In-situ plasma-grown silicon-oxide for polysilicon passivating contacts

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Keywords: solar cells, silicon, passivation, contacts

Large-scale manufacturing of polysilicon-based passivating contacts for high-efficiency crystalline silicon (c-Si) solar cells demands simple fabrication of thermally-stable SiOx films with well controlled microstructure and nanoscale thickness to enable quantum-mechanical tunneling. Here, we investigate plasma-dissociated CO2 to grow in-situ thin (<2nm) SiOx films on c-Si wafers as tunnel-oxides for plasma-deposited, hole-collecting (i.e. p-type) polysilicon contacts. We find that such plasma processing offers excellent thickness control and superior structural integrity upon thermal annealing at 1000 °C, compared to state-of-the-art wet-chemical oxides. As a result, we achieved p-type polysilicon contacts on n-type c-Si wafers that combine excellent surface passivation, resulting in an implied open-circuit voltage exceeding 700 mV, with a contact resistance as low as 0.02 Ω·cm².
1. Introduction

Silicon oxide (SiO$_x$) has been extensively studied for the electronic passivation of crystalline silicon (c-Si) surfaces, with applications in a range of electronic devices, including transistors and solar cells $^{[1, 2]}$. Increasingly, SiO$_x$ is also used in the fabrication of high-quality carrier-selective, passivating contacts for c-Si solar cells, aimed at effectively collecting one carrier type (e.g. holes), while avoiding recombination of the opposite carrier type (e.g. electrons) $^{[3]}$. In such contacts, the SiO$_x$ layer is inserted between the c-Si surface and a doped polysilicon (poly-Si) layer; these contacts are therefore sometimes referred to as tunnel-oxide passivating contacts (TOPCon) $^{[4]}$ or polysilicon on oxide (POLO) contacts $^{[5]}$. In this contact structure, the SiO$_x$ acts as a buffer layer to passivate the Si dangling bonds at the surface of the c-Si wafer, avoiding carrier recombination. To enable simultaneously efficient carrier collection by quantum-mechanical tunneling, its thickness should be < 2 nm $^{[2, 6]}$. Furthermore, this layer regulates the diffusion of dopants into the c-Si wafer during extended high-temperature thermal annealing, typically needed to crystallize the poly-Si film and activate the dopants in the Si film $^{[7]}$. However, it has been reported that for temperatures above 850 °C, the passivation properties of the poly-Si/SiO$_x$ stack degrade due to the formation of a high density of pinholes in the SiO$_x$, as well as due to excessive diffusion of dopants into the c-Si wafer $^{[8]}$; the extent and onset of the degradation may depend on the specific fabrication process $^{[6]}$. Several methods have been used to oxidize the c-Si surface, including wet-chemical and thermal processes. In the former case, the c-Si wafer is submersed in an oxidizing solution, typically HNO$_3$ (nitric acid) or ozonated water. However, the relatively high temperature required for the oxidation chemistry alters the acid composition, impacting the reproducibility, uniformity, and quality of the SiO$_x$ $^{[9]}$. In thermal processes, wafers are loaded in quartz-tube furnaces and exposed to an oxidizing atmosphere of O$_2$ (dry thermal oxidation) $^{[10, 11]}$ or H$_2$O (wet thermal oxidation) $^{[9, 12, 13]}$. An alternative dry-oxidization process is to expose the c-Si surface to UV/ozone $^{[9, 14]}$. 
However, the promise for these processes to be adopted by the photovoltaic industry is hampered by the fact that they introduce an additional processing step, increasing device fabrication costs. In this respect, *in-situ* oxide growth, combined with low pressure chemical vapor deposited (LPCVD) poly-Si may be appealing, but is inherently non-selective, coating both wafer sides, again increasing device fabrication complexity.

