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Synthesis and optimization of tungsten and tungsten oxide films produced by laser ablation

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Abstract. This work was aimed at achieving an optimal deposition process by pulsed laser ablation (PLA) on large area substrates, using pure tungsten as target. The films were deposited at different: wavelengths (355/532/1064 nm), fluences (1.5, 5 and 10 J/cm^2), oxygen pressures (100 and 200 mTorr), substrate temperatures (room temperature, 200, 300, and 400°C). The morpho-structural and compositional investigations have been carried out by profilometer, scanning electron microscopy, X-ray diffraction, Rutherford backscattering spectroscopy and Fourier transform infrared spectroscopy. The study has shown that optimal conditions for tungsten deposition on large area surfaces are at 355 nm/ 5 J/cm^2. Amorphous, orthorhombic and triclinic phases WO_3 films were obtained.

1. Introduction

Tungsten trioxide is one of the best electro-chromic materials used for windows, displays and color memory devices. Many research articles have been devoted to a better understanding of the correlation between the experimental parameters and film properties, and the precise control of the deposition process. In recent years significant effort has been devoted towards developing surface acoustic wave (SAW) sensors based on WO_3 sensing films, to be used for detection of gases like NO, H_2S, NO_2, SO_2, CO, CO_2. The WO_3 films have been deposited by various techniques as magnetron sputtering [1, 2, 3], electrochemical deposition [4, 5], chemical vapor deposition [6, 7], as well as laser ablation technique [8, 9, 10].

In this work, the tungsten trioxide thin films were deposited and investigated using pulsed laser deposition method (PLD). The deposition of tungsten trioxide thin films is strongly influenced by the laser wavelength, fluence, gas pressure and the substrate temperature. Initially, a preliminary study of

pure tungsten films and optimization of the deposition process was carried out, for a better understanding of the deposition process and film characterization, particularly interesting for large area films. The investigations on the surface morphology, elemental composition and structure have been achieved using profilometer, X-ray diffraction (XRD), scanning electron microscope (SEM), Rutherford backscattering spectroscopy (RBS) and Fourier transform infrared spectroscopy (FTIR).

2. Experimental

Tungsten and tungsten trioxide thin films were deposited by PLD on silicon substrates. As target, pure metallic tungsten was used, placed at 30 mm distance from the silicon substrate. The depositions were made in the following experimental conditions: wavelengths 355 nm / 532 nm / 1064 nm, laser pulse energy 46 mJ, fluences 1.5 J/cm^2, 5 J/cm^2, 10 J/cm^2, repetition frequency 10 Hz and the substrate temperature from room temperature (RT) to 400°C. Initially, the chamber was evacuated down to 4×10^{-6} Torr by a turbomolecular pump. The tungsten films, were deposited in vacuum at 5×10^{-6} Torr, while WO_3 thin films were deposited in the oxygen at 100, 200 mTorr. The deposition time was 30 and 60 min for W and WO_3 respectively.

For measurements, the following standard equipments were used: profilometer Tokyo Seimitsu Surfcom 130 A, X ray diffractometer RIGAKU, model RINT 2500HF+/PC, field emission scanning electron microscope JEOL (JSM 6700 F), Rutherford backscattering spectrometer NHV model (NT-1700HS), FTIR NICOLET model IMPACT 410.

3. Results and discussions

As previously mentioned the final goal was to produce stoechiometric, crystalline and compact WO_3 films by ablation of the tungsten in oxygen atmosphere. First, we considered necessary a preliminary study, to optimize the deposition by PLD of tungsten film in order to make a trade off between deposition rate and film quality (important aspect, especially for large area films).

Table 1. Tungsten films.

Wavelength (nm)	Fluence (J/cm^2)	Thickness (nm)	Deposition rate (nm/pulse)	Roughness (10^{-6} m)	No. droplets/mm	Droplet average size (10^{-6} m)
	1.5	40	0.002	0.015	0.12	0.110
355	5	800	0.044	0.017	1.06	0.342
	10	280	0.015	0.028	3.06	0.562
	1.5	180	0.01	0.012	2.06	0.166
532	5	520	0.028	0.024	3.06	0.410
	10	100	0.005	0.102	15	0.612
	1.5	-	-	-	-	-
1064	5	50	0.002	0.010	0.25	0.742
	10	100	0.005	0.010	0.81	0.340

