Thin Solid Films 610 (2016) 1–9

Contents lists available at ScienceDirect

Thin Solid Films

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

Effect of N_2 flow rate on the microstructure and electrochemical behavior of TaN_x films deposited by modulated pulsed power magnetron sputtering

L. Mendizabal [a,*], R. Bayón [b], E. G-Berasategui [a], J. Barriga [a], J.J. Gonzalez [c]

[a] IK4-TEKNIKER, Department of Surface Physics and Technology, Iñaki Goenaga 5, 20600 Eibar, Spain
[b] IK4-TEKNIKER, Department of Tribology, Iñaki Goenaga 5, 20600 Eibar, Spain
[c] ETSIB University of Basque Country, Department of Material Science, Alameda de Urquijo s/n, 48013 Bilbao, Spain

ARTICLE INFO

Article history:
Received 19 June 2015
Received in revised form 7 April 2016
Accepted 27 April 2016
Available online 30 April 2016

Keywords:
Tantalum nitride
Modulated pulsed power magnetron sputtering
Microstructure
Surface topography
Crystal structure
Corrosion resistance
Pitting potential

ABSTRACT

Modulated pulsed power magnetron sputtering (MPPMS) technology offers the possibility to grow high performance coatings compared to the ones developed by conventional dc magnetron sputtering. The high degree of ionization of sputtered particles developed during MPPMS can be usefully utilized to precisely tailor the properties of the growing films. One of the main advantages of such a high metal ion flux is related to the densification of the coatings due to enhance ion bombardment towards the growing film. The development of extremely dense and low-defect microstructure coatings can have a positive effect on the corrosion resistance of tantalum nitride (TaN_x) films.

In this study, TaN_x thin films have been deposited by MPPMS in a closed field unbalanced magnetron sputtering system. Structure, surface morphology, hardness and corrosion resistance of the developed coatings have been analyzed as a function of different N_2-to-Ar ratios (0, 0.25, 0.625, 1). X-ray diffraction and scanning electron microscopy analysis reveal high dependence of the grown crystal phases and the microstructure on N_2-to-Ar ratio. The hardness of the TaN_x coatings increases when increasing N_2-to-Ar ratio up to a maximum value of 25 GPa (N_2-to-Ar ratio of 0.625). The corrosion behavior was investigated using electrochemical impedance spectroscopy (EIS) and linear sweep voltammetry. EIS measurements registered at different immersion times show high impedance values (in the order of 10 MΩ cm^2) and corrosion resistance enhancement with time, indicating the formation of a passive protective oxide layer on the top of their surfaces. TaN_x film grown at 0.25 N_2-to-Ar ratio exhibits the highest corrosion resistance of 103.53 MΩ cm^2 and low porosity of 1.63×10^{-3} and is characterized by columnar-free microstructure.

1. Introduction

The protective properties of transition metal nitride films deposited by reactive magnetron sputtering have been thoroughly studied for the last decades. However, the majority of studies are focused on a limited number of metals, namely Ti, Al and Cr, while other potentially attractive compounds are barely investigated. Nevertheless, the industry is continuously demanding films with improved properties and therefore, an active research is ongoing in the development of new structures, materials and deposition technologies capable to withstand the increasingly severe working conditions present in current applications. The enhancement of corrosion resistance of the magnetron sputtered films is one of the most demanding concerns. The films deposited by this technology commonly exhibit a columnar structure and a considerable high porosity. The presence of columns and porosity in the coatings will give rise to corrosion on the substrate surface since grain boundaries and open pores or pinholes represent diffusion pathways for aggressive compounds [1].

