한국표면공학회지
Journal of the Korean Institute of Surface Engineering
Vol. 34, No. 5, Oct. 2001
<연구논문>

Hard TiN Coating by Magnetron-ICP PI^{3}D

S. A. Nikiforov*, G. H. Kim*, G. H. Rim*, K. W. Urm**, S. H. Lee**

** Korea Electrotechnology Research Institute (KERI), P. O. Box 20, Changwon, Korea*
*** Doosan Heavy Industries & Construction Co., 555 Guygok-Dong, Changwon, Korea*

Abstract

A 30-kV plasma immersion ion implantation setup (PI^3) has been equipped with a self-developed 6'-magnetron to perform hard coatings with enhanced adhesion by PI^{3}D (PI^3 assisted deposition) process. Using ICP source with immersed Ti antenna and reactive magnetron sputtering of Ti target in N_2/Ar ambient gas mixture, the TiN films were prepared on Si substrates at different pulse bias and ion-to-atom arrival ratio (J_i/J_{Me}). Prior to TiN film formation the nitrogen implantation was performed followed by deposition of Ti buffer layer under Ar^+ irradiation. Films grown at $J_i/J_{Me} = 0.003$ and $V_{pulse} = -20$ kV showed columnar grain morphology and (200) preferred orientation while those prepared at $J_i/J_{Me} = 0.08$ and $V_{pulse} = -5$ kV had dense and eqiaxed structure with (111) and (220) main peaks. X-ray diffraction patterns revealed some amount of Ti_xN_y in the films. The maximum microhardness of $H_V = 35\ GN/M^2$ was at the pulse bias of -5 kV. The PI^{3}D technique was applied to enhance wear properties of commercial tools of HSS (SKH51) and WC-Co alloy (P30). The specimens were 25-kV PII nitrogen implanted to the dose $4 \cdot 10^{17}\ cm^{-2}$ and then coated with 4-μm TiN film on Ti_xN_y buffer layer. Wear resistance was compared by measuring weight loss under sliding test (6-mm Al_2O_3 counter ball, 500-gf applied load). After 30000 cycles at 500 rpm the untreated P30 specimen lost $3 \cdot 10^{-4}$ g, and HSS specimens lost $9 \cdot 10^{-4}$ g after 40000 cycles while quite zero losses were demonstrated by TiN coated specimens.

1. Introduction

A great deal of effort has been made during last decades to commercialize the technology of surface modification by accelerated ions. Plasma immersion ion implantation (PI^3) is one of the novel techniques in this field1). In PI^3 an ion current density does not depend on the area to be irradiated which makes it especially attractive for the treatment of large-area articles and for a batch process. A small penetration depth of ions, limiting industrial application of implantation, become much less of concern when a high rate deposition technique combines with PI^3 thus forming PI^{3}D - a promising versatile tool for surface modification of different materials. Sputter cleaning of a substrate, formation of interface layer by ion mixing, a film deposition accompanied with energetic ion irradiation, and the film post implantation - all of these steps can be performed within single treatment cycle.

Different PI^{3}D arrangements have been tested for preparation of coatings with advanced properties at high productivity1, 2). Hard TiN coatings have been reactively deposited on Si substrate by PI^{3}D in 2 mtorr pure nitrogen using vacuum arc Ti plasma source[3]. The growing film was pulse irradiated with 20-50 keV Ti^+ ions. The hardness of the film was found to increase with increasing pulse voltage, and for -40 kV it was almost equal to that for -500 V dc bias while the crystal orientation in the film was different It was strongly (200) preferred orientation for high voltage pulse biasing while (111) and (220) for -500 V dc one. The considered technique revealed the possibility of 3-D treatment[4] but suffers of droplet problem inherent for the vacuum arc sources.

