Research Article

Surface Passivation and Antireflection Behavior of ALD TiO\textsubscript{2} on n-Type Silicon for Solar Cells

Ing-Song Yu,\textsuperscript{1} Yu-Wun Wang,\textsuperscript{2} Hsyi-En Cheng,\textsuperscript{2} Zu-Po Yang,\textsuperscript{3} and Chun-Tin Lin\textsuperscript{3}

\textsuperscript{1} Department of Materials Science and Engineering, National Dong Hwa University, Hualien 97401, Taiwan
\textsuperscript{2} Department of Electro-Optical Engineering, Southern Taiwan University of Science and Technology, Tainan 710, Taiwan
\textsuperscript{3} Institute of Photonic System, National Chiao Tung University, Tainan 71150, Taiwan

Correspondence should be addressed to Ing-Song Yu; isyu@mail.ndhu.edu.tw

Received 16 September 2013; Accepted 30 October 2013

Academic Editor: Jimmy Yu

Copyright © 2013 Ing-Song Yu et al. This is an open access article distributed under the Creative Commons Attribution License, which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.

Atomic layer deposition, a method of excellent step coverage and conformal deposition, was used to deposit TiO\textsubscript{2} thin films for the surface passivation and antireflection coating of silicon solar cells. TiO\textsubscript{2} thin films deposited at different temperatures (200\degree C, 300\degree C, 400\degree C, and 500\degree C) on FZ n-type silicon wafers are in the thickness of 66.4nm ± 1.1nm and in the form of self-limiting growth. For the properties of surface passivation, Si surface is effectively passivated by the 200\degree C deposition TiO\textsubscript{2} thin film. Its effective minority carrier lifetime, measured by the photoconductance decay method, is improved 133% at the injection level of 1×10\textsuperscript{15} cm\textsuperscript{-3}. Depending on different deposition parameters and annealing processes, we can control the crystallinity of TiO\textsubscript{2} and find low-temperature TiO\textsubscript{2} phase (anatase) better passivation performance than the high-temperature one (rutile), which is consistent with the results of work function measured by Kelvin probe. In addition, TiO\textsubscript{2} thin films on polished Si wafer serve as good ARC layers with refractive index between 2.13 and 2.44 at 632.8nm. Weighted average reflectance at AM1.5G reduces more than half after the deposition of TiO\textsubscript{2}. Finally, surface passivation and antireflection properties of TiO\textsubscript{2} are stable after the cofire process of conventional crystalline Si solar cells.

1. Introduction

Most commercially available solar cells are from silicon, and p-type crystalline silicon solar cells are the mainstream now. In order to increase the efficiency of crystalline silicon solar cells, people in industry try to find the better integration processes of conventional solar cells, to improve the quality of materials, and to cost down the fabrication. Besides, new structures of silicon solar cells with higher efficiency are studied. Passivated emitter and rear, locally diffused cell (PERL), proposed by University of New South Wales, Australia, in 1994, is also one of the designs, which performs very high efficiency up to 25% [1]. In industry, the conversion efficiency of 6 inch × 6 inch p-type crystalline silicon solar cells can be over 20% using the surface passivation technology with Al\textsubscript{2}O\textsubscript{3} thin films [2]. Unfortunately, the light induced degradation (LID) makes p-type crystalline silicon solar cells drop around 1% efficiency due to the formation of boron-oxygen clusters after light exposure [3]. Therefore, PERL with n-type silicon wafers attracts researchers’ great attention recently and will dominate the crystalline Si solar cell in the near future [4, 5].

