

# Excellent Passivation of Silicon Surfaces by Thin Films of Electron-Beam-Processed Titanium Dioxide

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**Abstract**—Dielectric of a titanium dioxide thin film is currently re-emerging as a passivating material for high-efficiency crystalline silicon (c-Si) solar cells, owing to its good passivation quality and appropriate band offset when in contact with c-Si. Here, we demonstrate effective passivation on c-Si substrates by electron-beam-processed titanium oxide layers, which are obtained by low-temperature thermal oxidation of predeposited pure titanium thin films. A derived titanium oxide layer by 3.5-nm titanium at 250 °C yields a surface recombination velocity down to 16 cm/s. Structural characterizations reveal that the resultant oxide layers are amorphous titanium dioxide. The passivation property is attributed to Si–O–Ti bonding at the Si–titanium dioxide interface as well as to the presence of an interfacial silicon dioxide layer. The easy processing and high-level passivation capability make these titanium dioxide thin films highly desirable to serve as a good passivating choice toward high-efficiency c-Si solar cells.

**Index Terms**—Silicon solar cells, surface passivation, titanium oxide thin film.

## I. INTRODUCTION

PASSIVATED contacts have received broad application in the photovoltaic (PV) devices, resulting from the great contribution to the performance gain by remarkable reduction of the surface recombination loss. Reduced density of interface states ( $D_{it}$ ) and/or depleted minority carriers (related to the fixed charges at interface) from the surface have been achieved by employing an array of dielectrics including silicon dioxide ( $\text{SiO}_2$ ) [1], silicon nitride ( $\text{SiN}_x$ ) [2], [3], amorphous silicon (a-Si)

[4], and aluminum oxide ( $\text{Al}_2\text{O}_3$ ) [5]. Such passivation layers have achieved great successes in the solar cells with configurations like tunnel-oxide-passivated carrier-selective contacts and amorphous/crystalline silicon heterojunction [6]–[9].

Another dielectric that is currently re-emerging as a suitable passivating material is titanium dioxide ( $\text{TiO}_2$ ) [10], [11]. Owing to its small conduction-band offset ( $\Delta E_c \sim 0.05$  eV) and large valence-band offset ( $\Delta E_v \sim 2.0$  eV) when in contact with c-Si, the c-Si/ $\text{TiO}_2$  heterojunction can effectively serve as passivating electron-selective contact [12], [13]. Many technologies have been explored for depositing  $\text{TiO}_2$ , including evaporation [14], sputtering [15], sol-gel method [16], chemical vapor deposition (CVD) [10], and atomic layer deposition (ALD) [17]–[19]. Coating with 60–70-nm CVD-deposited  $\text{TiO}_2$  layers, Thomson and McIntosh reported an effective minority carrier lifetime ( $\tau_{\text{eff}}$ ) of 500  $\mu\text{s}$  for 5- $\Omega$ -cm n-type c-Si float-zone (FZ) wafers [10]. Relying on ALD-deposited  $\text{TiO}_2$  (ALD- $\text{TiO}_2$ ) layers combining  $\text{N}_2$  anneal, Liao *et al.* received a high level of surface passivation for n-type c-Si, with surface recombination velocity ( $S_{\text{eff}}$ ) down to 11 cm/s [11]. The  $S_{\text{eff}}$  has been reduced to 2.8 cm/s when the ALD- $\text{TiO}_2$  was further annealed in  $\text{N}_2$  and soaked under light to fully activate its passivation quality [11]. With titanium tetra-isopropoxide as a precursor in the ALD process, Yang and Weber deposited 10-nm  $\text{TiO}_2$  on n-type c-Si, resulting in an implied open-circuit voltage ( $iV_{\text{oc}}$ ) of 687 mV [13]. Although ALD- $\text{TiO}_2$  looks good for surface passivation on the base of c-Si, the ALD process needs expensive and high-purity organic titanium sources, and it is also limited by the low utilization of precursors. Attempts by means of other deposition methods (e.g., RF sputtering, CVD, and Sol-gel), however, have given only modest passivating results.

