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Synthesis of ceramic films on metallic substrates using magnetron-sputtering deposition synchro-enhanced by microwave ECR plasma source ion implantation under high vacuum conditions

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Abstract: This paper introduced how to do simultaneous plasma source ion implantation enhanced deposition (PSII-IBED) and how to prepare the ceramic films on the metallic substrate using simultaneous PSII-IBED. The formula for calculating the deposition rate which matches the implantation rate was offered for the first time.

I. INTRODUCTION

The ceramic films on metallic substrate are increasingly being used in many technical areas. Various ceramic films have been deposited in different experimental conditions, by D.C. magnetron reactive sputtering, by ion beam enhanced deposition (IBED) and by PSII-IBED. There are two techniques for IBED: (1) nitrogen/oxygen ions are implanted in the metallic film while the film is being deposited (simultaneous process) (ref.1); (2) nitrogen/oxygen ions are implanted in the metal after a suitable thickness of metal film has been reached. This individual deposition and ion-implantation step can then be iterated until the desired total thickness is reached (iterated deposition and ion-implantation process) (ref. 2). But for PSII-IBED, there is only one technique, i. e. the iterated deposition and ion-implantation process which is a cumbersome process and is not suitable for industrial applications (ref. 3 and 4).

There are some problems which must be resolved for simultaneous PSII-IBED: (1) PSII is omnidirectional, the magnetron sputtering deposition is not; (2) PSII needs high vacuum (about 5×10^{-2} Pa), the deposition needs lower vacuum (about several Pa); (3) how to match the deposition rate with the implantation rate? In our laboratory, a simultaneous process for synthesis of various ceramic films on metallic substrate using PSII -IBED has been succeeded. In this paper, the experimental setup with a special work-piece manipulation which makes the magnetron sputtering deposition omnidirectional was introduced (Section II), so problem (1) was resolved. For problem (2), a special magnetron sputtering target (ref. 5) which can work well under high vacuum was used. For problem (3), we have deduced a formula of calculating the deposition rate matched with the implantation rate for the first time (Section III). Then we prepared some ceramic films using simultaneous PSII-IBED and made some analysis of samples and discussion (Section IV). At the last, we got some conclusion (Section V).

II. EXPERIMENTAL SETUP

Figure 1 shows the scheme of the experimental setup which was constructed in Dalian University of Technology, China. Its main chamber is a 600 mm-in-diameter and 700 mm-in-height cylinder with two ECR rooms on its top, a cylindrical-shaped magnetron sputtering target of 50 mm-in-diameter and 460 mm-in-length in the center and a rotatable platform on its bottom. The target has been made into a sleeve form which was tightly buckled with the magnetron device cooled with water and so it can be replaced easily. Four work-piece supports mounted on the platform are able to spin, so that an identical ion implantation dose and the same amount of the sputtered articles can been received for all over the work-piece surface. A 450 1 / s turbomolecular pump with a 8 l/s pre-pump can creates a base vacuum of 8×10^{-4} Pa in the main chamber. The work pressure in the main chamber was 8×10^{-2} Pa which was maintained by filling the work-gas ($Ar+N_2$) into the chamber. A two-channel mass flow controller was used to regulated the mass flows of Ar and N_2 (or O_2). For the experiment, the optimum input power of the microwave was 540 W. In the experimental process of, for example, making TiN film by the simultaneous PSII-IBED, after the sputtering cleaning of the work-piece surface by Ar^- under a -1200V bias voltage, the TiN film was deposited on the surface and enhanced by a synchronous ion implantation. The pulsed negative high voltage bias exerted on the work-piece was 30 kV in-amplitude, 30 μs-in-width and 50 Hz-in-frequency. The sputtering rate and the integrated film thickness was inspected with a quartz crystal monitor and the real film thickness on the work-piece surface was worked out from the measured value of the monitor aimed with some auxiliary experiments. For the sake of safety, the quartz detector must be mounted outside the high-voltage sheath.

