Chiang Mai J. Sci. 2013; 40(5) : 857-864
http://it.science.cmu.ac.th/ejournal/
Contributed Paper

Reactive Gas Feeding Technique in Deposition of Titanium Nitride Film by Magnetron Sputtering

Witthawat Wongpisan*, Kanin Ruthairung, Autcharaporn Srion, Suphakan Kijamnajsuk and Panadda Sheppard
National Metal and Materials Technology Center, National Science and Technology Development Agency, Pathumthani, Thailand.
*Author for correspondence; e-mail: witthaww@mtec.or.th

Received: 18 July 2012
Accepted: 18 February 2013

ABSTRACT

The paper discusses the effect of the reactive gas feeding parameters in a magnetron sputtering unit on the microstructural development of Titanium Nitride thin film. In this work, TiN films were deposited using DC reactive magnetron sputtering at substrate temperatures of 400°C, 200°C and at room temperature. The film fabrication employed four feeding configurations for the N_2 reactive gas. The nitrogen gas was fed through a distribution ring positioned above the Ti target into the plasma flux at 4 different distances from the target resulting in different gas distribution patterns and also different levels of gas warming prior to it entering the sputtering chamber. The effect of the plasma warming of the reactive gas caused the sputtering reaction, and hence the phase formation of the TiN, to alter. XRD and SEM were utilized in the microstructural study of the TiN films. It was found that for type D N_2 feeding configuration, where N_2 enters the deposition chamber at the middle of chamber, the lattice parameter of TiN film is not affected by the substrate temperature ranging from RT to 400°C. In practice, this means that altering the gas feeding technique can help to reduce the variation in the film structure caused by an uneven distribution in the substrate temperature.

Keywords: titanium nitride, reactive sputtering, gas feeding technique

1. INTRODUCTION

Titanium nitride (TiN) films deposited using PVD (physical vapor deposition) techniques are useful material for surface engineering because of properties such as high hardness, good corrosion resistance at room temperature and elevated temperatures, good thermal stability, low friction coefficient, good appearance and high electrical conductivity [1-5]. They have been successfully employed as hard coatings, diffusion barriers, optical coatings and anti-oxidation coatings.

Three main sputtering parameters affect the film structure, and consequently the properties of titanium nitride thin films. These are substrate temperature, range of nitrogen partial pressure and bias voltage.

The formation of TiN film depends on the supply of reactant N atoms from the plasma. N_2 gas consists of diatomic molecules. These molecules need to dissociate into N atoms before reacting with Ti atoms. This dissociation of N_2 molecules and the subsequent reaction to form TiN requires plasma energy. However, the diatomic N_2 molecules have internal rotational and vibrational electronic states that consume energy from the plasma [6].

In this paper, titanium nitride films prepared by DC pulse reactive magnetron sputtering using different nitrogen feeding configurations were investigated using X-ray diffractometry (XRD) and scanning electron microscopy (SEM). The work focused on the effect of nitrogen feeding configurations on the microstructural properties of the TiN films.

2. EXPERIMENTAL METHODS

TiN thin films were deposited on silicon (100) substrates using different nitrogen feeding configurations and substrate temperatures (RT, 200°C and 400°C) using pulsed direct current (DC) magnetron sputtering. Recently, pulsed sputtering has been developed for the deposition of highly adherent, uniform and dense coatings of nitrides and oxides. Si (100) is the substrate. The schematic diagram of a custom built magnetron sputtering system used in the present study is given in Figure 1.