In this work, we developed a plasma-based method to realize nanometer-scale SiO$_x$ layers, compatible with high-throughput solar cell processing [15]. We grow *in-situ* SiO$_x$ by exposing c-Si wafers to a CO$_2$ plasma prior to plasma-enhanced CVD (PE-CVD) of the doped Si layer, using the same reactor for both processes. CO$_2$ is a commonly available precursor gas in PE-CVD reactors; recent work discussed plasma-assisted oxidation using N$_2$O [15, 16]. We remark that achieving excellent surface passivation is known to be more challenging for hole-collecting than for electron-collecting passivating contacts [7, 17], hence our focus on poly-Si(p$^+$)/SiO$_x$/c-Si structures in this work. In particular, we study and evaluate the chemical composition of deposited SiO$_x$ capped by boron-doped, hydrogenated amorphous silicon [a-Si:H(p)] layers, which are subsequently crystallized to poly-Si(p$^+$) by thermal annealing. Our results show that our plasma-grown SiO$_x$ layer in the poly-Si(p$^+$) contact structure enables excellent passivation of c-Si surfaces, leading to implied open-circuit voltages ($iV_{oc}$) exceeding 700 mV. Besides this high $iV_{oc}$, low contact resistance ($\rho_c = 0.02$ Ω·cm$^2$) values for the poly-Si(p$^+$) contacts are obtained, making this contact system an ideal candidate for high efficiency c-Si solar cells. Moreover, we show accurate control of the oxide thickness and thermal stability of the SiO$_x$ upon annealing at 1000 °C.

**Results and discussion**

Figure 1(a) shows the thickness of SiO$_x$ grown at different CO$_2$ plasma-exposure times, ranging from 2 – 20s, determined by spectroscopic ellipsometry (SE). Starting from 2s, the initial thickness was 1.1 nm. We observe that the thickness then gradually increased by increasing the
exposure time, demonstrating precise thickness control for the growth of tunnel-oxides using this technique. We selected a plasma-exposure time of 6s for further experiments, corresponding to a device-relevant thickness of about 1.2 nm, allowing for tunneling of charge carriers. We investigated the change in effective excess-carrier lifetime (τ_{eff}) as a function of annealing temperature for the poly-Si(p^+)/SiO_x/c-Si(n) structure at an injection level of Δn = 10^{15} cm^{-3}, as shown in Figure 1(b), where the samples are forming-gas (FGA) annealed. Three peaks can be identified for samples annealed in the temperature range studied (200-1050 °C, steps of 100 °C for 10 min each). At low annealing temperatures (≤ 600 °C) a first peak is present at 500°C, which is the likely result of hydrogen passivation of the SiO_x/c-Si interface, resulting from hydrogen effusion from the a-Si:H(p) layer [18]. However, at annealing temperatures of 600-700 °C the a-Si:H(p) layer starts to crystallize, losing most of its hydrogen [19], which explains the local minimum in τ_{eff}. Subsequently, at annealing temperatures above 700 °C, τ_{eff} increases again, showing a second maximum at 900 °C. After that, τ_{eff} slightly decreases at 950 °C to recover at 1000 °C, giving the maximum τ_{eff} value we obtained: 2.7 ms. Moreover, we tested the passivation quality using wet-chemical oxide and we found that the iV_{oc} dropped to 672 mV.
From the lifetime measurements, we extracted the corresponding $iV_{oc}$ value for each annealing condition. We obtained the highest value at 1000 °C, with an $iV_{oc}$ value of 706 mV, corresponding to a saturation current density ($J_0$) of 12.7 $fA.cm^{-2}$, and an implied fill factor ($iFF$) value of 84%, as shown in Figures 1(c) and (d). Our results are comparable to those of other reports, for poly-Si(p+)/SiO$_x$/c-Si(n) structures using wet oxidation to form SiO$_x$\textsuperscript{11,20}. Fourier-transform infrared spectroscopy (FTIR) is a powerful technique to study the structure and chemical composition of poly-Si/SiO$_x$ films\textsuperscript{21}. We plot the FTIR spectra of our samples for different annealing temperatures in Figure 2(a). For poly-Si/SiO$_x$ passivating contacts two specific vibrational frequencies are relevant. Firstly, the Si-H stretching mode is located in the
range 1900-2100 cm\(^{-1}\). We find that these H-related absorption peak intensities decrease upon annealing above 500 °C, matching the decreasing trend in lifetime data in Figure 1. Notably, this signal disappears after annealing above 600 °C, suggesting complete outgassing of hydrogen from the doped Si film as it crystallizes.

