

Tunnel Oxide Passivated Carrier-Selective Contacts based on ultra-thin SiO₂ Layers grown by Photo-Oxidation or Wet-Chemical Oxidation in ozonized Water

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Abstract — A successful application of carrier selective contacts was demonstrated by using the tunnel oxide passivated contact (TOPCon) approach yielding a 24.9% efficient solar cell. A key factor of this contact is the ultra-thin SiO_x tunnel layer which reduces interface recombination significantly but must not restrict carrier flow. Within this paper a comparison between the standard wet-chemical HNO₃ oxide, a dry-grown UV/O₃ oxide, and a wet-chemically grown oxide by using ozonized DI-H₂O is drawn. The oxides' stoichiometry and structure are analyzed and will be set in relation with the effective surface passivation. It will be demonstrated that beneath certain UV/O₃ oxides also wet-chemically grown oxides offer a high thermal stability during the annealing and can improve the passivation of n-TOPCon, especially on textured surfaces.

Index Terms — carrier-selective contacts, interface structure, passivated contacts, tunnel oxide, TEM, XPS.

I. INTRODUCTION

The tunnel oxide passivated contact (TOPCon) [1] consists of a stack of an ultra-thin tunnel oxide layer and a doped Si layer which partially crystallizes upon annealing. In the case of the phosphorus-doped electron-selective contact (n-TOPCon) an excellent surface passivation was achieved ($J_{0, rear} < 10$ fA/cm²) [2]. Replacing the point contact scheme of an n-type silicon PERL solar cell with B-diffused emitter, the passivated contact enabled a high V_{OC} of 719 mV and very high fill factors of 83.4% due to its excellent carrier-selectivity and its one dimensional carrier flow pattern in the base. Altogether with an optimized front side a conversion efficiency of 24.9% was demonstrated [3–5].

Since the quality of the tunnel oxide is crucial for the surface passivation the main purpose of this publication is to draw a comparison between the standard wet-chemical HNO₃ oxide, a dry-grown UV/O₃ oxide [6], and a wet-chemical oxide grown in ozonized DI-H₂O (DIO₃). The different oxidation technologies are compared using microstructural analysis but also at device level.

Beside the potentially lower process costs for the ozone based oxide, it was already shown that UV/O₃ grown oxides compared to HNO₃ oxides allow for higher thermal annealing temperatures which can be attributed to a favorable interface stoichiometry of the grown oxide [6]. As described in

literature [7–10] ozone-grown oxides are found to exhibit improved structural (less strain, transition layer is reduced, high density and less defects due to more saturated Si-O bonds) and electrical properties due to the occurring damage-free oxidation of the silicon surface. In addition, it is assumed that atomic oxygen is the main driving force of the oxidation process because it is the most diffusion active species in the SiO_x layer and saturates silicon dangling bonds [11]. The resulting ozone grown oxide layers are supposed to have a higher density (2.20 to 2.24 g/cm³ for thermal oxide, 2.21 to 2.25 g/cm³ for O₃ based oxides and 2.11 g/cm³ for HNO₃ [10]), and to have a lower amount of defects [10] and their structure is closer to that of stoichiometric SiO₂ [6].

II. EXPERIMENTAL

A. Sample Preparation

Symmetrical lifetime samples were realized on planar (shiny-etched) and alkaline textured n-type 1 Ωcm (100)-oriented FZ silicon wafers with a thickness of 200 μm. The wafers were wet chemically cleaned according to the RCA procedure [12]. The tunnel oxide layer having an approximate thickness of 1.3 to 1.5 nm was either wet chemically grown in 68 wt.% nitric acid at 110°C for 10 minutes [13, 14] or in ozonized DI-H₂O with a constant ozone concentration of 30 ppm at 30 °C and varying exposure time ($t = 3, 5, 10$ and 15 min). Alternatively the oxide layer was generated by photo-oxidation with an UV excimer source [6, 15]. The UV excimer source emits monochromatic UV light at a wavelength of 172 nm which dissociates molecular oxygen (O₂) of the ambient atmosphere. The resulting atomic oxygen can then directly react with the silicon surface or with O₂ to form ozone (O₃) which is also a highly oxidizing species and interacts fast with the silicon surface. The oxide growth was influenced by varying the distance between wafer and source ($d = 0.2, 0.5, 1.5$ cm) as well as the exposure time ($t = 1, 3, 5$ min) [6]. Subsequently, a 15 nm thin phosphorus (P)-doped silicon layer was deposited on both sides. Upon deposition, the samples were annealed within a tube furnace process at the two

