

Manipulation of K center charge states in silicon nitride films to achieve excellent surface passivation for silicon solar cells

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High quality surface passivation ($S_{\text{eff}} < 5 \text{ cm/s}$) was achieved on polished float zone and textured p- and n-type solar grade Czochralski silicon substrates by externally injecting and storing positive or negative charges ($> \pm 8 \times 10^{12} \text{ cm}^{-2}$) into a dual layer stack of Plasma Enhanced Chemical Vapor Deposition (PECVD) Silicon Nitride (SiN_x)/PECVD Silicon Oxide (SiO_2) films using a corona charging tool. We demonstrate long term stability and uniform charge distribution in the SiN_x film by manipulating the charge on K center defects while negating the requirement of a high temperature thermal oxide step. © 2014 AIP Publishing LLC. [<http://dx.doi.org/10.1063/1.4863829>]

Hydrogenated silicon nitride (SiN_x) films used for passivation^{1–5} and anti-reflection purposes for standard p-type substrates with n^+ emitters (n^+ -p) crystalline silicon (c-Si) cells carry fixed positive charges ($Q_f \approx 5 \times 10^{11} \text{ cm}^{-2}$) originating from specific silicon-nitrogen dangling bond ($\bullet\text{SiN}_3$) defects, known as K centers.^{6–11} When applied to n-doped silicon surfaces, these fixed positive charges reduce surface recombination by keeping the minority holes away from the surface and, therefore, enhance the efficiency of a typical n^+ -p cell. However, when applied to moderately doped rear p-type surfaces, these same positive charges create a depletion layer and thus increase surface recombination. For more lightly doped p-type material, the surface will invert, reducing recombination but potentially leading to parasitic shunting depending on the metal contact structure.¹² Therefore, p-type surfaces require dielectric films carrying negative charge to shield minority electrons away from the surfaces. Thin ($\sim 10 \text{ nm}$) aluminum oxide (Al_2O_3) films with fixed negative charges that are currently being applied to the rear p-doped surfaces of the n^+ -p cells and to the front surfaces of the n-type cells with p^+ emitters provide excellent surface passivation.^{13–16} However, processes and tools needed to deposit Al_2O_3 films on a high volume industrial scale are not widely available yet, making it difficult to find a solution for films carrying negative charges to be applied on p-type surfaces.^{17,18} These issues with both SiN_x and Al_2O_3 films make it difficult to use them on all types (n or p-type) of silicon cell surfaces. Therefore, a fast and easy process to manipulate the polarity and control the amount of charge present in the SiN_x dielectric would be greatly beneficial.

This work demonstrates through minority carrier lifetime measurements that excellent and stable surface passivation can be achieved on both p- and n-type polished float zone (FZ) silicon and solar grade textured Czochralski (CZ) silicon substrates by appropriately charging the deposited SiN_x film. It utilizes an important property of the K center defects present in the SiN_x films that allows these centers to store either

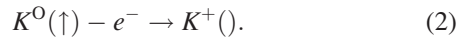
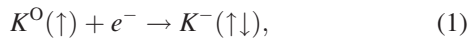
positive or negative charges, and this charge can be retained through use of a dual layer low temperature Plasma Enhanced Chemical Vapor Deposition (PECVD) $\text{SiN}_x/\text{SiO}_2$ film stack. It was found that the externally injected corona charges in the PECVD deposited SiN_x film on silicon substrates dissipated within 10 min of the charging treatment. To retain the injected charges of either polarity in the SiN_x film and to achieve surface passivation, a thin 20 nm PECVD SiO_2 layer was deposited underneath the SiN_x film to prevent charge transfer between the SiN_x film and the silicon substrate. Previous work by Weber and Jin¹⁹ used a high temperature (1000°C) thermal oxide film that is known to degrade the bulk lifetime of the sample. In this work, low temperature (200°C) PECVD SiO_2 film is used and deposited in the same PECVD tool used to deposit SiN_x films. The SiN_x films were thoroughly characterized and optimized as explained in our previous paper.²⁰ A custom built corona charging tool was used to externally inject positive or negative charges in the $\text{SiN}_x/\text{SiO}_2$ film stack deposited on the silicon substrate. The sample was placed approximately 2 cm underneath the corona discharge in atmospheric conditions. The charged ions of atmospheric gases settled on the top SiN_x layer and induced changes in the charged states of K center defects of the SiN_x film depending on the polarity of the discharge. The thin SiO_2 layer prevented any charge transfer between the SiN_x film and the silicon substrate. Through various design iterations of the charging tool, the charge injection process was tuned to inject uniform charges over a large area ($156 \text{ mm} \times 156 \text{ mm}$) of the sample. Moving the sample underneath the discharge allowed uniform charge injection throughout the sample area.

