Spectroscopic ellipsometrical studies of UV irradiation effects on the surface properties of the ultra thin native oxide film on titanium*

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Under ultraviolet (UV) irradiation, an ultra thin titanium native oxides film covered by a hydrocarbon contamination (HC) layer on the as-deposited titanium film was investigated by using spectroscopic ellipsometry (SE), atomic force microscopy (AFM) and contact angle meter. Using a stable silicon dioxide sample as a reference provided an insight of the structural change of the titanium native oxide film under UV irradiation. The SE results indicate that UV irradiation can completely remove the adsorbed HC layer both on the Ti sample and on Si sample after 337 min and 4059 min respectively. The titanium native oxide accelerates the HC removing process. The pseudo-optical constants (pseudo- n and pseudo- k) of the Ti composite and the thickness of the surface layer on Ti decreased during UV irradiation, which was considered to be contributed to the changes of the surface properties of the titanium composite film. AFM images on the surface of UV-treated titanium native oxide films present a less root-mean-square (RMS) roughness and many isolated grains with a size of about 10 nm. [DOI: 10.1380/ejssnt.2005.284]

Keywords: titanium oxide; ellipsometry; atomic force microscopy; native oxide; optical constant

I. INTRODUCTION

A titanium native oxide film covered with a hydrocarbon contaminations layer are of crucial importance to the application performance of titanium [1–4]. Understanding the UV-induced effect on the native oxide film on titanium covered with a layer of hydrocarbon contaminations and characterizing this film are of great interest both in scientific and engineering point of view.

Titanium has been widely recognized for its outstanding properties [5, 6]. Under the atmospheric conditions, a thin native oxide film, which is covered by a hydrocarbon contamination layer of rather complex compositions, would grow on the Ti surfaces [3]. Many application properties of titanium are closely related to this native oxide film [7]. For instance, the surface stability and corrosion resistance of titanium metal in ambient environments results from the presence of this surface oxide layer that acts as a kinetic barrier to the transport of ions, atoms, and electrons [8]. Although the oxide layer on metal is chemically stable in most oxidation conditions, recent reports demonstrate that microscopic defect sites within the oxide film can act as efficient shunt pathways for electron transport [9, 10]. So prior to next processing (such as passivation [11]), complete removal of the native oxide layer and the hydrocarbon contamination layer is essential to ensuring that a high density and excellent corrosion resistant passive film is formed. In some case, the native oxide film, which is one of dielectrics and generally resistant to further chemical reaction, makes problematic compatibility between titanium and organics. Localized variations in the thickness, stoichiometry, or crystallography of the oxide film are factors believed to influence the localized conductivity [2, 12].

A number of literatures have been devoted to tita-

nium oxides (mainly TiO_2) produced by various techniques such as sol-gel [13], chemical vapour deposition (CVD) [14], physical vapour deposition (PVD) and electrochemical anodization of bulk titanium (galvanostatic, potentiostatic or potentiodynamic pathways) [15], and reactive cathodic vacuum arc deposition [16]. Due to its remarkable optical, electronic, and chemical properties, titanium dioxide (TiO_2) film has been widely used in many fields of optical coating and protective layer on lenses and optical fibers, humidity and gas sensors, gate electrodes in semiconductors, photocatalytic purifier in environmental cleaning and photochemical solar cells. The recent increased interest in titanium films has led to the application and the fundamental research of this material from its remarkable photocatalysis and hydrophilicity induced by UV-light [17].

TiO_2 is a well-known photocatalyst material. When UV is irradiated onto TiO_2 , electron and hole pairs are generated, which reduce and oxidize adsorbates on the surface, respectively, thereby producing radical species, such as $\text{OH}\cdot$ and $\text{O}_2\cdot$. These radicals can decompose most organic compounds or bacteria [18, 19]. Many studies have been conducted on the application of TiO_2 to water and air purification [7]. Another charming phenomenon of TiO_2 is the generation of a highly hydrophilic TiO_2 surface by UV light [20, 21]. When UV light is irradiated onto the surface of TiO_2 , a highly hydrophilic surface is generated. Aside from fundamental investigations into this phenomenon [22, 23], a polycrystalline TiO_2 film coating has been applied on various industrial products, such as automobile side mirrors, window films, exterior tiles, and highway wall panels, utilizing this property [24].

However, very little attention has been focused on the titanium native oxide film and its conversion under UV irradiation [2, 3]. Though it was reported that the native oxide film on Ti is about 2–3 nm [7], and nominally consists of n -type TiO_2 , a large band-gap material ($E_g = 3.05$ eV), it still lacks a complete understanding for the native oxide on titanium comparing with bulk titanium dioxide film obtained by other methods. Since the properties of the TiO_2 layer depend on its treatment method, so it is quite interesting from both a scientific and an industrial

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FIG. 1: Schematic configuration of sample structure (a) Titanium sample, (b) Silicon sample.

standpoint to understand the surface properties of the titanium native oxides covered by a HC layer under UV irradiation.

