Passivating electron contact based on highly crystalline nanostructured silicon oxide layers for silicon solar cells

Josua Stuckelberger¹, Gizem Nogay¹, Philippe Wyss¹, Quentin Jeangros¹, Christophe Allebé², Fabien Debrot², Xavier Niquille¹, Martin Ledinsky³, Antonin Fejfar³, Matthieu Despeisse², Franz-Josef Haug¹, Philipp Löper¹, Christophe Ballif¹

¹ École Polytechnique Fédérale de Lausanne (EPFL), Institute of Microengineering (IMT), Photovoltaics and Thin-Film Electronics Laboratory, Rue de la Maladière 71b, 2002 Neuchâtel, Switzerland

² CSEM PV-Center, Jaquet-Droz 1, 2002 Neuchâtel, Switzerland

³ Laboratory of Nanostructures and Nanomaterials, Institute of Physics, Academy of Sciences of the Czech Republic, v. v. i., Cukrovarnická 10, 162 00 Prague, Czech Republic

ABSTRACT

We present a novel passivating contact structure based on a nanostructured silicon-based layer. Traditional poly-Si junctions feature excellent junction characteristics but their optical absorption induces current losses when applied to the solar cell front side. Targeting enhanced transparency, the poly-Si layer is replaced with a double-layer stack consisting of a nanostructured silicon oxide capped with a nanocrystalline silicon (nc-Si) layer. The nanostructured silicon oxide layer consists of an amorphous SiO_x matrix with incorporated Si filaments connecting one side of the layer to the other, and is referred to as nanocrystalline silicon oxide (nc- SiO_x) layer. We investigate passivation quality, measured as saturation current density, and nanostructural changes, characterized by Raman spectroscopy and transmission electron microscopy, carefully studying the influence of annealing dwell temperature. Excellent surface passivation on n-type and also p-type wafers is shown. An optimum annealing temperature of 950 °C is found, resulting in a saturation current density of 8.8 fA cm⁻² and 11.0 fA cm⁻² for n-type and p-type wafers, respectively. Efficient current extraction is presented with specific contact resistivities of 86 mΩ cm² on n-type wafer and 19 mΩ cm² on p-type wafers, respectively. High-resolution transmission electron microscopy reveals that the layer stack consists of intermixed SiO_x and Si phases with the Si phases being partly crystalline already in the as-deposited state. Thermal annealing at temperatures ≥ 850 °C further promotes crystallization of the Si-rich regions. We show that the addition of the SiO_x phase enhances the thermal stability of the contact and we expect it to allow to tune the refractive index and improve transparency while still providing efficient electrical transport thanks to the crystalline Si phase, which extends throughout almost the entire layer.

1. INTRODUCTION

Crystalline silicon (c-Si) solar cells have a market share of > 90% [1] and represent the most mature and promising photovoltaic technology to replace fossil fuels and nuclear energy sources. In most c-Si solar cells the Si wafer is in direct contact with the metallization, forming a metallurgical c-Si/metal junction. The direct metal-silicon interface is affected by very high recombination rates, resulting in a decrease of the solar cell's photovoltage and therefore energy conversion efficiency [2]. This voltage loss can be overcome by inserting passivating buffer layers between the silicon wafer and the metal contact. First approaches, based on thin silicon oxide buffer layers capped with doped poly-silicon or semi-insulating poly-silicon (SIPOS) were pioneered already in the 1980's [3]–[5]. Recently, impressive solar cell results were demonstrated using a similar approach as rear contact [6]–[9], with associated recombination current at the rear side of only 7 fA cm⁻² [10]. This contact structure is based on a very thin SiO_2 buffer layer coated by a highly doped silicon layer. During a thermal annealing step at typically 800-900 °C, dopants diffuse from the deposited silicon layer into the wafer forming a highly doped

region. Afterwards, a hydrogenation step [11] is applied to chemically passivate electronic defects at the wafer-SiO₂ interface to “switch on” the passivation [6].

With the excellent quality of poly-Si junctions employed as rear contact, the front side contacting scheme becomes the efficiency limiting element [10]. Consequently, in order to further increase the solar cell efficiency, passivating contacts are also needed at the front side.

While requirements for a full-area passivating front contact are similar to these for the rear contact in terms of passivation behavior and electrical transport, the front contact layer stack also has to be optically highly transparent to avoid parasitic absorption losses.

This can be achieved with thin and highly crystalline silicon layers since the absorption coefficient of crystalline silicon in the visible and infrared is much lower than of amorphous silicon. Full crystallization of thin Si layers can be reached by prolonged thermal annealing [12]. This might, however, lead to deteriorated surface passivation due to rupture of the SiO_x buffer layer [6], [13]–[15]. Alternatively, thicker SiO₂ buffer layers can be used [5], [7], but this approach requires a “SiO₂ break up” step at 1050 °C which might degrade surface passivation or alter the doping profile in an unwanted way. To overcome these limitations, we propose to choose deposition regimes that result in crystalline structures in the film already before thermal annealing, such that moderate temperatures (700-900 °C) are sufficient to achieve almost full crystallization.

