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# Growth of Industrial Scale Nanocrystalline TiN Film using Cylindrical Magnetron System

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**Abstract:** Development of large area industrial scale Nanocrystallite TiN thin films, using indigenously developed cylindrical magnetron sputtering (CMS) system is reported. Initially experimental parameters were optimized on 10 x 10 mm Si (111) sample and then same parameters were implemented over 220 x 110 mm large area ceramic tile. Effect of nitrogen flow rates (1.8-3.0 sccm) and substrate biases (0-120 V), on thin film growth has been investigated. Crystallite size, phase orientation, morphology and sheet resistivity of the film have been analyzed using XRD, SEM, AFM and four probe techniques, respectively. Grown TiN films found to have (111) preferred orientation phase. Average crystallite size calculated using Scherrer formula lies in the range of 15-30 nm. Nitrogen flow rates and substrate biases found to have strong influence on surface morphology and size of crystallite. Film become coarse for increasing nitrogen flow rates and denser for increasing substrate bias, respectively. Sheet resistivity of the films ranges from 80 to 300  $\mu\Omega$ .cm. Measurement indicates higher electrical resistivity of the films deposited using higher nitrogen flow rate.

**Keywords:** Cylindrical Magnetron, TiN Film, Nanostructure.

## 1 Introduction

Thick TiN coatings are extensively applied in machinery industry due to their high hardness, low friction coefficient, and excellent chemical stability and wear resistance. In recent years, it has been gaining the increased attention for its application in microresonator detector [1]. In micro-electronic instrumentation TiN also finds application for its electrical characteristics and for its diffusion barrier properties [2]. Also TiN films are recently used as charge collectors in dye synthesise solar cells [3]. TiN films are also proposed as a plasmonic material to replace silver and gold [4]. Apart from these, TiN films have application for decorative purpose due to its gold like shiny colour [5]. Due to various applications of TiN film it has been extensively studied and several techniques like magnetron sputtering [6,7,8], pulsed laser deposition [9,10], cathodic arc, chemical methods are mainly used for its growth. However, film properties greatly depend upon deposition technique and deposition parameters. Planar magnetron sputtering is effectively used for TiN coatings [6, 7, 8]. But for large area coating this technique gets limitation due to only racetrack erosion area and film homogeneity. All the target area is not utilized for the sputtering due to the existence of ExB drift in the limited region. On the other end cylindrical magnetron configuration provides uniform coating over the large surface area and complex geometries. Also

erosion area is maximized in the case of CMS. It is easy to upscale the system dimension as per the requirement [11,12]. In a CMS, homogeneous magnetic field is externally applied in the axial direction parallel to the cathode, and is homogeneous throughout the cathode length. In CMS high sputtering rate can be achieved as the ionization rate is greatly enhanced in the vicinity of cathode due to ExB effect. Therefore, we can vary not only the electric field but also the magnetic field and enhance the plasma density by electron confinement over large cathode area.

The formation of TiN thin film by reactive sputtering has been studied by many researchers [6-10]. In the case of reactive sputtering of TiN, nitrogen flow play an important role in determining structural properties. Nitrogen flow has strong influence in reactive DC planar Magnetron sputtered TiN films and at a critical nitrogen flow dense, isotropic, fine-grained microstructure could be developed. Effect of substrate bias on TiN film has also been studied by many researchers [7, 8]. But for industrial scale application these study has to be repeat on large area deposition technique like CMS. During the deposition of thin film, the packing density and preferred orientation of the film normally changes with process parameters and deposition techniques. Therefore, it is important to study how the properties of TiN films -

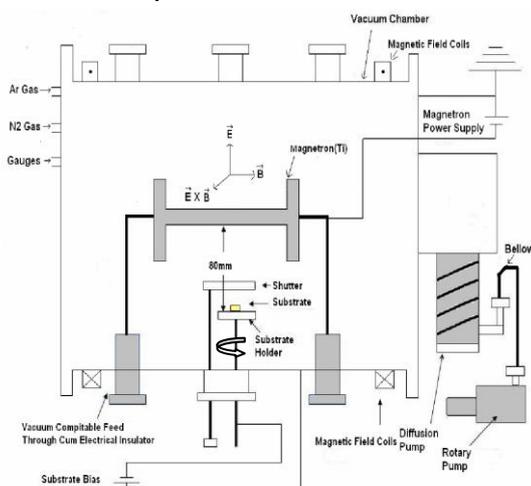
deviate with different deposition techniques during up scaling process. For example common problem in a large area industrial scale films is loss of homogeneity and pilling off due to developed stresses.

