Transactions of the Materials Research Society of Japan 27 [1] 55-58 (2002)

Surface Modification of Titanium Dioxide Irradiated by Pulse-Modulated High Power ICP

Takamasa Ishigaki¶, Nobuhiro Okada*, Hajime Haneda, Shunichi Hishita, and Shigeru Ito*

National Institute for Materials Science, Advanced Materials Laboratory
1-1 Namiki, Tsukuba-shi, Ibaraki 305-0044, Japan
*Science University of Tokyo, Department of Industrial Chemistry
Noda-shi, Chiba 278-8510, Japan
¶ Fax: +81-298-51-4005, e-mail: ISHIGAKI.Takamasa@nims.go.jp

Newly developed pulse-modulated high-power inductively coupled plasma [ICP] is expected to offer an unique physico-chemical condition, such as the increased concentration of chemically reactive species, as well as the appropriate heat flux for materials processing. Green compacts of titanium dioxide (TiO_2), whose characteristics strongly depend on the formation of lattice defects and the incorporation of hydrogen, were placed at the downstream of Ar-H_2 ICP and irradiated in the plasma of continuous [CN] and pulse-modulated [PM] modes. The sample position and the plasma generation pressure were changed as processing parameters. Comparing specimens treated in PM-ICP with those treated in CN-ICP, the disk specimens had less thermal effect of plasma. The CN-ICP irradiation at the position close to the plasma tail gave rise to the thermal reduction of oxides. In the PM-ICP irradiation, the degree of thermal reduction depended on the lower power level during pulse-off time, as well as the total electric power. Irradiation in PM-ICP led to the increased formation of oxygen vacancies, which would be related to the high concentration of hydrogen radicals in the plasma.

Key words: inductively coupled plasma, pulse-modulated generation, plasma irradiation, titanium dioxide, surface modification.

1. INTRODUCTION

Thermal plasma is characterized by its high enthalpy and chemical reactivity, and has been used for various kinds of advanced materials processing, such as the spray coating of metals and ceramics, the thin film deposition of high-temperature superconducting oxides and diamond, the particle spheroidization, and the synthesis of ultra-fine powders.

In order to increase the application potential of the thermal plasma materials processing, it is indispensable to develop a novel plasma generation source and extend further the plasma processing parameters. Some disadvantages of the thermal plasma pointed out so far are such as the radiation loss in powder processing, and the damage on substrates and grown films, which come from the non-controllable, too high enthalpy. In order to reduce the influence of the high enthalpy in materials processing, several methods have been tried by lowering the plasma generation pressure or the spatial position of substrate. As is distinct from the above methods, the time-domain control of the present work is expected to include a strong potential to control precisely the sort and concentration of chemical species as well as the energy level in thermal plasma.

Sakuta et al. reported numerically on a time-dependent RF inductively coupled plasma[ICP] and suggested about the possibility to generate pulse-modulated[PM] plasma[1]. Ishigaki et al. succeeded in the PM-ICP generation, for the first time, at an adequate frequency, 1 MHz, to the generation of sufficiently large volume, and at a sufficiently high electric power of 17 kW, for materials processing[2]. An important thing was that the total energy of plasma can be decreased, while the maximum temperature remained unchanged, at around ~12,000K, in the pulse-on time, which was almost the same as that of continuous[CN] generation. Also, it has been suggested by optical emission spectroscopy that the PM-ICP could produce intentionally a non equilibrium state of particle temperatures and the flux density of radical species [3,4]. The unique condition in the plasma is expected to offer the unique physico-chemical condition for materials processing.

In this work, the interaction between plasma and materials was examined, as the information is essential to the application of PM-ICP to the advanced materials processing. Disc compacts of titanium oxide were treated in Ar-H_2 plasma of CN and PM generation modes. The choice of material used in the present work was made thorough the following consideration of materials science. With respect to the thermally induced reduction, titanium dioxide, TiO_2, has an intermediate stage before going to the next reduction

state, Ti_nO_{2n-1}, that is, the formation of Ti^{3+} in TiO_2. The phase, Ti_nO_{2n-1}, can be easily identified by XRD. Also, It is known that the formation of Ti^{3+} in TiO_2 can be more easily identified by the change of color, even if the concentration of Ti^{3+} is quite low. Therefore, the titanium oxide in this work is regarded as the indicator of the degree of thermally induced reduction. Concerning on the chemical features of plasma, the high concentration of hydrogen radicals, which was suggested by the optical emission spectroscopy, may play an important role.

