Applied Surface Science 255 (2008) 2133–2138

Contents lists available at ScienceDirect

Applied Surface Science

journal homepage: www.elsevier.com/locate/apsusc

Effect of substrate temperature on the structural properties of magnetron sputtered titanium nitride thin films with brush plated nickel interlayer on mild steel

B. Subramanian *, K. Ashok, M. Jayachandran

ECMS Division, Central Electrochemical Research Institute, Karaikudi 630006, India

ARTICLE INFO

Article history:
Received 26 December 2007
Received in revised form 21 March 2008
Accepted 2 July 2008
Available online 19 July 2008

PACS:
81.15. Cd
68.55. Jk

Keywords:
Titanium nitride
Magnetron sputtering
Structural properties
Hard coatings

ABSTRACT

Thin films of titanium nitride (TiN) were prepared on mild steel (MS) by a physical vapor deposition (PVD) method namely direct current reactive magnetron sputtering. With the aim of improving the adhesion of TiN layer an additional Nickel interlayer was brush plated on the steel substrates prior to TiN film formation. The phase has been identified with X-ray diffraction (XRD) analysis, and the results show that the prominent peaks observed in the diffraction patterns correspond to the (1 1 1), (2 0 0) and (2 2 2) planes of TiN. Cross-sectional SEM indicated the presence of dense columnar structure. The mechanical properties (modulus and hardness) of these films were characterized by nanoindentation.

1. Introduction

In recent years, usage of thin, hard and wear resistant titanium nitride (TiN) ceramic coatings in metal cutting and metal forming tools applications has acquired increasing importance. It plays a vital role in many industrial applications because of its high hardness, high evaporation temperature (2950 °C), good chemical stability and metallic brightness [1]. Generally, techniques like physical vapor deposition (PVD) [2,3], plasma assisted chemical vapor deposition (PACVD), plasma enhanced chemical vapor deposition (PECVD) and hollow cathodic ionic plating [4] are used in developing hard coatings on various substrates.

The equilibrium phase diagram of TiN shows three stable solid phases. The cubic B1-NaCl crystal structure of δ-TiN phase is stable over a wide composition range ($0.6 < N/Ti < 1.2$) and the hexagonal α-Ti phase can dissolve up to 15 at.% nitrogen. The ε-Ti_2N crystallizes in a tetragonal structure and exists only at a composition range of 33 at.%. However, the δ-TiN phase is mostly used in technological applications [5]. Pelleg et al. [6] have shown that for these types of material, the actual plane of lowest surface energy is the (2 0 0). They also suggested that the (1 1 1) plane in TiN possesses the lowest strain energy, due to anisotropy of Young's modulus, and that this frequently observed orientation is due to a minimization of strain energy. The structure and the properties of films depend sensitively on the deposition conditions. The TiN coatings produced by PVD route like sputtering method have better materials properties and thermal stability [7]. The dependence of the structural and other physiochemical properties of TiN layers deposited by DC magnetron sputtering on the substrate bias voltage and substrate position was investigated. The formation of TiN compound depends mainly on neutral atomic and excited molecular nitrogen species arising within the magnetron discharge [8].

The aim of the present work is to study the effect of substrate temperature on structure of TiN thin film and with brush plated Ni interlayer on mild steel (MS) substrate deposited by reactive DC magnetron sputtering. The structural parameters, viz. the crystallinity, crystal phase, lattice constant, grain size, orientation,

* Corresponding author. Tel.: +91 4565 227555; fax: +91 4565 227713.
E-mail address: tspsenthil@yahoo.com (B. Subramanian).

0169-4332/$ – see front matter
doi:10.1016/j.apsusc.2008.07.083

internal stress and strain are strongly dependent on the substrate temperature. Scanning electron microscopy was applied for precise investigation of surface topography of nitride layers. Such information is essential for understanding the interaction of the outer surface of these layers with a biological environment [9].

2. Experimental

The used substrate was MS, consisting of 0.37 wt% C, 0.28 wt% Si, 0.66 wt% Mn and 98.69 wt% Fe. Coupons of the substrate were cut to size of 75 mm × 25 mm and the surface was ground with SiC paper to remove the oxides and other contamination. The polished substrates were degreased with acetone and then cathodically electro cleaned in alkali solution containing sodium hydroxide and sodium carbonate for 2 min at 70 °C, followed by rinsing with triple distilled water. These substrates were subsequently dipped in 5 vol.% H_2SO_4 solution for 1 min and thoroughly rinsed in distilled water.

A microprocessor controlled Selectron Power Pack Model 150 A to 40 V (USA) was used to transform AC current to DC current in the brush plating setup. The schematic of the brush plating system is given elsewhere [10]. The DC power pack has two leads, one is the anode connected to the plating tool and the other is the cathode connected to the work piece over which the coating has to be plated. The anode is covered with a porous absorbant material, which acts as the brush holds the solution. This wet brush can be moved on the surface of the work piece that is to be finished (coated). When the anode touches the work surface the electrical circuit is closed and deposition is produced. The nickel electrolyte bath, similar to Watt's bath, contained 240-g/l nickel sulphate, 40-g/l nickel chloride and 30-g/l boric acid. The pH and temperature was maintained at 4.0 and 28 °C (RT), respectively.