The sputtering was carried out in a stainless steel chamber of 40 cm diameter and 60 cm depth. A 99.995% Ti disc of 50.8 mm. (2") diameter and 3mm. thickness was used as a sputtering target. The deposition chamber was evacuated to a base pressure of 5×10^{-6} mbar using a pumping system consisting of rotary and turbomolecular

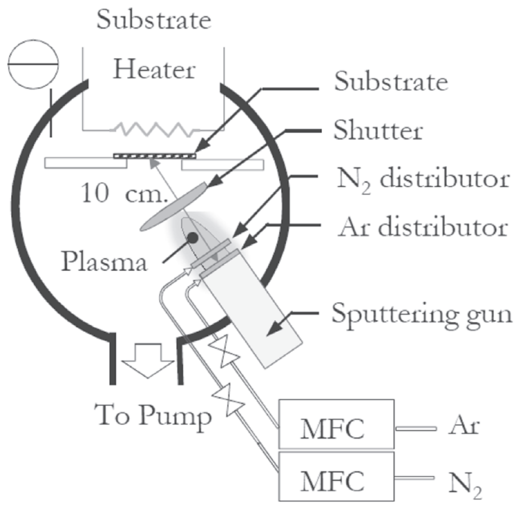


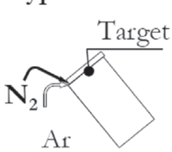
Figure 1. Magnetron sputtering setup.

pumps. Silicon substrates (size of 20mm×15mm×0.5mm) were first cleaned using soap solution and then ultrasonically cleaned in acetone for 10 min and dried before being placed in the deposition chamber. The flow rates of Ar (99.99%) and N_2 (99.999%) were controlled by MKS flow controllers. A Pinnacle Plus bipolar pulsed DC power supply (AE, USA) was used as the electrical power source for the thin film deposition. The substrate temperature was set at RT, 200°C and 400°C using two halogen lamp (1,000W) heaters with a digital programmable temperature controller. The substrate holder temperature was monitored using a chromel–alumel thermocouple. The thermocouple is placed in the rear side of substrate holder to avoid its contact with the plasma. The substrates were kept at each desired temperature for 30 minute to establish a homogeneous temperature distribution before each deposition. Substrate bias at -70 V was found to be best performing in a scratch adhesion test. Therefore a substrate bias of -70V was applied to the substrates during the deposition. Pre-sputtering of the Ti target was performed for 5 min before each deposition. The deposition conditions are given in Table 1.

Table 1. Deposition Parameters for TiN.

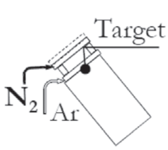
Objects	Specification
Target	Ti pure (99.995%)
Substrate	Si wafer
Target to substrate	100 mm.
Base pressure	5 x 10^{-6} mbar
Operating pressure	3 x 10^{-3} mbar
Argon	4 sccm.
Nitrogen	1 sccm.
Power	DC pulse 225W, f=100 kHz, T=2 μs
Bias	-70 V
Substrate temp.	Room temperature, 200°C, 400°C

Type A



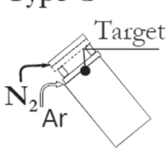
Ar and **N_2** was fed through gas distributor in front of the target

Type B



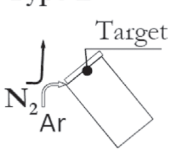
Ar was fed through gas distributor in front of the target
N_2 was fed through gas distributor at 30 mm. above the target

Type C



Ar was fed through gas distributor in front of the target
N_2 was fed through gas distributor at 50 mm. above the target

Type D



Ar was fed through gas distributor in front of the target
N_2 was fed into the middle of the vacuum chamber

Figure 2. Nitrogen feeding configurations.

There are 4 types of N_2 feeding configuration used in this work. They are explained using diagram Figure 2.

The crystallographic structure of the deposited films was analyzed by XRD in θ–2θ configuration. The diffractometer used the Cu Kα line at 1.5406 nm as the X-ray source. Scans were made in grazing angle mode with the incident radiation impinging the sample with an angle of approximately 3° with respect to the specimen surface. The average lattice parameter is analyzed with MDI Jade 6.0 software.

3. RESULTS AND DISCUSSION

3.1 Crystal Structure

TiN films deposited by various PVD methods generally have three kinds of preferred orientation, i.e. (111), (200) and (220) [6]. Figure 3-6 shown XRD patterns of the films in this work prepared at substrate temperature of room temperature, 200°C and 400°C by N_2 gas-feeding type A, B, C and D respectively. All of the diffraction peaks correspond to FCC TiN (JCPDS card no: 38-1420).