An Applied Materials PECVD cluster tool with 13.56 MHz RF generators at the Solar Power Lab at Arizona State University (ASU) was used to deposit $\text{SiN}_x/\text{SiO}_2$ film stacks. The SiN_x films were 76–80 nm thick (refractive index $n = 2.01$) deposited at 350°C and the SiO_2 films were 17–20 nm thick ($n = 1.46$) deposited at 200°C . C-V measurements were taken on p-doped, $1\text{--}5 \Omega\text{cm}$, $675 \mu\text{m}$ thick polished CZ silicon substrates using a mercury (Hg) probe tool to determine the polarity and quantify the amount of charge in the SiN_x films.²¹ All charge densities are reported

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as an effective fixed interface charge per unit area calculated from the flatband voltage, V_{FB} . Electron Spin Resonance (ESR) measurements were taken on SiN_x films deposited on silicon substrates to detect the neutral paramagnetic K^0 defects in the SiN_x film. All the ESR spectra were taken at room temperature using a Bruker ELEXSYS 580 X-band spectrometer, and the reported spin densities were calculated using Magnesium Chloride (MnCl_2) solution as a calibration standard. Photoconductance measurements using a Sinton WCT 120 tool were taken on FZ silicon test samples at 25 °C to quantify the effect of charge injection on minority carrier lifetime of the sample.

The K centers present in the SiN_x films exist in three different charged states: neutral K^0 , positive charged K^+ , and negative charged K^- defect, with one, zero, and two electrons on the dangling bond, respectively. Thus, the K center defects act as amphoteric defects that can change their charge state according to the following equations, thereby changing the net charge of the SiN_x film:



As shown in Eq. (1), the neutral K^0 defect present in the nitride film captures an electron during negative corona charging and converts to a negatively charged K^- defect with two electrons. Similarly, following positive corona charging, the neutral K^0 defect changes to a positively charged K^+ defect after donating its electron or capturing a hole as described by Eq. (2).

As shown in Fig. 1, C-V measurements taken on as-deposited SiN_x film gave a V_{FB} of -2.9 V indicating the presence of net positive charges with a density (N_f) of $+3.3 \times 10^{11} \text{ cm}^{-2}$. The silicon sample (p-type, CZ, 1–5 Ωcm) was then divided in two pieces; one received a positive charge injection and the other a negative charge injection. A 30 s treatment of the first sample in the corona charging tool for positive charge injection gave a V_{FB} of -7.5 V, equivalent to a higher positive charge density of $4.6 \times 10^{12} \text{ cm}^{-2}$ in

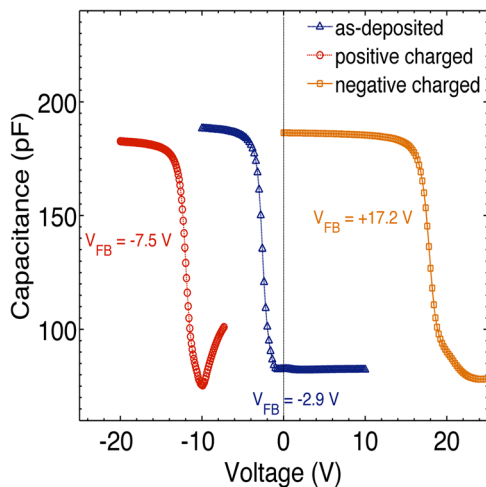


FIG. 1. Capacitance–voltage (C-V) plots of (1) as deposited ($N_f = +3.3 \times 10^{11} \text{ cm}^{-2}$), (2) positively charged ($N_f = +4.6 \times 10^{12} \text{ cm}^{-2}$), and (3) negatively charged ($N_f = -6.9 \times 10^{12} \text{ cm}^{-2}$) SiN_x films on a p-type, 1–5 Ωcm , CZ silicon wafer.

