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NANOSTRUCTURED TiN THIN FILMS SUITABLE FOR MEDICAL APPLICATIONS

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ABSTRACT

Titanium nitride thin films are widely used in biomedical implants because of their biocompatibility, good mechanical properties and high corrosion resistance. Titanium nitride (TiN) thin films on silicon and glass substrates were prepared using a dc magnetron sputtering system under conditions of systematically varying the nitrogen pressure and titanium magnetron power. The nano-structure and microstructure of the coatings was examined using a scanning electron microscope and atomic force microscope. The present studies show that the surface structure, grain size, deposition rate and microhardness of the coatings are strongly dependent on the nitrogen pressure and titanium magnetron power. The grain diameter increased from 35 to 100 nm with the increase in nitrogen partial pressure from 0.4 to 1.0 mTorr. The optimal nitrogen partial pressure found for making gold colour TiN thin films and increased hardness (about 2550 Vickers number) was determined to be between 0.4 – 0.6 mTorr. The grain size was found to decrease from 60 to 28 nm and the microhardness increased from 1600 to 2550 (Vickers number) as the titanium magnetron power increased from 100 to 250 W.

1. INTRODUCTION

Titanium nitride (TiN) thin films are widely used in the machine industry in the last few decades as refractory materials, as hard and wear resistance coatings on machine parts and cutting tools because of their high temperature stability, low friction coefficients and high hardness [1-4]. However in the last few years or so, the TiN thin films have come to the attention of the medical industry for use as coatings on devices as orthopaedic implants and screws used with knee and hip implants [5]. This is due to its biocompatibility and good corrosion resistant when comes in contact with the biological fluids [6, 7]. Polyurethane is often used as a material for external blood contacting materials but it is bioactive and for this reason it can not be used as an internal device. TiN is therefore an ideal perspective biomaterial [8, 9], because of its biological resistance. The surface of the polyurethane can be modified by applying a thin film of TiN to reduce the possibility of infection [10].

It was found that the highest hardness of the TiN film [11] depends on the preferred orientation of the lattice (111). The film thickness, the deposition rate and nitrogen partial pressure are all important parameters that affect the microhardness, surface structure and preferred orientation of the deposited coating. Consequently, before these types of coatings can be used for biological applications, an understanding of the surface morphology that is produced under various processing conditions is required.

The purpose of this paper is to systematically investigate the influence of the nitrogen partial pressure and titanium magnetron power on the microstructure, deposition rate and microhardness of the films. The variation of the film thickness, microstructure and morphology of the TiN films were investigated using Scanning Electron Microscope (SEM) and Atomic Force Microscope (AFM).

2. EXPERIMENTAL PROCEDURE

The depositions of Ti interlayer and TiN thin film on Si and glass substrates were carried out using a conventional dc magnetron sputtering system (Edward High Vacuum Ltd). A turbo molecular pump was used to evacuate the chamber below 5 x 10^{-6} Torr. The chamber pressure was monitored using hot cathode ionization gauge and a MKS mass gas flow controller was used to monitor the flow rate of the reactive gases Ar and N_2. Ultrahigh purity Ar and N_2 gases were used. A Ti target (99.999% purity) with a diameter of 9 cm was used and the target power was supplied by a MDX 1.5 kV power supply. The target to the substrate distance was kept constant at 6 cm and the Ti and TiN film deposition was performed at room temperature.

Before deposition, the substrates were cleaned using Ar ion beam etching for 2 minutes in the chamber. The Ti thin film with a thickness of ~ 60nm was first deposited as an interlayer and then TiN film was deposited by varying the N_2 partial pressure from 0 to 1.0 mTorr and Ti magnetron power from 100 to 250 W. The thickness of the TiN films varied from 1μm – 2.5 μm. The deposition was carried out at total pressure of Ar and N_2 of about 2.4 mTorr.

