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Studies on Reactive Magnetron Sputtered Tin Thin Films

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ABSTRACT

Titanium Nitride (TiN) is an interstitial nitride with remarkable hardness, adhesion and toughness making it ideal for thin film applications. In this work the effect of substrate bias and substrate temperature on crystallinity, morphology, hydrophobicity and adhesion of TiN films has been studied. The films were deposited by dc magnetron sputtering on well-cleaned substrates of glass, silicon (100) and stainless steel (AISISS304). The deposited films were analysed using X-ray Diffraction (XRD), Field Emission Scanning Electron Microscope (FE-SEM), contact angle measurement and scratch testing. Grains with globular and columnar morphology were formed and the films were predominantly hydrophilic in nature. In the absence of substrate bias amorphous films were formed and (111) and (200) planes appeared with substrate heating and bias. Improved adhesion was observed at lower bias and higher temperatures.

Key words: Magnetron sputtering, titanium nitride, crystallinity, wettability, adhesion

INTRODUCTION

TiN exhibits a combination of ceramic and metal-like properties viz., high hardness and strength, high electrical and thermal conductivity. In addition, chemical inertness, wear and corrosion resistance are some of the other properties of TiN that enable it to be used for a wide range of applications (Pierson, 1996. William Andrew Inc.). This combination of remarkable properties makes it ideal for coating high speed cutting tools to improve the tool's life (Scholl, 1997), as biocompatible coating on implants (Karagkiozaki *et al*., 2009), for protective and decorative purposes (Straumal *et al*., 2000). TiN coatings have also been used to improve conductivity of electrodes for electro-analytical (Kirchner *et al*., 2007) applications.

Thin films of TiN are deposited by both PVD (Roquiny *et al*., 1999; Mahieu *et al*., 2006) and CVD (Park *et al*., 2003) techniques. CVD techniques involve use of toxic precursors and limit their use for biological applications. On the other hand sputtering has the advantage of having good deposition rates and also a number of variable parameters which can be controlled to tailor the film properties (Ohring, 2001).

The effect of substrate bias and substrate temperature on the orientation and properties of the film has been studied. By keeping the other deposition parameters constant, substrate bias was varied from floating potential to -200 V and the substrate temperature was varied between room temperature to 200°C. By varying these two parameters the objective was to compare their influence on the film and identify an optimal deposition condition. The aim was to prepare a film

with good adhesion and hydrophilic nature which will enable it to be used for biological applications.

MATERIALS AND METHODS

In the present study the TiN films were deposited on to thoroughly cleaned silicon (100) and stainless steel (AISISS304) substrates using reactive dc magnetron sputtering technique. The substrates were thoroughly cleaned before loading in to the deposition chamber. Figure 1 shows block diagram of dc magnetron sputtering system. The deposition chamber was evacuated to a pressure better than 1×10^{-5} mbar using the combination of rotary pump and oil diffusion pump. Pure titanium disc (2 inch dia; 3.18 mm thick; 99.99% purity) was used as the target. Before the deposition, the Ti target was sputter cleaned for 10 min in order to avoid impurities. The flow of argon (99.9999%) and nitrogen (99.999%) was controlled by mass flow controllers. The cathode power and the deposition time were maintained as 120 W and 15 min, respectively, while the substrate temperature and the substrate bias voltage were varied systematically to obtain TiN films with different properties. The deposition parameters of the prepared samples have been given in Table 1.

