Low-Temperature, Chemically Grown Titanium Oxide Thin Films with a High Hole Tunneling Rate for Si Solar Cells

Yu-Tsu Lee 1, Fang-Ru Lin 1, Ting-Chun Lin 1, Chien-Hsun Chen 4 and Zingway Pei 1,2,3,*

1 Department of Electrical Engineering, National Chung Hsing University, Taichung 40227, Taiwan;
bill90867@hotmail.com (Y.-T.L.); ginkgo0518@hotmail.com (F.-R.L.); lin46094@gmail.com (T.-C.L.)
2 Graduate Institute of Optoelectronic Engineering, National Chung Hsing University, Taichung 40227, Taiwan
3 Research Center for Sustainable Energy and Nanotechnology, National Chung Hsing University,
   Taichung 40227, Taiwan
4 Green Energy and Environment Research Laboratories, Industrial Technology Research Institute,
   Chutung 310, Taiwan; tantalus@itri.org.tw
* Correspondence: zingway@dragon.nchu.edu.tw; Tel.: +886-4-2285-1549 (ext. 801)

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Abstract: In this paper, we propose a chemically grown titanium oxide (TiO₂) on Si to form a heterojunction for photovoltaic devices. The chemically grown TiO₂ does not block hole transport. Ultraviolet photoemission spectroscopy was used to study the band alignment. A substantial band offset at the TiO₂/Si interface was observed. X-ray photoemission spectroscopy (XPS) revealed that the chemically grown TiO₂ is oxygen-deficient and contains numerous gap states. A multiple-trap-assisted tunneling (TAT) model was used to explain the high hole injection rate. According to this model, the tunneling rate can be 10⁵ orders of magnitude higher for holes passing through TiO₂ than for flow through SiO₂. With 24-nm-thick TiO₂, a Si solar cell achieves a 33.2 mA/cm² photocurrent on a planar substrate, with a 9.4% power conversion efficiency. Plan-view scanning electron microscopy images indicate that a moth-eye-like structure formed during TiO₂ deposition. This structure enables light harvesting for a high photocurrent. The high photocurrent and ease of production of chemically grown TiO₂ imply that it is a suitable candidate for future low-cost, high-efficiency solar cell applications.

Keywords: titanium oxide; chemically grown; heterojunction; band alignment; hole tunneling

1. Introduction

Heterojunction solar cells have recently become leading candidates for high-efficiency cells with a considerably low production cost. Heterojunctions are widely used in optoelectronic devices such as light-emitting diodes (LEDs) [1–4], laser diodes [5,6], and photodiodes (PDs) [7–9] because they enable manipulating either hole or electron transport selectively by applying an appropriate band alignment. The specific band alignment can either increase carrier recombination in a LED or move photocarriers into appropriate contact in a PD. A solar cell, an energy harvesting device, is a type of PD. To achieve a high photocurrent, holes and electrons should arrive at a specific electrode properly. Therefore, several material systems have been proposed and demonstrated to achieve appropriate heterojunctions in Si solar cells. Amorphous Si is a well-known material system deposited on crystalline Si to construct a heterojunction for high-efficiency solar cells by setting front and back surface fields [10]. A very thin (5–10 nm) intrinsic amorphous Si (a-Si:H) layer and a heavily p-type-doped amorphous Si (p-a-Si:H) layer were deposited sequentially through plasma-enhanced chemical vapor deposition (PECVD). The purpose of the intrinsic a-Si:H is to passivate the Si surface with hydrogen to prevent carrier
recombination. However, this is a challenging process because PECVD involves ionic radicals that might damage the Si surface rather than passivate it. Although the a-Si:H-based heterojunction with intrinsic thin-film technology has demonstrated high efficiency, an alternative material that inherently exhibits excellent surface passivation and proper band alignment is required. Therefore, in addition to a-Si:H, metal oxides such as AlO$_x$ [11–13], SiO$_2$ [14,15], and TiO$_2$ [16,17] have been used in constructing carrier selective barriers with passivation ability on crystalline Si to achieve a high photocurrent. Pudasaini et al. [11] used ultrathin aluminum oxide (approximately 1.84 nm), grown through an atomic layer deposition, on an n-type Si wafer as a passivation layer in a poly(3,4-ethylenedioxythiophene) polystyrene sulfonate/Si hybrid heterojunction solar cell system. Sheng et al. [14] used a wet method to form silicon oxide on a Si wafer as a passivation layer. A 10.48% efficiency was achieved in a hybrid solar cell. Avasthi et al. [16] used low temperature chemical vapor deposition (CVD)-grown TiO$_2$ (3 nm) on a p-type wafer to block holes, thereby achieving a 7.02% photoelectric conversion efficiency. Among the aforementioned materials, TiO$_2$ is the most attractive because it exhibits a smaller bandgap that ensures efficient carrier tunneling. Furthermore, TiO$_2$ was demonstrated to be an alternative to silicon nitride as a Si surface passivation layer [18]. However, CVD is a slow and expensive process that might limit productivity in the future. Moreover, n-type Si is preferred to p-type Si in solar cells because electrons move faster than holes do. Therefore, chemically depositing TiO$_2$ at a low temperature is proposed for attaining a high hole tunneling rate on an n-type Si substrate for heterojunction solar cells.

