Materials properties of nanostructured titanium nitride thin films synthesised by DC reactive magnetron sputtering

B. Subramanian* and M. Jayachandran

Titanium nitride (TiN) films were deposited on different substrates by reactive magnetron sputtering. X-ray diffraction analysis showed a preferential orientation along (111) and (200) for the sputtered TiN films on Si wafer. These films had a maximum reflectance of about 60% at 850 nm and local minimum reflectance at a wavelength of 480 nm. The good optical quality of the film was confirmed from the room temperature photoluminescence spectrum. The electrical resistivity was found to be 20 μΩ cm. Scanning electron microscopy analysis indicated that the coatings are very regular with dense columnar structure. Surface topography was examined by atomic force microscopy. Laser Raman studies showed characteristic peaks were observed at 315 and 560 cm^{-1}.

Keywords: Titanium nitride films, Magnetron sputtering, PVD

Introduction

Titanium nitride (TiN) is currently one of the most widely used hard coatings in industrial applications. The deposition of TiN coatings on high speed tools by physical vapour deposition (PVD) methods results in a substantial increase in tool life, but it has also been shown that the performance of cutting tool inserts as well as the basic physical properties may depend on a number of process conditions.[1–3]

These coatings are increasingly being used in various applications such as in the tool industry, for machine parts, microelectronics, artificial jewellery, diffusion barriers and electrodes, because of their excellent properties such as extreme hardness, low electrical resistivity, high wear, excellent corrosion resistance and high thermal stability.[4,5] It is common to use techniques such as PVD,[6–8] plasma assisted chemical vapour deposition (PACVD),[9,10] and hollow cathodic ionic plating.[11] Chemical vapour deposition is a high temperature process ($\sim$1000°C) in which a gaseous metal precursor, usually titanium tetrachloride, is reacted with hydrogen, nitrogen and ammonia to form TiN. The high temperatures of the reaction and the subsequent need to heat treat CVD coated steel tooling to obtain the necessary substrate hardness cause some distortion, whereas PVD is a low temperature coating process carried out at less than 500°C. This temperature is below the tempering temperature of high speed steels; consequently PVD coating normally produces insignificant distortion and can be applied to high tolerance tooling.[12]

ECMS Division, Central Electrochemical Research Institute, Karaikudi 630 006, India

*Corresponding author, email tspsenthil@yahoo.com

Among the TiN coatings produced by PVD, films deposited by the sputtering method have better properties and thermal stability.[13]

In this investigation, the film was deposited on glass and Si substrates using the reactive DC magnetron sputtering process and the material's structural, microstructure, hardness and optical properties were characterised.

Experimental

The layers of TiN were deposited on well cleaned substrates glass, and Si wafer, with a DC magnetron sputter deposition unit HINDHI VAC. The base vacuum of the chamber was about 1×10^{-4} nm^{-2} and the substrate temperature was kept at 400°C. High purity argon was fed into the vacuum chamber for the plasma generation. The substrates were etched for 15 min at a DC power of 50 W and argon pressure of 2×10^{-1} nm^{-2} (1·33 Pa) A high purity (>99·999%) titanium target of 5 cm diameter was used as the cathode (TiTan, India). The deposition parameters for TiN reactive sputtering are summarised in Table 1.

The crystallographic structure of the deposited films was analysed with a diffractometer (X'pert pro, PANalytical) using the Cu K_α line. The microstructure of the coatings was examined using a Hitachi S 3000H scanning electron microscope and a molecular imaging atomic force microscope (AFM). The microhardness of the films on mild steel was evaluated by using a DM-400 microhardness tester (LECO) with Vickers indenters. A dwell time of 15 s and loads of 25 and 5 g were used for the measurement. The Raman spectroscopy measurements used an excitation wavelength of 632·8 nm. The data were collected with a 10 s data point acquisition time in the spectral region of 200–600 cm^{-1}. The

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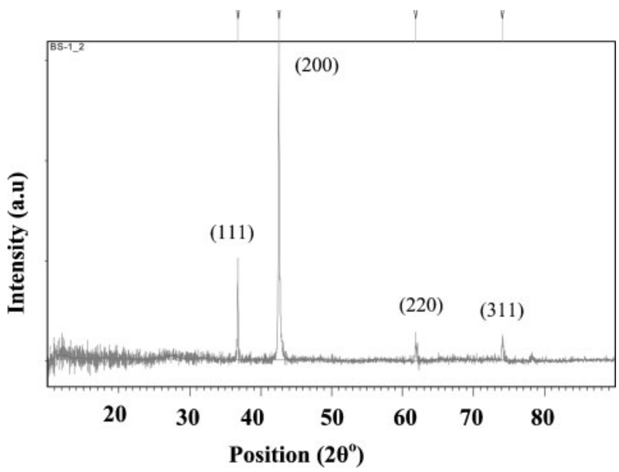


1 X-ray diffractogram of sputtered TiN film on Si wafer

photoluminescence (PL) measurements were made using a Cary Eclipse fluorescence spectrophotometer (VARIAN) employing a PbS photodetector and a 150 W Xe arc discharge lamp as the excitation light source.

