# Tuned Optical Reflection Characteristics of Chemically-Treated Ti Substrates

Ho-Gyeong Yun, Myoung Kim, and In-Kyu You

*Titanium foils for use in photoelectrochemical devices are treated with a $HNO_3$-HF solution. After this treatment, the optical reflection characteristics of the Ti substrates are markedly increased in terms of not only reflectivity but also optimized wavelength. Furthermore, the "multiple beam interference" theory and optical analysis of surface morphologies clearly verify the origin of the optimized optical reflection properties.*

*Keywords: Optical reflectance, color variation, titanium.*

## I. Introduction

$TiO_2$ on metal substrates allows for desirable photoelectrochemical devices, such as photovoltaic cells [1] and photocatalytic water splitting systems [2]. Particularly, the anatase form $TiO_2$ on Ti substrates is preferred, due to its high efficiency, low cost, chemical inertness, and photostability [3]. Regarding optical wavelength, different photoelectrochemical devices utilize different ranges. For example, an anatase form $TiO_2$-based photocatalytic water splitting system generates the $e^-/h^+$ precursor only with ultraviolet (UV) light (< 387.5 nm), rendering the use of solar irradiation inefficient [4]. On the other hand, a dye-sensitized solar cell (DSSC), a kind of photoelectrochemical device, produces a current using visible light. A considerable amount of visible light transmits the dye-coated $TiO_2$ electrode to generate the current in the DSSC system without causing an electron-generating reaction. Nevertheless, the performance of each device will significantly increase if the substrate reflects the transmitted light of the available wavelength well, because the light that is not utilized in the energy conversion process is reflected rather than absorbed [5]. In detail, if the substrate were to reflect the UV light or visible light well, it would be helpful to the anatase form $TiO_2$-based photocatalytic water splitting system or the DSSC, respectively. To strengthen the utilization of transmitted light, Poullou and others proposed an electrochemical method that uses the Ti substrates for multiple reflection [5]. However, the cavity for multiple reflection was formed by complicated processes, and the wavelength of the reflected light was not controlled in that structure. In the case of a DSSC, a bi-layer structure of $TiO_2$ was proposed for the use of transmitted light, including a 20-nm-sized photoactive layer and a 400-nm-sized scattering layer [6]. However, the light is illuminated from a counter electrode, that is, back illumination, in the DSSCs based on the $TiO_2$ on metal substrates [7]. The light-scattering layer should be located between 20-nm-sized $TiO_2$ particles and metal substrates accordingly. However, this structure causes poor adhesion of the scattering layer to the metal substrate because of the relatively large particle size of the scattering layer. The optical reflection characteristics of the substrates, therefore, could be very significant in the DSSCs with the back illumination system. In the present study, we report that acid treatment of the Ti substrates for the nanocrystalline-$TiO_2$ photoelectrode significantly improves the optical reflection characteristics in terms of not only reflectivity but also optimized wavelength.

## II. Experimentation

**Preparation.** Prior to chemical treatment, the surfaces of the Ti foils (Goodfellow, 0.1 mm thickness) are cleaned in both acetone and deionized water and then the substrates are

---

Manuscript received May 11, 2012; revised July 11, 2012; accepted July 19, 2012.

This work was supported by the ETRI and Small & Medium Business Administration, Rep. of Korea [SL122749].

Ho-Gyeong Yun (corresponding author, phone: +82 42 860 5017, yunhg@etri.re.kr), Myoung Kim (kimmyoung@etri.re.kr), and In-Kyu You (ikyou@etri.re.kr) are with the Convergence Components & Materials Research Laboratory, ETRI, Daejeon, Rep. of Korea.

http://dx.doi.org/10.4218/etrij.12.0212.0204

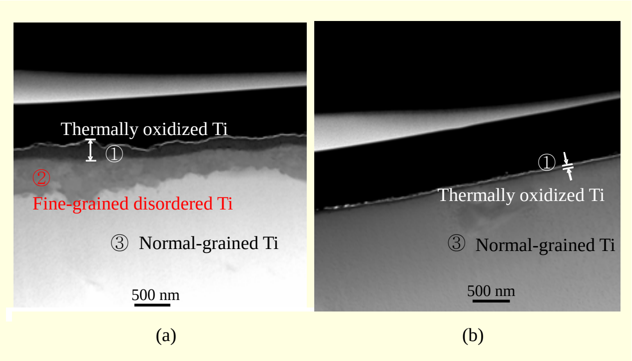


Fig. 1. Cross-sectional STEM images of (a) nontreated and (b) $HNO_3$-HF-treated Ti substrate after thermal annealing.

subjected to a chemical treatment in a 0.8 M ~ 3.5 M $HNO_3$-HF solution for three minutes, followed by another ultrasonic cleaning process. Among several metal-oxidation methods [8], thermal annealing at 550°C under an air atmosphere is performed for the oxidization of the Ti foil.