2. Experimental

An n-type, surface polished (100) Si wafer (1–10 $\Omega$-cm) 525 µm in thickness was diced into tiles with areas of $2 \times 2$ cm$^2$ and used as the substrate. Prior to deposition, the Si substrate was cleaned chemically in a solution with an HF:H$_2$O ratio of 1:10 for 30 s and then rinsed in deionized water. After the substrate was cleaned, a layer of TiO$_2$ 24–48 nm in thickness was deposited through liquid phase deposition (LPD). The deposition system consisted of:

(1) an environment that was temperature controlled at an accuracy of ±0.1 °C;
(2) a Teflon vessel containing the deposition solution.

To form the deposition solution, (NH$_4$)$_2$TiF$_6$ and H$_3$BO$_3$ were dissolved in deionized water at concentrations of 0.2 M and 0.6 M, respectively. To deposit TiO$_2$, this solution was saturated with TiO$_2$ powder. The deposition temperature was maintained at 40 °C.

The mechanism for chemically growing TiO$_2$ consists of two equilibrium reactions. The first is ligand exchange between metal-fluoro-complex ions (Equation (1)), and the second is an F$^-$ ion consuming reaction in which boric acid serves as an F$^-$ scavenger (Equation (2)) [19].

$$[\text{TiF}_6]^{2-} + n\text{H}_2\text{O} \leftrightarrow [\text{TiF}_{6-n}(\text{OH})_n]^{2-} + n\text{HF}$$

$$\text{H}_3\text{BO}_3 + 4\text{HF} \leftrightarrow \text{HBF}_4 + 3\text{H}_2\text{O}$$

H$_3$BO$_3$ reacts readily with F$^-$ to form stable BF$_4^-$ ions, thereby promoting the consumption of uncoordinated F ions. TiO$_2$ dissolves in the solution and reacts with (NH$_4$)$_2$TiF$_6$ to produce a TiO$_2$ film on the Si and HF in the solution. The formation of HF prohibits the growth of TiO$_2$. At this moment, the H$_3$BO$_3$ consumes HF, thereby sustaining the growth of TiO$_2$. The grown TiO$_2$ was then rinsed in deionized water and was air-dried with purified nitrogen. After TiO$_2$ deposition, a thin layer of B-doped a-Si:H (20 nm) was deposited through PECVD (13.56 MHz). A transparent conductor, indium–tin oxide (ITO), was then deposited through sputtering in a 80-nm-thick layer. Subsequently, front and back contacts, namely Ag (100 nm) and Al (200 nm), respectively, were deposited using a thermal evaporator. The dark current density-voltage characteristics of the fabricated solar cells were measured using an Agilent B2912A semiconductor parameter analyzer, and the photovoltaic characteristics were measured using the same setup equipped with a calibrated solar simulator under an air mass (AM) 1.5 G (100 mW/cm$^2$) condition. The external quantum efficiency (EQE) was measured.
using a Titan Electro-Optics QE-3000 system (Titan Electro-Optics Co., Taipei, Taiwan). Scanning electron microscopy (SEM) images were taken using a JEOL JSM-6700F (JEOL USA Inc., Peabody, MA, USA). Transmission electron microscopy (TEM) measurements were obtained using a JEOL JEM-2100F (JEOL USA Inc.). X-ray photoelectron spectroscopy (XPS) measurement was performed using a ULVAC-PHI PHI 5000 Versa Probe (Physical Electronics, Inc., Chanhassen, MN, USA).