2. EXPERIMENTAL

Schematic of PM plasma generation has been shown elsewhere[2]. The solid state amplifier (MP-22CY, Denki Kogyo Co., Ltd., Japan) was employed for the pulsing plasma generation. The inverter-type power source supplies the electric power of 22 kW continuously with nominal frequency of 1 MHz. The RF power was pulse-modulated by imposing the external pulsed signal generated by a pulse generator (HP 8116A) to switch a static induction transistor [SIT].

The plasma torch, as shown in Fig. 1, consists of two coaxial quartz tubes, between which cooling water flows, and is surrounded by a water-cooled copper coil. The inner diameter of inner quartz tube and the outer radius of outer tube are 55 and 70 mm, respectively. The induction coil consists of thirteen turns. The sheath gas was injected with swirl from outer slots of gas distributor. Except for the turn number of RF coil, the design of present torch is the same as that used in our previous study for continuous steady operation[5]. Operation conditions are as follows. The sheath gas is composed of Ar and H_2 at the flow rate of 98 l/min and 6 l/min, respectively. The plasma was firstly generated at the continuous power level of 13 kW and the reactor pressure was controlled at 26.6-99.8 ± 0.5 kPa. Then, the external pulsing signal was imposed to switch to the PM mode with pulse-on and -off times of 10 and 5 ms, respectively, and the shimmer current level, the current ratio of the lower level of pulse-off time to the higher one of pulse-on time, of 0.53-0.58. The detected signal of RF current through current transformer was stored in a digital oscilloscope (LeCroy, LC334A) with a minimum sampling time of 2 ns per step.

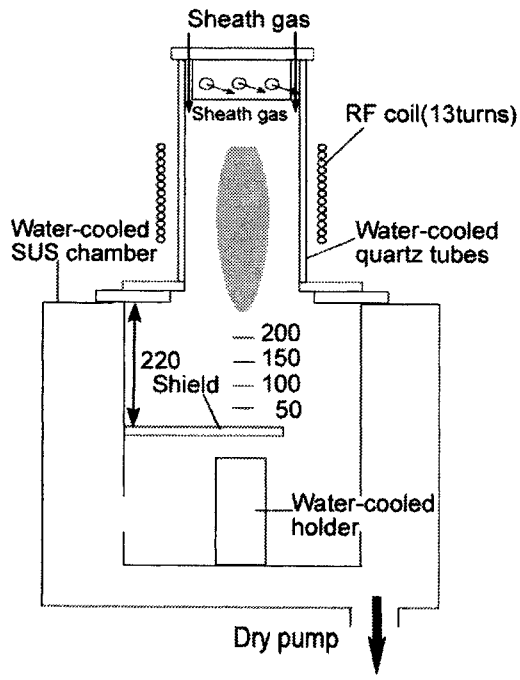

Fig. 1 Schematic of plasma torch and reactor.

Titanium oxide powder (TiO_2, purity, 4N; Kojundo Chemical Laboratory Co., Ltd, Japan) was composed of rutile phase. Disk specimens of ~10 mm in diameter and ~4 mm thick were formed by uniaxial pressing at 25 MPa, followed by pressing isostatically at 200 MPa. The green compacts were put on the water-cooled molybdenum holder and placed at the downstream of plasma flow, as shown in Fig. 1. The specimens were irradiated for 5 minutes in Ar-H_2 plasma of CN and PM generation modes. The sample position and the plasma generation pressure were changed as processing parameters.

3. RESULTS AND DISCUSSION

When the PM plasma is generated, the steep overshoot and undershoot of the amplitude of coil current is recognized at the time instance of pulse on and off, giving an abnormally large current flow in the electric circuit and the breakdown of transistors. The shimmer level was introduced accordingly for decreasing the magnitude of such overshooting, and the low power level in the pulse-off period became almost 1/3 of the higher one in the pulse-on period for Ar-H_2 plasma generated at the power level of 22 kW and the reactor pressure of 99.8 kPa[2]. Then, the modulation signal form of square wave was modified to give the relatively slow switching shown in the upper figure of Fig. 2, that is, the rise and decay signals of exponential form with the time constant of 940 μs. As a result of the slow switching, a little overshoot and no undershoot occurred with a little change of rise time and slightly longer decay time. The plasma was able to be generated down to the lower power level, 23% of higher level, for the same plasma condition[6].