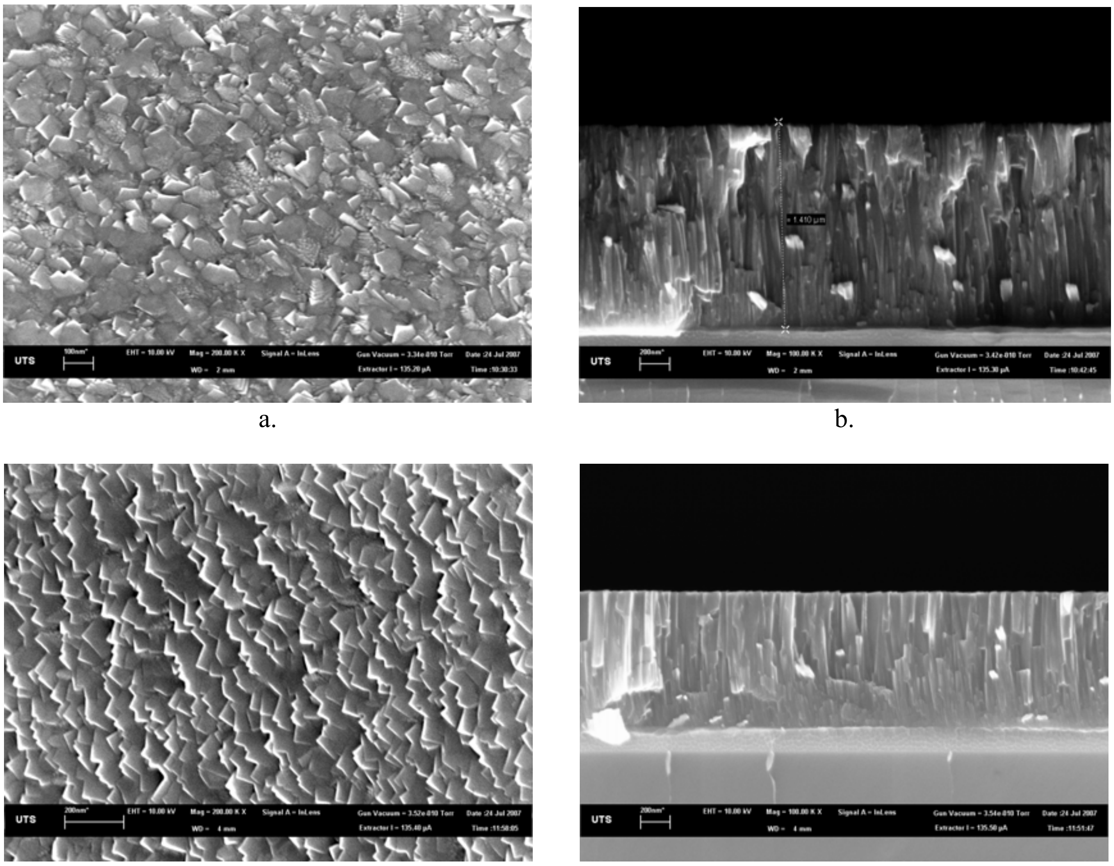
The surface morphology and microstructure of the TiN films were studied using a Zeiss Supra 55VP Scanning Electron Microscope (SEM) operated at 10kV and Atomic Force Microscope (Dimension 3100, with a 100 x 100 micron area scanner). The grain diameter of TiN films was measured from the AFM study. The composition of the films was determined using Energy Dispersive X-ray Spectroscopy (EDS) at 10 kV. The TiN film thickness was determined by preparing cross sections of the film for SEM analysis. The microhardness of the TiN film was measured using Leco M-400-H2 hardness instrument with 2g load to minimise any substrate effect.

3. RESULTS AND DISCUSSION

3.1 Effect of Nitrogen Pressure

The titanium nitride (TiN) thin films were prepared at various nitrogen pressure (0 to 1.0 mTorr) and Ti magnetron discharge power (100 to 250 Watts). Visual inspection revealed that the colour of the TiN films was golden when prepared at a nitrogen pressure of > 0.4 mTorr and < 0.8mTorr. Beyond the above limits of the nitrogen partial pressure the TiN film had a light-golden colour. It is evident that the flow of nitrogen is a critical factor in the preparation of stoichiometric TiN thin films.

The dependence of the surface morphology of the TiN films prepared at different nitrogen pressure is shown in Figure 1. It was found that the surface becomes rougher as the nitrogen pressure increases during deposition as shown in Figure 2 and 3. The variation of surface roughness with the nitrogen pressure is shown in Figure 3. The AFM images (Figure 2) of the surface of the films prepared at 0.4 mTorr and 1.0 mTorr nitrogen pressure demonstrates that as the N_2 pressure increases the grain size increases.



