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Titanium nitride nano-structure by DC magnetron sputtering plasma

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Abstract Titanium nitride is useful as hard coating for surface durability It also provides wear and corrosion resistance to the coated material Direct current magnetron sputtering is used for deposition of titanium nitride (TiN) on an alloy of copper and tin (bell-metal) substrate Plasma is produced in argon and nitrogen reactive gas environment with titanium (cathode) as the target for the sputtering mechanism Qualitative study of the deposited titanium nitride film shows the formation of nano-structure XRD study confirms the formation of TiN, SEM and AFM analyses are carried out to study the surface morphology of the deposited film The TiN film provides a permanent hard protective and anti-corrosive bright gold coloured coating to the bell-metal substrate

Keywords Magnetron, sputtering, hard coating, nano-structure

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1. Introduction

Direct current magnetron glow discharge process is used for sputter deposition of different compound films in a large number of technological fields [1, 2]. Some of the examples are as follows – multiple films on magnetic recording media or heads, metallic interconnects in microelectronics, thin film solar cells, various coatings namely optical, decorative or protective. It is also regarded as an environment friendly process since it fully avoids the use of various chemical reactants [3] Sputtering deposition has become a generic name for a variety of sputtering processes. Among the various sputtering processes, the one, which is most widely used today, involves the use of magnetic field perpendicular to the electric field and is known as magnetron sputtering. Magnetron sputtering uses confinement of excited plasma in crossed magnetic and electric fields that results in high deposition

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rates and good reproducibility [4, 5] Titanium nitride is a rocksalt structure (NaCl) compound consisting of Ti atoms filled in fcc based lattice with all octahedral sites filled with nitrogen atoms as shown in Figure 1 Some of its physical properties are as follows Lattice parameter , 0 424 nm , Melting point 3173 K Thermal stability (ΔH_f^{298}) . 336.6 kJmol^{-1}; Young's modulus 450 GPa TiN thin films have found applications as hard coatings, decorative coatings, wear resistant coatings and also diffusion barriers in IC technology [6] Here, we have presented an analysis of TiN thin film deposited on an alloy of copper and tin (bell-metal) in reactive N_2/Ar gas environment by direct current magnetron sputtering with X-ray diffraction (XRD), scanning electron microscope (SEM) and atomic force microscope (AFM) techniques

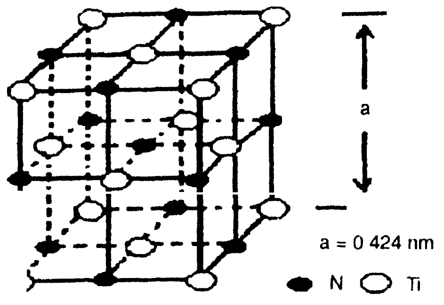

Figure 1. Schematic structure of TiN

2. Details

The experimental cylindrical magnetron device is a stainless steel chamber having dimensions of 30 cm in diameter and 100 cm in length A small titanium cylinder is placed coaxially inside the chamber which acts as the cathode The length of the cathode is 25 cm and its outer diameter is 3 25 cm A schematic diagram of the experimental set up is shown in Figure 2. For generation of a steady axial magnetic field, two uniform coils are placed around the body of the chamber Low pressure is created inside the chamber