Many instruments and techniques, such as X-ray photoelectron spectroscopy (XPS), ToF-SIMS (Time of Flight-Secondary Ion Mass Spectroscopy), AES (Auger Electron Spectroscopy), SEM (Scanning Electron Microscope) and TEM (Transmission Electron Microscope), AFM (Atomic Force Microscopy), and Spectroscopic ellipsometry (SE), were used for determining the thickness, surface morphology, microstructure and chemical compositions of a titanium oxide film. Recently, spectroscopic ellipsometry (SE) as a non-invasive and non-destructive technique has been employed to characterize the optical properties and structure of bulk solids and thin films. Especially, SE in air is a very powerful tool for studying the time evolution of the optical properties (n and k from one time measurement), layer thickness (also multilayer stacks), interface quality, microstructure, contamination, surface properties of materials during preparation and processing.

In this paper, Ti film was deposited by means of electron cyclotron resonance (ECR) plasma-ion sputtering. Under air exposure conditions, the ultra thin titanium native oxides film covered by a hydrocarbon contamination layer grown on the as-deposited titanium film was investigated by SE, and the thickness, surface morphology, microstructure and chemical compositions of a titanium oxide film were discussed on the base of SE results. AFM was also used to characterize the surface morphology of both UV-treated and non-UV-treated titanium native oxide film.

II. EXPERIMENTAL

Titanium thin films were deposited onto well-cleaned wafer substrates by ECR plasma-ion sputtering method. Disk-shaped pure titanium (99.98%) with a diameter of 4 inches and 2 mm thickness was used as a sputtering target, and a thermally oxidized 2 inches diameter and 0.5 mm thickness was used as the deposited substrate.

After sputter deposition, the as-deposited titanium film was placed in air for 51 days, a native titanium oxide film covered by a layer of hydrocarbon contaminations grown on titanium, which was considered as the model system used in this study, as shown in Fig. 1. Using silicon dioxide sample as a stable reference provides an insight of the structural change as a function of UV irradiation time.

The titanium samples were cut into small plates with a size of about $8 \times 8 \text{ mm}^2$. The plates were placed on the stage of ellipsometer and irradiated in air by UV light (derived from a Hg lamp, 254 nm wavelength, As-One Co., Japan) with intensity of 2.0 mW/cm^2 . For comparison, the silicon sample ($0.5 \mu\text{m}$ single-crystal silicon with $2\sim 3 \text{ nm}$ silicon dioxide surface layer) was simultaneously irradiated by UV-light. Spectroscopic ellipsometer (FE-5000, Otsuka Electronics Co., Japan) was used to perform measurements of the change of optical properties during UV irradiation and after UV irradiation, and parameters of $\tan \Psi$ and $\cos \Delta$, n and k , and thickness changes were used to evaluate the UV-induced effects on the surface of Ti and Si samples. The measurement wavelength of SE was set over the range of $230\sim 800 \text{ nm}$, and an incidence angle of 70° was selected. The temperature and relative humidity (RH%) in this experiment were not controlled, but they changed in $24\sim 27^\circ\text{C}$ and $25\sim 32\%$, respectively.

For calculating the thickness of the titanium native oxide film and silicon dioxide, which include the hydrocarbon layer, we proposed a single-layer model which was fitted between wavelength $500\sim 800 \text{ nm}$ with an nk -Cauchy dispersion law, an attached software with the ellipsometer. A refractive index of $n = 2.2$ and an extinction coefficient of $k = 0$ for titanium oxide, and $n = 1.45$ and $k = 0$ for silicon dioxide, were referred as the initial optical properties of fitting simulation [25]. A linear regression analysis (LRA) technique was used to minimize the mean square deviation between the calculated and experimental $\tan \Psi$ and $\cos \Delta$ data by adjusting the ellipsometric model parameters, and finally to obtain the results in terms of best-fit model parameters and the thickness of titanium native oxide film.

Surface topography of different titanium samples, non-UV-irradiated and UV-irradiated for 3 days, were characterized by atomic force microscopy (AFM, Nanoscope IIIa, Veeco Instruments) in air using a tapping mode with MPP21100 type cantilever (Veeco Instruments; resonant frequency 90 kHz). The scan rate was set at 1.5 Hz to scan over multiple $1000 \text{ nm} \times 1000 \text{ nm}$ and $300 \text{ nm} \times 300 \text{ nm}$ sampling areas. The root-mean-square (RMS) roughness analysis was also performed with the accompanying Nanoscope IIIa software. The contact angle of water on the non-UV-irradiated and UV-irradiated Ti film was measured by using Contact Angle Meter (Kyowa Interface Science Co.LTD).

III. RESULTS AND DISCUSSION

A. SE parameters $\tan \Psi$ and $\cos \Delta$

After having been placed in air at ambient conditions for 51 days, the as-deposited Ti sample was applied to UV irradiation. The effect of UV on the SE parameters $\tan \Psi$ and $\cos \Delta$ was studied with spectroscopic ellipsometry, and the results were shown in Fig. 2.