Recently, tantalum nitride (TaN) films are attracting increasing attention for thin film resistors and diffusion barriers in the microelectronics industry [2]. Likewise, they are characterized by high hardness, good wear resistance, chemical stability, excellent corrosion resistance and good shock- and heat-resistant properties. Tantalum metal (Ta) is one of the most corrosion resistant materials, exhibiting a corrosion performance similar to noble metals. It is not attacked by acids and it is biocompatible [3]. This resistance of tantalum to aggressive media is based on the formation of a highly stable and well-adherent tantalum oxide (Ta_2O_5) on the metal surface [4]. Moreover, tantalum is considered today as a possible candidate to replace electrodeposited (ED) chromium coatings often used for various tribological and corrosion resistance applications. The substitution of ED chromium coatings is expected in

* Corresponding author.
E-mail address: lucia.mendizabal@tekniker.es (L. Mendizabal).

http://dx.doi.org/10.1016/j.tsf.2016.04.043
0040-6090/

the near future due to the big concern about the generation of hexavalent chromium waste during the processing of this coating, a well-known carcinogen and environmental hazard [5].

Ta–N system is rather complex system, containing a variety of different compounds. In addition to the equilibrium phases, a lot of metastable phases have been reported [6]. Due to this complexity, the chemical and phase compositions of as-deposited TaN_x layers have been found to be critically dependent on growth conditions, primarily on nitrogen content, for all deposition techniques utilized. The mechanical and tribological properties of TaN_x films have been reported by several researchers [7–9], while the corrosion response of these films still remain unexplored.

Conventional dc magnetron sputtering is one of the state-of-art techniques for the depositions of hard coating materials, including TaN. However, when it comes to corrosion resistance evaluation, the large amount of defects typically present on sputtered films strongly jeopardizes their performance. To overcome this problem, the application of recently developed modulated pulsed power magnetron sputtering technology (MPPMS) is proposed [10].

MPPMS technique is a variation of the well-known high power impulse magnetron sputtering technology (HiPIMS) [11]. Both techniques have shown great advantages over the traditional magnetron sputtering techniques by the generation of a highly ionized metal plasma using short pulses of low duty cycle and frequency leading to peak power target densities of hundreds of $kWcm^{-2}$ [12]. The main difference between HiPIMS and MPPMS is the magnitude, duration and shape of the pulses as summarized in [13]. A typical HiPIMS pulse is a short (50–200 μs) and unique pulse which develops very high peak power densities, whereas the MPPMS pulse is much longer (500–3000 μs) and can be modulated in different steps and generally exhibits lower peak power densities than HiPIMS. This fact allows higher deposition rate values during MPPMS compared to HiPIMS which is a key feature for the successful industrialization of these processes. These modes of operation result in the generation of ultra-dense plasmas with unique properties, such as a high degree of ionization of the sputtered atoms and an off-normal transport of ionized species, with respect to the target. These features make possible the deposition of well-adherent, extremely dense and smooth coatings on complex-shaped substrates [14–15]. The possibility to deposit very dense and columnar-free microstructure Ta coatings by MPPMS technique has been demonstrated [16], but the influence of the microstructure on its corrosion response remains unknown. Moreover, the deposition of TaN films by MPPMS has not been reported yet.

Therefore, this paper deals with a preliminary investigation of corrosion resistance of TaN_x films deposited by MPPMS at different N_2-to-Ar ratios in NaCl 0.06 M electrolyte. The dependence of TaN_x corrosion response on nitrogen content in the film will be assessed. Corrosion characteristics will be also correlated with the film microstructure and crystal phases present in each coating. The final aim of this study is to select the best-performing TaN_x coating to particularly optimize it hereafter, to be applied either in biomedical implants and/or fuel cells where highly corrosion resistant coatings are needed [17,18].

2. Experimental

TaN_x films depositions were performed in a closed field unbalanced magnetron sputtering semi-industrial system designed at IK4-TEKNIKER equipped with three rectangular cathodes. A single Ta target of $133 \times 500\ mm^2$ size was sputtered in Ar/N_2 atmosphere. The base pressure of the vacuum chamber was 1×10^{-3} Pa. The employed MPPMS power supply was the SOLO/AXIS-180™ Pulsed DC Plasma Generator manufactured by Zpulser LLC, USA.

