

## TiN Coating to Three-Dimensional Materials by PBII Using Vacuum Titanium Arc Plasma

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Titanium nitride (TiN) films were coated on a silicon substrate (p-type, (111)) and titanium ions were simultaneously implanted in the substrate by Plasma Based Ion Implantation (PBII) using a titanium vacuum arc of DC 70A with a pulse voltage of -40kV/20 $\mu$ s. The XPS measurements indicated that the thickness of the implanted layer was independent of the tilt angle of the substrate, and that the deposition thickness depended on the tilt angle. When the Ti ions were implanted into the walls of the trench-shaped substrate holder, the implantation depth in the inner side wall was shorter than those in the outer side and bottom wall of the trench. The RBS measurements showed that the number of the Ti atoms in the deposited film and implanted layer varied with the tilt angle of the substrate.

Key words : PBII, TiN, metal arc, coating, ion implantation

### 1. INTRODUCTION

Plasma-based ion implantation (PBII) is a promising method for modifying the surface properties of materials in order to improve wear resistance and hardness in engineering fields[1]-[3]. Our PBII facility for obtaining metal ions includes a metal plasma source in the same vacuum chamber with a substrate. Although the PBII technique shows some similarities to ion-assisted coating or ion beam mixing, PBII has advantages of easy handling, large area and low cost treatment. PBII also has the advantage that the thin film preparation and the ion implantation are simultaneously carried out and it is possible to apply to the objects with three-dimensional topologies without using vacuum manipulation in order to obtain uniform doses.

Titanium nitride (TiN) thin films have been prepared from nitrogen ions reacting with titanium atoms [4],[5]. The advantage of using metal ions instead of gas ions is that they implant themselves more easily into the substrate while simultaneously forming the thin film.

In this study, the TiN films were coated using a vacuum arc as a titanium arc source in nitrogen gas. The formation of the implanted layer was explored in comparison with that prepared by applying DC bias. The tilt angle of the substrate to the arc source was varied in order to discuss the ion implantation and the number of the Ti atoms deposited and implanted in three-dimensional materials.

### 2. EXPERIMENTAL

A schematic diagram of the experimental facilities is shown in Fig.1. The inner dimensions of the width, depth and height of the vacuum chamber were 340, 550 and 380mm, respectively. A pulse voltage of negative polarity was supplied to a substrate via a feedthrough placed at the end of the chamber, opposite to the arc

source. A water-cooled titanium cathode was mounted with a trigger electrode at the other end of the chamber. The vacuum chamber was grounded to make an anode.

Both cathode and trigger electrodes were connected to a DC power source. The DC arc current and voltage were 70A and 20V, respectively. A trigger discharge was ignited by disconnecting the trigger electrode from the cathode to generate a DC metal-arc between the cathode and the grounded chamber. A resistance R in Fig.1 suppressed the trigger-discharge current after the main arc ignition. The process time was 2min for the measurements of X-ray photoelectron spectroscopy (XPS) and Rutherford backscattering spectrometry (RBS). The shapes of substrate holders were trench, sphere (40mm in diameter) and triangle (angles  $\phi$  of 30, 45 and 60 $^\circ$ ).

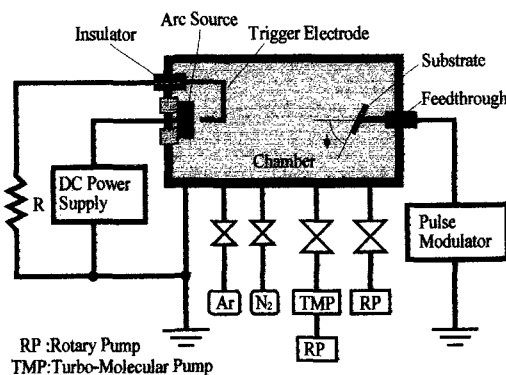


Fig.1. Schematic diagram of experimental facilities.

The pulse modulator was used for applying a pulse voltage of  $-40\text{kV}$  with the width of  $20\mu\text{s}$ . The repetition rate was  $400\text{Hz}$ . The deposition occurred during the DC arc between pulses. The nitrogen pressure was  $0.27\text{ Pa}$ .

