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Extended Anode Effect for Tube Inner Coating of Non-Conductive Ceramics by Pulsed Coaxial Magnetron Plasma

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Abstract

For uniform tube inner coating of non-conductive thin films, the double-ended coaxial magnetron pulsed plasma (DCMPP) method was investigated. In this study, coating of TiN and TiO_2 was performed. It was clearly shown that the extended anode effect was strongly influenced by the electric resistance of the coated thin films on the inner surface of an insulator tube. Additionally, high frequency (100 kHz) was better for relatively high plasma density. On the other hand, in the case of titanium oxide deposition, negative ion productions drastically decrease the deposition rate and the shifting velocity of plasma main position for coated TiO_2 films.

Keywords

Double-Ended Coaxial Magnetron Pulsed Plasma, Tube Inner Coating, Extended Anode Effect, Fine Ceramic Films, Titanium Nitride Films, Titanium Oxide Films

1. Introduction

Narrow tubes are commonly used in industry to deliver water, gas, cooling substances for many purposes and for other functional applications [1]. However, these tubes are often required to excel performances in terms of corrosion and wear resistance. It is, therefore, necessary to create enhanced protection inside of tubes. In this regard, several studies have been conducted [2]-[10]. In addition to the above methods, coaxial magnetron plasma (CMPP) method has been proposed for inner narrow tube coating by the use of extended anode effect proposed by H. Fujiyama *et al.* [10] [11]. The CMPP method enables us to coat films inside the whole inner surface of a long tube by sputtering with the use of extended anode effect. In the sputtering process, plasmas must be shifted along the tube, and the shifting of plasma is caused by the fact that the deposited conductive films play the role of an anode; this is the extended anode effect. Therefore, the shifting velocity increases with sputtering yield of the target material and decreases with the electric resistivity of the deposited film [10] [11]. The shifting velocity also depends on the properties of the target materials (cathode). As many physical parameters affect the extended anode effect, further studies on the effects of physical conditions on the extended anode effect are required.

In the present study, we investigated the extended anode effect for Ti-oxide and Ti-nitride films that have different electric resistivity, and discussed the extended anode effect from the viewpoints of electric resistivity and negative ions produced by the presence of O_2.

2. Experimental Methods

Figure 1 shows the experimental equipment for tube inner coating by double-ended coaxial magnetron pulsed plasmas. A long cylindrical vacuum chamber of 1300 mm in length and 320 mm in inner diameter was used, water-cooled solenoidal coil arranged coaxially around the chamber. DCMPP electrode was placed inside the chamber, pulsed discharge occurred between the long narrow cathode (Titanium rod of 3 mm in diameter) and the grounded anode, the anode was consisted of two connected parts, the first part was short ring Titanium at both sides of the tube (16 mm in outer diameter). The second part was glass tube (19 mm in outer diameter, 16.5 mm in inner diameter, and 500 mm in length). However,