Results and discussion

Structure and microhardness

The X-ray diffraction (XRD) pattern obtained for the reactive sputter deposited titanium nitride films on Si wafer with the Ar/N_2 ratio of 50 : 50 (Fig. 1) indicated a successful formation of TiN having a cubic crystal system with the lattice parameter of a=4·231 nm and belonging to a space group of Fm3m.

The observed interplanar distances 'd' (*hkl*) and expected values from phases described in JCPDS are given in Table 2.

The data show that the observed 'd' values are in very good agreement with the standard 'd' values. The peaks at 36·780 and 42·539 correspond to diffraction along (111) and (200) plane and these peaks agree with the standard values of TiN.

The grain size of these coatings could be determined by the equation

$$D = \frac{0{\cdot}94\lambda}{\beta \cos\theta} \qquad (1)$$

where D is the grain size, β is the full width at half maximum (FWHM) of the diffraction peak, λ is the wavelength of the incidental Cu K_α X-ray (1·514 Å) and θ is the diffraction angle. The grain size of the film was found to be $\sim$70 nm. Such a small grain size contributes to the smooth surface morphology and also may have a beneficial effect on the improvement of the microhardness of the coating.[14] In addition, the grain size reduction to the nanometer range results in considerable improvement in their resistance to localised corrosion.[15]

The microstrain ε was calculated from the slope of the $\beta\cos\theta$ versus $\sin\theta$ plot using the relation[16]

$$\beta = (\lambda / D\cos\theta) - \varepsilon\tan\theta \qquad (2)$$

The dislocation density δ,[16] defined as the length of the dislocation per unit volume of the crystal, was calculated from the formula

$$\delta = 15\varepsilon / aD \qquad (3)$$

The value of microstrain ε and the dislocation density δ of the as grown film were found to be $5{\cdot}065 \times 10^{-4}$ and $2{\cdot}0269 \times 10^{14}$ line m^{-2}.

During sputtering of TiN, argon ions in the plasma are attracted to the Ti target at high speeds and knock the atoms out through a momentum exchange process. Sputtered Ti atoms with relatively high momentum react with nitrogen gas, reach the substrate surface and get adsorbed on it. Depending on the adsorbing, the substrate temperature and the crystal structure of the adsorbing surface, TiN films of various structures would grow. Internal residual stresses could be built up in the deposited films due to lattice mismatch between the film structure and the substrate surface.

The surface microhardness values of TiN films on glass having the thickness value of 2·2 μm increases from $\sim$820 to $\sim$1750 HV with the decrease in applied load from 0·25 to 0·05 N.

The low hardness observed at the higher load may well be due to excessive penetration of coating and subsequent influence of substrate.

Microstructure analyses

SEM analysis

An overall microstructure of the film prepared with Ar/N_2 ratio of 50 : 50 is shown in Fig. 2.

The TiN coating has very smooth and dense columnar structure. A characteristic of the TiN coating is the presence of micro defects such as pinholes and droplets. The porosity of TiN coating is strictly related to the thickness and thick coatings are involved in anticorrosive applications, because the initiation and continuation of corrosion at the surface of underlying metal strongly depends on the barrier efficiency of the coating against the attack of corrosive environment.

AFM analysis

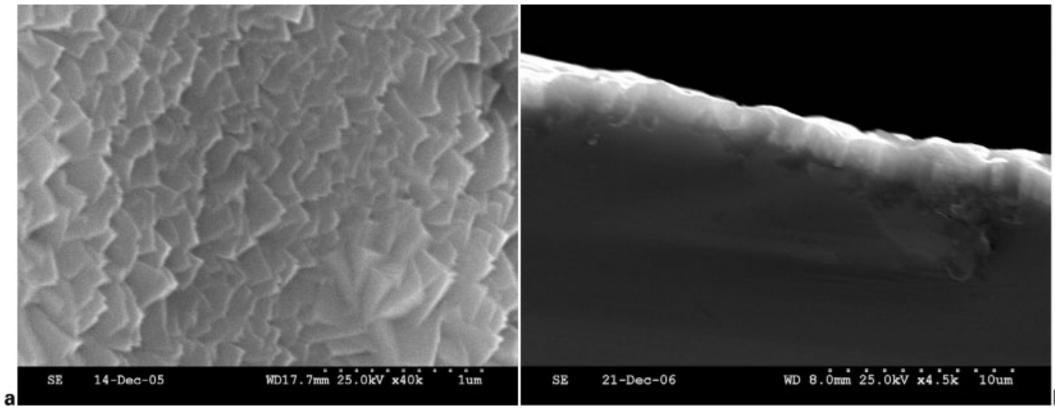
The surface topography of these TiN thin films was studied using AFM. The basic study comprised a three-dimensional representation for a scanned area of 5 × 5 μm and the section analysis method that allows

