

Preparation and Characterization of Metallic Oxides Using Photoelectrochemical Deposition

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The deposition of lead dioxide onto the single crystal and polycrystalline TiO_2 electrodes using the photoelectrochemical epitaxial growth (PEEG) and electroless oxidation technique was carried out, and the electrochemical behavior of the prepared $\text{PbO}_2/\text{TiO}_2$ electrode was studied. The crystal orientation of the deposited oxides strongly depended on the crystal misfit between the oxides and the TiO_2 substrate. The AFM images showed that the crystal growth of deposited PbO_2 was affected by the current density and the temperature. From the measurements of the current-potential curve of the $\text{PbO}_2/\text{TiO}_2$ electrode, it was found that the PbO_2 , deposited on the polycrystalline TiO_2 , produces a surface state leading to a large anode tunneling current. Therefore the present $\text{PbO}_2/\text{polycrystalline TiO}_2$ electrode was very useful as an inert anode.

Key words: titanium dioxide, photoelectrochemistry, lead dioxide, electroless

1. INTRODUCTION

It is well known that PbO_2 is very useful as an inert anode in acidic solution¹⁻⁴. Sometimes, these electrodes act as an anode for the generation of ozone because of the high overvoltage for the oxygen evolution reaction. PbO_2/Ti electrodes where α - and β - PbO_2 are anodically deposited on a Ti plate in the solution containing Pb^{2+} are very important in practical use. In this case, the TiO_2 film formed on the Ti plate must be released or some conducting mixed oxides must be coated on the Ti substrate before the PbO_2 electrodeposition, because the TiOx oxide produced on the Ti substrate under the anodic bias behaves as an insulator and disturbs the electrodeposition of PbO_2 ¹.

The deposition of PbO_2 onto the TiO_2 semiconductor is possible if we use the photoelectrochemical epitaxial growth (PEEG) or electroless oxidation technique. In the PEEG, the photoproduced OH radical on the illuminated electrode surface significantly contributes to the deposition of the metallic oxide⁵⁻⁶. On the other hand, some metal oxide films such as PbO_2 ⁷, MnO_2 ⁸, and Ti_2O_3 ⁸ have been electrolessly deposited on glass in solutions containing metal cations, where they are oxidized in heterogeneous reactions by an oxidizing agent, peroxydisulfate. In both cases, metal oxide films will be formed by similar electrochemical reactions to those in anodic oxidation. These processes will be very available for the preparation of the metallic oxide film, compared with other methods such as CVD and sputtering, since the film can be prepared easily using a simple apparatus and under simple conditions. Moreover, the prepared PbO_2 coated TiO_2 ($\text{PbO}_2/\text{TiO}_2$) electrode may be useful as an inert anode material in acidic solution, because a large tunneling current flows via the PbO_2 crystal formed at the surface under anodic bias.

In this paper, the preparation of PbO_2 on the single and polycrystalline TiO_2 electrode by PEEG was investigated and the electrochemical behavior of the prepared $\text{PbO}_2/\text{TiO}_2$ was measured. In comparing, the preparation and characterization of the PbO_2 by

electroless oxidation was also investigated.

2. EXPERIMENTAL

The polycrystalline TiO_2 used as a working electrode was prepared from titanium plate. After washing with acetone, the specimen was heated in air at 400 or 650°C for 3hr. The geometric area exposed to the electrolyte was reduced to 1 cm² on one side by epoxy resin to mask off the remainder of the electrode. The surfaces of TiO_2 single crystals with rutile type structure were used the (100) and (001) planes. The TiO_2 single crystal was reduced in H_2 at 800°C so as to increase conduction. Indium was deposited on the back side of TiO_2 for purpose of ohmic contact.