distinctive temperatures 800°C and 900°C. The amorphous structure of the doped Si layer can be entirely sustained with only negligible dopant diffusion into the c-Si at 800 °C. On the other hand, the 900 °C anneal leads to a partial crystallization of the Si layer and a shallow diffusion into c-Si. The partial crystallization of the Si film is also beneficial in terms of mitigating parasitic absorption when the TOPCon structure is placed on the front side [16]. The samples then received a 30 min anneal at 400 °C in an atomic hydrogen atmosphere (Remote Plasma Hydrogen Passivation (RPHP)) [17]. The injection-dependent carrier lifetime characteristics were measured by the quasi-steady-state photo-conductance (QSSPC) technique. These curves were then translated into implied J-V curves which yielded the iV_{oc} at one sun and the implied fill factor (iFF) [18].

III. RESULTS

A. Characterization of Tunnel Oxide Layer

Firstly, the thickness of the SiO_x layers was experimentally determined by spectral ellipsometry (SE) using a model for native oxide to allow for a rapid qualitative comparison. Both, the wet-chemical oxidation in HNO_3 or DIO_3 and the UV/ O_3 oxidation are self-limiting processes. Using UV/ O_3 oxidation, the oxide growth saturated after about 3 min exposure time and a final oxide thickness of 1.4 to 1.5 nm was determined by SE (Fig. 1). In comparison the HNO_3 oxide turned out to be of similar thickness (about 1.4 nm, Fig. 1).

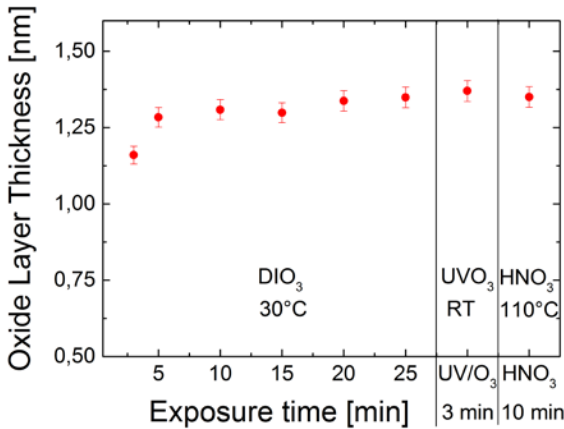


Fig. 1. Oxide layer thickness determined by SE plotted against process exposure time for DIO_3 oxides, for the UV/ O_3 (0.5 cm distance to irradiation source) and HNO_3 reference process. Process temperature is given.

To verify whether the obtained SiO_x layer thicknesses are accurate a comparative measurement was carried out by high resolution transmission electron microscopy (TEM) imaging. However, the values resulting from the SE measurement are supposed to be overestimated to some extent due to

inaccuracies regarding the applied model for the data interpretation. For the wet-chemical oxidation in ozonized DI- H_2O comparable oxide thicknesses in the range of 1.3 nm were obtained after 10 to 15 min whereby for shorter exposure times the oxide growth was not completed and a thickness of 1.1 to 1.2 nm was reached (Fig. 1).

In Fig. 2 the atomically resolved image of the Si-SiO₂ interface by TEM is depicted. On top of the SiO₂ layer a capping layer (Ti) was deposited for the purpose of protection against further oxidation induced by ambient-air oxygen. The obtained SiO₂ layer thickness averaged approximately 1.1 nm for several positions with a standard deviation of 0.2 nm for each single measurement.

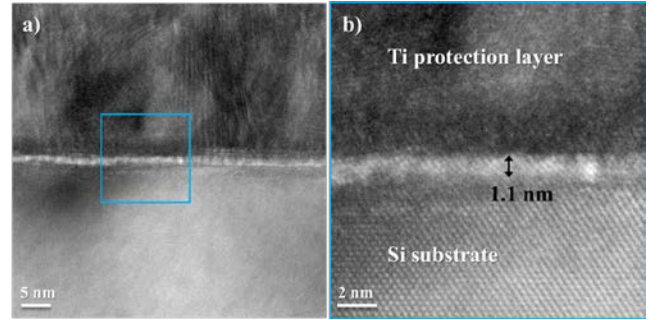


Fig. 2. a) TEM cross section (bright field image) of the Si-SiO₂ interface; the ultra-thin SiO₂ layer was prepared by UV/ O_3 oxidation (3 min exposure time, 0.5 cm distance to irradiation source). b) Enlarged illustration of the Si-SiO₂ interface.

