Effect of the rapid thermal annealing on the structural properties of TaO_xN_y thin films deposited by reactive magnetron sputtering

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Abstract. Tantalum oxynitride thin films are deposited by radio-frequency magnetron sputtering using a pure tantalum target under argon/oxygen/nitrogen gas mixture. The argon flow is kept constant while the oxygen and nitrogen flows are changed simultaneously in a way to keep constant the total flow of these reactive gases. We succeed to deposit TaO_xN_y films with stoichiometry ranging between those of TaN and Ta_2O_5. All films are deposited at room temperature without any biasing. A thermal annealing in a RTA furnace was applied to all the films in a nitrogen atmosphere. A phase transition was detected by XRD investigations and SEM scanning from as deposited to annealed films, noticing the crystallisation of all films which depends on the composition of each film.

1. Introduction

The integration of antireflective coatings in optical applications has made an important improvement in their performance. The simplest antireflective coating consists of a single layer of transparent material with an optimum refractive index. The efficiency is improved by a multilayer structure formed by a succession of layers with graded refractive indices. These films are the essential component of electroluminescent devices used particularly in lighting applications (panel backlighting to liquid crystal displays) providing good illumination by consuming relatively little electric power, and frequently used as protective and antireflection coating in eyeglass lenses and solar panels. Tantalum pentoxide (Ta_2O_5) is used as gate dielectric in electronics, optical devices and in antireflective coatings due to its high transparency, high dielectric constant [1, 2], large band gap and its large refractive index (~2.3 at 632.8 nm) [3]. Tantalum nitride (TaN) is a hard material, resistant to the corrosion and chemically inert, is used for hard and wear resistant coatings [4], as diffusion barrier [5], as well as film resistors since its electrical resistance is very stable [6] and it possesses metallic behavior. Combining the useful properties of oxide and nitride allows obtaining all the qualities in oxynitride material supervised by controlling the process parameters. Tantalum oxynitride films are promising candidates for applications as electroluminescent devices, decorative coatings, dielectric layers [7] diffusion barriers [8] and antireflective coatings due to the wide range of variation of their refractive index between 2.3 and 3.8.

The reactive magnetron sputtering represents a good candidate to deposit optical and electrical structures on sensitive substrates due to the lower work temperatures. The possibility of variation of several deposition parameters such as pressure, gas flows, target, power, etc. allows obtaining a wide range of film stoichiometry; thereby it permits to deposit layers with graded composition.

In this work we deposit TaO_xN_y thin films by reactive magnetron sputtering from a pure tantalum target with $Ar/O_2/N_2$ plasma. We focus our interest on the investigation of the annealing effect on the structural properties of our films and what advantage could this annealing provide to the optical properties which will be published later on.

2. Experimental details

TaO_xN_y thin films were deposited at room temperature by radio-frequency magnetron sputtering in an Alcatel A450 vacuum chamber, using a pure tantalum target (99.99%) under argon/oxygen/nitrogen gas mixture. A constant power density of 3.18 $W.cm^{-2}$ was applied. Initially, the chamber was evacuated to a base pressure of $5x10^{-4}$ Pa. The work pressure varied between 1 and 1.2 Pa. Prior to film deposition, target was cleaned in Argon plasma for 15 minutes. The argon supply was kept constant while oxygen and nitrogen were varied simultaneously in a way to keep a constant total flow of these reactive gases which is presented by the $R_F=F_{O2}/(F_{O2}+F_{N2})$ ratio. The choice of the total reactive gases value gives us the opportunity to deposit films with large variation of stoichiometry without being in a completely poisoned mode. Below this value all the films had a metallic appearance, with composition very rich on tantalum, and above this value only nitride-like and oxide-like films were obtained. In this study, we deposit the thin films on different substrates: quartz, silicon, and vitreous carbon. All the substrates were ultrasonically cleaned in ethanol (10 min). Rapid thermal annealing of the films was realised in a JIPELEC JETFIRST furnace at 900°C under nitrogen atmosphere after pumping the furnace chamber to eliminate the maximum of residual oxygen. The chemical composition was investigated by RBS at CEMHTI (Orléans-France), using 2 MeV alpha particles. The experimental results were correlated with numerical simulations made by SIMNRA code. Structural properties of as deposited and annealed films were studied by X-ray diffraction employing a PHILIPS X'PERT Diffractometer using CuK_α radiation. Typical patterns were recorded in 10°- 70° 2θ range. Surface morphology of the films was observed by scanning electron microscopy SEM using a ZEISS SUPRA 55VP, with an acceleration voltage of 50 kV.

