Controlling synthesis of Ti–O/Ti–N gradient films by PIII

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Abstract

Titanium oxide and titanium nitrogen gradient films were synthesized using plasma-immersion ion implantation and deposition (PIIID). An intelligent control system was developed to control pushing of the metal cathode source and variation of the gas composition by programmable logical control (PLC); cathode pushing rules can be conveniently set, multi-channel gas composition control was achieved by D/A and mass flow control (MFC), and gas change has quick dynamic response velocity and a good degree of linearity. The results show that the whole system is stable and reliable, has strong anti-interference capacity and sets flexibly correlative technological parameters. The mechanical properties of the films synthesized on silicon wafer, titanium and low-temperature isotropic carbon (LTIC) were analyzed by microhardness tests, pin-on-disc wear experiments and scratch adhesion tests. X-Ray diffraction (XRD) and scanning electron microscopy (SEM) were used to evaluate the properties. Good mechanical properties were achieved by controlling the synthesis of the Ti–O/Ti–N gradient films discussed in this paper. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Plasma immersion ion implantation (PIII); Programmable logical control (PLC); Mass flow control (MFC); Ti–O/Ti–N gradient film

1. Introduction

Titanium nitride is commonly used as a wear- and corrosion-resistant coating on cutting tools, machine components and biomaterials [1], due to its superior mechanical and chemical properties, including high hardness, low wear coefficient and chemical stability. The blood compatibility of titanium oxide has also been studied in recent years. Rutile-type titanium oxide ceramics, TiO2 and TiO layers or films prepared by thermal oxidation and ion beam-assisted deposition (IBAD) [2–6] generally have a blood compatibility better than that of clinically applied biomaterials, such as LTIC. Hence, titanium oxide is a candidate for use as a biomaterial. Combining titanium nitride and titanium oxide may help to obtain the advantages of both coatings. During synthesis of the films, duplex gradient films were fabricated in order to enhance adhesion. Several methods have been used to synthesize Ti–O/Ti–N gradient films, including metal–organic chemical vapor deposition, filter arc deposition, DC magnetron reactive sputtering, ion beam-enhanced deposition (IBED) [7,8], plasma-immersion ion implantation (PIII), etc. [6].

PIII, demonstrated by Conrad et al. in the late 1980s [9], shows great commercial potential in the fields of surface modification and semiconductor processing [10]. PIII circumvents the line-of-sight restriction inherent to conventional beam-line ion implantation, eliminates complex focusing elements in the instrument, is capable of processing complex-shaped components, such as artificial organs, and is potentially more economical [6]. Therefore, our interest has focused on Ti–O/Ti–N duplex gradient films synthesized by PIII in recent years. However, existing PIII facilities are usually equipped with relatively crude control systems, and some of them are even manually controlled [9]. The lack of a robust and reliable control system neither guarantees stability of the technology process, nor sets the technology parameters agilely. The workload imposed on operators can lead to operational failure.

By allusion to actual work, an intelligent control system was designed and used to control cathode push-
ing of metal vapor vacuum arc (MEVVA) and variation of the gas composition by programmable logical control (PLC). Ti–O/Ti–N gradient films were synthesized on Si(100) wafer, titanium and LTIC substrates by PIII, using titanium metal plasma and reactive plasma nitriding/oxidation. The mechanical properties of Ti–O/Ti–

2. System structure

Fig. 1 shows the complete schematic structure of the control panel, including the PLC, digital-to-analog converter (D/A), analog-to-digital converter (A/D) and mass flow control (MFC).

2.1. Hardware selection

PLC is the core of the whole control system. Cathode pushing and gas control are set by the PLC, with the output point directly linked to the cathode power switch.

The MFC is a voltage-controlled device, possessing the advantages of high definition, good linearity and repeatability, fairly quick velocity of dynamic response and reliable control. The gas flow can be controlled to between 1.2 and 100 sccm. PLC transfers data to the D/A, which then converts the digital signals to analog. The MFC receives a voltage signal from the D/A to control the gas flow. The whole process attains a stable controlling effect when the air pressure is within a definite range. A schematic diagram of the MFC structure is shown in Fig. 2. There are two screens on the control panel of the MFC; two channels of gas flow can be displayed on the screens in real time. Moreover, the MFC itself is a device with feedback function.

2.2. Software design

The program for cathode pushing produces a continuous square wave. During the high level, the cathode is

Fig. 3. Technology graph of gas composition control.
pushed and, during the low level, the cathode pushing process is stopped. The cycle and pulse duration of the square wave can be continuously adjusted by the software.