Table 1 Deposition parameters for TiN DC reactive magnetron sputtering

Objects	Specification
Target	Ti (99·999%)
Substrate	Si wafer
Target to substrate distance	50 mm
Ultimate vacuum	1×10^{-4} N m^{-2}
Operating vacuum	2×10^{-1} N m^{-2}
Sputtering gas (Ar/N_2)	50 : 50
Power	300 W
Substrate temperature 400°C	

Table 2 Comparison of d – values (JCPDS file no. 03-065-5774)

Pos. [2θ°]	d-spacing, Å	d-standard	d (*hkl*)
36·7808	2·441	2·448	111
42·5393	2·123	2·120	200
61·8643	1·498	1·499	220
74·0678	1·278	1·278	311



a plane view; *b* cross-sectional view
2 Sputtered titanium nitride thin film on Si wafer

the determination of the profile of the samples with a line drawn over the surface, which is shown in Fig. 3.

From the horizontal cross-section analysis, the globule size was estimated to be in the range of minimum 40 to maximum 80 nm. Some shallow valleys of ~10 nm depth were observed in sputtered Ni coatings.

Roughness analysis of the coating was carried out and the value of the mean roughness R_a was calculated as the deviations in height from the profile mean value[17]

$$R_a = \frac{1}{N}\sum_{i=1}^{N} |Z_i - Z| \tag{4}$$

where Z is defined as the sum of all height values divided by the number of data points (N) in the profile. The roughness value, estimated from these images using equation (4) was 12 nm which is similar to the value of roughness reported by Mei *et al.*[18]

Optical reflectance and laser Raman studies

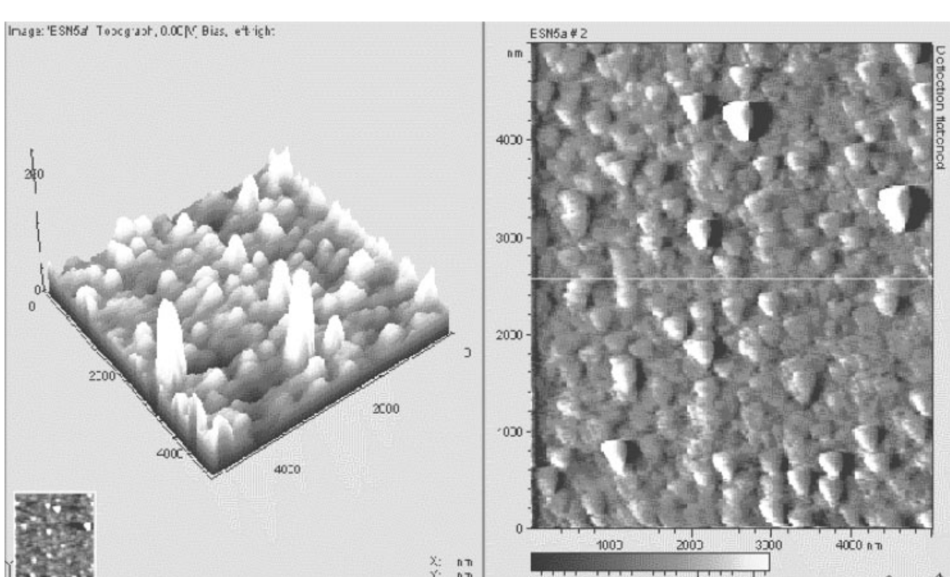
The reflectance of the TiN coatings was measured with a double beam spectrophotometer. A sputtered aluminium surface was used for the standard mirror. The reflectance measured was the so called relative reflectance. A typical reflectance spectrum taken for the wavelength region of 200–2000 nm of a titanium nitride film on low carbon steel substrate is shown in Fig. 4.