To further decrease optical absorption we introduce a high band gap material, namely silicon oxide, as a matrix around the silicon crystallites. The added SiO_x phase gives the opportunity to tune the refractive index of the mixed-phase material [16]. The concept of Si phases embedded in a SiO_x matrix is related to the early work on SIPOS-based junctions [3], [4], [17], [18]. SIPOS is a homogeneous material with Si inclusions surrounded by SiO₂ phases and features rather high specific resistances due to the transport barrier caused by the Si/SiO₂ band offsets.

In contrast to SIPOS like approach, we propose in this paper a layer structure in which the Si phases extend as pillars or filaments from one side to the other of the layer, thus enabling efficient current transport across the layer. We present an electron-selective passivating junction layer stack consisting of a phosphorus-doped nc-SiO_x/nc-Si double layer on top of a chemical oxide, prepared by plasma enhanced chemical vapor deposition (PECVD) and a thermal annealing step. The contact is investigated as n+/n and as n+/p junction using both n- and p-type wafers, respectively. We discuss the effect of annealing dwell temperature on passivation properties and nanostructural transformations.

2. EXPERIMENTAL

The investigation of the passivating electron contact was done using symmetrical structures based on 280 μm thick double side polished 4-inch (100) 2.8 Ω cm silicon wafers doped with phosphorus or boron (Figure 1). After cleaning using standard wet chemistry, a 1.2 nm thin SiO_x layer was formed by wet chemical oxidation [19], [20], also referred to as “chemical SiO_x”. Subsequently, a phosphorus-doped SiO_x/Si bilayer structure was deposited by PECVD on both sides. The individual layers are also referred to as “deposited SiO_x” and “deposited Si” in order to distinguish from the chemical SiO_x. The samples were then annealed for 15 minutes in nitrogen (N₂) atmosphere at temperatures from 750 °C to 950 °C. This was followed by a 30 min forming gas (4% H₂ in N₂) anneal at 500 °C to passivate electronic defects at the wafer-SiO_x interface. The effective minority carrier lifetime was measured by photoconductance decay and the method of Kane and Swanson [21] was applied to extract the emitter saturation current density at an excess carrier density of 1·10¹⁶ cm⁻³. The spatial homogeneity of the passivation was analyzed using photoluminescence imaging (PLI). The doping profile was analyzed by secondary

ion mass spectroscopy (SIMS) with a Cameca ims 4f-E6. For electrical characterization, coplanar aluminium (Al) contacts were thermally evaporated, and the specific contact resistivity was measured using the transfer length method (TLM). Crystallization of the Si phases and stress in the layer was characterized by Raman spectroscopy. Care was taken to suppress the signal of the silicon wafer in order to get a clear signal only from the deposited layers. This was done using a 442 nm laser, which has a Raman collection depth of only around 150 nm in c-Si [22], and additionally by polarizing the laser in such a way that the signal from the underlying wafer was minimized [23].

FIG. 1. Schematic of the symmetrical samples with the nc-SiO_x/nc-Si carrier-selective junction stack. The mixed-phase layer is indicated by silicon phases (red) embedded in an oxide matrix (green).

The structural changes were further characterized by several transmission electron microscopy (TEM) techniques in a FEI Titan Themis. The microscope was operated at 300 kV for experiments involving high-resolution (HR) TEM and scanning TEM (STEM) high-angle annular dark field (HAADF) imaging combined with energy-dispersive X-ray spectroscopy (EDX) and at 200 kV for STEM electron energy-loss spectroscopy (EELS) measurements, which were performed with a convergence of 28 mrad and a similar collection angle using a Gatan GIF Quantum ERS high energy resolution EELS spectrometer and energy filter (dispersion of 0.1 eV per channel). To this purpose, TEM lamellae were prepared from samples that were either as-deposited or annealed at 850 °C or 900 °C using the conventional focused ion beam (FIB) lift-out technique in a Zeiss Nvision 40.

3. RESULTS AND DISCUSSION

3.1 Surface passivation

We investigated the effect of the additional silicon oxide phase in our deposited passivating layer stack by varying the deposition time of the nc-SiO_x layer while keeping the total deposition time of the nc-SiO_x/nc-Si stack constant. The implied open-circuit voltage iV_{OC} and the emitter saturation current J_0 after annealing at 900 °C are plotted in Figure 2a for n-type wafers. The surface passivation is clearly enhanced with increasing nc-SiO_x thickness.

Additionally, we tested the tolerance of our contact structure to variations of dwell temperature for the case of a stack with 36% nc-SiO_x relative deposition time. The dependence of iV_{OC} and J_0 on annealing dwell temperature is shown in Figure 2 for n+/p junctions (b) and n+/n junctions (c). Excellent surface passivation is achieved for temperatures above 850 °C up to 950 °C for both n- and p-type wafers. In other studies, where the doped Si layer was deposited directly on the chemical SiO_x buffer layer, a degraded surface passivation was reported for annealing temperatures above 875 °C [9] or 900 °C [6] and attributed to a break-up of the SiO_x buffer layer [13].

