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Sputtering of the aqueous solution of $TiCl_3$ and the TiO_2 formation

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DC-plasma was generated between the substrate and the aqueous solution of $TiCl_3$ under the reduced pressure. Deposition was carried out for 1 h. The amount of the liquid loss and the morphology of the products were examined. A linear relationship existed between the liquid loss and the input power. The threshold power was 200 Watt, under which no stable discharge was established. The sputtering yield of H_2O molecules was between 100 and 900 at the applied voltages between 600 and 1300 V. TiO_2 thin films of microcrystalline rutile structure were deposited on the quartz glass substrates. On the titanium substrate, thick films of highly ⟨110⟩ oriented rutile structure were produced. © *2002 Kluwer Academic Publishers*

1. Introduction

DC-plasma-assisted synthesis of ceramic films using liquid is a new method [1]. When a highly positive bias is applied to the substrate above the liquid surface, glow discharge is generated between the substrate and the liquid surface. With the choice of a suitable carbon containing solution, diamond can be deposited. The approach offers greater flexibility over the selection of the starting materials than if the starting materials are limited to gases and solids as most of the conventional film formation by sputtering [2]. The present paper deals with the application of the dc-plasma above the liquid surface to grow TiO_2 films. Although TiO_2 films have applications in electronics such as photolysis [3] and gas sensor [4], our objective is to show that the dc-plasma above the liquid surface can provide a useful way of producing the oxide films, TiO_2 as an example, by sputtering the dilute aqueous solution. The effects of important process parameters are examined, including the relationship between the amount of the liquid loss during the deposition and the sputtering yield of H_2O molecules.

2. Experimental

Fig. 1 shows the schematic illustration of the apparatus. The reaction vessel was made of glass of 5 cm diameter and covered with a rubber stopper. The vessel was evacuated with an aspirator. Two kinds of substrate were used. Polycrystalline titanium rod of 6 mm diameter and 6 mm long was attached directly to the water-cooled electrode. The quartz glass disc of 6 mm diameter and 1 mm thick was set inside the stainless steel holder of 8 mm outer diameter, 6 mm inner diameter and 5 mm long. The solution was cooled and circulated. The surface level of the solution was kept constant with the aide of a reservoir. The substrate-liquid distance was 8 mm and the liquid layer thickness was 20 mm. The solution was prepared by diluting the reagent grade aqueous solution of 20 wt% $TiCl_3$ with water. The $TiCl_3$ concentration tried was 1×10^{-4}, 5×10^{-4}, 1×10^{-3}, 5×10^{-3} and 1×10^{-2} mol/*l*. The solution was biased negatively via graphite block. The deposition was carried out for 1 h under the constant substrate temperatures of 900, 1000 and 1100°C. The applied voltage was adjusted manually to keep the substrate temperature constant. The substrate temperature was measured by an optical pyrometer. The pressure was measured with a vacuum gauge. Details of the apparatus have been described elsewhere [5]. The deposits were examined with optical microscopy, scanning electron microscopy (SEM), X-ray diffraction (XRD) and Raman spectroscopy. The 514.5 nm line of an Argon laser was used to induce the Raman spectrum.

3. Results and discussion

3.1. Deposition parameters

Plasma fluctuated violently in the end composition of 1×10^{-4} and 1×10^{-2} mol/*l* with the titanium substrate. With the quartz glass substrate, it was impossible to produce stable plasma using 1×10^{-4} mol/*l* solution. For other compositions, plasma was stable. To maintain a given substrate temperature, it was necessary to apply a higher voltage for solutions with lower $TiCl_3$ concentration. During the deposition for 1 h, the first 5 min was unstable because of the transient time for the temperature stabilization. Generally, applied voltage decreased gradually with time and the corresponding