the SiN_x film compared to the as-deposited sample. Similarly, the second sample after negative charge injection treatment for 30 s gave a V_{FB} of $+17.1$ V, indicating the presence of negative charges of the order of $-6.9 \times 10^{12} \text{ cm}^{-2}$ in the film. C-V measurements taken on both the positively charged and negatively charged samples over a period of 1 year under indoor conditions showed stable flat band voltages demonstrating the long term stability of injected charges.

Minority carrier lifetime measurements were taken to determine the effect of SiN_x charge manipulation on the surface recombination velocity of various silicon samples. Substrates included n-type, 100 Ωcm 480 μm thick polished FZ silicon wafers, and both n- and p-type, 1–3 Ωcm as-cut, solar grade CZ silicon wafers. The solar CZ wafers went through standard KOH-based damage removal and texturing at 80 °C followed by RCA B and 10:1 buffered oxide etch (BOE) cleans. Test structures consisted of 80 nm thick PECVD SiN_x and 20 nm thick PECVD SiO_2 films deposited on both sides of the substrates.

Fig. 2 shows the effect of various charge manipulation treatments on minority carrier lifetime (τ_{eff}) measured on an n-FZ silicon sample. All the carrier lifetimes were measured at a minority carrier density of $1 \times 10^{15} \text{ cm}^{-3}$. Immediately after film deposition, the pre-charged sample had a minority carrier lifetime of 100 μs . After a forming gas anneal (FGA) at 400 °C for 20 min, the τ_{eff} improved to 865 μs due to hydrogen passivation of interface defects.²² Positive charges of $+7.1 \times 10^{12} \text{ cm}^{-2}$ were then externally injected in the SiN_x film using the corona charging tool and the τ_{eff} increased significantly to 4520 μs , giving a maximum effective surface recombination velocity (S_{eff})⁵ of 5 cm/s for the FZ silicon sample. Positive charges present on an n-doped silicon sample create a strong accumulation of majority electrons at the surfaces and significantly reduce the surface recombination activity. Finally, the sample was illuminated with high energy (~ 4.9 eV) ultra-violet (UV) radiation for 5 min to neutralize the injected charges ($N_f = +9.2 \times 10^{10} \text{ cm}^{-2}$) and the measured τ_{eff} dropped to just 45 μs equating to an increased S_{eff} of 533 cm/s. It should be noted that such high energy UV radiation does not exist in standard AM1.5G solar spectrum. From C-V measurements, we observe that the UV illumination annihilates all the charges, positive or negative, in the nitride film, setting the surfaces nearly at flat-band, maximizing the surface recombination and reducing the minority carrier lifetime of the sample.

Similarly, the minority carrier lifetimes of both n- and p-type CZ silicon substrates were measured at various stages: (1) after PECVD $\text{SiN}_x/\text{SiO}_2$ film deposition on both sides, (2) after FGA annealing, and (3) after charging the SiN_x film, again on both sides. As shown in Fig. 3 for the p-type substrates, while the as-deposited τ_{eff} was just 2.8 μs , it improved to 33 μs after FGA due to hydrogen passivation of the interface defects. After negative charge injection in the SiN_x film, the τ_{eff} further improved by over an order of magnitude to 252 μs , approaching the bulk lifetime of the CZ silicon sample, giving a significantly decreased S_{eff} of 16 cm/s. Similar behavior was seen on the n-CZ silicon sample but with positive charge injected in the SiN_x film. This improvement in minority carrier lifetime of the samples after