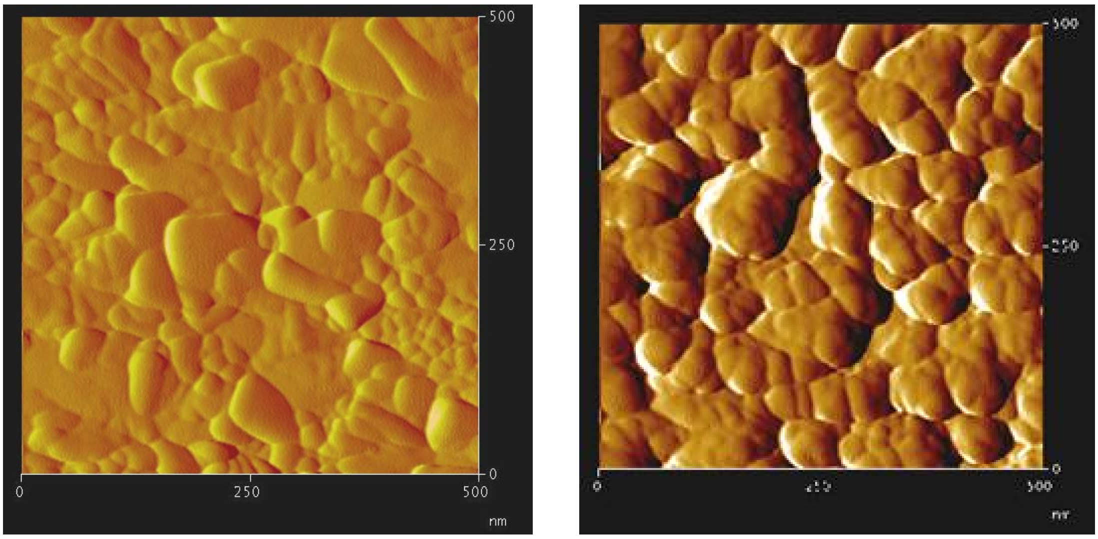
a.

b.

c.

d.

Figure 1. SEM images of the TiN thin films shows the effect of nitrogen pressure on the microstructure of the coatings a) 0.4 mTorr, b) 0.8 mTorr and the cross sectional view shows that the films are columnar structure c) 0.4 mTorr and d) 0.8 mTorr.



a. b.

Figure 2. AFM images on the TiN coatings prepared at a) 0.4 mTorr and b) 1.0 mTorr nitrogen pressure.

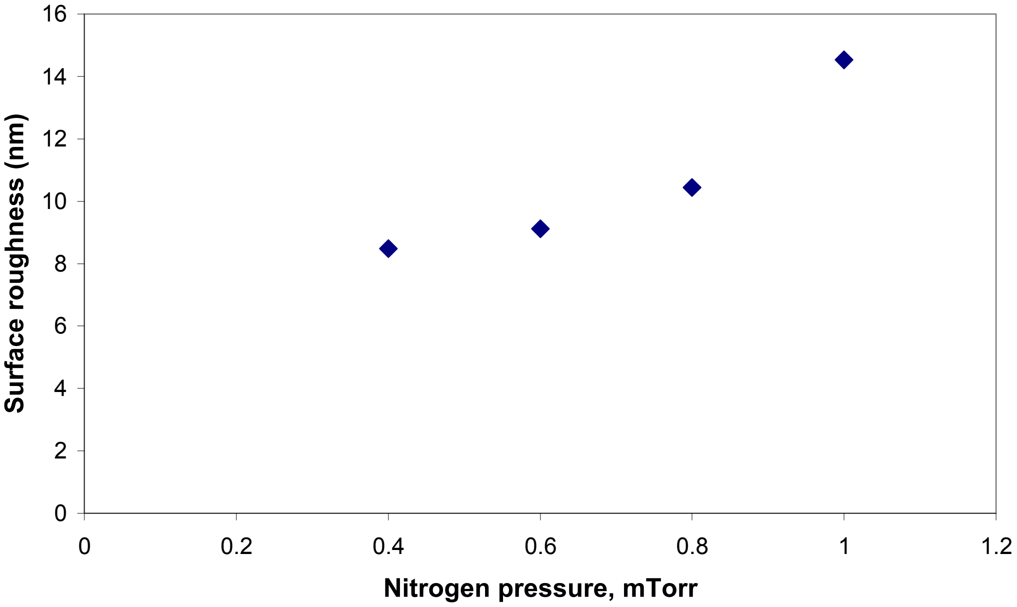


Figure 3. Variation of surface roughness with nitrogen partial pressure.