3. Results and Discussion

To determine the proper band alignment to n-type Si for carrier selection, ultraviolet (UV) photoemission spectroscopy (UPS) was performed to measure the energy levels of TiO₂ [20]. The UPS was performed by emitting UV photons with an energy of 21.2 eV to the TiO₂ film. The binding energy (BE) of photoelectrons was analyzed. A schematic of the mechanism is plotted in Figure 1a.

![Figure 1. (a) Schematic of work function of TiO₂ determined through ultraviolet (UV) photoemission spectroscopy (UPS) spectroscopy; (b) UPS spectrum of liquid phase deposition (LPD)-TiO₂; (c) optical bandgap of TiO₂ layer; (d) image of TiO₂/Si interface taken through transmission electron microscopy (TEM); and (e) I-V characteristics of Al/LPD-TiO₂/Si diode.](image)

The Fermi energy ($E_F$) of the solution-processed TiO₂ is suggested to have an energy level between the conduction band edge ($E_C$) and the valence band edge ($E_V$) of the TiO₂. Upon UV light illumination, valence electrons are excited and escape from the associated atoms with a kinetic energy ($KE$) measured by a detector. Therefore, the energy relationship of the system can be described by $BE = h\nu - KE - \Phi$, in which $BE$ is the binding energy of an electron, determined as the difference between the energy of the electron in the valence band and the $E_F$; $h\nu$ is the energy of the UV light; and $\Phi$ is the work function of the system, determined as the energy difference between the vacuum level and the $E_F$. Therefore, a $BE$ was obtained at each $KE$. The maximum $BE$ was obtained at zero $KE$, as shown in Figure 1b. The work function ($\Phi$) of the films was defined by $\Phi = h\nu - \Delta E$, in which $\Delta E$ is determined as the $BE$ at the cutoff edge of electron emission [20,21]. Extrapolation shows that the cutoff edge is 17 eV. Therefore, the work function is 4.2 eV in the LPD-grown TiO₂ film. The energy difference between $E_F$ and $E_V$ can be determined at the rising point of electron emission through extrapolation, because the electrons are occupied mostly in the valence band in a semiconductor. The calculated $E_F - E_V$ difference is 1.9 eV. Accordingly, the $E_V$ is 6.1 eV below the vacuum level. The transmission spectrum of TiO₂-grown glass was used to calculate the bandgap ($E_g$) of the TiO₂ through the following procedure. The absorbance ($A$) of the TiO₂ layer can be obtained using the relation $A = 1 - R - T$, in which $R$ is the reflectance, and
$T$ is the transmittance. With known thickness ($d$) and $A$, the absorption coefficient ($\alpha$) can be deduced according to the relation $A = \exp(-\alpha d)$. With the absorption coefficient, the optical bandgap of the TiO$_2$ can be obtained according to a Tauc plot, as shown in Figure 1c. The optical bandgap of the TiO$_2$ was determined to be 3 eV through this method. Accordingly, the $E_C$ is 3.1 eV from the vacuum level. In general, the $E_C$ and $E_V$ for Si are 4.05 eV and 5.17 eV, respectively. Therefore, the valence band barrier for the TiO$_2$/Si interface is 0.93 eV.