This break up can be explained with the phase separation $\text{SiO}_x \rightarrow (2-x)/2 \text{ Si} + (x/2) \text{ SiO}_2$ [12] occurring in thin SiO_x layers sandwiched between two Si phases, in conjunction with oxygen interstitial generation upon annealing of SiO_2 films on Si wafers in N_2 atmosphere ($\text{SiO}_2 + \text{Si} \rightarrow 2 \text{ SiO}$) [24].

We explain the beneficial effect of the nc- SiO_x layer (Fig. 2a), and the excellent passivation temperature stability shown in Figure 2b, c with an enhanced structural stability of the interfacial SiO_x buffer layer due to the larger amount of oxygen available from the deposited nc- SiO_x layer. With these temperatures as high as 950 °C, an iV_{oc} of 723 mV and J_0 of 11.0 fA cm^{-2} is reached for the n+/n junction and an iV_{oc} of 722 mV and a J_0 of 8.8 fA cm^{-2} for n+/n junction, respectively.

FIG.2. Measured implied open circuit voltage and emitter saturation current density of the contact structure (a) on a n-type wafer annealed at 900°C as a function of the relative deposition time of the nc- SiO_x layer compared to the deposition time of the whole bilayer stack, (b) on a p-type wafer and (c) on an n-type wafer as a function of the annealing dwell temperature.

3.2 Doping profiles

Figure 3 shows the doping profiles measured by SIMS on the same wafers as discussed above. Within a surface region in the wafer of about 20 nm from the wafer-SiO_x interface, they reveal a similar behavior for all studied temperatures. Beyond that region, they show the expected behavior of deeper in-diffusion at higher temperatures, reaching a depth of 290 nm for 950 °C. To understand the electrical properties of highly P doped regions the surface concentration C_s for the different temperatures can be related to the equilibrium concentration C_{eq} and saturation concentration C_{sat} given by [25]. For 750 °C, $C_{s,750} = 3.00 \cdot 10^{20}$ atoms cm⁻³ is higher than $C_{sat,750} = 2.16 \cdot 10^{20}$ atoms cm⁻³ meaning that a considerable amount of P is incorporated partially as SiP precipitates which are recombination active. For 850 °C annealing, $C_{s,850} = 3.51 \cdot 10^{20}$ atoms cm⁻³ lies in between $C_{sat,850} = 4.05 \cdot 10^{20}$ atoms cm⁻³ and $C_{eq,850} = 2.84 \cdot 10^{20}$ atoms cm⁻³ denoting that some phosphorus is inactive but not recombination active. After annealing at 900 °C and higher, $C_{s,950} = 3.92 \cdot 10^{20}$ atoms cm⁻³ is $\lesssim C_{eq,950} = 3.89 \cdot 10^{20}$ atoms cm⁻³, hence indicating that the phosphorus is electrically active. Integrating the doping profiles and calculating the sheet resistance R_{SH} according to the mobility model of Klaassen et al. as demonstrated by [26] gives values from 300 Ω/□ for 750 °C down to 160 Ω/□ for 950 °C. To separate the influence of intrinsic (Auger and radiative) recombination from recombination of the surface and explore further optimization potential, we perform simulations of the highly doped region using EDNA [27]. We assume zero Shockley-Read-Hall recombination in the bulk of the emitter. For simplicity we model our structure as a highly doped region in the wafer at a surface with an effective surface recombination velocity SRV. This effective SRV thus lumps all recombination, independent of its exact mechanism, occurring at the interface between wafer and the deposited layer stack and within the layer stack.

The simulation shows that the effective SRV at the wafer/chem. Oxide interface is below 10000 cm s⁻¹ for all annealing temperatures ≥ 850 °C. Figure 3b shows J_0 as function of the effective surface recombination velocity for the doping profile of the nc-SiO_x/nc-Si layer stack annealed at 950 °C. The simulation shows that for the doping profile of our 950 °C sample the saturation current density is largely independent on SRV for an SRV below $1 \cdot 10^4$ cm s⁻¹ with a lower limit of 13 fA cm⁻². This matches our experimental result within the experimental error, which is estimated to be ± 2 fA cm⁻². Consequently, our experimental result cannot be improved further by optimizing the recombination properties of the interface or the layer stack.

To explore possibilities for further J_0 reduction we compare with simulations for complementary error function (ERFC) doping profiles with the same sheet resistance. For the case of an ERFC doping profile with the same phosphorus surface concentration $C_{s,950}$ and same sheet resistance as the 950 °C annealed sample, leading to a junction depth z_f of 0.03 μm, a similar behavior can be seen. Lowering the surface concentration but keeping the sheet resistance constant leads to a deeper junction. For comparison, simulated ERFC doping profiles with deeper junction ($C_s = 9.95 \cdot 10^{18}$ atoms cm⁻³, $z_f = 0.5$ μm) and the junction depth of our 950 °C sample ($C_s = 2.08 \cdot 10^{19}$ atoms cm⁻³, $z_f = 0.29$ μm) are added to Figure 3. Consequently, to attain even lower J_0 values, the surface concentration has to be reduced while increasing the junction depth, an effect that might be accomplished by decreasing the phosphorus concentration in the deposited layer and increasing the annealing dwell time. However, this effect would come at the cost of the J_0 being more sensitive to the surface recombination properties. Our experimental profile has the advantage that it provides good passivation even in case of comparatively strong surface recombination.