A silicon substrate (p-type, (111),  $0.626\text{mm}$  in thickness) was used for the XPS measurement and a carbon substrate for the RBS measurement. The substrates were positioned about  $400\text{mm}$  (or  $150\text{mm}$ ) from the arc source. The pumping system consisted of a turbo-molecular pump and a rotary pump, which were positioned on the side-wall of the discharge chamber. The turbo-molecular pump could be separated from the discharge chamber by a gate valve.

XPS coupled with  $2\text{keV Ar}^+$  sputter depth profiling was also conducted to determine the composition profiles and the chemical bonding states of the constituents. An analysis was done with monochromatic  $\text{MgK}\alpha$  X-rays in a vacuum chamber after argon sputtering. The substrate was sputtered in Ar at pressure of  $5.0 \times 10^{-4}\text{Pa}$  for  $11\text{h}$  and the profiles were obtained every  $1\text{h}$ . The film thickness was measured by a thickness meter for the film implanted by applying  $-40\text{kV}$  at the substrate angle of  $90^\circ$ . On the basis of this result, the film thicknesses for other tilt angles were obtained using the XPS depth profile. The RBS measurement was performed with using a  $1.8\text{-MeV He}^+$  beam (collimated to  $1\text{-mm}$  diameter) backscattered at  $165^\circ$  to the beam direction. The quantity of the Ti atoms were estimated by a simulation.

### 3. RESULTS AND DISCUSSION

#### 3.1 TiN film and implantation layer

The depth profiles of Ti and N concentrations obtained from XPS measurements are shown in Fig.2 for some tilt angles of the substrate. For the tilt angle of  $90^\circ$ , the Ti concentration of the film prepared at a DC voltage of  $-0.2\text{ kV}$  is also shown. The concentration at an etch time of  $0\text{ h}$  corresponds to that at the surface of the deposition layer. The etch rate was about  $80.4\text{nm/h}$ .

In the profile for the tilt angle of  $90^\circ$ , there appears a coated layer of TiN at etch times of  $0$  to  $6\text{ h}$ . The atomic ratio of titanium to nitrogen for the TiN thin film is independent of the tilt angle of substrate and is approximately equal to  $4/3$ . The profiles at etch times from  $8$  to  $11\text{h}$  show that the implanted layer is formed in the substrate. The similar implanted layers were observed in the profiles for the tilt angles of  $0$  to  $60^\circ$ . However, the implanted layer is not recognized for the DC voltage application. The implanted layer is formed by the implantation of the titanium ions accelerated with the high voltage pulse. Thus, the implantation of the titanium ions through the coated thin film into the substrate is made by our PBI system.

The TiN film thickness varies with the tilt angle of substrate as shown in Fig.3. It is seen that the thickness is proportional to  $\sin \phi$  corresponding to the surface area seen from the arc source. On the other hand, the thickness of the implanted layer is independent of the tilt angle of substrate as shown in Fig.3. The Ti ions are implanted through the coated layer into the Si substrate. Therefore, the implantation depth in the Si substrate for each pulse decreases with increasing coating thickness. However, the deepest implantation in the Si substrate

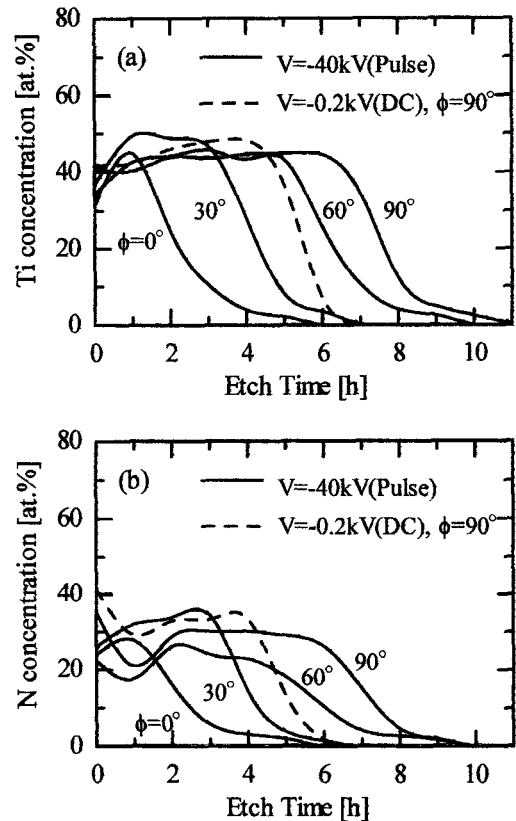


Fig.2. Depth profiles of TiN film on silicon substrate at various tilt angles.