Figure 3 shows the XRD patterns of the films prepared at different substrate

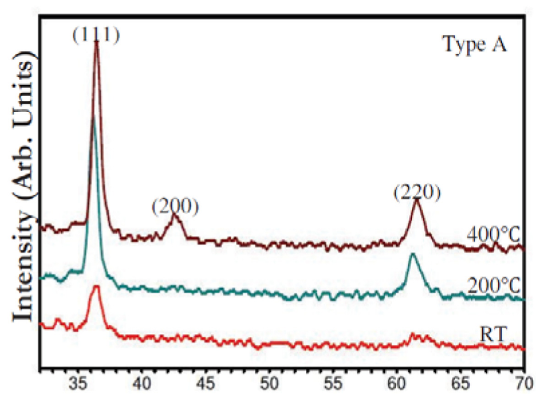


Figure 3. XRD pattern of the films prepared by N_2 gas-feeding type A at room temperature, 200°C and 400°C.

temperatures by using N_2 gas-feeding type A. The TiN (111) and (220) peak intensities increase with increasing substrate temperature. The TiN (200) appears in the film formed at the substrate temperature of 400°C.

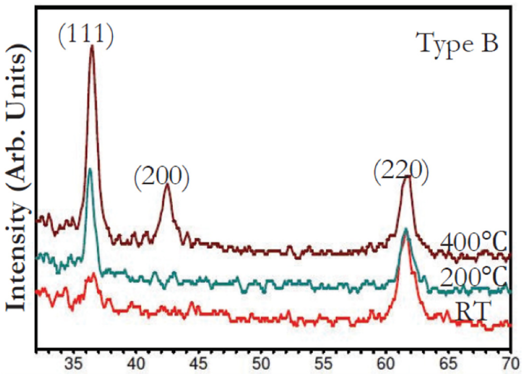


Figure 4. XRD pattern of the films prepared by N_2 gas-feeding type B at room temperature, 200°C and 400°C.

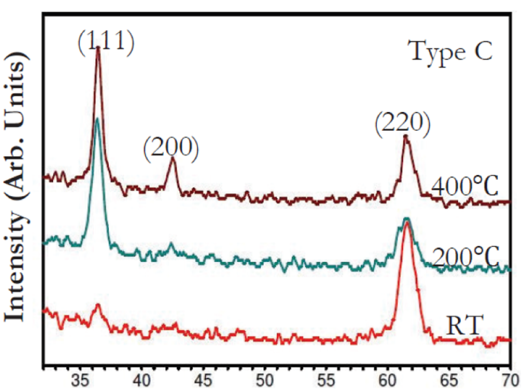


Figure 5. XRD pattern of the films prepared by N_2 gas-feeding type C at room temperature, 200°C and 400°C.

Figure 4 and 5 show the XRD patterns of the films prepared at different substrate temperatures using N_2 gas-feeding type B and C. This configuration of gas feeding fed N_2 into the plasma above the surface of the target. The intensity of the (220) peak is higher than that of the (111) peak at room temperature. The (220) peak and (111) peak change with increase in substrate temperature. The relative intensity of the (111) peak increases whilst that of the (200) peak is decreased. The TiN (200) peak appears at a substrate temperature of 400°C

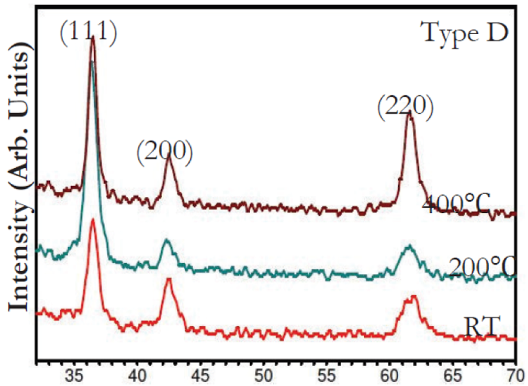


Figure 6. XRD pattern of the films prepared by N_2 gas-feeding type D at room temperature, 200°C and 400°C.

