Preparation of Pt-deposited TiO$_2$ films and evaluation of photocatalytic properties

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This research was designed for planning a progress of photocatalytic properties of TiO$_2$ thin films prepared by RF magnetron sputtering method with depositing Pt particles on top. The films prepared without heating substrate showed anatase structure. The organic-decomposition properties of TiO$_2$ thin films with Pt deposition showed large decomposition rate compared with these without Pt deposition. But optically excited hydrophilicity characteristics were decreased in the case of Pt deposition.

Keyword: TiO$_2$ thin films, RF magnetron sputtering, photocatalyst, Pt-deposition

1. INTRODUCTION

TiO$_2$ films have photocatalytic properties, for example organic-decomposition and photo-excited hydrophilicy by absorbing the ultraviolet light ($\lambda \leq 380$ nm)$^1$. 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 photo energy and rain water.$^2$-$^{10}$

TiO$_2$ has crystal structures of rutile, anatase and brookite. The anatase has the highest photocatalytic activity. Therefore, anatase type TiO$_2$ is chiefly used in photocatalytic reaction. To improve these photocatalytic properties, there are two methods. The one method is to make the light of long-wavelength side effective. The another method is to improve the light efficiency of the photocatalytic reaction. The former is desired to develop a catalyst that responds to not only the ultraviolet light but also visible light. The latter is the revitalization of photocatalytic properties by depositing the co-catalytic material on the films. When platinum (Pt) is deposited, it is said that the electrons in the conduction band of TiO$_2$ move to the Pt side, 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

The TiO$_2$ films were prepared on the glass substrate (Matsunami Glass Industry, non-alkali glass #1737) by using RF magnetron sputtering method. The TiO$_2$ films were coated with platinum films by using an ion-coater (Eiko Engineering IB-5). The insulating material like TiO$_2$ could be deposited by this RF magnetron sputtering method. A high rate sputtering of TiO$_2$ could be succeeded without O$_2$ flow.

Figure 1 shows a RF magnetron sputtering apparatus. It has three substrate holders and can deposit three films 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.

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Pt was deposited by using an ion coater. Figure 2 shows a schematic diagram. The uniform films with high sticking coefficient could be deposited by this apparatus. The vacuum pressure was 0.01 Torr or less. The ionization voltage was 1.5 kV and the ion current was 1 mA. The size of the platinum target is 40 mm φ, and the distance between the target and substrate is 55 mm. The Pt films were deposited at room temperature (R.T.).

The preparation condition of TiO$_2$ films is shown in Table 1. The RF power and sputtering pressure were 150, 200 W and 5, 10 Pa, respectively. Only the Ar gas was introduced. The deposition time was 120 minutes. Platinum films were deposited on the four sets of samples for 3 and 7 min, respectively.

### Table 1 Deposition condition of TiO$_2$ films

<table>
<thead>
<tr>
<th>Deposition Condition</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sputtering Target</td>
<td>TiO$_2$ Powder [99.9%]</td>
</tr>
<tr>
<td>Incident Power</td>
<td>150, 200 [W]</td>
</tr>
<tr>
<td>Reflected Power</td>
<td>2.7, 2.2, 0.2, 5.4 [W]</td>
</tr>
<tr>
<td>Ar Flow</td>
<td>4 [sccm]</td>
</tr>
<tr>
<td>Substrate Temp</td>
<td>R.T(96), R.T(122), R.T(106), R.T(140) [°C]</td>
</tr>
<tr>
<td>Gas Pressure</td>
<td>5, 10, 5, 10 [Pa]</td>
</tr>
<tr>
<td>Deposition Time</td>
<td>120 [min]</td>
</tr>
</tbody>
</table>

### Evaluation

<table>
<thead>
<tr>
<th>Type</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>Thickness</td>
<td>5546, 5936, 5882, 8448 [Å]</td>
</tr>
<tr>
<td>Deposition Rate</td>
<td>0.8, 0.8, 0.8, 1.2 [Å/sec]</td>
</tr>
<tr>
<td>Energy Gap</td>
<td>3.2, 3.2, 3.2, 3.2 [eV]</td>
</tr>
<tr>
<td>Energy Gap (Pt 3min)</td>
<td>3.14, 3.14, 3.16, 3.14 [eV]</td>
</tr>
<tr>
<td>Energy Gap (Pt 7min)</td>
<td>3.12, 3.1, 3.12, 3.1 [eV]</td>
</tr>
</tbody>
</table>

3. RESULTS AND DISCUSSION

3.1 Wavelength dependence of transmittance of TiO$_2$ films

Figure 3 shows the wavelength dependence of the transmittance of the TiO$_2$ films. Figure 3 (a) shows the data of the films deposited at R.F. power of 150 W and pressure of 5 Pa, respectively. The R.F. power and pressure were varied as follows. In Fig. 3 (b), the R.F. power of 150 W and the pressure of 10 Pa were used. In Fig. 3 (c), The R.F. power of 200 W and the pressure of 5 Pa were used. In Fig. 3 (d), the R.F. power of 200 W and the pressure of 10 Pa were used. In the case of sputtering pressure of 10 Pa, it has been understood that the amplitude of the transmission spectrum is smaller than that in the case of 5 Pa. This seems to be due to a formation of porous films because of a decrease of kinetic energy of sputtered particles at high pressure, and a decrease of the refractive index.

It has been understood that the energy gap decreases as increasing the deposition time of Pt. The energy gap was 3.1-3.12 in the case of 7-min deposition, while the energy gap was 3.2 eV in the case of without Pt-deposition.

3.2 Crystallographic structure of TiO$_2$ films

Figures 4(a) to (d) show the crystallographic structure of the TiO$_2$ thin films prepared with various preparation conditions as shown in figs. 3 (a) to (d). All these films show an anatase structure.

![Transmission spectrum](image1)

(a) RF Power 150 W Gas Pressure (Ar) 5 Pa

![Transmission spectrum](image2)

(b) RF Power 150 W Gas Pressure (Ar) 10 Pa

![Transmission spectrum](image3)

(c) RF Power 200 W Gas Pressure (Ar) 5 Pa
3.3 Photo-excited hydrophilicity characteristics of TiO$_2$ films

Figures 5(a) and (b) show the result of the photo-excited hydrophilicity characteristics of the TiO$_2$ films prepared with various preparation conditions as shown in Figs. 3 (a) to (d). The contact angle of dropped distilled water was measured after UV irradiation by using a Contact Angle System OCA 15 Plus (Data Physics).

Figures 5(a) and (b) show the data of the films prepared at the R.F. power of 150W and 200W, respectively. The films without Pt deposition show a super-hydrophilicity after UV-irradiation of 40 min. The super-hydrophilicity characteristics were deteriorated in the case of Pt-deposited films.

3.4 Organic-decomposition properties of TiO$_2$ films

Figure 6 shows the result of the organic-decomposition properties of the TiO$_2$ films prepared with various preparation conditions. The variation of methylene blue concentration after UV irradiation was measured by a V-550 spectrometer (Jasco).

Figures 6(a) and (b) show the data of the films prepared at the R.F. power of 150 and 200W, respectively. It was shown that the decomposition rate of the films prepared at 10Pa was bigger than those prepared at 5Pa. The decomposition rate has been improved as increasing the Pt deposition time.
4. CONCLUSION

The organic-decomposition properties were improved when platinum was deposited on the TiO$_2$ film. The TiO$_2$ films with Pt-deposition time of 7 min have higher organic-decomposition rate than those of 3 min Pt-deposition time. However, the photo-excited hydrophilicity characteristics decreased.

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REFERENCE


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