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Coating of titanium nitride thin film on stainless steel using an RF planar coil inductively coupled plasma

S.P. Chew and **C.S. Wong**

Plasma Research Laboratory, Department of Physics, Faculty of Science, University of Malaya, 50603 Kuala Lumpur, Malaysia

ABSTRACT Titanium nitride (TiN) thin film is grown on 304-stainless steel plate by Plasma Enhanced Physical Vapour Deposition (PEPVD) method in an RF Planar Coil Inductively Coupled Plasma (PC ICP) system. H-mode discharge in Ar-N_2 admixture is produced for this purpose. The titanium target is biased at a negative voltage of –800V, while the substrate is biased at voltage ranging from 0 to –160V in step of 20V to study the effect of substrate bias voltage on the quality of the TiN thin film obtained. The composition and structure of the films are studied and investigated by XRD, EPMA, AFM and SEM. The results show that bad quality TiN thin film is obtained when the substrate bias voltage is lower than –60 V. With a substrate bias voltage of greater than –80 V, a nominal TiN deposition rate of better than 1 μm per hour can be achieved.

ABSTRAK Pemendapan filem nipis titanium nitride (TiN) pada permukaan plat keluli nirkarat telah dilakukan melalui kaedah “Plasma Enhanced Physical Vapour Deposition” (PEPVD) dengan menggunakan sistem Plasma RF gandingan induktif gegelung satah (PC ICP). Nyahcas mod-H dalam gas camporan Ar-N_2 dihasilkan untuk tujuan tersebut. Sasaran titanium itu dibias dengan voltan negatif bernilai 800 V manakala substrat itu dibias pada voltan yang diubah antara 0 dan -160 V dengan langkah 20 V supaya kesan voltan bias substrat kepada kualiti filem nipis TiN dapat dikajikan. Kandungan dan struktur filem yang dihasil itu dikajikan dengan XRD, EPMA, AFM dan SEM. Didapati dari hasil tersebut bahawa filem nipis TiN berkualiti buruk mungkin dihasilkan bila voltan bias substrat itu kurang daripada -60 V.

(Titanium nitride thin film, RF planar coil inductively coupled plasma)

INTRODUCTION

Hard TiN thin films having superior tribology properties of good wear and chemical resistance [1-8] have been widely used in surface engineering, such as surface hardening of cutting tool, protective layer of hard disk, biomedical material, extremely high vacuum material, diffusion barrier layer and decorative coating[9-16]. The most commonly used systems for the coating of TiN thin film are RF or DC Reactive Sputtering systems where the electrodes are present inside the system. The coating of TiN thin film using the RF planar coil inductively coupled plasma is attempted for the first time and reported here. In particular, the effect of applied substrate bias voltage on the composition and microstructure of TiN thin film coated has been investigated.

The effect of substrate bias voltage on the morphology, composition and electrical properties of the TiN thin film had been studied by several researchers[1, 4, 17-24]. Sungren et al[18] studied the effect of substrate bias voltage on TiN thin film coating and found an increase in the non metal content in the film and a decrease in the lattice parameter with increasing bias voltage. These changes in the composition and structure were attributed to an enhancement of the surface energy due to increased ion bombardment. They also reported that the enhanced adatom mobility caused the grain size to increase for bias voltage less than –200V. At higher negative bias voltage the resputtering of the adatoms and the generation of nucleation sites become dominant and the grain size decreases.

In this work, similar effect of the substract bias voltage on the quality of the TiN thin film as observed by other workers has been observed. However, we show that with the use of the planar coil inductively coupled plasma as the sputter coater, the threshold bias voltage required for obtaining good quality TiN thin film is only -60V as compared to -200V.

EXPERIMENTAL SETUP

The deposition of the TiN thin film is performed using an RF PC ICP system operated in H-mode discharge with Ar-N_2 admixture at a pressure of 1 mbar. The deposition time is about 2 hours. The net power supplied by the 13.56MHz, 50Ω RF power generator is kept at 240W. The target is biased with negative DC voltage of 800V, while the substrate bias voltage is varied from 0V to –160V in step of 20V. The arrangement of the system is shown in Figure 1.

The substrate used in the experiments is 304 stainless steel plate with dimensions of 2.0 × 2.0 × 0.1 cm^3. It is mounted onto a rotating system by stainless steel wire so that it is rotating inside the plasma during the coating process in order to achieve uniform TiN coating. The target is also hung by a Ti wire so that it is located at the same level as the substrate as shown in Figure 1.