(a) Ti concentration, (b) N concentration

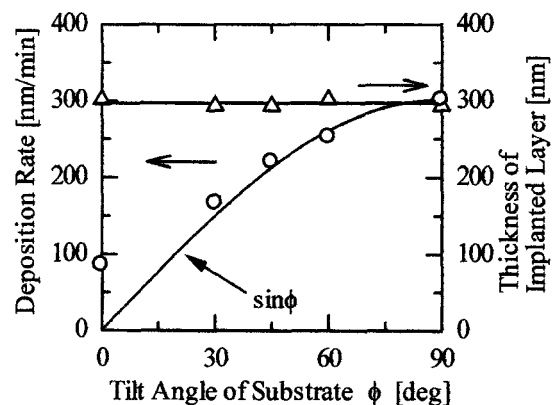


Fig.3. Deposition rate and thickness of implanted layer.

occurs at the first pulse, where the effect of coating on the implantation is least. The implantation depth at the first pulse is solely determined by the pulsed voltage. Thus the thickness of the implanted layer in the Si substrate is independent of substrate angle.

For DC bias of  $-200\text{V}$ , the thickness of the TiN film is approximately  $431.7\text{nm}$  which is less than that for the pulse voltage application, of which thickness is about  $602.7\text{nm}$  for the process time of  $2\text{min}$ . The smaller value of the thickness for the DC bias is attributable to the ion

sputtering due to the continuous application of the voltage to the substrate.

The XPS spectra of Ti 2p<sub>3/2</sub> and Ti 2p<sub>1/2</sub> in the film and substrate are shown in Fig.4(a), where the pulse voltage and the angle are -40kV and 90°, respectively. They show a change in chemical shifts. Ti in deposited layer shows the chemical shift of 1 eV, due to the Ti-N combination. In the meantime, Ti in implanted layer (etch time ≥ 9h) shows no chemical shift, which is attributable to the Ti-Si combination. On the other hand, the XPS spectra of N 1s in Fig.4(b) showed the constant binding energy of 396.6eV in both the deposited and implanted layers. This fact is consistent with the expected negligible difference in chemical shift between the combinations of N-Ti and N-Si in the deposited and implanted layer, respectively. Thus, Ti and N atoms in the implanted layer are mainly combined with Si atoms.

### 3.2. Implantation to trench

The trench and the sphere-shaped substrate holder are schematically shown in Fig.5. Both width and depth of the trench are 16mm, and the substrates were placed on the bottom, inner side, outer side and back walls of the trench.

The depth profiles of Ti concentration obtained from XPS are shown in Fig.6, where the pulse voltage is -40kV. The profiles show that implantation layers are formed in the substrate at etch times from 6 to 8h for the bottom and at 2.5 to 4h for the outer side wall. However, the implanted layer are diluted and thinner for the back (1-2h) and inner side wall (2-3h) compared to those for the bottom and outer side wall. The non-uniform depth of the implantation layer is due to that the ion sheath formed is long compared with the width of trench when the plasma density around the substrate is 10<sup>15</sup>-10<sup>16</sup>m<sup>-3</sup>.