As shown in Fig.2, the values of $\tan \Psi$ and $\cos \Delta$ at a certain wavelength decreased rapidly at the initial stage of UV irradiation. As UV irradiation was continuously implemented, the $\tan \Psi$ and $\cos \Delta$ had a different changing tendency. At UV irradiation time was 337 min, $\tan \Psi$ had a turning point, after which it almost keep constant

(a)

(b)

FIG. 2: Changes of SE parameters (a) $\tan \Psi$ and (b) $\cos \Delta$ of as-deposited Ti film under UV irradiation.

if it didn't decrease slightly, while for $\cos \Delta$ at 337 min, it dropped to its minimum, after which it slightly increased as UV irradiation time prolonged.

It is well known that the organic contaminants are accumulated at high-energy surfaces [26]. Since, TiO_2 also have high-energy surface, obviously it will adsorb the contaminants [27]. The adsorbed contaminants mainly consist of hydrocarbons [3], which would be removed under the UV irradiation of the TiO_2 surface. So during UV irradiation, the hydrocarbon contaminations were gradually removed, and the $\tan \Psi$ and $\cos \Delta$ decreased, as shown in Fig. 2. It was supposed that the hydrocarbon contaminations were completely removed when the UV irradiation time was up to 337 min.

After having been irradiated using UV lamp for a long time (8958 min=6.2 days), the sample Ti film was placed in air at ambient conditions. The changes of $\tan \Psi$ and $\cos \Delta$ of the composite film were also studied with spectroscopic ellipsometry, and the results were shown in Fig. 3. There are several reports says that the titanium surfaces would be easily contaminated within few days [27], which is consistent with the results shown in Fig. 3. During storage in the laboratory atmosphere, both $\tan \Psi$ and

(a)

(b)

FIG. 3: SE parameters (a) $\tan \Psi$ and (b) $\cos \Delta$ of the UV-treated Ti film and HC layer left in air at different time.

$\cos \Delta$ of the composite film gradually increased as time prolonged, which means that the hydrocarbon contaminants gradually adsorbed on the titanium oxide surface again. The thickness of the hydrocarbon contaminants layer formed on titanium oxides at different time in air were also shown in Fig. 3.

B. Pseudo-optical constants

The thickness of both the native Ti oxide film and the HC layer are very thin, about 2~3 nm [3], it is almost impossible to accurately calculate their optical constants, n and k , from such an ultra thin film [25]. So in this paper, for the composite film of several layers, including HC layer, Ti (or Si) oxide and substrate Ti (or Si), the optical constants is named pseudo-optical constants, n and k are respectively named as pseudo- n and pseudo- k , which could be easily calculated by using Substrate Analysis method of the SE software with good reproducibility. The pseudo-optical constants are the overall optical constants, and different from that of each layer which is one of part of the composite film. Because the substrate ti-

tanium metal film or crystal silicon (c-Si) film are thick enough and light can not penetrate through them, it is reasonable to assume that UV irradiation could not bring about any changes to their optical constants. That is to say, changes of SE measurement parameters are only correlated with changes of HC layer and Ti (or Si) oxide layer, and independent to the bulky substrate. Therefore, pseudo- n and pseudo- k of the composite film could be used to characterize the changes of surface properties, such as microstructure and chemical compositions of HC and Ti (or Si) oxide layer at the UV irradiation time or elapsed time after UV irradiation.

Two kinds of samples, Ti composite film and Si composite film were applied to UV irradiation. The effect of UV on the pseudo- n and pseudo- k of the Ti and Si composite film was studied at the meantime by using spectroscopic ellipsometry, and the results were shown in Fig. 4.

From Figs. 4 (a) and (b) it was found that the pseudo- n and pseudo- k values of Ti film at a certain wavelength increased rapidly at the initial stage of UV irradiation, which corresponded with the removing process of the HC which covered on Ti oxides. At this stage, the main function of UV irradiation was to degrade and remove HC. As UV irradiation continuously implemented, the pseudo- n or pseudo- k got a maximum, which indicated that the HC was completely removed. However, after this critical point, the pseudo- n or pseudo- k gradually decreased as UV irradiation time prolonged, which seemed to be contributed to the facts that UV light irradiated on the surface of Ti oxide and led to changes of its microstructure or chemical compositions.

From Figs. 4 (c) and (d) we could find that at the initial stage of UV irradiation, the pseudo- n values of Si film at a certain wavelength also increased with time, while the changing tendency of pseudo- k was much different from that of pseudo- n , it decreased at the initial stage of UV irradiation. As UV irradiation was continuously applied, the pseudo- n got its maximum and pseudo- k got its minimum at a certain wavelength, which meant the HC have completely removed. After this critical point, the pseudo- n or pseudo- k kept constant as UV irradiation time prolonged.