Beside SE and TEM, also X-ray photoelectron spectroscopy (XPS) analysis (under different detection angles, AR-XPS) can be used for thickness measurement of the interfacial SiO₂ layer. Hereby, the oxide layer thickness d_{oxide} is calculated according to the formula (1) suggested by Seah and Spencer [19, 20] whereby L_{SiO_2} corresponds to the attenuation length for the Si 2p photoelectrons in the upper SiO₂ layer, θ is the angle of emission of the photoelectrons from the surface normal, R_{expt} is the measured ratio of the oxide and substrate photoelectrons and R_0 is the ratio of electrons for these two states of the bulk samples.

$$d_{oxide} = L_{\text{SiO}_2} \cos \theta \ln \left(1 + \frac{R_{\text{expt}}}{R_0} \right) \quad (1)$$

Before the components of the Si 2p peak were fitted a Shirley background correction [21] was carried out. The Si substrate peak doublet Si 2p 3/2 and Si 2p 1/2 which originate from spin orbit coupling were fitted as two single peaks. The peaks resulting from the oxide component were fitted as single peak despite these are doublets, too. The simplification which was applied for the calculation of d_{oxide} is assumed to result in a deviation of approximately 3% from the real thickness [19]. For a detection angle of 70° (more surface sensitive) a SiO₂ thickness of 0.72 nm was obtained whereas for an angle of 0°

(less surface sensitive) a thickness value of 0.61 nm was reached [22].

In comparison, the d_{oxide} values obtained from SE and TEM analysis show only negligible differences. These can be attributed to inaccuracies concerning the applied model for the data interpretation for SE measurements or to inaccuracies that can be caused by intermixing of the Si and SiO₂ layers at the interface. However, the values determined by XPS analysis are significant lower. This might be a consequence of the fact that only Si-atoms which are chemically bonded to O-atoms are considered in the analysis.

The main results of oxide analysis obtained from an investigation reported in [6] were that there are structural differences concerning the stoichiometry of HNO₃ and UV/O₃ grown oxides and that a longer exposure time and/or a reduced distance lead to more stoichiometric oxides for the UV/O₃ oxides [6].

Similar tendencies are observed within the XPS analysis of the DIO₃ oxide layers in dependence of the exposure time. The “suboxide-ratio” which is defined in this paper as the ratio between the Si-rich (Si¹⁺) and the O-rich (Si²⁺, Si³⁺) suboxide species decreases with an extended exposure time and indicates that a higher amount of oxygen-rich Si-suboxides is present in the oxide layer. The comparison of the UV/O₃ (3 min exposure time, 0.5 cm distance to irradiation source) and the newly investigated wet-chemically grown DIO₃ oxides shows a comparable thickness and stoichiometric composition (higher amount of oxygen-rich Si-suboxides (expressed in the “suboxide-ratio”) after an exposure of approximately 15 to 25 min (Table I).

In contrast the HNO₃ oxide of approximately the same thickness has a significant higher “suboxide-ratio” and therefore a lower amount of oxygen-rich Si-suboxides (Table I). In summary, the obtained results indicate that the composition of the non-stoichiometric SiO_x layer is dependent on the oxidation mechanism and the kinetics of the occurring reactions [23].

In addition, the depth dependent distribution of the sub-oxide species can be determined by XPS depth profiling resolved over the sputter time (Fig. 3 left). Although each sub-oxide peak was fitted as one peak it is not possible to deduce the exact concentration from the depth profile. Nevertheless pronounced maxima of the different sub-oxide species with stoichiometric SiO₂ as a top layer can be found in the profile.

The maxima of the sub-oxide species follows in the order of decreasing oxygen content and indicate a layered interface structure. Angle resolved XPS measurements (with detection angles of 0°, 30°, 50°, 60° and 70°) support these findings.

The higher the detection angle, the more pronounced the signals resulting from the (O-rich) sub-oxide species which are located closer to the surface (Fig. 3b) [22].

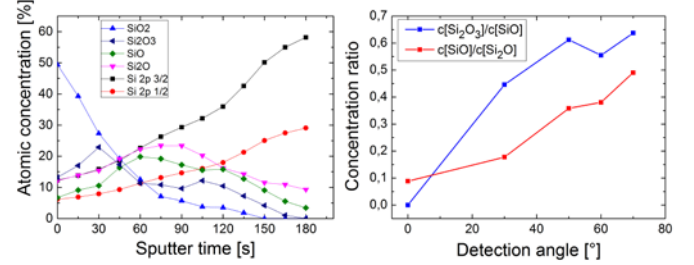


Fig. 3. The XPS depth profile shows pronounced concentration maxima for each of the oxide species. The depth corresponds to sputter time, $t = 0$ s represents the surface, $t > 180$ s represents the bulk silicon (left). ARXPS results show higher sub-oxide signal as the detection angle is increased, e.g. originating from near surface (right). Sample: UV/O₃ oxide ($t = 3$ min, $d = 0.5$ cm)