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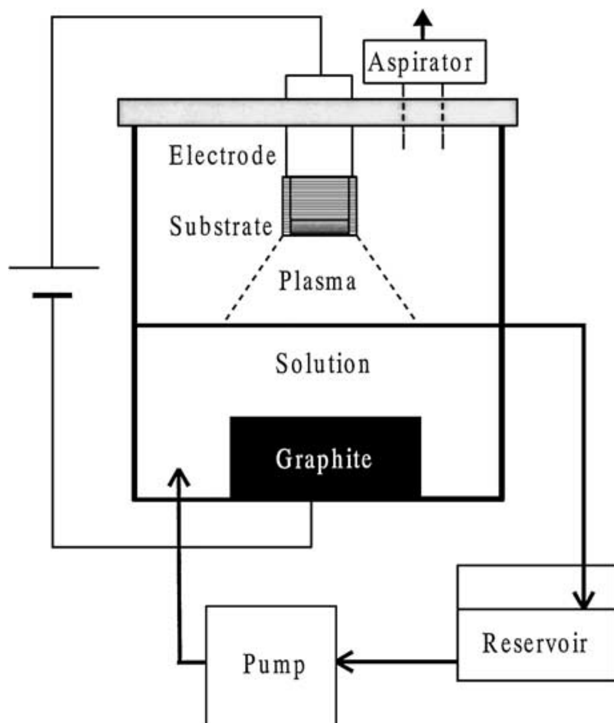


Figure 1 Schematic diagram of the experimental setup.

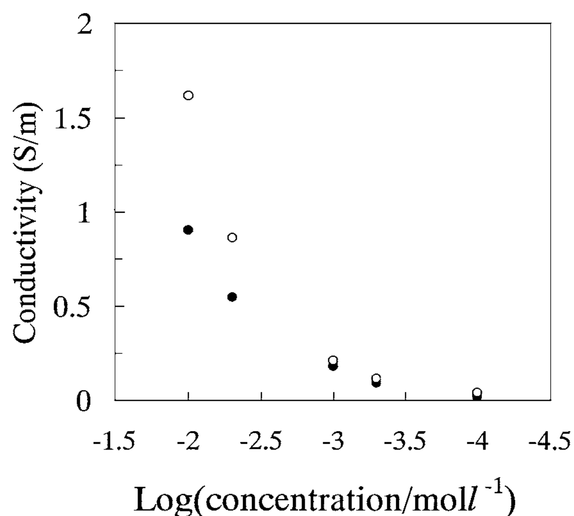


Figure 2 Conductivity change in solution as a function of log(concentration). Deposition was carried out at 1000°C for 1 h using the titanium substrate. (●) Before deposition and (○) after deposition.

variations in current and pressure were small. Therefore, average values of applied voltage, current and pressure were defined reasonably. The highest values of 1278 V, 647 mA and 22 kPa were obtained for deposition with the titanium substrate at 1100°C using 1×10^{-4} mol/*l* solution. On the other hand, the lowest values were 616 V, 304 mA and 10 kPa with the quartz glass substrate at 900°C using 5×10^{-3} mol/*l* solution. The conductivity of the solution, before and after the deposition at 1000°C, is plotted in Fig. 2 as a function of log(concentration) for the titanium substrate series. The room temperature resistances of the 2 cm deep liquid with the initial concentration of 1×10^{-4}, 5×10^{-4}, 1×10^{-3}, 5×10^{-3} and 1×10^{-2} mol/l were calculated to be 510, 112, 64, 19 and 11 Ω, respectively.

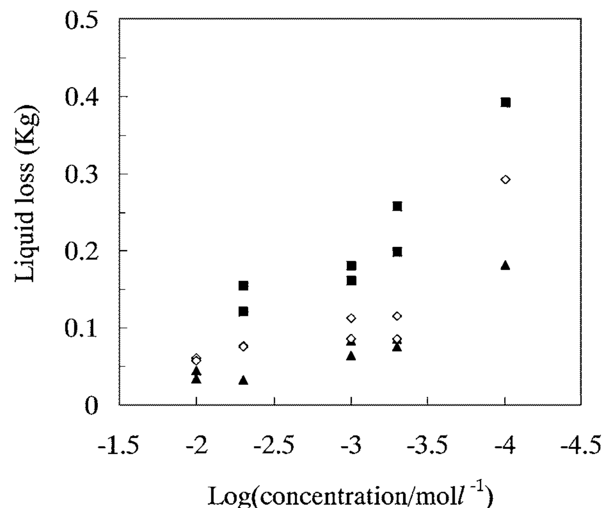


Figure 3 Liquid loss as a function of log(concentration). Deposition was carried out for 1 h using the titanium substrate. The substrate temperatures are (■) 1100, (◇) 1000 and (▲) 900°C.