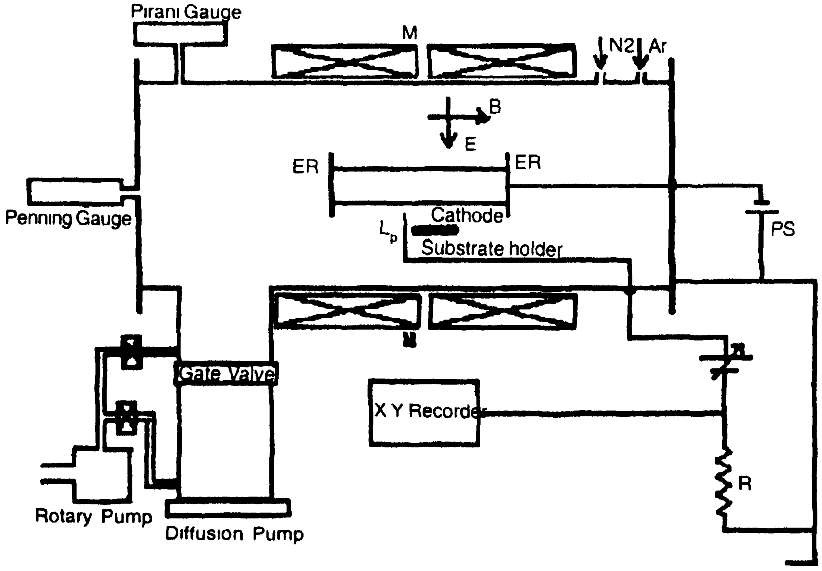

Figure 2. Schematic diagram of experimental set-up E – Electric field, B – Magnetic field, ER – End reflectors, L_p – Langmuir probe, MM – Magnetic coils, PS – Power supply

using a combination of rotary and diffusion pumps. The base pressure of the chamber is of the order of 10^{-6} Torr and working gas pressure is varied within the range of (1×10^{-3} – 3×10^{-3}) Torr. A Pirani gauge and an ionization gauge are used for measurement of pressure inside the chamber. The discharge power is supplied from a stabilized DC power supply (1500 V, 5 A) working in the voltage-regulated mode. Gas is 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 (fine control). Plasma is produced at a pressure of 2.5×10^{-3} Torr by applying 600 V DC bias between central post electrode as cathode and the grounded chamber as anode. Langmuir probe is used as a diagnostics for the estimation of various plasma parameters namely the electron temperature, the plasma potential and the plasma density.

X-ray diffraction (XRD) pattern of titanium nitride film deposited on bell-metal substrate is shown in Figure 3. Thin film XRD pattern is recorded using Cu K_α radiation source of wavelength, $\lambda = 1.54$ A in Bruker AXS make X-ray diffractometer installed at Nanotechnology Centre, IIT Guwahati. The deposition condition of the TiN film is as follows – discharge power is 60 watt, magnetic field is 200 gauss and gas pressure is 2.5×10^{-3} Torr. The deposition time is 30 minutes and the substrate is placed at a distance of 8 cm from the cathode. A sharp intense peak corresponding to TiN (200) is observed along with another peak TiN (220) of less intensity from the figure. The metallic Cu (111) and Cu(200) peaks seen corresponds to the bell-metal substrate.

