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FORMATION OF TiO_2 THIN FILM BY ION-BEAM-MIXING METHOD AND ITS APPLICATION AS THE CORROSION PROTECTING FILM

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ABSTRACT

One of the n-type semiconductor materials of TiO_2 has been expected to be used as photo-catalytic media in these days. A lot of studies have been conducted for applying TiO_2 film to anti-bacterium, water decomposing, anti-stain and deodorant coatings. The TiO_2's photo-catalytic function can be obtained under the condition of UV light illumination. Purpose of this study is to apply coated TiO_2 thin film as the corrosion protecting film of substrate metals using photocurrent obtained from UV ray irradiation. This implies the cathodic protection employing outer electric source. Therefore, even though when the thin film having some defect distribution in itself, the TiO_2 thin film shows corrosion protecting effects to substrate without a anodic dissolution of film itself. In this paper, formation and characterization of TiO_2 thin film made on AISI 304 stainless steel by Ion-Beam-Mixing method were conducted. Then, the cathodic protection performance of 0.15 μm thick TiO_2 thin film with some defect distribution was investigated in 0.3wt% NaCl aqueous solution. And also, effects of ion source upon the photo-catalytic function of TiO_2 thin film was investigated.

KEYWORDS

TiO_2 thin film, Ion-Beam-mixing Method, photo-catalytic function, corrosion protecting film, UV ray irradiation, defect distribution, cathodic protection performance

INTRODUCTION

Thin film coatings toward various types of materials such as metal and organic compound have been used for protecting substrate surface from harsh environment or adding a lot of functions to them [1]. However, nanometric defects and cracks were always existed in coated thin film from the initial stage [2]. In actual environment, degradation was generated as a result of the corrosive solution coming into substrate metals through the nanometric defect of coating.

Recently, one of the n-type semiconductor materials of TiO_2 has been expected to be used as photo-catalytic media.

And a lot of studies have been conducted for applying TiO_2 film to anti-bacterium, water decomposing, anti-stain and deodorant coatings[3-5] The TiO_2's photo-catalytic effect can be obtained under the condition of UV light illumination as shown in the following equation.

$$H_2O + 2h^+ \rightarrow 2H^+ + (1/2)\,O_2 \qquad (1)$$

Purpose of this study is to apply coated TiO_2 thin film to the corrosion protecting film of substrate metals using photocurrent obtained from UV ray irradiation. This implies the cathodic protection employing outer electric source. Therefore, even though when the film having defect in itself, the TiO_2 thin film shows corrosion protecting effects to substrate without an anodic dissolution of film itself. In this study, formation of TiO_2 thin film was conducted on AISI 304 stainless steel by Ion-Beam-Mixing method. Then, the characterization of the compositions and crystal structure of deposited thin films were conducted by XRD and ESCA. And also, cathodic protection performance of TiO_2 thin film with some defect distribution in itself was investigated under UV ray irradiation condition.

EXPERIMENTAL PROCEDURES

The Specimen

The specimen used in this study was 0.15 μm thick TiO_2 thin film coated on AISI 304 stainless steel plate (25×50 ×1.0mm) by Ion-Beam-Mixing method shown in Figure 1. Because, TiO_2 thin film made by Ion-Beam-Mixing method had superior adhesive strength. In this process ion beams of the inert gas of Ar and He have been used for assisting to obtain TiO_2 thin film with well-crystallized microstructure. The surface of AISI 304 substrate specimen was finished like mirror, and also degreased by methanol. Table 1 showed condition of TiO_2 thin film formation by this method. Chemical compositional profile of thin films was examined by X-ray Photoelectron Spectroscopy and the structure of coated layer was investigated by X-ray Diffraction.

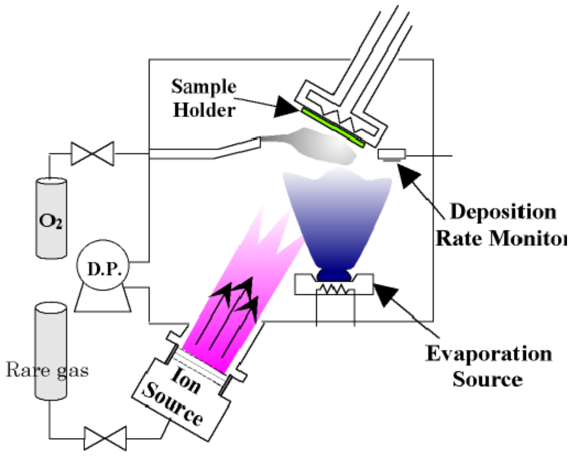


Figure 1: The chamber of Ion-Beam-Mixing equipment

TABLE 1 CONDITION OF TiO_2 FILMS FORMATION BY ION-BEAM-MIXING METHOD

Ion beam gas	Ar^+	He^+
Ar or He gas pressure (mPa)	3.0	4.0E-2
O_2 gas pressure (mPa)	14.0	18.0
Ar or He ion beam current (μA/cm^2)	20.0	15.0
Ti evaporation rate (μm/s)	0.5	0.5
Thickness of films (μm)	0.15	0.15