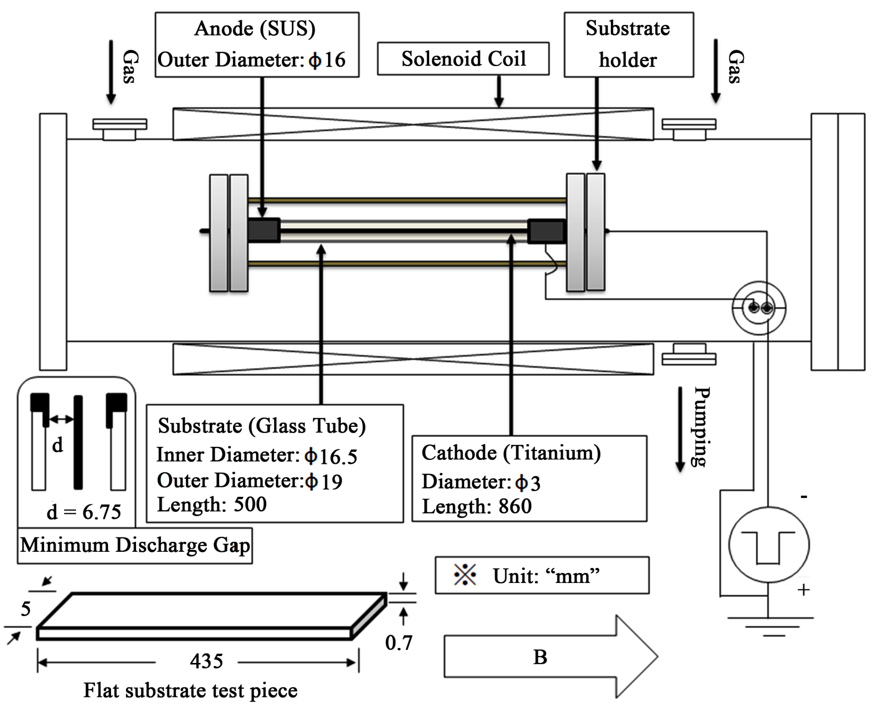

Figure 1. Experimental apparatus.

the coated part of the glass tube was only 435 mm in the middle of the tube, since the uncoated parts at the both edges of the glass tube were covered by the two ring Titanium anodes. Axial strong magnetic field (833 Gauss) was applied; this magnetron effect can make the breakdown easier in a narrow tube under low-pressure conditions than without axial magnetic field. Ti was deposited in Ar + N_2 mixture as well as Ar + O_2 gas. Discharge pressure was investigated from 0.5 - 2.5 Pa, and optimum discharge pressure was determined to be 1 Pa according to Paschen curve.

Film thickness was measured by placing a flat glass substrate test piece (435 mm in length and 5 mm in width and 0.7 mm thickness) inside the tube as shown in Figure 1, the flat substrate was marked by magic pen at several points to prevent coating at those points in order to make steps for the measurement of film thickness by Veecodektak 150 surface profilometer.

After the measurements of film thickness, the flat substrate was cut into several pieces at the points that they were marked by the magic pen, and then the electrical resistance R was measured by contacting ohmmeter probes at the end edges of a cut piece. Consequently, the resistivity ρ was measured by using the formula:

$$\rho = RA/L \tag{1}$$

where L and A are the distance between probe, and the cross sectional area of the film, respectively.

3. Results and Discussion

3.1. Influence of Nitrogen Fraction on Tube Inner Coating

The experimental conditions are shown in Table 1.

The effect of N_2 fraction in the gas mixture, f_{N2} on discharge current (I_d) and discharge voltage (V_d) were observed by oscilloscope and the monitor of the power supply. Under the constant power supply, the discharge voltage V_d increased and the discharge current I_d decreased with increasing of N_2 % amount as shown in Figure 2(a) and Figure 2(b).

Table 1. Experimental conditions.

Magnetic flux density [Gauss]	833
Gas pressure [Pa]	1
Mass flow rate of Ar [SCCM]	100, 90, 80, 70, 60, 50
Mass flow rate of N_2 [SCCM]	0, 10, 20, 30, 40, 50
Mass flow rate of O_2 [SCCM]	0, 5, 10, 15, 20, 25
Applied power [Watt]	300
Duty cycle [%]	55
Pulse repetition frequency [kHz]	100
Sputtering time [min]	2 (15 sec × 8)

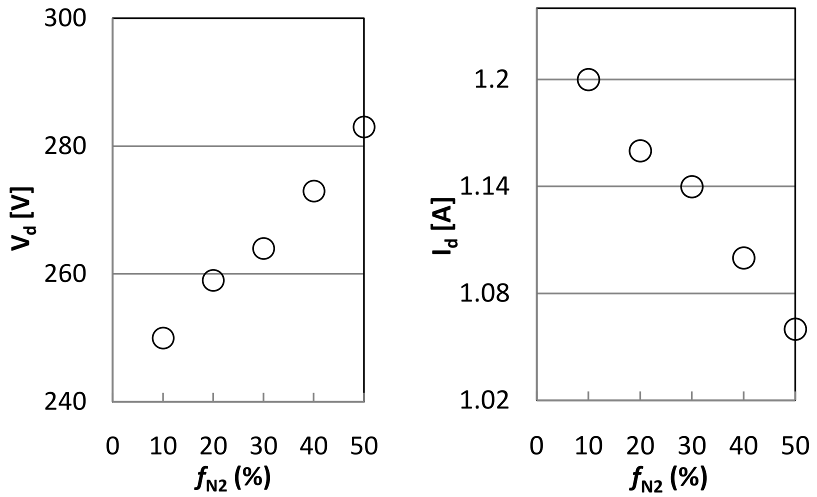

Figure 2. (a) Discharge voltage; (b) Discharge current as a function of fraction of N_2 f_{N2} %.

