Vol 13 No 8, August 2004
1009-1963/2004/13(08)/1309-06

Chinese Physics

© 2004 Chin. Phys. Soc.
and IOP Publishing Ltd

Properties of TiN coating on 45# steel for inner surface modification by grid-enhanced plasma source ion implantation method*

Zhang Gu-Ling(张谷令)†, Wang Jiu-Li(王久丽), Liu Yuan-Fu(刘元富), Liu Chi-Zi(刘赤子), and Yang Si-Ze(杨思泽)

Institute of Physics, Chinese Academy of Sciences, Beijing 100080, *China*

(Received 9 December 2003; revised manuscript received 8 April 2004)

Using a new inner surface modification method named GEPSII (grid-enhanced plasma source ion implantation), which is designed for inner surface modification of tubular work pieces, we successfully produced polycrystalline TiN coating on 0.45% C steel (45# steel) samples. Compared with the uncoated 45# steel sample, the electrochemical corrosion test on the coated 45# steel samples presents evident improvement in their corrosion resistance. Two implanted voltages, direct current (–2kV) and pulsed negative voltage (–10kV), are applied on the substrates. It is shown that the direct current implantation is more effective than the pulsed implantation in the surface corrosion resistance. AES depth profile shows that coating thickness is about tens of nanometres. The preferred orientations expressed by peaks at (111) and (200) can be seen clearly in XRD patterns.

Keywords: PSII, inner surface, TiN, corrosion resistance
PACC: 5275R, 6800, 8160

1. Introduction

It is well known that plasma source ion implantation (PSII) is a non-line-of-sight technique to modify the surface properties of materials with complex shapes such as metals, plastics, semiconductors, ceramics and so on.[1,2] However, there are still some difficulties in implanting the inner surface of devices or workpieces such as gun-barrel, cylindrical automobile and oil pipes; this has aroused considerable attention in some industrial applications. Therefore, some experiments have been developed to improve the inner surface properties of tubes.[3–7] But bad uniformity and film firmness are two chief obstacles thus far unresolved. Due to the still existing problems, recently, one new inner surface PSII method, called grid-enhanced plasma source ion implantation (GEPSII), has been proposed to uniformly modify the inner surface of workpieces.[8] In this new method, plasma is directly produced inside the tubular samples and the plasma ions are implanted into the inner surface by the applied pulsed negative or direct current (dc) potential. Thus the two difficulties are resolved at the same time.[8–10]

For current industrial applications, it is important to improve the material surface properties, such as the superficial hardness, rubbing fastness, and corrosion resistance in various kinds of materials. In titanium nitride (TiN) a novel combination of physical properties is seen, such as high hardness, high corrosion resistance, metallic electrical conductivity, good chemical inertness, temperature stability coefficient, and low friction; and what is more its electrical and thermal conductivities are close to those of pure metals.[11,12] So we choose TiN as the inner surface protection film in the experiment.

As is known, the coating properties are related to the implantation modes; and the pulsed negative high-voltage implantation and dc voltage implantation are two different growth modes. In pulsed negative high-voltage implantation mode, when a pulse begins, ions

*Project supported by the National High Technology Development Programme of China (Grant No 2002A331020), the National Natural Science Foundation of China (Grant Nos 50071068 and 10275088), the Science and Technology Program of Beijing Municipal Science and Technology Commission (Grant No H020420160130), and the ARO-FE (Grant No N62649-02-1-0010).
†E-mail: glzhang@aphy.iphy.ac.cn

strike into the substrate with a kilo-eV energy, and these ions are implanted into the substrate surface and the crystal restructure is completed in the pulse gap; while in the dc mode, ions impact the substrate continuously. Generally, the pulsed mode has a higher ion implantation energy but lower ion dosage than the dc mode does. Therefore, films obtained will show different characteristics under different growth mode. In this paper, we use two implantation modes, –10kV pulsed voltage and –2kV dc voltage, to implant TiN coating on the 0.45% C steel ($45^{\#}$ steel) samples.