Electrochemical Measurement

To examine the corrosion characteristics of TiO_2 coated specimen, the corrosion potential measurement and the anodic polarization measurement were conducted with and without the UV ray irradiation employing automatic polarization test system shown in Figure 2. For an electrochemical measurement, the specimen was coated by silicone for insulation from solution with non-coated area of $1cm^2$ left for testing. Each examination was conducted using three electrodes method that composed from specimen (working electrode), Pt (counter electrode) and the saturated calomel electrode (SCE)(referential electrode). Anodic polarization measurement was conducted in 0.3 wt% NaCl aqueous solution of 298K from –700 to 1000mV at a sweep rate of 20mV/min [3]. Natural corrosion potential measurement was conducted initially during 2 hours without UV ray irradiation, next 2 hours with UV illumination and final 2 hours in dark again. The light source was UV ray whose wave length λ =366nm and luminous intensity was $1.70mW/cm^2$. The distance of UV light from specimen was kept to be 60mm during testing.

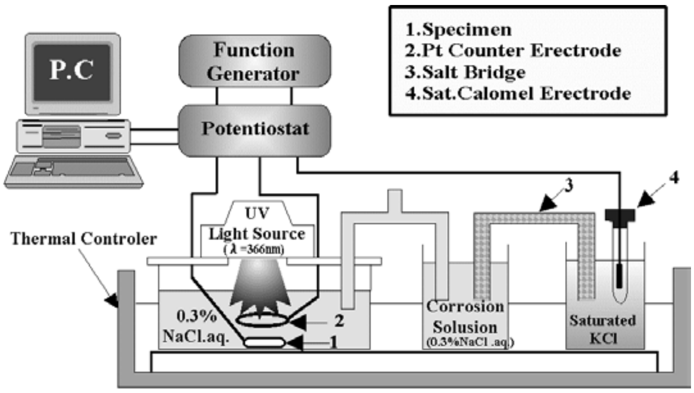


Figure 2: Schematic diagram of the system for electrochemical measurements

EXPERIMENTAL RESULTS AND DISCUSSIONS

Examination of the Compositions and Crystal Structure of Deposited Thin Films

The depth profiles of chemical composition and crystal structure of TiO_2 thin film made by Ion-Beam- Mixing method was investigated by XPS. The correlation between the composition ratio O/Ti and etching time was obtained and shown in Figure 3 together with those of other TiO_2 films made under different Ar ion

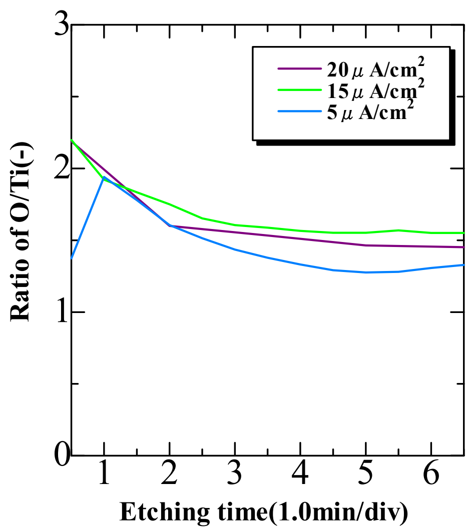


Figure 3: The composition ratio of TiO_2 thin films made under various Ar ion beam current

beam current. Almost of all the TiO_2 thin films made by this method is confirmed that oxygen in the films decreased from surface in the depth direction, and the other element of Ti in the films increase from surface toward the depth direction. Chemical compositional depth profile obtained in this study showed that the crystal structure of TiO_2 film obtained by using He ion beam had relative better crystallized structure.

Then, the crystal structure of the coated TiO_2 thin film was investigated by XRD and shown in Figure 4. From the result of crystal structure examined for thin films by X-ray Diffraction, no sharp peak strength was recognized both in Rutile structure and Anatase one. Therefore, the thin films obtained in this study by Ion-Beam-Mixing method showed relatively amorphous microstructure. However, in case when the TiO_2 thin film was obtained using He ion for assisting comparatively crystallized microstructure of Rutile was obtained .