FIG. 3. (a) Doping profile measured by SIMS for different annealing dwell temperatures. (b) Simulation of charge carrier recombination with EDNA [27] out of SIMS doping profiles of (a) for the 950 °C annealed sample in comparison with generated ERFC doping profiles for same C_s , same z_f and a deeper z_f .

3.3 Electrical characterization

TLM measurements were performed using the Berger structure [28]. We extracted the specific contact resistivity $\rho_{c,TLM}$ and sheet resistance $R_{SH,TLM}$ for structures on p-type wafers as well as on n-type wafers annealed at 900 °C. According to the SIMS measurements shown in Figure 3 these samples feature a highly P doped region in the wafer about 200 nm deep underneath the also highly P doped deposited layer stack. Generally, current could flow from one contact to the other both through the deposited layer stack, specifically through the topmost nc-Si layer, and through the in-diffused region in the wafer. In case of an n-type wafer, the lowly doped wafer itself can additionally contribute to conductance. To investigate the current pathway, the region between the TLM pads was repetitively etched for 2 s in a $SF_6/O_2/Ar$ plasma using the aluminium pads as etching mask, and the samples were measured after each etch process by TLM. In Figure 4a and 4b a representative behavior of $\rho_{c,TLM}$ and $R_{SH,TLM}$ as a function of etching depth is shown for n+/n and n+/p junctions, respectively. The specific contact resistivity and the sheet resistance both increase upon etching for etch depths exceeding 30 nm for n+/p junction and 50 nm for n+/n junction, respectively. Please note that the data points are unequally spaced despite of the constant etch time, which is caused by the lower etch rate of SiO_x compared to Si. Consequently, the region with closely spaced data points corresponds approximately to the SiO_x layer (low etch rate).

Both for the n+/n and n+/p junction, $\rho_{c,TLM}$ and $R_{SH,TLM}$ do not change upon etching of the deposited layer (the first 30 nm). This indicates that the deposited layer does not contribute to lateral current transport, but that current rather flows through the wafer

including the in-diffused region.

The sheet resistance on the n+/n junction is increasing from 45 $\Omega/\square$ before etching to a constant value of 52 $\Omega/\square$ after etching over 200 nm which matches fairly the total calculated sheet resistance of the wafer together with the diffused region at the opposite side of the contacts of 68 $\Omega/\square$ (calculated from the wafer thickness 280 μm , background doping $1.66 \cdot 10^{15} \text{ atoms cm}^{-3}$ and ERFC profile $C_{S,900} = 2.82 \cdot 10^{20} \text{ atoms cm}^{-3}$, $z_f = 0.027 \mu\text{m}$). This small increase indicates the loss of the current pathway within the surface-near region of the wafer below the chemical oxide. For the n+/p junction the sheet resistance is 70 $\Omega/\square$ before etching and is increasing sharply as soon as the diffused region starts to be etched away. For etch depths exceeding 100 nm the current pathway is too resistive to be measured. Consequently, for the n+/p structure, the lateral conductive channel is the in-diffused n+ region only, and current flow is blocked by the p/n+ junction.

The specific contact resistivity of the n+/n junction remains largely unchanged while etching the layer stack, but slightly increases from 86 $\text{m}\Omega \text{ cm}^2$ to 137 $\text{m}\Omega \text{ cm}^2$ once the layer stack is etched and also the diffused region within the wafer is removed. For the n+/p junction, a similar but more pronounced behavior is observed with an increase from 19 $\text{m}\Omega \text{ cm}^2$ to 85 $\text{m}\Omega \text{ cm}^2$. Please note that while the structures on n+/p junctions fulfill the assumptions made in the TLM theory, the latter is not strictly valid for the n+/n junction because the conductive channel is comparatively thick.

Interestingly, in case of the n+/p junction, the increase of the specific contact resistivity is more pronounced than for the n+/n junction and occurs at lower etch depth than the increase of the sheet resistance. For the n+/n junction this is opposite, the sheet resistance starts to increase at an etch depth of 30 nm, but $\rho_{c,\text{TLM}}$ starts to increase only for etch depths of $> 60 \text{ nm}$. This hints at current spreading in the first 20 to 40 nm in the wafer which are doped to $> 2 \cdot 10^{19}$ (cf.3 Figure 3a), before the current is laterally transported over the entire depth of the conductive channel. The current flow is qualitatively sketched in Figure 5. Current spreading increases the electrically effective area of the contact. Once the spreading is reduced (here by etching away the conductive channel) the contact resistivity increases. We explain the sharper increase of $\rho_{c,\text{TLM}}$ in case of the n+/p structures with current spreading being more pronounced than for n+/n junctions because the current is confined to a thin conductive channel and can spread only on the topmost first nm, see Fig. 5b. In the n-type wafer, on the other hand, current is transported over the entire wafer thickness and the spreading can thus take place over the entire n+ region, as depicted in Fig. 5a.

