Effect of defects in TiO₂ nanotube thin film on the photovoltaic properties of quantum dot-sensitized solar cells

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In the liquid-phase-deposition (LPD) method, the deposition temperature is considered to be one of the most important factors in TiO₂ nanotube crystal growth. We investigated the effects of the deposition temperature on the surface morphology and defects in TiO₂ nanotube (NT-TiO₂) thin film electrodes utilizing scanning-electron-microscopy (SEM), X-ray diffraction (XRD), and photoluminescence (PL), together with the effects of these on the photovoltaic characteristics of CdSe quantum dot (QD)-sensitized NT-TiO₂ solar cells. In addition, we studied the effect of these defects on the physical properties, such as the carrier recombination and electron transport at the TiO₂ and TiO₂/QD interface. NT-TiO₂ electrodes prepared at low temperatures have a more uniform surface and lower defects than those prepared at high temperatures. From the PL measurements and the photovoltaic characterization such as shunt resistance (R_{sh}) and open circuit voltage decay (OCVD), these defects can act as carrier recombination centers. The defect density increases with increasing deposition temperature, leading to an increase in carrier recombination. Series resistances (R_s) of the solar cells with NT-TiO₂ electrodes prepared at high temperatures were larger than those of the solar cells with NT-TiO₂ electrodes prepared at low temperatures, suggesting that the defects can also affect the carrier transport characteristics. Eventually, CdSe QD-sensitized NT-TiO₂ solar cells employing NT-TiO₂ prepared at low temperatures showed higher conversion efficiencies than those prepared at high temperatures.

KEYWORDS: TiO₂ nanotube electrode, CdSe quantum dot, quantum dot sensitized solar

cells, surface morphology, defect, recombination, back electron transfer, open circuit voltage decay, electron lifetime

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1. Introduction

Semiconductor quantum dot (QD)-sensitized solar cells (QDSSCs) have attracted much attention as third generation solar cells. QDs in QDSSCs act as photosensitizers, and they can be fabricated by more inexpensive procedures than conventional silicon-based solar cells.¹ QDSSCs possess various unique benefits and have the potential to overcome the Shockley-Queisser limit to the power conversion efficiency [1, 2]. Firstly, the energy gap of QDs can be tuned by controlling the size of the QDs to cover a suitable range of the solar spectrum [3]. Secondly, QDs have a large extinction coefficient due to the quantum confinement effect [4]. Thirdly, they have a large intrinsic dipole moment, leading to rapid charge separation [4]. Finally, they have the potential to generate multiple excitons by one-photon absorption, which can potentially increase the photovoltaic conversion efficiency up to 44%. This process is called multiple exciton generation (MEG) [5-8]. If MEG is used effectively, the photocurrent could be improved significantly.

Despite of the above attractive potential effects of QDSSCs, their maximum conversion efficiency still lags behind dye-sensitized solar cells (DSSCs) [9-12]. Fundamental studies are needed to shed light on the physics and chemistry governing the poor initial performance of QDSSCs when compared to dye-sensitized solar cells (DSSCs). To improve the present QDSSC performance, there are several approaches: (1) enhance the QD loading onto the TiO₂ surface, (2) passivate the surfaces of the QDs and the TiO₂ to reduce excited carrier recombination [13], and (3) develop novel electrolytes and counter electrodes for QDSSCs [14].

Presently, nanostructured TiO₂ thin films are widely used as working electrodes in QDSSCs for the adsorption of QDs. In particular, agglutinated TiO₂ nanoparticles (NPs) thin film electrodes have often been employed because of their high surface area for adsorbing QDs, resulting in enhanced photocurrent [15, 16]. Therefore, NP-TiO₂ electrodes have been used extensively for QDSSCs. On the other hand, there are many grain boundaries between the TiO₂ nanoparticles in NP-TiO₂ films. As a result, NP-TiO₂ has the disadvantage of low electron transport because of the interfacial resistance and electron scattering [17].