Comparing the pseudo- n , pseudo- k of titanium sample with those of Si sample under UV irradiation, three results could be deduced. Firstly, it took a shorter time of 337 min for pseudo- n and pseudo- k of Ti sample to get their critical point (Figs. 4a, 4b), while it took a longer time of 4059 min for Si sample (Figs. 4c, 4d). This meant that the hydrocarbon contaminants on Ti oxide film were more efficiently removed than that on Si sample. Secondly, after the hydrocarbon contaminants were completely removed, the pseudo- n and pseudo- k of Si composite film kept constant under UV irradiation, but for Ti composite film the pseudo- n and pseudo- k changed continuously. So we considered that, under UV irradiation, silicon dioxide is stable, while the microstructure or chemical components of the native oxide film on titanium changed. Thirdly, the effect of hydrocarbon contamination layer on the pseudo- n and pseudo- k of the composite film were different between Ti sample and Si sample. The existence of hydrocarbon contamination layer decreased the pseudo- n and pseudo- k of Ti sample, while it increased the pseudo- n and decreased the pseudo- k of Si sample. The reason for this

case was related with the n and k values of each component in the composite film.

It is known that at wavelength of 632.8 nm, the refractive index $n(\text{SiO}_2) = 1.45$ (the n value of HC is similar with that of SiO_2), but $n(\text{TiO}_2) = 2.20$. For the Ti sample, the n and k values of both Ti metal and Ti oxide are larger than that of hydrocarbon contaminations. For Si sample, the optical constant n of HC, which is similar with that of SiO_2 , are smaller than that of crystal silicon substrate, and the k values of HC, SiO_2 and the substrate c-Si, which are all dielectric materials, are near to zero in long wavelength region (for example, 500~800 nm), so the effect of the surface HC layer on pseudo- k of Si composite film is principally negligible, but as seen from this experimental results (Fig. 4d), the existence of the surface HC layer actually made the pseudo- k of Si composite sample increase, which was probably caused by the interfacial effect between HC layer and silicon dioxide layer.

In addition, comparing the optical constants (n and k) of pure Ti [28] with that of Ti composite film from this experiment shown in Fig. 4, it can be found that the shape of n (or k)-wavelength curve of them are almost the same, which means that the pseudo- n and pseudo- k of the Ti composite film are primarily determined by the substrate (Ti) and only modified by the top thin films (Ti oxide and HC layer). The same result can be got for Si composite sample.

In order to further verify the result mentioned above, UV lamp was shut off and taken away, and the long-term UV-irradiated Ti and Si composite film (UV irradiation for 8589 min), which were kept their position on the stage of ellipsometer, were exposed in air and continuously measured by using spectroscopic ellipsometer. The changes of the pseudo- n and pseudo- k of Ti and Si samples in air were shown in Fig. 5 and Fig. 6, respectively.

When Ti sample was exposed in air after long-time UV irradiation, the pseudo- n and pseudo- k of it at wavelength of 600 nm decreased rapidly at the beginning stage because HC adsorbed on the sample surface again. As time went by, the surface adsorption gradually became saturated, so the decreasing rate of pseudo- n and pseudo- k became slow (Fig. 5).

For the Si sample after long time UV irradiation, as seen in Fig. 6, the pseudo- n at the wavelength of 378 nm, where showed a peak, decreased rapidly at the beginning of exposure in air, but the pseudo- k increased rapidly. This meant that the adsorption layer of HC on Si sample decreased the pseudo- n and increased pseudo- k of the Si composite film.

Therefore, from the results of Figs. 4, 5 and 6 we can film with low n (or k) covered on high n (or k) substrate would decrease the pseudo- n (or pseudo- k), such as the changes of pseudo- n and pseudo- k of Ti composite film, and the pseudo- n of Si composite film. For a high n (or k) film on low index substrate the pseudo- n (or pseudo- k) would increase, such as the changes of pseudo- k value of Si composite film.

C. Change of thickness

To ensure fair comparison, one Ti sample and one Si sample were simultaneously irradiated by UV, and the

FIG. 4: Changes of optical constants of Ti and Si composite film under UV irradiation; (a) pseudo- n of Ti composite film; (b) pseudo- k of Ti composite film; (c) pseudo- n of Si composite film; (d) pseudo- k of Si composite film.

FIG. 5: Changes of the pseudo- n and pseudo- k of Ti composite sample exposed in air at wavelength 600 nm.

FIG. 6: Changes of the pseudo- n and pseudo- k of Si composite sample exposed in air at wavelength 378 nm.

changes of the thickness of the oxide film covered with HC were expressed in Fig. 7. After long time (8589 min) UV irradiation, those samples were exposed in air and measured by using spectroscopic ellipsometer, the thickness of the oxide film covered with HC was expressed in Fig. 8.

Figure 7 described the changes of thickness for the Ti composite film and Si composite film under UV irradiation, from which we could find that Ti film and Si film had

different response, and the thickness of Ti surface film decreased rapidly at the initial stage of UV irradiation, while the thickness of Si surface film decreased slowly.

