Nitric acid pretreatment for the passivation of boron emitters for *n*-type base silicon solar cells

Valentin D. Mihailetchi,[a)] Yuji Komatsu, and L. J. Geerligs
ECN Solar Energy, P.O. Box 1, 1755 ZG Petten, The Netherlands

We have developed a simple method to passivate industrially produced boron-doped emitters for *n*-type base silicon solar cells using an ultrathin (~ 1.5 nm) silicon dioxide layer between the silicon emitter and the silicon nitride antireflection coating film. This ultrathin oxide is grown at room temperature by soaking the silicon wafers in a solution of nitric acid prior to the deposition of the silicon nitride antireflection coating film. The *n*-type solar cells processed in such a way demonstrate a conversion efficiency enhancement of more than 2% absolute over the solar cells passivated without the silicon dioxide layer. © *2008 American Institute of Physics*. [DOI: 10.1063/1.2870202]

n-type base silicon has been proven to have a higher tolerance to common transition metal impurities, such as those present in silicon produced from quartz and carbon (i.e., metallurgical routes), potentially resulting in higher minority carrier diffusion lengths compared to *p*-type substrates.[1,2] Additionally, it does not suffer from degradation of recombination lifetime due to the boron-oxygen related defect.[3] In spite of these advantages, at present, with the exception of two particular high-efficiency cell types produced by two companies,[4,5] all silicon solar cells produced by the industry are based on *p*-type base substrates. This is caused mostly by an insufficient development and industry implementation of the *n*-type cell processes, which is in turn for a large part due to a poor development of an industrial low-cost technique for passivation of p^+ emitters.

Since the conventional way to passivate n^+ emitters, for the *p*-type solar cell process, using a plasma enhanced chemical vapor deposition (PECVD) of hydrogenated silicon nitride (SiN_x) resulted in a poor or no passivation at all for p^+ emitters,[6] a method to passivate p^+ surfaces needs to be developed. Reported approaches to solve this issue are by using an intermediate silicon dioxide (SiO_2) layer between SiN_x and the p^+ diffused emitter, or even by using PECVD silicon carbide (SiC_x) as a passivation layer instead of SiN_x.[6–8] However, the SiO_2 layer is thermally grown at high temperature for a long time, which could result in degradation of Si wafers[9] (especially if they are multicrystalline) and an increase in production cost of the cells. Recent results by Chen *et al.* demonstrated that SiN_x of particular composition can result in good passivation of boron doped emitters,[10] while Hoex *et al.* showed that Al_2O_3 films provide also an excellent level of surface passivation on highly doped boron surfaces.[11] Nevertheless, a simple and effective method to passivate p^+ emitters is still demanded by the industry if *n*-type solar cells are to be produced on large scale and in a cost-effective way.

In the present study, we demonstrate that an ultrathin SiO_2 layer formed by nitric acid oxidation of Si (NAOS) (Ref. 12–14) can be used in combination with SiN_x to passivate industrially produced p^+ (i.e., boron) doped emitters for *n*-type solar cells. This method relies on the same PECVD-SiN_x technology as is widely used in industry to passivate n^+ (i.e., phosphorous) emitters, which is industrially applicable with no substantial increase in cost or process time.

