OPTICAL PROPERTIES OF TANTALUM OXIDE THIN FILMS OBTAINED BY LASER DEPOSITION TEHNIQUES

George STANCIU[1], Mihaela FILIPESCU[2], Valentin ION[3], Ecaterina ANDRONESCU[4], Maria DINESCU[5]

Tantalum oxide is a compound with attractive properties and important applications in optoelectronis. It has a high refractive index and a good thermal and chemical stability. Tantalum oxide thin layers have been deposited by laser ablation-pulsed laser deposition (PLD) and radiofrequency assisted pulsed laser ablation (RF-PLD) starting from a Tantalum metallic target in oxygen atmosphere.

In the present paper the influence of deposition parameters (laser wavelength, substrate temperature and r[6]adiofrequency power) on the morphology and the optical propert[7]ies was studied.The investigation techniques used for the characterization of the deposited layers were atomic force microscopy and spectroellipsometry.

Keywords: Tantalum oxide thin films, pulsed laser deposition, radiofrequency oxygen plasma, spectroscopic ellipsometry

1. Introduction

Tantalum oxide dielectric thin films (in particularly Ta_2O_5) are widely used for optical and microelectronic applications. Due to their excellent transparency, chemical and thermal stabilities, tantalum oxides are used in optical communication technology. Thus, it is used as high refractive index and low loss materials for interference filters, anti-reflective coatings (solar cells, for example), optical waveguides and electroluminescent devices [1, 2]. Due to its high dielectric constant (□$_r \approx$ 25) it is likely to replace thin SiO_2 layers as capacitor insulators in high density dynamic random access memories [3, 4].

[1] Ph.D. student, Faculty of Applied Chemistry and Material Science, University POLITEHNICA of Bucharest, Romania; e-mail: georgestanciu00@yahoo.com
[2] National Institute for Laser, Plasma and Radiation Physics, Magurele, Bucharest, Romania
[3] National Institute for Laser, Plasma and Radiation Physics, Magurele, Faculty of Physics, University of Bucharest, Romania
[4] Prof., Faculty of Applied Chemistry and Material Science, University POLITEHNICA of Bucharest, Romania
[5] National Institute for Laser, Plasma and Radiation Physics, Magurele, Bucharest, Romania

The tantalum oxide as thin films can be produced by various techniques like Chemical Solution Deposition (CSD) [5], Metal Organic Chemical Vapor Deposition (MOCVD) [6], Plasma Enhanced Chemical Vapor Deposition (PECVD) [7], Low Pressure Chemical Vapor Deposition (LPCVD) [8], Reactive Magnetron Sputtering [9] and Pulsed Laser Deposition (PLD) [10,11].

The PLD is an advantageous technique that has demonstrated unique features for producing high-quality thin films of numerous materials which are chemically or structurally complex. High-temperature superconductors and ferroelectrics are examples of materials that were successfully grown by PLD [10,11]. Most of the depositions were performed using ArF excimer lasers (with a wavelength λ= 193 nm) [12,13], KrF excimer laser (λ = 248 nm) [14], or the second or third harmonic of Nd:YAG laser (λ = 532 or 355 nm, respectively) [15,16]. In order to increase the reactivity in the growth area on the substrate, a radio-frequency (RF) discharge plasma beam to the PLD system can be used [17].

The aim of this work is to obtain smooth and crystalline tantalum oxide (specially Ta_2O_5) thin films for application in optoelectronics.

2. Experimental

Thin films of tantalum oxide (Ta_xO_y) were obtained by PLD and RF-PLD starting from a tantalum metallic target and collected on silicon (Si) substrate at room temperature and platinum coated silicon (Pt/Si) substrates at 400 °C. A Nd:YAG laser operating in UV range with a laser fluence of about 3 J/cm^2 was used. All depositions were made in reactive oxygen atmosphere. The distance between target-substrate was fixed at 4 cm, oxygen gas pressure during deposition was 5×10^{-2} mbar and the power of RF plasma was of 150 W. The main deposition parameters are listed in Table 1.

The influence of deposition parameters (substrate temperature and radiofrequency power) on the morphological and optical properties was studied. As investigation techniques Atomic Force Microscopy (AFM) and Spectroellipsometry (SE) were used.

Table 1. Deposition parameters of Ta_xO_y thin films obtained by PLD and RF-PLD.