**Characterization.** The microstructures of the Ti substrates are inspected using scanning transmission electron microscopy (STEM) (Hitachi, HD2300A). Optical reflectance and color variations are identified using UV-VIS-NIR spectrophotometers combined with an integrated sphere (Varian, Cary 100 & DRA-CA-300) and a microlens system (Canon, EF 100 mm). The roughness factors and incident light angle of the substrates are optically identified with a scanning white light interferometer (Zygo, Newview7300).

## III. Results and Discussion

Ti is resistant to corrosion in many acidic solutions. However, hydrofluoric acid dissolves Ti, according to reaction (1) [9]:

$$Ti + 3HF \rightarrow Ti^{3+} + 3/2H_2 + 3F^-. \quad (1)$$

To avoid the formation of hydride, a solution of $HNO_3$-HF, rather than HF alone, is used. Figures 1(a) and 1(b) respectively show cross-sectional STEM images of nontreated and HF-$HNO_3$-treated Ti surfaces after thermal annealing. As shown in Fig. 1(a), a nontreated Ti substrate consists of three parts, that is, ① thermally oxidized Ti (ca. 100 nm), ② fine-grained disordered Ti, and ③ normal-grained Ti. The fine-grained disordered Ti layer at the outermost surface of the nontreated Ti substrate could be attributed to the thermomechanical manufacturing process [10]. In contrast, a more uniform and thinner thermally oxidized Ti layer (ca.<50 nm) is exhibited in a $HNO_3$-HF-treated Ti substrate. This means that the treatment of the Ti substrate both eliminates the fine-grained disordered Ti layer at the outermost surface and affects the surface morphology and characteristics of the thermally oxidized layer [11].

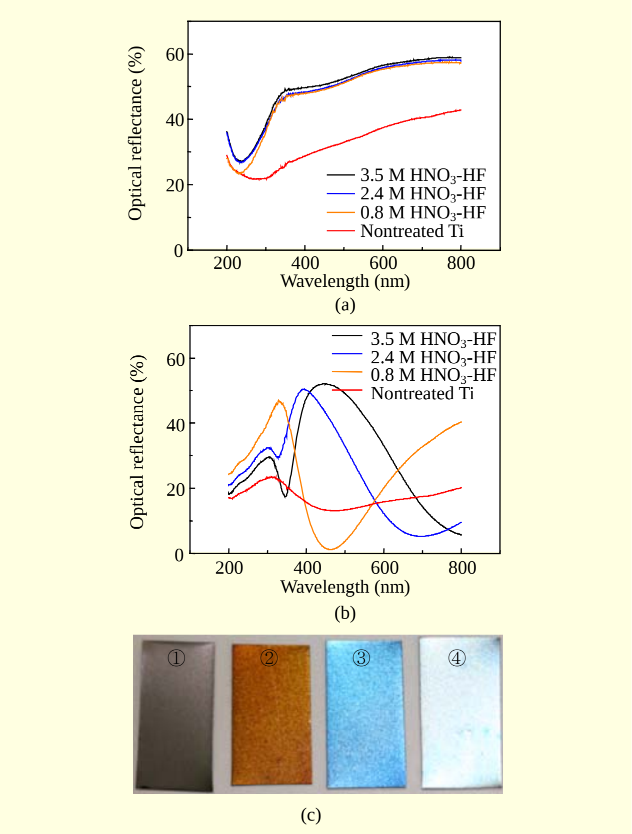
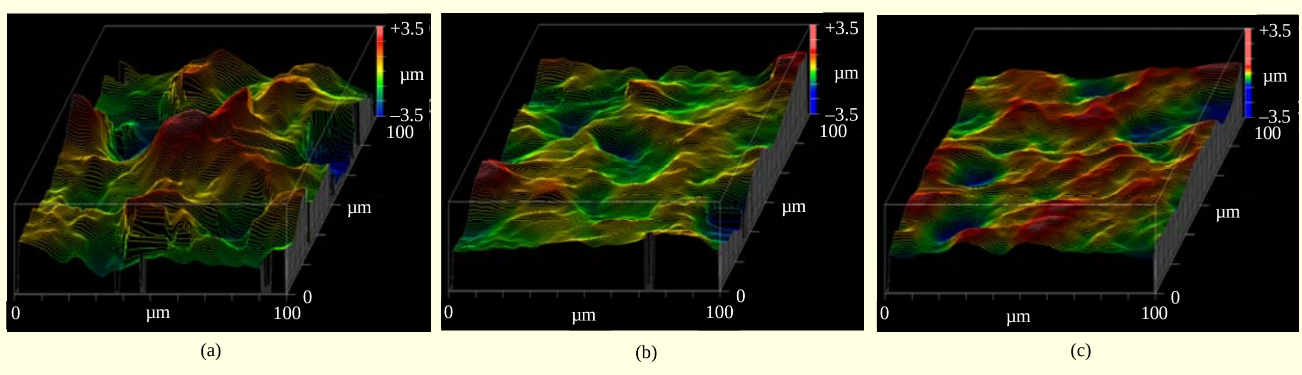