PbO_2 was photoelectrochemically deposited onto the single and polycrystalline TiO_2 surface under a constant current density for 30 min under illumination of a 500W ultra high-pressure mercury lamp. Pt and $\text{Hg}/\text{Hg}_2\text{SO}_4$ were used as the counter and reference electrodes, respectively. 0.1 M $\text{Pb}(\text{NO}_3)_2$ was used as the electrolyte.

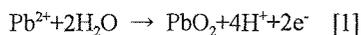
Electroless deposition of PbO_2 on TiO_2 substrate from a solution containing Pb^{2+} and an oxidizing agent was also investigated to compare the photoelectrochemical technique. The substrate was immersed in a vertical position into a mixed solution of $\text{Pb}(\text{NO}_3)_2$ and $(\text{NH}_4)_2\text{S}_2\text{O}_8$. $\text{CH}_3\text{COONH}_4$ were added to the solution as supporting electrolyte. The pH of the solution was adjusted to 6 by HNO_3 titration. After an induction time of several hours, the solution gradually turned brown, and after 12 hours a compact and continuous oxide film was precipitated on the substrate.

The deposited oxide films prepared on TiO_2 were washed in distilled water, followed by drying at room temperature. The structures of the oxide films were examined by X-ray diffraction analysis (XRD) using monochromatic $\text{CuK}\alpha$ radiation. Morphological observations of the oxide films were carried out with an atomic force microscope (AFM). The electrochemical behavior of the $\text{PbO}_2/\text{TiO}_2$ electrodes was obtained in H_2SO_4 .

3. RESULTS AND DISCUSSION

Figure 1 shows XRD patterns of the PbO_2 photoelectrochemically deposited onto the various TiO_2 electrode in 0.1 M $\text{Pb}(\text{NO}_3)_2$ with $\text{pH}=1$ at $50 \mu\text{A}/\text{cm}^2$ under illumination. No deposition occurred in darkness. 1 M $\text{Pb}(\text{NO}_3)_2$ solution was adjusted to $\text{pH}=1$ by HNO_3 titration, since the solution of 0.1 M $\text{Pb}(\text{NO}_3)_2$ was primarily $\text{pH}=4$. The product mainly consisted of a polycrystalline $\beta\text{-PbO}_2$ in low pH , but that a large amount of polycrystalline $\alpha\text{-PbO}_2$ was also deposited at relatively high pH . This result is quite similar to the case for the deposition of the PbO_2 onto the metal electrode⁹. In this figure, the same crystal orientation (100) and (001) was observed for the $\beta\text{-PbO}_2$ because of the same rutile structure. The result indicates that the orientation of deposited $\beta\text{-PbO}_2$ was strongly dependent on the crystal structure of the TiO_2 substrate surface.

On the other hand, figure 2 shows XRD patterns of the PbO_2 onto the various TiO_2 electrode by electroless oxidation technique. The following electroless deposition occurred for the PbO_2 deposition.



The same crystal orientation (100) and (001) was also observed for the $\beta\text{-PbO}_2$. In the short deposition time, $\alpha\text{-PbO}_2$ was observed with $\beta\text{-PbO}_2$, but $\beta\text{-PbO}_2$ only grew as the deposition advanced. Therefore, in the short deposition time the growth of electroless deposited $\beta\text{-PbO}_2$ is not only due to the mismatch but also due to other factors, such as change of the pH .

Figure 3 shows the AFM images of PbO_2 deposited on the single crystal TiO_2 by photoelectrochemical technique. In room temperature (A), PbO_2 was deposited