The grain size of the coating increases from 35 nm to 100 nm when the nitrogen pressure increases from 0.4 mTorr to 1.0 mTorr as shown in Figure 4. The cross sectional view of all TiN films prepared at different nitrogen pressure (0.4 mTorr and 0.8 mTorr) showed that the coatings contained columnar-type structure (Figure 1).

Figure 5 shows the variation of deposition rate of the TiN films with the nitrogen pressure. It was found that the deposition rate decreased from 30 to 16nm/min with the increase of nitrogen pressure from 0.4mTorr to 0.8 mTorr. The decrease of deposition rate and hence the increase of grain size might be due to an increase of scattering of the Ti atoms which decrease the number and kinetic energy of the incident atoms arriving at the substrates with the increase of nitrogen pressure. As a result the rate of nucleation will decrease and course grain structure develops [12, 13].

The microhardness of the TiN coatings was measured at 2g load to avoid the substrate effect. The thickness of the TiN coatings used in the microhardness measurements was in the range 1µm to 2.5µm. The indentation depth of the diamond indenter was roughly 30% of the film thickness to avoid substrate effect. Hardness values were obtained from the average of five measurements on each sample. The variation of microhardness with the nitrogen pressure is shown in Figure 6. It is observed that the hardness was almost constant for the coatings prepared at 0.4mTorr and 0.6mTorr nitrogen pressure then a drop is observed for a coating prepared below 0.8mTorr (Figure 6). Similar results were also observed by Munteanu and Vaz [14] on TiN thin films.

The compositions of the TiN thin films prepared at different nitrogen pressure were determined using Energy Dispersive Spectroscopy (EDS) at 10kV (results summarised in Table 1). It was found that the variation of nitrogen content is not significant at higher nitrogen pressure (1.0mTorr). For higher flow of nitrogen from 0.6mTorr to 1.0mTorr the nitrogen content rises only 5at% which is comparable with the previous results published by Munteanu and Vaz [14].

3.1 Effect of Discharge Power

The TiN thin films were prepared at different Ti magnetron discharge power from 100W to 250W to observe its effect on the microhardness, deposition rate and surface morphology of the films. The variation of the deposition rate and the grain size with the titanium magnetron power is shown in Figure 7 and 8 respectively. It is observed that the deposition rate and the grain size are strongly dependent when the Ti magnetron power increases from 100W to 200W but above 200W it became less dependent. At lower magnetron power (100W) the grains are almost uniform in size (50 – 60nm) but with higher magnetron power (>100W) small grains (<30nm) starts to dominate. The AFM image on the film prepared at 250W (Figure 9) shows the bimodal distribution of the grains with small number of bigger grains compared to smaller grains. The deposition rate increases from 20 to 43nm/min and the grain size decreases from 60 to 28nm when the Ti magnetron power increases from 100 to 250W. It was found that the surface of the films becomes smoother with an average grain size of 30nm when the films prepared with a magnetron power of above 250W as shown in the AFM images in Figure 9.

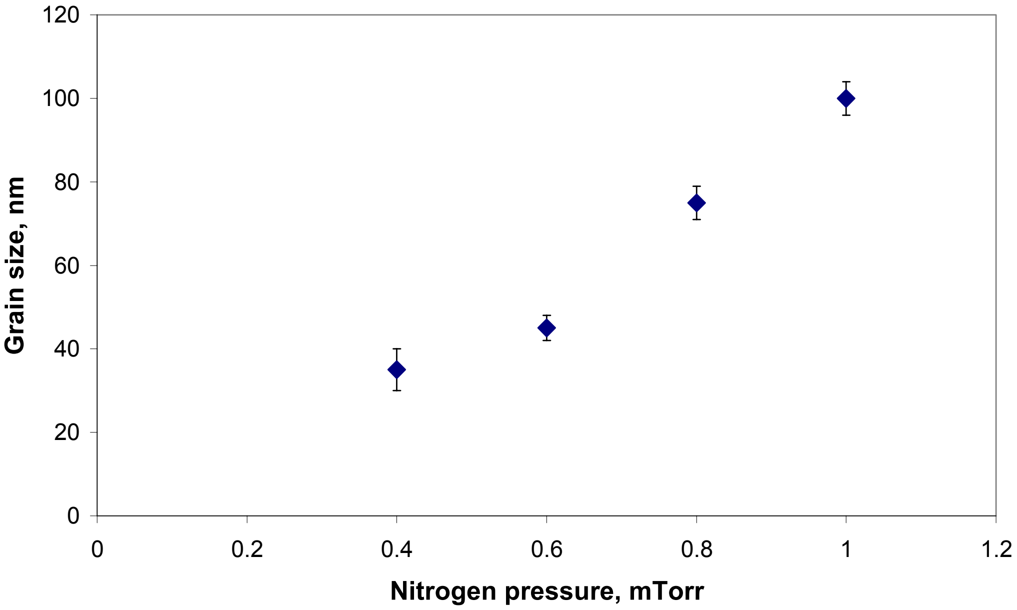


Figure 4. Variation of grain size with the nitrogen pressure.