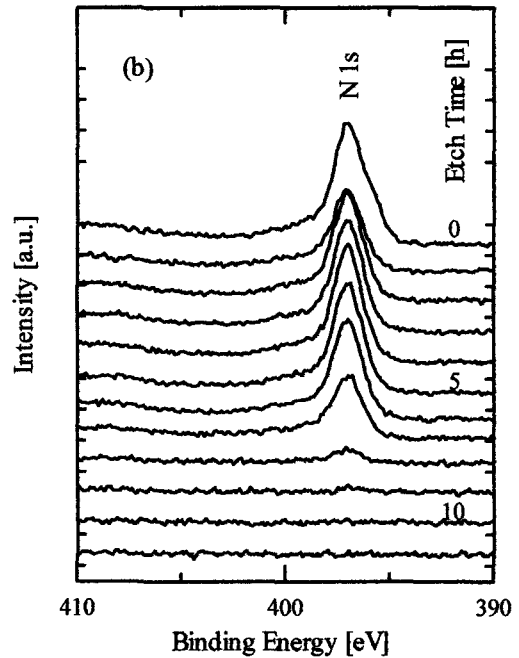
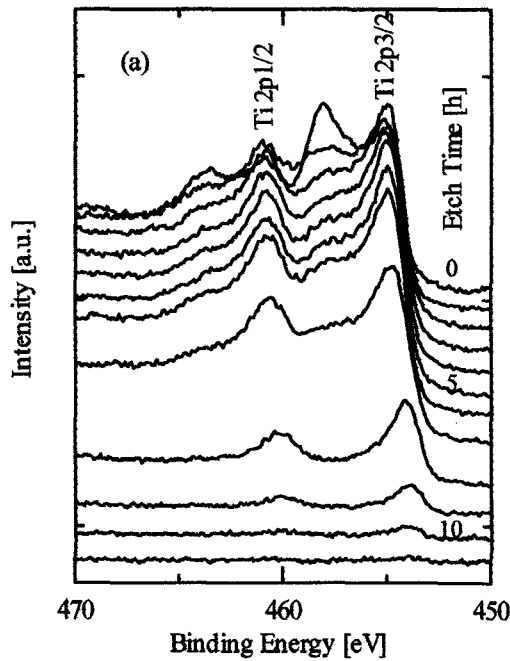


Fig.4. XPS spectra. (a) Ti 2p<sub>3/2</sub> and 2p<sub>1/2</sub>, (b) N 1s.

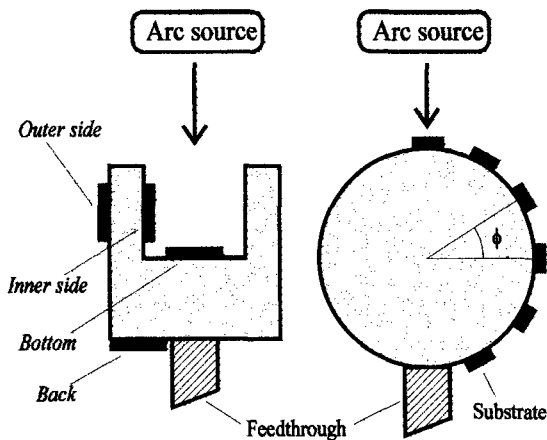


Fig.5. Substrate positions at the wall of trench and sphere-shaped substrate holder.

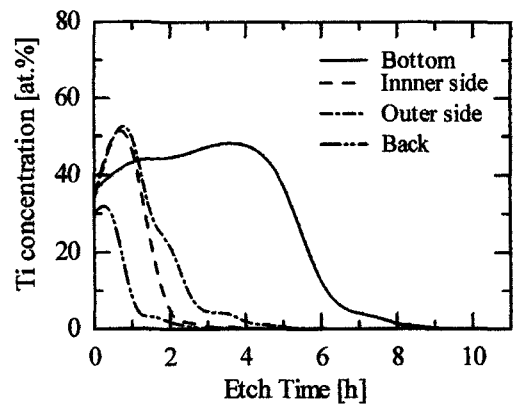


Fig.6. Depth profiles of Ti concentration on the substrate placed on the trench.

The plasma density was measured by a Langmuir probe. In order to carry out uniform implantation to the objects with uneven surfaces like the trench, it is necessary to extend the ion sheath with increasing the plasma density.