One of the main factors determining the photovoltaic performance is the morphology of the TiO₂ thin film electrodes. Recently, TiO₂ electrodes with various morphologies, for example, nanotubes (NTs) [18-22] and inverse opal (IO) [23, 24] structures, as well as

NP-TiO₂, have been studied to explore the effects of the TiO₂ morphology on various properties, such as the electron transfer and photovoltaic properties of QDSSCs. In particular, NT-TiO₂ thin films, which has the advantage of smooth electron transport because of its one-dimensional structure, has been reported as being a potential material for the electrodes for QDSSCs [25-29]. NT-TiO₂ thin films can be fabricated in various ways, such as by the sol-gel method [30, 31], template-assisted methods [32, 33], or the electrochemical-anodization-oxidation (ECAO) method [19-22]. Liquid-phase-deposition (LPD) has been proposed as a template-assisted method [34]. Of these synthetic methods for fabricating NT-TiO₂, LPD is a high-performance growth technique, which is particularly attractive because of its low cost and environmental friendliness [34]. Furthermore, through using the LPD method, transparent conductive films, such as fluorine-doped tin oxide (FTO) or indium tin oxide (ITO), can be employed as substrates for the NT-TiO₂ array. Therefore, the NT-TiO₂ electrodes and QD sensitizer can be directly illuminated by sunlight, resulting in high efficiency solar cells [34, 35]. This is difficult for NT electrodes prepared on titanium substrates using the ECAO method.

The LPD method contains a procedure in which TiO₂ is deposited on the surface of a ZnO nanorod (NR) template in a precursor solution [34]. To obtain high quality NT-TiO₂ with the TiO₂ layer stacked uniformly, it is important to control the TiO₂ growth rate on the ZnO-NR surface in the precursor solution. However, there are few reports that discuss these phenomena, especially the reaction temperature dependence of the NT-TiO₂ growth. The defects, disorder and surface morphology are dependent on the LPD preparation conditions, particularly the deposition temperature.

In general, chemical reaction rates can be expressed by the Arrhenius equation [36]. Therefore, the chemical reaction rate constant k is strongly dependent on the deposition temperature, and the deposition temperature greatly affects the TiO₂ growth rate. In other words, the formation of TiO₂ on the template can be varied by changing the deposition temperature. Thus, it is expected that the surface morphology and intrinsic state of the defects and disorder in the NT-TiO₂ can be changed by changing the deposition temperature. Consequently, the photovoltaic characteristics of QDSSCs using NT-TiO₂ electrodes correlate with the deposition temperature, as a result of differences in the surface morphology and the defects/disorder in the NT-TiO₂.

In this work, we report on the effects of the deposition temperature on the surface morphology and defects in NT-TiO₂ electrodes grown by the LPD method. The analysis was done using optical absorption, X-ray diffraction (XRD), photoluminescence (PL) and open circuit voltage decay (OCVD) measurements. We investigated the differences in the characteristics of the defects in NT-TiO₂ prepared at different deposition temperatures, and the effect of the defects on the photovoltaic characteristics of CdSe QD-sensitized NT-TiO₂ solar cells. In addition, we studied the effect of the defects on the physical properties, such as carrier recombination and electron transport, at the interface between the TiO₂ and the QDs.

2. Experimental details

2.1 Sample preparation

By the liquid phase deposition (LPD) method [34], NT-TiO₂ were prepared on FTO substrates (10 Ω/sq). First, a ZnO-NR template was fabricated using a method described in previous reports [34]. A ZnO seed-layer was formed on the FTO substrate by using spin coating method. The substrate was then deposited in an aqueous solution of Zn(NO₃)₂·6H₂O (25 mM) and Hexamethylenetetramine (25 mM) at 93°C for 9 h to fabricate the ZnO-NR template. After that, the substrate was removed from the solution and annealed at 400 °C for 1 h in air. Secondly, TiO₂ was deposited on the ZnO-NR template by the following LPD method. The substrates with ZnO-NR templates were immersed in aqueous solution including Ammonium-hexafluorotitanate (0.07 M) and boric acid (0.5 M) at various temperatures (in this study; 5°C - 50°C) for 3 h to deposit TiO₂ layers on the surfaces of the templates, and to simultaneously dissolve the templates. After preparing the NT-TiO₂, the substrate was removed from the solution and annealed at 450 °C for 2 h. Scanning electron microscopy (SEM) images of the NT-TiO₂ films were observed. The thickness of the NT-TiO₂ film was measured using a contact profilometer (ULVAC, DEKTAK).