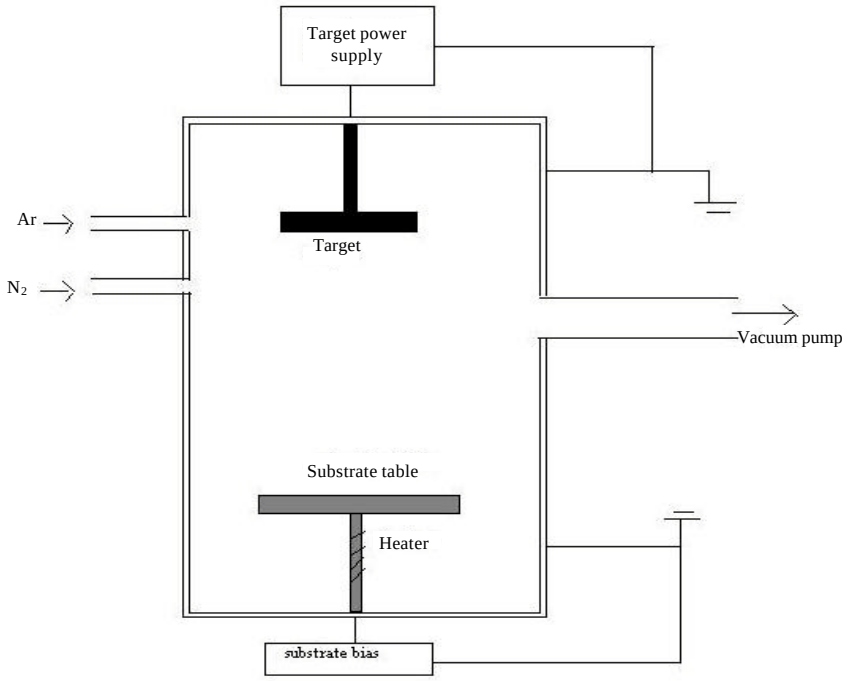

Fig. 1: Block diagram of dc magnetron sputtering system

Table 1: Deposition parameters of the prepared samples

Sample code	Ar pressure (mbar)	N_2 pressure (mbar)	Substrate temperature (°C)	Substrate bias (V)
A	3.5×10^{-3}	3.7×10^{-3}	room temperature	100
B	3.3×10^{-3}	3.8×10^{-3}	100	100
C	5.5×10^{-3}	5.6×10^{-3}	200	100
D	4.0×10^{-3}	4.3×10^{-3}	200	FP
E	3.8×10^{-3}	4.0×10^{-3}	200	200

The crystallinity of the films was studied using X-ray diffraction (XRD) (Burker D8 Focus X-ray Diffractometer). CuKα (λ = 0.154 nm) was the radiation source and scans were performed from 2θ = 30-60°. The surface morphology was analysed using field emission-scanning electron microscopy (FE-SEM: JEOL JSM-6701 F). The hydrophobicity of the TiN films was measured by the sessile drop method (Ramé-Hart 250 F1) with a standard goniometer to measure the contact angle of the water droplet on the film based on Young's equation. Scratch resistance of the films were measured by using a commercial scratch tester (CSM Instruments, Switzerland) coupled with a Rockwell spherical diamond indenter with a tip radius of 200 mm. Scratch tests were performed using progressive loads from 1-50 N for a transverse scratch length of 3 mm in dry and ambient atmospheric conditions. The scratch tester is equipped with an acoustic emission monitoring sensor which detects emission in the range of 20-80 kHz.

RESULTS

Structural properties: Figure 2a-e shows the XRD graphs of the deposited films. Figure 2a showed a peak at 2θ = 44° and this phase was identified as α-Ti_2N with tetragonal shape crystals. At higher temperature the same phase was formed but an increase in peak intensity was seen. With further increase in temperature Fig. 2c there was appearance of peak at 2θ = 38° which was identified as (111) plane of cubic-shape, d-TiN phase (Jeyachandran *et al.*, 2007). At floating potential (no intentional substrate biasing) (Fig. 2d) there was absence of any crystalline phases. At a higher bias Fig. 2e there was re-emergence of the (200) plane, which was consistent with formation of α-Ti_2N phase. The lattice parameter (Liu *et al.*, 1992) and grain size was calculated using the following equation:

$$a = \lambda/2\sin\theta \times (h^2+k^2+l^2)^{1/2} \quad (1)$$

where, a = lattice constant, λ = Wavelength of source X-ray (CuK_α=1.54Å), θ = Diffraction angle, h,k,l = Miller indices of crystallographic plane.

The crystalline size was measured using Scherrer's equation:

$$D = K\lambda/\beta\cos\theta \quad (2)$$

where, D = Grain size, K = Shape factor (0.9), λ = Wavelength of source X-ray (CuK_α = 1.54 Å), β = Full width half maxima, θ = Diffraction angle. The values have been tabulated and given in Table 2. (The calculated values are only approximate as internal stresses have not been taken into account).