In this paper, we demonstrate a new way to fabricate thin  $\text{TiO}_2$  passivation layers on c-Si wafers by annealing electron beam (E-beam) deposited pure titanium (Ti) films in  $\text{O}_2$  environment, yielding a  $\tau_{\text{eff}}$  as high as 1500  $\mu\text{s}$  ( $S_{\text{eff}} = 16$  cm/s). The influence of the anneal temperatures and the film thicknesses on the passivation quality is investigated. Series of structural characterizations are implemented to investigate the physical and chemical properties of the  $\text{TiO}_2$  films as well as the Si/ $\text{TiO}_2$  interface, aiming to reveal the origin of passivation.

## II. SAMPLE PREPARATION AND MEASUREMENT PROCEDURE

The fabrication procedures are illustrated in Fig. 1. Double-side-polished n-type FZ c-Si wafers with a thickness of  $500 \pm 10$   $\mu\text{m}$ , (100) surface orientation, and bulk resistivity of

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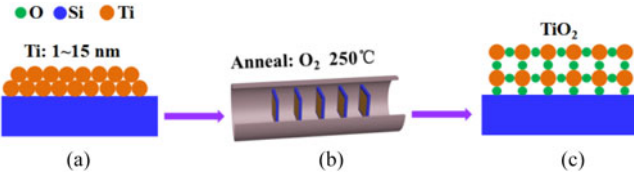


Fig. 1. Schematic of fabrication procedures for TiO<sub>2</sub> thin films. (a) E-beam deposited pure Ti thin films with thicknesses of 1–15 nm on c-Si. (b) Low-temperature thermal anneal of the Ti thin films in O<sub>2</sub> ambient. (c) TiO<sub>2</sub> layers that are converted from the Ti thin films.

5–10 Ω·cm were used to characterize the passivation quality. Before Ti film deposition, the substrates were cleaned with the standard RCA procedure [20] and dipped in a diluted hydrofluoric acid (HF 10%) to remove the native silicon oxide layer. Ti films with different thicknesses were first deposited on both sides of c-Si wafers by E-beam evaporation (Xinnan-Tech ZS-500) with a deposition rate of around 0.02 nm/s and pressure under  $6 \times 10^{-4}$  Pa. When depositing on one side, the other side of the wafer was protected by a clean glass slice to avoid contamination. Compact thin titanium oxide films were simply achieved by a 10-min thermal annealing in O<sub>2</sub> environment with temperature ranging from 200 to 400 °C.

The crystalline natures of the titanium oxide films were measured by grazing incidence X-ray diffraction (GIXRD, D8 Advance). Chemical analysis relates to the titanium oxide films and interfacial speciation was addressed by X-ray photoelectron spectroscopy (XPS, AXIS ULTRA) and Fourier transform infrared spectroscopy (FTIR, Nicolet 6700). The XPS measurements were performed in a dedicated ultrahigh vacuum chamber with a base pressure of  $< 2 \times 10^{-10}$  torr. Al K $\alpha$  radiation at 1486.6 eV was used in XPS, with an experimental resolution of 0.05 eV. The  $\tau_{\text{eff}}$  of wafers were characterized by quasi-steady-state photoconductance measurements, using a WCT-120 from Sinton instruments. Neglecting Shockley–Read–Hall recombination in the bulk of the wafer, the upper limit of the  $S_{\text{eff}}$  was calculated according to

$$\frac{1}{\tau_{\text{eff}}} = \frac{1}{\tau_{\text{bulk}}} + \frac{2S_{\text{eff}}}{d}$$

where  $d$  is the thickness of the Si substrate, and  $\tau_{\text{bulk}}$  is the intrinsic bulk lifetime in Si parameterized by Richter *et al.* [21]. Charge densities were determined with capacitance (conductance)–voltage ( $C$ – $V$ ) measurements. One-side-polished p-type Si wafer with a resistivity of 1–5 Ω·cm was used for the  $C$ – $V$  measurement, and a Ti film was deposited on the polished side followed by the oxidation process. Al circular electrode with a diameter of 1 mm was deposited upon the titanium oxide, and a GaSn electrode was used for back contact. During the  $C$ – $V$  measurements, high-frequency (1 MHz) measure was applied.