For the surface passivation and antireflection coating of p-type Si solar cells, amorphous SiN\textsubscript{x} films deposed by the technique of plasma-enhanced chemical vapor deposition (PECVD) were well developed in the early 1990s. SiN\textsubscript{x} thin films can reduce surface recombination and light reflection and additionally provide very efficient passivation for bulk defects of low cost Si materials [6, 7]. However, for the p-type diffused surface of n-type Si solar cells, SiN\textsubscript{x} dielectric coatings are not suitable for passivation, because its positive charge will decrease the properties of surface passivation. Thermal silicon oxide could be good for passivation initially, but the Si-SiO\textsubscript{2} interface on boron-diffused and undiffused surfaces degrades slowly over three months at room temperature [8, 9]. Besides, amorphous silicon (a-Si) and Al\textsubscript{2}O\textsubscript{3} are good passivation layers but are not suitable for ARC on the front surface of solar cells. Therefore, titanium
oxide (TiO$_2$) reattracts researchers’ attentions, which has been used in the photovoltaic industry as an antireflection coating for many years since the 1980s due to its low growth temperature, a nontoxic and noncorrosive liquid precursor, excellent chemical resistance, an optimal reflective index, and low absorbance at wavelengths relevant to silicon solar cells. Surface passivation properties of spray pyrolysis TiO$_2$ on silicon wafer were enhanced by the formation of a SiO$_2$ layer at TiO$_2$/Si interface after being annealed at 950°C without degradation [10, 11]. Nonstoichiometric TiO$_2$ films grown by pulsed laser deposition (PLD) had some degree of passivation for nondiffused p-type Si surface through the substrate placed at the edge of plasma [12]. Recently, Thomson et al. proposed that the TiO$_2$ thin films deposited by atmospheric pressure chemical vapor deposition (APCVD) can effectively passivate n-type silicon and Boron-diffused surfaces as better as the passivation performance of SiO$_2$. These films were annealed at 300°C in N$_2$ ambient and light soaked by halogen lamp to create negative charges for better surface passivation [8].

Many technologies can be employed to grow TiO$_2$ thin films, such as PECVD, APCVD, PLD, spray pyrolysis, reactive sputtering, and sol-gel [13]. In this paper, we grew TiO$_2$ thin films on Si wafers by atomic layer deposition (ALD) which performs excellent uniformity, accurate thickness control, and almost 100% step coverage on substrate surface [14]. Some characterization of TiO$_2$ thin films by ALD will be shown. An investigation of the surface passivation and antireflection coating on silicon relative to the growth temperatures of ALD will be discussed. The degradation and influence of cofire process for the metallization of Si solar cells will also be studied. This work is essential for the applications of ALD TiO$_2$ thin films in n-type crystalline silicon solar cells.

## 2. Experiment

In the experiment, we used n-type double-polished FZ silicon wafers with resistivity 1000 Ω-cm, thickness 500 μm, and orientation (100). Before the deposition of TiO$_2$, the cleanness of Si wafers was conducted by acetone to remove the organics and 5% hydrofluoric acid to remove the native oxide. Then, wafer was rinsed in deionized water and dried with N$_2$ gas. Right after the cleaning, Si substrate was placed in the reaction chamber of our ALD system which is shown in Figure 1. Until the base pressure of chamber reached 2 × 10$^{-7}$ torr, we set the deposition temperature as 200°C, 300°C, 400°C, and 500°C, respectively. For the deposition process of TiO$_2$ thin films, we employed TiCl$_4$ and H$_2$O as reactants and Ar (99.999%) as purging gas. The injection volume of TiCl$_4$ and H$_2$O was 0.10 cc and 0.06 cc, respectively, for each step according to the ideal gas law. One cycle of a monolayer deposition included eight steps (TiCl$_4$ reactant, pump-down, Ar purge, pump-down, H$_2$O reactant, pump-down, Ar purge, and pump-down), and it took eight seconds. After 1000-cycle deposition and cool-down to room temperature of the chamber, n-type FZ Si wafer with double-side TiO$_2$ coating was done for further analysis [15]. First, the characterization of TiO$_2$ films was made by scanning electron microscopy (SEM) and X-ray diffraction (XRD). Second, the study of surface passivation for ALD TiO$_2$ on n-type FZ silicon wafers was carried out by Sinton’s quasi-steady-state photoconductance (QSSPC) method and Kelvin probe for work function measurement [16, 17]. Finally, optical properties of TiO$_2$ thin films were decided by the spectroscopic ellipsometry measurement and reflection spectroscopy in the wavelength range of 300 nm–1200 nm.