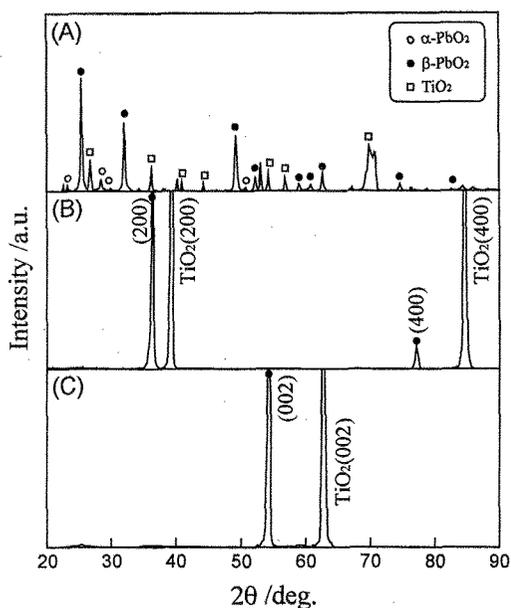


Figure 1. XRD patterns of the PbO_2 on the polycrystalline TiO_2 (A), single crystal TiO_2 (100) (B) and (001) (C) electrode by photoelectrochemical technique.

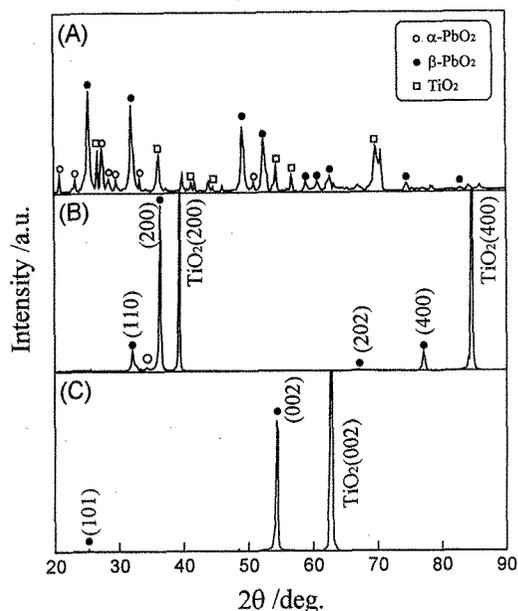


Figure 2. XRD patterns of the PbO_2 on the polycrystalline TiO_2 (A), single crystal TiO_2 (100) (B) and (001) (C) electrode by electroless technique.

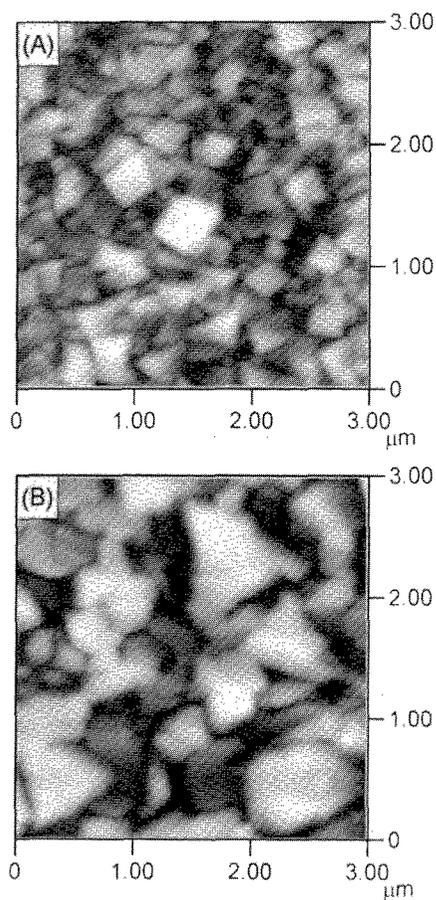


Figure 3. AFM images of the PbO_2 deposited on the single crystal TiO_2 at room temperature (A) and 80°C (B) by photoelectrochemical technique.

uniformly and the grain size was about 0.1-0.5 μm . The roughness of electrode surface and the grain size were increased with temperature under the photoelectrochemical deposition. On the other hand, a large island-like crystal growth was observed for PbO_2 on the polycrystalline TiO_2 in Figure 4. Moreover, the crystal shape was influenced by the current density. At low current density, the small crystal grew uniformly in Fig. 4(C). Therefore, in the PEEG technique, we can control the crystal shape of the deposited PbO_2 by the current density and the temperature.

