OPTICAL EMISSION SPECTROSCOPY OF SPUTTERING TYPE OXYGEN RADICAL SOURCE FOR THE DEPOSITION OF TiO_2 FILMS AT HIGH RATE

Hao Lei, Yoichi Hoshi, Daiki Ishihara, Meihan Wang, Yutaka Sawada

Center for Hyper Media Research, Tokyo Polytechnic University,1583 Iiyama, Atsugi, Kanagawa 243-0297, Japan.

Introduction

Titanium dioxide (TiO_2) thin films attracted considerable attention because of their potential applications in photocatalysis since 1980's. There are many methods to prepare TiO_2 films such as sol-gel, chemical vapour deposition, oxygen plasma assisted reactive evaporation and magnetron sputtering. As a most popular industrial tool, magnetron sputtering has advantages of preparing films with excellent uniformity, high packing density and strong adhesion. However, a rather low deposition rate was observed in the deposition of the films with anatase structure using a conventional magnetron sputtering system [1]. The reason for the low deposition rate was explained as follows; Ti target surface is covered with an oxide layer during the sputtering in Ar and O_2 mixture, resulting in the reduction of sputtering yield from the target. In addition, only the oxygen atoms are selectively sputtered from the oxide surface and the emission of titanium atoms is significantly suppressed. It should be noted that the oxygen defects produced on the surface by the sputter-emission is repaired immediately by the oxygen gas in the mixture [2].

In order to increase the deposition rate, we proposed a new reactive sputtering method using two sputtering sources working in a metallic mode and an oxide mode, respectively [3-4]. In the reactive sputtering method, the oxygen radicals produced in the oxide-mode sputtering source are supplied to the substrate surface to enhance the oxidation of titanium atoms supplied from the metallic-mode sputtering source. However, the performance of this sputtering type oxygen radical source was still not clear until now. Optical emission spectroscopy (OES) is a powerful tool with advantages of high space resolution and 'in situ' real time information of plasma as well as no any interference with the plasma. In the present study, investigation of OES of our sputtering type oxygen radical source was performed to clarify the relationship between the sputtering conditions and the formation of oxygen radicals.

Experimental

Figure 1 shows the DC planar magnetron reactive sputtering system with two sputtering sources conjunction of an optical emission spectroscopy including optical fiber, monochromator, detector and data processing system. The background pressure before the deposition was below 10^{-6} Torr. A sputtering source of Ti metallic target with diameter of 33 mm worked in a metallic mode and supplied Ti atoms. Another sputtering source with 100 mm Ti target cathode worked in the oxide mode and supplied oxygen radicals. Each sputtering sources were separated from the deposition chamber with a metal mesh of an open area ratio of 45%. O_2 (gas flow rate: 16 sccm) and Ar gases (up to 200 sccm) were introduced into the system through the oxygen radical source and the Ti source, respectively.

The oxygen gas pressure was maintained at 2×10^{-3} Torr, when Ar gas was not introduced. Oxygen radicals were produced using a DC power supply connected with a 20 kHz pulse generator. The plasma was analyzed by OES at a distance of 5 cm far from the Ti cathode via a quartz optical fiber. The spectral line intensities were recorded by means of an ATRAS-25 multi-spectrophotometer (Bunkoh-Keiki).

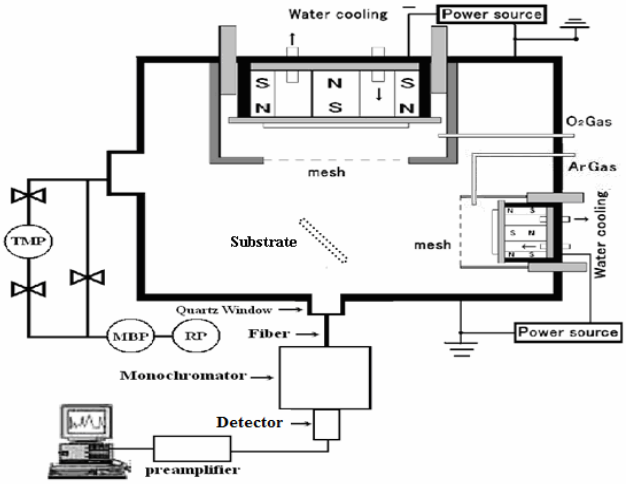

Fig. 1 Schematic configuration of reactive sputtering system with two sputtering sources combined with OES.

Results and Discussion

Figure 2 shows a typical optical emission

spectrum from the oxygen radical source at a discharge current of 1.5 A and sputtering voltage of 523 V. A strong emission peak appeared at 777.1 nm corresponding to atomic oxygen (O) [5]. Emission from oxygen molecule ions (O_2^+) were also detected but the intensity was very low compared with that of O. Figure 3 shows the changes in the O peak intensity and the intensity ratio of O_2^+/O with discharge current. It is clear from the figure that the emission spectrum from O increases monotonically as the discharge current increases. We also found that the absolute peak intensity of O_2^+ increased linearly with a discharge current. The intensity ratio of O_2^+/O, however, decreases continuously as shown in Fig. 3.