Figure 2. (a) FTIR spectra of poly-Si annealed at 200-1000 °C, (b) XPS Si 2p spectra of SiO\(_x\) prepared by using CO\(_2\) plasma (top) and wet processes (bottom), prior to Si film deposition or annealing. (c and d) cp-AFM for poly-Si(p\(^+\))/SiO\(_x\)/c-Si samples annealed at 1000 °C (SiO\(_x\) prepared using wet and plasma process, respectively).

Secondly, Si-O stretching modes between 1025 and 1076 cm\(^{-1}\), attributed to the tunnel oxide, are evident for all samples. Here, with increasing annealing temperature, the peak frequency slightly shifts to higher wavenumbers and the absorption intensity increases. This suggests that two (competing) mechanism may happen: i) the increase in SiO\(_x\) intensity indicates that more SiO\(_x\) bonds are formed during annealing, which likely comes from reconstruction of the plasma-grown SiO\(_x\) and ii) the decrease in intensity, noticeable above 900 °C, attributed to the
degassing of SiO via the reaction \( \text{Si} + \text{SiO}_2 \rightarrow 2\text{SiO}_{\text{gas}} \) \[^{12, 22}\]. The FTIR spectra at low annealing temperatures (below 400 °C) show that plasma-grown SiO\(_x\) contains Si-O bonds with O atoms in reconstruction mode. Under these annealing conditions, SiO\(_x\) is sub-stoichiometric (with respect to SiO\(_2\)) \[^{22}\]. At annealing temperatures above 700 °C, the signal intensity of Si-O peaks increases, which suggests a reduction in the Si dangling bond density at the \( e\)-Si interface and thus improved surface passivation; the Si-O bond represents the distinct factor, indicative for chemical passivation of SiO\(_x\) in which O atoms bond to adjacent Si surface atoms. Therefore, we attribute the change in the signal intensity and frequency position at 900 and 1000 °C, mainly to formation of stoichiometric SiO\(_2\) \[^{23}\]; its formation correlates well with improved passivation (Figure 1).

To demonstrate the structural integrity of the \textit{in-situ} plasma oxide we performed conductive probe atomic force microscopy (cp-AFM) to map the formation of pinholes. Figures 2(c) and (d) compare the cp-AFM mapping of the plasma oxide with a wet chemical oxide (using HNO\(_3\)) of comparable thickness (images are on the same scale). For the poly-Si/SiO\(_x/c\)-Si sample annealed at 1000 °C and prepared via the wet process, we found the presence of a significant amount of pinholes. These are absent in the plasma-processed samples, which further underlines the improved thermal stability of our plasma-grown SiO\(_x\).

To come to an improved microscopic understanding of these different oxides, high-resolution X-ray photoelectron spectroscopy (XPS) spectra of the Si 2p core line spectra for the wet and plasma-grown films, with SE-measured thicknesses of 1 nm and 1.2 nm respectively, are shown in Figure 2 (b). These films were first studied prior to any silicon deposition or annealing. The Si 2p\(_{3/2}\) and 2p\(_{1/2}\) doublet (separated by 0.60 eV) is shown here, where the position of Si 2p in both is adjusted to 99.5 eV to compensate for a slight surface charging \[^{24}\]. In accordance with previous analyses\[^{25}\] we interpret the main high binding energy peak at \(~103.6\) eV and its convoluted peaks to SiO\(_2\) (4+) and sub-stoichiometric Si oxides: Si\(_2\)O (1+), SiO (2+), Si\(_2\)O\(_3\) (3+) \[^{26, 27}\]. Comparing \( c\)-Si featuring wet tunnel-oxides with their plasma-grown counterparts, a
clear shoulder at 102.5 eV is observed for the former, indicating a less stoichiometric, silicon rich SiO$_2$ film. The spectra are deconvoluted into a further four Si 2p doublet ($\text{Si}^{1+}$, $\text{Si}^{2+}$, $\text{Si}^{3+}$, $\text{Si}^{4+}$) components, as described in detail in the experimental section, using the relative binding energy positions of the Si 2p$_{3/2}$ and peak full width at half maximum (FWHM) of the silicon oxides, as determined by Himpsel et al. $^{[26]}$ on SiO$_2$-$c$-$\text{Si}(111)$ and SiO$_2$-$c$-$\text{Si}(100)$ surfaces, and consistent with other reports using higher resolution soft XPS. $^{[28]}$ Here, the $\text{Si}^{4+}$ position is let free due to its well known binding-energy variation with film thickness and relatively fixed positions of $\text{Si}^{3+}$ and $\text{Si}^{1+}$. $^{[29]}$ Our analysis shows that the wet and plasma tunnel-oxides have contrasting distributions of SiO$_x$. These results are summarized in Table 1 $^{[26, 30]}$, where at an X-ray energy of 1486.7 eV, although affected by the vertical composition variation, the integrated peak-area distribution is directly proportional to the SiO$_x$ distribution. For clarity both the spectral distribution for all Si states (sensitive to the electron take-off angle $\theta$) as well as that for SiO$_x$ are shown. The SiO$_2$ film thickness can be estimated from the Si 2p XPS spectrum from the ratio of Si(0) to total SiO$_x$ peaks, as outlined by Seah et al. $^{[29]}$. This method is detailed in the supplementary information (S3) and calculated thicknesses are included in Table 1. Here we estimate thicknesses of approximately ~0.9 nm and ~0.8 nm for the wet and plasma film respectively, which is in reasonable agreement with the SE measurements.