There are four kinds of subprogram in the gas composition control program. Every subprogram controls a process. Fig. 3 shows four different technology process graphs. A flow chart for the control program for Ti–O$_y$Ti–N gradient films is shown in Fig. 4. When the program is executed, the system waits for operation commands to decide whether to begin pushing the cathode and gas flow or not. Thereafter, output for gas flow and cathode pushing is in terms of default values. When the process is over, gas flow and pushing of the cathode source immediately stop. If an error/failure or abnormality occurs, the program quickly sounds an alarm and shuts the system down.

3. Experimental

Synthesis of Ti–O$_y$Ti–N gradient films was performed in a multi-purpose plasma-immersion ion implanter equipped with several plasma-generating tools, including radio frequency (RF) discharge, hot-filament discharge and a vacuum arc metal plasma source [11]. Ti metal plasma, and nitrogen or oxygen gas plasma could be simultaneously generated inside the implanter to generate the films. Nitrogen and oxygen plasma was sustained by RF glow discharge in the main chamber, and the titanium plasma was generated in the metal-vapor vacuum-arc plasma source (MEVVA) and diffused into the vacuum chamber via a magnetic duct to eliminate deleterious macro-particles. When negative
Voltage pulses were applied to the sample and synchronized with the metal arc duration, titanium and nitrogen or oxygen ions were implanted into the exposed surface. During the off-cycles of the high-voltage power modulator, titanium ions condensed, while nitrogen or oxygen was absorbed onto the sample surface. Table 1 lists the parameters of the experiments performed in this work. Process curves Fig. 4a–d show different gas transition processes and pulse bias voltage for groups T1–T5 in Table 1.

The thickness of the Ti-O/Ti-N gradient films was measured with Taylor-Hobson thickness apparatus. The final thickness of the films was approximately 650 nm. The microhardness of the Ti-O/Ti-N gradient films on Si and Ti substrates was measured with HX1000 microhardness apparatus. The wear tests were performed on a pin-on-disk wear tester equipped with a 6-mm-diameter Si₃N₄ ball. The adhesion of gradient films on Ti and LTIC substrate was measured with WS-97 adhesion apparatus. The morphology of films after wear tests was observed by scanning electron microscopy.

4. Results and discussion

Fig. 5 shows the X-ray diffraction pattern of Ti-O/Ti-N gradient films deposited on a silicon wafer. It can be observed that the gradient film contains rutile TiO₂ and TiN. Fig. 6 displays the microhardness results of Ti-O/Ti-N gradient films on Si and Ti substrates, which were treated by processes T1, T2 and T3 (Table 1). The microhardness of the Ti-O/Ti-N gradient coatings reaches a maximum of approximately 1900 HV. For the measurements, a load of 5 g was used. Fig. 7 depicts the wear track widths after pin-on-disk wear tests using 50- and 25-g load/16 000 rotating cycles. Samples produced with the parameters of group T3 show a smaller track width than samples treated by processes T4 and T5. The friction coefficient as a function of the number of rotations is plotted in Fig. 8. The improvement is quite apparent for group T1.
frequency bias voltage of 2000 V will increase the wear resistance. Fig. 9 shows the result of adhesion tests of groups T3 and T5 on LTIC substrate. There are two curves in Fig. 9; the upper one shows the tangential force signal, with adhesion corresponding to the inflection point of tangential force; the lower curve shows the sound emission signal, with adhesion corresponding to the first peak of the sound emission curve. During experiments, measurement of the two curves was combined in order to decrease experimental errors. Adhesion on LTIC substrate of group T3 reaches a value of 69 N. This is 11 N higher than that of group T5. Adhesion on Ti substrate for groups T1–T3 is between 32 and 39 N, but that of groups T4 and T5 is approximately 16 N. This result was expected and indicates that high-frequency bias voltage will affect adhesion.

The morphology of the wear track was observed by SEM, which shows that the damage is due to abrading and fatigue wear. In Fig. 10, the films have still not completely flaked; only a few, small, exfoliated fields were observed. The edges of the wear track are ragged and deformation slip bands have been formed, indicating plastic deformation of the material close to the tracks.

5. Conclusion

Ti–O/Ti–N gradient films have been synthesized on silicon wafer, titanium alloys and LTIC by metal plasma-immersion ion implantation and reactive plasma nitriding/oxidation using a set of intelligent control systems. The whole process is stable and reliable; the control system improves the precision and decreases the workload of operators. Our result shows that the microhardness of gradient films can be as high as 1900 HV. Films also show good wear resistance and fairly good adhesion. We proved that the intelligent control system was successively developed, but much work needs to be carried out on the PIII system in order to improve the automation level of its control system.
Fig. 10. Morphology of wear track by SEM: (a) wear track of Ti substrate for group T1; and (b) wear track of LTIC substrate for group T3.

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