A high-resolution TEM image of the grown TiO$_2$ on crystalline Si is depicted in Figure 1d. The TiO$_2$ layer is approximately 24-nm-thick. The TEM images confirm that the solution-processed TiO$_2$ was smoothly deposited on the Si surface. To examine the ability of holes to tunnel through TiO$_2$, an Al/TiO$_2$/Si diode structure was used to measure the $I$-$V$ characteristics, as shown in Figure 1e. The current density, as high as 100 mA/cm$^2$, was obtained at a low voltage in the Al/TiO$_2$/Si diode under both positive and negative biases, indicating that both electrons and holes can flow through the 24-nm-thick TiO$_2$ efficiently without being blocked. The energy levels were measured through UPS as described. By contrast, without TiO$_2$, Al/n-Si exhibits a Schottky diode behavior [15] with a Schottky barrier height of 0.157 eV, as shown in Figure 1e.

To identify the reason for the efficient hole tunneling, the chemical structure of TiO$_2$ was explored through XPS. Figure 2a shows the atomic concentration depth profile for a thick TiO$_2$ film. Clear Ti and Si intermixing at the surface is evident. To further study the interface, the BE spectra of Ti 2p, O 1s, and Si 2p signals at the interface were analyzed and are shown in Figure 2b–d, respectively. After deconvolution, the Ti 2p 2p3/2 spectra have three peaks, which are associated with TiO (454.7 eV), Ti$_2$O$_3$ (457 eV), and TiO$_2$ (458.7 eV) [22], indicating that oxygen is deficient in the TiO$_2$ film. The O1s spectra also have three peaks, which are associated with TiO$_2$ (530.3 eV), oxygen-deficient TiO$_2$ (531.1 eV), and SiO$_2$ (532.2 eV) [22,23]. The oxygen deficiency implies the existence of Ti dangling bonds, which cause gap states in the LPD-TiO$_2$ film. These gap states stimulate trap-assisted tunneling (TAT), which ensures that the photogenerated holes in Si are transported through the TiO$_2$ to the ITO anode. The Si2p spectra have two peaks, which are associated with Si (99 eV) and Si–O (102 eV) [23,24]. The presence of Si–O bonding indicates that small amounts of SiO$_2$ exist inside the TiO$_2$ or at the Si surface. The incorporation of Si is an essential property of LPD-grown TiO$_2$ film. The Si dissolves into the solution through HF etching during LD of TiO$_2$. The dissolved Si then forms either Ti–O–Si or Si–O bonds at the TiO$_2$/Si interface. The coexistence of oxygen-deficient Ti and Si bonding and oxygen-bridging Ti and Si bonding may be responsible for the reduction of the measured barrier height for holes between Si and LPD-TiO$_2$.

Figure 2. (a) Ti 2p; (b) O 1s; (c) Si 2p core level atomic structures for LPD-TiO$_2$ obtained through X-ray photoelectron spectroscopy (XPS); and (d) depth profiles of these signals.
Figure 3a shows a schematic of band alignment in a fabricated heterojunction solar cell based on UPS measurement. According to the band alignment, the photogenerated electrons and holes are transported to the cathode and anode, respectively, by the established electrical field. The holes are probably blocked by barriers set by the TiO₂. However, the experimental observations indicated that holes can flow through such barriers, as shown in Figure 1d. A mechanism of TAT through the gap states in TiO₂ was proposed to be responsible for the high tunneling rate of holes. The physical theorem and calculation relevant to TAT have been discussed [25–29]. A multiple trap center model was used to simulate the tunneling current in the SiO₂. The current density attained through multiple-TAT was calculated to be approximately 8 orders of magnitude higher than the current density achieved through direct tunneling for 4.5-nm-thick SiO₂. In addition, the multiple-TAT current gradually decreases as the SiO₂ thickness increases. The carrier behavior in the valence band around TiO₂ based on this model is illustrated in Figure 3b.

