# Investigating the role of cathode in the surface modification of bell-metal by magnetron sputtering plasma

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***Abstract:***
Nano-structured titanium nitride (TiN) coating deposition has received significant interest for its excellent properties such as hardness and adhesion. The mode of the titanium cathode (target) plays an important role in the deposition of TiN coating over the bell-metal surface. Bell-metal, an alloy of copper and tin, is used for making various decorative items, idols, ornaments, musical instruments and utensils. One major problem faced by the industries is the degradation of the surface when kept in open air. A hard and corrosion resistant coating of TiN on bell-metal can solve this problem. Cylindrical magnetron sputtering can be a possible technique of obtaining such nano-structured uniform film coatings over a large area of the substrate material. Plasma discharge characteristics during titanium nitride deposition on bell-metal have been studied in a cylindrical magnetron system in reactive gas environment of argon and nitrogen. Changes in the plasma properties have been observed due to the introduction of the reactive nitrogen gas. Langmuir and emissive probes are used as diagnostics for the estimation of various plasma parameters – electron temperature, number density, plasma potential and potential profile. Optical emission spectroscopy (OES) provides useful information on the densities of the different species constituting the reactive gas mixture.

***Keywords:*** *Cylindrical magnetron, plasma sputtering, optical emission spectroscopy*

## 1. Introduction:

The process of direct current cylindrical magnetron glow discharge plasma is used for sputter deposition of different compound films in many technological fields such as multiple films on magnetic recording media or heads, metallic interconnects in microelectronics, thin film solar cells, various coatings namely optical, decorative or protective [1]. Such a system, regarded as an environment friendly system, uses externally applied magnetic field which traps the energetic electrons and effectively increases the ionization efficiency resulting in high deposition rate at a relatively low pressure. In a cylindrical magnetron device, the magnetic field ($B$) is applied in the axial direction parallel to the cathode having cylindrical geometry and is homogeneous throughout the cathode volume. The electric field ($E$) has radial direction and hence, the charged particles in the cylindrical magnetron discharge moves under the influence of the $E \times B$ field which greatly enhances the ionization rate in the vicinity of the cathode and high density plasma can be produced. Hence, high sputtering rate can be achieved. This type of configuration has the ability to coat a large area uniformly [2]. In reactive magnetron sputtering with metallic target, usually inert gas argon is used for sputtering of the target material while reactive gases like nitrogen, oxygen are used for the formation of different metal nitride/oxide films [3-4]. Generally, films are grown under low pressure to reduce collision events for higher surface mobility ensuring better quality of the deposited films. The cathode, also often referred as the target, has an important characteristic role in the sputter mechanism of the deposition process. The process of reactive sputtering is very complex in nature. It involves a variety of mechanisms namely physics of the plasma discharge, the sputtering process, chemical interactions at the target and film surfaces, transport of the sputtered and gas species and the kinetics of film growth. The reactive sputtering can be operated in different modes such as metallic, transition and reactive mode, depending on the inert/reactive gas partial pressure ratio. These modes are highly sensitive to the supply of the reactive gas. It is essential to have very good process control of these processes for proper deposition of the thin film. In the metallic mode, the sputtering rate of the target will be high but it will lead to understoichiometric composition of the deposited film. A very high supply of the reactive gas enables for stoichiometric deposition but it also leads to the poisoning of the target which lowers both the sputtering and the deposition rate. The optimum deposition condition is when both high rate and stoichiometric film can be grown.

Bell metal, an alloy of copper and tin, is used in different parts of India; particularly in North-Eastern states for making utensils, ornaments, musical instruments, idols and decorative items. The manufacturing of these items is mainly based on the manual technique of casting and beating. Degradation of the surface of the bell metal items when kept in open air is a major problem faced by the industries which can be overcomed by a corrosion resistant coating of titanium nitride.