The deposition increased the conductivity. The lowest concentration of 1×10^{-4} mol/*l*, for example, showed a change from 0.02 to 0.04 S/m. The conductivity change of a given initial concentration was almost the same regardless of the kind of substrate and its temperature. The chemical reactions taking place in the solution are responsible for the conductivity change, but it is very complicated according to the similar experiments in glow discharge electrolysis (GDE) [6, 7]. We will pay attention to the amount of the liquid loss.

3.2. Liquid loss

Total liquid volume was measured before and after the deposition for 1 h and the difference expressed in weight is the liquid loss. Fig. 3 shows the liquid loss as a function of log(concentration) in the titanium substrate series. The substrate temperatures are also indicated in the plots. The liquid loss of a given substrate temperature increased with decreasing concentration. The largest loss was 0.392 Kg, which was observed at the substrate temperature of 1100°C using 1×10^{-4} mol/*l* solution. The same liquid loss m is shown in Fig. 4 as a function of input power w (product of average voltage and

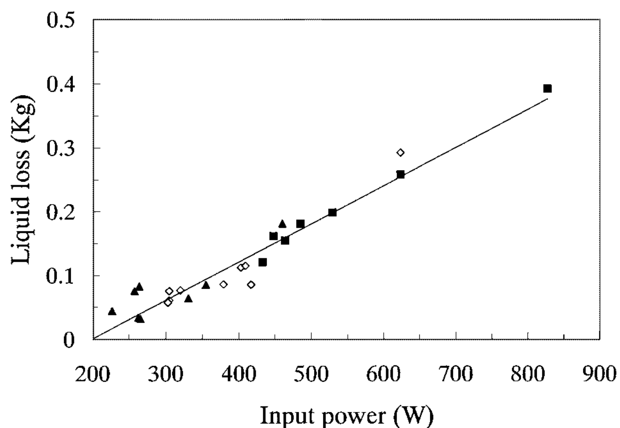


Figure 4 Liquid loss as a function of input power. Deposition was carried out for 1 h using the titanium substrate. The substrate temperatures are (■) 1100, (◇) 1000 and (▲) 900°C.

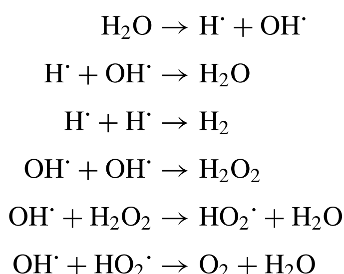
average current). The solid line was computed using a least squares program. The relationship is

$$m = 0.0006(w - 200) \quad (1)$$

There is a threshold power of 200 W: this is the minimum power necessary to establish a stable discharge. The origin of the liquid loss is attributed to GDE and sputtering. GDE and sputtering are the same in principle. However in GDE analysis, total H_2O loss is not discussed, instead, yields of H_2, O_2 and H_2O_2 are described in terms of Faraday's law. Thus we describe GDE and sputtering separately. Evacuating the reaction vessel also gives rise to the liquid loss. However, this was not considered.

3.2.1. GDE

It is generally accepted that aqueous solution experiences a kind of electrolysis under intense bombardment with H_2O^+ ions [6–8]. Some water molecules are broken into radicals. These radicals undergo several reactions, for example



$$H_2O \rightarrow H^{\cdot} + OH^{\cdot}$$
$$H^{\cdot} + OH^{\cdot} \rightarrow H_2O$$
$$H^{\cdot} + H^{\cdot} \rightarrow H_2$$
$$OH^{\cdot} + OH^{\cdot} \rightarrow H_2O_2$$
$$OH^{\cdot} + H_2O_2 \rightarrow HO_2^{\cdot} + H_2O$$
$$OH^{\cdot} + HO_2^{\cdot} \rightarrow O_2 + H_2O$$

Yields of H_2, O_2 and H_2O_2 are reported in significant excess of the Faraday's law values. However, even if we assume the yields 10 times the Faraday's law values, the consumption of H_2O is negligibly small compared with the present experimental values. For example, passing 1 A for 1 h consumes only 0.003 Kg of water in the electrolysis. Thus the evolution of H_2, O_2 and H_2O_2 in GDE contributes little to the liquid loss.