Figure 2 shows the temporal change of RF current for PM Ar-H_2 plasma generated at various pressures. Shimmer current ratio was set to be 58%, 56%, and 53%, for the reactor pressure of 99.8, 53.2, 26.6 kPa, respectively. The measured ratio of integrated RF power of PM mode to that of CN mode were 86%, 85%, 84% for 99.8, 53.2, 26.6 kPa, respectively.

The length of plasma flame changes depending on the plasma generating pressure, while the generation mode, CN or PM mode, did not give the difference of the apparent flame length. The decrease of reactor pressure gave the increase of flame length. The plasma flame generated at 26.6 kPa reached to the

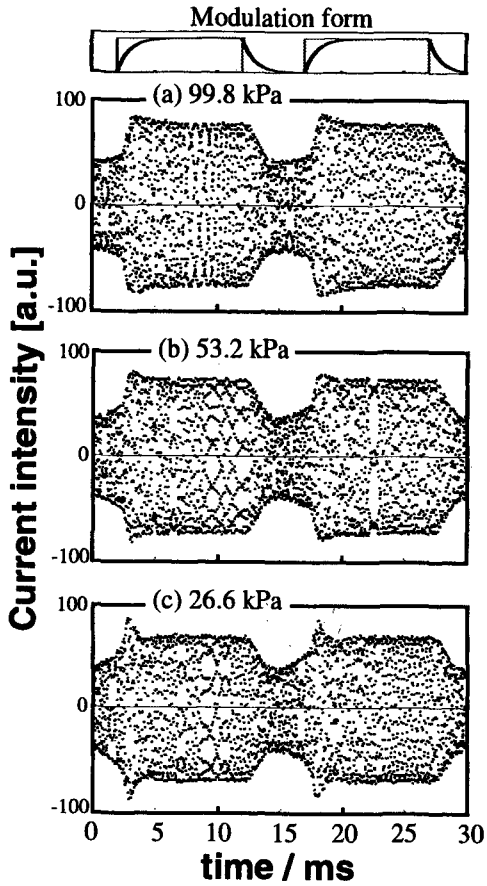

Fig. 2 Temporal change of RF current for Ar-H_2 plasma generated at various pressures: pulse-on time, 10 ms; pulse-off time, 5 ms.

specimen placed at the position of 200 mm, while the flame tail under the other conditions was above the specimens. The specimen placed in the plasma of CN mode at the positions of 200 and 150 mm was irradiated by the high-temperature flame, and the white disk changed to black. To the contrary, only the specimen placed at 200 mm in the plasma of PM mode showed the change of color in a restricted small area.

The specimen disks treated at the pressures of 53.2 and 99.8 kPa showed the similar tendency of coloration. Only the disks placed at the position of 200 mm in the CN plasma became black, while the other specimens showed almost no change of color. The difference came from the shorter flame length than that of the plasma at the pressure of 26.6 kPa.

Raw powder was composed of pure rutile phase. X-ray diffraction from the specimen disks treated in the plasma at the pressure of 26.6 kPa showed that the phase of all specimens, except a disk placed in the plasma of CN mode at the position of 200 mm, remained unchanged. Magnéli phases, Ti_nO_{2n-1}, were formed on the surface of colored disk. At the higher pressures of 53.2 and 99.8 kPa, no other phase than rutile was formed even on the colored surface of the specimens treated even at the highest position of 200 mm in the plasma of CN mode.

The color of Ti_nO_{2n-1} phases is known as black. The disk specimen treated at 200 mm under 26 kPa in the CN plasma was directly irradiated by the plasma flame and the surface was heated to the highest temperature among all specimens. Then the specimen was highly reduced from TiO_2 to Ti_nO_{2n-1}. It is well known that the formation of Ti^{3+} in TiO_2 gives the coloration, which agrees with he coloration of the specimen treated at 150 mm in the CN plasma. In the specimen, X-ray photoelectron spectroscopy[XPS] showed the existence of slightly reduced oxide constituent, although the phase change was not detected by XRD. The important point was that the specimens treated in the PM plasma were not reduced even at the highest position of 200 mm, where the temperature is highest and the concentration of hydrogen atoms is supposed to be highest among the three sample positions.

It was suggested that, in the PM plasma, the non-equilibrium effects should be considerable high and electron and heavy particle temperatures should be taken into account[3]. The difference of thermal effect between the plasmas would be further than what is comes from the small difference of electric power, that is, the difference of electric power was only ~15 % of CN generation mode.