Morphological properties: Figure 3a-e shows the FE-SEM micrographs of the TiN films deposited at different substrate bias voltages and substrate temperatures. Uniform dense, globular and void-free morphology was seen in Fig. 3a, b. An average grain size of 44.3 and 43 nm was seen. At higher deposition temperature, Fig. 3c showed dense columnar grains with inter-columnar spaces. At zero biasing, Fig. 3d the grains appeared flattened and inter-connected. Also, the grains were irregular in size. At higher biasing of -200 V (Fig. 3e), there was an appearance of globular morphology which was dense, void-free and not uniform throughout as there were few larger globules randomly scattered. The average grain size was 31 nm.

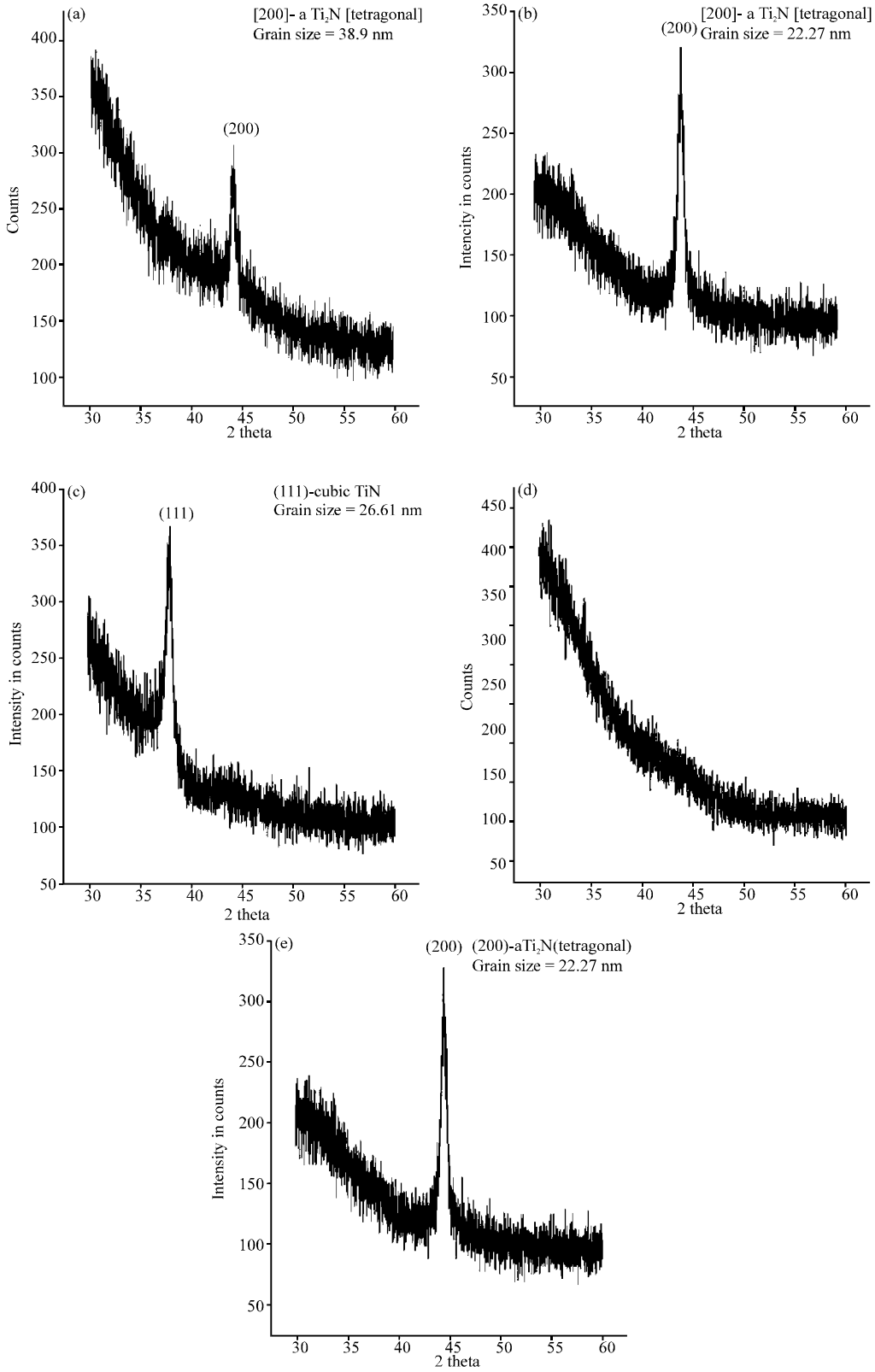

Fig. 2(a-e): XRD paterns of TiN film, (a) RT, -100 V, (b) 100°C, -100 V, (c) 200°C, -100 V, (d) 200°C, 0 V and (e) 200°C, -200 V

Table 2: Calculated lattice constant and grain size values

Sample code	Lattice constant (Å)	Grain size (nm)
A	4.0946	38.9
B	4.101	38.9
C	4.0826	26.61
D	Amorphons	Amorphons
E	4.0746	22.27

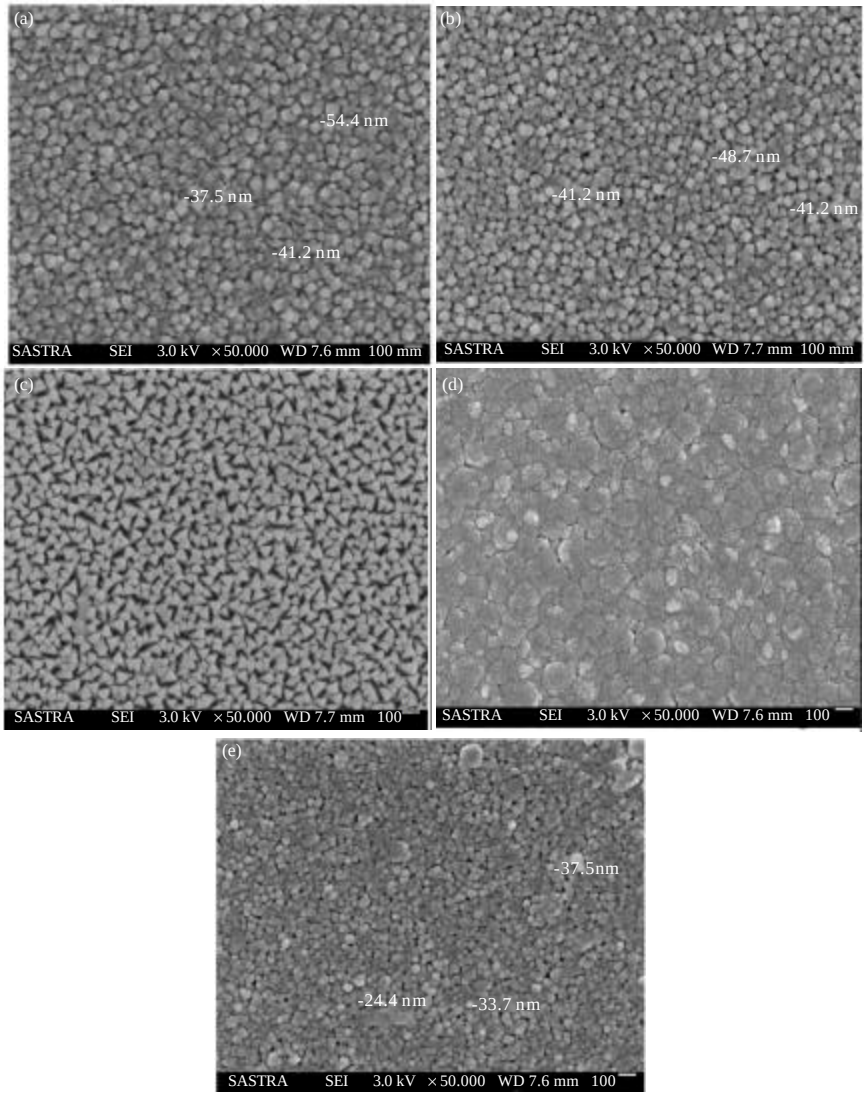

Fig. 3(a-e): FE-SEM micrographs of deposited TiN films (a) RT, -100 V, (b) 100°C, -100 V, (c) 200°C, -100 V, (d) 200°C, 0 V and (e) 200°C, -200 V

Contact angle measurement: The calculated values have been presented in Table 3. It is evident that the most of the films were predominantly hydrophilic with the exception of B.