Also it is hard to maintain extremely homogeneous plasma properties and hence sputtering from target and maintain homogeneous gas flow. In this study attempts are made to grow TiN coating over large area ceramic tiles as big as 220 x 110 mm rectangular in shape using Cylindrical Magnetron Sputtering (CMS) technique. First results optimized for small samples of 10 x 10 mm are discussed and then their implementation on the larger substrate area is presented.

## 2. Experimental

### 2.1 Experimental Setup

Developed CMS system shown in Fig.1. A cylindrical chamber of diameter 1200 mm length and 500 mm diameter pumped down to  $1 \times 10^{-5}$  mbar was used for this study. Titanium Rod of length 150 mm and outer diameter 15 mm acting as a cathode was placed co-axially inside the chamber. For the generation of a homogeneous axial magnetic field, Helmholtz coil configuration is placed around the body of the chamber as shown in Fig.1. Constant Voltage Source (D.C. Power Supply; 1kV/1A) was used for discharge formation. Magnetic field of 150 gauss was applied along the cathode (i.e. sputtering target) axis. During operation discharge voltage was between 600-700V, discharge current was 500-600 mA and operating pressure was maintained at  $5 \times 10^{-3}$  mbar. Plasma property and operating magnetron mode of this system are reported in [11].  $N_2$  flow rate was controlled through a mass flow controller. Two types of samples were chosen for the study, small Si (111) sample of 10 mm x 10 mm size and large ceramic tiles of 220 x 110 mm. Sample were biased with the help of a DC power supply from 0-120 V. Samples were sputtered clean by Ar plasma for 30 min prior to TiN deposition.



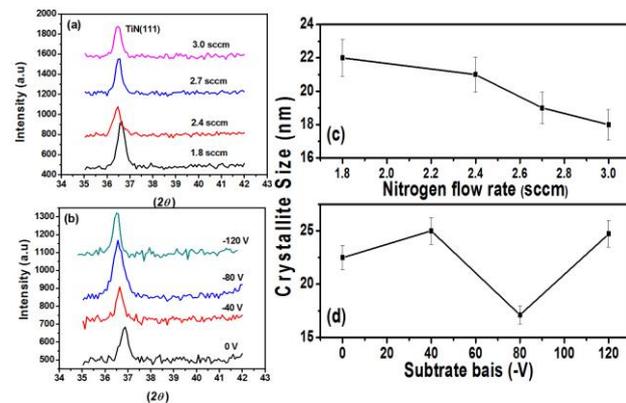
**Fig. 1:** Schematic diagram of the CMS system, used for TiN film deposition.

## 3 Results and Discussion

### 3.1 XRD Analysis

In Fig. 2 (a) and (b) X-Ray diffraction pattern of the film grown at various  $N_2$  flow rates and biasing voltages are shown, respectively. In both the cases we have observed TiN (111) preferred phase only. Depending on the deposition methods usually TiN films show (200), (111) and (220) preferred orientations. The preferred orientation in TiN film is decided by energy minimization of the available energies [13]. The competition between the surface energy, the strain energy and the stopping energy of different lattice planes leads to preferred orientations. Under high-stress conditions, (111) would become the preferred orientation. Ion bombardment induces intrinsic compressive stresses in the films through substitution and displacement of atoms on interstitial lattice sites [14, 15, 16]. In the sputtering process therefore usually (111) orientation is observed due to the bombardment of some plasma ion coming to the surface due to the floating potential.