As UV irradiation continuously implemented, the thickness of the Ti composite film obtained its minimum quickly (about 337 min), after which the thickness of the Ti composite film increased gradually as time. Though the thickness of the Si composite film also reached its minimum, but it took a long time up to 4089 min. After

FIG. 7: Changes of thickness of the oxide film covered with HC layer under UV irradiation.

FIG. 8: Changes of thickness of the oxide film covered with HC layer exposure in air.

this turning point, the thickness of the Si kept constant although UV irradiation time prolonged.

It is well known that UV irradiation could clean a contaminated surface, so the thickness decrease shown in Fig. 7 was contributed to the removing of the contaminants such as hydrocarbons (HC). As HC was removed completely, the thickness reached the minimum. From Fig. 7 it was found that HC both on Ti and Si could be removed by UV irradiation, but the removal rate was different. HC on Ti film was removed more quickly than that of Si, which suggested that the native oxide on Ti film could promote the remove of HC under UV, probably because Ti oxide has a strong photocatalytic effect and Ti also has a relatively stronger reflection coefficient than Si. That is, HC on Ti film was irradiated by not only incident UV light but also relatively stronger reflection light on Ti film surface than Si wafer surface.

After 8589 min passed, UV irradiation was stopped and the sample exposed in air again, and SE was used to measure the thickness of the composite film and the results was shown in Fig. 8. The thickness of the composite film increased quickly in air at first and then increased grad-

ually, but the thickness of HC-layer could not return its original values as shown in Fig. 8, even though the sample had exposed in air for a long time (31 days), which meant something had happened to the titanium oxide film by UV irradiation and the surface of titanium became not easy for HC contaminations to adsorb.

D. Chemical composition changes of the native Ti oxides layer

As shown in Fig. 4, after HC was removed completely, the pseudo- n and pseudo- k of titanium composite film decreased as a function of UV irradiation time, which means that the microstructure or chemical composition of the native oxide film on titanium changed.

It is known that the native oxide film on titanium is amorphous and mainly include TiO_2 , with a small quantities of other kinds of titanium oxides, such as TiO , Ti_2O_3 and Ti_3O_5 , existing in the native film. The main physical properties of Ti oxides are shown in Table 1.

The native oxide layer usually renders the inactivity of titanium. However, under UV irradiation, O_2 and H_2O vapor would be activated and formed O_2^- , OH^- or $\text{O}^\cdot$ free radical with high energy. Moreover, under UV irradiation the diffusing and penetrating ability of O_2 or $\text{O}^\cdot$ free radical through the native oxide film probably were also enhanced. So titanium bulk would react with O_2 in air to form titanium oxide.

The above reaction would increase the thickness of the native titanium oxide film as UV irradiation time prolonged. This suggestion is well consistent with the result shown in Fig. 7.

Besides the reaction between titanium metal and O_2 , there probably exists other oxidization reaction from low valence titanium oxides to high valence titanium dioxide. As shown in Table 1, there exists several titanium oxides in the native oxide film, some low valence titanium oxides are not stable under UV-light, so they would be oxidized to high valence titanium dioxide. For example, Ti_2O_3 is an unstable species, in contact with water it is rapidly oxidized to TiO_2 , the possible reaction is expressed as follows:

As a kind of dielectrics, the extinction coefficient k of each titanium oxide is supposed to be zero, but their refractive index n are different. It is reported that n of TiO_2 is 2.2, but no information about optical constants of other titanium oxides have been published. The n value of a substance is proportional to its density in many cases, so the n values of TiO , which has the highest density among these titanium oxides, is considered to be bigger than that of TiO_2 , which have the lowest density (Table 1). In addition, the oxygen concentration and Ti valence state in TiO_2 both are the biggest among all the titanium oxides (Table 1). It was reported that oxygen enough for reacting with titanium would produce TiO_2 , while low O_2

TABLE I: Properties of Ti oxides.

Property	TiO	Ti ₂ O ₃	Ti ₃ O ₅	TiO ₂
Valence state (Ti)	II	III	III, IV	IV
Formula weight	63.866	143.732	223.598	79.866
Melting point (°C)	1750	1842	1777	1800, 1843
Density (kg·m ⁻³)	4950	4490	4240	4230
O concentration (%)	25.05	33.39	35.78	40.07

pressure would preferably produce TiO [29]. Moreover, for the as-deposited TiO₂ amorphous films by using conventional unfiltered vacuum arc deposition, the refractive index of the film decreased with the pressure of O₂ [30]. From these results it is suggested that TiO₂ had the lowest refractive index n among all the titanium oxides.

Therefore, the oxidization reaction, including reaction between titanium metal and O₂ and the reaction from low valence titanium oxides to high valence titanium dioxide, would slightly decrease the n values of the native titanium oxide film, subsequently the pseudo- n of the Ti composite film. This is consistent with the result shown in Fig. 3. Of course, the chemical composition change of the native titanium oxide film is not the only reason for the decrease of the pseudo- n values, any changes in surface topography and microstructure of the native oxide induced by UV irradiation would also change the pseudo- n values of the Ti composite film.

