Stabilized Pt deposition on the TiO$_2$ films and their photocatalytic properties

Masaaki ISAI$^1$, Ikuta NAKAMURA$^1$, Takanori SATO$^1$ and Yoichi HOSHI$^2$

$^1$ Graduate School of Engineering, Shizuoka University 3-5-1 Johoku, Nakaku, Hamamatsu, 432-8561 Japan
$^2$ Faculty of Engineering, Shizuoka University 3-5-1 Johoku, Nakaku, Hamamatsu, 432-8561 Japan
#Graduate School of Engineering, Tokyo Polytechnic University 1583 Iiyama, Atsugi Kanagawa, E-mail: temisai@ipc.shizuoka.ac.jp

TiO$_2$ films were prepared with RF magnetron sputtering method. The platinum (Pt) films were deposited on the TiO$_2$ films. They act as cocatalysts which improve organic-decomposition properties, but deteriorate hydrophilicity because they have hydrophobic property. It seems that the thickness of Pt films is one of the most important parameters to improve the organic-decomposition properties. It was found that an optimum thickness of Pt films is from 500 to 700 Å to improve organic-decomposition properties without deteriorating hydrophilicity.

Keyword TiO$_2$ thin films, RF magnetron sputtering, Photocatalyst, Platinum deposition

1. INTRODUCTION

TiO$_2$ films have photocatalytic properties, for example, organic-decomposition and photo-excited hydrophilicity by irradiating the ultraviolet (UV) light ($\lambda \leq 380$ nm). They have been paid attention as an environmental clean-up material because the antimicrobial and self-cleaning effects are obtained without using chemicals and only using photon energy and rain water.$^{2-15}$

TiO$_2$ has crystal structures of rutile, anatase and brookite. The anatase has the highest photocatalytic activity. Therefore, anatase type TiO$_2$ is mainly used in photocatalytic reaction. There are two methods to improve these photocatalytic properties. The one method is to use the longer wavelength light effectively. The another method is to improve the light efficiency of the photocatalytic properties. The former is desired to develop a catalyst that responds to not only the UV light but also visible light. The latter is the revitalization of photocatalytic properties by depositing the co-catalystic material on the films. When platinum (Pt) is deposited, it is said that the electrons in the conduction band of TiO$_2$ successfully move to the Pt particles, and holes increase in the valence band of TiO$_2$ and react with water, and the active oxygens with a strong oxidizing power are generated more.

The purpose of this work is to improve the photocatalytic properties of TiO$_2$ films by depositing Pt on them.

2. EXPERIMENT

2.1 Sputtering apparatus

The TiO$_2$ films were prepared on the glass substrates (Matsunami Glass Industry, non-alkali glass #1737) by using RF magnetron sputtering method without flowing oxygen (O$_2$) gas. The TiO$_2$ films were coated with platinum films by using an ion-coater (Eiko Engineering IB-5).

Figure 1 shows a RF magnetron sputtering apparatus. It has three substrate holders. So, three films are successively deposited without breaking vacuum. It has the RF Power of 13.56 MHz, and 2 inch-TiO$_2$ target. The distance from the substrate to the target was 40 mm and a shutter is installed between them. The distance from the target to the shutter is 25 mm, and the distance from the shutter to substrate is 15 mm. The schale (hearth) of the target is made of duralumin. The substrate was heated with a halogen heater set up in the substrate holder. The substrate heater was not used through this study.

Fig. 1 Schematic of a RF magnetron sputtering apparatus.

Fig. 2 Schematic of an IB-5 ion coater.

The RF power and sputtering pressure were 200W and 10 Pa, respectively. Only the Ar gas was introduced. The Ar flow rate was 4 sccm.