We also performed sintering experiments to investigate the conditions required for establishing a good contact. Samples with the same structure as discussed above (Fig. 4b) were repeatedly sintered for 15 min on a hot plate in air at temperatures up to 400 $^{\circ}\text{C}$ and measured after each sintering step. We find a value of 59 $\text{m}\Omega \text{ cm}^2$ before the first sintering step. However, the specific contact resistivity could not be lowered by sintering for this contact structure.

The TLM measurements presented within this section show that this nc-SiO_x/nc-Si layer stack provides not only an excellent surface passivation but also a promising contact resistivity for a sufficient transport of the majority carriers for full-area contacts.

FIG. 4. Specific contact resistivity $\rho_{c,TLM}$ and sheet resistance R_{SH} for the passivating contact depicted in Fig. 1 annealed at 900 $^{\circ}C$, as a function of the etching depth for n+/n junction (a) and n+/p junction (b). In (c) $\rho_{c,TLM}$ is plotted as a function of post-metallization sintering temperature for an n+/n junction.

FIG. 5. Qualitative illustration of the current pathway during TLM measurements for an n+/n junction (a) and an n+/p junction (b), indicating the current spreading and the electrically effective area.

3.4 Structural changes

The crystallinity of the contact layer was analyzed by Raman spectroscopy, as illustrated in Figure 6a. Already in the as-deposited state, the Raman spectrum is dominated by the transverse optical (TO) c-Si phonon with a peak around 520.5 cm^{-1} . However, the signal still shows a pronounced shoulder at wavenumbers between 400 cm^{-1} and 510 cm^{-1} , which can be attributed to an amorphous Si phase [29]. After 15 min annealing at $750 \text{ }^{\circ}\text{C}$, measured at position 1, the amorphous fraction is still present. Measuring at a slightly different position only some micrometers apart (position 2), the amorphous fraction is hardly detectable. This means that annealing at $750 \text{ }^{\circ}\text{C}$ for 15 min is not sufficient to fully crystallize the layers homogeneously. For higher annealing temperatures, the amorphous fraction is decreasing further and lateral inhomogeneities vanish (not shown here). The amorphous contribution almost disappears for a dwell temperature of $950 \text{ }^{\circ}\text{C}$, meaning that the layer is almost fully crystalline.

A deviation of the Raman shift from its equilibrium position is a measure for internal stress in the layer system [30]. To extract the internal stress, the Raman peak is fitted by a Gaussian and the position x_0 of the crystalline peak is plotted as a function of the annealing dwell temperature in Figure 6b. The Raman peak shift from the equilibrium position of the c-Si TO phonon band at 520.5 cm^{-1} is directly proportional to internal stress in the silicon layer ($\Delta x = 1 \text{ cm}^{-1} \approx 250 \text{ MPa}$ [30]). A deviation towards higher wavenumbers is attributed to compressive stress whereas a deviation towards lower wavenumbers means tensile stress. In the as-deposited state the layer system is under tensile stress of 1225 MPa . After annealing at $750 \text{ }^{\circ}\text{C}$, the stress at position 1 that had more amorphous phase relaxed to 225 MPa while the stress at position 2 became compressive (625 MPa). By increasing the temperature to $950 \text{ }^{\circ}\text{C}$ the compressive stress is relaxing to a value of 300 MPa . This might be due to a reorganization of the nc-SiO_x layer, also accompanied by a phase separation towards a more stoichiometric SiO₂. Additionally a restructuring of the mixed phase takes place, which leads to a lower structural defect density as the stress in the film is lowered [31].

FIG. 6. (a) Raman spectra showing a clear tendency towards lower amorphous fraction with increasing temperature. (b) The stress in the layer system changes from a tensile stress in the as-deposited layer to a strong compressive stress in the layer that relaxes with higher temperature as the position of the c-Si peak is decreasing towards the bulk position at 520.5 cm⁻¹.

The nanostructure of the layer stack and its transformation upon thermal annealing were both investigated by TEM. STEM HAADF images and corresponding EDX maps and line scans of samples as-deposited, annealed at 850 °C and 900 °C are shown in Figure 7. Contrast variations in STEM HAADF images are related to differences in thickness (here approximately constant as a result of the FIB-preparation process) and atomic mass, with darker regions highlighting here positions richer in O and P when compared to Si-rich regions. In Figure 7, a ~2 nm thin continuous dark layer is distinguishable at the Si wafer interface in the HAADF image, which according to the EDX map corresponds to SiO_x. As the chemically grown oxide layer is 1.2 nm thick, the remaining ~0.8 nm is explained by a contribution from the deposited SiO_x layer. The EDX O signal is then observed to decrease over a range of ~15 nm as the layer evolves into phase-separated SiO_x (dark regions – green arrow) and Si (brighter regions – blue arrow) components with increasing Si content towards the top surface. In the upper 10-15 nm, a rather homogeneous silicon layer is visible, corresponding to the deposited Si layer. P doping appears to be homogeneously distributed in the nc-Si phase after deposition of the layers. The top surface is slightly oxidized and exhibits a roughness of ~5 nm.