CdSe QDs are used as sensitizers for QD sensitized NT-TiO₂ solar cells. The CdSe QDs were adsorbed onto the NT-TiO₂ electrodes by a chemical bath deposition (CBD) method [37]. The NT-TiO₂ electrodes were immersed into a mixture of CdSO₄ (80 mM), N(CH₂COONa)₃ (120 mM), and Na₂SeSO₃ (80mM) solution for 6 h at 10°C. After adsorption of the electrodes with CdSe QDs, they were coated with ZnS using a successive ionic layer adsorption and reaction (SILAR) method [38]. For the ZnS coating, the

TiO₂/CdSe-QD electrode was deposited in two different solutions for ~1 min each, one consisting of 0.1 M Zn(CH₃COO)₂ dissolved in distilled water and the other containing 0.1 M Na₂S dissolved in distilled water. Following each deposition, the films were rinsed with distilled water for 1 min. This deposition cycle was repeated two times.

2.2 Characterization

The TiO₂ electrodes strongly scatter the incident light. Hence, the PA technique, which is useful for opaque samples and those that optically scatter light [39, 40] was used for measuring the optical absorption spectra of the CdSe QD sensitized TiO₂ electrodes. In the PA technique, modulated light absorbed by a sample is converted into acoustic wave, which is then detected by a microphone, obtaining optical absorption spectra of the sample [39]. In this study, the PA technique was carried out in the wavelength range between 270 and 850 nm at a modulation frequency of 33 Hz at room temperature. The intensity of the PA signal is proportional to the optical absorption coefficient (α) the sample except in the saturation region of the PA signal [39].

The PL spectra of the NT-TiO₂ electrodes were measured at room temperature using a spectrophotometer (JASCO, FP-6500). A 150 W xenon lamp was used as the excitation light source. In this study, the excitation wavelength was 345 nm (3.6 eV).

Sandwich structure solar cells consisting of CdSe QD sensitized NT-TiO₂ working electrodes and Cu₂S counter electrodes were employed to measure the photocurrent density-photovoltage (J-V) characteristic. A polysulfide electrolyte including S (1M) and Na₂S (1M) solution was used as the regenerative redox couple [41, 42]. The active area of the solar cells was 0.25 cm². The photovoltaic characteristics of the solar cells were measured using a solar simulator (Peccell Technologies, Inc., PEC-L10) at one sun (AM1.5, 100 mW/cm²).

To measure the OCVD [43, 44], the above sandwich structure solar cells in the open-circuit condition were illuminated to a steady voltage under light emitted from a 405 nm laser diode. Then the illumination was turned off, and the voltage decay (from the initial steady-state voltage) was observed. The OCVD was recorded using a digital oscilloscope (IWATSU).

3. Results and discussion

Figure 1 show the surface morphologies of NT-TiO₂ electrodes deposited at different temperatures ((a) 5°C, (b) 10°C, (c) 30°C, (d) 50°C) magnified 20000 times. As shown in Figs. 1(a) and 1(b), the surface morphologies are very smooth. On the other hand, as shown in Fig. 1(c), the surface deposited at 30 °C is rougher than those deposited at 5 °C and 10 °C. Furthermore, as shown in Fig. 1(d), the surface of the NT-TiO₂ sample deposited at 50°C is the roughest, and a large number of small particles have been formed on the surface. These results indicate that at higher temperatures the TiO₂ growth rate is too fast to allow it to be uniformly deposited on the template, resulting in a rougher surface morphology for the electrode. J. H. Lee and co-workers reported that in the case of LPD method, tublar and end-closed NT-TiO₂ were obtained because TiO₂ could be deposited not only on the side-surface of ZnO-NR templates but also on the top-surface of the templates [34]. Therefore, we can consider that our fabricating samples also have tublar and end-closed structures. In addition, some end-opened tubular nanostructures in the same fabrication condition on NT-TiO₂ deposited at 5°C and 10°C could be observed (See Fig. A1).