Fig. 2. Optical reflectance of Ti substrates (a) before and (b) after thermal oxidation. (c) Photographs of Ti substrates after thermal oxidation: ① nontreated and treated in ② 0.8 M $HNO_3$-HF, ③ 2.4 M $HNO_3$-HF, and ④ 3.5 M $HNO_3$-HF.

The $HNO_3$-HF treatment combined with subsequent thermal annealing considerably alters the optical reflection properties of the Ti substrates in terms of reflectivity and optimized wavelength. Figures 2(a) and 2(b) respectively show the optical reflection of the Ti substrates with the UV-VIS-NIR spectrophotometers before and after thermal oxidation at 550°C. Although, the optical reflectivity at metal surfaces could be very high [12], the nontreated Ti substrate exhibits a poor reflection characteristic, as shown in Fig 2(a). However, chemical treatment of the Ti substrates using a $HNO_3$-HF solution, regardless of the solution composition, enhances the reflectivity of the Ti substrates before thermal annealing. The enhanced optical reflectance in the $HNO_3$-HF-treated Ti substrate could be attributed to the elimination of the fine-grained disordered region (Fig. 1), considering that the optical properties of solids are closely related to the size of the grain boundaries or to the degree of crystallinity [13].

After annealing at 550°C, more dramatic variations of optical reflection behavior, depending on the composition of the $HNO_3$-HF solution, are observed in the $HNO_3$-HF-treated Ti substrate (Fig. 2(b)). In addition, the positions of minimal



(a) (b) (c)

Fig. 3. Zygo images of $HNO_3$-HF-treated Ti surface after thermal annealing at 550°C for 30 min. Solution compositions were (a) 0.8 M $HNO_3$-HF, (b) 2.4 M $HNO_3$-HF, and (c) 3.5 M $HNO_3$-HF.

reflectance, that is, maximal absorbance, also shift from 463 nm, 694 nm, and > 800 nm. These variations of the optical properties in the visible light range also produce the diverse colors shown in Fig. 2(c).

According to [14], [15], the color variation of Ti passive films originates from interference (iridescence) of the reflected light from thin transparent oxides and the light reflected at the inner metal surface. Airy developed the multiple beam interference theory to explain these phenomena [16]. In addition, absorption or reflection by a range of wavelengths, rather than a single wavelength, is attributed to the nonuniform thickness of the oxide layer [12], [14]. Compared with the $HNO_3$-HF-treated Ti substrates (Fig. 1(b)), the thickness of the oxide layer of the nontreated Ti substrates is much greater and more variable (Fig. 1(a)), irrespective of the same oxidation condition. This thick and nonuniform oxide layer of the nontreated Ti substrate might result from the uneven distribution of the fine-grained disordered section at the outermost surface because development of the oxide layer is more pronounced at the disordered layer [17]. Thus, the low and flat reflection behavior of the nontreated Ti substrates after thermal annealing is attributed to the nonuniform thickness of the oxide layer and the inferior optical reflectance at the inner metal surface [11]. However, the optical characteristics of the $HNO_3$-HF-treated Ti substrates vary with the solution composition, though all of the fine-grained disordered regions are completely removed and oxide layers form under the same oxidation conditions, that is, 550ºC (Fig. 1(b)). This variation with different solution compositions could be attributed to the morphological changes as can be verified by the discussion given below. The phase lag $\delta$ is closely related to both the thickness of the oxide layer and the incident light angle [18]:

