RF Impulse Barrier Discharge for MgO Microparticle Formation In Sub-Atmospheric Pressure Regime

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Basic properties of RF impulse barrier discharge have been investigated in parallel plates and rod electrodes system. The impulse voltage, which is applied to a Mg-rod electrode, contains one sinusoidal waveform with period of about 10 μs with repetition frequency of 4.5 kHz. The effect of surface charges remained during the discharge-off interval on glass substrates, placed between the parallel plate electrodes, is quite important for microparticle formation as well as reduction of breakdown voltage. From the Raman and the SEM analysis, we have observed a formation of MgO microparticles with size less than several 100 nm. Most of the particles are in spherical shape. These particles are negatively charged and grew during their levitation in a space between the glass substrates.

Keywords: RF impulse discharge, Barrier Discharge, MgO, Spherical microparticle, Particle levitation.

1. Introduction

In manufacturing wide flat display panels by electric discharge in micro-cells, MgO film is acting as a protecting film from irradiation of the ions from the discharge and also acting as a transparent film with favorable secondary electron emission coefficient. The MgO film containing MgO microparticles were considered to provide efficient secondary electron emission surface because of the electric field concentration on the particles. The formation of flat MgO films with MgO microparticles was, therefore, important factor for developing the efficient wide display panels.

Moreover, MgO has been widely used as a buffer layer for the deposition of high T_c superconducting films. MgO can be also used as optical transmitters and substrates for thin film growth. Various methods for the formation and morphologies of MgO films have been reported [1-7].

In order to fabricate MgO thin film on inner wall of narrow glass tubes, we employed a plasma sputtering technique in Ar/O_2 plasma under atmospheric pressure condition [8]. Even in sub-atmospheric pressure regime, since the mean free paths of the electrons are still extremely short around micrometers, the electric discharge can be sustained in an extremely small region.

On the above basis, we developed RF impulse plasma generation method in order to apply to a surface modification on the glass plates. Here, we report basic characteristics of the impulse barrier discharge for generation of microparticles made of MgO on the glass surface by using sputtering technique in Ar/O_2 plasmas. The surface charges remained on the glass substrate was evaluated.

2. Experimental Apparatus and Condition

In order to perform a barrier discharge we employ a discharge system with parallel plates and rod electrodes as shown in Fig. 1. This system is convenient for an evaluation of the surface, on which MgO microparticles are deposited. We can easily analyze the surface condition of the glass substrate as well as the conditions of the plasmas parameters, produced between the glass plates. Using this system, we can also simulate a coaxial electrode system developed for an inner surface modification of small diameter glass tubes [8]. As shown in Fig. 1 we introduce two glass plates of 1 mm thick and 25 mm wide, inserted between two metal plate electrodes. The spacing between the glass plates is 2 mm. Inner electrode, made of 1.5-mm-diameter Mg rod, is installed in a center between both glass plates. The origin of axial direction is set at the upstream edge position of the metal electrode. The axial position of the tip of the inner

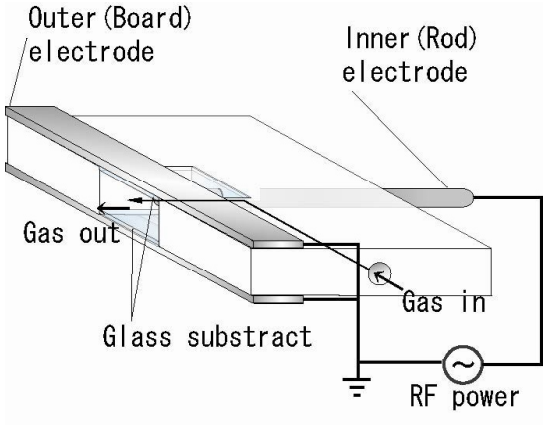

Fig. 1 Experimental apparatus.

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electrodes can be varied, but in this experiment the position was fixed at 5 mm in the upstream region.

RF impulse voltage is supplied to the inner electrode without using a matching circuit and a blocking condenser, while the outer electrode is grounded. RF power supply provides one cycle of sinusoidal waveform of about 10 μs in width, and the pulse amplitude and repetition frequency can be changed. The applied voltage can be raised up to 20 kV. Here, we can vary the pulse repetition frequency up to 4.5 kHz. The working gas is a mixture of Ar and O_2 in the pressure range 0.1 - 760 Torr. The total gas flow rate is fixed at 20 sccm. The properties of the depositions are mainly analyzed by the Raman spectroscopy. The surface morphology can be analyzed by the Scanning Electron Microscopy (SEM).

3. Experimental Results and Discussions

3.1 Discharge Property

We first measure lifetime of the plasma produced by the RF impulse discharge with finite repetition frequency.