PI^3 -assisted reactive deposition of TiN films was performed on 100Cr6 steel substrates in Ar/N_2 mixture at 0.85 mtorr by two large planar unbalanced magnetrons[5]. No other plasma source was used. Plasma density up to 1011 cm^{-3} was achievable in the stage vicinity at high magnetron power. During a pulse the growing film was irradiated with Ar^+ ions whereas between pulses the deposition of metal atoms was dominant. The pulses with amplitude 2.5-40 kV, pulse width 6-10 □s, and pulse-to-pause ratio 0.08-2 % were applied. The film microhardness was found to reduce with the voltage. At 5 kV it was nearly the same as that for conventional unbalanced magnetron sputtering at -50 V dc biasing. XRD patterns demonstrated (111) orientation for standard -50 V dc process, (200) preferred orientation for the pulse voltages up to 5 kV, and predominant rather week (111) texture for 10 - 40 kV. The use of unbalanced magnetron as a source of atoms to be deposited and the only source of plasma in PI^{3}D arrangement, indeed, allow to simplify the facility design but on the expense of flexibility. Additionally, spatial distribution of plasma is nonuniform in the cathode plane of unbalanced magnetron, and the plasma density reduces quite fast with the distance[6], thus make questionable the scaling up of the technique.

We modified a 30-kV experimental PI^3 setup[7, 8] to perform thin film deposition by PI^{3}D process using self-developed 6'-magnetron and ICP source with immersed antenna. Such arrangement seems to be attractive because both magnetron and ICP reveal good performance and are easily scaled up[8]. To explore the ability of the system, preparations of TiN film on Si, SS304, HSS (SKH51), and WC-Co alloy (P30) have been performed.

2. Experiment

The schematic diagram of an experimental arrangement is shown in Fig. 1a.

A 18-liter cylindrical processing chamber (diameter 300 mm and height 250 mm) is surrounded with full-line magnetic cusps for plasma confinement. A 6'- magnetron is mounted on the top flange. A 13.56-MHz ICP source is used to fill the chamber with dense uniform plasma. A one-turn water-cooled Ti antenna is placed between the magnetron and the substrate stage.

The antenna is grounded through a capacitor that allows to reduce the plasma potential and thus contamination from the chamber walls, and also results in the increase of the plasma density[9]. The same metal as to be deposited, namely Ti in our case, minimizes a contamination from RF antenna due to its self- biasing. Note that similar arrangement was used in[10] for directional PVD of metal ions into high aspect ratio surface features. Gas is introduced into the chamber through a shower, its flow rate and total pressure are controlled with a MKS mass flow controllers and a

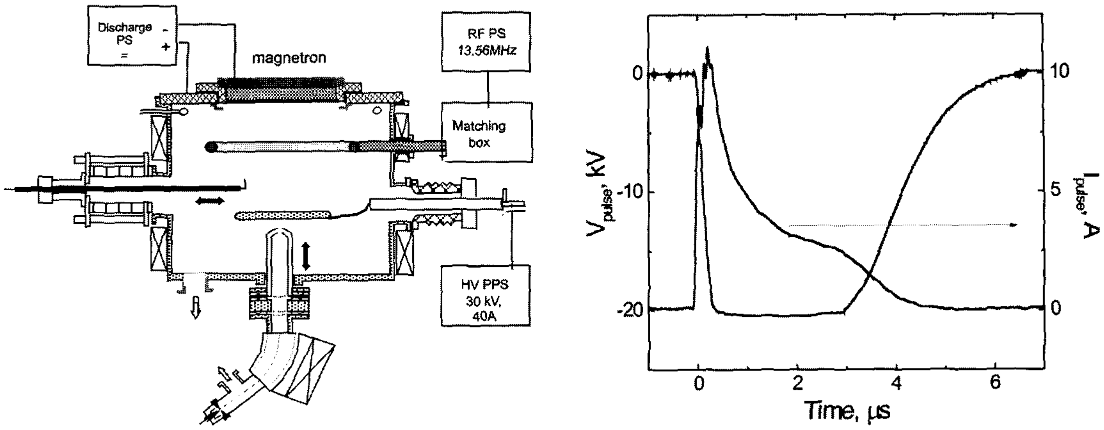

Fig. 1 (a) Schematic diagram of the 30-kV PI^{3}D setup. LP- Langmuir probe; MA - ion mass analizer.
(b) Typical traces of bias voltage and total pulse current through the stage.

baratron gauge. A diffusion pump equipped with LN_2 trap provides residual pressure of (1-2) $\cdot 10^{-6}$ torr.