The composition of the film obtained is analysed by using Electron Probe Micro Analysis (EPMA). The microstructure and crystallographic structure is identified using X-Ray Diffraction (XRD) analysis. The morphology of the film is studied by using Scanning Electron Microscope (SEM) and Atomic Force Microscope (AFM).

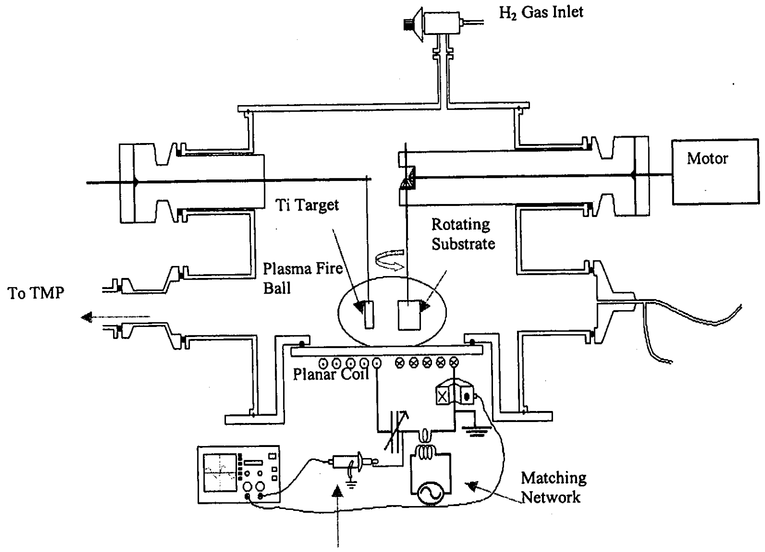

Figure 1. Schematic of the RF Planar Coil Inductively Coupled Plasma system (PC ICP).

RESULTS AND DISCUSSION

EPMA analyses of samples

A nominal TiN deposition rate of 1 µm per hour can be achieved with the present system operating at a substrate bias voltage greater than –80 V. For most of the samples analysed and presented in this paper, the process time used is 2 hours and hence the thickness of the TiN film obtained is about 2 µm. The compositions of the films determined by EPMA are shown in Figures 2 and 3. From visual observation of the appearance of the thin film obtained, the color of the film is golden for substrate bias voltage of –80V and above. The color changes to dark brown and eventually black at bias voltage of –60V and below. This is due to an increase in the atomic percentage of oxygen as shown in Figure 2. The source of oxygen is mainly due to leakage of the deposition chamber. From the graphs of Figure 2, the atomic percentage of oxygen remains at around 2% for bias voltage of –80V and above and it starts to increase exponentially for bias voltage below –80V. This indicates that the substrate bias voltage plays an important role of reducing the oxygen content of the TiN thin film. Figure 3 shows the variation of the Ti:N ratio with the substrate bias voltage. The ratio remains at around 0.64 for the substrate bias voltage range of –60V to –160V, which is found to be over-stoichiometry (TiN_x, x >1). One possible explanation of the observation of higher atomic percentage of nitrogen is due to the nitriding of the stainless steel substrate, which may occur prior to the titanium nitride coating process. Further decrease in the bias voltage gives rise to an increase of the Ti:N ratio until it reaches a maximum value of 0.92 at 0V substrate bias voltage.

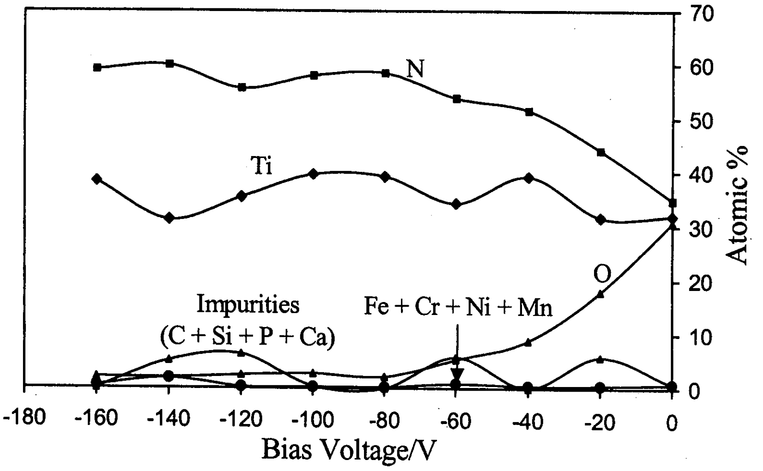

Figure 2. The effect of substrate bias voltage on the atomic percentage of TiN thin film's composition.