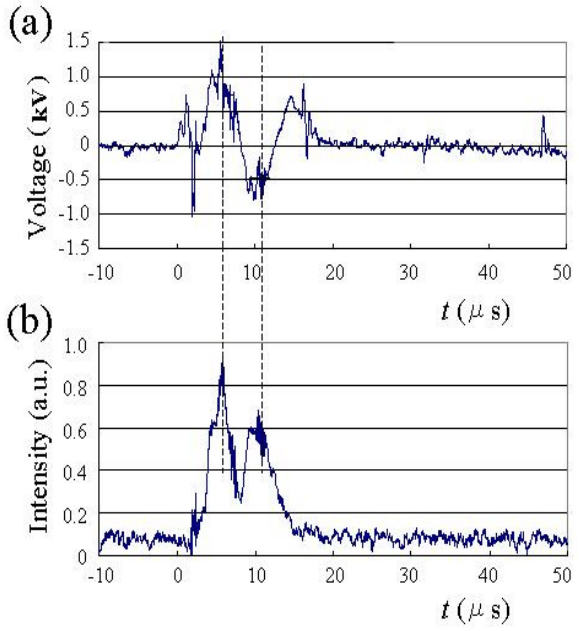

Fig. 2 Temporal variations of (a) applied voltage and (b) optical emission intensity.

Figures 2(a) and 2(b) show temporal variations of the voltage applied to the inner electrode and the optical emission intensity measured by a photo-diode, respectively. As clearly seen in Fig. 2(a), the impulse voltage applied to the electrode has almost one cycle of sinusoidal waveform with the period of about 10 μs. During the first half cycle with positive voltage the discharge was ignited, accompanied with a strong optical emission as shown in Fig. 2(b). During the next half cycle with negative voltage we can also observe a second peak of the optical emission. The discharge occurs, accompanied by the current against the forward current

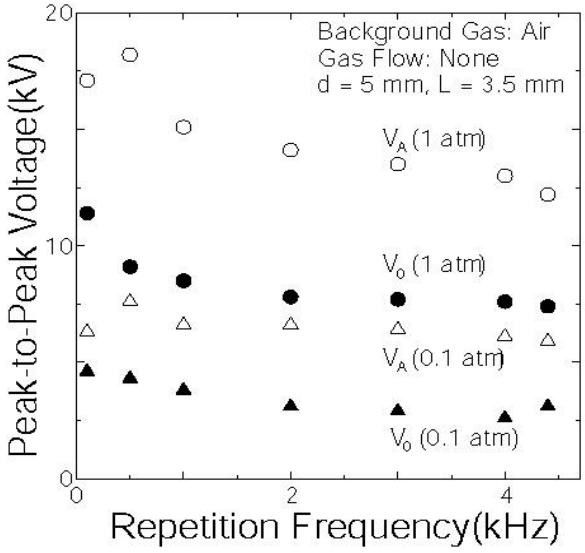

Fig. 3 Breakdown voltage V_0 for glow discharge and threshold voltage V_A for arc discharge as a function of repetition frequency with Ar pressure as a parameter.

during the first half cycle. However, the second positive voltage, coming as the third half cycle, did not trigger the discharge. We could not detect meaningful optical emission within this time phase. Dotted lines plotted in Fig. 2 show the time coincidences between the voltage peaks and the optical emission peaks. From Fig. 2(b) we could notice that the discharge ended soon after the second negative voltage and almost no optical emission was detected during the discharge-off interval of about 220 μs between the impulses. Here, the pulse repetition frequency was 4.5 k Hz. Note that the optical emission interval means the lifetime of neutral radicals, which might be quite important for the creation of materials. However, we could not ignore long lifetime radicals such as O* during discharge-off interval.

In order to analyze the effect of the discharge-off interval between the impulses we measured break down voltage V_0 as a function of the repetition frequency ω_R, as shown in Fig. 3 with gas pressure as a parameter. Once the breakdown took place, the plasma showed first a property of a glow discharge, in which the plasma distributed in rather broad region between the glass plates. Further increase in the voltage caused a gradual intensification of the optical emission. However, finally a very bright and localized discharge appeared, indicating a transition from the glow discharge to an arc discharge. We also measured the threshold voltage V_A for the transition from the glow to the arc discharges as shown in Fig. 3. From Fig. 3 we could know that the breakdown voltage V_0 for the glow discharge decreases first with an increase in the repetition frequency ω_R. Then, such decrease in V_0 was almost saturated in the range $\omega_R/2\pi$ > 1 kHz.