AISI 316L coupons, silicon wafers and high speed steel disks were used as substrates. After mechanical polishing to a mirror finish, the substrates were ultrasonically cleaned in acetone and ethanol for 10 min. The substrates were mounted on a substrate holder and installed at a distance of 70 mm from the target surface. The substrates were sputter etched in Ar plasma for 10 min prior to deposition for adhesion enhancement and native oxide removal from stainless steel surface. During the depositions, the working pressure was maintained at 0.7 Pa. The average power was set at 4 kW and the bias voltage was constant at −50 V. The substrate temperature was 350 °C. Prior to TaN_x coatings growth, a thin Ta interlayer film of 100 nm thickness was deposited for better adhesion between the substrate and the coating. Four different TaN_x deposition processes were carried out, characterized by different N_2-to-Ar ratio of 0, 0.25, 0.625 and 1.

The same MPP pulse was used for all depositions. The pulse length of the overall pulse is 1500 μs, which contains a 1000 μs weakly ionized micropulse to ignite the plasma in a stable condition, followed by a 500 μs stronger ionized micropulse as shown in Fig. 1.

Intrinsic parameters from MPPMS technology, i.e. voltage 'on' (τ_{on}) and voltage off (τ_{off}) times within the micropulses, are the ones developing different target voltage and current peak values and hence, are responsible for defining whether a micropulse is strong or not. τ_{on}/τ_{off} ratio is 10/30 and 12/10 for weakly and strongly ionized micropulses, respectively. The readers are referred to [19,20] for further explanation on MPPMS technique operation. The detailed deposition conditions for each TaN_x coating are summarized in Table 1.

During the processes, the voltage and current waveforms at the cathode were monitored and recorded on an oscilloscope (ISO-TECH, IDS 8064). Thickness of TaN_x films was estimated by cross-sectional scanning electron microscopy (SEM). 3 different zones along the cross-section were selected and 5 thickness measurements were made/per zone, obtaining 15 thickness values/per sample to calculate the average thickness of each TaN_x coating. The starting and ending points of the TaN_x films to measure the thickness were determined from perpendicular lines drawn using FESEM software at 90° angle with respect to the substrate Microstructure and surface morphology of TaN_x films was also analyzed by SEM.

The composition of the coatings was studied by glow discharge optical emission spectroscopy (GD-OES) measurements using a GDPROFILER 2 manufactured by Horiba Jobin Yvon. The crystal structure of the films was determined by X-ray diffraction (XRD) using grazing incidence. A Bruker AXS D8 Advance diffractometer operated in θ–2θ mode was employed using Cu Kα radiation. For hardness measurements, a Fischerscope H100VP was employed with Vickers indentation equipment, using Oliver and Pharr method [21].

Before the corrosion tests, the samples were cleaned with isopropyl alcohol and 1 cm^2 area was delimited with the help of a Slotowax coating for corrosion analysis. The corrosion performance was analyzed using a potentiostat PGSTAT 30N Autolab-Metrohm connected to a three-electrode electrochemical cell. The reference electrode was an Ag/AgCl (KCl 3 M) with a potential of 0.207 V versus standard hydrogen

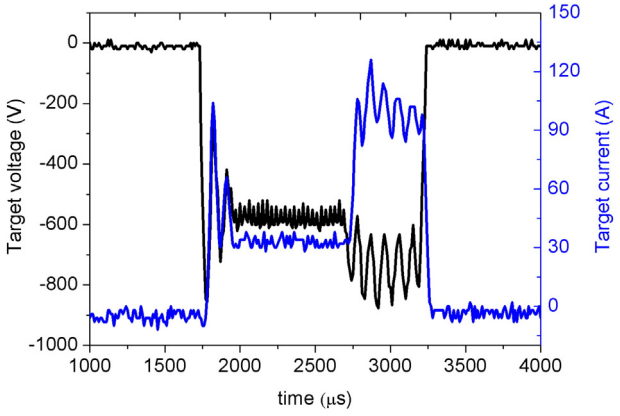

Fig. 1. Voltage–current characteristics of MPPMS pulse shape used for TaNx films deposition.