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ScienceDirect

Ceramics International 40 (2014) 5757–5764

CERAMICS INTERNATIONAL

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Effect of thickness on the structure, composition and properties of titanium nitride nano-coatings

G. Martinez[a], V. Shutthanandan[b], S. Thevuthasan[b], J.F. Chessa[a], C.V. Ramana[a,*]

[a]Department of Mechanical Engineering, University of Texas at El Paso, El Paso, TX 79968, USA
[b]Environmental Molecular Sciences Laboratory (EMSL), Pacific Northwest National Laboratory (PNNL), Richland, WA 99352, USA

Received 3 September 2013; received in revised form 5 November 2013; accepted 5 November 2013
Available online 25 November 2013

Abstract

Titanium nitride (TiN_x) coatings were grown by magnetron sputtering onto Si(100) substrates by varying time of deposition to produce coatings with variable thickness (d_{TiN}) in the range of 20–120 nm. TiN_x coatings were characterized by studying their structure, composition, and mechanical properties. Nuclear reaction analysis (NRA) combined with Rutherford backscattering spectrometry (RBS) analyses indicate that the grown coatings were stoichiometric TiN. Grazing incidence X-ray diffraction (GIXRD) measurements indicate that the texturing of TiN coatings changes as a function of d_{TiN}. The (111) and (002) peaks appear initially; (111) becomes intense while (002) disappears with increasing d_{TiN}. Dense, columnar grain structure was evident for all the coatings in electron microscopy analyses. The residual stress for TiN coatings with $d_{TiN} \sim 120$ nm was 1.07 GPa in compression while thinner samples exhibit higher values of stress.

Keywords: TiN; Coatings; Structure; RBS; Residual stress

1. Introduction

Titanium nitride (TiN) thin films and coatings have been the subject of intense research due to their exceptional chemical, physical, mechanical and electrical properties, such as a high degree of hardness, chemical stability, high thermal conductivity, resistance to wear and corrosion, chemical inertness and biocompatibility [1–9]. TiN coatings exhibit a number of properties similar to metals (good electrical conductivity) while retaining characteristics (covalent bonds, hardness, high melting point) found in insulating ceramics [1–4]. In addition to wear and corrosion, the lustrous color makes TiN useful for decorative applications [10–12]. TiN films serve as metallization materials or diffusion barriers for metal-interconnects in microelectronics [8,13,14]. Furthermore, optical properties of TiN coatings are increasingly gaining importance in view of their possible application in solar cells and plasmonics [11,15–17].

The structure, texturing, chemical composition and properties of TiN_x coatings are generally sensitive to the processing parameters employed during fabrication. For instance, the crystal structure and texture of the grown TiN_x layers are dependent on the ratio of nitrogen to argon in the reactive gas mixture during deposition [11–15,18–42]. Also, it has been reported that the texturing is strongly influenced by coatings thickness. Furthermore, TiN_x compounds with a wide range of stoichiometry i.e., x varying from 0.6 to 1.2, were found to be thermodynamically stable. Therefore, simultaneous determination of composition and crystal structure becomes important in order to optimize the processing conditions to obtain stoichiometric films for the aforementioned reasons. The present work was performed on the TiN coatings produced by direct current (DC) magnetron sputtering onto (100) silicon substrates. The impetus is to understand the effect of coatings thickness in the range of 10–120 nm on the microstructure and optical characteristics of the TiN_x nano-crystalline coatings. While the ultimate goal is to derive a comprehensive understanding of the thickness effects on the optical constants, the present work was focused on understanding the structure, morphology and residual stress of sputter-deposited TiN_x coatings.

*Corresponding author. Tel.: +1 915 747 8690; fax: +1 915 747 5019.
E-mail address: rvchintalapalle@utep.edu (C.V. Ramana).

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http://dx.doi.org/10.1016/j.ceramint.2013.11.014