$$\delta = \frac{2\pi}{\lambda} 2nd \cos\phi, \tag{2}$$

where $\phi$ is the incident light angle, $n$ is the refractive index, and $d$ is the distance between the surfaces, that is, the thickness of the oxide layer in this study. The morphological variations of the Ti substrates are optically analyzed using a scanning white light interferometer (Zygo).

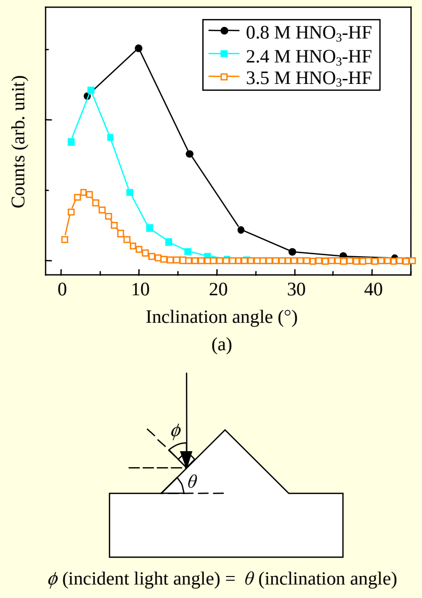
Figure 3 shows the surface morphologies, and Table 1 summarizes the roughness factors of the Ti substrates treated with a mixture of (a) 0.8 M $HNO_3$-HF, (b) 2.4 M $HNO_3$-HF, and (c) 3.5 M $HNO_3$-HF and subsequent thermal annealing at 550ºC. Figure 4(a) exhibits the distribution of the inclination angle treated with various compositions of a $HNO_3$-HF solution on the Ti substrate. The most dominant inclination angles of the treated Ti substrates, which are equal to the most dominant incident light angles, as depicted in Fig. 4(b), are 2.80°, 3.76°, and 9.89°. The irregular morphologies of the substrates make it difficult to derive any exact relationship. However, at the higher $HNO_3$ concentration, the roughness of the Ti substrates decline, which is indicative of a reduction in the incident light angle. Delplancke and others reported that the most strongly absorbed wavelength is affected by the oxide-film thickness [15]. However, because the oxidation condition is constant in the present study, we conclude that variations in the incident light angle, rather than the oxide-layer thickness, explain the shift in the most strongly absorbed wavelength that is observed when the $HNO_3$ concentration is changed.

Table 1. As function of solution composition, morphological properties of $HNO_3$-HF-treated Ti surface after thermal annealing at 550°C for 30 min.

(μm)

| No. | Roughness factors | | |
|---|---|---|---|
| | PV[a)] | RMS[b)] | Ra[c)] |
| 0.8 M $HNO_3$-HF | 7.248 | 1.198 | 0.937 |
| 2.4 M $HNO_3$-HF | 4.263 | 0.527 | 0.385 |
| 3.5 M $HNO_3$-HF | 2.805 | 0.371 | 0.300 |

a) maximum peak-to-valley height, b) root-mean-square roughness, c) arithmetical average roughness.



(a)

(b)

Fig. 4. (a) Distribution of inclination angle (incident light angle) of Ti substrates treated with various compositions of $HNO_3$-HF solution and (b) concept of inclination angle.

## IV. Conclusion

In summary, we introduced a very simple but highly-effective surface-treatment method of Ti substrates for use in photoelectrochemical devices, such as photovoltaic cells, including DSSCs and a photocatalytic water splitting system. By virtue of the proposed $HNO_3$-HF treatment, the reflectivity of the Ti substrate was significantly increased. In addition, the reflected wavelength of thermally annealed Ti substrates was optimized, that is, high reflectivity was obtained in the UV or visible region according to the solution compositions. Furthermore, the "multiple beam interference" theory and optical analysis of surface morphologies clearly confirmed that the origin of the optimized optical reflection properties of $HNO_3$-HF-treated Ti substrates are attributed to the varied inclination angles of the substrates.