Figure 3 clearly shows that the film thickness decreased with N_2 % amount increased until N_2 amount = 50%.

The reason is by increasing N_2 % amount; the film resistivity increased as shown in **Figure 4**, and the deposited film changed from metallic to nitride.

However, the resistivity of N_2 mixture is lower than those of O_2 mixture case as shown in **Figure 5** by 1 order. This can be attributed to the production of negative ions in case of O_2 mixture as it will be discussed later.

3.2. Influence of Oxygen Fraction on Tube Inner Coating

It was found that film thickness decreased with O_2 % increased as shown in **Figure 6**.

In the case of TiO_2 inner coating, both the negative ion production and electrical resistance would strongly influenced to the extended anode effect. Here, to comparing TiO_2 with coating that does not produce negative ions; we performed TiN inner coating experiments.

The film thickness decreased as O_2 % fraction increased in the gas mixture, and this can be attributed to the increase of the deposited film resistivity as well as to the negative ions production.

Figure 5 shows the increase of the electric resistivity of deposited film due to increase of O_2 % fraction in the gas mixture until the amount of O_2 was around 9.1%, the film resistance becomes very large. This result is due to the formation of TiO_2 film instead of Ti film as shown in **Figure 7**.

Figure 7 shows the XPS analysis results. XPS studies are conducted to understand the chemical environment of Titanium in the presence of different fraction of O_2.

The characteristic peak of metal Titanium for binding energy around 456 eV was observed for the conditions of O_2 % fraction at; 0%, 3.2%, and 6.2%. This confirms the explanation for the above results in **Figure 5** and **Figure 6**.

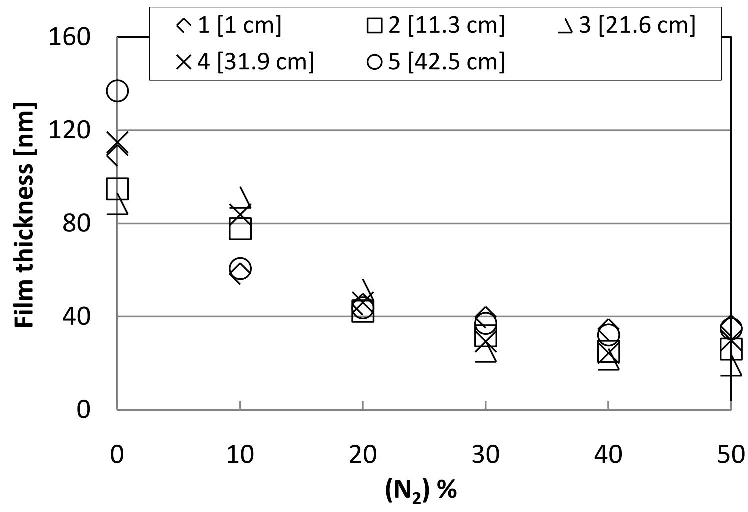

Figure 3. Film thickness as a function of N_2 %.

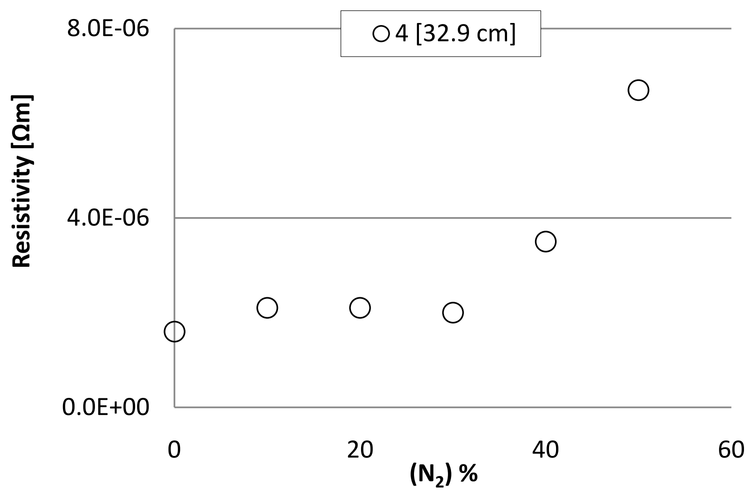

Figure 4. Film resistivity as a function of N_2 %.