**Table 1:** Peak-area percentages determined from the XPS spectra fitting of the Si 2p region for wet and plasma oxidation process of $c$-$\text{Si}(100)$, to grow SiO$_2$-$c$-$\text{Si}(100)$ interfaces without the presence of a poly-$\text{Si}(p^+)$ overlayer or annealing. The parantheses indicate the relative percentages of SiO$_x$ contributions.

<table>
<thead>
<tr>
<th>Deposition method</th>
<th>Thickness/nm (XPS) ±0.15</th>
<th>Si(0)</th>
<th>$\text{Si}^{1+}$</th>
<th>Si(2+)</th>
<th>$\text{Si}^{3+}$</th>
<th>Si(4+)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wet</td>
<td>0.9</td>
<td>73.14</td>
<td>3.16(11.77)</td>
<td>0.66(2.46)</td>
<td>3.40(12.66)</td>
<td>19.64(73.11)</td>
</tr>
<tr>
<td>Plasma</td>
<td>0.8 nm</td>
<td>75.91</td>
<td>2.77(11.49)</td>
<td>0.65(2.70)</td>
<td>1.84 (7.64)</td>
<td>18.83(78.17)</td>
</tr>
</tbody>
</table>

Overall, this suggests that a lower amount of silicon-rich, sub-oxide species (Si$_2$O, SiO and Si$_2$O) and a higher amount of stoichiometric SiO$_2$ is required for the as-grown film, to obtain a thermally and structurally stable film at annealing temperatures in excess of 1000 °C. In this regime a more abrupt and thinner Si(100)-to-SiO$_2$ transition region and a more uniform SiO$_2$ film would be expected. While analysis of the annealed SiO$_x$ layer in the actual contact stack (with overlaying polysilicon) would be ideal, XPS analysis requires in this case removal of the poly-Si(p$^+$) film via Ar$^+$ sputtering or wet chemical processes, which would likely change the SiO$_x$ stoichiometry and structure. An analysis of SiO$_x$/c-Si films annealed to 1000 °C without a poly-Si(p$^+$) layer is presented in the supplementary information, where we observed an increase in SiO$_x$ thickness to ~3.0 nm indicating further Si(100) oxidation and a more relatively uniform SiO$_x$ and SiO$_2$ stoichiometric composition between both samples. In actual contact stacks it is unlikely the interfacial oxide would increase to such an extent during annealing.

To verify the carrier-collection properties of our passivating contacts, we also performed contact resistivity measurements following the Cox and Strack method using Ag/poly-Si(p$^+$)/SiO$_x$/c-Si(p)/Ag samples annealed at different temperatures prior to metallization. The current-voltage response shows clear Ohmic behavior within the probed voltage range with a reduction of the contact resistance to values as low as 0.144, 0.03 and 0.02 Ω·cm$^2$ for the samples annealed at 900, 950, and 1000 °C respectively. These values are comparable to those reported in literature, obtained from wet oxidation in terms of stability at high temperature and performances$^{7,22}$. We were not able to extract the contact resistivity for the samples annealed below 900 °C.