The electroless deposited PbO_2 onto the TiO_2 (100) single crystal was distributed uniformly as small clusters as shown in Fig. 5-(A). The grain size of the deposited PbO_2 film for 3 hours was about 0.1-0.3 μm , where the deposited film was determined to be mixed phases of α - and β - PbO_2 by X-ray analysis. The grain size increased together with the increase of the deposition time (Fig. 5-(B)), where only the β - PbO_2 phase grew. In the electroless technique, control the crystal shape was difficult compared with the photoelectrochemical deposition, but the crystal growth with large size of the deposited PbO_2 was more advanced.

Figure 6 shows the current-potential curves of PbO_2 /single crystal TiO_2 (A) and PbO_2 /polycrystalline TiO_2 (B) where the PbO_2 was photoelectrochemically deposited at $500 \mu\text{A}/\text{cm}^2$ for 30 min. The deposited PbO_2 completely covered the surface of the TiO_2 based on an EPMA measurement. No photocurrent was

observed for either of the electrodes because the PbO_2 completely interrupts the illumination onto the TiO_2 surface. Dark current was scarcely observed under the anodic bias, while the cathodic current due to the PbO_2 reduction was observed in the potential region more negative than about the flatband potential for single crystal TiO_2 as shown in Fig. 6 (A). The flatband potential of the single crystal TiO_2 electrode was about -800 mV (vs. $\text{Hg}/\text{Hg}_2\text{SO}_4$) according to the M-S plot measurement. On the other hand, a large dark tunneling current due to the oxygen evolution reaction was observed under the anodic bias, and a cathodic current due to the reduction from PbO_2 to PbSO_4 was observed in the potential region more negative than the equilibrium potential of $\text{PbO}_2/\text{PbSO}_4$, $E(\text{PbO}_2/\text{PbSO}_4)$ at the β - PbO_2 /polycrystalline TiO_2 electrode, as shown in Fig. 6 (B). The electrochemical behavior of the present PbO_2 /polycrystalline TiO_2 electrode is quite similar to the case of the general metal electrode.

Figure 6 (C) shows the current-potential curves of the PbO_2 /polycrystalline TiO_2 , where the PbO_2 was electroless deposited for 12 hours. This electrode is also the same behavior as the photoelectrochemically deposited $\text{PbO}_2/\text{TiO}_2$ electrode.

The result indicates that no surface state bringing about the dark tunneling current under anodic bias in the present potential region exists at the interface of the single crystal TiO_2 . Under a cathodic bias, a large cathodic current due to the reduction of PbO_2 flows

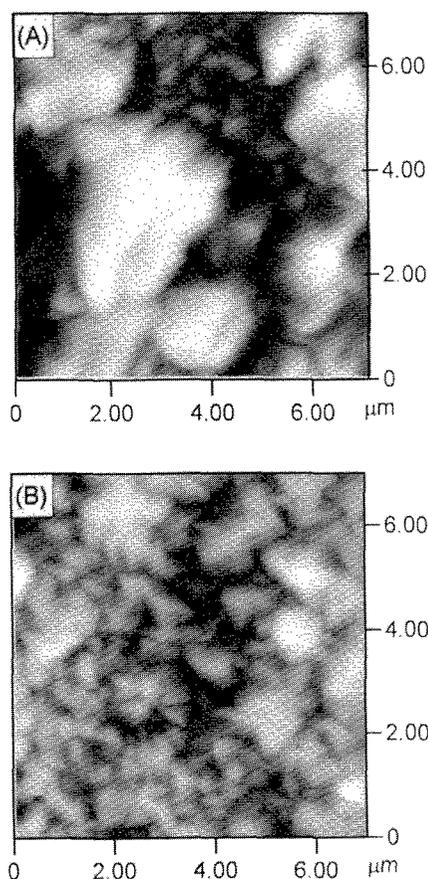


Figure 4. AFM images of the PbO_2 deposited on the polycrystalline TiO_2 at $500 \mu\text{A}/\text{cm}^2$ (A) and $50 \mu\text{A}/\text{cm}^2$ (B) by photoelectrochemical technique.