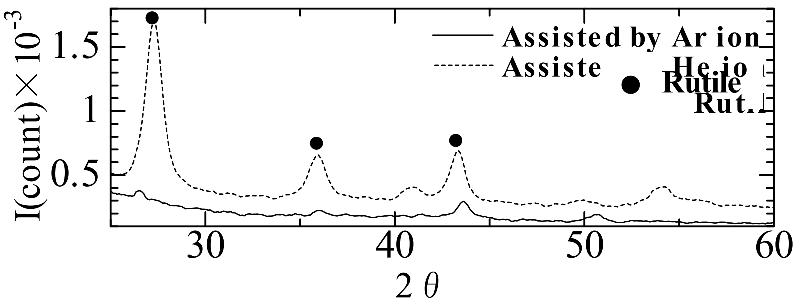


Figure 4:TiO_2 films diffraction pattern by XRD

Natural Corrosion Potentials of TiO_2 Thin Films in 0.3% NaCl Aqueous Solution

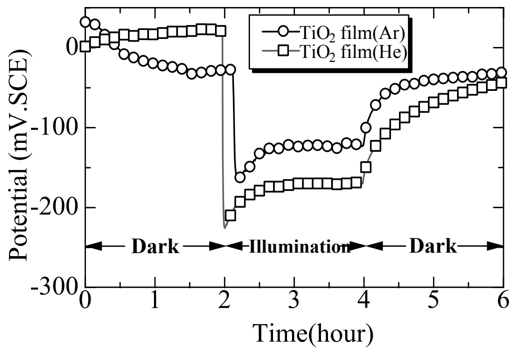
Natural corrosion potentials of TiO_2 thin coatings film were measured in 0.3% NaCl aqueous solution of 298K under the conditions of initial 2 hours without UV ray irradiation, next 2 hours with UV illumination and final 2 hours in dark again for both of Ar and He ions assisted films. In Figure 5 obtained results were indicated. From this figure, abrupt drop was recognized in the potential values when UV ray illumination was conducted. And then, gradual recover in the potential was recognized after UV ray was turned off. From these results, it was understood that the potentials gaps between UV ray illumination and dark were about 200mV and 120mV for He and Ar assisted TiO_2 thin films, respectively. Therefor, it is confirmed that the shift of potential was generated in the negative direction. Therefore, TiO_2 thin films showed the photo-catalytic function under UV ray illumination.

Anodic Polarization Measurement of TiO_2 Thin Films Coated Specimen in 0.3% NaCl Aqueous Solution

The polarization curves of TiO_2 thin films coated AISI 304 stainless steel specimen were obtained under UV ray illumination and non-illumination conditions in 0.3% NaCl aqueous solution of 298K and shown in Figure 6. Under UV ray illuminating condition both specimens made by Ar and He ions assisting showed no remarkable current density increase. In contrast, in case of non UV ray irradiated condition abrupt increase in the current density was recognized especially in He assisted TiO_2 thin film and resulted in the pitting corrosion with local exfoliation of thin film. Therefore, TiO_2 thin film has corrosion protecting performance under UV ray irradiating condition, even when TiO_2 thin film has some inherent defect distribution in itself. Under dark condition, however, distributed inherent defects such as pinhole and so on played an important role in the localized corrosion process of TiO_2 thin film coated SISI 304 stainless steel specimen. The adhesion strength between TiO_2 thin film and substrate metal became relatively low especially in case when He ion assisted thin film in spite of having better photo-catalytic function. As a result, the pitting corrosion with local exfoliation was generated in this film.

Cathodic Protection Performance of TiO_2 Thin Film with Some Artificial Defect

In the previous chapter, cathodic protection performance of TiO_2 film was indicated under UV ray irradiation condition. Usually, ceramic coatings inevitably have various defects even when appropriate coating



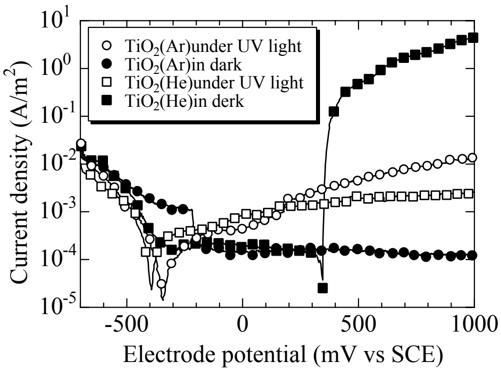


Figure 5:Spontaneous potential shift of TiO_2 films with and without UV illumination

Figure 6: Polarization curves of TiO_2 films (Ar and He) with and without UV illumination

conditions were selected for formation of thin films. For this reason, corrosion resisting property may be affected by distributed defects in thin film itself. Therefore, results shown in the previous section may be obtained from the situation that few large sized defects were existed in the TiO_2 thin film especially made by Ar ion assisted condition.

In this chapter, the dependency of TiO_2's photo-catalytic effect upon defect size that limited the cathodic protection performance of thin film was investigated. For this purpose, artificial scratch defect, whose width and defect ratio were about 200 μ m and about 2 %, was introduced on the coated thin film by diamond cutter as shown in Figure 5. By using Ar ion assisted TiO_2 thin film coated specimens with and without such scratch defect anodic polarization measurements were conducted under UV ray irradiating condition and shown in Figure 6 together with the result obtained using substrate AISI 304 stainless steel specimen. At the same time, above-mentioned measurements were conducted also under non UV ray irradiating condition and shown in Figure 7.