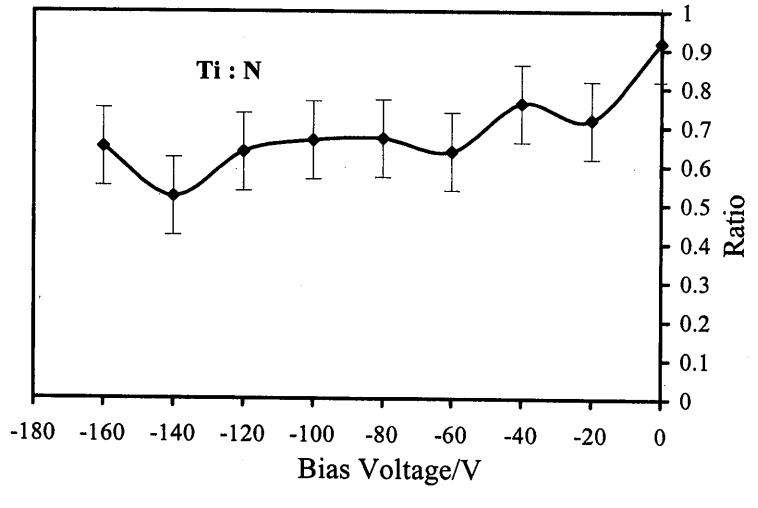

Figure 3. The effect of substrate bias voltage on the atomic percentage of titanium to nitrogen.

XRD analyses

The film obtained is confirmed to be crystallised TiN by XRD analyses (Figure 4). All the peaks observed are identified as TiN and 304 stainless steel for all substrate bias voltage except at –20V and 0V where zeta titanium nitride (Ti_4N_{3-x}) is observed. This compound contributes to the black color of the coating obtained.

There is no titanium oxy nitride ($TiO_{0.34}N_{0.74}$) or titanium oxide peak detected, contradicting the expectation from EPMA results. This may be due to their low concentrations and hence it is unable to detect their presence under XRD.

Figure 5 shows the enlarged view of the (111) diffraction peak of the XRD profiles in Figure 4. The diffraction peak becomes weaker and wider and is shifted to higher angle with decreasing substrate bias voltage, indicating some degradation of the crystal quality. The intensity or the number of diffracting crystal in the film decreases with the substrate bias voltage. It can be explained to be due to the presence of oxygen in the films as detected by EPMA, which causes some changes in the film structure and a change in film density.

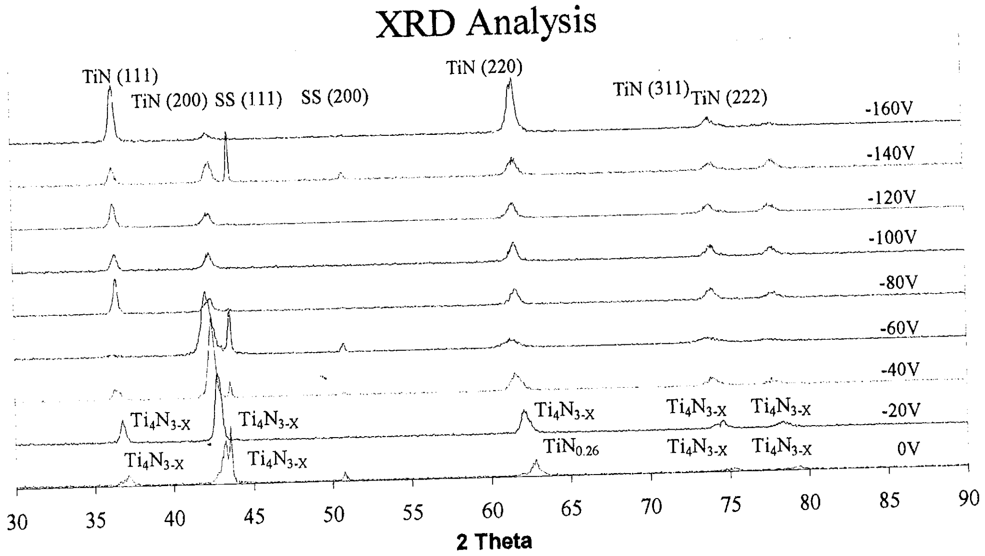

Figure 4. XRD profiles of titanium nitride films prepared at different substrate bias voltages.