2. Experiment

Figure 1 schematically shows our GEPSII experimental set-up for inner surface modification of a cylindrical tube. The modification system consists mainly of two coaxial electrodes, the central axial electrode and the coaxial-earthed grid electrode. N_2 plasma can be produced between them in a 13.56MHz radio frequency (RF) oscillation. The produced plasma can diffuse through the grid into the tube. Thus there are two plasma regions, the core plasma region and the diffused plasma region in the system. In addition, because of the self-produced bias voltage between the two electrodes of capacitive RF glow discharge, the central electrode has a negative electric potential, compared with the grid-earthed electrode, and it can be controlled between –200V and –400 V in this experiment. This self-produced bias produces an ion sheath outside the central electrode, and ions in the ion sheath are accelerated by the negative electric field and impact the central Ti electrode with an energy of hundreds of electron volts. The sputtering efficiency of 300eV Ar^+ to sputter the Ti target is 0.33, and that of 300eV N^+ is a little lower than 0.3. So a certain amount of Ti atoms can be sputtered from the central electrode. When the Ti atoms move through the ion sheath into the plasma region, they can be ionized by electron collisions

$$e + Ti \rightarrow 2e + Ti^+ \quad (1)$$

This ionization process only needs 3.3eV of electron energy.[13] In classical RF capacitive glow discharge, the plasma density is at a scale of $10^{10}/cm^2$ and the electron temperature is about 5eV. When a pulsed or dc negative potential is applied on the tube, nitrogen and titanium ions can be accelerated by the radial electric field between the grid electrode and the inner surface. The implanted active nitrogen and titanium ions can accordingly form TiN_x structure in the sample surface. Since the plasma is produced between the two coaxial electrodes, the produced plasma inside the tube is uniform along the axial and radial directions; and this will accordingly improve the axial uniformity of the implantation.

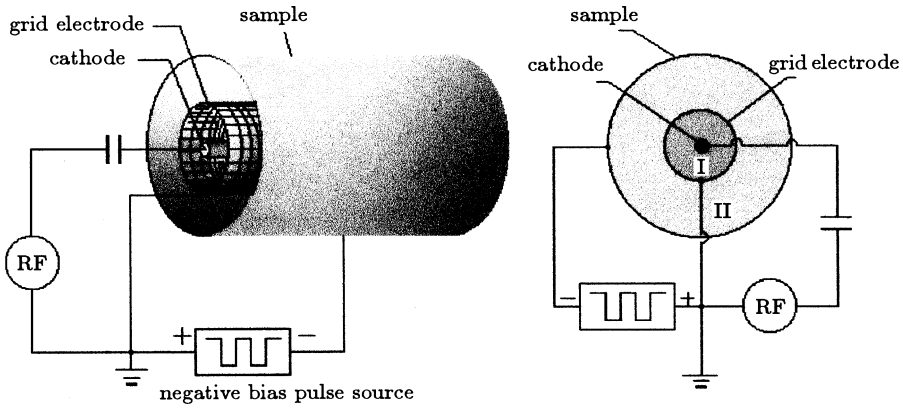


Fig.1. Schematic diagram of the GEPSII experimental system.

Although we assume that the plasma density distribution and the ion implantation along the axial direction are uniform, actually the axial density distribution will show a little difference at the two ends. Lengthening the tube in industrial applications can solve this problem. The axial and radial density distributions have been measured and published in Ref.[8].

In this experiment, for the convenience of experimental detection, we placed several 45# steel samples on the inner surface bottom side of the tube along the axial direction. The tube was really the cylinder of an automobile with a diameter of 100mm and a length of 210mm; the cylindrical grid electrode, made of stainless steel net with the mesh of a size 0.9mm×0.9mm, had a diameter of 48mm and a length of 230mm. The 45# steel, which is composed of ferrite (α-Fe) and cementite (Fe_3C), had a poor corrosion resistance and low hardness. We used two implantation voltages, pulsed and dc voltages. The parameters used are as follows: pulsed high voltage V_{pulse}=−10kV; pulse frequency f_{pulse}=60Hz; pulse width W_{pulse}=100μs; dc voltage V_{dc}=−2kV; nitrogen pressure p_{N_2}=10Pa; RF power P_{rf}=150W; self-bias of RF source $V_{rf-self} = -300$V; and the processing time durations are all 2h. The 45# steel samples were hand polished with dimensions of 15mm in diameter and 2mm in thickness.