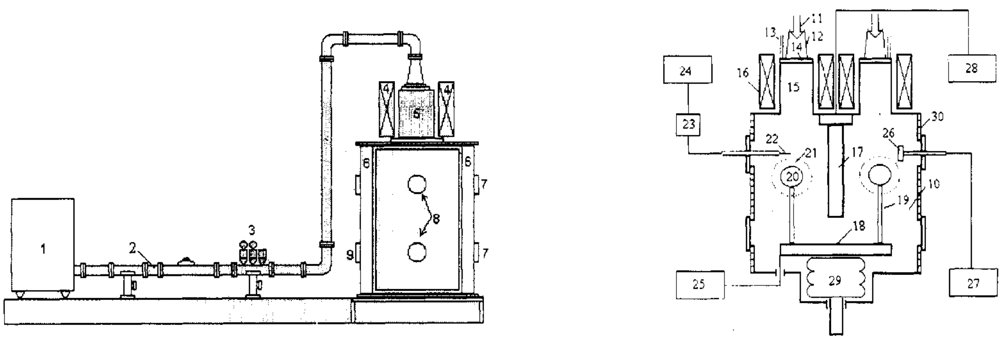

Fig. 1 A scheme of the experimental setup. (a). full view of the system; (b). the details in the main chamber.

1. the microwave power source. 2. the waveguide structure. 3. the impedance matching device. 4. the coil for magnetic field of 875 G. 5. the ECR cavity. 6. the main chamber. 7. the view ports. 8. the ports for diagnostics. 9. the port for vacuum pump. 10. the main chamber. 11. the incoming microwave. 12. the microwave guide. 13. the work-gas inlet. 14. the quartz window. 15. ECR cavity. 16. the magnetic coil. 17. the magnetron sputtering target. 18. the work-piece platform. 19. the work-piece supports. 20. the work-piece. 21. the sheath. 22. Langmuir probe. 23.D/A and A/D converter. 24. the micro-computer. 25. the pulsed negative high voltage power supply. 26. the sensor of the quartz crystal monitor. 27. the quartz crystal monitor. 28. the low-voltage bias power supply. 29. the insulator. 30. the confinement magnets.

III. HOW TO MATCH DEPOSITION RATE WITH IMPLANTATION RATE?

It is the crux of the simultaneous PSII-IBED process to match the deposition rate with implantation rate. The matched atomic ratio requires that the atom number N_x deposited on the unit area of the work-piece surface per second is equal to the implantation rate R_i (which is the number of the nitrogen atoms implanted into unit area of the work-piece surface per second) multiplied by m (here m is stoichiometrical constant), we can get:

$$N_x = m R_i \qquad (1)$$

It is known that the implantation rate R_i can be determined according to the following formula:

$$R_i = c f N_i (1 - \eta) V / S \qquad (2)$$

where f symbolizes the frequency of the negative high voltage pulse; N_i the ion density of the plasma in the main chamber; V the total volume of the sheath induced by the negative high voltage pulse exerted on the work-piece; S the total surface area of the work-piece; c the correction coefficient considering the existence of the nitrogen molecule ions each of which consist of two atoms and η the percentage of the Ar^+ component in the plasma ions. It was reported that 75% of the ions in the nitrogen plasma were molecule ions and therefore c = 1.75. Supposing the matched deposition rate being R_d (nm/s),N_x can be calculated as following expression:

$$N_x = R_d \rho_x N_A \times 10^{-7}/A_x \qquad (3)$$

where ρ_x, N_A and A_x represent the density of target material x, the Avogadro constant and the atomic mass of x. Therefore the following relation can be derived:

$$R_d = m\, c f N_i\, (1-\eta) V A_x \times 10^7 / S \rho_x N_A \qquad (4)$$

For example, for preparing TiN film by the simultaneous PSII-IBED, the experimental parameters we used are: c = 1.75, f = 50Hz, $N_i = 1.8 \times 10^{10}/cm^3$ and η = 30%, a global substrate with diameter of 2 cm was used as the work-piece sample. When the negative high voltage pulse is 30 kV in-amplitude and 30 μs in-width, the sheath volume has been experimentally measured by Langmuir probe to be 5568 cm^3. With A_{Ti} = 47.90, ρ_{Ti} =4.54 g/cm^3 and $N_A = 6.02 \times 10^{23}$/mol, the matched deposition rate R_d can be evaluated to be 0.086 nm/s, which can be easily achieved under the high vacuum condition by adjusting the bias voltage acted on the sputtering target.