Table 3: Contact angle measurements sample code lattice constant grain size

Sample code	Mean value (°)
A	59.9
B	109.5
C	Superhydrophilc
D	60.7
E	65

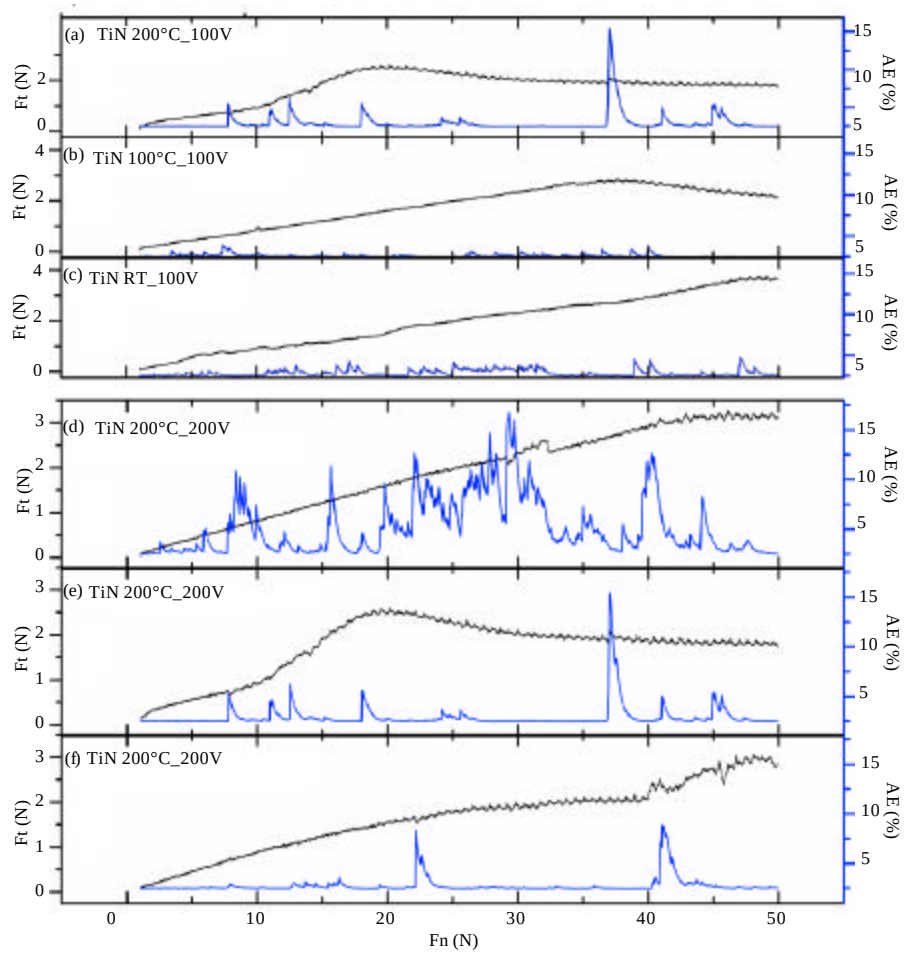

Fig. 4(a-f): (a, b, c) Adhesion strength of TiN films deposited at different substrate temperature, (d, e, f)Adhesion strength of TiN films deposited at different substrate bias

Scratch test: Figure 4 shows the adhesion strength of the deposited TiN films. The scratch resistance property was found be high in TiN films deposited at 200°C as represented in Fig. 4a. In this case initially there was no film failure and at certain extent of load, film started to fail at 7 N. In case of lower temperatures (100°C and RT) the film failed initially exhibiting poor adhesion as indicated in (Fig. 4a-b) and (Fig. 4a-c). Figure 4b shows that films deposited at higher biasing failed at early stages (Fig. 4d) compared to films deposited at 100 V and ay floating potential (0 V). So, better adhesion of the film was obtained at film deposited at lower biasing voltage. The amorphous film does not indicate any signs of failure up to 24 N.

