Nonthermal and nonequilibrium effects in high-power pulsed ICP and application to surface modification of materials*

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Abstract: Newly developed pulse-modulated high-power inductively coupled plasma (ICP) is expected to offer the unique physicochemical condition, such as the increased concentration of chemically reactive species, as well as the appropriate heat flux for materials processing. Two kinds of oxide materials, titanium and zinc oxide, were placed at the downstream of Ar–H2 ICP and irradiated in the plasma of continuous (CN) and pulse-modulated (PM) modes. 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 in titanium dioxide. In the case of zinc oxide, the UV emission efficiency was improved by PM-ICP irradiation, while the green emission became predominant by CN-ICP irradiation at the appropriate position. Induced effects in the two oxides by PM-ICP would be related to the high concentration of hydrogen radicals in the plasma.

NONEQUILIBRIUM CONDITION IN PULSE-MODULATED HIGH-POWER ICP

Pulse-modulated RF inductively coupled plasma (PM-ICP), in which nonequilibrium situation is expected to be induced at the instance of pulse-on and off, is an appropriate tool for advanced materials processing. Ishigaki et al. succeeded in PM-ICP generation, for the first time, at an adequate frequency, 1 MHz, to sustain a plasma with considerably large volume, and at a sufficiently high electric power of 17 kW, for materials processing [1]. An important feature was that the total energy of plasma can be decreased, while the maximum temperature, around 12 000 K, remained unchanged in the pulse-on time, which was almost the same as that of continuous generation [2]. Also, it has been suggested by optical emission spectroscopy that PM-ICP could produce intentionally a nonequilibrium state of particle temperatures and flux density of radical species [3,4]. Such conditions in PM-ICP plasma are expected to offer a unique physicochemical condition for materials processing. Also, it was predicted that the pulse modulation gives the higher cooling rate at the plasma tail [5].

Figure 1 shows the optical emission from Ar (751 nm) and Hα lines detected at the middle and 10 mm below the bottom of RF coil of the induction plasma torch used. After the time instance of pulse-on, the emission at the middle of RF coil shows the overshoot with a maximum, and this became larger for the low shimmer level. The overshoot of emission comes from the nonequilibrated situation induced by the rapid heating of plasma. It should be noted that hydrogen emission shows the overshoot even at


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the downstream, while the emission from Ar atoms shows no overshoot. When the plasma flow leaves from the high-temperature coil region, the temperature drops very rapidly to deviate from the equilibrium concentration of chemical species. In the pulsed-plasma, the quenching effect is enhanced by the induced condition following switching on and off. The overshoot of hydrogen emission at the downstream is higher than that at the middle of coil, which should be the evidence of overpopulated concentration of chemically reactive hydrogen radicals.

**IRRADIATION OF PULSE-MODULATED ICP ON CERAMIC MATERIALS**

The interaction between plasma and materials was examined, as the information is essential to the advanced materials processing by PM-ICP. Disc compacts of titanium and zinc oxides placed at the downstream of plasma were treated in Ar–H₂ plasma of continuous (CN) and pulse-modulated (PM) generation modes.

A schematic of PM plasma generation has been shown elsewhere [1]. The inverter-type solid-state power source supplies the electric power of 22 kW continuously with nominal frequency of 1 MHz. The RF power was modulated by imposing the external pulse signal from a pulse generator to switch a static induction transistor (SIT). As shown in Fig. 2, the mixture of Ar and H₂ was injected with swirl at the flow rate of 98 and 6 l/min, respectively. The torch design is the same as that used in our previous study.
for continuous steady operation [6]. Operation conditions are as follows. The plasma was firstly generated at the continuous power level of 13 kW, and the reactor pressure was controlled at 26.6–99.8 kPa. Then, the external pulsing signal was imposed to switch to the pulse-modulated mode with pulse-on and pulse-off times of 10 and 5 ms, respectively. The shimmer current level, which is the current ratio of the lower level of pulse-off time to the higher one of pulse-on time, is 0.53–0.58. Disk specimens, which were formed from TiO₂ and ZnO powders by isostatical pressing, were put on the water-cooled molybdenum holder and irradiated for 5 min in Ar–H₂ plasma of CN and PM generation modes.

**Surface modification of titanium dioxide**

Titanium dioxide is known to show photocatalytic activity, which is applicable to the air and water purification, the deodorization, 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, 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 hydrophobic surface.

The plasma in the present work has induced the thermal reduction of titanium oxide. When the relatively heavy reduction occurs, the color of the specimen changed to black [7]. The coloration depended on the lower current level in PM mode as well as the sample position. As mentioned in the preceding paragraph, the useful surface should be the slightly reduced one, that is, the color 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. 3a, which attributes to the hydroxyl groups chemisorbed on surface and/or

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

diffused into the near surface. In the specimens after long-term storage in air (Fig. 3b), the desorption peak appeared in the range above 500 °C. The hydrogen desorption came from the hydrogen atoms in the relatively deep region, as the chemisorbed hydroxyl groups incorporate into vacancies during long-term storage in the air. 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.

**Improvement of UV and green emission of zinc oxide**

Zinc oxide (ZnO) is known to be a high-efficiency phosphor compound under low-energy beam irradiation, which has been used for vacuum florescent devices and field emission displays. Recently, intensive efforts have been made to realize the UV emitting devices. It has been reported that the microwave hydrogen plasma irradiation enhances the UV emission, while the green emission is suppressed [8]. It was suggested that the dissolution of hydrogen should take a role in the improvement.

The influence of PM plasma irradiation was compared with the CN plasma irradiation on the cathodoluminescence. As is the same in titanium oxide, the CN plasma irradiation gave rise to the change of color on the specimens placed at the highest position. The effects of CN and PM plasma irradiation were considerably different on the emission spectra. As is clearly seen in Fig. 4, efficiency of UV luminescence was significantly improved and the visible emission was suppressed by the PM plasma treatment. On the other hand, ZnO powder giving green emission with high efficiency was obtained by the CN plasma treatment.

![Cathodoluminescence spectra of original and plasma-treated ZnO.](image)

**SUMMARY**

The effects of pulse modulation (PM) on the characteristic of ICP have been demonstrated in the plasma-irradiation processing of two oxides, titanium and zinc oxides. The PM-ICP plasma, which distinctly showed nonequilibrium chemical aspect of thermal plasma, is expected to give further extension of thermal plasma materials processing.
REFERENCES