![Figure 3. (a) Band alignment of proposed TiO₂/Si heterojunction solar cell; (b) enlarged part of band diagram at E_V around interface of TiO₂/Si; and (c) ratio of tunneling current through TiO₂ to that through SiO₂ (J_{TiO2}/J_{SiO2}) according to gap state concentration.](image)

When holes become close to TiO₂, they are captured by traps (gap states) and then emitted to a-Si:H by the internal field. Therefore, the capture rate (Rci) and emission rate (Rci) are dominant factors influencing the tunneling current. The current density can be expressed as the sum of the capture and emission rates R_i in each trap multiplied by the trap cross section ΔX_i, as shown in Equation (3).

\[ J = q \sum_i R_i \Delta X_i \]  

(3)

Under a high internal field, the carriers must tunnel through the TiO₂, and the emission rate must be higher or equal to the capture rate. Therefore, the calculation focuses on the emission rate. The emission rate can be expressed as the emission lifetime multiplied by the density of gap states, as shown in Equation (4). Furthermore, the emission lifetime can also be expressed by the relationship between the carrier distribution probability and the effective mass and energy levels, as shown in Equation (5). Finally, the tunneling current can be expressed by Equations (3) and (4) as expressed in Equation (6).

\[ R_{ci} \propto \tau_{ei}^{-1} \times N_{hi} \propto \frac{1}{(m_{\text{die}})^2 \times E_T \times E_g} \exp \left[ -\left( E - E_T \right) \right] \times N_{hi} \]  

(4)

\[ \tau_{ei}^{-1} \propto \frac{1}{(m_{\text{die}})^2 \times E_T \times E_g} \exp \left[ -\left( E - E_T \right) \right] \]  

(5)

\[ J \propto \frac{1}{(m_{\text{die}})^2 \times E_T \times E_g} \exp \left[ -\left( E - E_T \right) \right] \times N_{hi} \times \frac{1}{\sqrt{m_{\text{die}} \times E_T}} \]  

(6)

In the preceding equations, m_{die} is the effective hole mass (approximately 0.71 m₀) in the dielectric, E_T is the E_V of TiO₂, τ_{ei}^{-1} is the emission lifetime, and N_{hi} is the gap state concentration in the TiO₂. On the basis of these equations, we can calculate the ratio of the tunneling current density in the TiO₂ to
that in the SiO2 at different gap state concentrations. In this calculation, the gap state density for SiO2 is fixed at $9 \times 10^{17}$ cm$^{-3}$, as described in the literature [27]. This ratio is shown in Figure 3c. According to Figure 3c, at the same gap state density, the tunneling current through TiO is more than 100 times higher than that through SiO2. With an increase of the gap state density in the TiO to $10^{21}$ cm$^{-3}$, the tunneling current ratio becomes higher than $10^5$. Such a high gap state density is reasonable. An oxygen-deficient signal was evident in XPS for TiO, and TiO$_2$ occupied approximately two thirds of the Ti signal, whereas stoichiometric TiO$_2$ occupied only approximately one third. Therefore, chemically grown TiO$_2$ can withstand a high hole tunneling rate without blocking the holes.

The dark and photocurrent-voltage characteristics are illustrated in Figure 4a,b, respectively. All solar cells with a TiO$_2$ layer ranging from 24 nm to 48 nm in thickness exhibit favorable junction behavior. The rectifier ratio calculated at 0.5 V is approximately 7500 for a device with 24-nm-thick TiO$_2$. Other devices have similar values. The ideal factors for solar cells with 24-, 32-, 40-, and 48-nm-thick TiO$_2$ layers are 1.63, 1.75, 1.71, and 1.45, respectively. Such moderate ideal factors indicate that carrier recombination is not high at the TiO$_2$/Si interface. However, if the TiO$_2$ layer is absent in the heterojunction solar cell, the reverse saturation current clearly increases. The reverse saturation current density, $J_0$, for a reference device (without TiO$_2$) is $7.12 \times 10^{-7}$ A/cm$^2$, and it is $3.54 \times 10^{-7}$ A/cm$^2$ for a device with 24-nm-thick TiO$_2$. In addition, the reference device exhibits a relatively high ideal factor (>2) at a forward voltage. These findings indicate that TiO$_2$ can properly passivate the interface between a-Si:H and Si as well as further improve the electrical contact behavior between them.