In order to investigate this passivation method on p^+ emitters, we have fabricated solar cell devices made from phosphorous-doped *n*-type Czochralski (Cz) Si (100) wafers of 1.4–1.6 Ω cm resistivity and 210 μm thickness. Both surfaces of the wafers received a texture etch with random pyramids in NaOH/isopropanol solution. Subsequently, a p^+ emitter with a sheet resistance of 60 Ω/sq was diffused on the front side (light receiving side) of the wafers from a boron tribromide source in a quartz tube furnace of an industry-compatible scale. A n^+ (phosphorous) doped region with a sheet resistance of 30 Ω/sq was also diffused at the back side of the solar cells to serve as a back surface field (BSF) and to provide a good electrical contact to the *n*-type base. After the diffusion processes, all wafers received a standard cleaning followed by etching with a diluted hydrofluoric acid (HF) immediately before the application of the passivating layers. From here, the wafers were randomly divided in three groups in which one group received directly SiN_x on both sides. The other two groups were immersed in a nitric acid aqueous solution of azeotropic concentration (68%) at room temperature for 15 min. During this period, a SiO_2 layer with a thickness of approximately 1.5 nm (as determined by our ellipsometry measurements) is grown on the wafer surfaces. After rinsing with de-ionized water, one of the groups received again a diluted HF dip in order to strip off the SiO_2 deposited by the NAOS method and to allow for the investigation of a nitric acid cleaning effect on the passivation quality of the p^+ emitters. Then, the same SiN_x was deposited on both sides of these two groups followed by screen printing of the front and back contacts on the wafers of all groups, in order to complete the solar cell devices. It should be noted that firing at a high peak temperature (typically greater than 750 °C) for a short period is necessary to be able to make Ohmic contact between printed metal contacts and Si.

In addition to the solar cells, symmetric $p^+/n/p^+$ devices were also fabricated by diffusion of boron emitter on both side of polished Cz wafers. This device structure is widely used in literature in order to study the surface passivation or the emitter quality of a cell process by measuring the effective lifetime of minority charge carriers using quasi-steady-

---

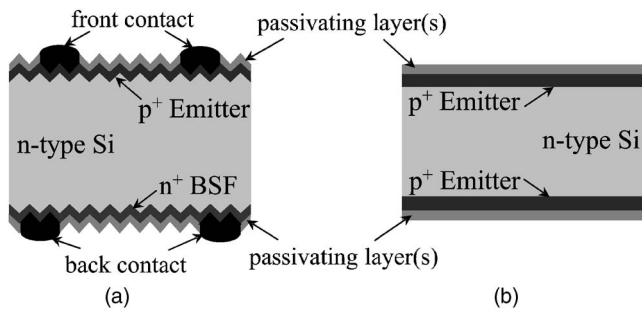[a)]Electronic mail: mihailetchi@ecn.nl.

FIG. 1. Schematic layout of the fabricated solar cells (a) and lifetime test devices (b).

FIG. 2. IQE data of *n*-type solar cells fabricated using different surface passivating layers based on PECVD SiN$_x$ method.

state photoconductance (QSSPC) setup.[6,7] A schematic layout of the fabricated devices is shown in Fig. 1.

Table I shows the mean values of the solar cell parameters processed using different passivation treatments as described above. For each passivation method tested a total of ten solar cells were fabricated with a cell area of 155.72 cm^2. These measurements were carried out under standard test conditions (STCs) using a class A solar simulator. As can be seen from the table, a substantial enhancement of 2% points in the conversion efficiency (η) is observed for the solar cells passivated using nitric acid SiO$_2$/SiN$_x$ stack layers as compared with the solar cells which do not have the ultrathin SiO$_2$ layer. Furthermore, the results shown in Table I demonstrate that there is no statistical significant difference at 95% confidence intervals between solar cells passivated using only the SiN$_x$ layer and those that received an extra nitric acid SiO$_2$ which was stripped off prior to the SiN$_x$ deposition (denoted as SiO$_2$/HF/SiN$_x$). This clearly indicates that just the cleaning effect of the wafer surfaces by nitric acid is not the cause of the observed enhancement in efficiency but the enhancement is rather caused by the ultrathin (≈ 1.5 nm) SiO$_2$ grown by the NAOS method. With the measured efficiency reaching 18.3%, the highest reported so far for this type of solar cells,[16] the results clearly demonstrate the superior performance of nitric acid SiO$_2$/SiN$_x$ passivation.