The electrochemical corrosion tests were carried out using a M351 potentiometer, which gave the testing Tafel curves. The corrosion test was performed in 2% NaCl solution. We used an x-ray photoelectron spectroscope (XPS/ESCALAB5) to analyse the coating content and an x-ray diffractometer (D/max-RB) with Cu$K\alpha$ (λ=0.154nm, 50kV, 200mA, with a monochromator, step width 0.02°, sampling time 3s) to characterize the microstructure of the coatings. The depth profile was analysed by a scanning Auger electron spectroscope (PHI-610/SAM, electron gun voltage 3kV, energy resolution 0.3%, entrance angle 30°).

3. Results and discussions

3.1. Electrochemical corrosion

The electrochemical corrosion test gives the log (I)–V polarization curves called the Tafel curves. We can obtain the pitting corrosion potential (E_{corr}) and corrosion rates from the Tafel curves. The pitting corrosion potential is obtained at the beginning of the test and taken as the start of the voltage axis; the corrosion rates are represented by the free corrosion current (I_k). The electrochemistry parameters of the processed samples are shown in Table 1 and Fig. 2. The value of E_{corr}, which is related to the Gibbs free energy of the sample, stands for the resistance ability against the pitting corrosion. The sample with a higher Gibbs free energy has a relatively high positive value of E_{corr}, and accordingly a higher corrosion resistance ability.[14] The passivating phenomenon in the curves in Fig.2 shows that the coated films work well. Here the passivated film which refers to the coated TiN film is different from that produced on the steel passivated by itself in a strong acid. For passivating curves the current value at the passivating inflection point is I_k of the film, and for the curve without passivating phenomenon, it is the current value at the intersection point of x-axis and the tangent of the curve at about 100mV above the E_{corr}. The lower I_k means a lower corrosion rate, and thus means a higher anticorrosion ability. E_{corr} and I_k given in Table 1 and Fig.2 indicate that all the coated films have a higher corrosion resistance than the uncoated sample does. The dc-implanted film, with E_{corr}=−8mV and I_k=1.5×10^{-8}A/cm^2, is several hundred times improved. And the pulsed negative high-voltage implanted film, with $E_{corr} = -319$mV and I_k=2.82×10^{-6}A/cm^2, is about 10 times improved. Because the total injection current of the dc implantation is larger than that of the pulsed implantation, the dc-implanted film has a higher corrosion resistance than the pulsed implanted film does. In anodic reaction, iron atoms lose electrons and dissolve into the salt solution. The coated film protects the 45# steel substrate with a dense microstructure to prevent corrosion reactions.

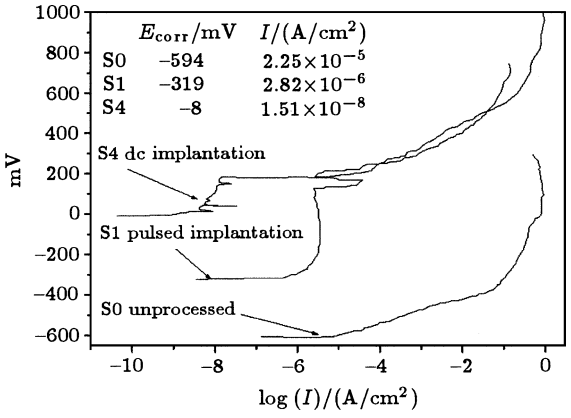


Fig.2. Tafel curves of different voltages for implanted coatings (anode reactive).

Table 1. Electrochemistry corrosion characters of different samples.