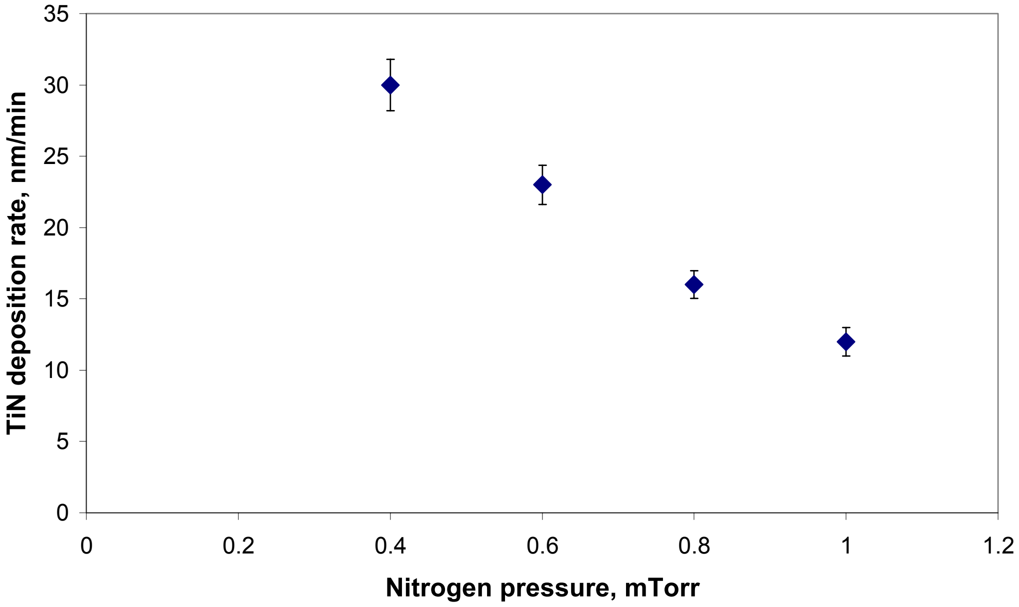


Figure 5. Shows the variation of TiN deposition rate with the nitrogen pressure.

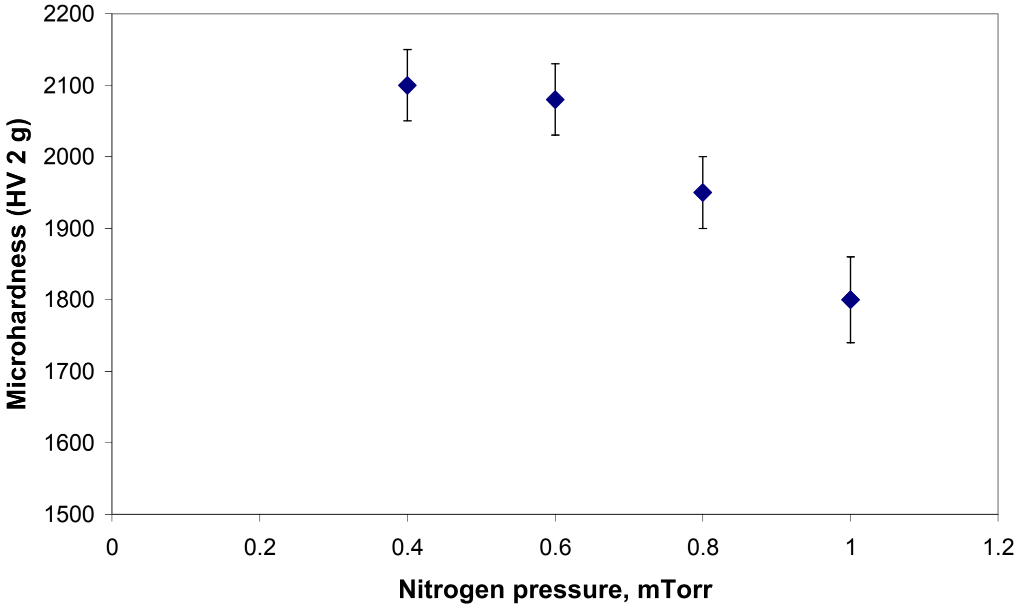


Figure 6. Graphical presentation indicating the dependence of microhardness on the nitrogen pressure.