3.2.2. Sputtering

It is suggested that gaseous ions entering the liquid have on the average energy of 100–200 eV [8, 9]. The value is two orders of magnitude larger than that needed to evaporate water. This signifies an important occurrence of sputtering. The chemical reaction occurring at the liquid-gas interface is very complex as mentioned in Section 3.2.1. We simply assume that all current near the liquid surface is carried by the gaseous H_2O^+ ions entering the solution and that the sputtered species are H_2O molecules or can be counted as H_2O even if H_2O is broken to smaller chemical species. Let us then calculate how many H_2O molecules are sputtered by collision with one H_2O^+ ion. The sputtering yield s of water can be expressed using the measured values of liquid loss

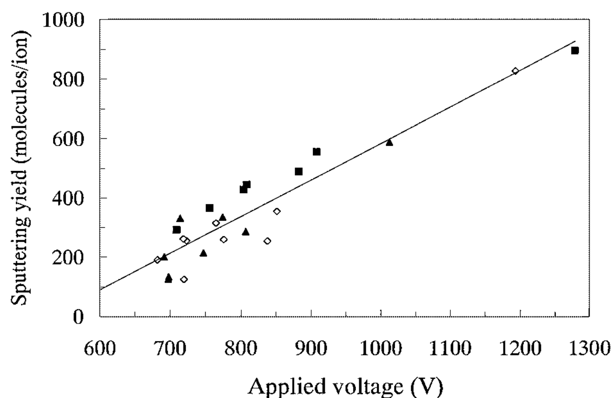


Figure 5 Sputtering yield of water as a function of applied voltage. Deposition was carried out for 1 h using the titanium substrate. The substrate temperatures are (■) 1100, (◇) 1000 and (▲) 900°C.

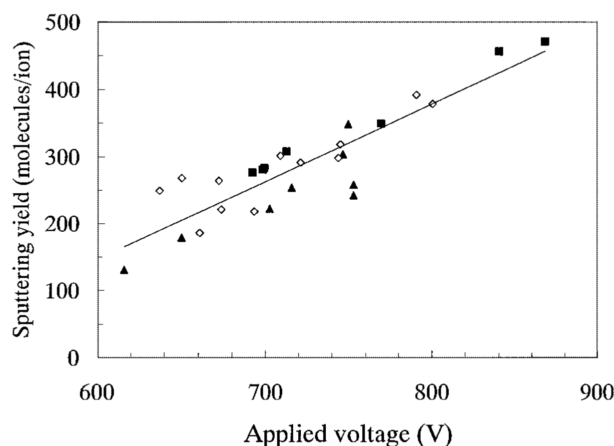


Figure 6 Sputtering yield of water as a function of applied voltage. Deposition was carried out for 1 h using the quartz glass substrate. The substrate temperatures are (■) 1100, (◇) 1000 and (▲) 900°C.

and the current as

$$s = \frac{1.54mNe}{I} \times 10^{-2} \quad (2)$$

where N is the Avogadro's constant and e is the elementary electric charge. For the deposition on the titanium substrate at 1000°C under 851 V, putting $m = 0.115$ Kg and $I = 0.48$ A, we obtain $s = 354$. The sputtering yields in the titanium substrate series are plotted as a function of applied voltage V_a (Fig. 5). The linear relationship gives

$$s = 1.23(V_a - 527) \quad (3)$$

Fig. 6 shows the yield in the quartz glass substrate series. Although the plots are fairly scattered, linear approximation gives

$$s = 1.16(V_a - 473) \quad (4)$$

Difference in Equations 3 and 4 reflects differences of shape and materials quality between the titanium substrate and the stainless steel holder. Lack of the data near the threshold voltage made the linear extrapolation rather arbitrary and thus it is difficult to discuss the implication of 527 and 473 V. We believe the cathode drop

to be around 500 V. Further research is underway for detailed examination in the sputtering yield. When we compare the sputtering yield of water with that of metal, we see a great difference. The present yields ($s = 100$–900) are two orders of magnitude greater than the yield of copper ($s = 2$ for Ar^+ at 600 V) [10]. One reason is attributed to the difference in the binding energy of water and copper. A weak hydrogen bonding works among the water molecules, whereas copper atoms are condensed with a strong metallic bonding. As a measure of binding energy, let us take the enthalpy of vaporization. For water it is 41 kJ/mol and for copper it is 305 kJ/mol. Even if the sputtering yield is inversely proportional to the enthalpy of vaporization, the measured yield is still one order of magnitude greater than expected from the copper sputtering. Another reason is attributed to the collision of H_2O^+ ions with H_2O molecules in the cathode drop layer. Mean free path of H_2O molecules under 15 kPa is about 2 μm at 1300 K [11]. On the other hand, the layer thickness of cathode drop is at least 500 μm [8]. Therefore, H_2O^+ ion will collide with H_2O molecules and some of them will hit the solution together with the H_2O^+ ion. So far, the sputtering yield has been interpreted as the number of H_2O molecules scattered per incident H_2O^+ ion. Now it is better to understand the yield as the number of H_2O molecules sputtered with the influence of one H_2O^+ ion entering the solution. This definition includes the

