Contents lists available at ScienceDirect

Solar Energy Materials & Solar Cells

journal homepage: www.elsevier.com/locate/solmat

Titanium oxide: A re-emerging optical and passivating material for silicon solar cells

Jie Cui [a,*], Tom Allen [a], Yimao Wan [a], Josephine Mckeon [a], Christian Samundsett [a], Di Yan [a], Xinyu Zhang [a], Yanfeng Cui [b], Yifeng Chen [b], Pierre Verlinden [b], Andres Cuevas [a]

[a] Research school of engineering, The Australian National University, Canberra ACT 2601, Australia
[b] Trina Solar, Changzhou, Jiangsu 213031, China

ARTICLE INFO

ABSTRACT

We demonstrate effective passivation of a variety of crystalline silicon (c-Si) surfaces by a thin layer of thermal atomic layer deposited (ALD) titanium oxide (TiO_2). Surface recombination velocities of 0.8 cm/s, 2.5 cm/s and 9.8 cm/s have been obtained on n-type 10 cm, 1 Ω cm and p-type 1 Ω cm undiffused wafers, respectively. Recombination current densities of 19 fA/cm^2 and 780 fA/cm^2 have been measured on 120 $\Omega/\square$ boron diffused p^+ and 100 $\Omega/\square$ phosphorus diffused n^+ regions. In addition to providing a superior passivation on p^+ over n^+ (c-Si) surfaces, the ALD TiO_2 layers produces a strong injection-dependent effective lifetime on the n-type substrates, , both of which are consistent with the possible presence of negative charge in the passivating layer. The recombination at the interface between TiO_2 and planar $<100>$, planar $<111>$ and alkaline textured (c-Si) surfaces with upright pyramids is compared. We find that (i) a planar $<111>$ surface exhibits a 1.39 times higher recombination than a planar $<100>$ surface, and (ii) after area correction, the ratio of recombination on the textured and planar $<111>$ surfaces is 1.37. A thin film of TiO_2 deposited by ALD has been applied to the front surface of a rear locally diffused p^+nn^+ front junction solar cell, performing the dual role of surface passivation and single-layer antireflection coating on the textured p^+ diffusion. The best solar cell achieved $V_{oc}=655$ mV, $FF=79.9\%$ and efficiency$=20.45\%$. The results presented in this work demonstrate that TiO_2 re-emerging as a suitable optical and passivating material to produce high performance solar cells.

© 2016 Elsevier B.V. All rights reserved.

1. Introduction

In recent years, double-side passivated silicon solar cells featuring localized contacts on the rear surface have received broad acceptance in the solar photovoltaic (PV) industry, due to higher open circuit voltage, improved electrical and optical performance parameters and improved efficiency. The performance gain is largely attributed to the reduction of the surface recombination loss, which is obtained by a reduced density of interface states (D_{it}) and/or depletion of minority carriers from the surface. Dielectrics with negative charge are especially favoured in the p-type rear passivated cell and n-type cell with a boron-diffused p^+ front surface. Aluminium oxide (Al_2O_3) is so far the best candidate, because of its low D_{it} and strong negative charge (elementary charge concentration in the range $\sim 10^{12}$–10^{13} cm^{-2}) [1–4]. Large efforts have been spent in the development of alternative materials to Al_2O_3, such as titanium oxide (TiO_2) [5–7], hafnium oxide

[8,9], aluminium nitride [10], gallium oxide [11], and tantalum oxide [12], with various levels of surface passivation reported.

Titanium oxide was used extensively from the 1970s to 1990s in the PV industry as an antireflection coating (ARC) for screen-printed solar cells [13]. Its high refractive index (typically $n=1.9$–2.45) and low extinction coefficient (i.e., $k < 0.1$ for $\lambda > 350$ nm) make it well-suited for reducing reflection losses of glass-encapsulated silicon solar cells [14]. Many technologies for depositing TiO_2 have been explored, including evaporation [15,16], sputtering [17], sol-gel method [5], spray pyrolysis deposition [13,18], atmospheric pressure chemical vapour deposition (APCVD) [6,19] and, more recently, ALD [7]. With respect to the application of TiO_2 to surface passivation, however, only modest results have been reported, either using APCVD [6] or the sol-gel method [5]. Very recently, effective passivation by ALD was reported, but only after complex post deposition annealing and extended light soaking [7].