### 3.3. Number of Ti atoms to three dimensional topologies

The RBS spectra for the film prepared at the pulse voltage of -30kV are shown in Fig.7. For the substrate distance from the arc source 150 and 400mm, numbers of Ti atoms per unit area are about  $2040 \times 10^{15}$  and  $320 \times 10^{15}$  atoms/cm<sup>2</sup>, respectively. Thus, the plasma density increases with decreasing distance from the arc source. Indicating that there is a divergent flow of Ti ion to the substrate from the arc source.

Number of Ti atoms is shown in Fig.8 as a function of tilt angle of substrate. The substrate is placed on the sphere-shaped substrate holder and the pulse voltage is -30kV. The profile is similar to that in Fig.3, that is, the numbers of the Ti atoms are proportional to  $\sin \phi$  corresponding to the surface area seen from the arc source. However, the Ti atoms were observed on the back wall ( $\phi = 0^\circ$  to  $-60^\circ$ ) of the substrate holder.

Thus PBII is proved to be useful for the conformal ion implantation to the three dimensional materials, since the plasma of high density can be formed by an application of pulsed bias. For the conformal ion implantation into the substrate with uneven surfaces like the trench, however, it is required that a more uniform plasma with a higher density and a smaller size of the ion sheath should be formed around the substrate. The smaller size of the ion sheath is attained by a shorter pulse width of the applied voltage. Furthermore, a multiple setting of the arc source is thought to be effective in realizing the more uniform plasma with a higher density, because there was a divergent flow of the plasma from the arc source in the above-described metal plasma.

## 4. CONCLUSIONS

A TiN thin film can be coated on a silicon substrate by means of PBII using titanium arc plasma (DC 70A) in nitrogen gas. The Ti ions are implanted inside the silicon substrate for all the substrate tilt angles and the applied pulse voltages. In the case of DC bias, the implanted layer is not formed. The thickness of the implanted layer is almost constant for various tilt angles of substrate, whereas the thickness of the deposited film depends on the tilt angle. There is a divergent flow from the arc source. That is, the plasma density decreases with increasing distance from the arc source. The XPS results show that both Ti and N atoms in the implanted layer are mainly combined with Si atoms.

For the implantation to the trench, the implanted layers are formed on all sides of wall. However, the implanted layers are diluted and thinner for the back and inner side wall compared to dose for the bottom and outer side wall. This fact is due to that the ion sheath formed is long compared with the width of the trench.

In order to carry out uniform implantation to the objects with uneven surfaces like the trench, it is necessary to extend the ion sheath with increasing the plasma density.

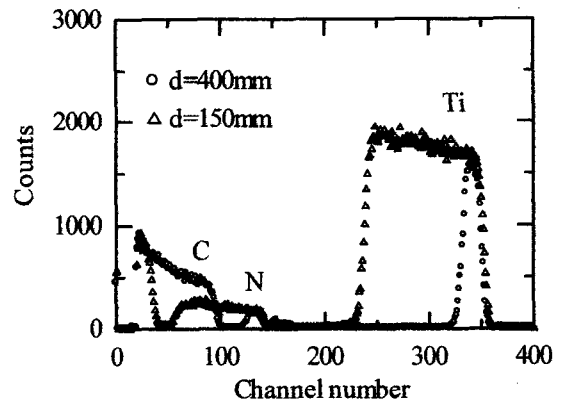


Fig.7. RBS spectra.

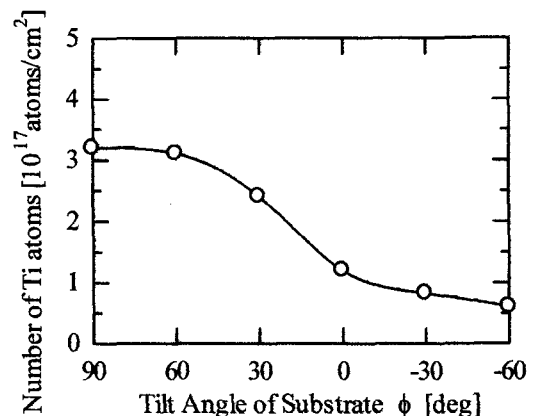


Fig.8. Number of Ti atoms as a function of tilt angle of substrate.

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