In N_2 gas-feeding type D, the TiN three strong peaks, (111), (200) and (220), appear at room temperature. Intensities of each peak increased with increasing substrate temperature.

The preference in the orientation of a film is due to its lowest overall energy, which depends on competition between the surface energy, the strain energy and the bombardment energy of different lattice planes. The (200) plane has the lowest surface energy, the (111) plane has the lowest strain energy and the (220) has the lowest bombardment energy [7,8].

Each gas flow configuration affects the preferred orientation of titanium nitride thin film differently especially at room temperature. Figure 7 shows the XRD pattern of the films prepared at room temperature by the four types of N_2 gas-feeding configuration.

At room temperature, the (220) peak achieved using the gas feeding configurations type B and C dominates due to the effect of bombardment energy. At the N_2

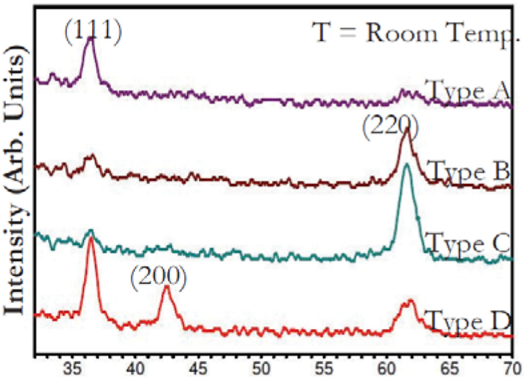


Figure 7. XRD pattern of the films prepared by the different N_2 gas-feeding methods at room temperature.

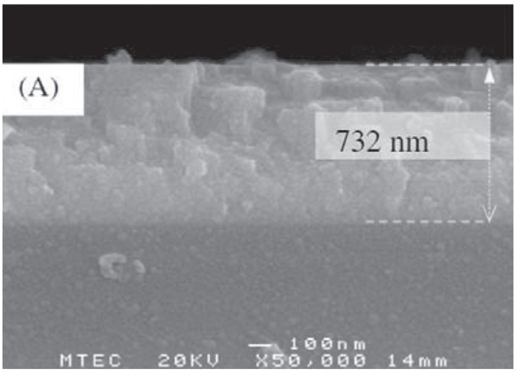


Figure 8. SEM micrographs of TiN cross sections prepared using N_2 gas-feeding configuration type A at 400°C.

distributor outlet in the plasma, N_2 dissociate into N atoms. High energy of N moves near the substrate and some N acts as bombardment atoms. This XRD pattern is similar to a TiN*x* thin film prepared using high bias voltage reported in other literature [9].

3.2 Microstructural Studies

The cross-sectional observations from Figure 8,9 and 11 indicate that the films have columnar structures. However, the columnar structures exhibited some differences in thickness and lattice parameter as shown in Table 2 and Table 3, respectively.

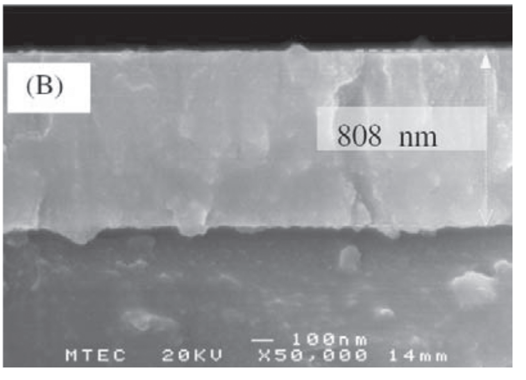


Figure 9. SEM micrographs of TiN cross sections prepared using N_2 gas-feeding configuration type B at 400°C.

Table 2. The film thickness and deposition rate in samples prepared using different N_2 feeding configurations.