3. Results and discussion

3.1 Chemical composition

Figure 1 shows the ratio of O/O+N content of the films as a function of R_F before and after annealing. We notice that tantalum content on the films before and after annealing varies only between 27 and 33 at. %. A wide variation of stoichiometry between those of TaN and Ta_2O_5 was obtained by controlling plasma composition in oxygen and nitrogen. The annealed films show a little increase of oxygen content in their composition; In fact, even in a pure nitrogen atmosphere, some residual oxygen persists on the chamber of the furnace. During the annealing, atoms will reorganized and the residual oxygen benefits to incorporate in the structure. This is due to the fact that oxygen atoms have a stronger affinity to tantalum atoms than that of nitrogen [9].

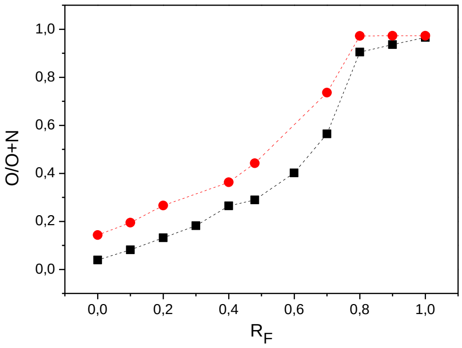

Figure 1. Oxygen and nitrogen content in the films as a function of R_F for as deposited (square) and annealed (circle) films.

3.2 Structure and morphology

XRD patterns of the as deposited films (figure 2) exhibit a variation of the structure with the deposition conditions. Films deposited in a nitrogen/argon plasma (R_F=0), exhibit 4 diffraction peaks which correspond to the cubic phase of TaN, same structure was obtained by other authors [10]. This crystallite structure is well seen by the granular surface showed by SEM image (figure 3,a). To assume, the grain size calculated using the Debey Sherrer's formula from the diffraction peaks and that estimated from the SEM image are in coherence (between 3.2 and 5.4 nm). For oxynitride films, the diffraction peaks disappear and a large peak remains around 2θ=34°, it could be assigned to a quasi-amorphous structure with nanocrystallites embedded in an amorphous matrix [11] which leads to a smoother surface showed by SEM (figure 3.b). For oxygen-rich films (R_F>0.48), no diffraction peaks were observed in the diffraction patterns and the SEM image (figure 3.c) shows a completely smooth surface which puts in evidence the amorphous structure of these films.

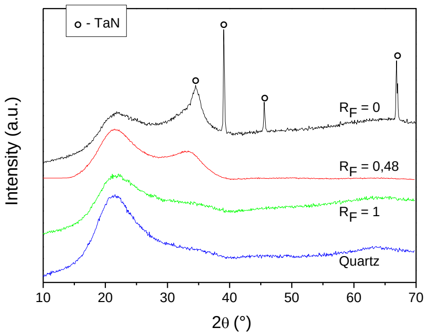

Figure 2. XRD patterns for as deposited films at RF = (b) 0; (c) 0.48 and (d) 1.

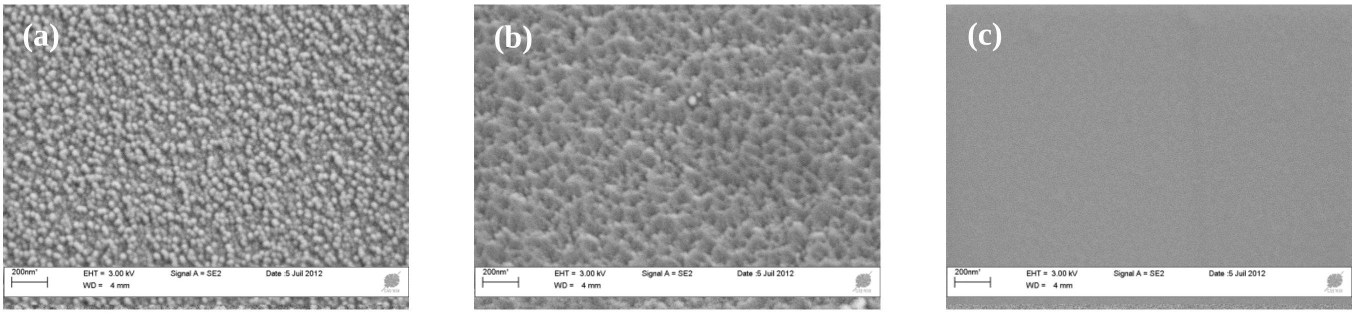

Figure 3. SEM images for as deposited films at RF = (a) 0; (b) 0.48 and (c) 1.