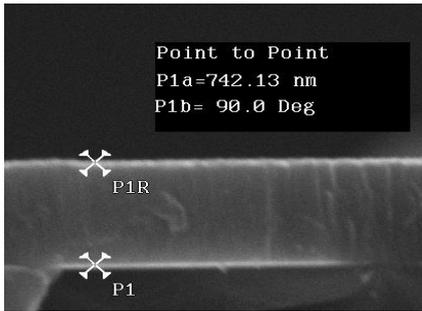
It can be observed in Fig. 2 (a), when the Nitrogen content increases from 1.8 sccm to 3.0 sccm, the XRD peaks shift to the lower diffraction angle. Trend of crystallite size calculated using Scherrer equation is shown in Fig. 2 (c). For 1.8 sccm the crystallite size is 22.5 nm that goes down to 17 nm at 3 sccm. This means, when there are more Ar ions in the plasma, the more Ti will be sputtered from the target and essentially will increase the deposition flux resulting in the higher crystallite size.



**Fig. 2 :** (a) XRD for different nitrogen flow rates (1.8 to 3.0 sccm), no substrate bias. (b) XRD for different substrate bias (0 to -120V), Nitrogen flow rate of 2.4 sccm. Crystallite size for different flow rate (c) and substrate bias (d).

Increasing the substrate bias voltage from 0 V to -120 V also results in the shift of XRD pattern to the lower diffraction angle (Fig. 2 (b)). Usually substrate biasing attracts the ions on the surface and results in roughing the surface, creating defects and dislocation in the substrate [13]. As a result film become more strained and hence peak shift to lower diffraction angle. Biasing at higher energies leads to the re-sputtering of the surface and also

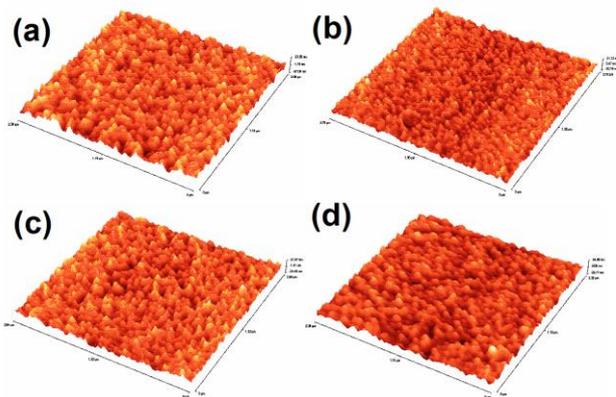
increases surface roughness, this again should results in lower crystallite size, but such effects are prominent in the higher energy regime. In the biasing range chosen in the current experiments a slight peak shift is observed in the XRD pattern but the variation in the crystallite size is not significant (Fig. 2(d)). In the biasing experiments  $N_2$  flow rate of 1.8 sccm was chosen, and at this flow rate we have already mentioned the higher crystallite size of about 22.5 nm at no biasing voltage.



**Fig. 3:** Cross-sectional view of TiN film grown at 2.4 sccm nitrogen flow rate without any biasing.

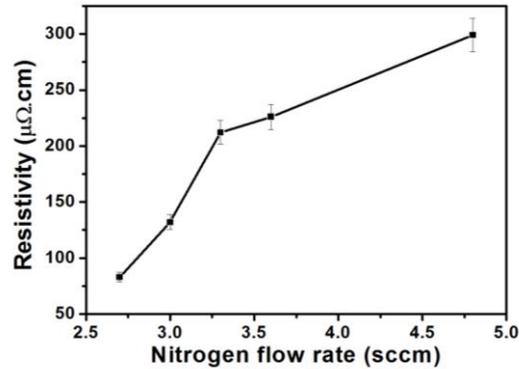
**3.2 SEM and AFM analysis:**

The morphology of the deposited TiN film was observed by means of the scanning electron microscope (SEM) and atomic force microscope (AFM). Cross-sectional SEM image shows highly dense TiN film of about 742 nm thicknesses (Fig. 3). Such a film is grown at no biasing voltage and 2.4 sccm flow of Nitrogen. Under such conditions we have already seen that crystallite size is relatively higher and results in highly dense film. In this case even the columnar growth is also disturbed, due to the energy of the adatom their surface migration is enhanced.



**Fig. 4 :** Surface morphology for substrate bias of (a) -40 V (b) -120 V and Nitrogen flow rate of (c) 2.4 sccm (d) 3 sccm, respectively. Height scale varies from 0 to 22 nm.

