Scientific Report

Regarding the project development during JANUARY– DECEMBER 2012

Introduction

Nowadays, due to industrial development, the environmental pollution becomes a very important issue. Every day, industry and motor vehicles produce toxic gases such as nitrogen oxides, carbon monoxide, sulfur dioxide, etc. The development of detection systems and building sensors that detect these gases, particularly nitrogen oxides, showed the interest for researchers and industry specialists. A compound that presents great interest for applications in sensors is tungsten oxide (WO_X). Particularly, it shows high sensitivity for NO_2 detection.

The necessity for miniaturization and lower production costs imposed the obtaining of different nanostructures such as nanoparticles, nanofibers, nanotubes, nanostructured thin films, clusters that allow an increase of sensitivity due to the high specific area and small grains size.

In last decades, in order to obtain nanostructures, numerous techniques more or less laborious with advantages and disadvantages have been developed. A simple, clean and versatile technique is laser ablation (Pulsed Laser Deposition - PLD). The addition of a radio frequency (RF) generator to the PLD system produces a discharge in reactive or inert gas and leads to an increase of reactivity in the growth area of the film onto substrate, contributing to the control of compound stoechiometry. Also, the nanostructures size can be controlled.

The aim of this project is the deposition of tungsten oxide (WO_X) as nanostructured thin films and cluster assembled (CA) by PLD and RF-PLD. These structures should be crystalline, the grains or clusters should have regular and controllable sizes for applications in sensors field.

Activity 1.1: *Preparation of deposition and characterization equipments;*

The experimental set-up for the WO_X nanostructures growth consists from a laser (ArF - 193 nm or YAG: Nd - 532 nm, 1064 nm), a reaction chamber, a vacuum pump system, a temperature controller, a heater onto the substrates (Si (100) and Corning glass) are placed, a translational-rotation system for the target (WO_3 ceramic) and a gas flow controller. The radio-frequency generator is working at 13.56 MHz and a maximum power of 1000 W.

In order to characterize the obtained structures, next techniques were used: Raman spectroscopy and X-ray diffraction - XRD for structure determination, atomic force microscopy - AFM and scanning electron microscopy - SEM (morphological study), secondary ion mass spectrometry - SIMS (composition determination) and ellipsometry (optical properties).

Activity 1.2: *The obtaining of WO_X nanostructured thin films by PLD and RF-PLD;*

In order to obtain nanostructured thin films, a number of thirty samples of tungsten oxide were deposited in different conditions of temperature (21°C to 600° C), pressure (10^{-5} mbar, 0.01 mbar, 0.1 mbar) and gas composition (oxygen, argon or a mixture of 50% Ar + 50% O_2). The RF discharge power was fixed at 150 W and the laser fluence was set to 3 J/cm^2. The number of laser pulses ranged between 10000 and 40000.

Activity 1.3: *Structural, morphological and compositional characterization of WO_X nanostructured films;*

From X-ray diffraction can be observed that the target is monoclinic predominantly. The substrate temperature (Ts) is an important factor that influences the WO_X thin films structure. The films deposited at λ = 1064 nm and room temperature (RT = 21 °C) show an amorphous character and those deposited at Ts = 600 °C have a crystalline structure. The wavelength (λ) is another parameter that influences the crystallinity: the films grown by PLD and RF-PLD at high Ts and λ = 1064 nm exhibits a predominantly monoclinic WO_3 as that of the target (Fig. 1).

In order to determine the structure of thin films grown at λ=193 nm, the Raman spectroscopy was used. The influence of pressure at constant temperature or vice versa on the structural modification was investigated. It was observed that the films deposited by RF-PLD at 600°C and 0.01 mbar of (Ar + O_2) show a mixture of two dominant phases (so called *new* - ***N***) and also a monoclinic-γ phase. The spectrum peaks from Fig. 2a shows a stoechiometric WO_3 thin film. The band from 960 cm^{-1} is attributed to the "stretching" mode of $W^{6+} = O$ bond, probably located on the surface of clusters and "nanovoids" in the film, being a fingerprint of nanostructure development in the film.