While the wafer/SiO_x interface remains intact when annealing at 850 and 900 °C, the surface oxide layer is observed to thicken with annealing temperature, probably due to residual oxygen present in the furnace (Figure 7b-c). In addition, the P distribution within the contact becomes inhomogeneously distributed during annealing. Indeed, as observed in Fig 7b.4, which shows a larger magnification of the structure annealed at 850 °C, P has

accumulated at the interface between the chemical SiO_x and the wafer (black arrow), while the interfacial SiO_x itself remains P depleted.

FIG. 7. STEM HAADF images (1) of the bilayer structure as-deposited (a), annealed at 850 °C (b) and at 900 °C (c) along with corresponding EDX maps (2) and line scans (3, EDX integrated signal of each element normalized to unity – in arbitrary units, extracted from the dashed region shown in 2). The inset b.4 shows a high-resolution STEM HAADF image, EDX map and line scan of the wafer/contact interface at 850 °C.

In order to investigate in detail the presence of silicon phases within the deposited SiO_x layer, low-loss EEL spectra were recorded in STEM. Using the methodology presented in [32], [33], three 4 eV wide images centered at 10 eV, 17.5 eV and 23 eV were extracted from the spectrum image. From the first and last images, a linear background was extrapolated and subtracted to the second image taken at the position of the Si plasmon peak as illustrated in Figure 8a. The contrast in the resulting image is related to differences in plasmon signal between Si (bright) and SiO_x (dark) and hence reveals fluctuations in composition within the SiO_x layer. At the wafer surface, a 2-3 nm continuous SiO_x layer is distinguishable both after deposition and annealing at 850 °C (Fig. 8b-c). Directly above, the results demonstrate the mixed-phase nature of the deposited SiO_x layer even after annealing, with vertically oriented silicon rich phases (arrowed in Fig. 8b-c) of a few nanometers in diameter extending throughout the oxide matrix up to the silicon layer deposited on top. Please note that the resolution of the STEM EEL spectrum images is limited by the delocalization of the plasmon signal (on the order of 2 nm [34]) which is inherent to the technique.

FIG. 8. (a) EEL spectra of c-Si and mixed Si/SiO_x regions; (b.1-2) STEM HAADF and corresponding EELS spectrum image of plasmons after background subtraction (colored region of the spectrum shown in a) of the as-deposited sample; (c.1-2) STEM HAADF and plasmons EELS spectrum image of the sample annealed at 850 °C.

The crystallinity of the layers was assessed by high-resolution TEM imaging. Figure 9 shows HRTEM micrographs of the contact as-deposited and annealed at 850 and 900 °C along with their Fourier transforms and colored inverse Fourier transforms of selected reflections. The results demonstrate a clear increase in crystallinity of the contact layer when annealed at 850 °C with grain sizes of up to ~10 nm, while annealing at 900 °C leads to larger grains up to ~30 nm. This finding corroborates the high crystallinity observed by Raman spectroscopy shown in Figure 6a. Moreover, the crystalline Si phases matrix extend locally to about 3 nm of the wafer interface building a percolating crystalline network through most of the contact structure. From comparison with Figure 8 we conclude that the Si filaments in the lower part of the deposited SiO_x layer remain amorphous even after annealing, while silicon crystallites are observed mostly further away from the interface and in the nc-Si layer. At the interface with the wafer, the SiO_x appears to remain amorphous.

FIG. 9. HRTEM micrographs, Fourier transforms and inverse Fourier transforms of selected reflections colored and superimposed to the HRTEM image of the contact structure as-deposited (a), annealed at 850 °C (b) and annealed at 900 °C (c)

4. CONCLUSION

A novel passivating electron contact structure based on a tunnel-oxide and a highly phosphorus-doped nc-SiO_x/nc-Si double layer is presented. High-resolution (S)TEM micrographs and EDX chemical maps show an interfacial amorphous SiO_x layer of ca. 2 nm thickness, followed by a nanocrystalline SiO_x/Si mixed-phase layer and a continuous nanocrystalline Si layer. The mixed-phase layer (called nc-SiO_x) consists of a SiO_x matrix with Si filaments extending through almost the entire SiO_x layer, and shows increasing Si concentration and crystallinity towards its top interface. The addition of the nc-SiO_x layer between the chemical oxide and the nc-Si layer was shown to enhance the thermal stability of the surface passivation. The amorphous volume fraction decreases significantly upon thermal annealing at temperatures ≥ 800 °C, which is believed to be beneficial for electrical transport and a promising result towards minimized parasitic absorption. In-diffusion of phosphorus creates a doping profile with surface concentration of $3.92 \cdot 10^{20}$ atoms cm⁻³. Thus, an excellent surface passivation is achieved with emitter saturation currents of 11.0 fA cm⁻² for n+/p junction and 8.8 fA cm⁻² for n+/n junctions, respectively, yielding specific contact resistivities between 19 mΩ cm² and 86 mΩ cm².