Sample	**Substrate**	**$T_{Substrate}$ (°C)**	**N_{Pulse}**	**P_{RF} (W)**
1	Si	RT (~ 23)	20000	-
2	Si	RT (~ 23)	20000	150
3	Pt/Si	400	15000	150
4	Pt/Si	400	15000	-

2.1. Atomic Force Microscopy

The atomic force microscope was a XE 100 model from Park System. It has the capability to scan the samples in contact mode, non-contact mode and intermittent contact mode. The maximum horizontal scan range is about 50×50 μm² and the maximum vertical movement is 8 μm. Depending on the scanning mode, on the nature of the surface and on the tips we use, a lateral resolution of tens of nanometers can be achieved.

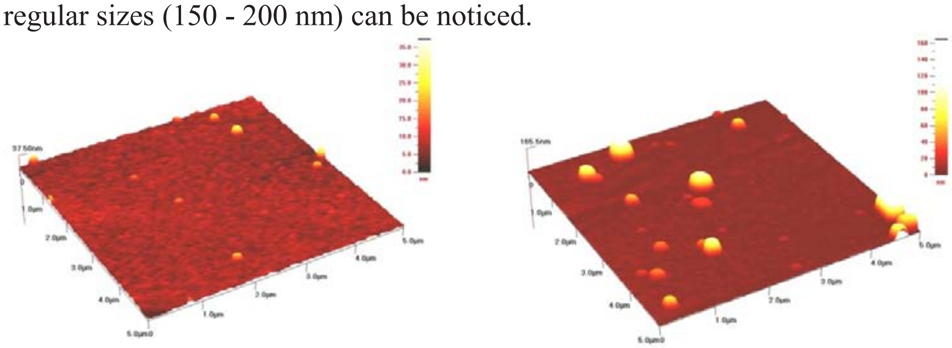
Atomic Force Microscopy, working in non-contact mode, was performed in order to analyze the films surface features and roughness, on different areas (20 × 20 μm² and 5 × 5 μm²).

2.2. Spectroellipsometry

Ellipsometry measures the change in polarization state of reflected or transmitted light of a material. An ellipsometer essentially measures two quantities. These are Delta, the phase difference between the p-waves and the s-waves induced by the reflection from sample, and Psi, the ratio of the diminution of the field intensity of the two wave components. A rather complex data analysis is required in order to determine thickness and index values from the Delta and Psi values [18]. The detail theory of ellipsometry is covered in various other works and will not be repeated here.

3. Results and discussion

Studying the morphology of the samples 3 and 4 obtained in the same conditions of temperature and pressure but using different techniques (PLD) and (RF-PLD) was observed that addition of radiofrequency plasma leads to considerable decreasing of the surface roughness (from 14 nm for sample obtained by PLD to 2 nm for sample obtained by RF-PLD). In the presence of the RF plasma the surface of the thin film becomes uniform, without droplets or pores. In the figure 1 a), the presence of compact “grains” with round shapes and regular sizes (150 - 200 nm) can be noticed.



a) **b)**

Fig. 1. AFM images for Ta_xO_y thin films deposited on (Pt/Si) heated at 400 °C in 5×10^{-2} mbar of oxygen by: a) RF-PLD and b) PLD.

In order to obtain the dielectric function in the wavelength interval 300-1550 nm, the spectroscopic ellipsometry technique was use. The optical model was necessary to be build.

In this case, the optical model consists of 4 layers: the silicon substrate, the native SiO_2, the Ta_xO_y layer and the rough top layer which is set to have half air and half Ta_xO_y. The dielectric function of the rough layer is calculated using the Bruggeman effective medium approximation [18]. The dielectric function for substrates are taken from literature [19, 20].

For films deposited on Pt/Si, the platinum layer is thick enough (150 nm) to be considered as a substrate. In ellipsometry there are 3 unknown parameters: the thickness, the refractive indices and the extinction coefficients. The best quality of the fit can be obtained when one or two parameters are fixed. Also, the behavior of optical constants (or dielectric function) needs to respect the Kramers-Kroning law [18].

In order to have one fixed parameter, the experimental data are fitted using the Cauchy formalism in the range of 600 - 1200 nm wavelength. Using this step, the thickness of samples, the thickness of top rough layers and also the preliminary optical constants are obtained. The Cauchy parameters and the roughness comparison between AFM (RMS) and SE are presented in table 2.

Table 2

Cauchy parameters for Ta_xO_y thin films obtained by PLD and RF-PLD.

Sample	Thickness (nm)	Roughness (nm)	An	Bn	RMS (nm)	MSE
1	148.918±0.525	23.189±1.02	1.7513±0.00202	0.006082±0.00104	7.3	12.98
2	311.122±3.1	3.49±0.02	1.7185±0.00743	0.0094681±0.00178	3.9	80.21
3	147.182±1.08	9.021±1.56	1.9732±0.00694	0.025962±0.00198	1.8	13.37
4	130.788±0.915	4.908±1.18	2.1171±0.00917	0.023432±0.00253	14.4	1.989

For Cauchy the dependence of refractive indices with wavelength is given by equation:

$$N_n = A_n + B_n/\lambda^2 + C_n/\lambda^4 \quad (1)$$

where: A_n, B_n and C_n are constants.