Table 1. Relative Ti and N_2 composition in the TiN films

Nitrogen pressure (mTorr)	Atomic %	
	Nitrogen	Titanium
0.4	55	45
0.6	59	41
0.8	61	39
1.0	62	38

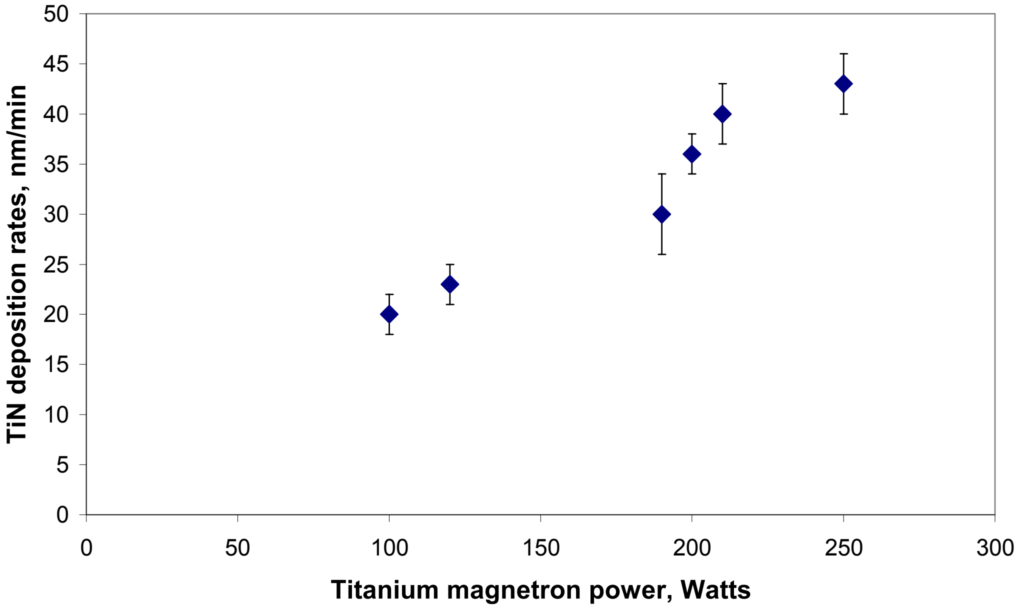


Figure 7. The dependence of TiN deposition rate on titanium magnetron power.

