Available online at www.sciencedirect.com
SCIENCE DIRECT
Thin Solid Films 513 (2006) 136–141
thin solid films
www.elsevier.com/locate/tsf

Optical and mechanical properties of tantalum oxynitride thin films deposited by reactive magnetron sputtering

O. Banakh *, P.-A. Steinmann, L. Dumitrescu-Buforn

University of Applied Sciences, HE-ARC, Avenue de l'Hôtel-de-Ville, 7, CH-2400 Le Locle, Switzerland

Received 29 July 2005; received in revised form 7 November 2005; accepted 24 January 2006
Available online 2 March 2006

Abstract

Ta–O–N thin films were deposited by reactive magnetron sputtering from a metallic Ta target in a mixed O_2/N_2/Ar atmosphere. The ratio between Ar and the reactive gas mixture in the plasma was 1 : 1, and the O_2/N_2 ratio varied between 0.08 and 1.33. The depositions were performed without substrate heating.

The oxygen fraction $f(O) = O/(O+N)$ in the films increases linearly with O_2/N_2 ratio in the plasma and stabilises at $O_2/N_2 \geq 0.75$ corresponding to $f(O) = 0.93–0.96$.Physical and chemical properties of the Ta–O–N films strongly depend on $f(O)$. Three groups can be distinguished: films with 1) low (0.06–0.19); 2) intermediate (0.31–0.70); and 3) high (0.80–0.96) $f(O)$.

Ta–O–N films with low $f(O)$ have a metallic character and are opaque. Their optical properties show similar behaviour as that of Ta–N films, while the optical properties of the films with high $f(O)$ are identical with those of insulating Ta_2O_5. The index of refraction of the films with intermediate $f(O)$ decreases from 2.5 to 2.1 with $f(O)$. Most films are poorly crystallized and film amorphisation becomes more pronounced with increasing $f(O)$.

The nanohardness decreases with $f(O)$ and varies from 27 GPa for $f(O) = 0.06$ to 5 GPa for $f(O) = 0.96$, fluctuating around 12 GPa for the films with intermediate $f(O)$.

Keywords: Tantalum oxinitrides; Sputtering; Optical constants; Hardness; Scanning electron microscopy

1. Introduction

Transition metal oxynitrides are a relatively new class of materials with yet unexplored physical and chemical properties and a great potential for industrial applications. Tantalum oxynitride films are promising candidates for application as decorative coatings [1], dielectric layers [2,3], diffusion barriers [4–6].

Tantalum nitride is known as a chemically inert, corrosion resistant, hard material. It is used as diffusion barrier and resistor in micro- and optoelectronics [7], heat-resistant layer in mechanical industry [8], and biocompatible coating [9]. Tantalum oxide is widely used in electronics as gate dielectric and in optical devices due to its high transparency and high dielectric constant [10,11]. A combination of beneficial properties of tantalum nitride and tantalum oxide results in a new material — tantalum oxynitride — with variable composition and functionality. Changing the oxygen-to-nitrogen ratio in Ta–O–N in a wide range offers a possibility to tune the film properties by controlling the process parameters.

The paper aims at the physical and chemical characterization of reactively sputtered Ta–O–N films with emphasis on their optical and mechanical properties.

2. Experimental details

The deposition experiments were performed in an Alcatel A450 vacuum chamber (volume 48 l) evacuated with a pumping unit (mechanical and turbomolecular pumps) to a base pressure of 10^{-5} Pa. Thin Ta–O–N films were deposited by direct current (DC) reactive magnetron sputtering from a metallic Ta target (purity 99.99%, diameter 100 mm) using O_2 and N_2 as reactive gases. The applied power was kept constant at 400 W. Prior to the deposition the target was pre-sputtered in Ar plasma for 10 min. Then, the reactive gases were slowly introduced into the chamber, first nitrogen then oxygen gas, in order to prevent the plasma interruption by arcing. After a short period, needed to stabilize the target potential, the shutter on the target was opened and the depositions of the films started. Ar flow was kept

* Corresponding author. Tel.: +41 32 930 1382; fax: +41 32 930 2930.
E-mail address: oksana.banakh@he-arc.ch (O. Banakh).

0040-6090/$ - see front matter © 2006 Elsevier B.V. All rights reserved.
doi:10.1016/j.tsf.2006.01.060

constant at 7 sccm, providing a pressure of 0.5 Pa. The pumping speed was 47 l/s. The ratio between Ar and (O_2+N_2) mixture flows was 1:1. The reactive gas (O_2 and N_2) flow rates were systematically changed (increased and decreased, respectively) for each deposition, resulting in O_2/N_2 flow ratios between 0.08 and 1.33. The total working pressure was 0.7 Pa. The substrates (Si wafers, microscopic glass and stainless steel AISI 304 L) were ultrasonically cleaned in acetone (5 min) and isopropanol (5 min) prior to deposition. Then, the substrates were etched in Ar plasma using a radio-frequency generator (13.56 MHz) applying a negative voltage (U_b = −170 V) for 10 min. The substrates were not additionally heated and no bias voltage was applied during the deposition. The target-to-substrate distance was 80 mm, and the deposition time was 15 min, resulting in the film thickness between 650 and 1100 nm. No interfacial layer was used to improve the film adhesion to the substrate.