Figure 4 shows the XRD patterns of the films after rapid thermal annealing. We note a variation on the structure for all films after annealing. Nitrogen-rich film (R_F=0) shows three peaks at 2θ = 35; 36 and 61° associated to the Ta_3N_5 orthorhombic phase. Its SEM image (figure 5.a) shows granular surface with some pores. Film with intermediate composition (R_F=4.8) exhibits crystalline TaON peaks with monoclinic structure. Its SEM image (figure 5.b) shows granular surface with some pores and a crack due to the thermal stress in the film. Upon increasing the oxygen content, orthorhombic Ta_2O_5 thin films have been formed after annealing for films deposited at R_F=1, with islands of grains surrounded by well-defined grain boundaries (figure 5.c)

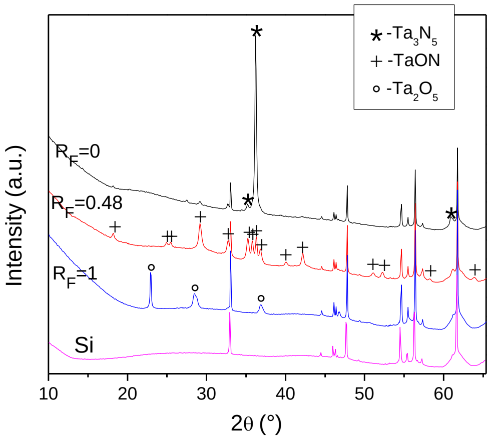

Figure 4. XRD patterns for films deposited at RF = (b) 0; (c) 0.48 and (d) 1 after RTA annealing at 900°C.

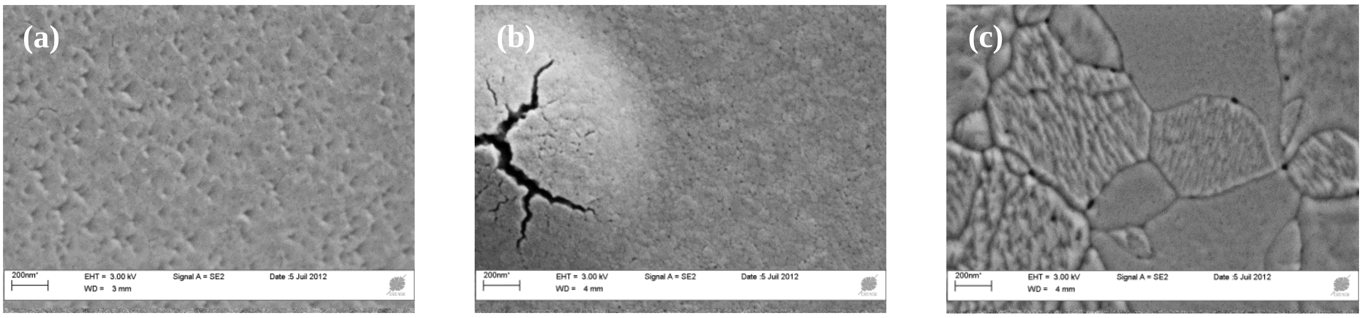

Figure 5. SEM images for films deposited at RF = (a) 0; (b) 0.48 and (c) 1 after RTA annealing at 900°C.

4. Conclusion

Thin TaO_xN_y films were deposited by reactive magnetron sputtering in an $Ar/O_2/N_2$ atmosphere. Wide variation of stoichiometry spanning the range between tantalum nitride and tantalum oxide was obtained by controlling the plasma composition. Rapid thermal annealing under nitrogen atmosphere leads to a little increase of oxygen content due to the residual oxygen in the furnace chamber but conserve the wide variation of stoichiometry. Structural and morphological variations were investigated for three types of films before and after RTA. As deposited TaN_x films shows a cubic TaN structure which transforms to orthorhombic Ta_3N_5 after annealing. TaO_xN_y films with intermediate composition show, before annealing, amorphous structure with nanocristallytes embedded on an amorphous matrix which is transformed into monoclinic TaON structure after annealing. And films with high oxygen content, TaO_x-like films, exhibit an amorphous structure which became orthorhombic Ta_2O_5 structure after annealing. The controlled variation of film's stoichiometry as well as the variation of the structure with the annealing gives us the opportunity to study their effects on the optical properties in view of their use as antireflective graded layers.

5. References

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