Sample	RF Power/W	Voltage/kV	Pressure/Pa	time/min	E_{corr}/mV	I_k/(A/cm^2)
S1	150	−10, 62Hz	10	120	−319	2.82×10^{-6}
S4	150	dc −2	10	120	−8	1.51×10^{-8}
S0	Unprocessed 45# steel sample				−594	2.25×10^{-5}

3.2. XRD analysis

Figure 3 shows the XRD patterns of the implanted samples. S1 denotes the pulsed implanted sample and S4 the dc-implanted sample. It can be seen from the positions of the peaks that the implanted films contain several possible forms of TiN_x: TiN (111), Ti_2N (210), TiN (200), TiN (220), Ti (103) and TiN (222), and only the TiN (111) and (200) peaks are remarkable. So the films have preferred orientations of [111] and [200]. The appearance of several TiO_2 peaks indicates oxidation of the films. Since TiN peaks are very weak compared with the α-Fe phase in the substrate, we think that the thickness of the film is thin. In addition, peaks are not sharp with several degrees of 2θ width. As is known, the crystal orientations are related to the substrate temperature; the implantation takes place at room temperature while the substrate temperature will rise during the implantation process, so we can observe TiO_2 peaks in the curves. Table 2 gives the measured values of TiN peaks compared with standard JCPDS data. There is no obvious difference between the two implantation modes, but still we can see that the dc-implanted coating has more clear small peaks, especially the titanium oxide peaks.

Table 2. The measured values of TiN peaks compared with the JCPDS standard data.

TiN peaks (hkl)	measured value d/nm	JCPDS date d/nm
111	0.2400	0.2440
200	0.2115	0.2120
220	0.1500	0.1496
222	0.1224	0.1223

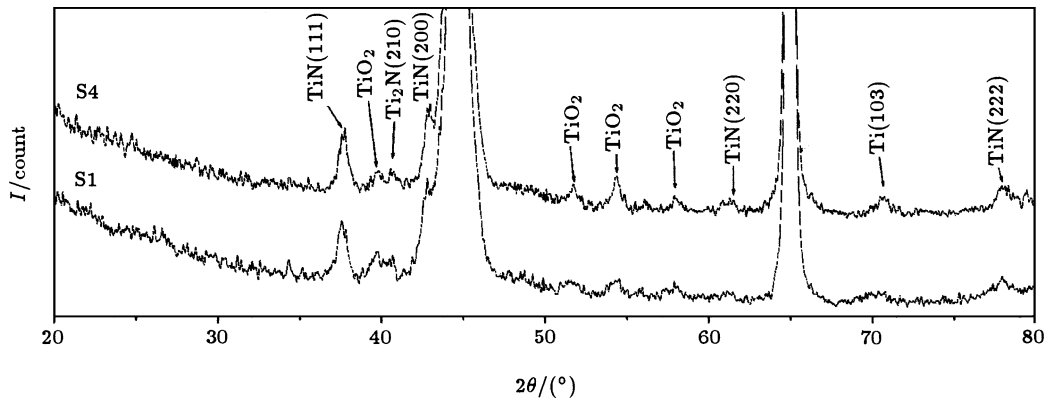


Fig.3. XRD patterns of implanted coatings (the strongest peaks are α-Fe).

3.3. Auger depth properties

Figure 4 shows the AES depth profiles of pulsed and dc-implanted coatings. The scanning area of Ar^+ sputtering gun is 1mm×1mm, and the sputtering rate is about 30nm/min, with 3.0keV energy and 25mA emission current, and the guide sample is SiO_2/Si. It can be seen that the thickness of the dc-implanted coating is about 48.75nm, but it is only 22.5nm for pulsed implanted coating. This can explain why the dc-implanted coating has a higher corrosion resistant ability than the pulsed implanted ones. Implanted coatings have good integrating interface with substrates, and about 20nm width integrated interface can be seen in the figures. The ratio of N/Ti is about 2 at all times, which also demonstrates the superabundance of the N circumstance. Considering that the Ti source is derived from the central electrode sputtering, the lower content of Ti in the film can demonstrate the lower sputtering ratio of Ti from the central electrode. Furthermore, the high content of oxygen can explain the Ti peaks in the XRD pattern. There are several reasons why there is so much oxygen in the coating: in the background gas pressure of about 3×10^{-3} Pa,

Ti is very easy to react with O_2, so there will be a quantity of Ti_2O_3 or TiO_2 in the coating. The temperature of vacuum chamber will increase during the implantation process, and oxygenization will become easier. In addition, the coating thickness is only tens of nanometres, so surface air oxidizing will be easy and severe after samples are taken out of the chamber.