N_2 feeding	Film thickness (nm)	Deposition rate (nm/s)
Type A	732	0.305
Type B	808	0.337
Type C	757	0.315
Type D	819	0.341

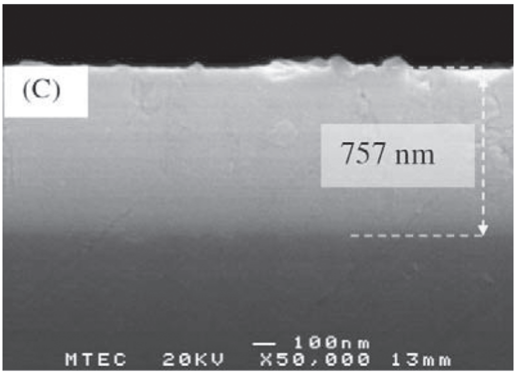


Figure 10. SEM micrographs of TiN cross sections prepared using N_2 gas-feeding configuration type C at 400°C.

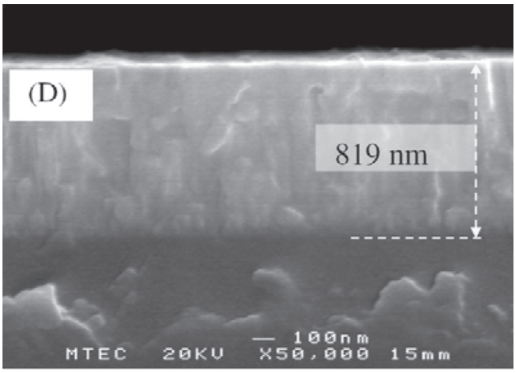


Figure 11. SEM micrographs of TiN cross sections prepared using N_2 gas-feeding configuration type D at 400°C.

Table 3. The average lattice parameter in samples prepared using different N_2 feeding configurations.

N_2 feeding Config.	Substrate temperature (°C)	Average lattice parameter (nm)
Type A	RT	0.42776 ± 0.00301
	200	0.43057 ± 0.00309
	400	0.42610 ± 0.00098
Type B	RT	0.42425 ± 0.00195
	200	0.42727 ± 0.00127
	400	0.42508 ± 0.00199
Type C	RT	0.42646 ± 0.00099
	200	0.42787 ± 0.00037
	400	0.42628 ± 0.00187
Type D	RT	0.42606 ± 0.00099
	200	0.42548 ± 0.00040
	400	0.42605 ± 0.00043

The microstructure of film shown in Figure 10 is very fine, dense and well-bonded to the substrate. This indicates that at suitable plasma energy conditions and deposition rate coatings may be produced free of open pores or pin-holes, which often appear in TiN film produced by PVD techniques.

The factors that reduce sputtering yield of the target are: (i) TiN compound formation on the target surface and (ii) lower effective bombardment ion in plasma or lower relative concentration of Ar. The main reason for lowest deposition rate in type A sample is the forming a compound of TiN. Compound formation will also take place at the surface of the sputtering target and the sputtering yield of the TiN is substantially lower than the sputtering yield of the Ti target material. The cause of the highest deposition rate in type D is due to the lowest amount of compound formation on the target and the highest relative concentration of Ar in the sputtering zone.

For this experiment, the lattice parameters calculated for each specimen are shown in Figure 12. The lattice parameters change with a change in the substrate temperature especially in type A and B N_2 feeding configurations, respective. But for type D feeding configuration, the lattice parameter does not alter significantly.

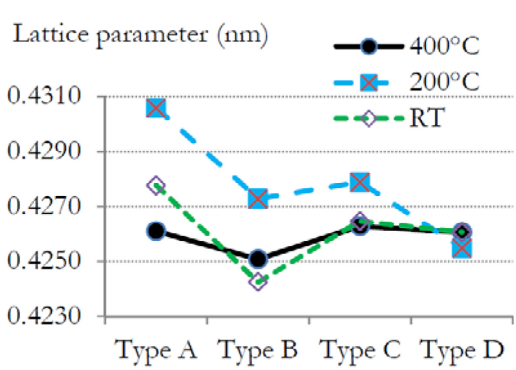


Figure 12. Lattice parameter of titanium nitride in different type N_2 feeding configurations.