### III. MEASUREMENT RESULTS AND DISCUSSION

For our E-beam-processed titanium oxide films, the temperature of thermal annealing and the initial thickness of Ti thin films play two key roles on the final passivating quality. For distinguishing, the titanium oxide films were named by the thickness of Ti films, for example, Ti<sub>10</sub> nm. Fig. 2 shows

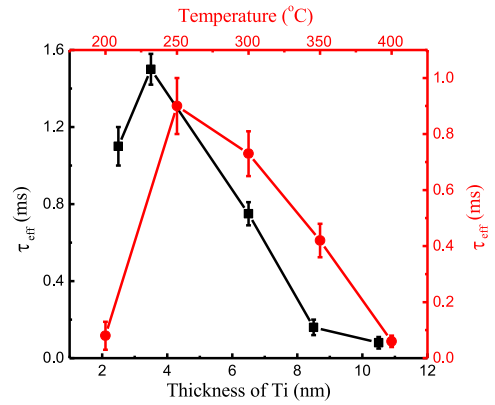


Fig. 2. Relations of  $\tau_{\text{eff}}$  with different annealing temperatures and Ti thicknesses. The temperature-dependent  $\tau_{\text{eff}}$  curve (red) was extracted on a Ti thickness of 6.5 nm, and the thickness-dependent  $\tau_{\text{eff}}$  curve (black) was performed at an annealing temperature of 250 °C.

the Ti-film-thickness- and annealing-temperature-dependent  $\tau_{\text{eff}}$  curves. The temperature curve in red was extracted on Ti thickness of 6.5 nm (Ti<sub>6.5</sub> nm), and the thickness in black was performed at an annealing temperature of 250 °C. As shown in Fig. 2, a clear trend of first improving and then reducing passivating quality with increasing thermal annealing temperature was observed, showing the best annealing temperature around 250 °C. In order to study the influence of the thickness of titanium oxide layers on the surface passivation quality, five symmetrical lifetime samples with Ti<sub>2.5</sub> nm, Ti<sub>3.5</sub> nm, Ti<sub>6.5</sub> nm, Ti<sub>8.5</sub> nm, and Ti<sub>10.5</sub> nm were prepared at the optimum annealing temperature of 250 °C (the black line in Fig. 2). It shown that the  $\tau_{\text{eff}}$  (i.e., the level of surface passivation) dramatically increases with the Ti thickness and reaches its maximum  $\tau_{\text{eff}}$  of 1500  $\mu\text{s}$  at Ti<sub>3.5</sub> nm and then decreases sharply above Ti<sub>6.5</sub> nm (780  $\mu\text{s}$ ) until to below 100  $\mu\text{s}$  for the Ti<sub>10.5</sub>-nm sample. The highest level of surface passivation was given by the Ti<sub>3.5</sub>-nm titanium oxide layers corresponding to an  $S_{\text{eff}}$  as low as 16 cm/s.

The enhancement in surface passivating quality at 250 °C indicates that the thermal energy at 200 °C is not high enough to thoroughly convert the pure Ti to titanium oxide. To elucidate why the passivation quality lost at 400 °C, GIXRD was carried out to investigate the crystalline natures of the titanium oxide films. As shown in Fig. 3(a), there is no crystalline phase signal present in the 250 °C annealed sample, while clear crystalline phase signals present for the 400 °C annealed sample. It should deserve mentioning that TiO<sub>2</sub> films are amorphous under 350 °C, and a metastable crystalline phase of anatase will form beyond this annealing temperature [22]. According to the previous reports, the TiO<sub>2</sub> films with crystalline phase, whether it is anatase or rutile, can only provide a poor surface passivation on c-Si because of the related high tensile stress [17], [23]. We can now draw a conclusion that annealing Ti film at 250 °C is optimal for passivation because this temperature not only ensures a complete conversion from Ti to titanium oxide, but also maintains the resultant film at amorphous nature.

