NON-THERMAL/EQUILIBRIUM EFFECTS IN HIGH POWER PULSED ICP AND APPLICATION TO SURFACE MODIFICATION OF MATERIALS

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1. Pulse-modulated ICP plasma for advanced materials processing

Pulse-modulated RF inductively coupled plasma (ICP), in which non-equilibrium situation is induced at the instance of pulse-on and off, is appropriate for advanced materials processing. Ishigaki et al. succeeded in the pulse-modulated 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[1]. An important thing was that the total energy of plasma can be decreased, while the maximum temperature remained unchanged, that is, the plasma temperature, ~12,000K, in the pulse-on time was almost the same as that of continuous generation[2]. Also, it has been suggested by optical emission spectroscopy that the pulse-modulated 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.

The solid state amplifier was employed for the pulsing plasma generation. The inverter-type power source has a high energy efficiency of 90%, the power level of 17 kW corresponds to equivalently to the power level of 30 kW introduced by the ordinal plate-type power source, which has a relatively low energy efficiency blow 50%. The RF power was pulse-modulated by imposing the external pulsed signal generated by a pulse generator to switch a static induction transistor. When the pulse-modulated 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. Then, the modulation signal form of square wave was modified to give the relatively slow switching, 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 the rise time, 0.7 ms, and slightly longer decay time, 2.4 ms for the argon-hydrogen plasma generated at 750 Torr. The plasma was able to be generated down to the lower power level, 4 kW, at which power level the continuous plasma generation was unable to be sustained[4]. Also, it was predicted that the pulse modulation gives the higher cooling rate at the tail[5].

2. Plasma irradiation of titanium dioxide

The interaction between plasma and materials was examined, as the information is essential to the application of the pulse-modulated RF induction plasma to the advanced
materials processing. Disc compacts of titanium oxide placed at the downstream of plasma were treated in Ar-H$_2$ plasma of continuous[CN] and pulse-modulated[PM] generation modes.

Titanium dioxide is known to show photocatalytic activity, which is applicable to air and water purification, deodorizaton, and antibacterial and self-cleaning coating. Recently, the visible-light-responsive photocatalyst was prepared 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 has been limited in the ultraviolet region. The extention of photocatalytic activity region to the visible light region 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 crucial 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, that is, the incorporation of hydrogen lead to hydrophobic surface.

It was shown in the present work that the thermal effect was much predominant over the chemical effect, when the relatively heavy reduction occurs, that is, the color of specimen changed to black[6]. However, 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 much sensitively. The increase of desorption after the plasma irradiation attributes to the hydroxyl groups chemisorbed on surface and/or diffused into the near surface. In the case of the specimens after storage in air, the desorbed hydrogen came from the hydrogen in bulk, as the chemisorbed hydroxyl groups incorporate into vacancies on long-term storage in the air.

3. Improvement of green and UV emission efficiency 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 hydrogen plasma irradiation leads to the improvement of UV emission efficiency.

The influence of PM irradiation was compared with that of the CN irradiation on the cathodoluminescence. Pressed powder samples were treated in the downstream of argon-hydrogen plasma. The effects of continuous and pulse-modulated irradiation were considerably different on the emission spectra. Efficiency of UV luminescence was significantly improved and the visible emission was suppressed by the pulse-modulated treatment. On the other hand, ZnO powder giving green emission with high efficiency was obtained by the CN treatment.

References