To obtain direct insight into the poly-Si(p$^+$)/SiO$_x$/c-Si(n) structure we acquired cross-sectional high-resolution transmission electron microscopy (HR-TEM) images, together with Si and O
energy-dispersive X-ray spectroscopy (EDX) elemental maps (Figure 3) on a sample annealed at 800 °C. The inset in Figure 3(a) shows the Fourier-transform image corresponding to the poly-Si(p⁺) region, representing clear c-Si lattice fringes. The ultra-thin plasma-grown SiOₓ layer of around ~1.4 nm is visible as a darker region between the poly-SiOₓ and c-Si bulk as shown in Figure 3(b), consistent with our ellipsometry measurements. From the elemental mapping, taking a zoomed-in view of the SiOₓ/c-Si(n) interface, we find an atomically sharp interface and well defined distribution of the oxide layer.

Figure 3 HR-TEM image of the poly-Si(p⁺)/SiOₓ/c-Si structure annealed at 800 °C, including EDX elemental mapping of Si and O signals. The insets (a) Fourier-transform image corresponding to this area and (b) the thickness of tunneling layer SiOₓ is 1.4 nm.

Conclusion
In this article we demonstrated the combined excellent passivation and low contact resistance for the poly-Si(p⁺)/SiOₓ/c-Si(n) hole-collecting contact structure prepared in via in-situ oxide growth, resulting from a brief exposure of the c-Si wafer to a CO₂ plasma prior to PECVD deposition of the doped a-Si:H layer, in the same reactor. In particular, our results show a high thermal stability and structural integrity at annealing temperatures in excess of 1000 °C, of
these contact stacks, which we ascribe to the stoichiometry of the interfacial SiO\textsubscript{x} layer, determined by FTIR. This is supported by XPS compositional analysis of the as-grown SiO\textsubscript{x}. The structural integrity of the oxide after annealing at 1000 °C was confirmed by conductive probe AFM measurements, which showed a minimal pinhole density compared to similar maps of an equivalent wet-chemical oxide. Overall, our passivation technique enabled an \( iV_\text{oc} \) of 706 mV with a low \( J_0 \) of 12.65 fA.cm\(^{-2}\) and \( \rho \) 0.02 Ω·cm\(^{-2}\), which is comparable with state-of-the-art \( p \)-type polysilicon contacts with less robust, \textit{ex-situ} oxide formation.

