of ALD compared to sputtering. For instance, it has been reported by Macco et al. that the sputter deposition of TCOs on thin a-Si:H passivation layers results in the significant reduction of the passivation quality due to plasma damage by ion-bombardment or UV-photons, whereas no reduction in passivation quality was observed when the ZnO was deposited by ALD.14 Note that the TEM cross-section in Fig. 2 shows that the ALD ZnO layer forms a sharp interface with the underlying SiO2 interface oxide, which could be indicative of such “soft” deposition. It is plausible that surface passivation can be achieved by sputtered ZnO films when such plasma damage can be mitigated.

C. The influence of the ALD Al2O3 capping layer on the interface hydrogenation

The lifetime results of Fig. 1 already showed that poor levels of surface passivation were obtained when the ZnO films were not capped by Al2O3 prior to annealing. In fact, when the ZnO films without Al2O3 capping layer were annealed in forming a gas at 450 °C, stains appeared on ZnO, which originate from mild etching of ZnO by hydrogen during the FGA. Such stains did not appear on similar samples that were annealed in nitrogen ambient. Nevertheless, also after prolonged annealing in nitrogen ambient, no surface passivation could be achieved by the ZnO films without Al2O3 capping layer. The presence of the Al2O3 capping layer is thus apparently critical in achieving surface passivation.

To understand how the Al2O3 capping layer assists in achieving surface passivation by the ZnO films, secondary ion-mass spectrometry and thermal effusion measurements were carried out on samples with and without Al2O3 capping layer. The results are shown in Figs. 4–6. To facilitate the tracing of the hydrogen throughout the passivation stack, for selected experiments the Al2O3 was prepared using deuterated TMA [i.e., Al(CD3)3] and D2O as precursors rather than Al(CH3)3 and H2O.

Figure 4 shows the distribution of hydrogen throughout ZnO:B films and ZnO:B/Al2O3 passivation stacks as obtained

![Figure 4](link)
with SIMS. Without Al₂O₃ capping layer, a relatively high concentration of hydrogen was present in as-deposited ZnO:B and at the underlying SiO₂ interface layer [Fig. 4(a)]. However, the amount of hydrogen in the ZnO:B film as well as in the SiO₂ film is reduced by over an order of magnitude after FGA. In contrast, for the samples that were capped by Al₂O₃, the amount of hydrogen in the ZnO and the underlying SiO₂ interlayer remained high after FGA, and similar in concentration to as-deposited samples. Importantly, the hydrogen concentration at the c-Si/SiO₂ interface remains high after annealing in presence with the Al₂O₃ capping layer. The differences in hydrogen concentration at the c-Si/SiO₂ interface between the annealed capped and uncapped ZnO samples could well explain the observed differences in surface passivation quality.

The large difference in hydrogen concentration between the capped and uncapped ZnO samples after annealing can qualitatively be well-explained by the results in Figs. 5 and 6. When considering the isotope labeling results of Fig. 5, a complete redistribution of ²H and ³H throughout the entire passivation stack is observed after annealing, which demonstrates that hydrogen became very mobile during the FGA at 450 °C. Specifically, in the as-deposited state, a high concentration of ³H was present in the Al₂O₃:³H, whereas the ZnO film contained predominantly hydrogen. After FGA however, ²H and ³H followed a similar distribution profile throughout the entire film stack. Note that a large part of the deuterium in the SiO₂/ZnO/Al₂O₃ system has exchanged with hydrogen from the forming gas during annealing, as has also been observed in comparable isotope labeling experiments on SiO₂/poly-Si/Al₂O₃ stacks.37

Thermal effusion measurements in Fig. 6 reveal a strong effusion of H₂ around 400 °C for the uncapped ZnO films, whereas such effusion was not observed for samples that were capped by Al₂O₃. The rapid redistribution of deuterium in ZnO and the effusion of H₂ during annealing at ~400 °C have also been observed by Beyer et al., who attributed this to the fast transport of molecular hydrogen through interconnected voids, i.e., the ZnO grain boundaries.30 As the amorphous Al₂O₃ capping layer prepared at 200 °C does not allow for the transport of molecular hydrogen at 400–450 °C, it is plausible that the capping layer impedes the transport and consecutive effusion of molecular hydrogen through the grain boundaries of ZnO and the underlying SiO₂ interlayer. This would explain why the hydrogen concentration of ZnO films that are capped with Al₂O₃ remains high after annealing. Note that in addition to blocking the effusion of molecular hydrogen from ZnO, the Al₂O₃ capping layer might also act as a hydrogen source for the underlying films during annealing. This is also supported by Fig. 5, which shows high concentrations of ²H—originating from the Al₂O₃:²H—at the passivated c-Si/SiO₂ interface after FGA.