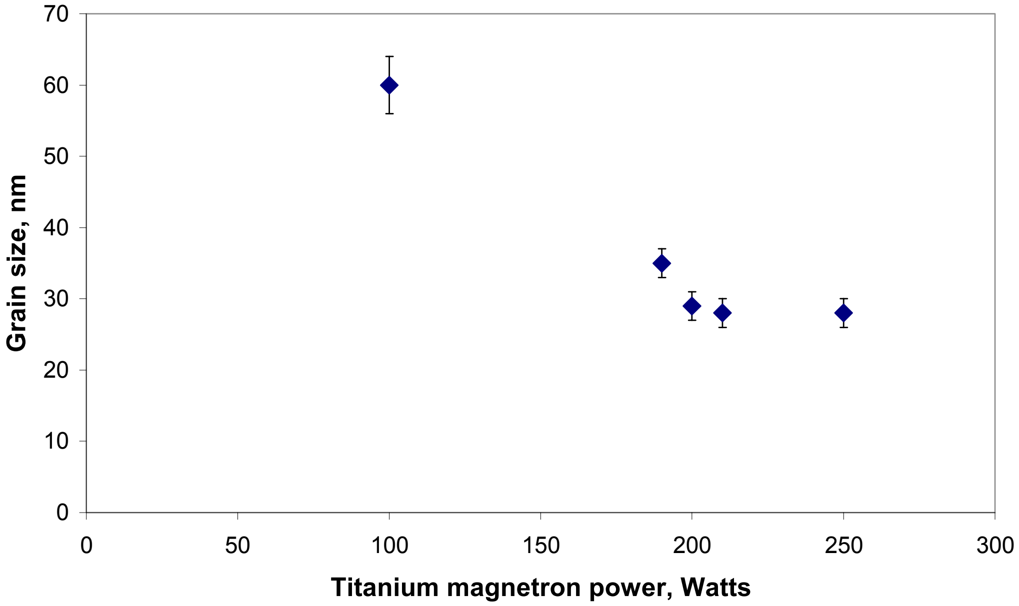
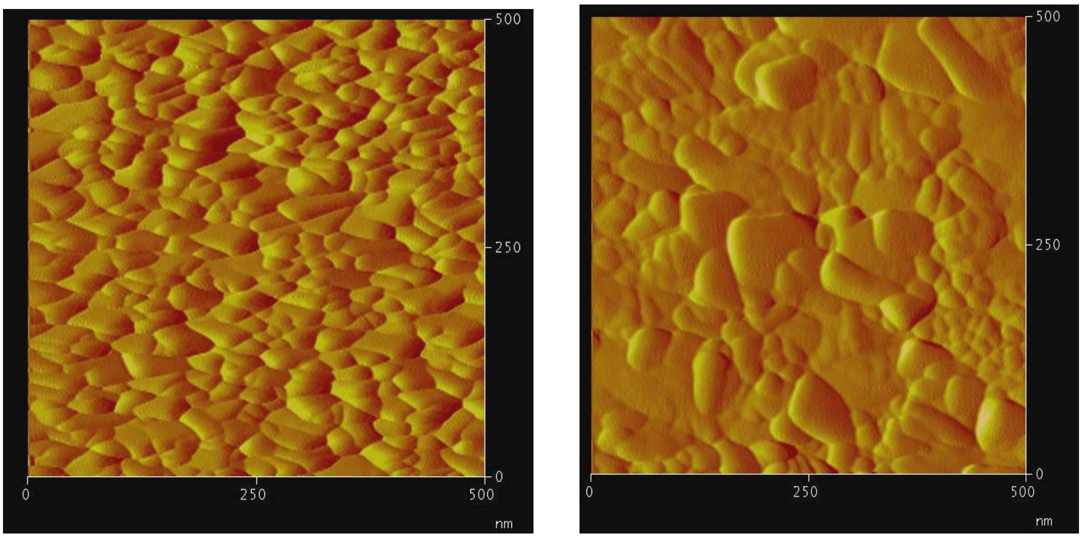


Figure 8. The dependence of grain size on the titanium magnetron power.



(a) (b)

Figure 9. AFM images of the TiN films prepared at different Ti magnetron power a) 100W and b) 250W. Average surface roughness a) 9.5 nm and b) 6.8 nm.

The variation of the microhardness of the films prepared with different magnetron power is shown in Figure 10. The microhardness of the TiN films increases with an increase of Ti magnetron power up to 210W then becomes independent of magnetron power. A maximum hardness of about 2550 (vickers number) was found at 210 - 250W magnetron discharge power. A close correlation was found between the grain size and microhardness, as shown in Figure 11. As the grain size decreases the microhardness increases.

The microstructure and surface morphology of the films is dependant on the mobility or kinetic energy of the incident atoms [15]. It was found that the grain diameter decreased with the increase of magnetron power or deposition rate of the TiN films as shown in Figure 8. This could be due to the fact that at higher deposition rates the incident atoms or molecules increased the density of the nanostructure of the TiN films which in turn refined the grains on the films. Similar results were also obtained by Wuhrer and Yeung [16] in TiAlN thin films.