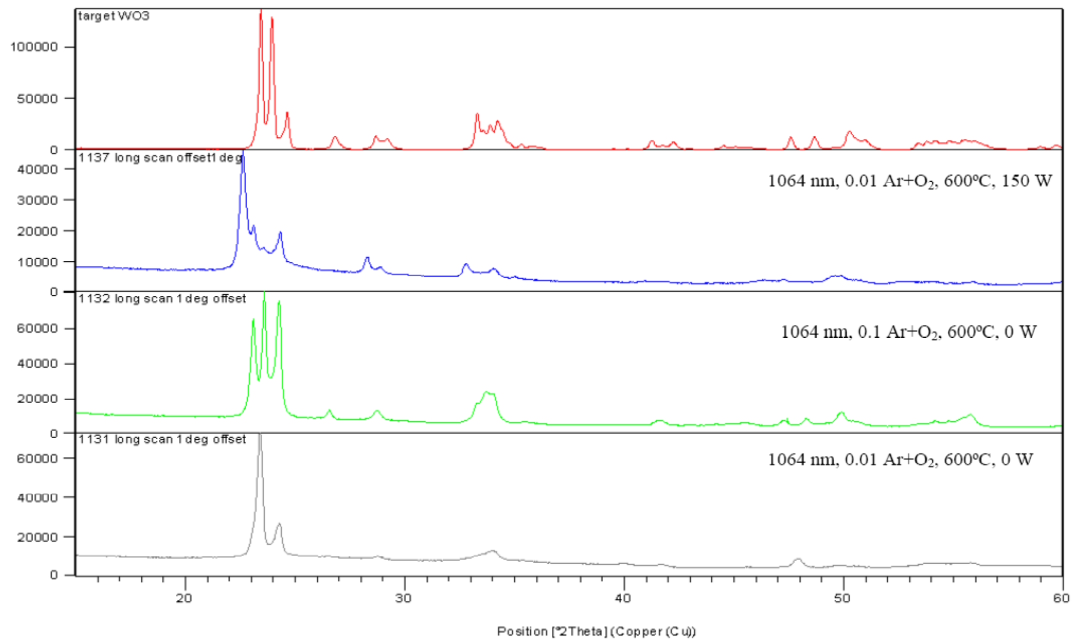
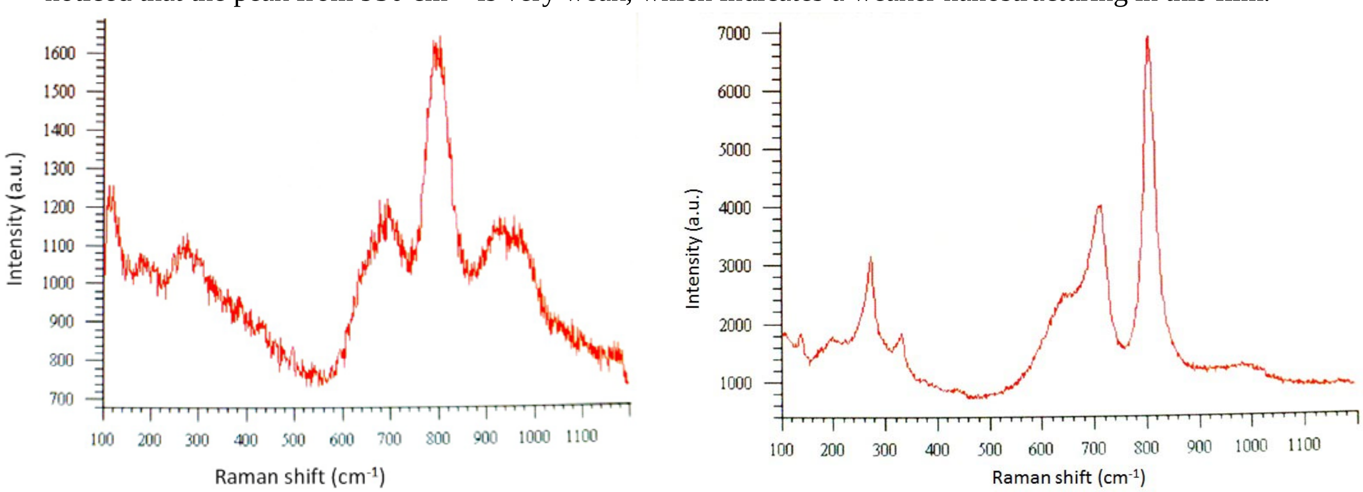


Fig. 1 XRD spectra of WO_x thin films grown on Si (100) in different conditions in comparison with WO_3 target

Increasing the pressure at 0.1 mbar and keeping constant the other experimental conditions as the previous film, the same trends described above can be observed.

Also, the role of RF plasma presence on the films nanostructuring has been investigated.

Fig. 2b shows the spectrum of a sample obtained by PLD at 600 °C and 0.1 mbar of (Ar + O_2). Again, there are two phases N (685 cm^{-1}) and γ-monoclinic (640 cm^{-1}) as well as the triclinic-δ phase. It was noticed that the peak from 950 cm^{-1} is very weak, which indicates a weaker nanostructuring in this film.



