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Full Length Article

In-situ XRD vs ex-situ vacuum annealing of tantalum oxynitride thin films: Assessments on the structural evolution

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ABSTRACT

The purpose of this work is to discuss the main structural characteristics of a group of tantalum oxynitride (TaN_xO_y) thin films, with different compositions, prepared by magnetron sputtering, and to interpret and compare the structural changes, by X-ray diffraction (XRD), when the samples are vacuum annealed under two different conditions: i) annealing, followed by ex-situ XRD: one sample of each deposition run was annealed at a different temperature, until a maximum of 800 °C, and the XRD patterns were obtained, at room temperature, after each annealing process; ii) annealing with in-situ XRD: the diffraction patterns are obtained, at certain temperatures, during the annealing process, using always the same sample. In-situ XRD annealing could be an interesting process to perform annealing, and analysing the evolution of the structure with the temperature, when compared to the classical process.

A higher structural stability was observed in some of the samples, particularly on those with highest oxygen content, but also on the sample with non-metal (O + N) to metal (Ta) ratio around 0.5.

1. Introduction

Tantalum (Ta) thin films and tantalum ceramic thin films (oxides, nitrides and oxynitrides) have extraordinary properties allowing them to be used in several interesting applications. Tantalum (refractory metal with melting temperature around 3050 °C) and tantalum nitride can be used as resistors and heaters, in the case of Ta, but also diffusion barriers, pressure sensors and protective layers [1–7]. Particularly, the formation of a tantalum oxide layer on the surface of Ta or Ta-nitrides allows them to have high resistance to chemical attacks [2].

The potential of these materials as thin films to be used in high temperature applications is significant. Several publications can be found where the behaviour of tantalum and tantalum nitride films under annealing is studied. To the best of our knowledge, the number of studies referring the behaviour of tantalum oxynitride subjected to thermal treatments is limited. The authors have published a study about the structural stability of a set of tantalum oxynitride films [8], while J.H. Hsieh et al. [9] discussed the behaviour of TaN_xO_y thin films with and without rapid thermal annealing.

Generally, concerning the structural stability with the temperature of any material, most of the studies follow the same pattern: annealing execution, generally in vacuum, followed by structural evaluation, normally by XRD, at room temperature. Only a few studies refer to the study of the structure evolution, obtaining the XRD patterns at specific temperatures, simultaneously with the annealing process. In this work, the differences concerning the structural evolution of magnetron sputtered TaN_xO_y films are discussed, after vacuum annealing, in two conditions: the diffraction patterns were captured at room temperature, after vacuum annealing, and compared to in-situ annealing and structural evaluation by XRD.

2. Experimental details

TaN_xO_y thin films were deposited onto silicon (100) substrates by DC reactive magnetron sputtering. Before being inserted in the chamber, the substrates were cleaned with ethanol. Prior to the etching process and subsequent deposition, the chamber was evacuated to a base pressure of $1.1 \div 1.3 \times 10^{-3}$ Pa. The substrates were plasma etched for a period of 500 s, using pure argon with a partial

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pressure of ~0.3 Pa (60 sccm) and a pulsed current of approximately 0.6 A.

The substrate holder was positioned at 70 mm during all runs. A DC current density of 50 A/m^2 on the tantalum target (99.6% purity) was used. The gas atmosphere during deposition was composed of argon as plasma gas, injected from a bottle (99.999% purity) and a mixture of nitrogen + oxygen, as reactive gas, injected from a bottle with composition 85% ± 2% of N_2 and 15% ± 2% of O_2. The argon flow (70 sccm) was kept constant during all depositions, while the $N_2 + O_2$ gas mixture flow was varied from 2.5 to 35 sccm, corresponding to a partial pressure of the reactive gases ($P(N_2 + O_2)$) varying from 0.02 Pa to 0.24 Pa, which resulted in 5 different deposition conditions. The partial pressure values were registered before the plasma ignition. The films were deposited maintaining the sample holder grounded. The substrate temperature was maintained at 100 °C for all depositions. The deposition period was 1 h.

The structural stability of the TaN_xO_y films, deposited with varying reactive gas partial pressures, was studied under two different situations:

i) Annealing, followed by ex-situ XRD: The vacuum annealing of the as-deposited samples was done using a vacuum furnace, with a base pressure of 10^{-4} Pa. One as-deposited sample of each of the 5 batches suffered a thermal treatment cycle with three steps: a) an increase of the furnace temperature, with a heating rate of 5° C/min, up to the programmed temperature (T_{max} = 800 °C); b) isothermal period of 1 h at the programmed temperature; c) free cooling until reaching room temperature. X-ray diffraction patterns were obtained after the annealing process, at room temperature, using a Philips PW diffractometer (Cu-Kα radiation) in a Bragg-Brentano geometry configuration. From this point forward, this process is called "ex-situ annealing" or "ex-situ process".
ii) Annealing with in-situ XRD: The annealing was performed during High Temperature X-ray diffraction (HT-XRD) measurements, using a Bragg-Brentano geometry XRD diffractometer and Cu Kα radiation (λ = 0.154 nm). The device operated at a working voltage of 40 kV and 40 mA current, respectively. The annealings were performed in a specially designed oven (Anton Paar HTK 1200) coupled to the diffractometer. The experiments were performed at low pressure (~10^{-2} Pa). The samples were fixed on an Al_2O_3 plate and heated from room temperature gradually, to 500 °C, followed by 100 °C steps up to 800 °C. The heating rate was 30 °C/min with 60 min isothermal periods, at each temperature, for annealing and thermal stabilization. The XRD acquisition took 20 min at each selected temperature. At the end of the experiments the pressure reached in the oven was ~10^{-2} Pa. XRD diffraction patterns were obtained until the maximum in-situ annealing temperature of 800 °C, in order to compare with the ex-situ process results. From this point forward, this process is called "im room temperature gradually, to 500 °C, followed by 100 °C steps up to 800 °C. The heating rate was 30 °C/min with 60 min isothermal periods, at each temperature, for annealing and thermal stabilization. The XRD acquisition took 20 min at each selected temperature. At the end of the experiments the pressure reached in the oven was ~10^{-2} Pa. XRD diffraction patterns were obtained until the maximum in-situ annealing temperature of 800 °C, in order to compare with the ex-situ process results. From this point forward, this process is called "in-situ annealing" or "in-situ process". The annealing parameters for both processes are presented in detail in Table 1.

The in-situ and ex-situ annealing of most of the samples will be discussed and compared, with the exception of one sample (B1 of Table 2) due to the lack of data concerning the in-situ annealing. Table 2 summarizes the partial pressure of the reactive gases mixture during the deposition and the atomic composition and atomic ratios of the as-deposited samples. Nevertheless, the results obtained with sample B1 are interesting enough to be included in this study.

Table 1
Annealing temperatures of both processes and the parameter Q correspondent to the integral of the annealing temperature with time.

Annealing temperature [°C]	Type of annealing	Q [°C s]
400	ex-situ	7.23×10^4
600	ex-situ	1.37×10^5
800	ex-situ	1.98×10^5
500	in-situ	3.34×10^4
600	in-situ	7.06×10^4
700	in-situ	1.14×10^5
800	in-situ	1.62×10^5

It has to be taken in consideration that: the XRD patterns of the ex-situ annealing are obtained at room temperature, at atmospheric pressure, after the vacuum annealing at a specified temperature, while the in-situ annealing is performed in vacuum, at the specified temperature; the XRD patterns of the ex-situ process were obtained for different samples from the same batch, for each temperature, after the annealing at the specified temperature, while in the in-situ process, the same sample from one batch suffered the treatment at all the programmed annealing temperatures. During the in-situ process, at each specified temperature the sample accumulates the consequences of the annealing at lower temperatures.

The eventual structural changes of the films during the thermal annealing process are due to the amount of thermal energy transferred to the samples. The amount of thermal energy effectively transferred to the film during the annealing that causes the structural changes cannot be easily obtained. Besides structural changes, there may be other consequences, such as desorption of volatile species and/or film oxidation. Nevertheless, Table 1 presents, for each type of annealing process and for each annealing temperature, Q) calculated using Eq. (1). This parameter takes into account the temperature variation, but also the duration of the annealing until the moment of XRD pattern extraction and allows to compare the intensity of the thermal treatment imposed to the samples. Table 1 contains the results for Q, for each specified temperature (T) and type of annealing.

$$Q = \int_{t_0}^{t_f} \Delta T dt \quad (1)$$

The heating rate of the ex-situ annealing is six times lower. This is one of the reasons why the Q value for the ex-situ process at the highest temperature (800 °C), is larger than the one of the in-situ process at the same temperature. Another reason is that in the ex-situ process, the Q value is calculated from the beginning of the process (at room temperature) until the end of the annealing, when the temperature drops to room temperature. The duration of the cooling process is significant. During the in-situ process, the Q value is calculated from the beginning of the process (at room temperature) until the end of the considered annealing temperature, not considering the cooling time, because the XRD pattern is obtained at the considered temperature. In the in-situ process the annealing continues until 800 °C. Just to reinforce this, even at the lowest temperature (400 °C) of the ex-situ thermal treatment, Q has a larger value than in the case of the in-situ thermal treatment at T=600 °C.

Elastic Back Scattering (EBS) [10,11] measurements were made in a chamber with three installed detectors: one at 140° scattering angle, and two pin-diode detectors located symmetrical to each

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