**Experimental Section**

Throughout this work, phosphorous-doped, double-side mirror-polished float zone (FZ) (100) \( c \)-Si(n) wafers, with resistivity of 1-5 Ωcm, were used. Initially, all samples were immersed in dilute HF to remove the native oxide, followed by rinsing in deionized water and drying by N\(_2\). This was followed by the growth of SiO\textsubscript{x} layers on the wafers at 200 °C, RF power in the range of 400-600 W, and the pressure 4.5 Torr. by exposure to a CO\(_2\) plasma in a PECVD reactor (Indotect, Octopus 2). For the wet-chemical oxide fabrication process, the samples were immersed in a HNO\(_3\) solution at the 120 °C process temperature for 15 minutes, then the samples were rinsed 3 times in deionized water. Subsequently, a 35 nm thick \( a \)-Si:H(p) layer was deposited via PECVD using silane (SiH\(_4\)) and trimethylboron diluted in H\(_2\) (2%TMB/H\(_2\)). Samples were then annealed at different temperatures ranging from 200-1000°C to partially crystallize the \( a \)-Si:H(p) to form poly-Si(p\(^+\)) in a forming-gas ambient (4% H\(_2\)/N\(_2\)); no post-hydrogenation treatments were applied. To further improve the passivation quality, hydrogenated silicon nitride (SiN:H) might be needed on top of the poly-Si \[31\]. For carrier-lifetime measurements, symmetrical samples were prepared by depositing the polySi(p\(^+\))/SiO\textsubscript{x} stack on both wafer sides. The effective excess-carrier lifetime (\( \tau_\text{eff} \)) was measured using a Sinton (WCT-120) instrument \[32\], operated in either transient or quasi-steady state mode. Using the same tool, the implied open-circuit voltage (\( iV_\text{oc} \)), implied fill factor (\( iFF \)) and
saturation current density \( (J_0) \) were extracted; \( J_0 \) was calculated from high-injection \( \tau_{\text{eff}} \) data according Ref. \(^{[33]}\). The SiO\(_x\) thickness was determined by spectroscopic ellipsometry (J.A Woollam) using a Tauc-Lorentz model. For contact-resistance measurements, the sample structure was Ag/polySi(p\(^+\))/SiO\(_x\)/c-Si(p)/Ag, 300 nm thermally evaporated Ag metal and measured using the Cox and Strack method \(^{[34]}\), using low resistivity (0.1-0.2 \( \Omega \)cm) planar boron-doped FZ c-Si(p) wafers. Fourier-transform infrared spectroscopy (FTIR) measurements were carried out immediately using an Agilent Cary 680 FTIR instrument with a resolution of 8 cm\(^{-1}\), applying 100 scans in the 400–4000 cm\(^{-1}\) wavenumber range. High-resolution transmission electron microscopy (HR-TEM; FEI Titan 80–300 electron microscope) was used to study the microstructure of the poly-Si/SiO\(_x\) contact stack. The composition and stoichiometry of the SiO\(_x\) films were analysed by X-ray photoelectron spectroscopy (XPS) in an Omicron multi-probe chamber, equipped with a monochromatic Al Ka X-ray source (XM1000; \( h\nu = 1486.7 \) eV) operated at 390 W, with multiple channeltron detector (Sphera II) under a vacuum of \( \sim 10^{-10} \) mbar. High-resolution spectra were recorded with a constant 15 eV pass energy, sampling an area of \( \sim 60 \) \( \mu \)m with an electron take-off angle of 33\(^\circ\) from normal indidence to the surface and \( \pm 7^\circ \) acceptance angle. The Si 2p spectra are deconvoluted by first subtracting a Shirley background and then fitting the Si\(^0\) component with with Gaussain/Lorenztian (40/60) and Si\(^{1+}\), Si\(^{2+}\), Si\(^{3+}\) and Si\(^{4+}\) with Gaussian doublets respectively. The doublets have a fixed branching ratio of 0.5 and binding energy splitting of 0.6 eV. Here the Si\(^{3+}\)2p\(_{3/2}\)−Si\(^{0}\)2p\(_{3/2}\) peak offsets are contrained to 0.95 eV(Si\(^{1+}\)), 1.8 eV(Si\(^{2+}\)) and 2.55 eV(Si\(^{3+}\)) respectively. The FWHM are fixed relative to the Si\(^{4+}\) value. Finally, conductive atomic force microscopy (cp-AFM) measurements were realized by Solver Next (NT-MDT, Russia), using a tip (PFTuna, PtIr coated, Bruker, USA) with a nominal spring constant of 0.4 N/m at a bias of 7V. The scanning area was 1×1 \( \mu \)m.
Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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References


The table of contents: This paper deals with the fabrication of a new hole selective contact for silicon solar cell. Silicon solar cells are industrially by far the most dominant technology. Here, a new type of passivating contact is introduced, leading to much less surface recombination while being resilient to high processing temperatures. This is done in simple and elegant way, where all contact-stack layers are deposited in the same plasma-deposition chamber.

Keyword: solar cells, silicon, passivation, contacts

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Supporting Information

*In-situ* plasma-grown silicon-oxide for polysilicon passivating contacts

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S1: The effective excess-carrier lifetime

![Graph showing effective lifetime as a function of excess carrier density](image)

**Figure S1.** Effective lifetime measured ($\tau_{\text{eff}}$) as a function of excess carrier density of $\Delta n = 10^{15}$ $\text{cm}^{-3}$

The effective lifetime ($\tau_{\text{eff}}$) is measured by using a Sinton (WCT-120) instrument. $\tau_{\text{eff}}$ shows that the passivation quality is enhanced with increase in the annealing temperatures. These measurements were performed on n-type float zone (FZ) Si wafers at injection level of $\Delta n = 10^{15}$ $\text{cm}^{-3}$. Here, we highlight that the $T_{\text{eff}}$ increment reaches 2.7 ms at 1000 °C.