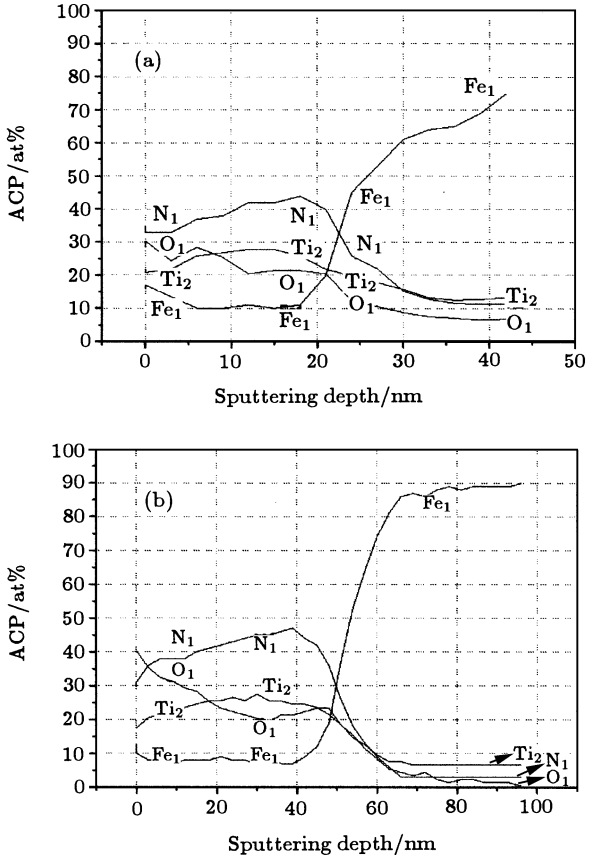


Fig.4. Auger depth spectra of pulsed coating (a) and dc coating (b).

3.4. XPS coating contents

Figure 5 gives the 0–1000eV XPS spectra of 5min sputtered sample S1, from which we can see Ti, N, C, O elements. The N peak is lower compared with the Ti peak, which means that Ti does not combine with N well, and there must be a certain titanium oxide (TiO_2). Figure 6 (a) shows Ti $2P_{3/2}$ and N 1S XPS spectra of 5min sputtered surface of sample S1, and Ti $2P_{3/2}$ XPS spectra of 5min sputtered surface of sample S4. At the surface there is only TiO_2 component, and Ti $2P_{3/2}$ peak is at 458.4eV. After 5min sputtering, the TiN signal arises. The Ti $2P_{3/2}$ peak of pure TiN is at 455.8eV, and it is 454eV for pure Ti. Figure 6 (b) also gives the fitting curves of the Ti $2P_{3/2}$ XPS spectra of 5min sputtered sample S1, from which we can see the Ti—O, Ti—N, and Ti—Ti valence bonds, and the amount of Ti—O bond is the highest. N 1s is at 396.5eV after 5min sputtering, but it is at 402eV at the surface, which corresponds to the absorption of nitrogen. The Ar^+ sputtering speed used in XPS is about 1.5nm per minute, so the sputtered depth is about 8 nm. From the AES data we can see that oxidation is still very high.

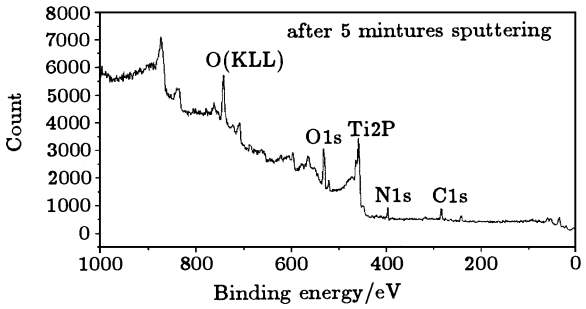
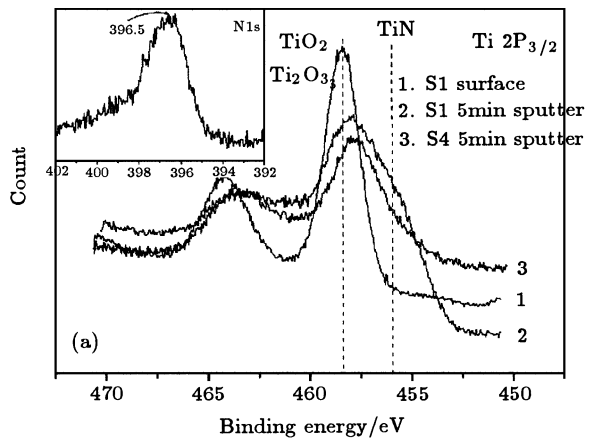


Fig.5. The 0–1000eV XPS spectra of 5min sputtered S1 sample surface.