Figure 2 and Table 1 show the tube diameters and tube lengths of the NT-TiO₂ for different deposition temperatures. As shown in Fig. 2 ((a) diameter, (b) length), both the diameter and length of the NT-TiO₂ increase with increasing deposition temperature. These results indicate that the growth rate of NT-TiO₂ on the template increases with increasing deposition temperature, and these growth rates change rapidly for temperatures above 30°C. The changing growth rate could affect the characteristics of the surface and the defects/disorders in NT-TiO₂.

It may be that the growth rate of the TiO₂ affects the crystal quality, which is related to the defects and disorder in the NT-TiO₂. To examine the crystal quality of each sample, XRD patterns were measured. Figure 3 shows the XRD patterns ((a) $2\theta = 20^\circ - 60^\circ$, (b) $2\theta = 20^\circ - 30^\circ$), and Table 2 shows the FWHMs of the peaks for each NT-TiO₂ sample. As shown in Fig. 3(a), the XRD patterns of each NT-TiO₂ sample indicate the anatase structure. Furthermore, as shown in Fig. 3(b) and Table 2, the FWHM of the peaks for the (101) phase for samples prepared at 5 °C and 10 °C are almost the same. On the other hand, the value of the FWHM of NT-TiO₂ increases with increasing deposition temperature above 10°C. Therefore, the results indicate that the crystal quality of NT-TiO₂ prepared at higher deposition temperatures

(30°C and 50°C) decreases compared with lower deposition temperatures (5°C and 10°C), as a result of the TiO₂ growth rate being too fast (discussed below).

To characterize the defect states in each NT-TiO₂, we applied PL spectroscopy. According to previous reports, in the case of anatase TiO₂, the PL peak signal appears at around 3.3 eV (interband), 3.0 eV, 2.6 eV and 2.3 eV, resulting from defects, for example, oxygen vacancies and/or surface defects [45, 46]. Figure 4 shows the PL spectra (normalized at 3.3 eV) of NT-TiO₂ for different deposition temperatures. The PL spectra for 5°C (black line) and 10°C (red line) are almost the same, suggesting that the defects in these samples are similar to each other. On the other hand, the PL intensity below 3.0 eV for NT-TiO₂ (which is considered to result from defects in the TiO₂) deposited at 30°C and 50°C are higher than those deposited at 5°C and 10°C. As a result, both the shallow level (around 3.0 eV) and the deep level (around 2.6 eV and 2.3 eV) increase with increasing deposition temperature. These results imply that there are more defects in NT-TiO₂ deposited at 30°C and 50°C than at 5°C and 10°C, indicating that the defect density in NT-TiO₂ increases with deposition temperature. These results are consistent with the XRD measurement results. Moreover, these PL measurement results indicate that the rate of electron trapping by deep states caused by the defects and disorder in the NT-TiO₂ increase with increasing deposition temperature. It is considered that these deep states might act as recombination centers. The density of these deep states in NT-TiO₂ can affect the photovoltaic characteristics of CdSe QD-sensitized NT-TiO₂ solar cells (discussed below).