## 2. Experimental set up

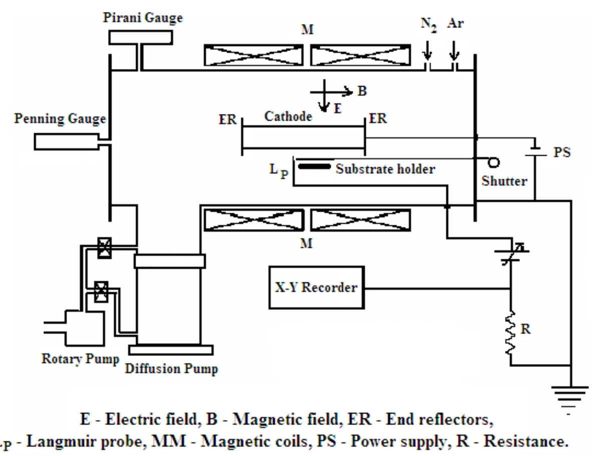


*Fig. 1: Schematic diagram of the experimental set up: E – Electric field, B – Magnetic field, ER – End reflectors, Lp – Langmuir probe, MM – Magnetic field coils, PS – DC discharge power supply (1500 V, 5 A), R – 200 Ω.*

The experimental magnetron device is a stainless steel cylindrical chamber having dimensions of 30 cm diameter and 100 cm length. A small titanium cylinder of length 25 cm and outer diameter 3.25 cm is placed co-axially inside the chamber which acts as the cathode. A schematic diagram of the experimental set up is shown in figure 1. For generation of a steady axial magnetic field, two coils are placed around the body of the chamber. Each coil consists of enamel coated copper wire and contains 1500 numbers of turns. Direct current is passed through both the coils in the same direction which produces an axial magnetic field parallel to the cathode surface that is uniform within a length of ~ 40 cm at the central region of the chamber. One ampere current through the coils generates a magnetic field of 0.0025 Tesla at the central region of the plasma chamber.

The vacuum system consists of a rotary pump having a displacement capacity of 350 lt/min and a diffusion pump with an effective pumping speed of 700 lt/sec. The base and working gas pressures of the chamber are of the order of $10^{-6}$ Torr and $10^{-3}$ Torr measured using a combination of an ionization gauge and a Pirani gauge. The discharge power is supplied from a stabilized DC power supply (1500 V, 5 A) working in the voltage-regulated mode. The working gas environment inside the magnetron chamber consists of a mixture of argon and nitrogen gases in different proportions. The gases are injected to the chamber to raise the neutral pressure up to $10^{-3}$ Torr by using a double valve system consisting of a stop valve and a needle valve (for fine control). The bell-metal substrates (dimension 1 cm in length and 1 cm in breadth) after polishing using diamond paste are ultrasonically cleaned with propan-2-ol organic solvent and dried properly. The samples are then suitably placed atop the substrate holder below the titanium cathode. Ti target (99.99% purity) and substrate are sputter cleaned prior to the actual deposition of the film for 10 minutes to remove oxide and any other contaminant layer existing on their surfaces. Typical discharge parameters for producing plasma are as follows - discharge voltage is 600 V and discharge current is in the range of (50-250) mA. The substrates are kept in floating condition without the supply of any bias voltage. Plasma parameters measured with the help of a cylindrical Langmuir probe are – density ~ $10^9$ $cm^{-3}$ and electron temperature ~ (2-4) eV. The deposition is done for time duration of 75 minutes under controlled discharge parameters. The optical emission spectra of discharge are recorded using BENTHAM M300 Monochromator through optical fiber cable. Focal length of the Monochromator is 30 cm and it is coupled with a photomultiplier tube (PMT) and a programmable motor controller. The output signal from the PMT is transferred to a personal computer (PC) through an analog to digital converter.