Figure 2 shows a schematic diagram an IB-5
Pt films were deposited by using an ion coater at room temperature (R.T.). The size of the platinum target is 40mm $\Phi$, and the distance between the target and substrate is 55 mm. The deposition condition is as follows. The vacuum pressure was 0.01 Torr or less. The ionization voltage was 1.5 kV and the ion current was 1 mA. The Pt deposition rate was successfully controlled by using a metallic mesh installing between Pt target and substrate in the ion-coater.

Figure 3 shows the Pt film thickness as a function of deposition time. The thickness of Pt films linearly increases as increasing the deposition time.

![Figure 3: Sputtering time dependence of the thickness of Pt films.](image)

2.2 Evaluation method

2.2.1 Evaluation of photo-excited hydrophillicity

Figure 4 shows a principle of measuring contact angle by a titration method. The photo-excited hydrophillicity was evaluated by measuring the contact angle by using a Protractor. A measuring procedure is as follows. The sample is put in a darkroom for 24 hours before measurement. The first measurement is done without irradiation of ultraviolet light. It is the starting point of measurement which denotes an initial condition. After irradiation of UV light (Toshiba FL20S BLB, peak wavelength : 352 nm ; 3.52 eV) of 1mW/cm$^2$, the contact angle was successively measured with the interval of 10 min until 1 hour. After that, the contact angle was measured at the periods of 2 and 3 hours. It means that this process involves 8 times of measurement stage. The contact angle was calculated after averaging the data of 5 points in each measurement stage.

The hydrophillicity means the contact angle under 30 degree. The super-hydrophillicity means the contact angle under 5 degree. The contact angle under 7 degree shows an anti-fog property. It is very useful for mirrors and window shields of the vehicles.

2.2.2 Evaluation of organic-decomposition Properties

The organic-decomposition properties were evaluated by measuring a discoloration rate of methylene blue solution. Fig.5 shows a schematic diagram of measuring apparatus.

A methylene blue (C$_{16}$H$_{18}$N$_3$S$\cdot$Cl) is one of the thiazine basic dyes. It has a pure blue color and is a representative dye to evaluate photocatalytic properties. This blue dye is stable under irradiation of ultraviolet light of 352 nm (3.52eV). The methylene blue adsorbed on the TiO$_2$ films is photocatalytically decomposed and easily decolorized after irradiating this UV light. The decomposition mechanism is as follows. The electrons and hole pairs could be generated in the TiO$_2$ under the irradiation of this UV light. The reason is as follows. The energy of UV light (3.52 eV) is larger than the band gap of TiO$_2$ (3.2 eV). The electrons could be excited from valence band to conduction band in the TiO$_2$. So, the electrons and holes in the TiO$_2$ contribute to the photocatalytic activities.

The measuring sequence is as follows. At first, the sample is irradiated by ultraviolet light of 1mW/cm$^2$ for 24 hours to decompose residual organics on the sample surface. Then, the sample is dipped into a methylene blue solution in the darkroom for 12 hours. In this process, a methylene blue color is adsorbed on the sample surface. After irradiating UV light for 20 min, an absorption spectra of wavelength range between 600 to 700 nm is measured. This measurement is repeated until the accumulation of irradiation time is reached to 3 hours. It means that the nine times of data acquisition is proceeded.

![Figure 5: Schematic diagram of measuring apparatus by using discoloration of methylene blue solution.](image)

3. RESULTS AND DISCUSSION
3.1 Surface structure of sputtered TiO$_2$ films.

Figure 6 shows a SEM image of the sputtered TiO$_2$ films without depositing Pt films on them. The thickness of the TiO$_2$ is about 8500 Å.

![Fig. 6 A representative SEM image of TiO$_2$ film (without Pt deposition).](image1)

Figure 7 shows a SEM image of the sputtered TiO$_2$ films with depositing Pt films on them. The thicknesses of the TiO$_2$ and Pt films are about 8500 Å and 300 Å, respectively. It seems that there is not so difference between these two SEM images.