In fact, the simultaneous PSII-IBED is a multi-channel-process (Fig. 2). A small fraction of the sputtered Ti atoms reacts into TiN groups with the N^+ in the nitrogen plasma and then some of them arrive at and deposit on the surface of the work-piece. Another fraction of the sputtered Ti atoms firstly were deposited on the surface of the work-piece and then probably react into TiN or Ti_2N with those N^+ that were implanted into the film. Some of the deposited Ti atoms may remain in atomic state. Therefore, the practical deposition rate should be higher than the calculated one. The optimum deposition rate and the implantation rate can only be found out through repetitive trial. There are many factors influencing the deposition rate strongly. Three of them , that are the partial pressure of Argon, the bias voltage of the sputtering target and the plasma density, are the most important. The characteristics of the negative high voltage pulse (i. e. amplitude, frequency and duty factor etc.) and the plasma density are the most effective factors to the implantation rate. There are two experimental operation modes for the simultaneous PSII-IBED, a continuous deposition process with a pulsed implantation and a pulsed deposition with a pulsed implantation (Fig.3). It has been found out that the full pulsed mode is more reliable and safer.

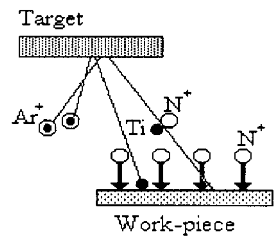

Fig. 2. A scheme of the multi-channel-process.

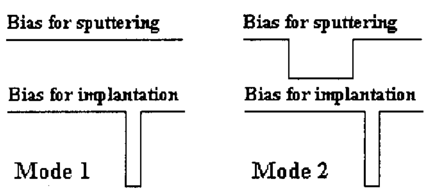

Fig. 3 The two operation modes.

IV. RESULT AND DISCUSSION

Using simultaneous PSII-IBED, we prepared some ceramic films: ZrN, TiN and ZrO_2 etc. on the substrate made of stainless steel. In PSII-IBED, energetic ions are useful in that they tailor surface structure and chemistry to further improve film properties such as hardness, wear, friction, corrosion resistance, or fracture toughness. Energetic ions also promote film adhesion to substrates through the creation of a graded interface , or through radiation damage to reduce compressive stress that often accompanies deposition. Figure 4 shows the Auger depth profile of the TiN film prepared by simultaneous PSII-IBED. There is a obvious graded interface between the film and the substrate. Figure 5 shows the scratch test results of (a) ZrN prepared by

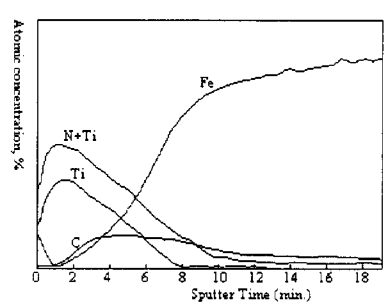

Fig. 4 Auger profile of TiN

simultaneous PSII-IBED and (b) ZrN prepared by the magnetron sputtering deposition. The adhesions between the substrate and the film prepared by simultaneous PSII-IBED are strong. The crystal structure of films was investigated by X-ray diffraction (XRD). Figure 6 shows the X-ray diffraction patterns of (a) ZrN and (b) ZrO_2 all prepared by PSII-IBED.

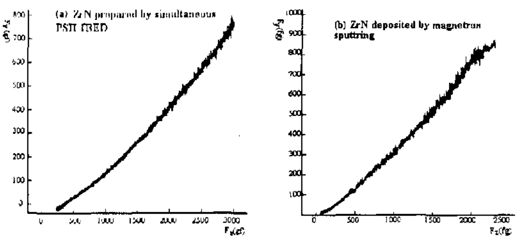

Fig. 5 Scratch test curve of (a) ZrN prepared by PSII-IBED and (b) ZrN by magnetron sputtering deposition

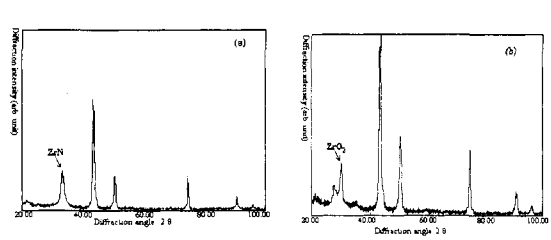

Fig. 6 X-ray diffraction patterns of (a) ZrN and (b) ZrO_2

V. CONCLUSION

1. The simultaneous PSII--IBED possess simple procedure and controllable parameters, a higher deposition rate will be obtained when a higher frequency of negative-high-voltage-pulse is used, so it is suitable for industrial application.

2. Using simultaneous PSII-IBED, the ceramic films of various thickness with graded surface and modified film can be made.

3. The matching formula is a approximate one, but it can offer the initial data for repetitive trials.

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