Since in this study, both front and back surfaces of the solar cells were passivated using the same method, internal quantum efficiency (IQE) measurements of the solar cells were used to disentangle front side (boron emitter) and back side (phosphorous BSF) contributions of improved passivation. Figure 2 shows the IQE data of solar cells selected from each of the groups of Table I. Since the absorption coefficient of Si for blue light (short wavelength photons) is very large, this light is absorbed directly near the front surface of the cell. Therefore, the IQE for short wavelength photons strongly reflects the recombination at the front surface of a cell, thus, it reflects the passivation of boron emitter in our solar cells. As can be seen in Fig. 2, the IQE of the solar ce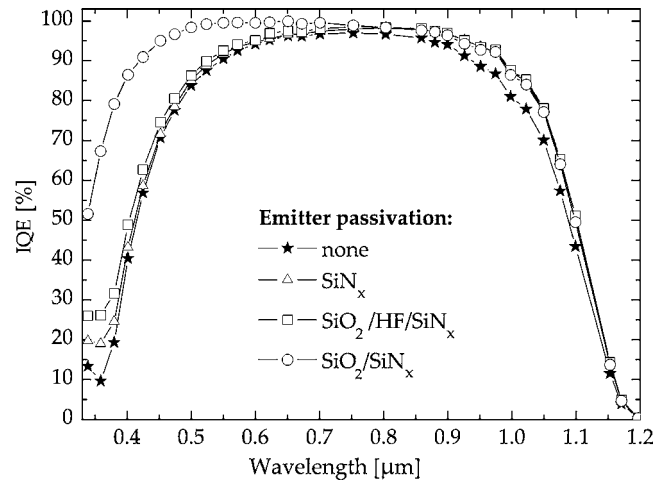ll passivated using the SiO$_2$/SiN$_x$ stack shows a strong improvement for wavelengths below 0.6 μm, as compared with the cells passivated using the other two methods of Table I or with an unpassivated front surface. Consequently, the open-circuit voltage (V_{OC}) and short-circuit current (J_{SC}) are increased, as can be seen in the table. On the other hand, the IQE for high wavelength photons, which reveal the amount of back surface recombination is nearly identical for all cells. These two observations clearly indicate that the improvement in the boron emitter passivation is the cause for the much better solar cell performance when using the ultrathin nitric acid SiO$_2$/SiN$_x$ stack layers.

To get further insight into the possible passivation mechanisms of p^+ (boron) emitters using the ultrathin nitric acid SiO$_2$, we have investigated the effective lifetime of symmetric $p^+/n/p^+$ devices [see Fig. 1(b)] passivated using SiN$_x$ or SiO$_2$/SiN$_x$ stack. For the high quality Cz wafers which were processed here, the bulk lifetime is specified by the supplier to be higher than 1 ms. Thus, the effective lifetime remains limited by the surface and emitter recombination, where the latter only plays a significant role at high injection levels (typically more than 10^{15} cm^{-3}). Figure 3 shows the effective lifetime as a function of excess carrier density measured before and after a firing step similar to the one performed for solar cell devices. The experimental data show that the effective lifetime increases an order of magnitude for the devices passivated using the SiO$_2$/SiN$_x$ stack after the firing step, while no significant enhancement is observed for devices passivated with only SiN$_x$. Without this high temperature firing step, the SiO$_2$/SiN$_x$ stack does not appear to be a good passivation scheme for p^+ emitters. This suggests that the effect of SiN$_x$ on the ultrathin SiO$_2$ layer is similar to that observed by annealed aluminum layer and is, therefore, likely that the atomic hydrogen in the SiN$_x$ layer is

TABLE I. Mean values and 95% Tukey HSD intervals (Ref. 15) (for efficiency) of the solar cells parameters measured under STC (AM1.5G, 100 mW/cm^2, 25 °C).