The difference in surface morphology of the NT-TiO₂ can be expected to have some effect on the adsorption of CdSe QDs on the NT-TiO₂ electrodes and the corresponding photovoltaic properties. To confirm the growth and evaluate the average diameter of the CdSe QDs, their PA spectra were measured (SEM images of NT-TiO₂ adsorbed with CdSe QDs at each deposition temperature are shown in Fig. A2 ((a) 5°C, (b) 10°C, (c) 30°C, (d) 50°C)). Figure 5 shows the PA spectra of NT-TiO₂ electrodes sensitized with CdSe QDs for which the TiO₂ was deposited at different temperatures. Optical absorption by the NT-TiO₂ sensitized with CdSe QDs occurs in the visible region and redshifts in the PA spectra can clearly be observed. These results demonstrate the growth of the CdSe QDs on the TiO₂ electrodes. The average diameter of the QDs was estimated by the effective mass approximation (EMA) [47, 48] as shown in eq. (1),

$$\Delta E = E_1 - E_g = \frac{h^2}{8r^2} \left(\frac{1}{m_e} - \frac{1}{m_h} \right), \quad (1)$$

where ΔE is the bandgap shift, E_1 is the first excitation energy level, E_g is the bandgap energy, r is the quantum dot radius, and m_e , m_h , and m_0 are the effective electron mass, hole mass, and electron rest mass, respectively ($m_e = 0.13 m_0$, $m_h = 0.44 m_0$, and $m_0 = 9.11 \times 10^{-31}$ kg [49]). Determination of the bandgap by the energy of the shoulder position in the PA spectrum has previously been reported [50, 51]. Thereby, the average diameter of the QDs can be calculated from the photon energy of the shoulder position in the PA spectra, which is assumed to correspond to the first excitation energy E_1 of the QDs [50-52]. Table 3 shows E_1 and the average diameters of the CdSe QDs, which are identical for the different temperatures at which the NT-TiO₂ was deposited.

Figure 6 shows the J-V characteristics of the CdSe QDSCCs using NT-TiO₂ electrodes. The values of J_{sc} , V_{oc} , FF, η , series resistance (R_s), and shunt resistance (R_{sh}) of the TiO₂ electrodes prepared at different deposition temperatures are shown in Table 4. At relatively low deposition temperatures the values of J_{sc} , V_{oc} , and FF are almost same (the values at 10°C are slightly higher than those at 5°C). On the other hand, J_{sc} , V_{oc} , and FF dramatically decrease for deposition temperatures higher than 10°C. As a result, the maximum value of the photovoltaic conversion efficiency η is 3.1 % at 10°C. Similarly, the values of R_{sh} for 5°C and 10°C are almost the same, and decrease dramatically above 10°C. In general, R_{sh} is related to the recombination of electrons injected into the TiO₂ with the holes in the QDs and/or in the electrolyte (back electron transfer) [53]. A higher R_{sh} indicates less back electron transfer [43, 53]. As shown in Table 4, R_{sh} for NT-TiO₂ prepared at 5°C and 10°C is more than two and three times higher than that for NT-TiO₂ prepared at 30°C and 50°C, respectively, suggesting that the back electron transfer rate from the NT-TiO₂ to the QDs and/or electrolyte is less in the former than in the latter. The back electron transfer rate could also affect the open circuit voltage V_{oc} of the solar cells [53]. Less back electron transfer results in a higher V_{oc} and R_{sh} . As shown in Table 4, the value of V_{oc} of CdSe-QD-sensitized NT-TiO₂ electrodes prepared at 5°C and 10°C is 13 % and 38 % higher than that for electrodes prepared at 30°C and 50°C, respectively. From the results of the surface morphologies and PL spectra of NT-TiO₂ prepared at different deposition temperatures