It is reported that ALD-TiO<sub>2</sub> gives a degradation of the surface passivating quality for thickness above 5.5 nm, and it attributed this to a stress-induced phase transitions inside the TiO<sub>2</sub> films

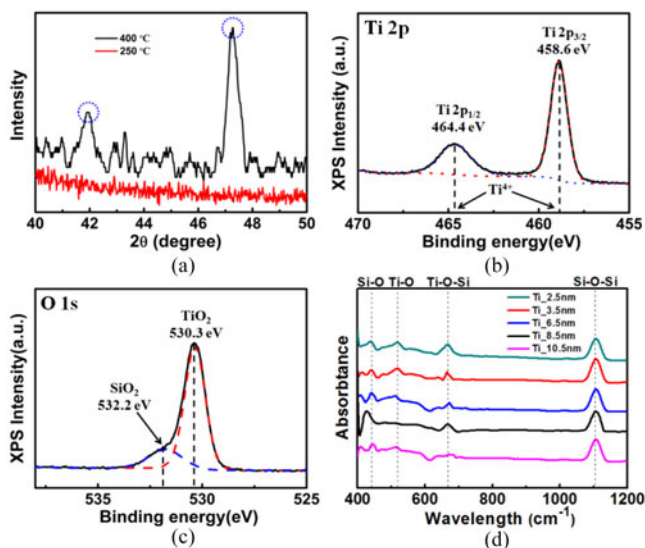


Fig. 3. (a) GIXRD spectra of the 250 and 400 °C processed titanium oxide films. (b) Ti 2p and (c) O 1s XPS spectra of the titanium oxide thin layer (from Ti\_3.5 nm) on Si substrates. (d) FTIR spectra of titanium oxide layers derived from Ti films with different thickness.

[13], [18], [23]. An amorphous TiO<sub>2</sub> layer formed in the beginning of the ALD deposition leads to a high tensile stress at the interface, which decreases gradually with increasing TiO<sub>2</sub> thickness and eventually becomes compressive stress, inducing phase transitions and leading to grain growth [17], [23]. However, we cannot simply attribute the degradation in our case to only a stress effect, because of the totally different fabrication procedures. We speculate that thickness-dependent thermal oxidation may play an important role in this degradation although lacking of more detailed supports at this time. Anyway, the results indicate that our E-beam-processed titanium oxide exhibits a better passivating performance than that of CVD-TiO<sub>2</sub> and even comparable with that of ALD-TiO<sub>2</sub>.

In order to understand the chemical oxidation state of the titanium oxide at the molecular level, XPS characterizations of the titanium oxide sample of Ti\_3.5 nm were examined and showed in Fig. 3(b) and (c), with Ti 2p and O 1s spectrum, respectively. As shown in Fig. 3(b), the Ti 2p spectrum shows two peaks at binding energies of 458.6 and 464.4 eV, respectively. The peak position of Ti 2p<sub>3/2</sub> at 458.6 eV is compared well with the peak position for Ti 2p<sub>3/2</sub> for Ti<sup>4+</sup> in TiO<sub>2</sub> (458.6–459.2 eV) and is significantly different from the Ti 2p<sub>3/2</sub> peak of Ti<sup>2+</sup> (454.9–455.2 eV) and Ti<sup>0</sup> (453.7–454.2 eV) [24], [25]. With no discernible signal for any lower valent Ti species, XPS measurements confirm the presence of TiO<sub>2</sub> on the surface. The O 1s spectrum in Fig. 3(c) also has two peaks, which are associated with TiO<sub>2</sub> (530.3 eV) and SiO<sub>2</sub> (532.2 eV) [24]. With no distinct signals relate to the oxygen-deficient TiO<sub>2</sub> or SiO<sub>2</sub> have been found in the O 1s spectrum again confirms that the derivative from thermal-annealed Ti is mainly TiO<sub>2</sub>. The identified SiO<sub>2</sub> is believed to be exist at the Si/TiO<sub>2</sub> interface, which is formed during the oxidation process.