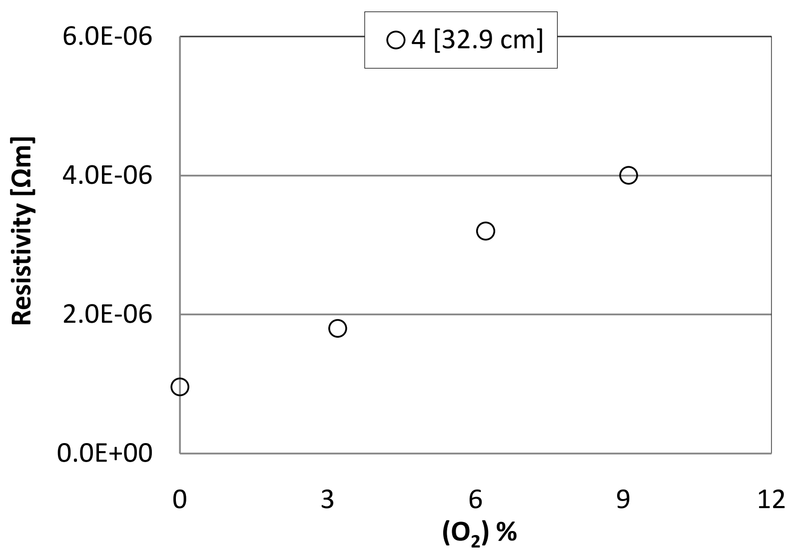

Figure 5. Film resistivity as a function of O_2 %.

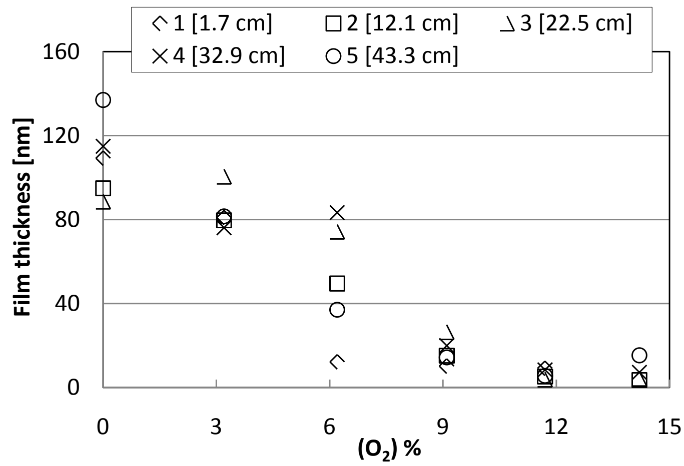

Figure 6. Film thickness as a function of O_2 % for different axial positions along the tube starting from the edge of the tube.