![Figure 4. Photocurrent-voltage characteristics for heterojunction solar cells containing TiO$_2$ at different thicknesses: (a) dark I-V characteristics; (b) photocurrent-voltage characteristics obtained under AM 1.5G; (c) external quantum efficiency (EQE) of solar cells; and (d) ratio of EQE enhancement of solar cells with TiO$_2$ interlayer relative to the reference cell.](image-url)

The photocurrent-voltage characteristics of heterojunction solar cells with and without TiO$_2$, measured under an AM 1.5 G (100 mW/cm$^2$) illumination condition by using a calibrated solar
The short-circuit current density ($J_{sc}$), open-circuit voltage ($V_{oc}$), and fill factor for a heterojunction solar cell with TiO$_2$ (24 nm) are 33.2 mA/cm$^2$, 0.49 V, and 0.579, respectively, yielding a power conversion efficiency (PCE) of 9.42. By contrast, without a TiO$_2$ interlayer, the values of those solar cell performance indicators are 29.9 mA/cm$^2$, 0.47 V, and 0.586, yielding an 8.23% PCE. The enhanced performance is attributed to the properly aligned and passivated interfaces for hole tunneling between a-Si:H and Si achieved by inserting the TiO$_2$ layer.

The $J_{sc}$ is quite high for a planar solar cell containing no surface microstructure for light harvesting. As the thickness of TiO$_2$ is increased to 48 nm, the $J_{sc}$ decreases gradually to 26.3 mA/cm$^2$. This implies that the PCE also gradually decreases, reaching 5.52% for a solar cell with 48-nm-thick TiO$_2$. The details are listed in Table 1. This reduction is inversely proportional to the increase in the series resistance. Consequently, the reduction of the $J_{sc}$ was attributed to slight current blocking by the thicker TiO$_2$.

The EQE of several fabricated solar cells is shown in Figure 4c. The solar cells with a TiO$_2$ interlayer (24 nm and 32 nm) exhibit higher EQE than that of the solar cell without a TiO$_2$ interlayer (reference) in both the short wavelength (400–580 nm) and near infrared (750–1100 nm) ranges. The enhanced EQE for the solar cells with a TiO$_2$ interlayer indicates the probability of passivation at interfaces. It also indicates that the solar cells with a TiO$_2$ interlayer may establish a higher internal electrical field than that of the reference cell inside the n-Si. Notably, the EQE of solar cells with thicker TiO$_2$ interlayers (40 nm and 48 nm) is lower than that of the reference cell at 580–750 nm. This phenomenon is clearly explained by the enhancement ratio, which is expressed as the EQE of a solar cell with a TiO$_2$ interlayer divided by the EQE of the reference cell. Figure 4d depicts the enhancement ratio for four samples; the EQE of solar cells with thicker TiO$_2$ interlayers (40 nm and 48 nm) is 95% of the EQE of the reference cell. This may be attributed to slight carrier blocking by the TiO$_2$. The calculated $J_{sc}$ is listed in Table 1 and denoted by $J_{sc}$(EQE). The measured $J_{sc}$ and $J_{sc}$(EQE) are highly similar for the reference sample. By contrast, the $J_{sc}$(EQE) for the solar cell with a 24-nm-thick TiO$_2$ interlayer is lower than that of the measured $J_{sc}$. This may be due to the difference in the measurement setup between the solar simulator and the quantum efficiency spectrometer. However, the $J_{sc}$(EQE) also shows a decreasing trend as the TiO$_2$ thickness increases, which is consistent with the proposed mechanism. The PCE based on $J_{sc}$(EQE) is also listed in Table 1.