The FTIR spectra for the TiO<sub>2</sub> samples formed by different Ti films are further collected and compared in Fig. 3(d), in order to

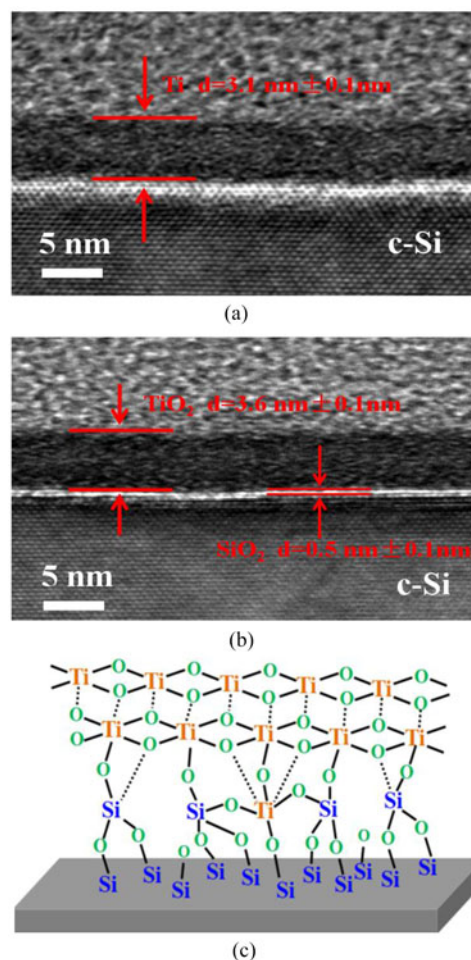


Fig. 4. HR-TEM micrographs of c-Si/Ti (a) before and (b) after thermal oxidation. (c) Proposed bonding structures near the Si/TiO<sub>2</sub> interface. From bottom to top, Si substrate, SiO<sub>2</sub> interfacial layer, Ti-O-Si bonds, and TiO<sub>2</sub> overlayer are shown.

reveal the roles of chemical bonds on the passivation as well as their evolutions with film thickness. According to [26] and [27], the absorbance peaks at about 439, 517, 670, and 1107 cm<sup>-1</sup> are assigned to vibrational modes of Si-O, Ti-O, Ti-O-Si, and Si-O-Si, respectively. The peak at ~1107 cm<sup>-1</sup> is related to the stretching vibrational mode of SiO<sub>2</sub>, indicating formation of a SiO<sub>2</sub> layer between the TiO<sub>2</sub> film and the substrate in all films. The other important feature to be noted here is the presence of the Ti-O-Si absorption peak located at ~670 cm<sup>-1</sup>, and its relative intensity decreases with the film thickness. We propose that the Ti-O-Si is formed between the surfaces Si- or/and Si-O (related to the interfacial SiO<sub>2</sub> layer) and the Ti-O groups of the TiO<sub>2</sub> overlayer. It is reported that when the Ti-O-Si bonding is present at the interface, the passivating quality can be improved significantly [28].

Cross-sectional high-resolution transmission electron microscopy (HR-TEM) images of c-Si/Ti samples before and after thermal oxidation were shown in Fig. 4(a) and (b), respectively. We can clearly see that the thickness of TiO<sub>2</sub> is about 3.6 nm, a slight increase from the 3.1 nm for the initial Ti film. Before the oxidation process, a clear boundary can be found