discussed above, it is considered that the defects increase with increasing deposition temperature. This suggests that the electron trapping states resulting from defects in the NT-TiO₂ increase with increasing deposition temperature. As a result, the back electron transfer rates of CdSe QD-sensitized NT-TiO₂ electrodes prepared at higher deposition temperatures (30°C and 50°C) were larger compared with those prepared at lower deposition temperatures (5°C and 10°C). Consequently, the values of R_{sh} and V_{oc} for NT-TiO₂ electrodes prepared at higher temperatures were smaller than those prepared at lower temperatures. Similarly, the values of FF for the former electrodes (prepared at 30°C and 50°C) were smaller than those for the latter ones (prepared at 5°C and 10°C) due to lower R_{sh} . Furthermore, it is considered that, since the back electron transfer rate increases with the temperature at which the NT-TiO₂ was prepared due to the increasing number of defects, the number of electrons extracted to the external circuit would be reduced. As a result, the values of J_{sc} of the CdSe QD-sensitized NT-TiO₂ electrodes prepared at higher temperatures were smaller than those prepared at lower temperatures. As shown in Table 4, R_s for the solar cells including NT-TiO₂ electrodes prepared at higher deposition temperatures (30°C and 50°C) were larger compared with those of the solar cells with NT-TiO₂ electrodes prepared at lower deposition temperatures (5°C and 10°C). R_s includes the resistance against electron (hole) transfer to the forward direction through the TiO₂ and the QD/TiO₂ interface. The diffusion and scattering of the electrons (holes) by defects can be considered to also affect R_s [17, 53]. since electron diffusion in NT-TiO₂ would become lower and the scattering rate would increase with defect density increasing. However, R_s didn't dramatically change compared with R_{sh} . Electron trapping and detrapping at shallow levels in anatase-TiO₂ are very important factors for the electron transport [17]. As shown in Fig. 4, the PL intensity at around 3.0 eV of NT-TiO₂ prepared at higher deposition temperatures is larger than that prepared at lower deposition temperatures. Therefore, it is expected that electron trapping and detrapping increases with increasing shallow levels. To confirm this expectation, future studies (evaluation of diffusion coefficients in NT-TiO₂, and so on) are needed.

To further investigate the defects in NT-TiO₂ prepared at each of the deposition temperatures, we measured the OCVD of the CdSe QD-sensitized NT-TiO₂ solar cells. In using the OCVD measurement, the electron lifetime in NT-TiO₂ can be understood from the decay of V_{oc} , following equation (2) [43]. This shows the OCVD measurement to be a

powerful tool for studying the electron lifetime in NT-TiO₂ [43].

$$\tau = \frac{k_B T}{e} \left(\frac{dV_{oc}}{dt} \right)^{-1}, \quad (2)$$

where τ is the electron lifetime, k_B is Boltzmann's constant, T is the absolute temperature, and V_{oc} is the open circuit voltage. Figure 7 shows the V_{oc} decay curves of CdSe QD-sensitized NT-TiO₂ solar cells prepared at different deposition temperatures under open circuit conditions. As shown in Fig. 7, in the range of deposition temperatures from 5°C to 10°C, with increasing deposition temperature, the decay of V_{oc} in the solar cells becomes slower. On the other hand, as the deposition temperature increases from 10°C to 50°C, the decay of V_{oc} becomes faster. In this case, V_{oc} depends on the electron density in the TiO₂ [43]. When the recombination rate in the TiO₂ is larger, the V_{oc} decay is faster because the excited electrons in the TiO₂ disappear quickly, resulting in a lower Fermi level. These results suggest that the recombination rate in NT-TiO₂ prepared at 5°C is larger than that prepared at 10°C. There are two possible reasons for these differences. One is that there is a larger defect density in NT-TiO₂ prepared at 5°C compared with that prepared at 10°C, and the other is that NT-TiO₂/CdSe interfaces have different properties for NT-TiO₂ prepared at different temperatures. According to XRD and PL results of NT-TiO₂ prepared at 5°C and 10°C as discussed earlier, we can know that the defect characteristic in these samples were almost the same. Therefore, we can consider that the second one, that is the difference in NT-TiO₂/CdSe interface may affect V_{oc} decay (electron lifetime), is more reasonable. Further study will be carried out to understand the differences.