## 3. Results and Discussions

### 3.1. The Characterization of ALD TiO$_2$ Thin Films

The surface morphology and cross-section of our TiO$_2$ thin films were observed by a JSM-6700F SEM with accelerating voltage 10 kV. In Figure 2, SEM images of TiO$_2$ thin films deposited at different temperatures show that these films are polycrystalline and have grain sizes in the range of 45 nm and 110 nm. Cross-section SEM images, in the inset of Figure 3, were used to decide the thickness of TiO$_2$ thin films. The thickness of TiO$_2$ thin films is 66.4 nm ± 1.1 nm for all growth temperatures shown in Figure 3. Here, we can find that the growth rate is independent of the substrate’s temperature, which indicates that the reaction is self-limited by the saturated surface adsorption of reactants. The adsorption thickness, 0.066 nm, is almost the same for each cycle of ALD process. Our ALD system demonstrates very large growth windows for the TiO$_2$ thin films deposited on Si wafers.

The crystallinity of ALD TiO$_2$ thin films at different temperatures was studied by Bruker X-ray diffractometry. In Figure 4, XRD patterns demonstrate that TiO$_2$ thin films deposited at low temperatures are primarily with anatase phase. As the deposition temperature increased up to 500°C, rutile phase began to be obtained in TiO$_2$ thin films. When the TiO$_2$ films are annealed with the parameter of 900°C, 60 seconds, and O$_2$ ambient, rutile phase dominated in the films. Rapid thermal annealing (RTA) induces phase transformation of TiO$_2$ films from low-temperature anatase phase to high-temperature rutile phase. The higher RTA temperature is, the more rutile phase we observe. From this work, we can control the phase of TiO$_2$ thin films for the following studies of surface passivation and antireflection coating on n-type Si.

In addition, grain size of ALD TiO$_2$ can be estimated by SEM images and Scherrer equation of XRD, which is summarized in Table 1. We get smaller grain size by XRD than the one by SEM, but their trends are the same at different deposition temperatures. For TiO$_2$ films only with anatase phase (at deposition temperatures 200°C, 300°C, and 400°C), the lower deposition temperature we set, the larger grain size we observe. According to the growth mechanism of TiO$_2$ thin films, higher-temperature deposition results in significant

| Table 1: Estimation of grain size of TiO$_2$ thin films by SEM and XRD. |
|---------------------|-------|-------|-------|-------|
|                    | ALD 200°C | ALD 300°C | ALD 400°C | ALD 500°C |
| Grain size from SEM (nm) | 110 | 70   | 45   | 70   |
| Grain size from XRD (nm)  | 39   | 31   | 22   | 25   |
**Figure 1:** Schematic of the ALD system.

**Figure 2:** SEM images of TiO$_2$ thin films at different growth temperatures: (a) 200°C, (b) 300°C, (c) 400°C, and (d) 500°C.
Inset is the cross-section SEM image.

3.2. Surface Passivation Properties of ALD TiO₂. Sinton’s WCT-120, a photoconductance decay method, was employed to measure the effective minority carrier lifetime of samples. The effective lifetime (τ_{eff}) is a combination of bulk lifetime (τ_{bulk}) and surface lifetime (τ_{sur}) as follows:

\[
\frac{1}{\tau_{eff}} = \frac{1}{\tau_{bulk}} + \frac{1}{\tau_{sur}}, \quad \frac{1}{\tau_{sur}} = \frac{2S}{W},
\]