In this work, we investigate the surface recombination on n, p, p^+ and n^+ (c-Si) surfaces passivated with ALD TiO_2, as well as its dependence on crystal orientation. We demonstrate excellent ARC and surface passivation of (c-Si) by a thin layer of thermal ALD

TiO$_2$ deposited at 75 °C without any post deposition treatment. An average conversion efficiency over 20% is achieved, when such a layer is deposited on the front boron diffused p^+ surface of a rear locally diffused p^+nn^+ solar cell.

2. Experimental

Samples for surface recombination investigation were fabricated on (*i*) undiffused 1 Ω cm *p*-type and *n*-type as well as 10 Ω cm *n*-type, < 100 > float-zone (FZ) (c-Si) wafers, with a thickness of 180 μm, and (*ii*) phosphorus diffused (n^+) 100 Ω cm *p*-type and boron diffused (p^+) 100 Ω cm *n*-type FZ (c-Si) wafers with a thickness of 390 and 280 μm, respectively. In Section 3.2, surface recombination was also studied on (*i*) *n*-type FZ 1 Ω cm < 111 > oriented planar wafer, with a thickness of 290 μm, and (*ii*) alkaline textured silicon wafers with random upright pyramids. Texturing was performed by immersing < 100 > oriented wafers into an alkaline solution of tetramethylammonium hydroxide (TMAH, 25 wt%), isopropyl alcohol (IPA), deionized water and dissolved silicon at a temperature of 85 °C for 60 min [20–23].

All wafers were firstly etched in 25 wt% TMAH at ∼85 °C for 5 min to remove any saw damage. Phosphorus and boron diffusions were performed in quartz tube furnaces using liquid POCl$_3$ and BBr$_3$ precursors, resulting in sheet resistance of 100 Ω/□ and 120 Ω/□, respectively, as measured by four-point probe. Wafers then went through a full RCA (Radio Corporation of America) clean process [24] and dipped in a 1% w/v HF solution to remove any native oxide prior to TiO$_2$ deposition. The TiO$_2$ films were deposited by a thermal ALD system (TFS200, BENEQ) using titanium tetrachloride (TiCl$_4$) as titanium precursor, deionized water as the oxidant and high purity nitrogen (N$_2$) as purge gas. The deposition temperature was 75 °C, and the deposition rate was determined to be 0.76 Å/cycle by spectroscopic ellipsometry (M2000, J.A. Woolam). The film thickness and wavelength-dependent refractive index n and extinction coefficient k were determined by fitting polarized reflectance using a Cauchy model in the transparent wavelength range (e.g., $\lambda > 600$ nm) and a B-Spline model in the absorbing wavelength range with determined film thickness. The number of deposition cycles was varied to obtain a range of film thickness.

The effective carrier lifetime τ_{eff} as a function of excess carrier density Δn was measured using a Sinton Instruments WCT-120 photoconductance tool. Neglecting Shockley–Read–Hall recombination in the bulk of the wafer, the upper limit of the effective surface recombination velocity $S_{eff,UL}$ was calculated according to Eq. (1),

$$S_{eff.UL} = \frac{W}{2}\left(\frac{1}{\tau_{eff}} - \frac{1}{\tau_{bulk}}\right) \qquad (1)$$

where W is the thickness of the Si substrate, and τ_{bulk} is the intrinsic bulk lifetime in Si parameterized by Richter et al. [25]. For diffused p^+ and n^+ Si samples, the recombination current density J_0 was extracted from the lifetime measurement by employing the Kane and Swanson [26] method with an intrinsic carrier concentration $n_i = 9.65 \times 10^9$ cm^{-3} at 300 K [27]. The measurement was performed in the transient mode, which is independent of the optical properties of the sample.