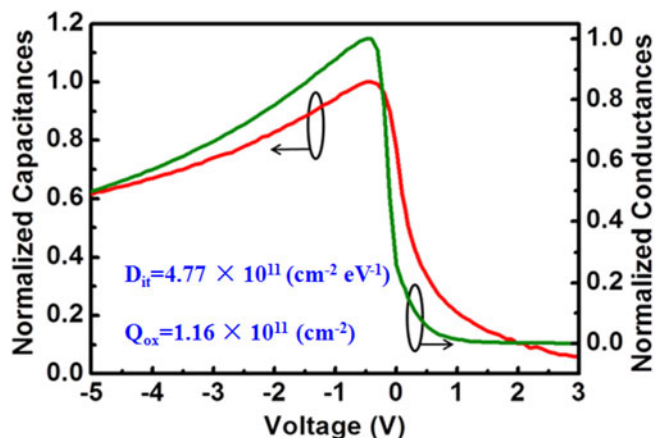


Fig. 5.  $C$ - $V$  characteristics of the deposited  $\text{TiO}_2$  layers.

between the Si and Ti films, and no amorphous  $\text{SiO}_2$  layer is present at this interface. However, after the thermal oxidization, a thin amorphous  $\text{SiO}_2$  layer with thickness about 0.5 nm can be distinguished at the Si and  $\text{TiO}_2$  interface. Based on above discussion, we can tentatively give a scheme of the bonding structures, as shown in Fig. 4(c), which shows how the effective lifetime depends on the chemical nature of the Si/ $\text{TiO}_2$  interface. The main conclusion is that both the presence of  $\text{SiO}_2$  interfacial layer and a high density of Ti–O–Si bonds are responsible for the excellent passivating capability for our E-beam-processed amorphous  $\text{TiO}_2$  thin films. Further studies will be emphasized on how to elevate the ratio of Ti–O–Si and Si–O–Si over Si–bonds, through well tuning the fabrication process.

$C$ - $V$  measurements were performed to probe the electronic properties of the  $\text{TiO}_2$  films, and the normalized capacitance (conductance)–voltage curves were shown in Fig. 5. The effective insulator fixed charge density ( $Q_{\text{ox}}$ ) and the interfacial defect density ( $D_{\text{it}}$ ) value were calculated from the curves with the Terman method [29]. For the  $\text{TiO}_2$  film with the best passivation property, a  $Q_{\text{ox}}$  of  $1.16 \times 10^{11} \text{ cm}^{-2}$  and  $D_{\text{it}}$  of  $4.77 \times 10^{11} \text{ cm}^{-2} \text{ eV}^{-1}$  were achieved. Although the Terman method shows an error when testing this  $\text{TiO}_2$  film, the ultralow  $D_{\text{it}}$  is comparable with the CVD- $\text{TiO}_2$  ( $1 - 5 \times 10^{11} \text{ cm}^{-2} \text{ eV}^{-1}$ ) that was deposited on  $\text{SiO}_2$ -passivated silicon [30], indicating a high level of chemical passivation. The state-of-the-art passivation layers of  $\text{SiN}_x/\text{SiO}_2$  stack, which were deposited by plasma-enhanced CVD, have been reported possessing a  $Q_{\text{ox}}$  of  $3 \times 10^{12} \text{ cm}^{-2}$  [6]. In comparison, our E-beam-processed  $\text{TiO}_2$  thin film shows even neutral property, which makes it a promising candidate to effectively passivate both n-type and p-type c-Si wafers.

#### IV. CONCLUSION

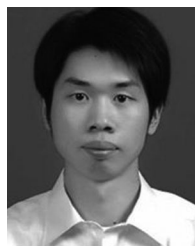
In summary, we have developed a new strategy of a low-temperature thermal oxidation method to fabricate high-quality passivation layers of  $\text{TiO}_2$  on c-Si wafers. The thin  $\text{TiO}_2$  layers derived from 3.5-nm Ti films provide a surprisingly high level of surface passivation with  $S_{\text{eff}} = 16 \text{ cm}^2/\text{s}$  on  $8\text{-}\Omega\text{-cm}$  n-type c-Si wafers, without any postdeposition anneals. Chemical

investigations showed that the low density of interfacial defects is related to the presence of  $\text{SiO}_2$  interfacial layer and Ti–O–Si bonds. The  $C$ - $V$  tests demonstrated a near neutral property for the  $\text{TiO}_2$  layers, and the chemical passivation could dominate the total surface passivation character. From an application perspective, the high surface passivation quality connected with an easy processing offers our method a great potential for an industrially feasible process.