Additionally, Table 5 shows the value of τ (τ is the value determined when V_{oc} is 0.5 V.) in CdSe QD-sensitized NT-TiO₂ solar cells prepared at different deposition temperatures estimated using equation (2). Similar to the V_{oc} decay curves shown in Fig.7, τ for the electrodes prepared at 10°C is larger than for those prepared at 5°C. Then, τ decreases dramatically as the deposition temperature for the NT-TiO₂ increases from 10°C to 50°C. The electron lifetime τ is related to the recombination rate [43] between electrons in the TiO₂ and holes in the QDs and/or the electrolyte. In the case of recombination between electrons in the TiO₂ and holes in the QDs and/or electrolyte, this recombination occurs after back electron transfer from the TiO₂ to the QDs and/or the electrolyte. The electron lifetime τ becomes

larger with lower recombination rates. Therefore, these results suggest that the recombination rate of CdSe QD-sensitized solar cells with NT-TiO₂ prepared at 10°C is the lowest. That is to say, the defects in the NT-TiO₂ are considered to act as recombination centers. The carrier recombination increases with the increasing defect density in NT-TiO₂ prepared at higher temperatures.

These results imply that at relatively low deposition temperatures, especially at 10°C, a regularly structured Ti-O network is formed in the NT-TiO₂. On the other hand, at higher temperatures, it is expected that the TiO₂ reaction rate is too fast to form a regularly structured Ti-O network. Therefore, the ensuing defect density is higher for NT-TiO₂ prepared at higher deposition temperatures than at lower ones. As a result, the electron lifetime τ for the solar cells with NT-TiO₂ prepared at higher temperatures is much smaller than those prepared at lower temperatures.

4. Conclusions

Using SEM images, XRD analysis and PL spectroscopy, we observed that NT-TiO₂ thin films prepared at low deposition temperatures (5°C and 10°C) have smoother surfaces and fewer defects than those prepared at high deposition temperatures (30°C and 50°C). These differences can be considered to result from the differences between the TiO₂ growth conditions on the template or on the previously stacked TiO₂ layer due to the different deposition temperatures. The results indicate that low temperature deposition conditions for the growth of the TiO₂ are needed to obtain a smooth surface and few defects in the NT-TiO₂.

From the photovoltaic characterization, the value of V_{oc} and R_{sh} decrease with increasing deposition temperature. In addition, the V_{oc} decay of CdSe QD-sensitized solar cells with NT-TiO₂ electrodes prepared at high deposition temperatures is much faster than that of those prepared at low deposition temperatures. These results suggest that the carrier recombination increases as the defect density increases. R_s on the solar cells with NT-TiO₂ electrodes prepared at high temperatures increase compared with those with NT-TiO₂ electrodes prepared at low temperatures, suggesting that the defects can also affect the carrier transport characteristics.

As a result, CdSe QD-sensitized NT-TiO₂ solar cells using NT-TiO₂ prepared at low temperatures showed higher conversion efficiencies than those prepared at high temperatures.

In this work, a maximum photovoltaic conversion efficiency of 3.1% was achieved for the CdSe QD-sensitized NT-TiO₂ solar cells prepared at 10°C.

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Table

Table 1. Diameters and lengths of NT-TiO₂ thin films deposited at different temperature in the TiO₂ precursor solution.

Deposition Temperature (°C)	diameter (nm)	length (μm)
5	100	2.5
10	110	2.6
30	160	2.7
50	330	4.0

Table 2. The values of full width at half maximum (FWHM) of the (101) phase NT-TiO₂ thin films.

Deposition Temperature (°C)	FWHM (deg)
5	0.3
10	0.4
30	0.8
50	1.0

Table 3. The first excitation energy level (E_1) and diameter of the CdSe QDs adsorbed on the NT-TiO₂ thin film electrodes.

Deposition Temperature (°C)	E_1 (eV)	Diameters (nm)
5	2.0	7.6
10	2.0	7.6
30	2.0	7.6
50	2.0	7.6

Table 4. Photovoltaic properties of solar cells using NT-TiO₂ electrodes deposited at different temperatures adsorbed with CdSe QDs. J_{sc}, V_{oc}, FF, η, R_{sh}, and R_s are the short-circuit current density, open-circuit voltage, fill factor, photovoltaic conversion efficiency, shunt resistance, and series resistance, respectively.