In figure 2 the experimental data and the model data obtained by fitting with a Cauchy equation in range of wavelength 500 - 1200 nm, are presented. The value of MSE, that express a difference between experimental and model, is very small for sample 1 (MSE = 12.98). The experimental and model curves are the same and this is an indication of good fitting procedure.

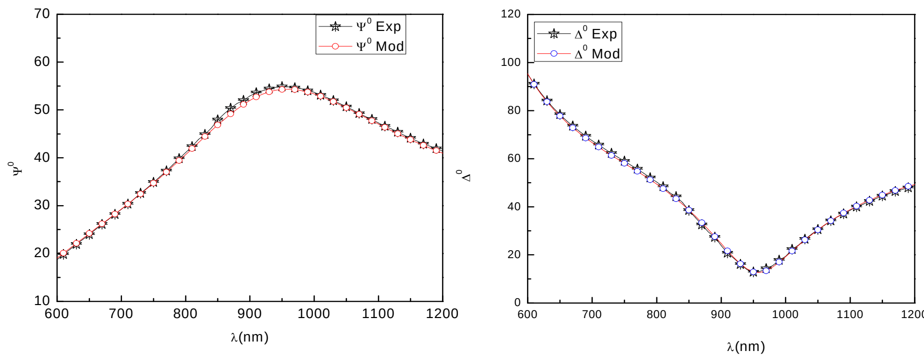


Fig. 2. Experimental and model curve for ψ and Δ for the sample 1 obtained by fitting with Cauchy dispersion formula.

After the thickness of samples and thickness of their rough layer were fixed, the range of wavelength was extended on full measured spectrum, between 300 - 1500 nm. The Cauchy equation was replaced with a Tauc-Lorentz oscillators [21] that well models the dielectric function of many amorphous materials and having the dielectric function written as: $\varepsilon = \varepsilon_1 + j\varepsilon_2 = (n + jk)^2$.

$$\varepsilon_{n\_T-L} = \varepsilon_{n1} + i\varepsilon_{n2}, \tag{2}$$

$$\varepsilon_{n2} = \left[\frac{A_n E_{0n} C_n (E - Eg_n)^2}{(E^2 - E_{0n}^2)^2 + C_n^2 E^2} \cdot \frac{1}{E} \right] \qquad E > Eg_n \tag{3}$$

$$\varepsilon_{n2} = 0 \qquad E \le Eg_n$$

$$\varepsilon_{n1} = \frac{2}{\pi} p \int_{Eg_n}^{\infty} \frac{\zeta \varepsilon_{n2}(\zeta)}{\zeta^2 - E^2} d\zeta \tag{4}$$

$$Ampn = A_n(eV),\ Enn = E_{0n}(eV),\ Cn = C_n(eV),\ Egn = Eg_n(eV)$$

where: A, E_0 and C are dispersion parameters in the following limits: $E_0 > Eg$ and $C < 2E_0$. The total dielectric function is expressed as: $\varepsilon = \varepsilon_\infty + \varepsilon_{TL}$ where ε_∞ is permittivity at ∞ frequency (e_1 in table 3).

In figure 3 are presented the experimental and generate data for the sample 1, resulted from fitting with a Tauc-Lorentz oscillator on entire measured range of wavelength (300 - 1550 nm). The Tauc-Lorentz parameters, obtained for all samples are presented in table 3.

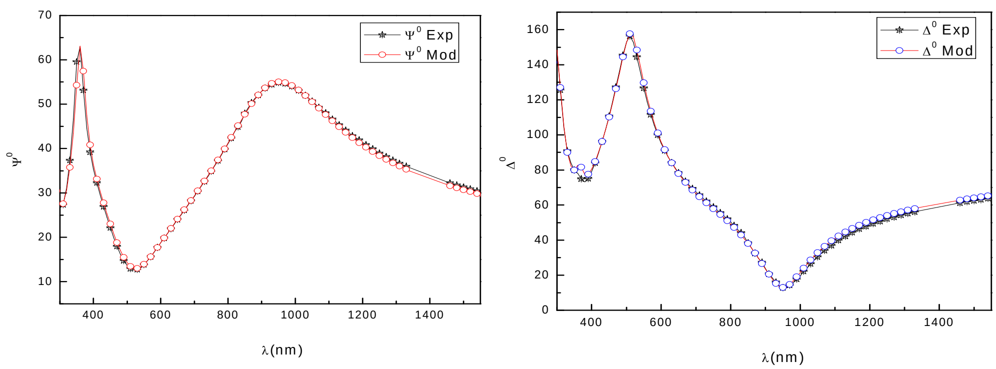


Fig. 3. Experimental and model curve for ψ and Δ for the sample 1 obtained by fitting with Tauc-Lorentz oscillator.