Titanium dioxide is known to show photocatalytic activity, which is applicable to the air and water purification, the deodorizatipon, and the antibacterial and self-cleaning coating. Recently, the visible-light-responsive photocatalyst has been reported by the plasma treatment of anatase-type titanium dioxide powder in an inductive-type RF hydrogen discharge at the pressure of 130 Pa[7], although the photocatalytic activity was limited in the ultraviolet region. The extension of photocatalytic activity region to the visible light was explained by a new energy state due to the formation of oxygen vacancies. It is also pointed out that oxygen vacancies may play a crucible role of the other distinguished property of titanium dioxide, the hydrophilic surface, which is antifogging and self-cleaning. To the contrary, the substitution of oxygen by hydroxyl group, i.e., the incorporation of hydrogen, leads to hydrofobic surface[8].

As mentioned in the preceding paragraph, the useful surface should be the slightly reduced one, that is, the colour should be kept white or beige. Quite low concentration of induced oxygen vacancies was characterized by thermal desorption spectroscopy, in which the hydrogen desorption is able to be detected with high sensitivity. The increase of desorption in the temperature range from 200 to 500°C for as-irradiated specimens is shown in Fig. 3(a), which attributes to the hydroxyl groups chemisorbed on surface and/or diffused into the near surface. In the specimens after long-term storage in air (Fig. 3(b)), the desorption peak appeared in the range of 900-1,000°C. The hydrogen desorption came from the hydrogen atoms in the

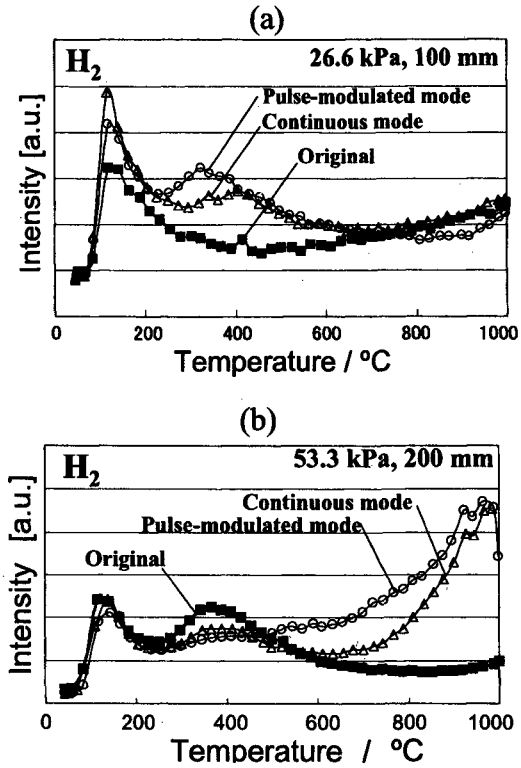

Fig. 3 Hydrogen desorption from original and plasma-treated titanium dioxide; (a) as-irradiated powders, (b) powders after long-term storage in air.

relatively deep region, as the chemisorbed hydroxyl groups incorporate into vacancies during long-term storage in the air[9]. It is shown that the PM plasma irradiation gave rise to the formation of higher concentration of oxygen vacancies than the CN plasma irradiation. The difference would be related to the increased concentration of hydrogen radicals in the PM plasma, as the hydrogen radicals take out easily oxygen atoms to form oxygen vacancies.

Finally, the main advantage of present treatment in PM-ICP is that the potential surface can be prepared even at the position close to the plasma flame where the high concentration of hydrogen atoms should exist. The modification by the present high-pressure plasma may be rapid and effective compared to the low-pressure plasma treatment.

4. SUMMARY

The disk specimens of titanium oxide were treated in the RF induction plasma of CN and PM modes. There were some different changes induced by the plasma treatments. Judging from the change of color, and the X-ray diffraction, the difference of thermal effect between the CN and PM plasmas was clearly recognized. The thermal effect was much predominant over the chemical effect in the heavy reduction of titanium oxide. Chemical aspect of PM-ICP was recognized on the slightly reduced surface. Higher concentration of oxygen vacancies was formed with the help of chemically reactive hydrogen radicals in the PM plasma irradiation. The results of present work gave the basic information about promising applications of plasma-treated titanium oxide as well as plasma characteristics.

ACKNOWLEDGEMENT

This work was performed through Special Coordination Funds of the Ministry of Education, Culture, Sports, Science and Technology (MEXT) of the Japanese Government.

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(Received December 21, 2001; Accepted January 30, 2002)