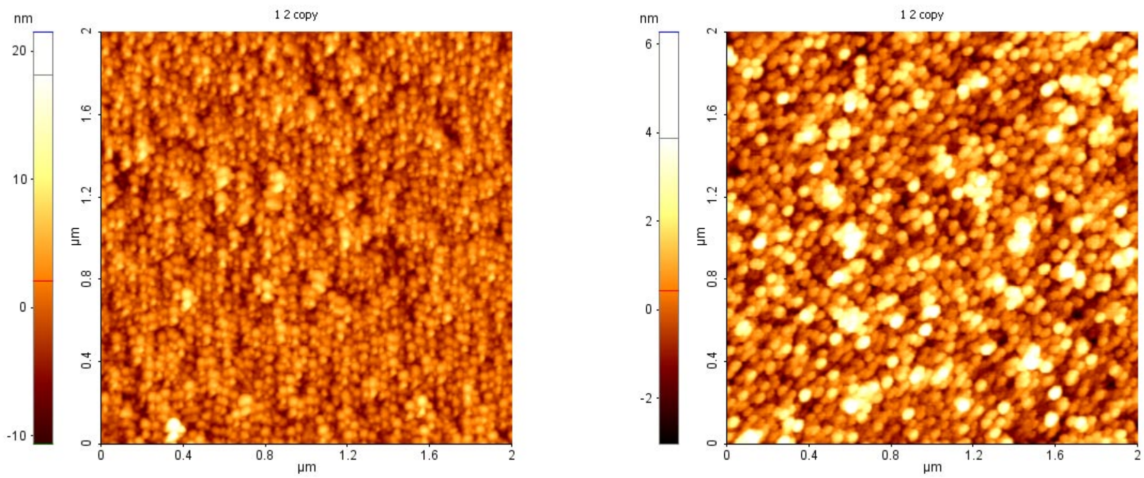
a) b)

Fig. 2 The Raman spectra of WO_3 thin films grown on Corning substrate with λ=193 nm, at 600°C in Ar+O_2 at a) 0.01 mbar by RF-PLD, b) 0.1 mbar by PLD

The thin films deposited at RT either at 0.01 mbar or 0.1 mbar of (Ar + O_2) present a similar behavior irrespective of the growth method (RF-PLD or PLD). Different phases as triclinic-δ, γ-monoclinic, N, with a lower degree of nanostructuring development than for films deposited at higher Ts appeared. The peak at 910 cm^{-1} indicates a $WO_{3-\gamma}$ non-stoechiometric compound.

Besides the desired crystalline structure, the nanoparticles with controllable sizes are important for the increasing sensitivity. On small areas of 2 × 2 μm^2 nanostructured topography can be observed.

Studying the surfaces of two thin films obtained with λ = 193 nm at 600 º C in 0.1 mbar (Ar + O_2), one grown by PLD and the other by RF-PLD, it can be observed that the addition of RF discharge (150 W) leads to nanoparticles with regular sizes of 50-60 nm (Fig. 3a), while the sample grown without RF (Fig. 3b) is formed by bigger nanoparticles (70-80 nm). The same effect of nanoparticles size decreasing for films grown at RT in the presence of RF discharge is remarked.



a) b)

Fig. 3 The AFM images for WO_3 samples grown on Corning glass with λ=193 nm, in 0.1 bar of (O_2+Ar) by a) RF-PLD at 600ºC, b) PLD at 600ºC

When the target is irradiated with a wavelength of 532 nm, on the films surface droplets occur. On the small area, nanoparticles with sizes of 50-60 nm and pores with sizes of about 50-60 nm were observed. Increasing the wavelength to 1064 nm, the surfaces films show droplets and pores with micrometric sizes. On area of 2×2 μm^2 nanoparticles with sizes of 100 nm that form agglomerations of about 300 nm were observed.

SIMS investigations have shown that thin films obtained by RF-PLD in gas mixture at 0.1 mbar and Ts = 600 º C are homogeneous, showing a sharp interface, without interdiffusion of elements from the deposited layer in Si (100) substrate. In contrast, at low temperature (RT), the films obtained in the same conditions (150 W, 0.1 mbar) have a non-homogeneous distribution of oxygen in the layer.