where W is the sample thickness and S is surface recombination velocity. In order to study the surface passivation of ALD TiO₂ thin films, we used FZ n-type Si substrate which has very large bulk lifetime. Therefore, the effective lifetime measured is close to surface lifetime to calculate the surface recombination velocity. Figure 5 shows the effective lifetime as function of minority carrier density by WCT-120. The effective lifetime without ALD TiO₂ passivation is 9.2 μs at the injection level of \(1 \times 10^{15} \text{ cm}^{-3}\) (\(S = 2717\) cm/s). After the deposition of TiO₂ at 200°C, the effective lifetime is 21.5 μs at the injection level of \(1 \times 10^{15} \text{ cm}^{-3}\) (\(S = 1163\) cm/s). Si surface is effectively passivated by the ALD TiO₂ thin films, especially for the one deposited at the low temperature. At the deposition temperature 500°C, when rutile phase can be observed, the degree of surface passivation does not exist anymore. For the samples with RTA 900°C, their effective lifetimes are very low (not shown). From the results of the effective lifetime measurement, we can find that TiO₂ thin film deposited at 200°C has the best performance for surface passivation on n-type Si.

Moreover, we study the degradation and influence of metallization process in crystalline solar cells. In Figure 6, the effective lifetime of 30 nm TiO₂ thin film grown at temperature 200°C slightly increased after five months of deposition. After cofire process of belt-type furnace at peak temperature 800°C, the effective lifetime decreased a little but is still good enough for surface passivation. We can summarize that ALD TiO₂ thin films have high stability for the applications in crystalline silicon solar cells.

In the study of solar cells, work function is sensitive to the voltage across the barrier of p-n junction and the surface traps in the passivation emitter interface. In this work, nonscanning ambient Kelvin probe, KP 020, was used to measure the work function of TiO₂ thin films at different deposition temperatures. In Figure 7, the higher deposition temperature we use, the larger work function of TiO₂ we measure, which is consistent with the result of effective
and cofire.
films deposited at 200 °C at the interface of TiO$_2$ as (ARC), the refractive index of coating layer has to be chosen for crystalline silicon solar cells. For lower deposition temperature of TiO$_2$, the reflectance from Si backside surface starts to contribute at around 1000 nm is observed for all samples. This is because the reflectance from Si backside surface starts to contribute the measured reflectance as wavelength approaching the band gap wavelength of Si.

Figure 6: Effective minority carrier lifetime of 30 nm TiO$_2$ thin films deposited at 200 °C in three cases: after deposition, five months, and cofire.

Figure 7: Work function (●) and effective lifetime (▲) of TiO$_2$ thin films at different deposition temperatures.

Effective lifetime (µs) vs. Minority carrier density (cm$^{-3}$)

- ALD 200°C (after deposition) 15.7 µs
- ALD 200°C (after five months) 17.8 µs
- ALD 200°C (after cofire) 16.6 µs

Figure 8: Work function (●) and effective lifetime (▲) of TiO$_2$ thin films at different deposition temperatures.

3.3. Optical Properties of ALD TiO$_2$. Now we will demonstrate that our ALD TiO$_2$ thin films are an excellent antireflection coating layer for crystalline silicon solar cells. For the conventional quarter-wavelength antireflection coating (ARC), the refractive index of coating layer has to be chosen as $\sqrt{n_2}$, where $n_2$ is the refractive index of substrate, that is, Si in this case. For example, considering the refractive index of Si in the spectral ranges of 400 nm–800 nm [20], the refractive index of quarter-wavelength ARC thin films should be in the range of ~2.36–1.92. To verify this, we performed the spectroscopic ellipsometry measurements and extracted the refractive index of our ALD TiO$_2$ thin films. Figure 9 shows the refractive index as a function of wavelength for our TiO$_2$ thin film deposited at temperature 200 °C. Its refractive index decreases monotonically from 2.65 to 2.25 as wavelength decreases from 375 nm to 900 nm, showing a similar trend as anatase-phase bulk TiO$_2$ [21] but having a little lower value of index, which probably is because of polycrystal structure in our films (see SEM images in Figure 2). Most importantly, the results show that our ALD TiO$_2$ thin films are an excellent choice of quarter-wavelength ARC layer for Si solar cells.