DISCUSSION

Effect of substrate temperature: Heating the substrate provides additional energy for the incoming adatoms to diffuse around and arrange them at the most stable and preferred orientation. At RT and 100°C, the appearance of globular grains Fig. 2(a-b) can be attributed to presence of impurities like oxygen or water vapor which causes repeated renucleation during the film growth stage as the coalescence step is blocked (Petrov *et al*., 2003). The grain size calculated using Eq. 2 showed that the grain size remains constant with increase in temperature from RT to 100°C but there is decrease to 26.61 nm at 200°C. This could be due to the columnar nature of the grains which are smaller than the globular grains.

At 200°C, there is formation of columnar grain structure Fig. 2c. This type of morphology is associated with higher surface roughness and porosity. These columns are elongated grains which are formed due to competitive growth and limited coarsening (Petrov *et al*., 2003).

At higher temperature oxygen and other impurities are removed due to substrate heating. The increased intensity at higher temperature Fig. 3b indicates improved crystallinity. At 200°C, the appearance of (111) plane shows that it is the preferred orientation at higher temperatures. Hydrophobicity exhibited by sample B could be due to surface contamination. The columnar morphology with pores is the cause for superhydrophilic nature of sample C.

There are two types of failure modes to explain the poorly adhered films at lower temperatures, in the case of Fig. 4a, b and Fig. 4a, c. it is observed that the intensity of acoustic emission is poor which signifies there is no strong interfacial bonding at the interface and therefore no elastic energy is released showing poor adhesion. In case of Fig. 4c the intensity of acoustic emission is high which indicates that the interfacial bonding is strong. When interface fails the release of elastic energy is high. High adhesion in TiN films deposited at 200°C can be due the formation of a reaction layer Si_3N_4 at the interface. At lower temperature, Si substrate is subjected to oxygen contamination which prevents the formation of Si_3N_4. But at higher temperature this oxygen is removed from the Si surface and Nitrogen is prompt to make the bonding with Si which forms Si_3N_4 as reaction layer at the interface. Once Si_3N_4 has formed there is no free Si which can continuously nucleate with N_2 that causes to form TiN. The coefficient of friction in the case of Fig. 4b, c is not due to the effect of TiN film but comes with the interaction from Si substrate. In case of Fig. 4a the trend of friction coefficient is stable before the failure of film. Further instability of this value is caused by interfacial cracks and fracture (Nose *et al*., 2003).

Effect of substrate bias: The application of negative bias serves to improve crystallinity by reorienting the film due to ion bombardment during growth. Applying a negative substrate bias has the same effect as heating on the film. The flattened grain structure (Fig. 2d) could be due to arcing effect during deposition. Arcing is caused due to charge accumulation. The absence of crystalline phases at zero substrate bias (Fig. 3d) is due to incoming atoms coming getting fixed at the point of impingement due to limited surface diffusion. In spite 200°C substrate temperature being applied the amorphous nature results. This could be due to perpendicular deposition which also causes limited diffusion (Shieh *et al*., 1998).

At bias of -200 V (Fig. 3e) appearance of (200) plane indicates that increased bias has caused re-orientation from (111) to (200) plane. It can be understood that by varying the bias the preferred orientation can be obtained. There is shift in peaks towards higher angles which is indicative of tensile stresses formed due to energetic ion bombardment by ions, Ar^+ being the predominant one. It gets trapped within the growing film and affects film quality (Namazu *et al*.,

2005). There is no change in wettability (Table 3) with increase in bias. The films are hydrophilic. This method is imperfect and errors due to surface irregularity and contamination are common. The poor adhesion exhibited at higher bias in Fig. 4b is also due to film damage caused by ions hitting the surface.

CONCLUSION

With increase in temperature there is change in morphology from globular to columnar and formation of (111) plane is observed. The films also show improved adherence at higher temperature. With increase in bias, the adhesion was found to decrease considerably and also distinct variation in the crystallographic orientation was seen. Film depositied at 200°C-100 V exhibited good adherence, crystallinity and hydrophilicity. These features will enable these coatings to be used for biological applications. From the studies it can be concluded that substrate bias and temperature have strong influence on film properties and based on the application intended the properties can be tailored by suitably adjusting these two parameters.

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