E. Microstructure of the native Ti oxides surface

In order to further determining the effect of UV irradiation on the surface morphology of titanium native oxide, a tapping-mode AFM was used and the images of non-UV-treated and UV-treated titanium composite film were obtained, as seen in Fig. 9.

As shown in Fig. 9, it is obvious that there have some differences between UV-treated and non-UV-treated Ti composite film. In the case of the non-UV-treated film, the surfaces of Ti oxides were relatively rough, and some bright peaks and dark valleys were easily observed (Figs. 9a, 9c), and the bright regions seemed to be consisted of many small grains (Fig. 9c). However, after long-time UV irradiation (3 days), the surfaces of Ti native oxides became relatively smooth, the big peaks and big valleys existed in the AFM image of non-UV-treated Ti surface (Figs. 9a, 9c), were reduced or disappeared, and instead of many single bright dots corresponding with the small grain with almost the same shape and size (about 10 nm in diameter) presented on the surface.

By analyzing the images shown in Fig. 9 we also found that the root-mean-square (RMS) surface roughness for samples without UV irradiation was 0.438 nm (Fig. 9a) and 0.466 nm (Fig. 9c) for scanning area 1000×1000 nm² and 300×300nm² respectively, but decreased to 0.415 nm (Fig. 9b) and 0.352 nm (Fig. 9d) for UV-treated samples. Namely UV irradiation slightly decreased the roughness of the native oxide film on Ti.

There are many studies focusing on the structure changes of metal oxide film induced by UV-light [24, 31]. The effect of VUV (UV in vacuum conditions) pretreat-

ment on the crystallization of anatase in sol-gel-derived TiO₂ precursor films was reported by Nakajima *et al.* [32], and it was found that VUV irradiation changed the film structure and the degree of the microstructure evolution depends on the intensity and duration of the VUV irradiation [32]. It was also found that a fixed energy value was required to arise the TiO₂ surface structural change [17]. For sol-gel derived anatase polycrystalline films the total energies of illuminated UV light to produce the highly hydrophilic state was more than 3.5°J/cm² [32], which was almost the same with the total energy needed to induce the native oxide film surface into a hydrophilic one. In this experiment, a UV lamp with power of 2 mW/cm² was used to irradiate the sample surface at least 60 min, the total energy was about 72 kJ/cm², which was high enough to produce hydrophilic surface on Ti oxides. So under the UV irradiation applied in this experiment, it is possible that the surface structure of native titanium oxide changed and became more hydrophilic after UV irradiation.

So, the AFM findings in this experiment can be explained by the fact that the titanium native oxide is activated by UV irradiation, and electron-hole pairs are generated and then promoted the producing and crystallizing of the native titanium oxide. The titanium metal film is expected, at least partially, to recrystallize following deposition, inducing grain-size-congregated and grain-orientation-related topographic features at the surface [33], so its surface is relatively rough (Figs. 9a, 9c), even if a very thin layer of native oxide is formed on it at room conditions. Comparison with amorphous titanium oxide, crystalline titanium oxide is a more stable material and has minimum surface energy, and more resistant to irradiation of UV light. When UV-light was applied to it, the native oxide surface was activated, which tended to minimize the surface area and the total surface energy of the native oxide film, and produced a relatively low roughness surface (Figs. 9b, 9d). In the meantime, more titanium oxides were formed (mentioned in above) and partially crystallized under UV irradiation, which made the gains on the surface become isolated and the film surface looked like somewhat chalking comparing with the non-UV-treated sample (Figs. 9b, 9d). Therefore, it was also assumable that a long-term UV irradiation converted the partial grains in the titanium native oxide film to hydrophilic ones, resulting in an entirely hydrophilic surface, which was confirmed by the results of water contact angle on the non-UV-irradiated and UV-irradiated Ti film. The non-UV-irradiated Ti sample was firstly cleaned with 0.1M H₂SO₄ and supersonic to remove HC, then the contact angle measurement was applied on it, and the water contact angle is 78.7°. After treated by UV light for

FIG. 9: AFM images of UV-treated (3 day) and non-UV-treated Ti composite film (Height=5 nm) (a) non-UV-treated, $1000 \times 1000 \text{ nm}^2$, (b) UV-treated, $1000 \times 1000 \text{ nm}^2$, (c) non-UV-treated, $300 \times 300 \text{ nm}^2$, (d) UV-treated, $300 \times 300 \text{ nm}^2$.

3 days, the water contact angle of this sample became 18.8° . Those results indicated that UV irradiation on the as-deposited Ti sample would induce a hydrophilic surface.

F. Mechanisms of removing HC contaminations on Ti native oxides surface

From the changes of the film thickness (Figs. 7, 8) and optical constants, including $\tan \Psi$ and $\cos \Delta$ (Figs. 2, 3), n and k (Figs. 4, 5, 6), derived from SE analysis, we found that HC contaminations on Ti composite film were more easily remove by UV light than that on Si substrate.