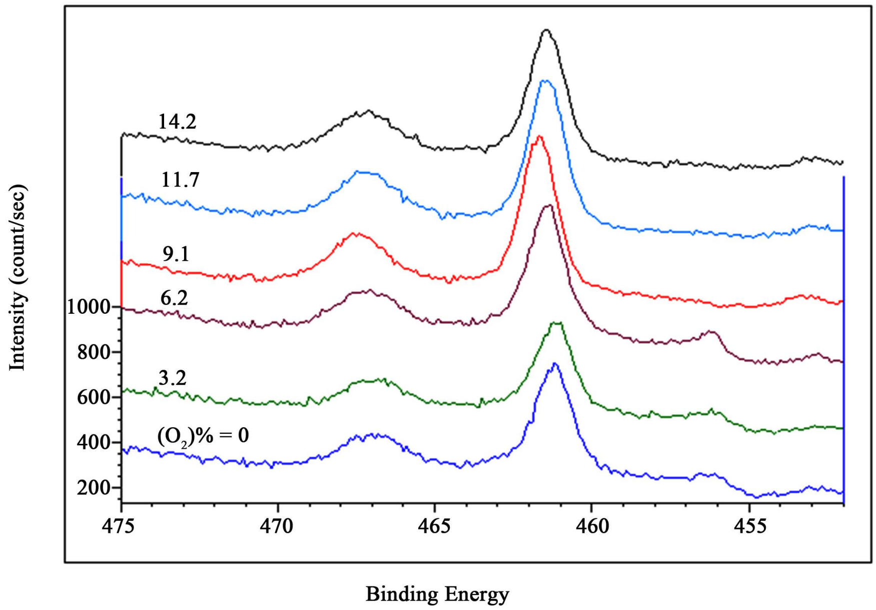

Figure 7. XPS analysis results.

The increase in film resistivity will decrease the shifting velocity of plasma along the tube and that will affect the extended anode effect.

Thus, this increase in the film resistivity affected the shifting velocity of main plasma position along the tube, as the shifting velocity decreased with increasing the electrical resistivity of the deposited film. Furthermore, the shifting velocity of main plasma position along the tube was influenced by decreasing of deposition rate by the decreasing electron density caused by the negative ion production. This will be discussed later.

Moreover, **Figure 8** shows film thickness as a function of axial position; this graph indicates the obvious difference in film thickness for O_2 % ≤ 11.7 which has smaller film thickness due to decreased plasma density by negative ion production and/or the formation of TiO_2 film with higher electrical resistivity

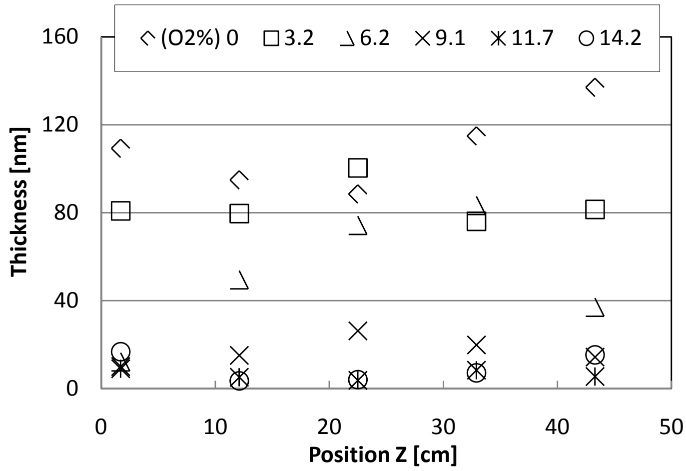

Figure 8. Film thickness as a function of axial position.

comparing with Ti film without O_2 mixture. Therefore extended anode effect seems to work only for conductive films, like Ti film in this experiment for O_2 ratio less than 11.7%.

Negative ions are produced during the sputtering time because of the presence of O_2 as shown in Equation (2).

$$O_2 + 2e^- \rightarrow O^{2-} \tag{2}$$

During sputtering time negative ions will be produced, and these negative ions and electrons will be attracted to the tube (anode), and since the target is cathode, so electron density would be decreased and plasma generation might be ceased for long exposure time. Thus, the production of negative ions lead to a decrease in the electron density, therefore this leads to decrease of the thickness of TiO_2 thin film. However, the use of pulse power helps in reducing the effect of negative ions production by means of pulse off-time. As refreshing time during pulse off-time is indispensable for sustaining the plasma generation and for relatively high density plasma as well. Because during on-time negative charges accumulate on the inner walls of glass tube (anode), then during off-time electrons and negative ions repel each other. Which make the anode ready for next discharge during on-time. Therefore, the obtained experimental results support the assumption of the production of negative ions, as it can be seen in the difference in the film thickness between TiO_2 and TiN profiles.

3.3. Influence of Pulse Repetition Frequency on Tube Inner Coating

Figure 9 shows the waveform of I_d and V_d, plasma production during on time. Meanwhile, the negative charges flow to anode (glass tube), while positive charges flow to cathode (target). Thus as a result negative charges are accumulated on the inner walls of glass tube. Therefore, during off-time negative charges will be canceled.