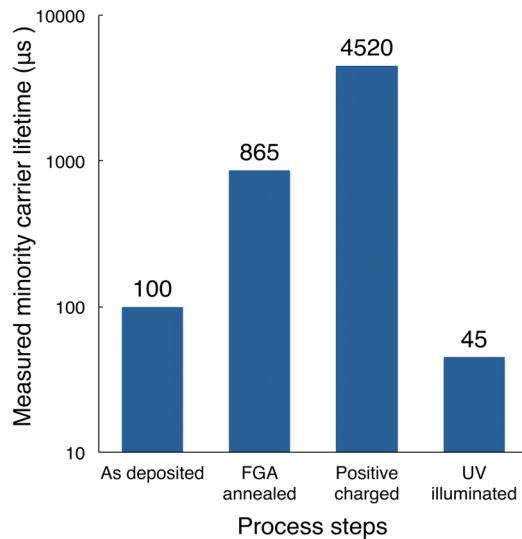


FIG. 2. Measured minority carrier lifetimes τ_{eff} on PECVD $\text{SiN}_x/\text{SiO}_2$ film stack deposited on an n-type, 100 $\Omega\cdot\text{cm}$, 480 μm thick polished FZ silicon sample for (1) as-deposited sample ($N_f = +2.9 \times 10^{11} \text{ cm}^{-2}$), (2) after FGA treatment of as-deposited sample ($N_f = +1.5 \times 10^{11} \text{ cm}^{-2}$), (3) after injecting positive charges in the SiN_x film ($N_f = +7.1 \times 10^{12} \text{ cm}^{-2}$), and (4) after UV illumination of the sample ($N_f = +9.2 \times 10^{10} \text{ cm}^{-2}$).

external charge injection in SiN_x films shows how the charge induced field effect passivation plays a crucial role in improving the effective lifetime by inducing accumulation of majority carriers at the surfaces and thus minimizing the surface recombination.

To determine the location and distribution of externally injected charges in the SiN_x film, C-V and ESR measurements were taken on standard SiN_x film test samples after an etch-back process. The etch-back C-V technique allows determining the distribution of charge in the film with respect to the film thickness. For the C-V experiment, $\sim 150 \text{ nm}$ SiN_x / 20 nm SiO_2 film was deposited on a 6 in. round p-type CZ silicon sample. The SiN_x film was first negatively charged, cleaved into 4 smaller samples and then each of these four charged samples were etched in 10:1 BOE solution for different durations of time to achieve target SiN_x film thicknesses.

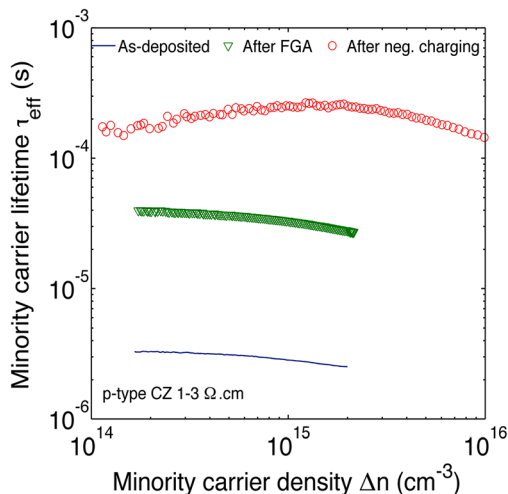


FIG. 3. Effective lifetime (τ_{eff}) vs. carrier density (Δn) for p-type CZ silicon solar substrate measured (1) after PECVD $\text{SiN}_x/\text{SiO}_2$ deposition, (2) after FGA anneal, and (3) after negative charging of SiN_x film.

TABLE I. Flat-band voltage (V_{FB}) and fixed charge density (N_f) measured after etching negatively charged SiN_x samples.

Sample	SiN_x film thickness (nm)	Flat-band voltage V_{FB} (V)	Fixed charge density N_f (cm^{-2})
A	153 (no etching)	17.7	-2.2×10^{12}
B	124	10.8	-1.7×10^{12}
C	105	7.6	-1.4×10^{12}
D	81	4.6	-9.8×10^{11}