Based on the results of ellipsometry, the thickness of HC layer was calculated by using the software attached with the ellipsometer, and the results were shown in Fig. 10. The refractive index $n = 1.324$ and extinction coefficient $k = 0$ was used to fit the experimental data. It took 337 min and 4059 min for removing HC layer from titanium oxide film and from silicon oxide film respectively.

From Fig. 10, we could get the average removing rate of HC layer on titanium oxide film and on silicon oxide film, it was about $5.81 \times 10^{-3} \text{ nm/min}$ and $4.14 \times 10^{-4} \text{ nm/min}$, the former was over twenty times bigger than that of the latter. This is to say again that the native titanium oxides grown on titanium promoted the removing process of HC.

In this experiment, two main mechanisms are used to explain the removing process of HC, one is through the UV-induced photocatalytic degradation, another is

FIG. 10: Changes of thickness of the HC layer on Ti or Si composite film under UV irradiation.

through the HC desorption from the native oxide surface with UV-induced hydrophilicity. The UV-induced photocatalytic activity is widely studied. It is suggested that photocatalysis plays an important role in removing HC contaminations through two ways [34]: (1) decomposing the HC contaminations into H_2O , CO_2 and other small molecular organic compounds directly; (2) decomposing

the HC contaminations to recover the surface hydrophilicity and making HC contaminations easily replaced by H₂O, N₂ or O₂ in air.

The photocatalytic mechanism is initiated by the absorption of a photon with energy equal to or greater than the band gap (E_b) of TiO₂ ($E_b = 3.23$ eV for anatase, $E_b = 3.05$ eV for rutile) producing an electron-hole pair on the TiO₂ surface [35]. An electron is promoted to the conduction band (CB) while a positive hole is formed in the valence band (VB). In order for this process to have a net chemical effect, the volume recombination of the electron-hole pair has to be precluded. The natural fate for h_{vb}^+ and e_{cb}^- is the removal of either of them by means of redox reactions involving the organic compounds adsorbed on the semiconductor surface. The standard chemical reactions have been given as [36]:

Hydroxyl radicals (HO•) and super-oxide ions (O₂⁻) are highly reactive species that will oxidize the organic compounds adsorbed on the titanium native oxide surface.

Besides UV-induced degradation, another routine for removing HC is the desorption of HC from the titanium native oxide surface. This routine is closely related to the UV-induced hydrophilic conversion of the titanium oxide surface due to the surface structural changes. It is suggested that the hydrophilicity is probably more important than the photocatalysis for removing HC contaminations on Ti native oxides layer [34].

IV. CONCLUSIONS

An ultra thin titanium native oxides film covered by a HC layer grown on the as-deposited titanium film was treated by UV irradiation and the treated surface was evaluated by using SE and AFM.

Under UV irradiation, SE parameters $\tan \Psi$ and $\cos \Delta$ decreased, and optical constants pseudo- n and pseudo- k increased as time passed by. When the HC layer was removed completely, these parameters all reached their critical point. After this critical point, these experimental parameters presented a complicated change tendency, which was related to the change of surface microstructure and chemical component of the native oxide film. At the initial stage of UV irradiation, the thickness of Ti surface film decreased rapidly, while the thickness of Si surface film decreased slowly. On the thickness of the composite film, the Ti composite film obtained its minimum thickness after irradiated for 337 min (the average removing rate of HC layer on titanium oxide film was 5.81×10^{-3} nm/min), which was quite shorter than 4089 min for the Si composite film (the average removing rate of HC layer on silicon oxide film is 4.14×10^{-4} nm/min).

The SE results indicated that UV irradiation applying to the Ti sample for about 337 min could completely remove the adsorbed HC layer. The titanium native oxide accelerated the HC removing process. The pseudo- n and pseudo- k values of the Ti composite and the thickness of the surface layer on Ti all decreased during UV irradiation. Compared with non-UV-treated Ti sample, AFM images from the surface of UV-treated titanium native oxide films presented a less RMS roughness and many isolated gains with a size of about 10 nm. The water contact angle on the non-UV-irradiated and UV-irradiated Ti film were 78.7° and 18.8° respectively, which indicated that UV irradiation on the as-deposited Ti sample would induce a hydrophilic surface.