![Fig. 7 A representative SEM image of TiO$_2$ film. (with Pt deposition:30min).](image2)

3.2 Photo-excited hydrophilicity of the Pt-deposited TiO$_2$ films

Figure 8 shows a hydrophilicity characteristics of TiO$_2$ films. Almost all samples have excellent properties.

![Fig. 8 Hydrophilicity characteristics of TiO$_2$ films.](image3)

The initial values of contact angles were different between Pt-deposited TiO$_2$ films and TiO$_2$ films. They were measured without UV irradiation.

The reason is as follows. The contact angles strongly depend on the adsorption condition of contaminants and organic materials on the films. They also depend on the time before measurement. Especially, in the case of Pt-deposited TiO$_2$ films, Pt was deposited in the different apparatus (ion coater) after depositing TiO$_2$ films. So, they have different surface conditions. They caused different initial values of contact angles.

The mechanism of hydrophilicity could not be satisfactorily explained with only photocatalytic activity. It seems to involve some another unidentified factors which govern the hydrophilicity.

![Fig.9 Contact angles as a function of Pt-deposition time. The contact angles were measured after 3h-irradiation of UV light.](image4)
### 3.3 Organic decomposition of the Pt-deposited TiO$_2$ films

Figure 10 (a) and (b) show the organic decomposition of the Pt-deposited TiO$_2$ films. Figure 10 (a) shows the data with Pt-deposition time from 0 to 60 min. It means the thickness of Pt films are varied from 0 to 500 Å. Figure 10 (b) shows the data with Pt-deposition time from 80 to 160 min. It means the thickness of Pt films are varied from 700 to 1400 Å.

![Graph showing organic decomposition of TiO$_2$ films](image)

(a) Pt-deposition (0~60 min).

(b) Pt-deposition (80~160 min).

Fig. 10 Organic decomposition of TiO$_2$ films.

(a) Pt-deposition time from 0 to 60 min.
(b) Pt-deposition time from 80 to 160 min.

The organic decomposition properties increase as increasing the Pt-deposition time. But, they turn to decrease as increasing the Pt-deposition time larger than 100 min. It means there is an optimum Pt-deposition time. This optimum Pt-deposition time is recognized as from 60 to 80 min. It means an optimum thickness of Pt film is from 500 to 700 Å.

![Graph showing the relationship between organic-decomposition rate and Pt-deposition time](image)

Fig.11 The relationship between organic-decomposition rate and Pt-deposition time.

Figure 11 shows the dependence of decomposition revitalization index on the Pt-deposition time. The index has a peak at the Pt-deposition time of from 60 to 80 min. It means an optimum thickness of Pt film is from 500 to 700 Å.

In the case of hydrophilicity, an optimum Pt-deposition time is 20 min, as shown in Fig. 8. This means the thickness of Pt film is 200 Å. The hydrophilicity deteriorates as increasing the Pt-surface coverage on the TiO$_2$ films.

There is a clear discrepancy between the optimum Pt-thicknesses for organic decomposition and hydrophilicity. The mechanism of deterioration of contact angle could not be satisfactorily explained with only photocatalytic activity. There are some other effects which govern the hydrophilicity. The investigation on this problem is now under way.

### 4. CONCLUSION

It was shown that the organic-decomposition properties improved when the Pt films were deposited on the TiO$_2$ films. The organic-decomposition revitalization index has a peak at the thickness of Pt film from 500 to 700 Å. But, it turns to decrease as increasing the Pt-film thickness larger than 1000 Å. It means an optimum thickness of Pt film is from 500 to 700 Å.

The photo-excited hydrophilicity characteristics were also decreased as increasing the Pt-film thickness larger than 1000 Å.

### 5. ACKNOWLEDGEMENT

We wish sincerely to express our gratitude to everyone in the thin film device laboratory of Tokyo Polytechnic University. We have received a lot of advices and fruitful comments from them during measurements.
REFERENCE


(Received December 22, 2011; Accepted February 14, 2013)