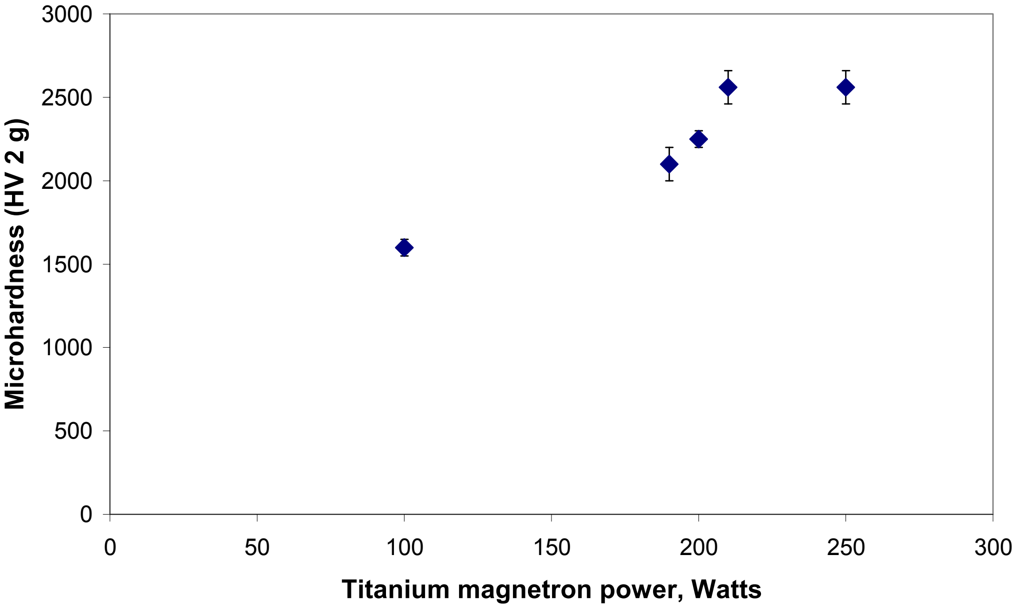


Figure 10. The variation of microhardness of the TiN film on the Ti magnetron power.

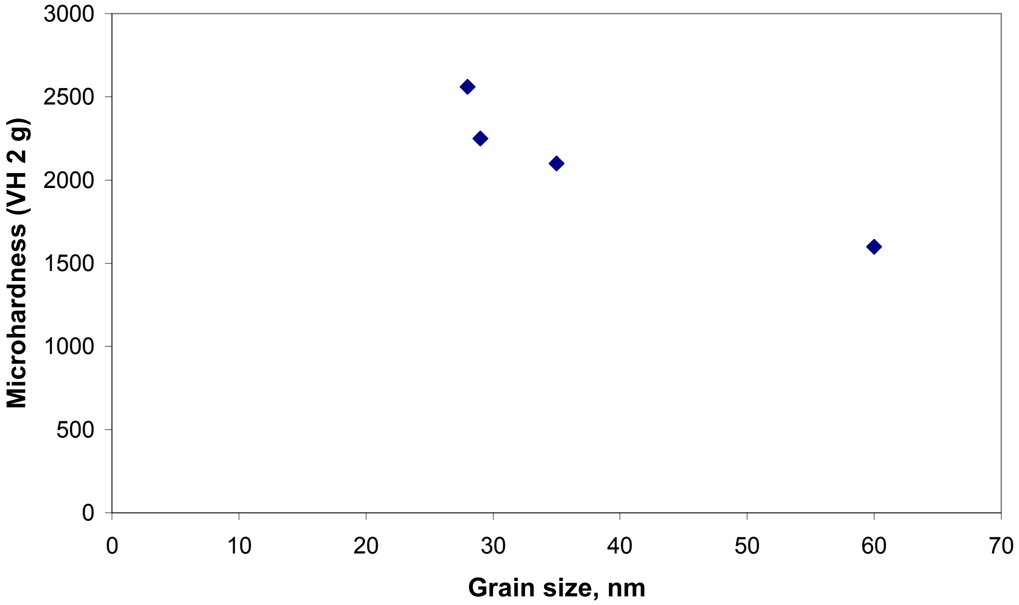


Figure 11. Shows the positive relationship between microhardness and grain size.

4. CONCLUSIONS

The TiN thin films were prepared at different nitrogen partial pressure (0 to 1.0mTorr) and with various titanium magnetron discharge power (100 to 250W) using a dc magnetron sputtering system. It was found that the grain diameter increased from 35 to 100nm and the deposition rate decreased from 30 to12nm/min as the nitrogen partial pressure increases from 0.4 to 1.0 mTorr. The microhardness of the films remained constant at about 2100 (Vickers number) with the increase of nitrogen partial pressure from 0.4 to 0.6mTorr but a decrease (1800-Vickers number) was found at 1.0mTorr nitrogen pressure. It was found that the microhardness and grain size of the TiN films are strongly dependent on the titanium magnetron power or deposition rate of the film. The grain diameter decreased from 60 to 28nm and the hardness increased from 1600 to 2550 (Vickers number) as the titanium magnetron power increased from 100 to 250W. An optimum nitrogen partial pressure of 0.4 to 0.6mTorr was found for better quality (highest hardness of about 2550 Vickers number) and uniform golden colour TiN thin films. Films produced with these conditions will now be implemented for biological investigations

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