The rear locally diffused p^+nn^+ solar cells were fabricated on Czochralski (Cz), *n*-type, 3 Ω cm (c-Si) substrates, with a thickness of ∼180 μm. After alkaline pyramidal texturing, a 120 Ω/□ boron diffused p^+ region was formed symmetrically. After etching away the rear p^+ region, a 40 Ω/□ rear localised n^+ region was formed via full-area phosphorus diffusion and etch back though a photolithography defined mask. The p^+ surface was passivated by a thermal ALD TiO$_2$ film with the thickness tuned for maximising
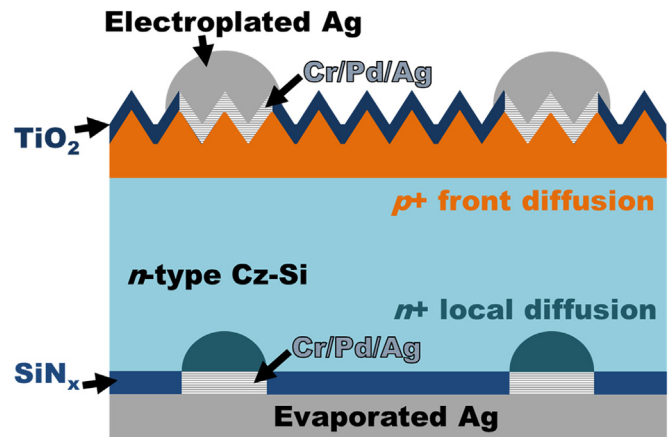

Fig. 1. Schematic representation of rear locally diffused p^+nn^+ solar cell with front ALD TiO$_2$ ARC and rear PECVD SiN$_x$ surface passivation.

the photocurrent generation in the substrate, while an 85 nm SiN$_x$ layer was deposited on the n^+ surface at 300 °C by remote PECVD (AK400, Roth & Rou). The passivation dielectrics were then patterned by etching in a buffered HF solution through a photolithography defined mask. Following this, a stack layer of chromium, palladium and silver (Cr/Pd/Ag) was thermally evaporated to both surfaces, forming direct contacts with Si. After the photoresist lift-off, leaving only local contacts of Cr/Pd/Ag covering 1% of cell area, a 1.2 μm layer of Ag was thermally evaporated to the rear surface, connecting the rear point contacts. An approximate 10 μm thick layer of Ag was electro-plated to the front metal grids for a reduced metal series resistance. Light *J-V* characteristics were measured under standard 1 sun conditions (AM1.5G spectrum, 100 mW cm^{-2}, 25 °C) with a steady state solar simulator (Photo Emission Tech., Inc.), and the external quantum efficiency (EQE) was measured using a QE1400 (Protoflex) instrument. Reflectance was measured with a spectrophotometer (Lambda 1050, Perkin Elmer). Fig. 1 outlines the schematic structure of the p^+nn^+ solar cell explored in this work.

3. Results and discussion

3.1. Surface passivation of (c-Si): p, n, p^+ and n^+

Fig. 2 shows the measured surface passivation quality presented as a recombination current density, J_0 (extracted at $\Delta n = 10^{16}$ cm^{-3}), provided by thermal ALD TiO$_2$ on p, n, and p^+ (c-Si) substrates. Fig. 2(a) depicts the effect of TiO$_2$ film thickness on J_0 on FZ *n*-type 10 Ω cm undiffused wafers. As shown in the figure, an ultra-thin TiO$_2$ with thickness less than 2.2 nm provides poor surface passivation, with J_0 close to 1000 fA cm^{-2}. The level of surface passivation is dramatically improved with a thickness over 4.3 nm and reaches its minimum J_0 of 6.4 fA cm^{-2} at a thickness of 15 nm with a τ_{eff} of 8.2 ms. A further increase of the TiO$_2$ thickness up to 62.7 nm, which is the optimised thickness for an ARC, only marginally increases the J_0, which remains approximately constant within measurement error. Therefore, a 15 nm TiO$_2$ film was consistently used in the study of surface recombination thereafter, unless otherwise specified. Fig. 2(b) shows the Auger-corrected inverse τ_{eff} as a function of excess carrier density for undiffused and diffused (c-Si) substrates. The J_0 of FZ *n*-type 10 Ω cm and *p*-type 1 Ω cm substrates are as low as 6.4 fA cm^{-2} and 7.3 fA cm^{-2}, respectively. These values correspond to an upper limit of the corresponding effective surface recombination velocity, $S_{eff,UL}$, as low as 0.8 cm s^{-1} and 9.8 cm s^{-1}, using the bulk lifetime parameterized by [25]. Moreover, a J_0 of 10 fA cm^{-2} and