B. Surface Passivation

The surface passivation quality of these different oxides was tested on symmetrical lifetime samples. Fig. 4 depicts the implied V_{oc} values achieved with the DIO₃ oxides (for O₃ concentration of 30 ppm and exposure times of 3, 5, 10 and 15 min) and those of the UV/O₃ (0.5 cm distance to irradiation source, 1 and 3 min exposure time) and HNO₃ oxides as a reference. For an annealing at 800 °C (closed symbols) each oxide yielded a good surface passivation characterized by an $iV_{\text{oc}} > 715$ mV on planar and an $iV_{\text{oc}} > 700$ mV on textured surfaces. For both, UV/O₃ and wet-chemically grown O₃ oxide, a longer oxidation time is required to get a good passivation quality for the samples annealed at 900 °C (open symbols). Especially on textured surfaces (triangular symbols) and for 900°C annealing, the O₃ based oxides ($iV_{\text{oc}} = 705$ to 720 mV) outperform the HNO₃ oxide ($iV_{\text{oc}} = 635$ mV). Compared to UV/O₃, the DIO₃ oxidation process seems to be more sensitive since partially a significant variation of the iV_{OC} values can be observed (Fig. 4).

TABLE I. XPS results for DIO₃, UV/O₃ and HNO₃ oxides

Oxide	Si ¹⁺ [%]	Si ²⁺ [%]	Si ³⁺ [%]	Si ¹⁺ /(Si ²⁺ +Si ³⁺)	Oxide thickness [nm]
DIO ₃ (30 ppm, 5 min)	4.53	0.52	0.30	5.52	1.3
DIO ₃ (30 ppm, 10 min)	3.85	0.46	0.31	5.00	1.3
DIO ₃ (30 ppm, 15 min)	3.97	0.51	0.33	4.73	1.3
DIO ₃ (30 ppm, 25 min)	4.14	0.57	0.35	4.50	1.4
UV/O ₃ (0.5 cm, 3 min)	3.77	0.49	0.39	4.28	1.4
HNO ₃ Reference	4.17	0.17	0.27	9.48	1.4

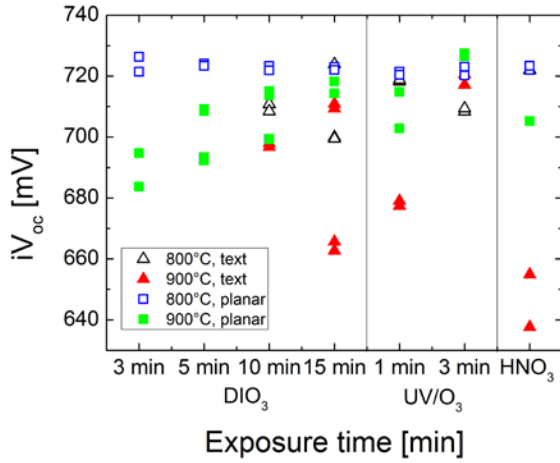


Fig. 4. iV_{OC} data of symmetrical lifetime samples of the TOPCon n-contact for the three investigated oxidation processes for different exposure times. Annealing temperature 800 and 900°C.

C. Impact of stoichiometry on iV_{OC}

For the quantification of the passivation quality in dependence of the stoichiometry the “suboxide-ratio” is set in correlation with the iV_{OC} values obtained at an annealing temperature of 900 °C for samples with a textured surface (Fig. 5). It can be assumed that oxide layers with a more SiO_2 stoichiometric structure provide a better passivation quality and result in a higher iV_{OC} .

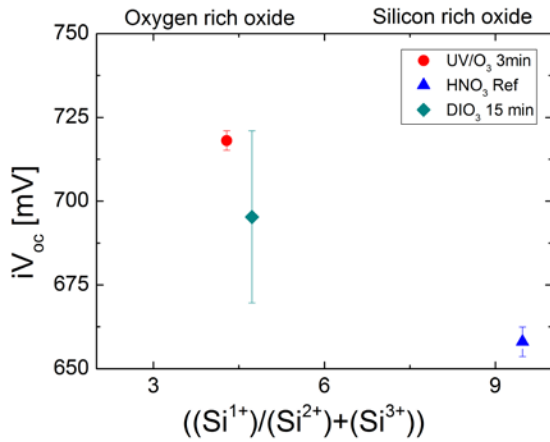
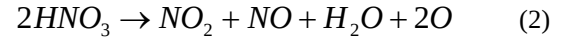


Fig. 5. iV_{OC} in dependence of the “suboxide-ratio”, comparison of HNO_3 , UV/O_3 and DIO_3 oxide layers, data from Table I.