#### REFERENCES

- [1] M. J. Kerr and A. Cuevas, "Very low bulk and surface recombination in oxidized silicon wafers," *Semicond. Sci. Technol.*, vol. 17, no. 1, 2002, Art. no. 35.
- [2] J. Schmidt and M. Kerr, "Highest-quality surface passivation of low-resistivity p-type silicon using stoichiometric PECVD silicon nitride," *Sol. Energy Mater. Sol. Cells*, vol. 65, no. 1, pp. 585–591, 2001.
- [3] Y. Wan, K. R. McIntosh, A. F. Thomson, and A. Cuevas, "Low surface recombination velocity by low-absorption silicon nitride on c-Si," *IEEE J. Photovolt.*, vol. 3, no. 1, pp. 554–559, Jan. 2013.
- [4] S. De Wolf and M. Kondo, "Abruptness of a-Si:H/c-Si interface revealed by carrier lifetime measurements," *Appl. Phys. Lett.*, vol. 90, no. 4, 2007, Art. no. 042111.
- [5] J. Schmidt *et al.*, "Surface passivation of high-efficiency silicon solar cells by atomic-layer-deposited  $\text{Al}_2\text{O}_3$ ," *Prog. Photovolt. Res. Appl.*, vol. 16, no. 6, pp. 461–466, 2008.
- [6] G. Dingemans and W. M. M. Kessels, "Status and prospects of  $\text{Al}_2\text{O}_3$ -based surface passivation schemes for silicon solar cells," *J. Vacuum Sci. Technol., A*, vol. 30, no. 4, 2012, Art. no. 040802.
- [7] K. M. Gad *et al.*, "Improved Si/ $\text{SiO}_x$  interface passivation by ultra-thin tunneling oxide layers prepared by rapid thermal oxidation," *Appl. Surf. Sci.*, vol. 353, pp. 1269–1276, 2015.
- [8] F. Feldmann *et al.*, "Efficient carrier-selective p- and n-contacts for Si solar cells," *Sol. Energy Mater. Sol. Cells*, vol. 131, pp. 100–104, 2014.
- [9] S. W. Glunz, F. Feldmann, A. Richter, M. Bivour, and C. Reichel, "The irresistible charm of a simple current flow pattern—25% with a solar cell featuring a full-area back contact," in *Proc. 31st Eur. Photovolt. Sol. Energy Conf. Exhib.*, 2015, pp. 259–263.
- [10] A. F. Thomson and K. R. McIntosh, "Light-enhanced surface passivation of  $\text{TiO}_2$ -coated silicon," *Prog. Photovolt. Res. Appl.*, vol. 20, pp. 343–349, 2012.
- [11] B. Liao, B. Hoex, A. G. Aberle, D. Chi, and C. S. Bhatia, "Excellent c-Si surface passivation by low-temperature atomic layer deposited titanium oxide," *Appl. Phys. Lett.*, vol. 104, 2014, Art. no. 253903.
- [12] J. Jhaveri *et al.*, "Hole-blocking crystalline silicon/titanium-oxide heterojunction with very low interface recombination velocity," in *Proc. IEEE 39th Photovolt. Spec. Conf.*, 2013, pp. 3292–3296.
- [13] X. Yang and K. Weber, "N-type silicon solar cells featuring an electron selective  $\text{TiO}_2$  contact," in *Proc. IEEE 42nd Photovolt. Spec. Conf.*, 2015, pp. 1–4.
- [14] D. G. Cahill, and T. H. Allen, "Thermal conductivity of sputtered and evaporated  $\text{SiO}_2$  and  $\text{TiO}_2$  optical coatings," *Appl. Phys. Lett.*, vol. 65, 1994, Art. no. 309.
- [15] Z. Wang, N. Yao, and X. Hu, "Single material  $\text{TiO}_2$  double layers antireflection coating with photocatalytic property prepared by magnetron sputtering technique," *Vacuum*, vol. 108, pp. 20–26, 2014.
- [16] J. Barbé, A. F. Thomson, E. C. Wang, K. McIntosh, and K. Catchpole, "Nanoimprinted  $\text{TiO}_2$  sol-gel passivating diffraction gratings for solar cell applications," *Prog. Photovolt., Res. Appl.*, vol. 20, pp. 143–148, 2012.
- [17] J. Cui *et al.*, "Titanium oxide: A re-emerging optical and passivating material for silicon solar cells," *Sol. Energy Mater. Sol. Cells*, vol. 158, pp. 115–121, 2016.
- [18] K. M. Gad *et al.*, "Ultrathin titanium dioxide nanolayers by atomic layer deposition for surface passivation of crystalline silicon," *IEEE J. Photovolt.*, vol. 6, no. 3, pp. 649–653, May 2016.
- [19] L. B. Hoex, K. D. Shetty, P. K. Basu, and C. S. Bhatia, "Passivation of boron-doped industrial silicon emitters by thermal atomic layer deposited titanium oxide," *IEEE J. Photovolt.*, vol. 5, no. 4, pp. 1062–1066, Jul. 2015.
- [20] W. Kern and D. Puotinen, "The RCA-clean," *RCA Rev.*, vol. 31, 1970, Art. no. 197.