Deposition Temperature (°C)	J _{sc} (mA/cm ²)	V _{oc} (V)	FF	η (%)	R _{sh} (10 ³ Ωcm ²)	R _s (Ωcm ²)
5	8.5	0.72	0.50	3.0	0.41	30
10	8.6	0.72	0.51	3.1	0.40	30
30	6.7	0.64	0.47	2.0	0.19	50
50	4.5	0.53	0.37	0.87	0.13	40

Table 5. Electron lifetime (τ) in NT-TiO₂ electrodes deposited at different temperatures in the TiO₂ precursor solution. τ is the estimated value at which V_{oc} is 0.5 V.

Deposition temperature (°C)	τ (s)
5	12
10	20
30	2.8
50	1.2

Figure Captions

Fig. 1. SEM images of NT-TiO₂ thin film electrodes deposited at different temperatures in the TiO₂ precursor solution [(a) 5 °C, (b) 10 °C, (c) 30 °C, and (d) 50 °C].

Fig. 2. Dependence of the (a) tube diameter and (b) tube length on the temperature of the TiO₂ precursor solution.

Fig. 3. XRD patterns of NT-TiO₂ thin film electrodes deposited at different temperatures in the TiO₂ precursor solution [(a) from $2\theta = 20^\circ$ to 60° , (b) from $2\theta = 20^\circ$ to 30°].

Fig. 4. PL spectra of the NT-TiO₂ thin films deposited at different temperatures in the TiO₂ precursor solution.

Fig. 5. PA spectra of CdSe QDs adsorbed on NT-TiO₂ electrodes deposited at different temperatures in the TiO₂ precursor solution.

Fig. 6. Photovoltaic characteristics of CdSe QD-sensitized NT-TiO₂ solar cells for which the NT-TiO₂ was deposited at different temperatures in the TiO₂ precursor solution.

Fig. 7. Decay curves of V_{oc} on CdSe QD-sensitized NT-TiO₂ solar cells for which the NT-TiO₂ was deposited at different temperatures in the TiO₂ precursor solution.

Fig. A1. SEM images of NT-TiO₂ in the same fabrication condition on those shown in Fig 1 [(a) 5 °C, (b) 10 °C].

Fig. A2. SEM images of NT-TiO₂ thin film electrodes deposited at different temperatures in the TiO₂ precursor solution adsorbed with CdSe [(a) 5 °C, (b) 10 °C, (c) 30 °C, and (d) 50 °C].

Figure

Fig. 1 Masaya Akimoto et al.

Fig. 2 Masaya Akimoto et al.

Fig. 3 Masaya Akimoto et al.

Fig. 4 Masaya Akimoto et al.

Fig. 5 Masaya Akimoto et al.

Fig. 6 Masaya Akimoto et al.

Fig.7 Masaya Akimoto et al.

Appendix

NT-TiO₂ prepared at a deposition
temperature of 5°C (× 50,000)
in same fabrication condition
on Fig. 1 (a) sample

NT-TiO₂ prepared at a deposition
temperature of 10°C (× 50,000)
in same fabrication condition
on Fig. 1 (b) sample

Fig. A1 Masaya Akimoto et al.

(a) NT-TiO₂ prepared at a deposition temperature of 5°C adsorbed with CdSe ($\times 50,000$)

(b) NT-TiO₂ prepared at a deposition temperature of 10°C adsorbed with CdSe ($\times 50,000$)

(c) NT-TiO₂ prepared at a deposition temperature of 30°C adsorbed with CdSe ($\times 50,000$)

(d) NT-TiO₂ prepared at a deposition temperature of 50°C adsorbed with CdSe ($\times 50,000$)

Fig. A2 Masaya Akimoto et al.