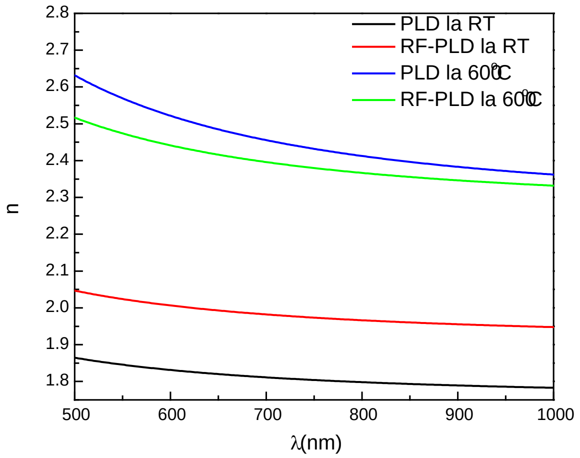


Fig. 4 Refractive indices vs. wavelength for thin films grown on Si in 0.1 mbar of (O_2+Ar)

Optical properties, in particular the refractive indices, were determined using ellipsometry. In Fig. 4 the behavior of refractive indices depending on wavelength is shown.

When films are grown by PLD and RF-PLD at Ts = 600 ° C in 0.1 mbar of (O_2 + Ar), high refractive indices (2.4 - 2.6) corresponding to polycrystalline phase of WO_3 are obtained; the tungsten oxide layers grown at RT show low refractive indices (1.8-2) assign to a low crystallinity. Decreasing pressure gas mixture at 0.01 mbar and maintaining a high substrate temperature it is observed that only if the growth process is assisted by RF, thin films with refractive indices corresponding to crystalline phase (n ~ 2.4) are obtained. The same behavior is observed to WO_X thin films obtained after target irradiation with λ = 532 nm. Due to the presence of pores and micrometric droplets on the surface of films grown by ablation of the ceramic target at λ = 1064 nm, the measurements could not be performed.

***Activity 1.4**: The obtaining of WO_X-CA structures by PLD and RF-PLD;*

Clusters are formed mainly by collision during ablation plasma propagation and land on the substrate where migrate and aggregate between them.

Depending on the equilibrium between the particle average kinetic energy that lands onto the substrate and the cohesion (attraction) energy of clusters/nanoparticles (NP), the film growth keeps a memory of building accumulations. This affects the nanostructure and the morphology.

In order to obtain WO_X-CA films, a number of 54 samples were deposited. Plates of Si (100) and Corning Glass were used as substrates. The ceramic target was irradiated with different wavelengths (193 nm, 532 nm and 1064 nm) in oxygen or argon atmosphere or mixed atmosphere of oxygen and argon (in equal proportions). The depositions were made either by classical PLD or by RF-PLD, in order to find the best conditions for obtaining films based on CA. The substrate was placed parallel to the target at a distance of 4 cm, being kept at room temperature (21 °C) or 600 °C. The gas pressure was varied from 1 to 7 mbar. Laser fluence was set at 3 J/cm^2. The RF discharge power was set at 150 W.

***Activity 1.5**: Morphological investigations on WO_X-CA structures;*

The dependence of tungsten oxide films properties on deposition parameters was investigated. The pressure gas mixture is an important parameter that influences the growth of CA-WO_X films. Using the wavelength of 193 nm, the films grown at Ts = 600°C by PLD at different pressures show significant morphological differences. Thus, at low pressure (1 mbar), "grains" with sizes of about 300 nm on the surface of the film are observed; increasing the pressure up to 7 mbar their size shrinks (~ 50 nm) and their presence is increasingly less dense (Fig. 5a-d).