As listed in Table I and shown in Fig. 4, as the nitride film was gradually etched, the flat-band voltage (V_{FB}) and the fixed charge density (N_f) of the samples measured by the C-V tool decreased. While sample A with 153 nm SiN_x film (non-etched) gave a $N_f = -2.2 \times 10^{12} \text{ cm}^{-2}$, sample D with 81 nm of SiN_x left after etching still gave a $N_f = -9.8 \times 10^{11} \text{ cm}^{-2}$. The negative charge injected in the $\sim 150 \text{ nm}$ SiN_x film prior to etching was present in all the other three samples even after etching and rinsing the nitride film, with a quadratic dependence of V_{FB} on thickness indicating that the charge injected in the SiN_x film by the corona charging tool was distributed uniformly in the bulk of the SiN_x film.²³ The K center defects that are present in the SiN_x film trapped the externally injected electrons and converted to negatively charged K^- defects giving a net negative charge density in the SiN_x film. Also, etching the charged SiN_x film sample in BOE solution and rinsing it with De-ionized (DI) water or Isopropyl Alcohol (IPA) did not erase the charge present in the sample, further confirming the stability of injected charges.

To further confirm the presence of K centers in the bulk of the SiN_x film and to compare the density of K centers with the quantified charge, ESR measurements were taken on two silicon substrate samples: one with an 80 nm SiN_x film and the second with a 1 μm thick SiN_x film. As shown in Fig. 5, the sample with the 1 μm thick SiN_x film gave a significantly larger ESR signal compared to the sample with the 80 nm thick SiN_x film. The area under the ESR signal is proportional to the density of neutral paramagnetic K^0

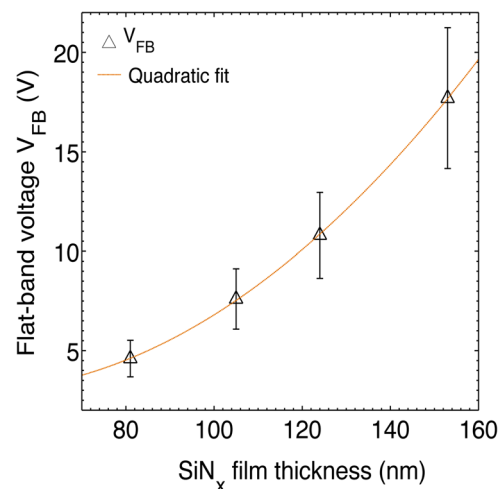


FIG. 4. Flat-band voltage (V_{FB}) as a function of SiN_x film thickness measured after etching charged SiN_x film samples.

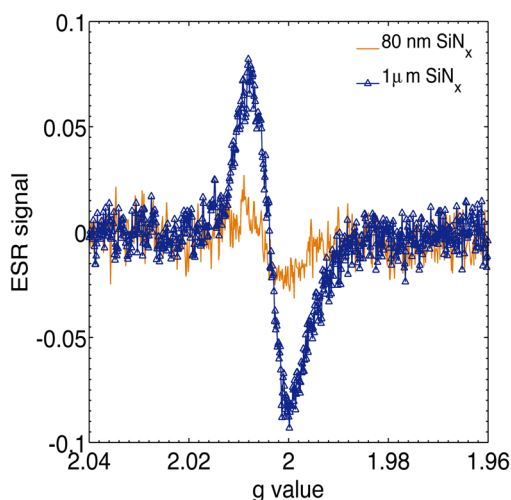


FIG. 5. ESR data: 80 nm vs. 1 μm thick SiN_x samples showing the distribution of K centers throughout the bulk of the SiN_x film.

centers (spins/ cm^2) present in the SiN_x film. While the 80 nm thick SiN_x film sample carried 1.2×10^{12} spins/ cm^2 , the 1 μm thick SiN_x film sample had 1.24×10^{13} spins/ cm^2 . The K center density is consistent with the measured magnitudes of the stored injected charge. ESR results thus show that the magnitude of neutral K center defects, participating in the charge injection process, increases as the thickness of the SiN_x film increases, indicating that these K center defects are distributed throughout the bulk of the SiN_x films and are not just near the Si- SiN_x interface as proposed earlier.¹¹

In summary, we used a corona charging technique to inject and store either polarity of charges in the SiN_x film. Externally injected charges greater than the as-deposited charge of the SiN_x film significantly improved the minority carrier lifetime of the samples by field effect passivation. We also showed using C-V and ESR measurements that the K center defects, responsible for charge trapping in the SiN_x film, scale with the SiN_x film thickness and are of a density consistent with the electrically measured stored charge. This ability to manipulate and control the charges in the SiN_x film and achieve stability when integrated as a dual layer low temperature PECVD $\text{SiN}_x/\text{SiO}_2$ film stack is extremely beneficial for solar cell applications, wherein the same SiN_x film

carrying either polarity of charge can be applied to either type of doped surfaces of silicon solar cells.