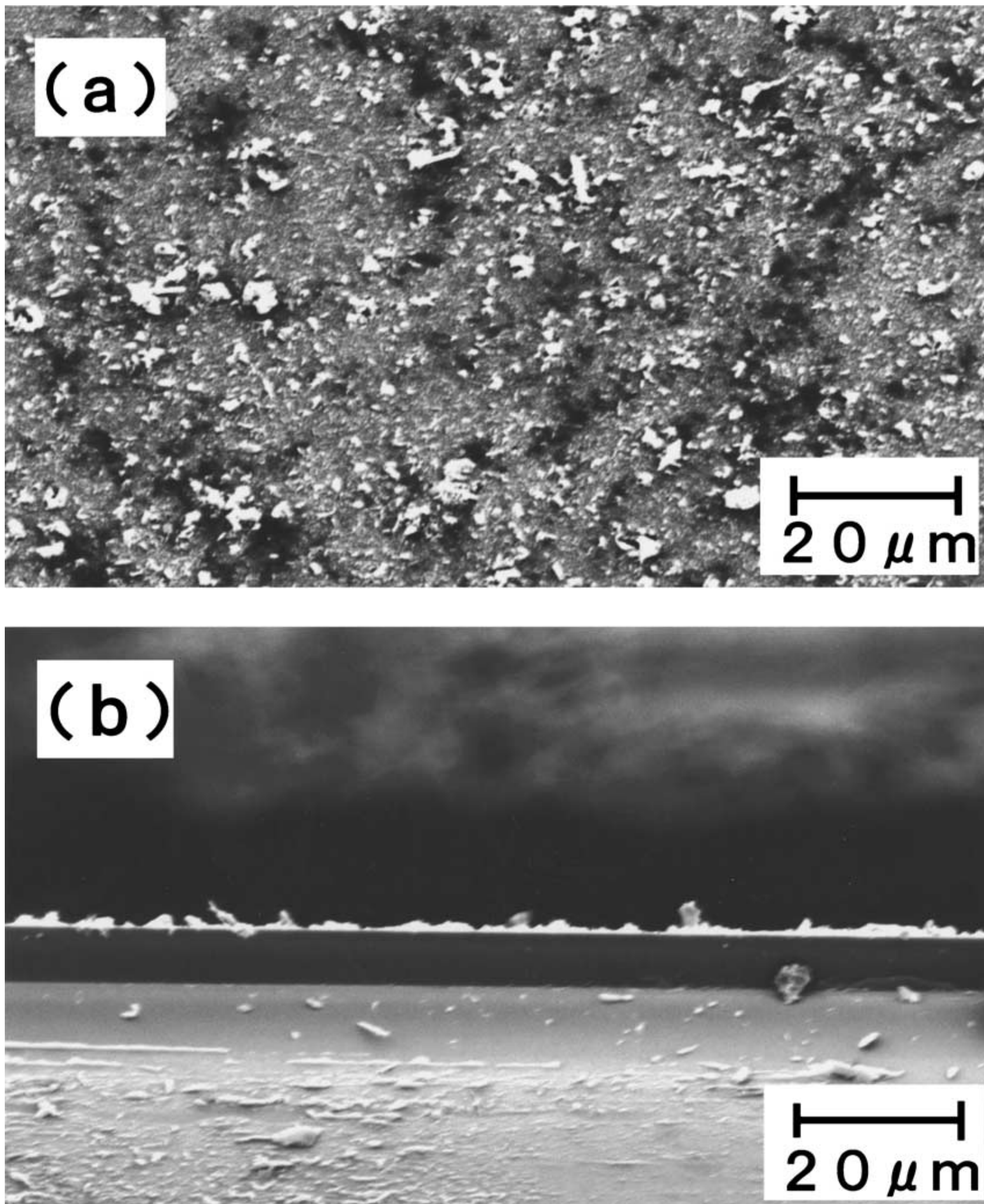


Figure 7 SEM photographs of deposit prepared on the quartz glass substrate at 1000°C for 1 h using 1×10^{-3} mol/*l* solution. (a) Surface morphology and (b) cleaved cross-sectional view.

accompanying H_2O molecules and does not change the present experimental findings.