## 3. Experimental results and discussion

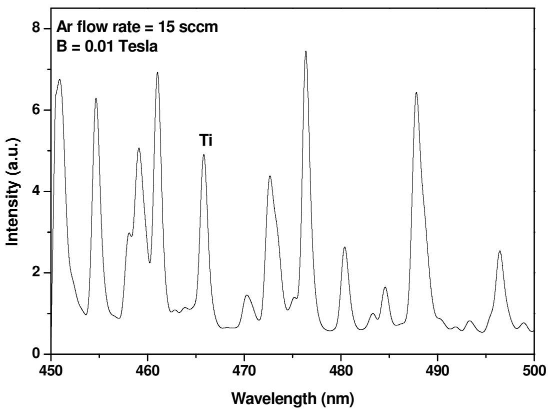


*Fig. 2: Titanium emission line recorded using OES.*

The titanium emission line (466.7 nm) recorded by OES during sputtering of the titanium target at an argon flow rate of 15 sccm, discharge current 100 mA and magnetic field 0.01 Tesla is shown is figure 2 which is considered to be resonant line to the ground state and its intensity can be considered as a representative of the density of that particular species in the plasma.

Figure 3 shows the variation of titanium emission intensity with increase in the flow rate of nitrogen gas. It should be mentioned here that with the increase in the nitrogen flow rate, the targeted titanium line is dominated by nitrogen line near to that peak. Therefore, after 5 sccm of nitrogen gas flow rate, it becomes impossible to determine the titanium emission intensity and the emission intensity, therefore, is shown as zero.

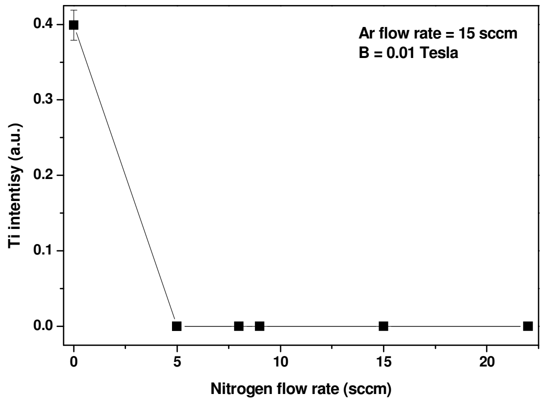


*Fig. 3: Titanium intensity at different $N_2$ flow rates.*

Figures 4(a), 4(b) and 4(c) represents the change of discharge voltage with the change of nitrogen flow rate for titanium at magnetic field 0.01 Tesla, discharge current 100 mA and argon flow rates of 10, 15 and 20 sccm respectively. At an argon flow rate of 10 sccm, the discharge voltage varies almost along a straight line with the increase and the decrease of nitrogen flow rate. However, when argon flow rate is raised to 15 sccm, the discharge voltage decreases sharply at nitrogen flow rate from 15 sccm to 23 sccm, after which it again decreases gradually. This means that as the argon flow rate increases, there is an abrupt change of the target to the reactive mode at the nitrogen flow rate of 15 sccm. At argon flow rate of 20 sccm, the discharge voltage decreases gradually up to nitrogen flow rate of 12 sccm. It then decreases sharply to nitrogen flow rate of 17 sccm and after that, again the discharge voltage decreases gradually. The hysteresis behaviour is not prominent indicating less reactivity between nitrogen and titanium in contrast to nitrogen and aluminium which shows more hysteresis.