5. ACKNOWLEDGEMENT

The authors gratefully acknowledge support by the Swiss National Science Foundation (SNF) under grant No. 200021_14588/1 and No. IZLIZ2_156641 and by the Swiss Federal Office for Energy (SFOE) under grant No. SI/501253-01. The Interdisciplinary Centre for Electron Microscopy of EPFL is acknowledged for FIB and TEM access. The authors thank also Aïcha Hessler-Wyser for her support and discussions.

REFERENCES

- [1] IEA-PVPS, "TRENDS 2014 in Photovoltaic Applications: Survey Report of Selected IEA Countries between 1992 and 2013," 2014.
- [2] A. Cuevas, "Physical model of back line-contact front-junction solar cells," *J. Appl. Phys.*, vol. 113, no. 16, 2013.
- [3] Y. H. Kwark, R. Sinton, and R. M. Swanson, "SIPOS Heterojunction contacts to silicon (1984)," vol. 94305, no. 415, pp. 742–745, 1984.
- [4] E. Yablonovitch, T. Gmitter, R. M. Swanson, and Y. H. Kwark, "A 720 mV open circuit voltage SiO_x:c-Si:SiO_x double heterostructure solar cell," *Appl. Phys. Lett.*, vol. 47, no. 11, p. 1211, 1985.
- [5] J. Y. Gan and R. M. Swanson, "Polysilicon Emitters for Silicon Concentrator Solar Cells," *Proc. 21st IEEE PVSC*, pp. 245–250, 1990.
- [6] F. Feldmann, M. Bivour, C. Reichel, H. Steinkemper, M. Hermle, and S. W. Glunz, "Tunnel oxide passivated contacts as an alternative to partial rear contacts," *Sol. Energy Mater. Sol. Cells*, vol. 131, pp. 46–50, 2014.
- [7] U. Römer, R. Peibst, T. Ohrdes, B. Lim, J. Krügener, E. Bugiel, T. Wietler, and R. Brendel, "Recombination behavior and contact resistance of n⁺ and p⁺ poly-crystalline Si/mono-crystalline Si junctions," *Sol. Energy Mater. Sol. Cells*, vol. 131, pp. 85–91, 2014.
- [8] D. L. Young, W. Nemeth, S. Grover, A. Norman, B. G. Lee, and P. Stradins, "Carrier-selective, passivated contacts for high efficiency silicon solar cells based on transparent conducting oxides," *2014 IEEE 40th Photovolt. Spec. Conf.*, pp. 1–5, 2014.
- [9] Y. Tao, E. L. Chang, A. Upadhyaya, B. Roundaville, Y. Ok, K. Madani, C. Chen, K. Tate, V. Upadhyaya, F. Zimbardi, J. Keane, A. Payne, and A. Rohatgi, "730 mV implied Voc enabled by tunnel oxide passivated contact with PECVD grown and crystallized n⁺ polycrystalline Si," *2015 IEEE 42nd Photovolt. Spec. Conf.*, pp. 1–5, 2015.
- [10] S. W. Glunz, F. Feldmann, A. Richter, M. Bivour, C. Reichel, H. Steinkemper, J. Benick, and M. Hermle, "THE IRRESISTIBLE CHARM OF A SIMPLE CURRENT FLOW PATTERN - 25% with a solar cell featuring a full area back contact," *Proc. 31th EUPVSEC*, 2015.
- [11] S. J. Pearton, J. W. Corbett, and M. Stavola, *Hydrogen in Crystalline Semiconductors*. Springer, 1992.
- [12] M. Zacharias and P. Streitenberger, "Crystallization of amorphous superlattices in the limit of ultrathin films with oxide interfaces," *Phys. Rev. B*, vol. 62, no. 12, pp. 8391–8396, Sep. 2000.
- [13] G. R. Wolstenholme, N. Jorgensen, P. Ashburn, and G. R. Booker, "An investigation of the thermal stability of the interfacial oxide in polycrystalline silicon emitter bipolar transistors by comparing device results with high-resolution electron microscopy observations," *J. Appl. Phys.*, vol. 61, no. 1, pp. 225–233, 1987.
- [14] A. Moldovan, F. Feldmann, G. Krugel, M. Zimmer, J. Rentsch, M. Hermle, A. Roth-Fölsch, K. Kaufmann, and C. Hagendorf, "Simple cleaning and conditioning of silicon surfaces with UV/ozone Sources," *Energy Procedia*, vol. 55, pp. 834–844, 2014.
- [15] F. Feldmann, M. Bivour, and C. Reichel, "Advanced Passivated Contacts and their Applications to High-efficiency Cells," *NREL Silicon Work.*, 2015.
- [16] P. Cuony, M. Marending, D. T. L. Alexander, M. Boccard, G. Bugnon, M. Despeisse, and C. Ballif, "Mixed-phase p-type silicon oxide containing silicon nanocrystals and its role in thin-film silicon solar cells," *Appl. Phys. Lett.*, vol. 97, no. 21, p. 213502, 2010.
- [17] P. Brüesch, T. Stockmeier, F. Stucki, and P. A. Buffat, "Physical properties of semi-insulating polycrystalline silicon. I. Structure, electronic properties, and electrical conductivity," *J. Appl. Phys.*, vol. 73, no. 11, pp. 7677–7689, 1993.