3.3. Deposit on the quartz glass substrate

Sputtering the 5×10^{-4} mol/*l* solution produced no appreciable deposit at 900, 1000 and 1100°C. For other concentrations at 900°C, deposits were appreciable but little. Much deposits with nearly the same quantity were observed at 1000 and 1100°C. With the stainless steel holder, the discharge took place only at the holder surface. This influenced the distribution of plasma density on the substrate. A few closed curves like annual rings were sometimes observed on the deposit surface by optical microscopy. Fig. 7 shows the SEM photographs of deposit obtained at 1000°C using 1×10^{-3} mol/*l* solution. Surface morphology of the central part (Fig. 7a) and its cleaved cross-sectional image (Fig. 7b) show that the surface has numbered spikes and hollows. However, the bulk is quite flat and seemingly dense with 7 μm thickness. Thicker films were deposited with higher concentration. The film thickness prepared at 1000°C was 15 μm with 5×10^{-3} mol/*l* solution and 21 μm with 1×10^{-2} mol/*l* solution. A trial of deposition using 5×10^{-2} mol/*l* solution failed because of the instability of plasma. This is due to the high initial conductivity of 3 S/m in the solution. XRD analysis of the deposit showed no sharp peak useful for crystal identification. Therefore, Raman spectra from the TiO_2 powder (purity: 99.9%) and deposits were compared. Deposits examined were prepared at 1000°C using 1×10^{-3}, 5×10^{-3} and 1×10^{-2} mol/*l* solution. Fig. 8a shows the spectrum from deposit using 1×10^{-2} mol/*l* solution and Fig. 8b is the powder pattern. Two of the powder peaks agree with the literature data of rutile; E_g mode at 448 cm^{-1} and A_{1g} mode at 610 cm^{-1} [12]. The other small powder peak at 516 cm^{-1} is identified as the $A_{1g} + B_{1g}$ mode from anatase [13]. Although the deposit spectra have a fairly weak intensity, their peak positions agree well with rutile. Other deposits showed exactly the same Raman pattern with Fig. 8a. Thus we conclude that deposits are microcrystalline TiO_2 films of rutile structure.

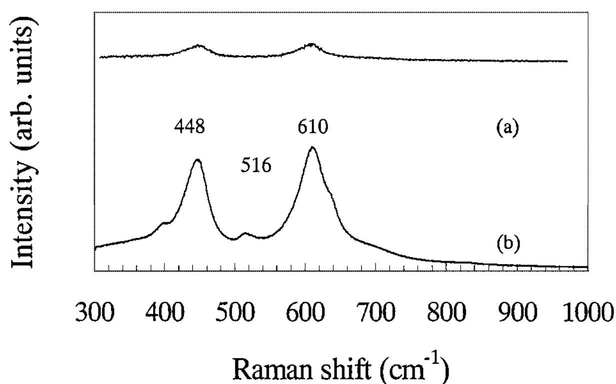


Figure 8 Raman spectra from deposit and TiO_2 powder. (a) Raman spectrum from deposit prepared on the quartz glass substrate at 1000°C for 1 h using 1×10^{-2} mol/*l* solution and (b) Raman spectrum from the TiO_2 powder.

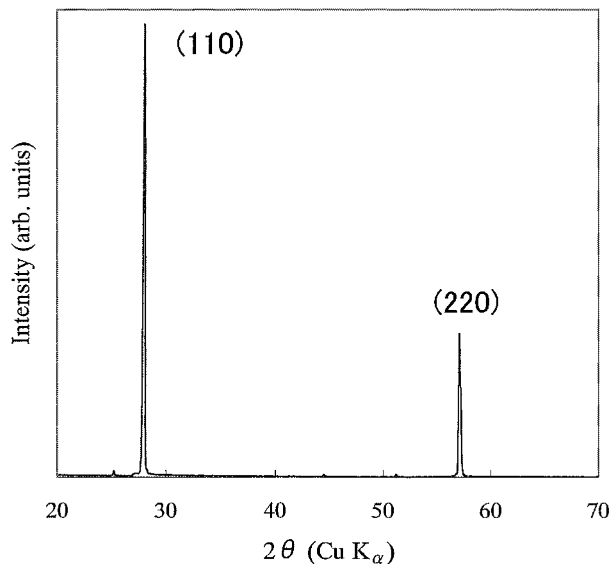
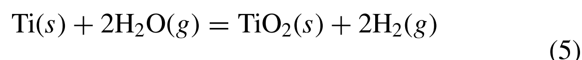