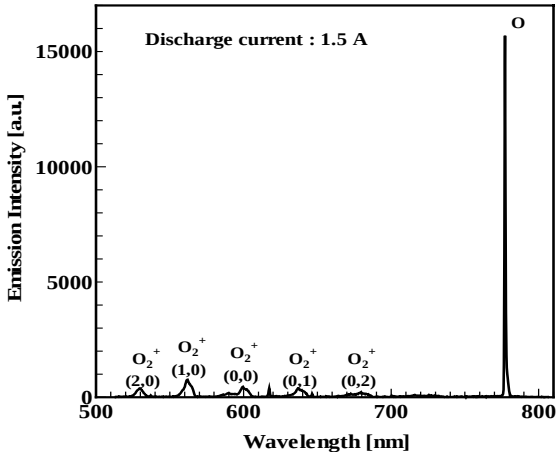

Fig. 2 Optical emission spectrum from oxygen radical source.

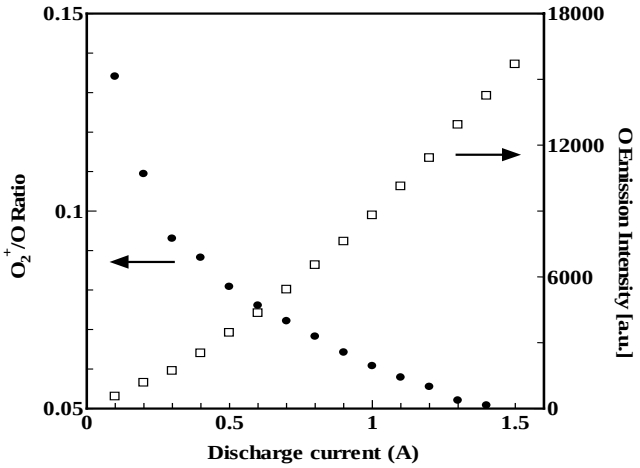

Fig. 3 Changes in the O peak intensity and the intensity ratio of O_2^+/O with discharge current.

These results indicate that the increase in discharge current promotes the production of the atomic oxygen. Usually oxygen molecules were excited by the collisions with high energy secondary electrons. If the atomic oxygen were only produced by such collisions between the oxygen molecules and the high energy electrons, the ratio of O_2^+/O should depend a little on the discharge current. Our results suggest that atomic oxygen was produced remarkably at high discharge current conditions. This may be attributable to the selective sputtering of oxygen atoms from the target surface, that is, larger amount of atomic oxygen is produced by the sputter-emission from the target surface at such a high sputtering current condition.

When a mixture of Ar (200 sccm) and O_2 (16 sccm) gas was introduced into the chamber, the absolute intensity of O and O_2^+ decreased to about one fifth of that in pure oxygen gas. The peak intensity ratio of O_2^+/O was almost no change.

It was also confirmed that the supply of large amount atomic oxygen to substrate surface was effective to deposit the TiO_2 films at high rate. Structure and photocatalytic properties of the films deposited by using our sputtering type oxygen radical source will be shown in the symposium.

Conclusion

Optical mission spectrum from a sputtering type oxygen radical source with titanium metal cathode was investigated in detail. As a result, it became clear that the amount of atomic oxygen was increased steeply by the increase of discharge current, and the atomic oxygen was the main product in the radical source, which is attributed to the selective sputtering of oxygen atoms from the target surface. This sputtering type oxygen radical source is useful for the promotion of oxidization of titanium atoms in the deposition of TiO_2 films at high rate.

References

1.Noguchi, D., Kawamata, Y. and Nagatomo, T. Relationship between the photocatalytic characteristics and the oxygen partial pressure of TiO_2 thin films prepared by a DC reactive sputtering method. *Jpn. J. Appl. Phy.,* **43** (2004) 1581-1585.

2.Hoshi, Y. and Takahashi, T. High Rate Sputter Deposition of TiO_2 Films Using Oxide Target. *IEICE Trans. Electron.,* **87-C** (2004) 227-231.

3.Sakai, T., Kamiya, O., Hoshi, Y. and Shimizu, H. High rate reactive sputter-deposition of TiO2 films by using two sputtering sources. *IEICE. Tech. Rep.*, **107** (2007) 23-27.

4.Hoshi, Y. Ishihara, H., Sakai, T., Lei, H. and Shimizu, H. Structure and Photo-catalytic Properties of TiO2 Films Deposited by High Rate Reactive Sputtering. *IEICE. Tech. Rep.*, **108** (2008) 75-79.

5.Karuppasamya, A. and Subrahmanyam, A. Studies on the room temperature growth of nanoanatase phase TiO_2 thin films by pulsed dc magnetron with oxygen as sputter gas. *J. Appl. Phy.,* **101** (2007) 064318.