A stage of diameter 120 mm is placed 200 mm downward the sputtering cathode and is connected alternatively to a 30-kV, 40-A (40 mA average) pulsed power supply or to a 3 - kV dc power supply. Pulses with width (pulse = 2 - 20 □s (FWHM), and frequency f = 100 - 5000 Hz were applied. A typical waveform of pulse bias and current through the stage is shown in Fig. 1b. Between pulses the stage was at nearly floating potential.

The setup was equipped with RF-compensated single Langmuir probe (LP) and an ion mass analyzer (MA) for plasma diagnostics[7].

PI^3-assisted reactive deposition of TiN films on different substrates has been performed at different operational conditions using Ti sputtering target and Ar/N_2 mixture. All the results presented in the following section were obtained at the total pressure of 1 mtorr, dc magnetron power of 1.5 kW, and FR power of the ICP source of 170 - 370 W.

Thickness of prepared films was measured by (-step profilometer. X-ray diffraction, SEM, AES were used to investigate the films properties. Microhardness of the films was measured by MZT -4 Akashi Co. nanoindenter.

3. Results and discussion

Fig. 2 (a) shows the parameters of argon plasma in the ICP source measured at 65 mm above the stage Density of 10^{11} cm^{-3} is obtained at relatively low RF-power of 360 W. Plasma is uniform within few percents across the stage[11]. Both, high plasma density and independent control of deposition rate and ion flux onto substrate are desirable in PI^{3}D process. Ion mass composition in the stage vicinity during PI^3-assisted deposition of TiN in Ar/N_2 mixture is shown in Fig. 2b. The ion mass spectrum in pure nitrogen ICP discharge at the same pressure is plotted for comparison too. It is seen that, unlike the results of[9] where high amount of Ti^+ ions was detected at a pressure of

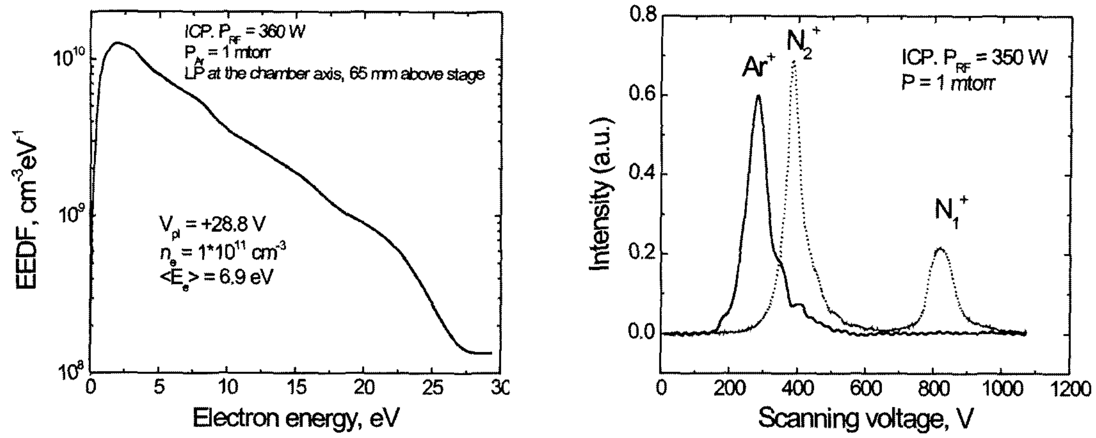

Fig. 2 (a) Electron energy distribution (EEDF), plasma density ne, average electron energy $<E_e>$, and plasma potential V_{pl} in ICP plasma.
(b) Ion mass composition in plasma at the substrate position. Solid line-during TiN reactive PI^{3}D in Ar/N_2 mixture, $P_{magnetron} = 1.5$ kW; dot line-in pure N_2 discharge ($P_{magnetron} = 0$).

some tens mtorr, in our case the plasma is mainly composed of Ar^+ ions. Hence during a pulse a growing film is mainly irradiated by Ar^+ ions; contents of $N_{1,2}^+$ and Ti^+ ions is negligible.