Table 3

Tauc-Lorentz parameters for Ta_xO_y thin films obtained by PLD and RF-PLD.

Sample	Amp	En (eV)	C	e1	Eg (eV)	MSE
1	61.702±9.09	6.3446±0.196	1.9084±0.55	1.7662±0.156	3.9335±0.071	32.17
2	96.856±5.3	6.3701±0.578	3.6776±0.25	1.4995±0.556	4.1372±0.143	93.69
3	24.381±1.84	5.9322±0.0582	0.77945±0.0439	2.2232±0.0646	4.1221±0.0731	21.96
4	242.15±39.2	5.5573±0.125	3.0289±0.61	1.3025±0.295	4.0093±0.0355	4.763

Using these Tauc-Lorentz parameters the values of refractive indices are generated for all samples obtained by PLD and RF-PLD (see figure 4). The value of extinction coefficients is zero (k = 0) on whole measured range because the optical band-gap for almost of samples are higher than 4 eV (λ < 310 nm).

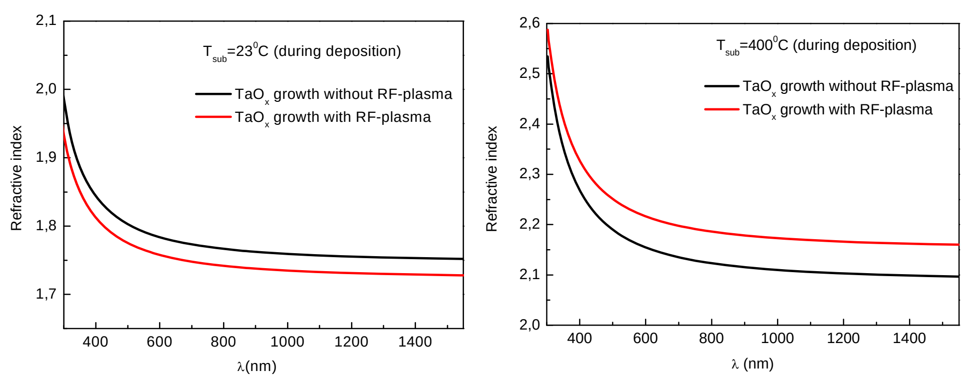


Fig. 4. The refractive index behavior for: left – Ta_xO_y thin films obtained at room temperature on Si substrate and right - Ta_xO_y thin films obtained at 400 °C substrate temperature on Pt/Si.

When the thin films are growth at room temperature on silicon substrates covered by amorphous native oxide, a smaller value of refractive indices than the normal value (in crystalline phases) is obtained. In figure 4 in left sides it can observe the variation in values of refractive indices when the pulsed laser deposition is assisted by RF plasma. The refractive index is smaller than the value obtained by simple PLD but the value of optical band gap is increased from Eg = 3.93 eV (PLD) to Eg = 4.13 eV (RF-PLD) and this behavior is an indication of a good transparency of the Ta_xO_y films.

When the temperature of substrates (400 $^{\circ}$C) is changed, during the deposition process a higher value (right side of figure 4) of refractive indices ($n > 2$) it is obtained, which is a normal behavior for this material [22]. The values of refractive indices increase when the thin film are deposited using a RF plasma in PLD process and the value of optical band-gap Eg = 4.12 is higher than Eg obtained by PLD (Eg = 4.00). A values of 4.1 - 4.2 eV was reported in literature for Ta_2O_5 [22].

For both cases the addition of RF plasma in pulsed laser deposition process has a high influence on optical transparency of tantalum oxide thin films, even if the layer are obtained on substrates at room temperature.

4. Conclusions

Smooth and highly transparent tantalum oxide thin films have been obtained by conventional laser ablation and RF assisted laser ablation starting from metallic tantalum target in oxygen reactive atmosphere. Spectroscopic ellipsometry studies were used to characterize the deposited thin films and the dispersion of the refractive index of the obtained layers was presented. Complementary analysis performed with the AFM confirms the surface roughness and show that the deposited layers are cracks and pore free. The higher value of the band gap, for both cases of substrate and substrate temperature during deposition was obtained when the reactive RF plasma was used.