UV/O_3 oxide layers are supposed to be less prone to disruption at higher annealing temperatures. This can be attributed to their structural composition which includes more O-saturated Si-bonds and results from the fast kinetics of the oxidation and diffusion reaction. In addition, a high amount of reactive oxygen species (atomic oxygen and ozone) is

available for the reaction due to the high energy input of the excimer radiation source. The reaction mechanism of the DIO_3 oxidation proceeds in a comparable manner as the UV/O_3 oxidation (as the same reactive oxygen species are available). However, the kinetics of the reaction is slower in aqueous solution, so that extended exposure times are required to produce oxide layers with a more stoichiometric structure comparable to that of the UV/O_3 oxide (Fig. 5).

Unless carried out at elevated temperature the reaction kinetics of HNO_3 are slower than the kinetics of the O_3 -based oxidation as HNO_3 has to decompose first to provide reactive oxygen species [13].



It can be assumed that due to the slower oxidation reaction more defects in the sub-stoichiometric interface layer are present when the oxidation of the first monolayers is accomplished. Furthermore, less diffusion through the stoichiometric amorphous SiO_2 layer that grows on top of the sub-stoichiometric interface layer is possible to saturate Si-dangling bonds.

D. Nanostructure analysis of the Si- SiO_2 interface

TEM cross sections of the textured iV_{OC} samples with HNO_3 and UV/O_3 oxide annealed at 900 °C were fabricated to verify if the decreased iV_{OC} value of the HNO_3 oxide sample can be attributed to disruptions of the SiO_x layer. As depicted in Fig. 6a the HNO_3 oxide layer is inhomogeneous and partially disrupted whereas the UV/O_3 oxide layer (Fig. 6) is homogeneous and continuous. Hence, the recent findings give further evidence for the hypothesis that the stability of the passivation is dependent on the stoichiometry of the interfacial SiO_x layer.

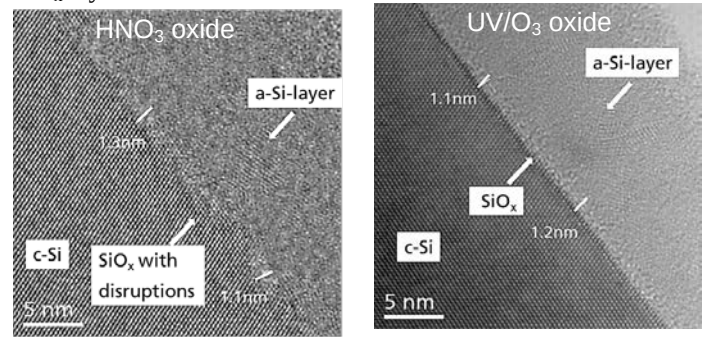


Fig. 6. TEM cross section of iV_{OC} sample with HNO_3 oxide (left). Cross section of iV_{OC} sample with UV/O_3 oxide (right). Both annealed at 900 °C.

IV. SUMMARY AND CONCLUSION

In this paper, several methods for a detailed study of ultrathin oxides were presented. These oxides are used as tunnel oxide layer for TOPCon solar cells. Tunneling oxides can be fabricated using hot concentrated nitric acid, which was used as a baseline process. Economically and ecologically preferable processes are based on ozone as an oxidation agent: DIO_3 and UV/O_3 . The oxides' stoichiometry and thicknesses were evaluated and compared to the HNO_3 reference. It was found that the oxidation in DIO_3 can result in thermally more stable oxides compared to HNO_3 oxides and also enabled an improved surface passivation quality for n-TOPCon on textured surfaces. Detailed analyses concerning oxide properties and possible correlations between these properties and the stability of the passivation layer have been demonstrated. The recent findings of the XPS and TEM analysis give further evidence to the hypothesis that the stability of the passivation depends on the stoichiometry of the interfacial SiO_x layer.

Applying the different oxide layers to solar cells featuring TOPCon as a full area passivated rear contact resulted in high V_{OC} values for all investigated tunnel oxide layers. High efficiencies could be obtained especially for the HNO_3 reference process ($T_{\text{anneal}} = 800^\circ\text{C}$) and for UV/O_3 and DIO_3 oxidation at $T_{\text{anneal}} = 900^\circ\text{C}$ [4].

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