### Table 1. Photovoltaic characteristics of TiO$_2$/Si heterojunction solar cells.

| Parameter | Ref. $^a$ | 24 nm | 32 nm | 40 nm | 48 nm |
|-----------|-----------|-------|-------|-------|-------|
| $V_{oc}$ (V) | 0.47 | 0.49 | 0.47 | 0.46 | 0.44 |
| $J_{sc}$ (mA/cm$^2$) | 29.9 | 33.2 | 29.5 | 27.1 | 26.3 |
| $J_{sc}$(EQE) (mA/cm$^2$) | 30.5 | 31.77 | 31.88 | 31.42 | 30.59 |
| Fill Factor | 0.586 | 0.579 | 0.583 | 0.556 | 0.477 |
| Efficiency (%) | 8.23 | 9.42 | 8.09 | 6.93 | 5.52 |
| Efficiency EQE (%) | 8.40 | 9.01 | 7.98 | 6.42 |
| $R_s$ (Ω-cm$^2$) | 3.8 | 3 | 3.5 | 4.44 | 5.35 |
| $R_{sh}$ (Ω-cm$^2$) | 1855 | 1875 | 1727 | 11,875 | 5369 |

$^a$ p-a-Si:H/n-Si heterojunction solar cell.

The reduction in the barrier height and the ease of tunneling for carriers through the TiO$_2$/Si interface can only ensure that the photocarrier is collected. They do not increase the light harvesting ability. To identify the reason for the high photocurrent (33.2 mA/cm$^2$) obtained in the LPD-grown TiO$_2$ heterojunction solar cell based on a polished Si substrate, the surface morphology of LPD-grown TiO$_2$ on Si was characterized through SEM.

Figure 5a depicts plan-view SEM images of the LPD-grown TiO$_2$ with different thicknesses. Many randomly arranged circular protrusions in a moth-eye-like structure were found over the LPD-TiO$_2$ surface. The density of these structures increases as the TiO$_2$ thickness increases. The diameter for each structure is approximately 100 nm. This dimension is close to the quarter wavelength of visible light in TiO$_2$. Therefore, the interaction of incident light and LPD-grown TiO$_2$ can be expressed by...
Mie scattering [30–32]. In the mechanism of Mie scattering, the percentage of back scattering is lower than that of Rayleigh scattering. Therefore, most of the incident light can be coupled into Si with high deflection. The deflected light can be reflected back and forth many times inside Si, increasing the absorbance of the incident light. This scattering mechanism is illustrated in Figure 5b. The reflectance of the LPD-grown TiO$_2$ on Si at 300–800 nm is shown in Figure 5c. In the figure, thick TiO$_2$ exhibits lower reflectance than that of thin TiO$_2$, indicating that the incident light is more intense for the thick TiO$_2$. However, the solar cell with the thick TiO$_2$ exhibits a lower $J_{sc}$ than that of the solar cell with the thin TiO$_2$. Therefore, as the TiO$_2$ thickness increases, hole transport through TiO$_2$ to the anode becomes less easy, causing the current density to decrease. Consequently, the improved performance of the device is due to the enhanced hole transport rather than increased light trapping.

![Figure 5](image)

**Figure 5.** (a) Plan-view scanning electron microscopy (SEM) images of LPD-TiO$_2$ on Si; (b) proposed light scattering process in TiO$_2$ solar cell. The inset of (c) shows the measured surface reflectance of planar Si and LPD-TiO$_2$ on Si.

4. Conclusions

In conclusion, we demonstrated enhancements in Si-based heterojunction solar cells fabricated using a low temperature and liquid-phase-processed TiO$_2$. LPD enables high throughput and low cost solar cell production. The LPD-TiO$_2$ can passivate the Si surface, preventing plasma and chemical damage in subsequent processes. Through UPS investigation, the work function, $E_C$, and $E_V$ for LPD-TiO$_2$ were obtained. The band alignment indicates that electrons and holes could be collected properly. On the polished Si substrate, a 33.2-mA/cm$^2$ short-circuit current was obtained. A moth-eye-like structure was observed on the LPD-grown TiO$_2$ surface. Mie scattering in these structures ensures light harvesting and is responsible for the high photocurrent.

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