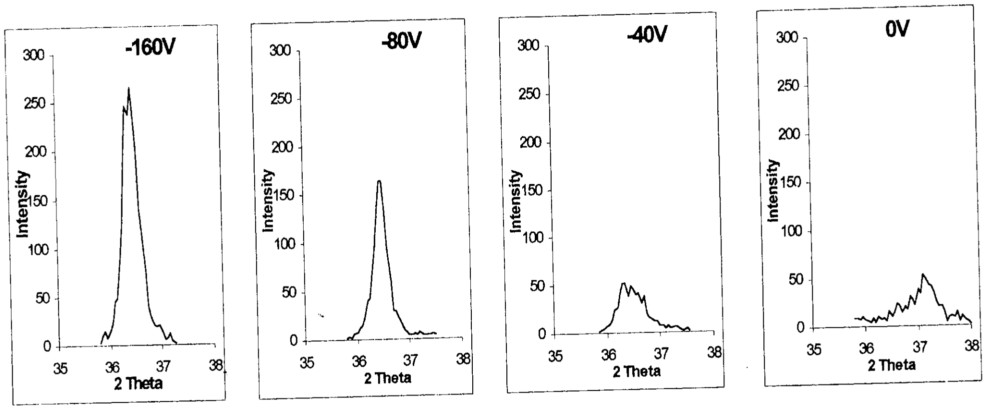

Figure 5. TiN (111) XRD peak at various substrate bias voltages.

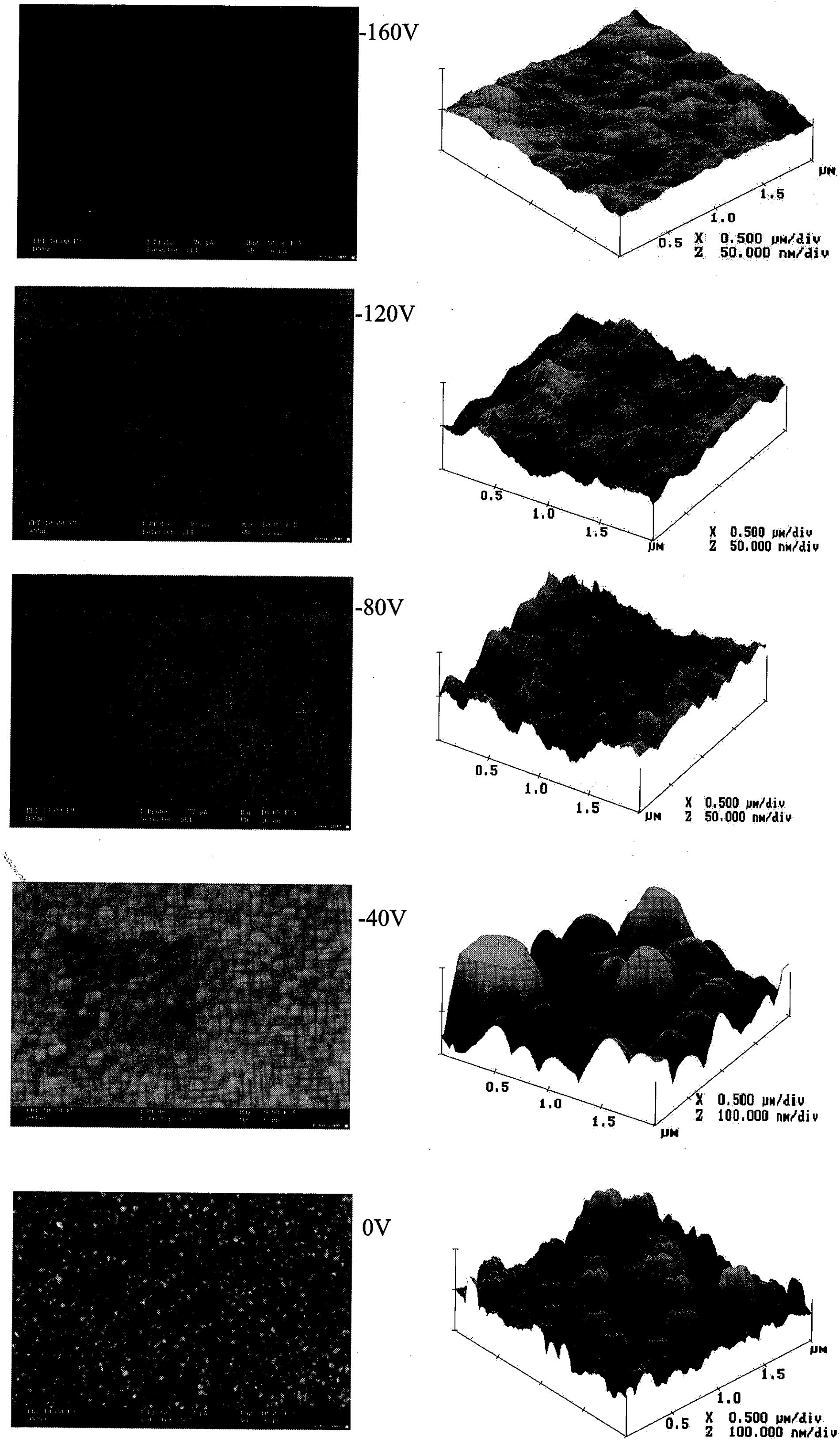

Figure 6. SEM and AFM images showing the surface morphology of TiN thin film at various substract bias