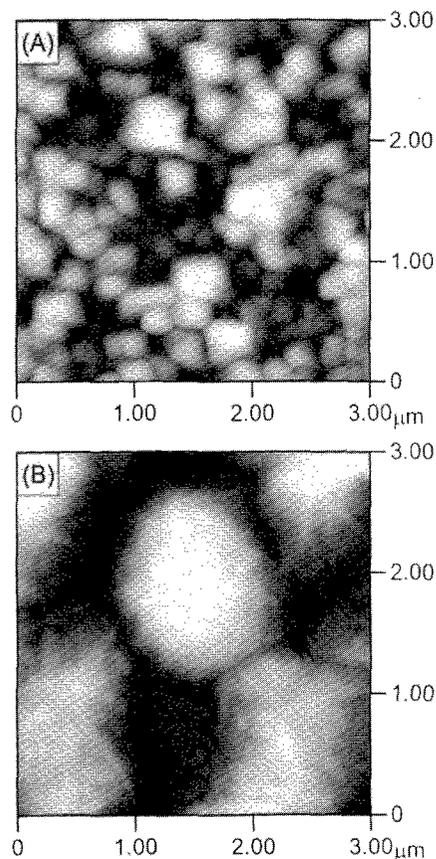


Figure 5. AFM images of the PbO_2 deposited on the single crystal TiO_2 by electroless oxidation. Deposition time for 3 hour (A) and 40 hour (B).

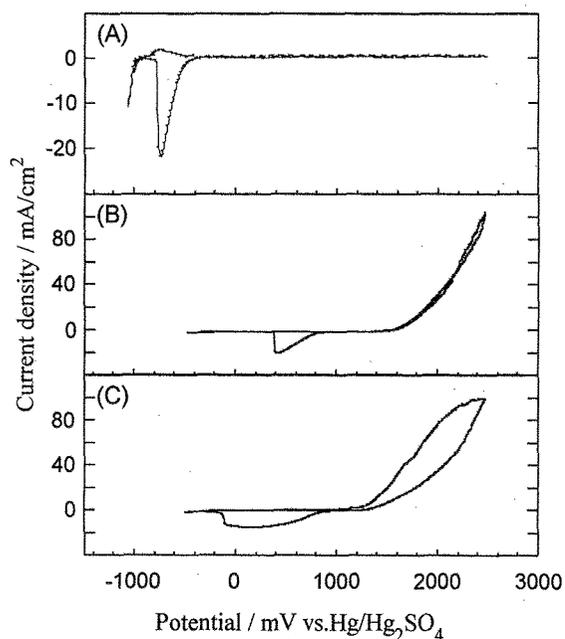


Figure 6. Current-potential curves of the photoelectrochemical deposited PbO_2 on the single crystal TiO_2 (A), polycrystalline TiO_2 (B), and electroless deposited PbO_2 on polycrystalline TiO_2 (C) in 0.5M H_2SO_4 .

because schottky barrier scarcely forms at the $\text{PbO}_2/\text{TiO}_2$ interface in the potential region more negative than the flatband potential.

On the other hand, Fermi level pinning occurred at the $\text{PbO}_2/\text{polycrystalline TiO}_2$ interface where a surface state has a large electron density. This surface state consists of Ti-Pb-O which is formed at the crystal edges

or grain boundaries or some defects at the polycrystalline TiO_2 in the interface, because no dark tunneling current was observed for the $\text{PbO}_2/\text{single crystal TiO}_2$. Therefore the prepared PbO_2 on the polycrystalline TiO_2 electrode by photoelectrochemical technique may be useful as an inert anode material in acidic solution.

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