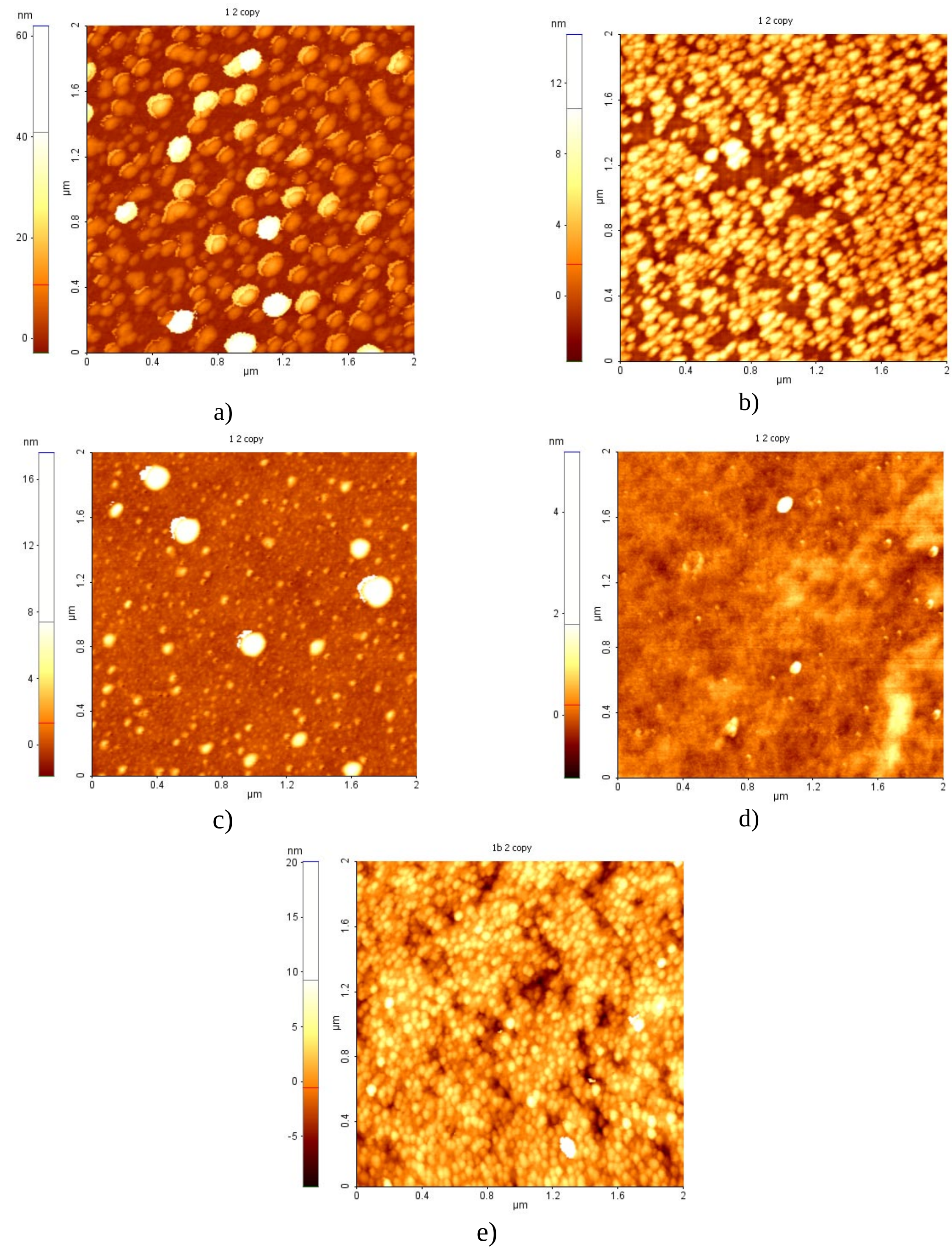


Fig.5 AFM images of CA-WOx films grown with λ=193 nm, at Ts=600°C by a) PLD lat 1 mbar, b) PLD at 3 mbar, c) PLD at 5 mbar, d) PLD at 7 mbar and e) RF-PLD at 7 mbar

During deposition process when an RF discharge is applied, the film obtained at Ts = 600 °C in 7 mbar of (Ar + O_2) shows a completely different morphology than the morphology of the film grown in the same conditions but with PLD (Fig. 5d): clusters with regular sizes (40-50 nm) and a high densification (Fig. 5e) appear.

Increasing the wavelength to 532 nm and then to 1064, on the surface of CA-WO_X films micrometer-sized droplets appear.

Conclusions

Tungsten oxide as nanostructured thin films and CA-WO_X films were obtained by laser ablation. The addition of radio-frequency discharge to the classical PLD system corroborated with a high substrate temperature and a pressure of 0.1 mbar Ar +O_2 leads to the synthesis of crystalline WO_3 films with regular size nanoparticles. The films obtained in these conditions show a stoechiometric composition with a high degree of structural order and homogeneous distribution of the elements in the film. A high roughness (3 nm) and regular size of particles (50-60 nm) show that a high specific area is achieved in the presence of RF beam.

In the case of CA-WO_X films, the presence of RF associated with a high temperature (600 °C) and high pressure (7 mbar) leads to regular sized dense clusters obtaining.

In conclusion, these results may lead to obtaining of tungsten oxide films with high sensitivity to be used in building of devices for toxic gases detection.

The objectives of this stage were fully realized.

Dissemination

1) **paper:** M. Filipescu, V. Ion, D. Colceag, P. M. Ossi, M. Dinescu, Growth and characterizations of nanostructured tungsten oxides, Romanian Reports in Physics, Vol. 64, Supplement, P. 1213–1225, 2012

2) **poster:** M. Filipescu, D. Colceag, V. Ion, R. Birjega, M. Dinescu, P. M. Ossi, Growth and characterizations of nanostructured tungsten oxides obtained by laser ablation, ICPEPA-8 Conference, Rochester – SUA, 12-17 August 2012

Project Director

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