- [21] R. S. W. Glunz, F. Werner, J. Schmidt, and A. Cuevas, "Improved quantitative description of Auger recombination in crystalline silicon," *Phys. Rev. B.*, vol. 86, 2012, Art. no. 165202.
- [22] K. N. Rao and S. Mohan, "Optical properties of electron-beam evaporated TiO<sub>2</sub> films deposited in an ionized oxygen medium," *J. Vacuum Sci. Technol. A.*, vol. 8, 1990, Art. no. 3260.
- [23] I. S. Yu, I. H. Chang, H. E. Cheng, and Y. S. Lin, "Surface passivation of c-Si by atomic layer deposition TiO<sub>2</sub> thin films deposited at low temperature," in *Proc. IEEE 40th Photovolt. Spec. Conf.*, 2014, pp. 1271–1274.
- [24] C. D. Wagner, W. M. Riggs, L. E. Davis, and J. F. Moulder, *Handbook of X-Ray Photoelectron Spectroscopy*. Chanhassen, MN, USA: Physical Electronics, 1979.
- [25] S. Avasthi *et al.*, "Hole-blocking titanium-oxide/silicon heterojunction and its application to photovoltaics," *Appl. Phys. Lett.*, vol. 102, 2013, Art. no. 203901.
- [26] A. D. Barros, K. F. Albertin, J. Miyoshi, I. Doi, and J. A. Diniz, "Thin titanium oxide films deposited by e-beam evaporation with additional rapid thermal oxidation and annealing for ISFET applications," *Microelectron. Eng.*, vol. 87, pp. 443–446, 2010.
- [27] D. K. Sarkar, D. Brassard, M. A. El Khakani, and L. Ouellet, "Dielectric properties of sol-gel derived high-k titanium silicate thin films," *Thin Solid Films*, vol. 515, pp. 4788–4793, 2007.
- [28] G. Sahasrabudhe *et al.*, "Low-temperature synthesis of a TiO<sub>2</sub>/Si heterojunction," *J. Amer. Chem. Soc.*, vol. 137, pp. 14842–14845, 2015.
- [29] L. M. Terman, "An investigation of surface states at a silicon/silicon oxide interface employing metal-oxide-silicon diodes," *Solid State Electron.*, vol. 5, pp. 285–299, 1962.
- [30] K. R. McIntosh *et al.*, "Charge density in atmospheric pressure chemical vapor deposition TiO<sub>2</sub> on SiO<sub>2</sub>-passivated silicon," *J. Electrochem. Soc.*, vol. 156, pp. G190–G195, 2009.



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