SEM and AFM analyses

The crystal structure of the film deposited on the substrate surface may undergo some changes during film deposition as a result of ion bombardment. The changes can be attributed to enhanced mobility of deposited ions or atoms on the surface of substrate [17, 24]. The crystalline structure of the film may vary according to the substrate bias voltage [8, 17-19, 23, 25]. Figure 6 shows the changes in the surface structure of the films resulted from the application of increasing bias voltage as observed by SEM and AFM. Clear columnar structure is obtained for the substrate bias voltage of –40V and below due to low and insufficient surface energy.

The film prepared at higher substrate bias voltage (above –60V) appears to have flat smooth surface. This can be explained to be due to the enhancement of surface mobility of deposited atoms as the bias voltage is increased [25]. The enhanced surface mobility destroys the columnar structure and fills the valleys between the columns resulting in a fine grain structure and hence a smooth surface. Another possible explanation is that with the increase in the substrate bias voltage, the deposited surface may be sputtered harder particularly at the columnar structure thus resulting in a flatter surface.

The deposition rate has been reported to decrease with increasing substrate bias voltage by several researchers [1,17,18]. Igasaki and Mitsuhashi [17] suggested that the decrease in the deposition rate was a consequence of the fact that the increase in substrate bias voltage resulted in flat surface and the formation of denser film. They further explained that the kinetic energy of the argon ions impinging on the film was absorbed by the deposited atoms or ions and their surface mobility was thus enhanced. This made it possible for the valleys on the surface to be filled by the migrating atoms or ions. Sundgren et al [25] explained that as the energy of the impinging ion was increased, the penetration into the lattice of the condensed film and the generation of defect would be increased. This gave rise to an increased number of preferential nucleation sites, resulting in smaller grains and a destruction of the columnar growth morphology [24].

Figure 7 shows the variation of the roughness of the film surface obtained by AFM with the substrate bias voltage. The roughness is below 10nm for substrate surface coated by using bias voltage of –60V and above. For bias voltage below –60V the surface roughness increases linearly to 49.61nm at –40V, 91.47nm at –20V and reduces slightly to 82.21nm at 0V.

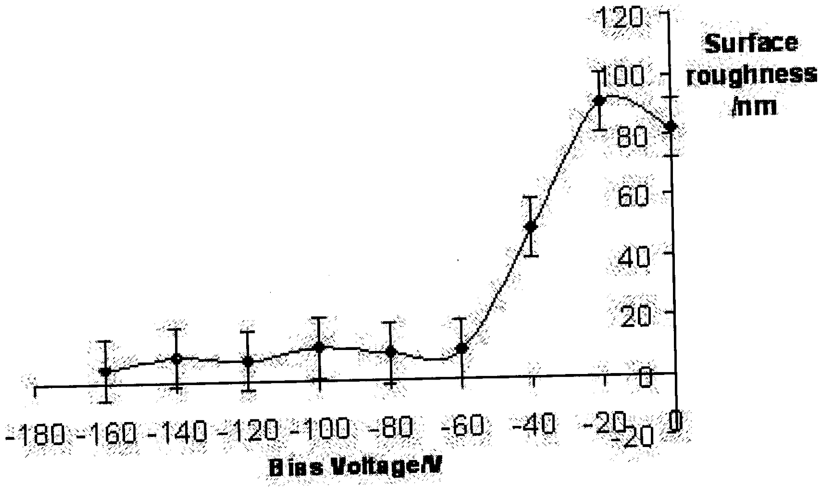

Figure 7. Variation of surface roughness of the TiN film with substrate bias voltage.

CONCLUSION

The coating of TiN thin film onto 304 stainless steel substract using the planar coil inductively coupled plasma system has been successfully demonstrated. It is observed that the substract bias voltage plays an important role in determining the quality of the thin film coated. In the present experiments, good quality crystallised TiN film can be obtained with substrate bias voltage higher than -60V. The surface smoothness is also greatly enhanced when substrate bias voltage higher than -60V is used.

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