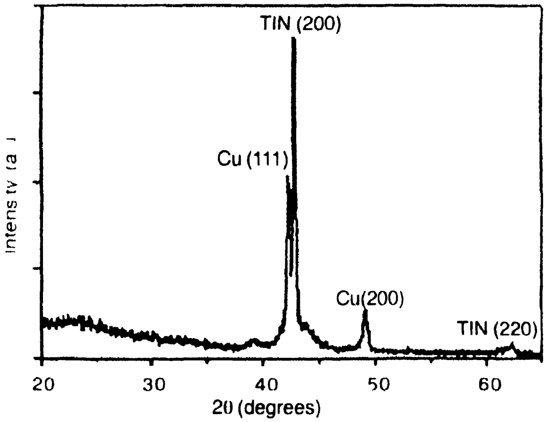

Figure 3. XRD pattern of TiN on bell-metal substrate

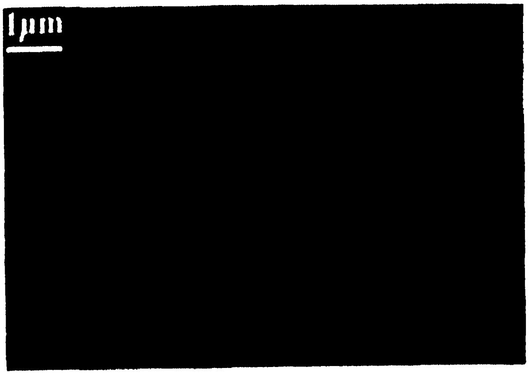

Figure 4. SEM picture of TiN film

Figure 4 shows SEM picture of the deposited TiN film obtained using LEO-143VP make scanning electron microscope installed at Central Instrumentation Facility, IIT Guwahati. The picture shows the formation of TiN structures resembling black dots distributed throughout the scanned film surface. The dimensions of these structures are measured and are found to be in the nano-scale range with an average size of ~ 180 nm. The presence of nano-structure in the deposited TiN film is of great importance and utility as it will lead a very hard coating to the substrate material. No inter-metallic phase peaks are found in this study using SEM EDX.

The surface morphology of the deposited TiN film has been further examined using atomic force microscope (AFM) This study is done in a SMENA-B make AFM instrument at Physics Department, IIT Guwahati The surface image recording is done by operating the instrument in the tapping mode

Figure 5(a) shows the surface of the deposited TiN film in the presence of both argon and nitrogen gases (Ar N_2 = 1 1) which is found to be the optimized deposition condition of the film In Figure 5(b), the surface morphology of the film in the presence of nitrogen gas only has been shown The maximum roughness of the deposited film is of the order of 100 nm But at most places, it has a value of ~ 40 nm On careful observation of the two figures, one can see the formation of dotted net like structures on both the deposited TiN films which are found to maintain a distinct pattern throughout the surfaces of both films Hardness study by nano-indentation method shows that the deposited TiN film over the bell-metal substrate increases the surface hardness by a factor of 13 under the above deposition condition The Copper Acetic Acid Salt Spray (CASS) test was done to determine the anti-corrosive property of the TiN thin films The CASS test is now covered by BS 5466 Part III 1977 (ISO 3770 and ASTM B368) [7] The film exhibited no change in its surface morphology for 48 hours This indicates that the TiN coating is able to shield the bell-metal surface from the severe and hostile environment and thus, provide a good protective cover to it

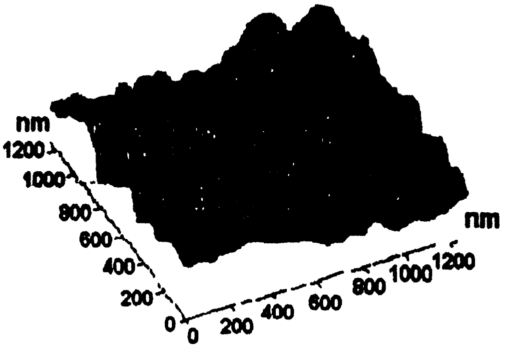

Figure 5(a). AFM picture of TiN in argon and nitrogen

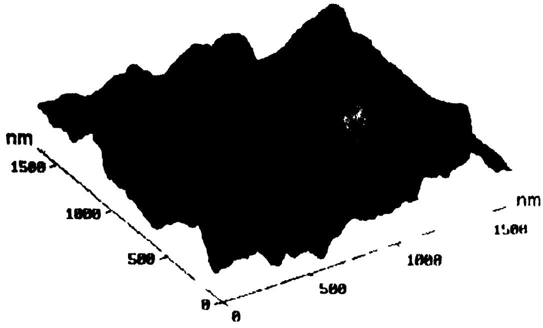

Figure 5(b) AFM picture of TiN in nitrogen only

3. Summary

TiN thin film deposited on bell-metal substrate is found to form nano-structures under the above mentioned deposition condition The nano-structures possess a definite structural pattern and it provides a very hard coating over the substrate material The film coating acts as a protective layer and prevents the bell-metal surface from corrosion and getting oxidized Further, the golden colour of the TiN film enhances the beauty of the surface

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