Figure 9 XRD pattern of product prepared on the titanium substrate at 1000°C for 1 h using 5×10^{-3} mol/*l* solution. Product is identified as rutile-TiO_2 mixed with a small amount of anatase. Deposit exhibited preferred ⟨110⟩ orientation.

3.4. Product on the titanium substrate

In all temperatures and concentrations, discharge took place at the entire front surface of the substrate. White product, thicker than that on the quartz substrate, covered the substrate including the side. XRD analysis showed that the product is rutile-TiO_2 with a preferred ⟨110⟩ orientation (Fig. 9). The (110) surface has the highest atomic density. The rutile-TiO_2 contained a small amount of anatase as indicated by a weak peak at $2\theta = 25.3°$. TiO_2 can be produced by the deposition from the gas phase and possibly by the oxidation of the titanium substrate. Although the present plasma method is not an equilibrium process, thermodynamic analysis will be a help to understand the possible occurrence of the oxidation [14]. Oxidation of the titanium substrate exposed to water vapor at 1300 K is expressed as



$$\mathrm{Ti}(s) + 2\mathrm{H_2O}(g) = \mathrm{TiO_2}(s) + 2\mathrm{H_2}(g)$$

$$\Delta G(\mathrm{kJ}) = -357.7 + 21.6 \log \frac{P_{\mathrm{H_2}}}{P_{\mathrm{H_2O}}} \quad (5)$$

This indicates the possibility of titanium oxidation to TiO_2 since the partial pressure of water vapor is always greater than that of hydrogen molecule. The amount of the weight increase of the substrate was measured to understand the process of the TiO_2 formation for samples treated at 1000°C for 1 h. The increase per unit surface area was 0.064 g/cm^2 with 5×10^{-4} mol/*l* solution. The corresponding TiO_2 thickness should be 150 μm if all is deposited from the gas phase. On the other hand, it becomes 380 μm if all is formed by the oxidation of the titanium substrate. Fig. 10 shows the SEM photographs of product prepared at 1000°C for 1 h using 5×10^{-4} mol/*l* solution. Surface morphology of the central part (Fig. 10a) and its cross-sectional image (Fig. 10b) show that the products are crystallized well and rich in pores. The film thickness was 600 μm. This indicates the porous TiO_2 formation via oxidation of the