The layers of TiN were deposited on well-cleaned MS substrates and brush plated Ni/MS specimen using a DC magnetron sputtering unit HIND HIVAC. The base pressure of the chamber was below 10^{-6} Torr (1.33×10^{-4} Pa) and the substrate temperature was varied between 200 °C and 500 °C. High purity argon was fed into the vacuum chamber for the plasma generation. The substrates were etched for 5 min at a DC power of 50 W and an argon pressure of 10 mTorr (1.33 Pa). A high purity (>99.999%) Ti target of 7.5 cm diameter was used as cathode.

X-ray diffraction (XRD) was used to examine the changes in preferred grain orientation. XRD patterns were recorded using an X'pert pro diffractometer using Cu Kα (1.541 Å) radiation from 40 kV X-ray source running at 30 mA. The surface of the coating was characterized by scanning electron microscopy (SEM) using a Hitachi S 3000H microscope. The hardness of the TiN thin films was measured using nanoindentation. The loading and unloading phases of indentation were carried out over a time span of approximately 20 s in all the experiments. At the maximum load, a dwell period of 20 s was imposed before unloading, and another dwell period of 20 s at 90% of unloading, so as to correct for any thermal drift in the system. At least 20 indents were made for each specimen, with the adjacent indents separated by at least 10 μm.

3. Results and discussion

3.1. Structural properties

The XRD patterns of DC magnetron sputtered TiN thin films deposited at various substrate temperatures (T_s) are shown in Fig. 1(a)–(d). The *d* spacing values matches with JCPDS card no. 38-1420 for TiN thin film. Only a single-phase TiN structure with FCC and the peaks corresponding to (1 1 1) and (2 0 0) planes are observed at $2\theta = 36.4^\circ$ and 42.2°. The outcome revealed that the homogeneous coating displays a strong preferred (1 1 1) orientation parallel to the substrate surface. The (1 1 1) plane of TiN has the lowest strain energy due to anisotropy in Young's modulus as observed from nanoindendation studies also. Therefore, its alignment normal to the growing direction will minimize the total energy under strain–energy dominated growth [5]. When the substrate temperature increased, the peak intensity of (1 1 1) plane was found decreasing whereas the intensity of (2 0 0) plane showed an increasing trend. This means that the crystallographic orientation of the film changes from the presence of (1 1 1) to both (1 1 1) and (2 0 0) with the increase of T_s. Comparatively, one can observe that the sample prepared at $T_s = 400$ °C shows good crystalline nature as observed from (1 1 1) (2 0 0) and (2 2 2) planes. It confirms the textured growth of the film with different planes to improve its strength.

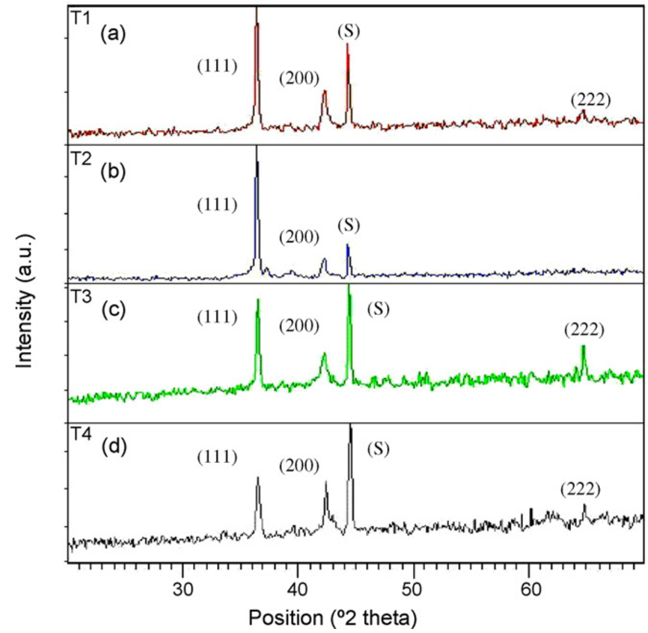

Fig. 1. XRD pattern for TiN at different substrate temperatures: (a) 200 °C, (b) 300 °C, (c) 400 °C and (d) 500 °C.

XRD patterns of TiN coatings with Ni interlayer on MS substrates at different substrate temperatures (T_s) are shown in Fig. 2(a)–(d). The patterns show the predominant peaks for FCC Ni (JCPDS card no. 04-0850) interlayer along (1 1 1) and (2 0 0) planes in addition to that peaks identified for TiN along (1 1 1) and (2 0 0) planes at $2\theta = 36.4^\circ$ and 42.3°. A constant thickness of about (~5 μm) Ni interlayer was maintained for all the samples. Up to 400 °C the peak intensity of TiN (1 1 1) plane increases and the intensity of (2 0 0) was found to increase at 500 °C.

The structural parameters calculated for both (1 1 1) and (2 0 0) planes were compared and both behave close to one another. The lattice parameter of the TiN sample prepared at 200 °C (T_s) was calculated to be 4.27 Å, which is in good agreement with the reported value (JCPDS No. 38-1420) lattice constant vs. substrate temperature graph for both (1 1 1) and (2 0 0) planes are shown in Fig. 3a. When T_s increases the lattice parameter decreases [11] in accordance with the decrease of crystallographic volume. The value of the lattice parameter for the TiN thin film is lower than the reported value for the bulk [12] means that the lattice has many nitrogen vacancies [13]. These vacancies increase with the temperature because the re-sputtering process affects the lighter N atoms more than heavier Ti atoms.