For comparison, Ta–N and Ta–O films were prepared with N_2 and O_2 as the reactive gas, respectively.

The film thickness was measured by a profilometer (Alpha-step 500, TENCOR). The chemical composition of the films on Si substrates was determined by Electron Probe Microanalysis — Wavelength Dispersive X-ray spectroscopy (EPMA — WDX; Cameca, Camebax Microbeam) using a voltage of 5 keV. The elemental concentration was calculated averaging 3 measurements performed at different areas. Complementary Rutherford Backscattering Spectroscopy (RBS) was performed on one Ta–O–N film. Cross-sectional scanning electron microscopy (SEM) observations of the films deposited on Si substrates were performed with a JEOL JMS-6400F field emission SEM at an acceleration voltage of 5 keV. The surface topography was analysed by Atomic Force Microscopy (AFM; Nanoscope III, Digital Instruments) in contact-mode on the sample area 1 μm^2 with a scanning frequency of 1 μm/s. The average surface roughness (R_a) of the films was calculated over the total analysed area. The structure of the films was studied by X-ray diffraction (XRD; Rigaku) at grazing incidence (4°) using a CuK_α radiation. Optical properties (refractive index n and extinction coefficient k) of the films deposited on Si were determined with a phase-modulated spectroscopic ellipsometer (UVISEL HR460, Jobin-Yvon Horiba Group) at an incidence angle of 70° in the energy range 0.75–4.50 eV. Hardness H and elastic modulus E of the coatings were determined by a nanoindentation depth-sensing technique (Nanohardness Tester, CSM Instruments SA) using a Berkovich-type diamond indenter. The maximum load (5 mN) was adjusted in order to ensure a penetration depth of less than 10% of the coating thickness. The values of H and E were determined by using the method described by Oliver and Pharr [12].

The residual stress of the films was determined by Stoney's equation [13] using substrate curvature radii before and after film deposition.

3. Results and discussion

3.1. Chemical composition, film structure and morphology

The chemical composition of the films was correlated with the process parameters, namely with partial reactive gas flow rate ($N_2/(N_2+Ar)$ or $O_2/(O_2+Ar)$ for Ta–N and Ta–O system, respectively) and with O_2/N_2 flow ratio for Ta–O–N films.

The N/Ta ratio of the Ta–N films increases linearly with N_2 partial flow rate, reaching 1.71 (most likely, Ta_3N_5) at N_2 partial flow rate of 57%, whereas the residual oxygen content decreases from 8 (for pure Ta) to 4 at.%. The oxygen level is quite high, especially in the Ta and Ta–N films with low N content. Although a very low base pressure in the vacuum chamber was reached, it does not prevent against film oxidation due to high reactivity of oxygen with metallic tantalum. By contrast, the addition of nitrogen hinders Ta atoms from oxidation.

The major problem encountered during the deposition of the Ta–N films is their poor adhesion to the substrate. Films deposited with high N_2 partial flow rate in the plasma stayed adherent to the steel only, but peeled off the Si and glass due to the induced by the deposition internal stress and a structural mismatch between the growing film and the substrate. Therefore, only silicon substrates were used for the film characterization, except for the Ta–N films deposited at N_2 flow higher than 25% in the plasma.

The O/Ta ratio of the Ta–O films follows the increase of the O_2 partial flow ratio. The highest O/Ta achieved in the films is 2.8, which is higher than the maximum theoretical value of 2.5 for stoichiometric Ta_2O_5. Over-stoichiometric TaO_x films with x up to 3.2 were reported previously [14]. This was attributed to O atoms trapped interstitially in the film. It is also possible that an over-estimation of O/Ta ratio occurs because of EPMA

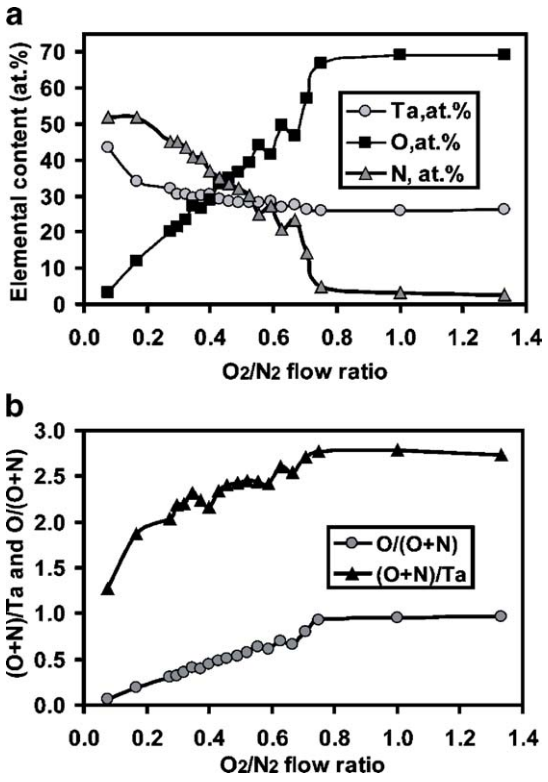

Fig. 1. (a) Elemental composition (in at.%) of the Ta–O–N films as measured by WDX. (b) Change of the metalloid-to-metal (O+N)/Ta ratio and oxygen fraction O/(O+N) in the Ta–O–N films vs. O_2/N_2 flow ratio. The estimated maximum relative error is 10%.