The reasons that explain the fluctuation of lattice parameter are:

(i) The effect of different nitrogen feeding positions on the plasma energy, especially for a small size sputtering target. Different plasma energy can be an additional source of substrate heating, and this can make a difference to the effects of the substrate temperature.

(ii) Different nitrogen feeding positions affect N/Ti ratio since sputtering rate of the titanium atom is changed and the nitrogen has different time to incorporate into the film, respectively. In addition, some nitrogen feeding positions could enhance the mobility of nitrogen atoms on the growing film surface. Previous literature has also shown that the lattice parameter increases with increasing (N/Ti) ratio in the deposition of TiN film using sputtering techniques [7,10].

In large-scale production using a large chamber and many small sputtering targets, an even temperature distribution of the substrates is a factor that can be difficult to control. In this case, the type D N_2 feeding configuration can be used in order to minimize the effect of the temperature fluctuation, thus reducing the changing of lattice parameter of TiN related to stress in the thin film.

4. CONCLUSIONS

1. N_2 gas feeding configuration affects the preferred orientation and the lattice parameter of TiN thin film deposited at low temperature.

2. For type A, B and C N_2 gas feeding configurations, the change in the temperature of the substrate affects the lattice parameter of the deposited TiN film.

3. For type D N_2 gas feeding configuration, the lattice parameter is not affected by the substrate temperature ranging from RT to 400°C.

5. REFERENCES

[1] Fanga Q. and Zhang J.Y., Nanoporous TiN thin films deposited by reactive sputtering method, *Int. J. Inorg. Mater.*, 2001; **3**: 1193-1196.

[2] Makinoa Y., Moria, Miyakea S., Saitob K. and Asami K., Characterization of Zr–Al–N films synthesized by a magnetron sputtering method, *Surf. Coat. Tech.,* 2005; **193**: 219-222.

[3] Carrascoa C.A. and Vergara V., The relationship between residual stress and process parameters in TiN coatings on copper alloy substrates, *Mater. Charact.,* 2002; **48**: 81-88.

[4] Kraft O., Rattunde O., Rusu A., and Haberland H., Thin films from fast clusters: golden TiN layers on a room temperature substrate, *Surf. Coat. Tech.*, 2002; **158-159**: 131-135.

[5] Vasu K., Krishn M.G. and Padmanabhan K.A., Substrate-temperature dependent structure and composition variations in RF magnetron sputtered titanium nitride thin films, *Appl. Surf. Sci.*, 2011; **257**: 3069-3074.

[6] Arshi N., Lu J., Joo Y.K., Lee C.G., Yoon J.H. and Ahmed F., Study on structural, morphological and electrical properties of sputtered titanium nitride films under different argon gas flow, *Mater. Chem. Phys.*, 2012; **134:** 839-844.

[7] Pelleg J., Zevin L.Z. and Lungo S., Reactive-sputter-deposited TiN Films on glass substrates, *Thin Solid Films*, 1991; **197**: 117-128.

[8] Zhao J.P., Wang X., Chen Z.Y., Yang S.Q., Shi T.S. and Liu X.H., Evolution of the texture of TiN films prepared by filtered arc deposition, *J. Phys. D: Appl. Phys*. 1997; **30**: 5-12.

[9] Chen Jingsheng,Yu Guoqing b., Shi Ying b., Pan Haochang b. and Zhu Dezhang b., Investigation of titanium nitride films deposited at room temperature by energetic cluster impact, *Thin Solid Films*, 2009; **517**: 200-204.

[10] Kang J.H. and Kim K.J., Structural, optical, and electronic properties of cubic TiN_x compounds, *J. Appl. Phys*., 1999; **86**: 346-350.