Shining gold TiN films were prepared on SUS304 and Si specimens at different high voltage pulse biasing and plasma density. The average energy per deposited atom defined as $<E_d> = E_i(J_i/J_{Me})$, where Ei is an ion energy and J_i/J_{Me} is the ratio of the accelerated-ion to deposited-thermal-particle fluxes incident at the growing film, is often used as a parameter of an ion assisted deposition[12, 13]. Even though a different film structure can be formed for the same $<E_d>$ depending on whether Ei or J_i/J_{Me} is high[14], we evaluated $<E_d>$ along with Ei and J_i/J_{Me} when compared the characteristics of prepared films. In PVD general trend is that the high ion flux is preferable rather than the increase of an ion energy (dc bias)[15]. In PI^{3}D high energy ions irradiate a substrate in pulse mode, and an average ion current should be rather small to keep the deposition rate higher than the resputtering rate. A mechanism of energy transfer in PVD differs from that in PI^{3}D where keV-range ions bombard a growing film and penetrate far below the surface.

To investigate the dependence of TiN film properties on irradiation parameters a series of treatment, when keeping V_{pulse}·□pulse·f = 8 V·Hz·□s = Const. in order to provide nearly the same resputtering rate, has been performed. The measured deposition rate was about 2 □m/h in all cases, treatment time was 1 h. Prior to TiN film formation the nitrogen implantation was performed followed by the deposition of Ti buffer layer under Ar^+ irradiation. To compare the film properties, PVD process at -(50÷300) V dc bias also was carried out. Substrate temperature did not exceed 300 ℃ in all cases. XRD patterns and corresponding cross sectional SEM pictures of the TiN films deposited on Si at -20 kV and -5 kV pulse, and -200 V dc bias are shown in Fig. 3. Films grown at $J_i/J_{Me} = 0.003$ and $V_{pulse} = -20$ kV

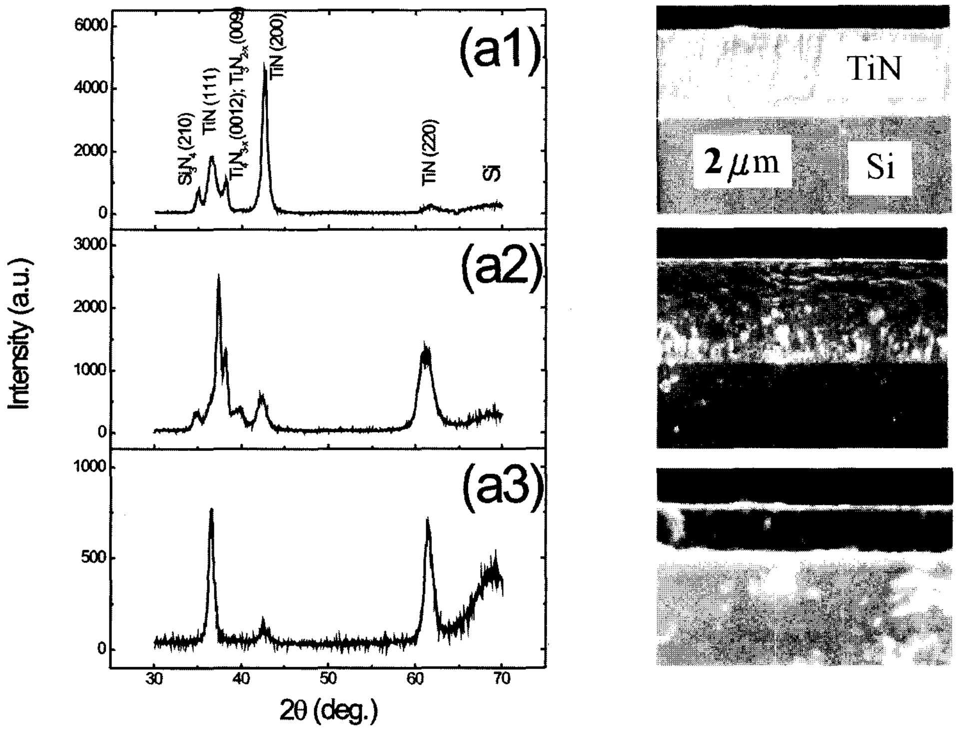

Fig. 3 X-ray diffraction patterns (a) and corresponding cross sectional SEM pictures (b) of TiN films deposited on Si.

(a1) : V_{pulse} = -20 kV, τ_{pulse} = 4 □s, f = 100 Hz; P_{RF} = 170 W; $<E_e>$ = 60 eV, J_i/J_{Ti} = 0.003.