Acknowledgements

This work has been funded by Sectoral Operational Programme Human Resources Development 2007 - 2013, POSDRU/88/1.5/S/61178.

R E F E R E N C E S

[1] *K.D. Pollard, R.J. Puddephatt,* Chem. Mater. **11** (1999) 1069.
[2] *C.L. Tien,* Influence of ejection angle on residual stress and optical properties of sputtering Ta_2O_5 thin films, Applied Surface Science **255** (2008) 2890–2895.

[3] *S. Boughaba, G.I. Sproule, J.P. McCaffrey, M. Islam, M.J. Graham,* Synthesis of tantalum pentoxide films by pulsed laser deposition: material characterization and scale-up, Thin Solid Films **358** (2000) 104-113.
[4] *K. Schmitt, K. Oehse, G. Sulz and C. Hoffmann,* Evanescent field Sensors Based on Tantalum Pentoxide Waveguides – A Review, Sensors 2008, **8**, 711-738.
[5] *P.C. Joshi, M.W. Cole,* Influence of postdeposition annealing on the enhanced structural and electrical properties of amorphous and crystalline Ta_2O_5 thin films for dynamic random access memory applications. J. Appl. Phys. 1999, **86,** 871-880.
[6] M.S. Mattsson, G.A. Niklasson, A frequency response and transient current study of ß-Ta_2O_5: methods of estimating the dielectric constant, direct current conductivity and ion mobility, J. Appl. Phys. 1999, **85**, 2185-2191.
[7] *B.C. Lai, J.C. Yu, J.Y. Lee,* Ta_2O_5/Silicon barrier height measured from MOSFETs fabricated with Ta_2O_5 gate dielectric, IEEE Electron Device Letters 2001, **22**, 221-223.
[8] *J.W. Kim, S.D. Nam, S.H Lee, S.J. Won, W.D Kim, C.Y. Yoo, Y.W. Park, S.I. Lee, M.Y. Lee,* Electrical properties of crysatalline Ta_2O_5 with Ru electrode, Jpn. J. Appl. Phys. 2000, **39**, 2094-2097.
[9] *B.R. Jooste, H.J. Viljoen,* A study of piezoelectric orthorombic Ta_2O_5, J. Mater. Res. 1998, **13**, 475-482.
[10] *D.B. Chrisey, G.K. Hubler,* Pulsed Laser Deposition, Wiley, New York, 1994.
[11] *D. Bäuerle,* Laser Processing and Chemistry, Springer-Verlag, Berlin 1996, p. 397.
[12] *Y. Nishimura, A. Shinkawa, H. Ujita, M. Tsuji, M. Nakamura,* Appl. Surf. Sci. **136** (1998) 22.
[13] *N. Inoue, T. Monnaka, S. Kashiwabara, R. Fujimoto,* Appl. Surf. Sci. **127-129** (1998) 536.
[14] *T. Ooie, T. Yano, M. Yoneda, M. Katsumura,* in: *W. Duley, K. Shibata, R. Poprawe (Eds.),* Proc. ICALEO'96, Vol. **81** Laser Institute of America, Orlando, FL, 1996, p. 161.
[15] *Z. Mingfei et al.,* Appl. Surf. Sci. **108** (3) (1997) 399.
[16] *J.Y. Zhang, Q. Fang, I.W. Boyd,* Appl. Surf. Sci. **138/139** (1999) 320.
[17] *G. Dinescu et al.,* Influence of the radiofrequency plasma beam addition on the properties of pulsed laser deposited films, Proceedings SPIE **5448** (2004) 136-143.
[18] *H. Fujiwara*, Spectroscopic Ellipsometry Principles and Applications, Maruzen Co. Ltd., Tokyo, Japan, 2007.
[19] *C.M. Herzinger, B. Johs, W.A. McGahan*, J.A. Woollam,W. Paulson, Ellipsometric determination of optical constants for silicon and thermally grown silicon diox- ide via a multi-sample, multi-wavelength, multi-angle investigation, J. Appl. Phys. **83** (615) (1998) 3323–3336
[20] Palik, Edward D., Handbooks of optical constants of solids: Platinum, pp. 340-341, 1998
[21] *G.E. Jellison, Jr. and F.A. Modine,* Parameterization of the optical functions of amorphous materials in the interband region, Appl. Phys. Lett. **69**, 371 (1996), Erratum, Appl. Phys. Lett. 69, 2137 (1996).
[22] *K. Postava, M. Aoyama, T. Yamaguchi, H. Oda,* Spectroellipsometric characterization of materials for multilayer coatings, Applied Surface Science **175-176** (2001) 276-280.