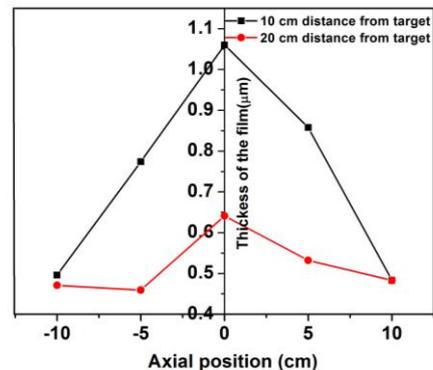
Effects of substrate bias and flow rate on the surface roughness of TiN film have been confirmed with the help of AFM studies shown in Fig. 4. The film grown at -120 V (Fig. 4(b)) is denser as comparable to -40V bias (Fig. 4(a)). This effect is clear as discussed earlier, energetic ions increase the surface roughness. At a lower flow rate of 2.4 sccm compare to 3.0 sccm Ar gas flux to the surface is higher and results in more surface roughness (Fig. 4(c, d)). Typical surface roughness in all the cases was around 22 nm.



**Fig. 5:** Electrical resistivity variation at different nitrogen flow rate.

**3.3 Resistivity Measurement**

The electrical resistivity of the film is measured by four probe technique. Resistivity of the TiN thin film increases with nitrogen flow rate (Fig. 5). Resistivity increases from 75  $\mu\Omega.cm$  to 300  $\mu\Omega.cm$  when the Nitrogen flow rate increases from 2.75 sccm to 5 sccm. Increase of resistivity with increase in nitrogen content could be explained by impurity scattering due to incorporation of excess nitrogen atoms in the film. This significantly reduces the free career concentration and their mean free path and results in increase of resistivity of the film [16, 17].



**Fig. 6:** TiN film thickness variation parallel to the target

### 3.4 Large area coating

Results presented so far were optimized over a small Si (111) sample of size 10 x 10 mm. But when same experimental parameters (2.4 sccm N<sub>2</sub> flow /- 80 V bias) were implemented over a larger ceramic tile of size 220 x 110 mm for decorative purpose results were not impressive. Film homogeneity was the major issue, initially the sample was kept at a 10 cm distance from the cathode. There was almost 50 % variation in the film thickness from the centre to the edge of the sample (Fig. 6). When the distance was increased to 20 cm there was very less variation observed in the film thickness. To minimize this variation even further sample rotation was performed at a 12 rpm speed as shown in the schematic diagram of the experimental system (Fig. 1). Rotation solved the problem of inhomogeneity. Fig.7 show the actual ceramic tile coated by TiN film showing characteristic golden colour. Strong light in the centre of the image is due to the camera flash.



**Fig. 7:** Coated tiles with TiN, showing the characteristic golden colour.

Eventhough we have presented the example of rectangular shape but in this configuration different shape and geometries can be coated. Film properties at different locations were tested and found to be similar like in the case of film thickness. Length of the cathode rod is crucial in CMS configuration; it limits the length of the structure to be deposited.

### 4. Conclusions

TiN thin films have been synthesized by DC cylindrical magnetron sputtering technique. TiN coating on the substrate appears to be smooth and dense with nanocrystallite structures and displays characteristic golden colour. Effect of biasing and Nitrogen flow rate on films crystallite size is demonstrated. At a lower flow of Nitrogen higher crystallite size is observed due to the higher erosion by Ar ion and increase in the rate of deposition. No significant effect of the biasing voltage in the range chosen for this study is observed. Surface morphology by AFM indicates nanostructured TiN thin film on the Si substrate. TiN (111) phase in the film is confirmed by XRD study. The crystallite size calculated by Scherrer formula lies in the range of 15-30 nm. Results from SEM and AFM micrographs show that for the lower nitrogen flow rates and higher substrate biases

nanocrystallites can be achieved and film becomes denser and smoother. Electrical resistivity is found to be more for higher flow rates. Later TiN film on actual industry scale sample is demonstrated. Sample distance from the target, cathode rod length and sample rotation found to be crucial for homogeneous large area coating.

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