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- ¹T. Lauinger, J. Schmidt, A. G. Aberle, and R. Hezel, *Appl. Phys. Lett.* **68**, 1232 (1996).
- ²P. Doshi, G. E. Jellison, and A. Rohatgi, *Appl. Opt.* **36**, 7826 (1997).
- ³J. D. Moschner, J. Henze, J. Schmidt, and R. Hezel, *Prog. Photovolt: Res. Appl.* **12**, 21 (2004).
- ⁴W. Soppe, H. Rieffe, and A. Weeber, *Prog. Photovolt: Res. Appl.* **13**, 551 (2005).
- ⁵A. G. Aberle, *Crystalline Silicon Solar Cells—Advanced Surface Passivation and Analysis* (Center for Photovoltaic Engineering, University of New South Wales, Sydney NSW 2052, Australia, 1999).
- ⁶D. T. Krick, P. M. Lenahan, and J. Kanicki, *Phys. Rev. B* **38**, 8226 (1988).
- ⁷J. Kanicki, W. L. Warren, C. H. Seager, M. S. Crowder, and P. M. Lenahan, *J. Non-Cryst. Solids* **137**, 291 (1991).
- ⁸W. L. Warren, F. C. Rong, E. H. Poindexter, G. J. Gerardi, and J. Kanicki, *J. Appl. Phys.* **70**, 346 (1991).
- ⁹R. Hezel and R. Schörner, *J. Appl. Phys.* **52**, 3076 (1981).
- ¹⁰H. Mäckel and R. Lüdemann, *J. Appl. Phys.* **92**, 2602 (2002).
- ¹¹A. Aberle, *Sol. Energy Mater. Sol. Cells* **65**, 239 (2001).
- ¹²S. Dauwe, L. Mittelstädt, A. Metz, and R. Hezel, *Prog. Photovolt: Res. Appl.* **10**, 271 (2002).
- ¹³G. Agostinelli, A. Delabie, P. Vitanov, Z. Alexieva, H. F. W. Dekkers, S. De Wolf, and G. Beaucarne, *Sol. Energy Mater. Sol. Cells* **90**, 3438 (2006).
- ¹⁴B. Hoex, J. Schmidt, P. Pohl, M. C. M. Van de Sanden, and W. M. M. Kessels, *J. Appl. Phys.* **104**, 044903 (2008).
- ¹⁵N. M. Terlinden, G. Dingemans, M. C. Van de Sanden, and W. M. M. Kessels, *Appl. Phys. Lett.* **96**, 112101 (2010).
- ¹⁶G. Dingemans and E. Kessels, *J. Vac. Sci. Technol., A* **30**, 040802 (2012).
- ¹⁷J. Benick, A. Richter, M. Hermle, and S. W. Glunz, *Phys. Status Solidi RRL* **3**, 233 (2009).
- ¹⁸B. Veith, F. Werner, D. Zielke, R. Brendel, and J. Schmidt, *Energy Procedia* **8**, 307 (2011).
- ¹⁹K. J. Weber and H. Jin, *Appl. Phys. Lett.* **94**, 063509 (2009).
- ²⁰V. Sharma, A. Bailey, B. Dauksher, C. Tracy, S. Bowden, and B. O'Brien, *J. Vac. Sci. Technol., A* **30**, 021201 (2012).
- ²¹ASTM standard F1153-88, *Standard Test Method for Characterization of Metal-Oxide-Semiconductor (MOS) Structures by Capacitance-Voltage Measurements*, (American Society for Testing and Materials, 1988).
- ²²B. L. Sopori, X. Deng, J. P. Benner, A. Rohatgi, P. Sana, S. K. Estreicher, Y. K. Park, and M. A. Roberson, *Sol. Energy Mater. Sol. Cells* **41**, 159 (1996).
- ²³D. K. Schroder, *Semiconductor Material and Device Characterization*, 3rd ed. (Wiley-Interscience Publication, Hoboken, New Jersey, USA, 2006).