As a mechanism of the decrease in the breakdown voltage with an increase in ω_R, we consider an effect of the surface charge remained during the discharge-off interval on the glass substrates. During the discharge the electrons reaching the glass surface are remained on it to build up surface negative charges. Since the conductively on the glass surface is extremely low, the surface electrons could not rapidly escape from the surface but remained for a long period. Once the surface was negatively charged, we need not much voltage to achieve a successively coming breakdown. Therefore, the breakdown voltage can be reduced. This effect well acts when the discharge-off interval is short, On the contrary, when ω_R is decreased and then the discharge-off interval is increased, there appears a chance for the surface charges to escape from the surface to reduce the surface charged-up voltage. Then, the breakdown voltage will be raised up. This means that so long as ω_R is kept high, negative charges can remain on the glass surface during the discharge-off interval.

The reason why the breakdown voltage was low in the low gas pressure regime shown in Fig. 3 can be explained by an increase in the collision mean-free pass. The electrons can be much accelerated to get higher energy to ionize the gasses even when the low voltage is applied. The transition form the glow discharge to the arc discharge occurs at an applied voltage higher than V_0. The arc discharge might occur by an increase of the inner electrode temperature with increasing the discharge current. Therefore, the transition voltage V_A depends on the discharge current which is a function of V_A - V_0. As shown in Fig. 3, we found that the dependency of V_A on ω_R was roughly the same as that of the breakdown voltage V_0.

3.2 Microparticle Deposition

Usually, under typical experimental condition, we find many microparticles deposited on the glass surface as shown in Fig. 4. Here, we did not adopt a heating system for the glass surface. The temperature of the glass surface will be increased locally by irradiation of the ions. However, the maximum temperature is at most less than several ten degrees centigrade, because the impulse duty is very small (～ 5 %). We first examine the effect of oxygen on the formation of microparticles in relatively low gas pressure regime. Here, we notice that the oxidization processes of Mg atoms sputtered from the Mg inner electrode are of crucial. Though the discharge proceeded mainly between the electrodes, the deposited materials were much observed on the glass substrate near the inner electrode. This fact was attributed to plasma concentration and localization near the inner rod electrode because of an asymmetry electrode system. A short mean free path of Mg atom reaction was also of crucial, because Mg atoms sputtered from the Mg inner electrode might immediately react with the oxygen within a very short distance. We also found that the size of the particles was widely spread in the range from the order of nanometers to a few micrometers.

From a careful observation of the shape of the microparticles, especially for a smaller one, we found that they are produced in principle as small spherical balls. Especially, smaller ones have a quite symmetric shape of

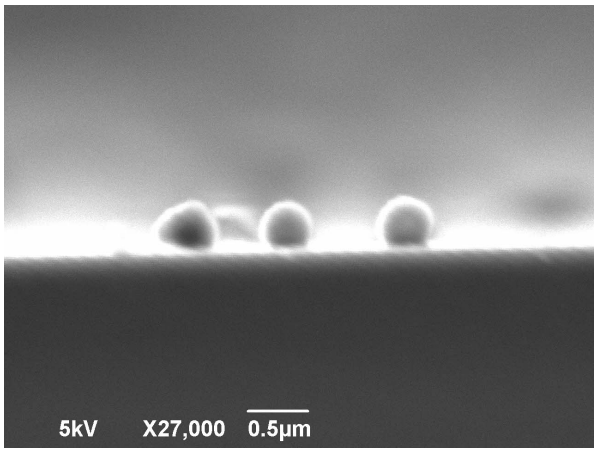

Fig. 4 SEM image of side view of microparticles

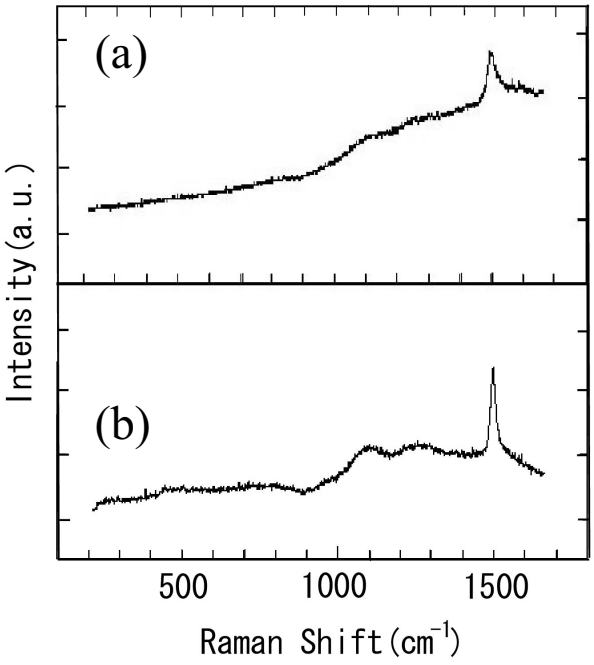

Fig. 5 Raman spectra of (a) microparticles and (b) MgO sample particles.

spherical balls. With increasing the particles size, although the shape is a little bit deformed, we can still regard these microparticles in principle as spherical balls. On the other hand, the structures of the bigger particles were quite irregular. However, these particles seemed to be also formed by accumulation and coagulation of many

small spherical particles. These results show that the start time of the nucleation of these particles is random. So, the particles, which started to grow just before the end of the deposition experiment, would be small. Therefore, the size of the particles spreads widely.