Altogether, the variety of experimental results demonstrates that sufficient hydrogen should remain present at the c-Si/SiO₂ interface after annealing to passivate Si dangling bonds. For samples which were not annealed, the lack of sufficient surface passivation can be explained as, apart from having sufficient hydrogen at the c-Si/SiO₂ interface, also the thermal budget provided by the FGA is needed to activate chemical passivation of Si dangling bonds, as has, e.g., also been found for SiO₂/poly-Si/Al₂O₃ passivation stacks.31 The Al₂O₃ helps in achieving surface passivation by ZnO as it suppresses a rapid effusion of hydrogen from the ZnO and the underlying c-Si/SiO₂ interface during FGA. After such FGA, we have verified that the Al₂O₃ capping layer can be removed from the passivation stack by highly diluted HF without severely impairing the surface passivation (with corresponding lifetimes of 1.31 and 1.08 ms prior to and after the removal of the Al₂O₃ layer, respectively). Therefore, the Al₂O₃ capping layer thus also can be used as a sacrificial layer which only needs to be present during annealing. Note that HF etches both Al₂O₃ as well as ZnO. Therefore, a carefully timed etch is required to minimize the etching of the ZnO layer. However, in principle, ALD Al₂O₃ can be etched with high selectivity (>400:1) over ALD ZnO.31

The beneficial effect of a sacrificial Al₂O₃ capping layer on the (chemical) surface passivation has also been reported for other materials, including SiO₂,30,42,43 and SiO₂/poly-Si.30 For the case of SiO₂/poly-Si, other dense capping layers can also be used for interface hydrogenation, such as SiNₓ.30 Potentially, such other dense and amorphous materials could therefore serve as capping material to enable passivation by ZnO as well.

D. Influence of the ZnO doping level on the field-effect passivation

It is well known that surface recombination can be reduced by reducing either the electron or the hole concentration at the surface. Such “field-effect passivation” can be induced by, e.g., a fixed charge density or the work function of a passivation layer. For ZnO, the work function can be effectively lowered by the addition of extrinsic n-type dopants.15 Figure 7 shows the effect of the electron density for extrinsically doped ZnO films on the effective minority carrier lifetime.

Interestingly, the lifetime increases strongly with the electron density in ZnO. This can most likely be related to a change in field-effect passivation. Specifically, the evaluation of the Tauc optical bandgap of the ZnO films shows an increase from 3.25 eV for the lowest electron density (Nₑ = 8.0·10¹⁹ cm⁻³) to 3.73 eV for the film with the highest electron density (i.e., Nₑ = 4.05·10²⁸ cm⁻³). This strong increase in the optical bandgap by ~0.5 eV is known as the Burstein–Moss shift and can be primarily attributed to the shift of the Fermi level into the conduction band of ZnO, and thus a lowered work function.31 Simulations of the c-Si/SiO₂/ZnO band alignment in Fig. 8 show how such a change in the doping level and work function affect the field-effect passivation. In this example, the hole concentration at the c-Si surface is three orders of magnitude lower in the case of highly-doped ZnO than for lowly-doped ZnO. The highly-doped ZnO yields a surface hole concentration which is eight orders of magnitude lower than the electron concentration at the surface. This asymmetry in carrier concentrations at the
surface can significantly reduce the recombination rate through surface defect states, as this will be limited by the capturing of holes. Note that the ZnO films evaluated in this work have electron densities up to $\sim 4 \times 10^{20}$ cm$^{-3}$, while in principle electron densities of $\sim 10^{21}$ cm$^{-3}$ can even be reached for highly-doped ZnO. This thus leaves the potential for further enhancements of the field-effect passivation.

IV. CONCLUSION AND OUTLOOK

We have demonstrated that the ALD ZnO films can provide excellent passivation of lowly-doped n- and p-type c-Si surfaces. It was found that the presence of a high-quality $\text{SiO}_2$ interface layer between c-Si and ZnO was key in achieving high levels of surface passivation. Moreover, it was required to cap ZnO by $\text{Al}_2\text{O}_3$ prior to FGA to obtain surface passivation. SIMS and thermal effusion measurements showed that the $\text{Al}_2\text{O}_3$ capping layer prevents the effusion of hydrogen from ZnO and the underlying c-Si/$\text{SiO}_2$ interface. Such effusion can most likely be attributed to the rapid transport of molecular hydrogen through the ZnO grain boundaries. After FGA, $\text{Al}_2\text{O}_3$ can be removed from ZnO without impairing the improved levels of passivation, making it possible to use $\text{Al}_2\text{O}_3$ as a “sacrificial” layer. Finally, it has been established that the level of surface passivation improves with increasing electron densities in the ZnO films. The addition of extrinsic dopants reduces the work function of ZnO, which leads to enhanced field-effect passivation by reducing the hole concentration at the c-Si surface.

The doped ZnO films described in this work are highly transparent, conductive, suitable as anti-reflection coating, and moreover provide high levels of surface passivation. Due to these properties, the ZnO films provide new opportunities for c-Si solar cells. For instance, the ZnO films could potentially serve as an alternative to SiN$i$ as a passivating antireflection coating at the front surface of solar cells. In this way, it would loosen the lateral conduction requirements of the emitter or omit the use of firing-through metallization. Moreover, the passivating ZnO films are of specific interest as a highly transparent passivating electron contact. For this application to be successful, a sufficiently low contact resistivity of passivating ZnO with c-Si will be a prerequisite. Finally, it is expected that the approach and insights presented in this work will be more generally applicable and can aid the development of other (emerging) surface passivation and passivating contact materials.

SUPPLEMENTARY MATERIAL

See the supplementary material for a more in-depth study on the influence of the ZnO film thickness on the passivation quality. Moreover, it provides the $n$ and $k$ values of the ZnO film of Table I that are used for OPAL2 simulations.

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REFERENCES