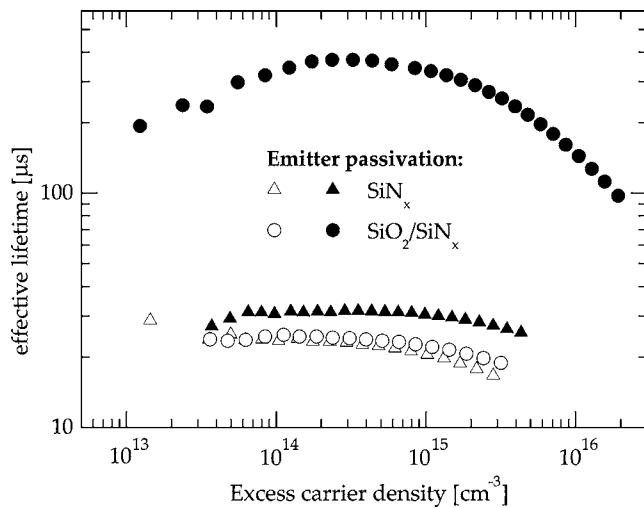| Passivating layer(s)	Counts (–)	J_{SC} (mA/cm^2)	V_{OC} (mV)	FF (%)	η (%)
SiN$_x$	10	35.1	599	75.4	15.9($\pm$0.14)
SiO$_2$/HF/SiN$_x$	10	35.2	600	75.7	16.0($\pm$0.15)
SiO$_2$/SiN$_x$	10	37.3	627	76.7	17.9($\pm$0.14)

FIG. 3. Effective lifetime of minority charge carriers as a function of injection level measured using QSSPC setup performed on lifetime test devices [see Fig. 1(b)] before (empty symbols) and after (filled symbols) firing step.

FIG. 4. Accelerated ageing test of solar cells passivated using either a SiN_x layer or a stack of nitric acid SiO_2/SiN_x layers (see legend).

diffusing to the SiO_2/Si interface during the firing step and passivate dangling bonds.[12–14] A similar scenario is reported also for the thermal SiO_2/SiN_x scheme.[17,18] However, the reasons why the nitric acid SiO_2/SiN_x stack is able to passivate better the p^+ diffused surfaces than just a SiN_x layer still needs to be understood. The passivation quality of nitric acid SiO_2/SiN_x stack shown in Fig. 3 was further quantified by the emitter saturation current density (J_{0e}), which is determined at high injection level (up to 2×10^{16} cm^{-3}). The obtained J_{0e} of ≈ 23 fA/cm^2 (per side) is in a good agreement with the best literature values for the same boron sheet resistance (≈ 60 Ω/sq).[10,11]

One of the most important criteria for commercialization of solar cells is their stability under normal operational conditions of temperature and illumination. The passivation method for p^+ emitters introduced here is proven to be very effective but it must also be stable during the operational lifetime of a solar cell. Therefore, accelerated aging tests under the influence of illumination and an elevated temperature of 60 °C was carried out, in order to study and compare the behavior of the solar cells passivated with the nitric acid SiO_2/SiN_x stack or with SiN_x. Solar cells were light soaked under open-circuit condition for a period of 1000 h by a xenon lamp at one-sun intensity. The lamp light was filtered with a UVB and infrared cutoff filter. During this period, the solar cells received a total radiation dose of 2×10^9 J/m^2 (or 555 kW h/m^2). Figure 4 shows the power conversion efficiency as a function of illumination time for the two solar cells investigated. Even after extensive light soaking of 1000 h and strong UVB radiation, the cell efficiency decreases by less than 2% relative to the initial value for both passivation schemes used. This shows that the ultrathin nitric acid SiO_2/SiN_x stack can be expected to be a reliable passivation scheme for p^+ emitters.

In summary, we have shown conclusive evidence that an ultrathin silicon dioxide layer grown by soaking the silicon wafers in a solution of nitric acid prior to the deposition of silicon nitride antireflection film is a reliable and effective method to passivate boron doped emitters for n-type solar cells. This method demonstrates an efficiency enhancement of more than 2% points, which leads to a record-high effi-
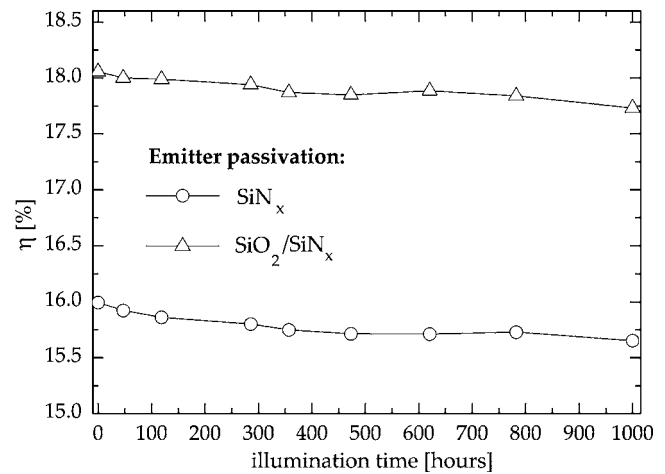
ciency of 18.3% on phosphorous-doped Czochralski silicon. These results open up the possibility to explore the higher potential possessed by n-type silicon using an easy-to-fabricate and industrially feasible process.

