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Control of Crystalline Structures of Titanium Dioxide in a Low-Pressure O_2/Ar plasma

低圧Ar/O₂プラズマによる二酸化チタンの結晶構造制御

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In this study, we investigated a production of titanium dioxide (TiO_2) on a surface of Si substrate by using a low-pressure O_2/Ar discharge with coaxial electrodes. We observed depositions of thin films made of TiO_2 with anatase and rutile, the property of which was controlled by the discharge power, mixing flow-rate ratio, and total pressure of the working gases. We observed also spherical particles with a scale of a few 100 nm, attached on the Si surface. Shape of nanoparticles could be changed from baroque to spherical by controlling the discharge condition. From the electron refraction patterns it turned out that the nanoparticles with a size of 20-30 nm were made of anatase.

1. Introduction

Titanium dioxide TiO_2 is a wide band-gap semiconductor with superior chemical stability. For this reason, TiO_2 has been used in many fields such as, for instance, sunscreen agent, white paints, solar cell, and photocatalyst. Today, TiO_2 has attracted much attention for application to energy and environmental problem. TiO_2 acts as photocatalyst for cleaning environments by exploiting sunlight energy. Superior photochemical properties of TiO_2 are also applied to photochemical reaction of an electrode of dye-sensitized solar cells. The application to medical treatments such as self-cleaning effect, purification, sterilization, and deodorization, has also been considered.

TiO_2 has typically two crystallites, i.e., anatase and rutile. The former is useful for photoactivities, and the latter is widely used as white dye powder.

Several types of TiO_2 nanostructures have been reported, such as, for instance, baroque and spherical structures. If the solar cell electrode consists of superficial TiO_2 nanoparticles, surface electrode area becomes larger for the reaction, which may lead to an increase of electric power generation. For this reason, spherical TiO_2 particles are paid attention for applying to the electrode of dye-sensitized solar cells.

In this study, we report a control of crystalline structure of thin TiO_2 films, together with a creation of nanostructures, containing spherical particles, by changing the experimental condition such as discharge power, mixing ratio, and total pressure of working gases O_2/Ar.

2. Experimental apparatus and method

Figure 1 shows a schematic drawing of the experimental apparatus used for plasma sputtering [1]. As a source of Ti, a Ti rod electrode was used and installed in a ceramic pipe. The flow rates of Ar and O_2 gases were adjusted by mass flow controllers independently and the mixed gas was introduced into a stainless tube. Rectified dc voltage was supplied to the titanium rod.

Using this system we can change the discharge parameters such as O_2/Ar flow rates, pressure in the discharge region, and applied voltage. The discharge took place between the tip of the titanium electrode and a titanium plate electrode with an open hole at the center.

We selected the partial pressure ratio and supplied voltage as a parameter. Typically, O_2/Ar =1/1 and 1500 [V] for sample 1, and O_2/Ar =1/3 and 4500 [V] for sample 2. Other parameters were fixed constant through the experiment. The total pressure of O_2/Ar was kept at 0.50 [Torr].

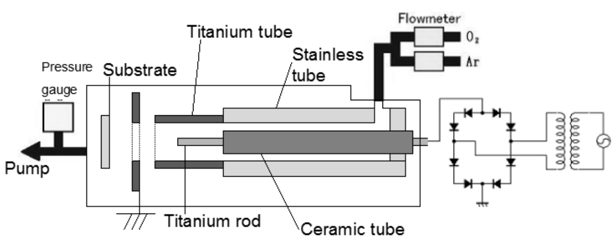

Fig.1. Schematic drawing of experimental apparatus.

3. Experimental results

Deposition experiment was carried out by changing the discharge parameters. From the detailed evaluation of the crystallites, it turned out that anatase seemed to be deposited in outer region apart from the main discharge. Here, we concentrated mainly on the case of anatase formation.