(a2) : V_{pulse} = -5 kV, τ_{pulse} = 4 □s, f = 400 Hz; P_{RF} = 370 W; $<E_e>$ = 40 eV, J_i/J_{Ti} = 0.008.

(a3) : V_{dc} = -200 V, P_{RF} = 360 W, $<E_e>$ = 1200 eV, J_i/J_{Ti} = 6.

showed columnar grain morphology and (200) preferred orientation while those prepared at J_i/J_{Me} = 0.08 and V_{pulse} = -5 kV had dense and eqiaxed structure with (111) and (220) main peaks. The films prepared at -5kV pulse and -0.2 kV dc biasing demonstrate similar preferred orientation even though the value of ⟨Eα⟩ was 30 times higher in the latter. When applying -0.2 kV dc bias at such a high ion flux (J_i/J_{Me} = 6), the deposition rate was twice less than that for the pulse bias. X-ray diffraction patterns revealed some amount of Ti_xN_y in the films in case of pulse biasing that is attributed in part to the interfacerlayer.

The hardness of TiN films prepared at different pulse biasing is shown in Fig. 4.

The results obtained in[3] and[5] are depicted for comparison. The maximum microhardness of H_V = 35 GN/M^2 was obtained at the pulse bias of -5 kV and other parameters the same as in Fig. 3. This value is higher than that obtained by other researches[3, 5], and even 1.5 times higher than the typical hardness value for bulk TiN (20 GN/M^2). It can be attributed in part to the presence of Ti_2N in a film because the hardest films are formed in the two-phase region with Ti_2N and TiN[16]. Detailed analysis is out of scope of this paper.

The PI^{3}D technique was applied to enhance the

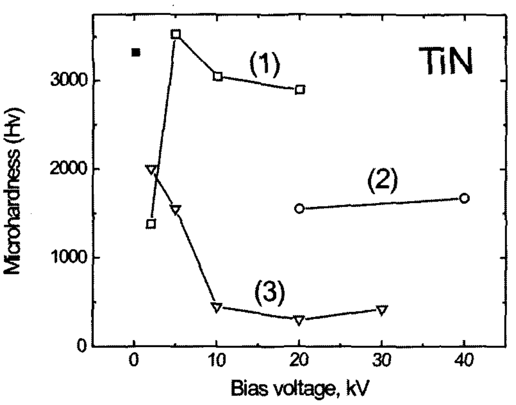

Fig. 4 Microhardness of TiN films prepared by PI^{3}D vs pulse voltage. Film thickness - 1-2 □m, and load - 1gf in all cases.
(1) - this work (the product V_{pulse}·□$_{pulse}$·f = 8 V·Hz·□s = const.). Microhardness for the film deposited at -200 V dc is depicted too (solid square);
(2) - M. Sano et al$^{3)}$; (3) - S. Schser et al$^{5)}$.

wear properties of commercial tools of HSS (SKH51) and WC-Co alloy (P30). The test specimens were 25-kV PII nitrogen implanted to the dose $4 \cdot 10^{17}$ cm^{-2} and than coated with 4-μm TiN film on Ti_xN_y buffer layer. Wear resistance was analyzed by measuring the weight loss under sliding test (6 - mm Al_2O_3 counter ball, 500-gf applied load). Coefficient of sliding friction for TiN coated and uncoated specimens of HSS and WC-Co is shown in Fig. 5. After 30000 cycles the untreated P30 specimen lost $3 \cdot 10^{-4}$ g, and HSS specimens lost $9 \cdot 10^{-4}$ g after 40000 cycles while quite zero loss was demonstrated by TiN coated specimens.

4. Conclusions

A 30-kV PI^3 setup has been modified to provide PI^3-assisted deposition using dc magnetron and ICP source. High density, uniform plasma and independent control of metal atoms and ion flux to the substrate are both desirable for obtaining good film properties. Besides high performance such arrangement shows good ability of scaling up.

Measurement of ion composition showed that in our case, during PI^{3}D process of TiN reactive deposition in Ar/N_2 mixture at the pressure 0.5-2 mtorr, a substrate is mainly irradiated with Ar^+ ions.