Based on the results in Figure 9 the pulse repetition frequency was adjusted, Figure 10 shows the discharge current (I_d) as a function of the pulse repetition

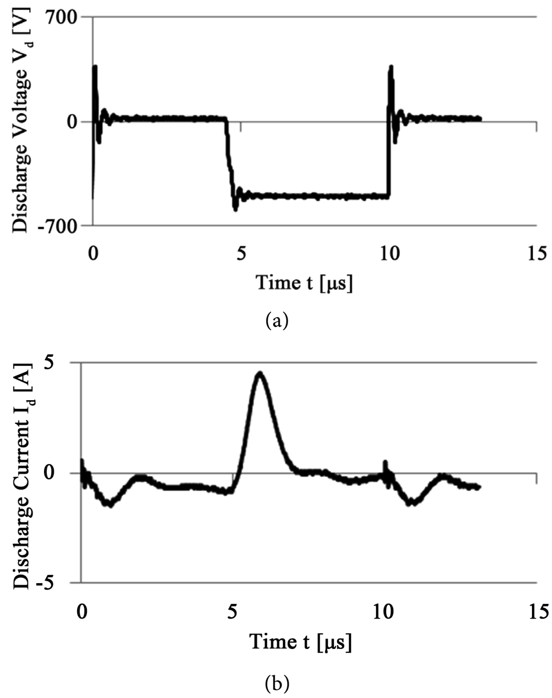

Figure 9. Waveforms of (a) Discharge voltage (V_d) and (b) Discharge current (I_d).

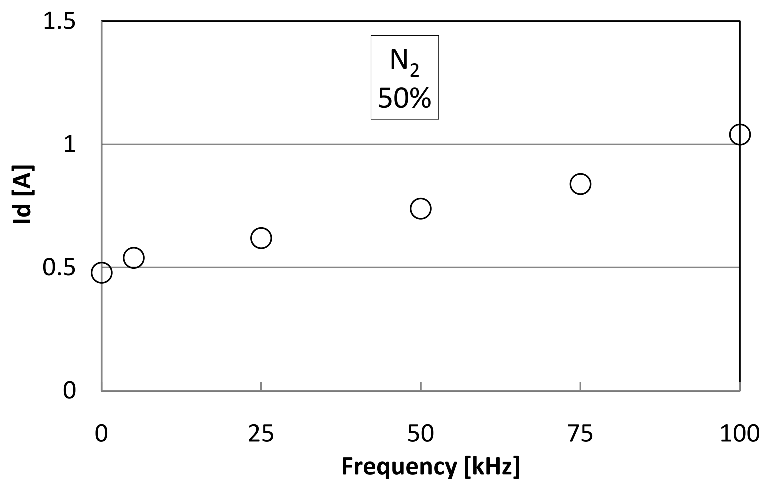

Figure 10. Discharge current (I_d) as a function of pulse repetition frequency.

frequency of the applied voltage, the I_d increased with the frequency. Therefore, it was better to use high frequency (100 kHz) for relatively high plasma density.

4. Conclusion

For uniform tube inner coating of non-conductive thin films, the extended anode effect in double-ended coaxial magnetron pulsed plasma was investigated. Thus coating experiments have been performed for various thin films made of metal to ceramics like TiO_2 or TiN with different electrical conductivity. The deposited film profile and thickness changed by the film electrical resistivity. Therefore, it can be concluded that the extended anode effect is strongly influenced by the electrical resistance of coated thin film on the inner surface of insulator tube. Moreover, the shifting velocity of the main position of plasma was affected the production of negative ions in case of O_2. Furthermore, the effect of the production of negative ions can be seen in the difference of shifting velocity of the main poison of plasma along the tube between the thickness profile of TiO_2 film and TiN film. Since shifting velocity was slower for O_2 comparing to N_2, thus TiN film supposed to reach anodic state before TiO_2 film. Therefore, other methods for uniform coating of non-conductive thin film on the whole inner surface of insulator tubes should be developed.

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