[1]A. Cuevas, M. J. Kerr, C. Ferrazza, and G. Coletti, Appl. Phys. Lett. **81**, 4952 (2002).
[2]D. MacDonald and L. J. Geerligs, Appl. Phys. Lett. **85**, 4061 (2004).
[3]K. Bothe, R. Sinton, and J. Schmidt, Prog. Photovoltaics **13**, 287 (2005).
[4]M. Taguchi, A. Terakawa, E. Maruyama, and M. Tanaka, Prog. Photovoltaics **13**, 481 (2005).
[5]K. R. McIntosh, Proceedings of the third World Conference on Photovoltaic Energy Conversion, 2003 (unpublished), p. 971.
[6]J. Libal, R. Petres, T. Buck, R. Kopecek, G. Hahn, R. Ferre, M. Vetter, I. Martín, K. Wambach, I. Roever, and P. Fath, Proceedings of the 20th European Photovoltaic Solar Energy Conference, 2005 (unpublished), p. 793.
[7]R. Petres, J. Libal, R. Kopecek, M. Vetter, R. Ferre, I. Martín, D. Borchert, I. Röver, K. Wambach, and P. Fath, Proceedings of the 15th International Photovoltaic Science and Engineering Conference, 2005 (unpublished), p. 128.
[8]I. Martín, M. Vetter, A. Orpella, J. Puigdollers, A. Cuevas, and R. Alcubilla, Appl. Phys. Lett. **79**, 2199 (2001).
[9]P. J. Cousins and J. E. Cotter, Sol. Energy Mater. Sol. Cells **90**, 228 (2006).
[10]F. W. Chen, T. T. A. Li, and J. E. Cotter, Appl. Phys. Lett. **88**, 263514 (2006).
[11]B. Hoex, J. Schmidt, R. Bock, P. P. Altermatt, M. C. M. van de Sanden, and W. M. M. Kessels, Appl. Phys. Lett. **91**, 112107 (2007).
[12]A. Asuha, T. Kobayashi, O. Maida, M. Inoue, M. Takahashi, Y. Todokoro, and H. Kobayashi, Appl. Phys. Lett. **81**, 3410 (2002).
[13]A. Asuha, S. Imai, M. Takahashi, and H. Kobayashi, Appl. Phys. Lett. **85**, 3783 (2004).
[14]A. Asuha, Y. Liu, O. Maida, M. Takahashi, and H. Kobayashi, J. Electrochem. Soc. **151**, 824 (2004).
[15]D. C. Montgomery, *Design and Analysis of Experiments*, 6th ed. (Wiley, New York, 2005).
[16]T. Buck, R. Kopecek, J. Libal, A. Herguth, K. Peter, I. Röver, K. Wambach, and L. J. Geerligs, Proceedings of the 21th European Photovoltaic Solar Energy Conference, 2006 (unpublished), p. 1264.
[17]J. D. Moschner, P. Doshi, D. S. Ruby, T. Lauinger, A. G. Aberle, and A. Rohatgi, Proceedings of the second World Conference on Photovoltaic Energy Conversion, 1998 (unpublished), p. 1894.
[18]M. J. Kerr, J. Schmidt, A. Cuevas, and J. H. Bultman, J. Appl. Phys. **89**, 3821 (2001).