Golden shining TiN films with the hardness of up to H_V=35 GN/M^2 were prepared by PI^{3}D at the

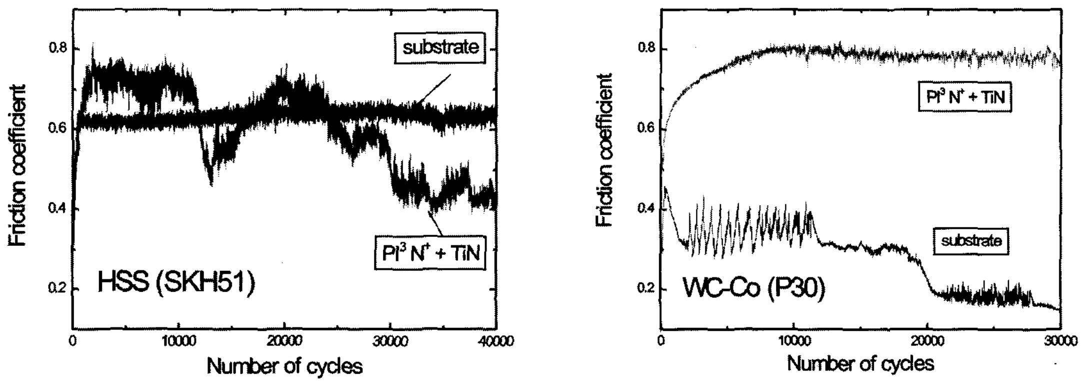

Fig. 5 Coefficient of friction for TiN coated and uncoated specimens of HSS and WC-Co under sliding test (6-mm Al_2O_3 counter ball, 500 rpm, 500-gf applied load).
(a) HSS. Sliding velocity - 0.4 m/s, track diameter - 15 mm, sliding distance - 1885 m;
(b) WC-Co. Sliding velocity - 0.2 m/s, track diameter - 8 mm, sliding distance - 754 m.

pulse bias of -(5-10) kV and at pressure of 1 mtorr. For 1.5-kW magnetron power, the deposition rate was about 2 □m/h as measured with □-step profiler and SEM.

Competitive preferred crystal orientation of (111), (200) and (220) was found in the entire rage of the treatment parameters applied. The hardest films had the (111) and (220) preferred orientation.

Further researches are required to understand better a film formation in PI^{3}D media and to reveal advantages of PI^{3}D technology comparing with others already established in industry.

References

1. Handbook of Plasma Immersion Ion Implantation and Deposition, Ed. by A. Anders, John Wiley & Sons, New York, 2000.
2. Papers from the 5th Int. Workshop on Plasma-Based Ion Implantation (PBII-99), Surf. Coat. Technol. 136 (2001).
3. K. Yukimura, M. Sano, et al, J. Vac. Sci. Technol. B 17 (1999) 840-844.
4. M. Sano, T. Teramoto, et al, Surf. Coat. Technol. 136 (2001) 168-171.
5. S. Schoser, J. Forget, K. Kohlhof, Surf. Coat. Technol., 93 (1997) 339-342.
6. P. Spatenka, I. Leipner, et al, Musil, Plasma Sources Sci. Technol. 6 (1997) 46-52.
7. G. H. Kim, G. H. Rim, S. A. Nikiforov, Surf. Coat. Technol. 136 (2001) 255-260.
8. G. Kim, G. Rim, et al, Proceed. of the ISPP-2000, Korea (2000) 191-197.
9. S. M. Rossnagel and J. Hopwood, Appl. Phys. Lett. 63 (1993) 3285-3287.
10. K. Suzuki, K. Konishi, et al, Plasma Sources Sci. Technol. 9 (2000) 199-204.
11. G. H. Kim, S. Nikiforov et al, Proceed. of the ICOPS'99 (1999) 206
12. L. Hultman, J. Sundgren, et al, J. Appl. Phys. 78 (1995) 5395-5403.
13. S. Logothetidis, I. Alexandrou, S. Kokkou, Surf. Coat. Technol. 80 (1996) 66-71
14. F. Adibi, I. Petrov, et al, J. Appl. Phys. 73 (1993) 8580-8589.
15. K. Laing, J. Hampshire, et al, Surf. Coat. Technol. 112 (1999) 177-80
16. F. A. Smidt, International Materials Reviews, 35 (1990) 61-128.