These films had a maximum reflectance of ~60% at 850 nm which is in good agreement with the value of 65% reported for TiN films produced by unfiltered arc sources and 80% for the films prepared by filtered arc evaporation.[19] The local minimum reflectance around a wavelength of 480 nm was observed which is similar to observation made by other researchers.[20]

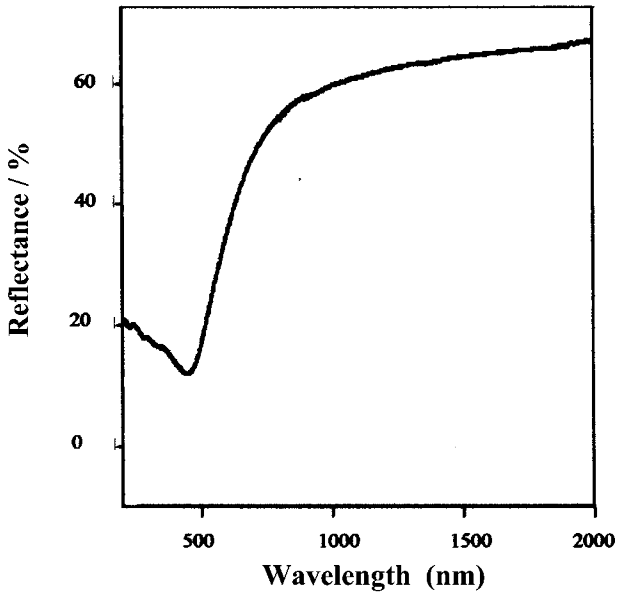
A room temperature PL spectrum of the titanium nitride film taken for the excitation wavelength of 391 nm is shown in Fig. 5. It is interesting to note that emissions appearing at 482 and 531 nm are only in the visible region. This implies that the titanium nitride films prepared by DC reactive magnetron sputtering are of good optical quality.

The characteristic peaks at 315 and 560 cm^{-1}, related to longitudinal acoustic and transverse optical modes of TiN respectively, were observed in the Raman spectra of TiN films (Fig. 6) prepared by reactive sputtering process. This is in good agreement with the reported values for TiN films prepared by cathodic vacuum arc technique.[21]

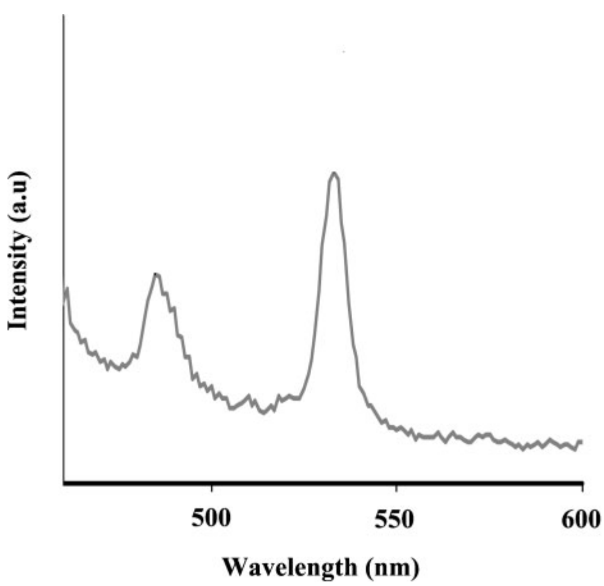
Electrical resistivity measurements were performed using the four probe method at room temperature. The



3 Image (AFM) showing topography of TiN film on Si wafer



4 Reflectance of titanium nitride film deposited on glass at an Ar/N_2 ratio of 50 : 50

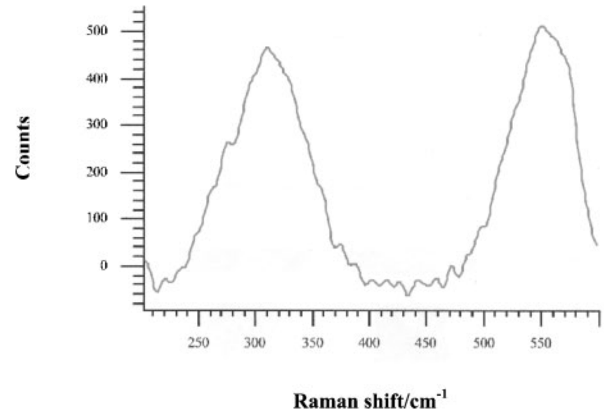


5 Photoluminescence spectrum obtained for magnetron sputtered titanium nitride film on glass substrate

value was found to be 20 μΩ cm for the DC magnetron sputtered TiN on glass substrate.

Conclusions

Titanium nitride (TiN) films were successfully grown by reactive DC magnetron sputtering on Si wafer substrates. The structural analysis using XRD reveals that the films are polycrystalline in nature possessing cubic structure and having the lattice parameter a= 4·2314 nm. A dense columnar structure was observed from SEM analysis. These films had a maximum reflectance of ∼60% at 850 nm and the local minimum



6 Laser Raman spectrum obtained for titanium nitride film on Si wafer

reflectance at a wavelength of 480 nm. Good optical quality of these films was observed from PL studies. The characteristic Raman peaks were observed for the DC magnetron sputtered TiN films.

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