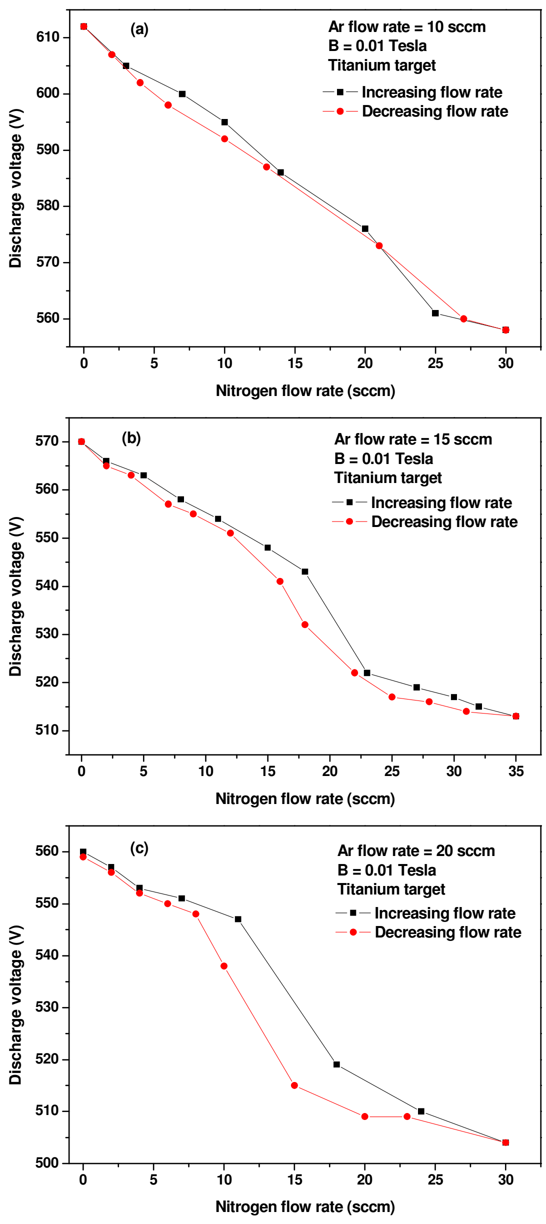


*Fig. 4: Variation of discharge voltage with nitrogen flow rate for titanium target at discharge current 100 mA , B = 0.01 Tesla and Ar flow rate (a) 10 sccm, (b) 15 sccm and (c) 20 sccm.*

However, at 20 sccm of argon flow rate, there is an indication of the formation of the hysteresis. This is because at higher argon flow rate, the discharge prevents the target to convert into the reactive or the transition mode. At higher argon flow rate of 20 sccm, the sputtering rate is higher and therefore, the gas consumption of the reactive gas is higher in the metallic mode. Therefore, at higher argon flow rate, the transition of the discharge from the metallic to the reactive mode is steep and the hysteresis is formed. Variation of the discharge voltages with that of the nitrogen flow rate at argon flow rate of 15 sccm, discharge current 100 mA and magnetic fields of 0.005 Tesla and 0.015 Tesla respectively for titanium target are shown in figures 5(a) and 5(b) respectively. No formation of hysteresis is observed in both these cases.

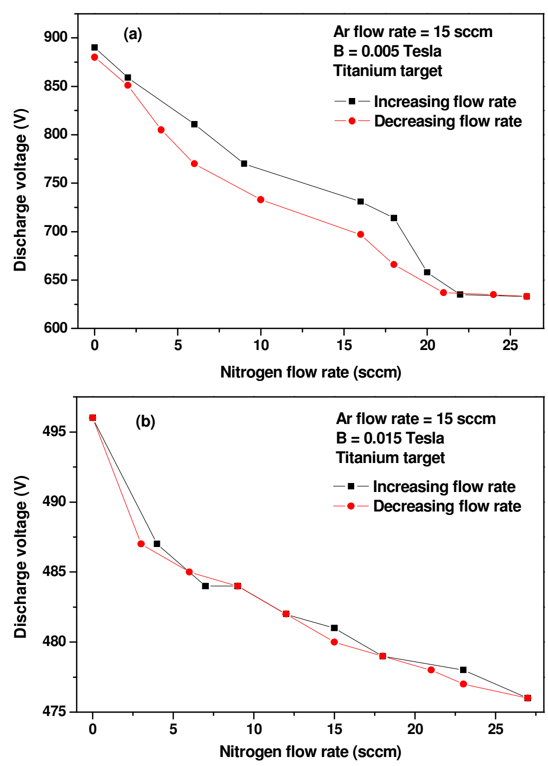


*Fig. 5: Variation of discharge voltage with nitrogen flow rate for titanium target at discharge current 100 mA, Ar flow rate = 15 sccm and B = (a) 0.005 Tesla and (b) 0.015 Tesla.*

## 4. Conclusion

The partial pressures of argon and nitrogen gases determine the sputtering mode of the cathode which is an important factor during the deposition of titanium nitride film coating on bell-metal for its surface modification. The gas pressures should be such that the sputtering occurs in the transition mode for obtaining high yield.

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