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- [1] P. Bourdet, F. Vacandio, L. Argeme, S. Rossi, and Y. Massiani. *Thin Solid Films* **483**, 205 (2005).
 - [2] C. J. Boxley, H. S. White, C. E. Gardner, and J. V. Macpherson. *J. Phys. Chem. B* **107**, 9677 (2003).
 - [3] J. Lausmaa, B. Kasemo, and H. Mattsson. *Appl. Surf. Sci.* **44**, 133 (1990).
 - [4] E. S. Gawalt, M. J. Avaltroni, N. Koch, and J. Schwartz. *Langmuir* **17**, 5736 (2001).
 - [5] Xiao-Xiang Wang, Lei Xie and Rizhi Wang. *Biomaterials* **26**, 6229 (2001).
 - [6] F. Barrere, M. M. E. Snel, C. A. van Blitterswijk, Klaas de Groot and P. Layrolle. *Biomaterials* **25**, 2901 (2004).
 - [7] P. S. M. Dunlop, J. A. Byrne, N. Manga and B. R. Eggins. *J. Photochem. Photobiol., A Chem.* **148**, 355 (2002).
 - [8] K. Katsumata, A. Nakajima, H. Yoshikawa, T. Shiota, N. Yoshida, T. Watanabe, Y. Kameshima, and K. Okada. *Surf. Sci.* **579**, 123 (2005).
 - [9] S. B. Basame, H. S. White. *J. Electrochem. Soc.* **147**, 1376 (2000).
 - [10] N. Casillas, S. J. Charlebois, and W. H. Smyrl. *J. Electrochem. Soc.* **141**, 636 (1994).
 - [11] H. Nanjo, N. J. Laycock, H. Deng, I. Ishikawa and N. Sanada. *Curr. Appl. Phys.* **4**, 156 (2004).
 - [12] S. B. Basame, H. S. White. *J. Phys. Chem. B* **102**, 9812 (1998).
 - [13] C. Su, B.-Y. Hong and C.-M. Tseng. *Catalysis Today* **96**, 119 (2004).
 - [14] P. Zeman, S. Takabayashi. *Surf. Coat. Technol.* **153**, 93 (2002).
 - [15] S. K. Poznyak, D. V. Talapin and A. I. Kulak. *J. Electroanal. Chem.* **579**, 299 (2005).
 - [16] H. Takikawa, T. Matsui, T. Sakakibara, A. Bendavid, and Philip J. Martin. *Thin Solid Films* **348**, 145 (1999).
 - [17] K. Katsumata, A. Nakajima, H. Yoshikawa, T. Shiota, N. Yoshida, T. Watanabe, Y. Kameshima and K. Okada. *Surf. Sci.* **579**, 123 (2005).

- [18] I. Losito, A. Amorisco, F. Palmisano and P. G. Zambonin. Appl. Surf. Sci. **240**, 180 (2005).
- [19] C. C. Trapalis, P. Keivanidis, G. Kordas, M. Zaharescu, M. Crisan, A. Szatvanyi, and M. Gartner. Thin Solid Films **433**, 186 (2003).
- [20] A. Mills, S. LeHunte, J. Photochem. Photobiol. A: Chem. **108**, 1 (1997).
- [21] R. Wang, K. Hashimoto, A. Fujishima, M. Chikuni, E. Kojima, A. Kitamura, M. Shimohigoshi, and T. Watanabe. Nature **388**, 431 (1997).
- [22] L. Sirghi, Y. Hatanaka. Surf. Sci. Lett. **530**, L323 (2003).
- [23] N. Sakai, A. Fujishima, T. Watanabe, and K. Hashimoto. J. Phys. Chem. B **107**, 1028 (2003).
- [24] A. Fujishima, K. Hashimoto, and T. Watanebe. *TiO₂ Photocatalyst, Fundamentals and Applications*, BKC Inc., Tokyo, 1999, p. 66.
- [25] H. G. Tompkins and W. A. McGahan. *Spectroscopic Ellipsometry and Reflectometry: a user's guide*, John Wiley & Sons, Inc., 1999, p. 113.
- [26] S. Karuppuchamy, J. Mun Jeong. Mater. Chem. Phys. **93**, 251 (2005).
- [27] S. Takeda, M. Fukawa, Y. Hayashi, K. Matsumoto. Thin Solid Films **339**, 220 (1999).
- [28] Edward D. Palik. *Handbook of Optical Constants of Solids (Vol. III)*, Academic Press, Boston, USA, 1997.
- [29] Xianghui Wang, Feng Zhang, Zhihong Zheng, Changrong Li, Lizhi Chen, Huimin Wang, and Xianghuai Lui. Mater. Lett. **44**, 105 (2000).
- [30] H. Takikawa, T. Matsui, T. Sakakibara, Avi Bendavid, and Philip J. Martin. Thin Solid Films **348**, 145 (1999).
- [31] H. Nanjo, H. Deng, I. S. Oconer, I. Ishikawa and T. M. Suzuki. Jpn J. Appl. Phys. **44-1B**, 539 (2005).
- [32] A. Nakajima, N. Hayashi, Y. Taniguchi, Y. Kameshima, K. Okada. Surf. Coat. Technol. **192**, 112 (2005).
- [33] S. Tosatti, R. Michel, M. Textor, and N.D. Spencer. Langmuir **18**, 3537 (2002).
- [34] K. Guan. Surf. Coat. Technol. **191**, 155 (2005).
- [35] J. O. Carneiro, V. Teixeira, A. Portinha, L. Dupa ka, A. Magalhaes, and P. Coutinho. Vacuum **78**, 37 (2005).
- [36] S. G. Schrank, H. J. Jose, and R. F. Moreira. J. Photochem. Photobiol. A: Chem. **147**, 71 (2002).