## References

[1] S. Ito et al., "High-Efficiency (7.2%) Flexible Dye-Sensitized Solar Cells with Ti-Metal Substrate for Nanocrystalline-$TiO_2$ Photoanode," *Chem. Commun.*, 2006, pp. 4004-4006.

[2] A.L. Linsebigler, G. Lu, and J.T. Yates, Jr., "Photocatalysis on $TiO_2$ Surfaces: Principles, Mechanisms, and Selected Results," *Chem. Rev.*, vol. 95, 1995, pp. 735-758.

[3] G.K. Mor et al., "A Review on Highly Ordered, Vertically Oriented $TiO_2$ Nanotube Arrays: Fabrication, Material Properties, and Solar Energy Applications," *Solar Energy Mat. Solar Cells*, vol. 90, 2006, pp. 2011-2075.

[4] J.H. Park, S. Kim, and A.J. Bard, "Novel Carbon-Doped $TiO_2$ Nanotube Arrays with High Aspect Ratios for Efficient Solar Water Splitting," *Nano Lett.*, vol. 6, 2006, pp. 24-28.

[5] M. Poullou et al., "Titanium Wave-like Surface Microstructure for Multiple Reflections in Solar Cell Substrates Prepared by an All-Solution Process," *Scripta Materialia*, vol. 62, 2010, pp. 411-414.

[6] S. Ito et al., "High-Efficiency Organic-Dye-Sensitized Solar Cells Controlled by Nanocrystalline-$TiO_2$ Electrode Thickness," *Adv. Mat.*, vol. 18, 2006, pp. 1202-1205.

[7] H.-G. Yun et al., "Effect of Increased Surface Area of Stainless Steel Substrates on the Efficiency of Dye-Sensitized Solar Cells," *Appl. Phy. Lett.*, vol. 93, 2008, 133311.

[8] H.C. Oh et al., "Improved Stability of Atomic Layer Deposited ZnO Thin Film Transistor by Intercycle Oxidation," *ETRI J.*, vol. 34, no. 2, Apr. 2012, pp. 280-283.

[9] E.M.M. Sutter and G.J. Goetz-Grandmont, "The Behavior of Titanium in Nitric-Hydrofluoric Acid Solutions," *Corro. Sci.*, vol. 30, 1990, pp. 461-476.

[10] P.R.F. Barnes et al., "The Influence of Substrate Etching on the Photoelectrochemical Performance of Thermally Oxidized $TiO_2$ Films," *J. Electrochem. Soc.*, vol. 154, 2007, pp. H249-H257.

[11] H.-G. Yun, B.-S. Bae, and M.G. Kang, "A Simple and Highly Efficient Method for Surface Treatment of Ti Substrates for Use in Dye-Sensitized Solar Cells," *Adv. Energy Mater.*, vol. 1, no. 3, May 2011, pp. 337-342.

[12] W.-Y. Kwong, "High System Performance with Plasmonic Waveguides and Functional Devices," *ETRI J.*, vol. 32, no. 2, Apr. 2010, pp. 319-326.

[13] A. Tamiowy, R. Mania, and M. Rekas, "The Effect of Thermal Treatment on the Structure, Optical, and Electrical Properties of Amorphous Titanium Nitride Thin Films," *Thin Solid Films*, vol. 311, 1997, pp. 93-100.

[14] G. Jerkiewicz, H. Strzelecki, and A. Wieckowski, "A New Procedure of Formation of Multicolor Passive Films on Titanium: Compositional Depth Profile Analysis," *Langmuir*, vol. 12, 1996, pp. 1005-1010.

[15] J.-L. Delplancke et al., "Self-Colour Anodizing of Titanium," *Surface Tech.*, vol. 16, 1982, pp. 153-162.

[16] G.B. Airy, *Mathematical Tracts on the Lunar and Planetary Theories, the Figure of the Earth, Precession and Nutation, the Calculus of Variations, and the Undulatory Theory of Optics*, 2nd ed., Cambridge, UK: University of Cambridge (for J. & J.J. Deighton), 1831, p. 381.

[17] S. Hrapovic et al., "Morphology, Chemical Composition, and Electrochemical Characteristics of Colored Titanium Passive Layers," *Langmuir*, vol. 17, 2001, pp. 3051-3060.

[18] S. Tolansky, *Multiple-Beam Interferometry of Surfaces and Films*, London: Oxford at the Clarendon Press, 1949, ch. 2.