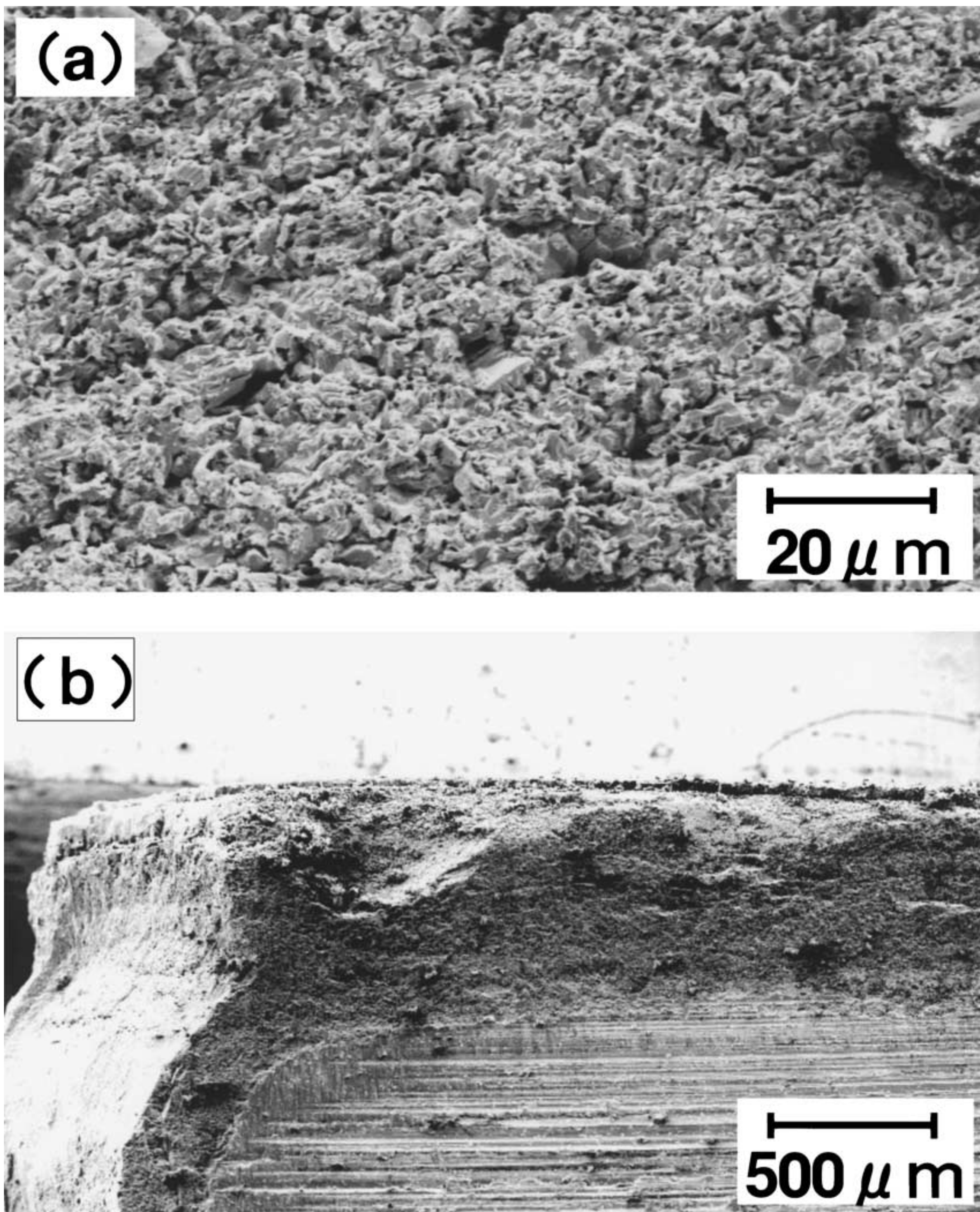


Figure 10 SEM photographs of product prepared on the titanium substrate at 1000°C for 1 h using 5×10^{-4} mol/*l* solution. (a) Surface morphology and (b) cross-sectional view.

titanium substrate. The rectangular corner of the original titanium substrate was rounded as shown in Fig. 10b. The corner is the active diffusion site of charged ions, because the substrate is intensively biased.

4. Conclusions

DC-plasma was generated between the substrate and the aqueous solution of $TiCl_3$. Deposition was carried out for 1 h at the substrate temperature of 900, 1000 and 1100°C under the reduced pressures between 10 and 22 kPa. The amount of the liquid loss and the morphology of the products were examined. The results were as follows.

1. There existed the linear relationship between the input power and the amount of the liquid loss. The threshold power was 200 Watt, under which no stable discharge occurred.

2. The liquid loss was mostly due to the sputtering. GDE was not the predominant factor to introduce the liquid loss.

3. The sputtering yield of H_2O molecules by one H_2O^+ ion was between 100 and 900 under the applied voltages between 600 and 900 V. The yield was 2 orders of magnitude greater than the yield of copper atoms sputtered by an argon ion.

4. The large sputtering yield was attributed to two factors. One was the weak hydrogen bond working

among the H_2O molecules and the other was the bombarding H_2O molecules accompanying the H_2O^+ ion entering the solution.

5. Microcrystalline TiO_2 films of rutile structure were deposited on the quartz glass. The surface was rugged but the bulk was flat. The film thickness prepared at 1000°C was 15 μm with 5×10^{-3} mol/*l* solution and 21 μm with 1×10^{-2} mol/*l* solution.

6. Polycrustalline TiO_2 films of rutile structure were produced on the titanium substrate. The film showed preferred $\langle 110 \rangle$ orientation. The products were porous and the thickness was 600 μm when prepared at 1000°C using 5×10^{-4} mol/*l* solution. Thick film formation is mainly due to the oxidation of the titanium substrate.

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