- [18] Y. Pan, "Study on the optical absorption of oxygen-doped polysilicon thin films," *Opt. Eng.*, vol. 32, no. 3, p. 589, 1993.
- [19] H. Kobayashi Asuha, O. Maida, M. Takahashi, and H. Iwasa, "Nitric acid oxidation of Si to form ultrathin silicon dioxide layers with a low leakage current density," *J. Appl. Phys.*, vol. 94, no. 11, p. 7328, 2003.
- [20] N. E. Grant and K. R. McIntosh, "Surface Passivation Attained by Silicon Dioxide Grown at Low Temperature in Nitric Acid," *24th Eur. Photovolt. Sol. Energy Conf.*, pp. 1676–1679, 2009.
- [21] D. E. Kane and R. M. Swanson, "Measurement of the emitter saturation current by a contactless photoconductivity decay method," *Proc. 18th IEEE Photovolt. Spec. Conf.*, pp. 578–583, 1985.
- [22] M. Ledinsky, A. Vetushka, J. Stuchlik, T. Mates, A. Fejfar, J. Kocka, and J. Stepanek, "Crystallinity of the mixed phase silicon thin films by Raman spectroscopy," *J. Non. Cryst. Solids*, vol. 354, no. 19–25, pp. 2253–2257, 2008.
- [23] W. S. Yoo, H. Harima, and M. Yoshimoto, "Polarized Raman Signals from Si Wafers : Dependence of In-Plane Incident Orientation of Probing Light," vol. 4, no. 9, pp. 356–363, 2015.
- [24] R. A. B. Devine, D. Mathiot, W. L. Warren, and B. Aspar, "O interstitial generation and diffusion in high temperature annealed Si / SiO₂ / Si structures," *J. Appl. Phys.*, vol. 79, pp. 2302–2308, 1996.
- [25] S. Solmi, a. Parisini, R. Angelucci, a. Armigliato, D. Nobili, and L. Moro, "Dopant and carrier concentration in Si in equilibrium with monoclinic SiP precipitates," *Phys. Rev. B*, vol. 53, no. 12, pp. 7836–7841, 1996.
- [26] D. B. M. Klaassen, "A unified mobility model for device simulation-I. Model equations and concentration dependence," *Solid State Electron.*, vol. 35, no. 7, pp. 953–959, 1992.
- [27] PVLighthouse, "EDNA2," 2016. [Online]. Available: <https://www2.pvlighthouse.com.au/calculators>.
- [28] H. H. Berger, "Contact resistance and contact resistivity," *J. Electrochem. Soc.*, vol. 119, no. 4, p. 507, 1972.
- [29] Z. Iqbal and S. Veprek, "Raman scattering from hydrogenated microcrystalline and amorphous silicon," *J. Phys. C Solid State Phys.*, vol. 377, 1982.
- [30] I. DeWolf, "Micro-Raman spectroscopy to study local mechanical stress in silicon integrated circuits," *Semicond. Sci. Technol.*, vol. 11, no. 2, pp. 139–154, 1996.
- [31] M. Zacharias, J. Bläsing, P. Veit, L. Tsybeskov, K. Hirschman, and P. M. Fauchet, "Thermal crystallization of amorphous Si/SiO₂ superlattices," *Appl. Phys. Lett.*, vol. 74, no. 1999, p. 2614, 1999.
- [32] S. Schamm, C. Bonafos, H. Coffin, N. Cherkashin, M. Carrada, G. Ben Assayag, A. Claverie, M. Tencé, and C. Colliex, "Imaging Si nanoparticles embedded in SiO₂ layers by (S)TEM-EELS," *Ultramicroscopy*, vol. 108, no. 4, pp. 346–357, 2008.
- [33] P. Cuony, D. T. L. Alexander, I. Perez-Wurfl, M. Despeisse, G. Bugnon, M. Boccard, T. Söderström, A. Hessler-Wyser, C. Hébert, and C. Ballif, "Silicon filaments in silicon oxide for next-generation photovoltaics," *Adv. Mater.*, vol. 24, no. 9, pp. 1182–1186, 2012.
- [34] R. F. Egerton, "Electron energy-loss spectroscopy in the TEM," *Reports Prog. Phys.*, vol. 72, no. 1, p. 016502, 2008.