Scanning electron microscopy (SEM) images of the surface of sample 1 is shown in Fig. 2(a). It was observed that many spherical particles of 100 ~1500 [nm] in diameter were deposited. In addition,

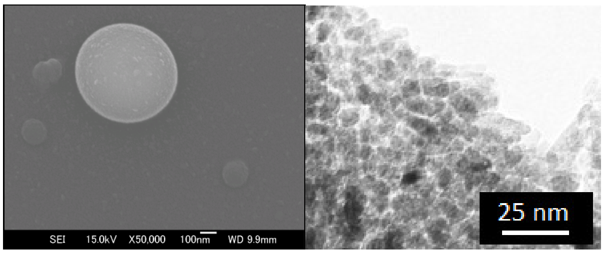

Fig.2. (a)SEM and (b) TEM images of sample1.

the particles with a distorted shape also existed at the periphery. Even on the Si substrate we observed a thin film, which was quite similar to that on the surface of the spherical particles.

In order to clarify the crystallite of the particles, transmission electron microscopy (TEM) image of sample 1 was taken as shown in Fig. 2(b), where many coagulated nanoparticles with a size of about 10~20 nm were found. This meant that the particles of a few 100 nm were composed by small nanoparticles with a size of 10 ~20 nm.

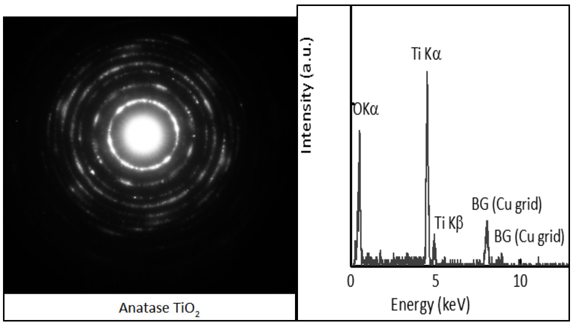

Fig.3 (a) Electron refraction pattern and (b) EDX spectrum of sample1.

Figure 3(a) shows the electron refraction pattern of the particles of sample 1. We find several refraction spots, which are well distributed on the positions of TiO_2 anatase. The atomic components were also analyzed by EDX spectrum as shown in Fig. 3(b), where typical peaks corresponding to Ti and O were observed. Any other atomic components were not found. Therefore, it was concluded that the particles were consisted of TiO_2 and the crystalline structure was anatase.

We also found many spherical nanoparticles on the surface of sample 2. Distribution of the particles on the substrate is shown in Fig. 4. Almost no particles was observed in the center region of the substrate. The position of the peak was around 4 mm, which was a little bit outer than the edge of the anode hole. The particle deposition position was shifted outward by the discharge power.

4. Discussion

In the case of sample 1, it was found that spherical particulate was consisted of many nanoparticles, made of anatase, with a size of 10~20 nm. It is considered that these larger particles have grown like snowballs. Deposited thin films were also considered to be anatase. From the result of sample 2, it was shown that the larger particles were distributed in the outer region. As an origin of the spherical particles, the growth around the sheath

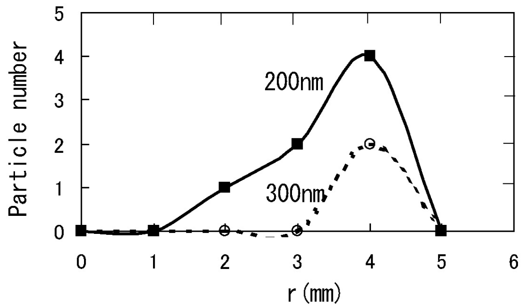

Fig.4 Distribution of particles on the substrate of sample 2.

edge was considered. They were transported to the substrate by a gas flow along the periphery of the plasma column. The particles may grow via coagulation during the trapping around the sheath. When the deposition condition was changed, the composition rate, the size, and the number of particles were changed. The transition between rutile and anatase was dependent on the discharge condition. TiO_2 anatase seemed to be deposited in a low power discharge. During the growth of crystallites, anatase might turn to rutile in the high power plasma.

5. Conclusion

It was verified that the crystalline structure of TiO_2 , i.e., anatase and rutile, could be controlled by the discharge parameters, which also gave an effect on the shape and distribution. We observed spherical particles of 100-1500 nm, formed by 20-30 nm nanoparticles made of anatase. Particle distribution depended on the particle size.

Reference

[1] T. Muraoka et al., Thin Solid Films, **518,** 1012(2009).