In order to analyze the materials consisting of microparticles we carried out the Raman spectroscopy. As shown in Fig. 4 the microparticles did not occupy whole region of the glass surface. The microparicles were distributed randomly on the glass surface. Therefore, there exist two domains on the glass surface. One is a domain containing microparticles and the other is a flat domain between microparticles. The flat domain was not simply a naked glass surface, but was covered by smooth thin films. Typical Raman spectrum of the microparticle domains is shown in Fig. 5(a). From this trace, we find a strong peak around 1500 cm^{-1}. We also found weak broad peaks around 1100 cm^{-1} – 1300 cm^{-1}. Since these peaks well coincided with those of MgO powder sample shown in Fig. 5(b), we concluded that these microparticles were made of MgO. We also found similar peak in the spectrum of the flat domain. This fact indicated that the flat domain was also consisting of MgO thin film whose surface was quite smooth. Therefore, MgO flat domain was regarded as MgO background layer, independent of the microparticle growth. Note that, in the case of Ar/O_2 = 0/20, we did neither much detect MgO particles nor thin film in the flat domain. This was attributed to a change of the discharge condition, including dissociation and excitation of molecular oxygen, together with oxidization of Mg rod surface.

From a close-up SEM image in Fig. 4 two characteristic features are found. First, they are quite symmetrical ball structure as mentioned above. Secondly, these particles seem to be just put on the substrate surface. If these particles are grown from the surface, their cross-sectional shape should be a pressed hemisphere on the substrate. In order to produce such a spherical structure these particles should grow up in the plasma without touching any places. Further, from our experimental conditions, it should be emphasized that it would be rather difficult for the particles to grow up to the size of about 0.5 nm during only one period (～10 μs) of the impulse discharge. The particle growth time were supposed to be much longer than one period of the impulse. Therefore, the particles should be confined and levitated in the space between the glass substrates even during the discharge-off interval.

We propose a following model for the formation of MgO flat domain and spherical microparticles. Owing to the sheath potential in front of the Mg rod electrode, Mg atoms can be sputtered by energetic Ar ions. Theses Mg atoms immediately react with O* atoms to form MgO nuclei. We also note that these clusters are charged up negatively by the effect of energetic electrons in the plasma. As shown in Fig. 3, since $\omega_R/2\pi$ > 1 kHz, the surface of the glass substrate can be also charged negatively even during the discharge-off interval. Therefore, the microparticles, which were charged negatively, could be confined electrically in the plasma during the discharge and also in the space between the glass substrates during the discharge-off interval for a long period. Therefore, the nuclei of MgO might grow up during the impulse discharges repeated many times before arriving at the substrate surface.

Another important factor is about its spherical shape. We think that these MgO clusters are able to rotate in the plasma space. Therefore, a symmetrical growth in the three-dimensional directions was possible to occur to make the particle shape spherical. The ion drag force will be one of the most presumable candidates for the driving forces. On the other hand, Mg atoms and small size MgO clusters arriving at the substrate can form a relatively flat thin film consisting of MgO on the substrate surface.

As described in the introduction, we note that MgO microparticles on the MgO thin film can act as efficient electron emitters, because the electric filed applied can be concentrated and strengthen on the surface of the microparticles. Therefore, the MgO films containing MgO microparticles seem to provide an efficient secondary electron emission surface.

4. Conclusion

We have carried out RF impulse discharge with a use of plate-rod electrode system in a narrow space between glass plates. We found that the higher repetition frequency of the impulse was important for the reduction of the breakdown voltage due to the negative surface charges remained during the discharge-off interval. We also found a spherical microparticle deposition on the glass surface. The particles are dominantly deposited on the area close to the inner Mg electrode. From the Raman spectrum these materials consist of MgO. For the growth of these microparticles, the surface charges remained during the discharge-off interval are of crucial. Therefore, negatively charged particles were confined electrically for a long period in a space between the glass substrates. It is demonstrated that the discharge technique employed here is very useful for MgO thin film formation with MgO microparticles.

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