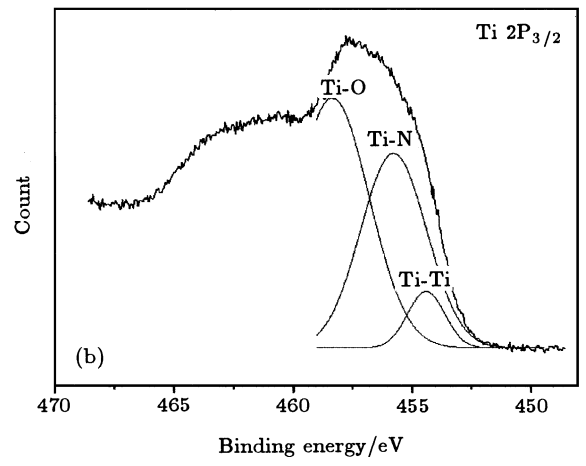


Fig.6. Ti 2P and N 1S spectrum of (a) Ti 2P XPS spectra surface and 5min sputtered surface of sample S1 and S4, and N 1S XPS spectra of 5min sputtered surface of sample S1; (b) fitting curves of Ti $2P_{3/2}$ XPS spectra of 5min sputtered S1 surface.

4. Conclusion

GEPSII is a new and effective method for material inner surface modification. In this paper we have successfully implanted TiN protective coating on $45^{\#}$ steel samples by GEPSII. The protective TiN coatings can improve the surface corrosion resistance of $45^{\#}$ steel samples. Because of the higher implanted dose, the dc-implanted sample has a better surface corrosion resistance than the pulsed implanted sample does. The XRD, AES and XPS analyses indicate that TiN coating is polycrystalline and contains some oxide components. Introducing the grid electrode in the experimental system is a trial and it needs further research on properties of the plasma source and the film growth.

References

[1] Chen J, Blanchard J, Conrad J R and Dodd R A 1992 *Surf. Coat. Technol.* **53** 267
[2] Mantese J V, Brown I G, Cheung N W and Collins G A 1996 *MRS Bull.* **21** 52
[3] Ensinger W 1996*Rev. Sci. Instrum.* **67** 318
[4] Demokan O 2000 *IEEE Transactions on Plasma Science* **28** 1720
[5] Shinji S, Yoshikawa M and Naito K 1998 *Thin Solid Films* **316** 165
[6] Sugimoto S, Uchikawa Y, Kuwahara K, Fujiyama H and Kuwahara H 1999 *Jpn. J. Appl. Phys.* **38** 4342
[7] Sun M, Li B, Liu C Z and Yang S Z 1996 *J. Vac. Sci. Technol.* A **14** 367
[8] Liu B, Zhang G L and Yang S Z 2001 *J. Vac. Sci. Technol.* A **19** 2958
[9] Zhang G L, Wang J L, Liu C Z and Yang S Z 2003 *Acta Phys. Sin.* **52** 2213 (in Chinese)
[10] Wang J L, Zhang G L, Liu C Z and Yang S Z 2004 *Chin. Phys.* **13** 458
[11] Nouvellon C, Konstantinidis S, Dauchot J P, Wautelet M, Jouan P Y, Ricard A and Hecq M 2002 *J. Appl. Phys.* **92** 32
[12] Hoang N H, McKenzie D R, McFall W D and Yin Y 1996 *J. Appl. Phys.* **80** 6279
[13] Adachia S 2000 *J. Appl. Phys.* **87** 1264
[14] Liu B, Liu C Z and Yang S Z 1999 *Thin Solid Films* **349** 110