To further prove this, we used Hitachi U-4100 to measure the reflectance spectra of our ALD TiO$_2$ thin films and a Si wafer as a reference, shown in Figure 10. Firstly, all of TiO$_2$ deposited Si wafers show a much lower reflectance than those of a bare Si wafer over the measured spectral range. Secondly, a minimum reflectance of TiO$_2$ deposited Si wafers is observed at ~550 nm, which is consistent with the requirement of film thickness for quarter-wavelength ARC; that is, $d = \lambda/4n_{TiO_2}$. Taking λ = 550 nm and $n_{TiO_2} \approx 2.15$, we have $d \approx 64$ nm, which agrees with our SEM results. Again, this indicates that our TiO$_2$ thin films serve as an ARC layer. Thirdly, the reflectance of all TiO$_2$ deposited Si increases monotonically from ~550 nm to ~1000 nm. This is because the thickness (66.4 nm) of our TiO$_2$ film deviates the $d = \lambda/4n_{TiO_2}$ further and further as wavelength increases. Fourthly, a bump rising at around 1000 nm is observed for all samples. This is because the reflectance from Si backside surface starts to contribute the measured reflectance as wavelength approaching the band gap wavelength of Si.

To overall justify the ARC performance of our TiO$_2$ thin films for solar cells, we calculate the weight average reflectance (WAR) at AM1.5G in the range of 300 nm to 1200 nm. The results show that all of our ALD TiO$_2$ thin films have WAR (16.68%–18.92%) less than the half of WAR (38.36%) of bare Si. The TiO$_2$ thin film grown at 200 °C shows the lowest value of WAR because it has the lowest refractive index deduced from ellipsometry. A lower WAR value can be achieved with optimized growth conditions and film thickness. Moreover, the reflectance spectra as well as the WAR are almost the same after cofire process by belt-type furnace at peak temperature 800 °C (not shown), which indicates that our ALD TiO$_2$ thin films are suitable for the fabrication processes of crystalline silicon solar cells.

4. Conclusion

Growth window of self-limiting can be from 200 °C to 500 °C in our TiO$_2$ ALD system with the growth rate 0.066 nm per cycle. All these films are excellent antireflection coating layers for Si. For lower deposition temperature of TiO$_2$ thin films, we find smaller energy band bending in the interface of TiO$_2$/Si and better surface passivation performance. The best surface passivation and antireflection coating on Si wafers are carried out at the deposition temperature 200 °C, mainly
Figure 8: The left hand side is energy band diagrams of TiO$_2$ and Si before contact. After contact, band bending occurs at the interface of TiO$_2$ and Si.

![Energy Band Diagram](image)

Figure 9: Refractive index as function of wavelength for TiO$_2$ thin film grown at 200°C.

![Refractive Index](image)

Figure 10: Reflectance of bare Si wafer and Si with TiO$_2$ thin films grown at different temperatures as function of wavelength from 300 nm to 1200 nm.

![Reflectance](image)

anatase phase in TiO$_2$ film. Once the rutile appears via high-temperature depositions or annealing processes, the degree of surface passivation will not exist. After the cofire process of conventional crystalline Si solar cells, we prove that their surface passivation and antireflection properties are very stable, which can be applied for n-type crystalline silicon solar cells.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

Acknowledgments

The authors acknowledge National Science Council of Taiwan (NSC 101-2218-E-259-001) for financially supporting this study and E-Ton Solar Tech. Co., Ltd., for the measurement of Sinton WCT-120 and Hitachi U-4100.

References


Submit your manuscripts at http://www.hindawi.com