2. Experimental details

2.1. Fabrication

Titanium nitride (TiN_x) coatings were deposited by DC magnetron sputtering method using a Ti-metal target(3" diameter; 0.125" thick) for sputtering. The deposition was made silicon (Si) (100) substrates. All the substrates were thoroughly cleaned using the RCA (Radio Corporation of America) procedure. Briefly, the RCA cleaning procedure removes organic, alkali ions and heavy metal contaminants present on the surface of the substrate. The cleaning procedure has three major steps. (1) Removal of insoluble organic contaminants using $5{:}1{:}1 \cdot H_2O/H_2O_2/NH_4OH$ solution. (2) Removal of ionic and heavy metal atomic components using a solution of $6{:}1{:}1 \cdot H_2O/H_2O_2/HCl$ solution. (3) Removal of native oxide by buffered oxide etching solution. Finally, the substrates were dried with nitrogen before introducing them into the vacuum chamber. The fabrication conditions employed for TiN coatings are listed in Table 1. The deposition was made using a gas mixture containing argon (Ar) and nitrogen (N_2), where Ar and N_2 were the working and reactive gases, respectively. High purity Ar (99.999%) and N_2 (99.999%) were employed for TiN depositions. A rotary feedthrough unit holds the substrate to be deposited and turns 2–3 rpm to achieve a more uniform deposition. The chamber was pumped down to a base pressure of 5×10^{-8} Torr before nitrogen and argon were introduced. The gas mixture was N_2/Ar with a ratio of 25/1. The flow rate of N_2 and Arduring deposition was controlled using gas flow meters. A sputtering power of 40 W was initially applied to the Ti-target while introducing Ar into the chamber to ignite the plasma. Once the plasma was ignited the power was increased to 200 W and high purity N_2 was released into the chamber for reactive deposition. The deposition temperature was kept constant at 400 °C for all samples with varying time of deposition to produce TiN coatings in the thickness range of 10–120 nm. The deposition rate and coating thickness were calibrated in a special control experiment. In thickness control experiments, the samples were first deposited for 5 min and then examined for thickness. In the control experiments, X-ray reflectivity (XRR) in combination with Rutherford backscattering spectrometry (RBS) was employed to determine thickness. Then, the deposition time was set to produce TiN_x coatings in the thickness (d_{TiN}) range of 10–120 nm. However, the accurate thickness for each and every deposition was determined again after film deposition i.e., ex-situ.

Table 1
Fabrication conditions of TiN coatings.

Deposition parameter	Set value
Base pressure	5×10^{-8} Torr
Target	Ti pure (99.99%) (5 cm × 0.40 cm)
Substrate	Si (100)
Substrate temperature	400 °C
Target substrate distance	8 cm
Target power	200 W
Film thickness	10–120 nm

2.2. Characterization

The grown TiN_x coatings were characterized by evaluating their structure, morphology and residual stress. In order to avoid interference by the substrate and obtain structural information of only the TiN coatings, grazing incidence X-ray diffraction (GIXRD) was performed. GIXRD measurements were performed using a BrukerD8 Advance X-ray diffractometer. GIXRD patterns were recorded using Cu Kα radiation ($\lambda = 1.54056$ Å). The X-ray beam was fixed at a grazing incidence of 0.5°. The scanning was performed in a 2θ range of 15–60° using the "detector scan" mode. The detector was independently moved to collect the diffraction pattern. From X-ray diffraction data, the interplanar spacing (d_{hkl}) between atomic planes can be determined using the Bragg's relation:

$$2d_{hkl}Sin\theta = n\lambda \quad (1)$$

where λ is wavelength of the X-rays. Titanium nitride exhibits cubic structure in a wide range of compositions. Therefore, the lattice parameter (a) of the grown coatings can be determined using the relation:

$$a = d_{\mathrm{hkl}}\sqrt{h^2+k^2+l^2} \quad (2)$$

where (hkl) are Miller indices for the diffraction planes responsible for observed XRD peaks. Surface imaging analysis was performed using scanning electron microscopy (SEM) via a high-performance and high resolution scanning electron microscope (Hitachi S-4800).

The chemical composition of grown TiN_x coatings as a function of d_{TiN} was determined by Rutherford backscattering spectroscopy (RBS) analysis using a 2.0-MeV tandem electrostatic ion accelerator that provides two stages of acceleration (negative ion acceleration from the source end to the terminal in the middle and positive ion acceleration from the middle to the high-energy end), were the final energy can be controlled depending on the charge state of the ion [43]. The accelerated ions are focused through the high-energy beam line using a magnetic quadrupole and a y-axis electrostatic steerer. The helium ion source used for this analysis was the radio frequency (Alphatross) plasma which accelerated helium ions to the sample to be analyzed in the end station where ion-scattering measurements were performed in the second level using a fixed-position detector at a scattering angle of 150° for RBS spectrometry. The beam of 2 MeV helium ions was used at the incident angle $\alpha = 7°$, the exit angle $\beta = 15°$, a scattering angle $\theta = 150°$ and a detector resolution of 20 KeV. RBS results are very accurate with heavy elements such as titanium. However, RBS is not accurate for obtaining the concentration of nitrogen incorporation into the films. For this reason, Nuclear Reaction Analysis (NRA) was also performed in order to get the accurate composition of nitrogen in the films. NRA is a well suited nuclear method to obtain concentration of lighter elements (such as oxygen and nitrogen) in a solid. A deuterium (d) beam of 0.94 MeV was used to irradiate the samples. The target elements then undergo a