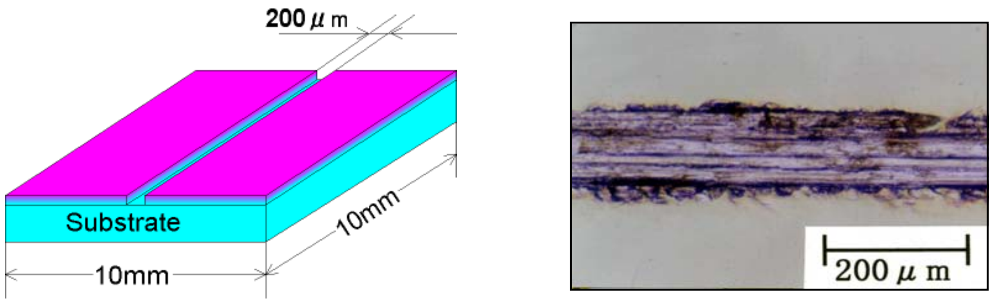


Figure 5: The scratch defect size and surface photograph

Some increase in the current density was recognized in TiO_2 thin film coated specimen with scratched defect when polarization measurement was conducted even under UV ray irradiating condition as shown in Figure 6. However, no localized corrosion was generated on the specimen surface after anodic polarization measurement. In contrast, remarkable increase in the current density was generated in TiO_2 thin film coated specimen with scratched defect when polarization measurement was conducted under non UV ray irradiating condition as shown in Figure 7. In this case, the pitting corrosion was recognized after electrochemical test as shown in Figure 8. Therefore, the cathodic protection performance of 0.15 μ m thick TiO_2 film coated on
AISI 304 stainless steel by Ion-Beam-Mixing method with Ar ion beam assisting can be obtained due to its photo-catalytic effect even when the film has artificially scratched defect whose width was about 200 μ m.

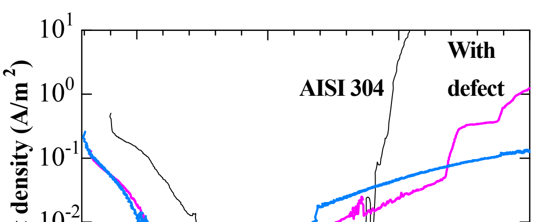


Figure 6: Polarization curves of TiO_2 film under UV ray irradiating condition

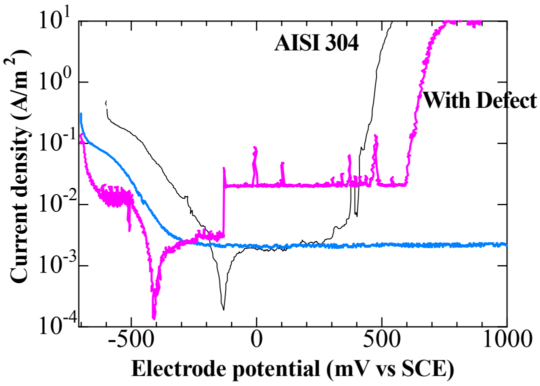


Figure 7: Polarization curves of TiO_2 films under the dark

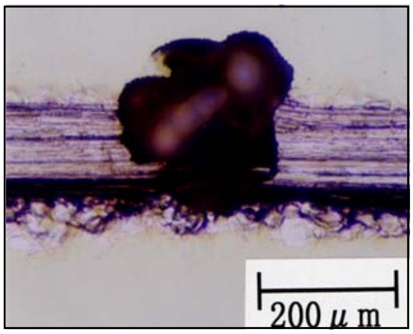


Figure 8:Pitting corrosion recognized after polarization measurement

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CONCLUSIONS

In this study, formation and characterization of TiO_2 thin film made on AISI 304 stainless steel by Ion-Beam-Mixing method were conducted. Then, the cathodic protection performance of 0.15 μ m thick TiO_2 thin film with some artificially scratched defect was investigated in 0.3wt% NaCl aqueous solution. And also, effects of ion source upon the photo-catalytic function of TiO_2 thin film was investigated.
The results of obtained were summarized as follows:

1. TiO_2 thin films made by Ion-Beam Mixing method shows the cathodic protection performance due to its photo-catalytic effect even when TiO_2 thin film has some inherent defect distribution in itself.
2. 0.15 μ m thick TiO_2 thin films shows the cathodic protection performance under UV ray irradiating condition in 0.3% NaCl aqueous solution of 298K even when it has artificially scratched defect whose width was about 200 μ m.

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