S2: Contact resistivity
Figure S2. Contact resistivity measurement of the poly-Si(p+)/SiOx/c-Si structure annealed at 900 °C, 950 °C, and 1000 °C.

We performed contact resistivity measurement using the Cox and Strack method for poly-Si(p+)/SiOx/c-Si structure annealed at 900 °C, 950 °C, and 1000 °C. These measurements have been performed on low resistivity (0.5-0.1 Ωcm) planar boron-doped FZ c-Si(p) wafers. We
noticed that with increase annealing temperature the contact resistivity decrease from 0.144 to 0.03 and 0.02 Ω·cm².

**S3: X-ray Photoelectron Spectroscopy**

The thickness of the SiO₂ overlayer $d_{SiO₂}$ can be determined by analysis of the Si 2p XPS spectra. The area of the $Si_0$ peak, which is equivalent to the unoxidised substrate and the areas of the $Si_x$ (where $x = 1,2,3,4$) (suboxides) are determined first via a fitting procedure. The common method used widely and outlined by Seah et al.¹ is then employed. This utilises the SiO₂ attenuation length (3.448 eV Al Si 2p) and experimental electron take-off angle $θ$ and makes use of equations 1 and 2 shown below,

$$\frac{S_{SiO_2}^\infty}{S_{Si_{sub}}^\infty} = \frac{S_{SiO_2}^\infty}{S_{Si_{sub}}^\infty} \left\{ 1 - e^{-\frac{d_{oxide}}{L_{SiO_2} E_{Si} \cos(\theta)}} \right\}$$

$$d_{SiO_2/\text{nm}} = L_{SiO_2} (E_{Si} \cos(\theta)) Ln \left( 1 + \frac{R_{exp}}{R_0} \right)$$

where $\frac{S_{SiO_2}^\infty}{S_{Si_{sub}}^\infty}$ is the integrated area of Si 2p SiO₂ and SiOₓ peaks (SiSiO₂) and the Si⁰ peaks (SiSub), referred to as $R_{exp}$ in equation 2. The ratio $\frac{S_{SiO_2}^\infty}{S_{Si_{sub}}^\infty}$ is the intensity of infinitely thick layers of silicon substrate and oxide respectively and referred to as $R_0$ in equation 2, here the literature value of 0.88¹ is used. The thicknesss of SiO₂ is $d_{SiO_2}$. The attenuation length of the SiO₂ layer $L_{SiO_2}$ at 1386.7 eV is 3.448 nm¹ and $θ$ is the angle from normal.

Plasma and wet SiOₓ/Si without poly-Si(p⁺) were also studied by XPS after annealling at 1000 °C in the forming-gas furnace and spectral information is shown in Table S1.
Table S1: Peak area percentages determined from the XPS spectra fitting of Si 2p region for wet and plasma oxidation process of c-Si(100), to grow SiO$_x$/c-Si(100) interfaces after annealing at 1000 °C without a poly-Si(p$^+$) layer. The parantheses indicate the relative percentages of SiO$_x$ contributors.

<table>
<thead>
<tr>
<th>Deposition method</th>
<th>Thickness/nm (XPS) ±0.15</th>
<th>Si(0)</th>
<th>Si(1+) (Si$_2$O)</th>
<th>Si(2+) (SiO)</th>
<th>Si(3+) (Si$_2$O$_3$)</th>
<th>Si(4+) (SiO$_2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wet annealed</td>
<td>3.25 nm</td>
<td>34.76</td>
<td>1.29 (1.97)</td>
<td>0.55(0.84)</td>
<td>1.60 (2.45)</td>
<td>61.80(94.73)</td>
</tr>
<tr>
<td>Plasma annealed</td>
<td>2.96 nm</td>
<td>36.69</td>
<td>1.51 (2.39)</td>
<td>0.50(0.79)</td>
<td>1.34(2.12)</td>
<td>59.96(94.71)</td>
</tr>
</tbody>
</table>