In table1 are shown the investigation results regarding tungsten film thickness, deposition rate, roughness and droplets, at different deposition parameters. We must underline that the thickness has been measured without taking into account the droplets, but the compact region only. One can see an interesting behaviour: at 355 nm the deposition rate is increasing for fluences from 1.5 to 5 J/cm^2, while at 10 J/cm^2 it is strongly decreased. The reduced deposition rate at 10J/cm^2, is due to the plume shielding. The same thickness/ deposition rate behaviour occured at 532 nm, but their values were smaller than at 355 nm, excepting 1.5 J/cm^2 fluence; at 1064 nm, when the laser beam is much less absorbed, one can observe that the ablation process started just from 5 J/cm^2, and deposition rate was two orders less than at 355 nm. It is clear that the IR radiation is not suitable for ablation of tungsten. Concerning the roughness, the data from table 1 demonstrated that in UV the films are much smoother. Thus, because we are interested to have an efficient deposition rate on large areas, and at

the same time to maintain a good roughness (without droplets as much as possible), one can conclude that 355 nm / 5J/cm^2 were the optimal conditions for deposition of tungsten films (deposition rate of 0.044 nm/pulse, and 17 nm roughness).

Since the main goal of this work was deposition of high quality WO_3 films, the optimal deposition conditions found for W were later on applied to WO_3 as well. Thus, in these conditions we have studied of WO_3 deposited at two pressures, 100 and 200 mTorr of oxygen, and substrate temperature from RT to 400°C. In figure 1 are shown several XRD spectra for the films deposited at 100 mTorr oxygen. One can notice that the films deposited at RT have presented only an amorphous phase, and a mixture of amorphous and crystalline phases or weak crystalline at 200°C, 300°C, 400°C (as an example, in Figure 1 are shown only the XRD spectra of WO_3 films deposited at RT and 200°C). Moreover if the pressure was increased to 200 mTorr, the film structure was also amorphous.

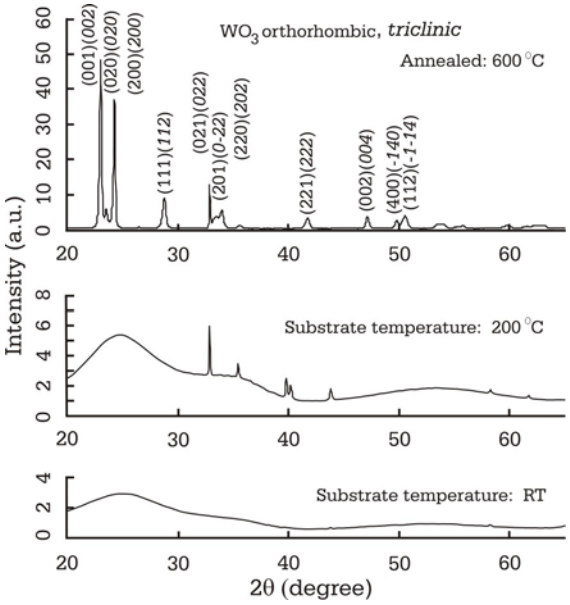

Figure 1. X ray diffraction spectra for the films deposited at room temperature, 200°C and annealed at 600°C.

We were interested to know if the films were WO_3 or not; from XRD analysis of such films we could not draw any conclusions on the film composition and therefore the next step was to investigate the composition of such films by RBS. Figure 2 depicts the Rutherford backscattering spectrum for a film deposited at 200°C and 100 mTorr oxygen. The simulation shows that the best fit was for a film with the elemental composition W:O=1:3 (± 10%); this confirms that the amorphous film was WO_3. The same conclusion was drawn for all amorphous films deposited in the experimental range of pressure or temperature.

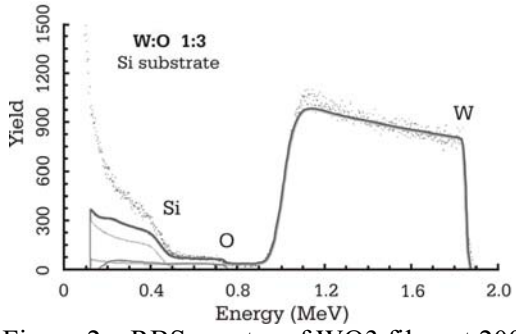

Figure 2. RBS spectra of WO3 film, at 200 °C and 100 mTorr

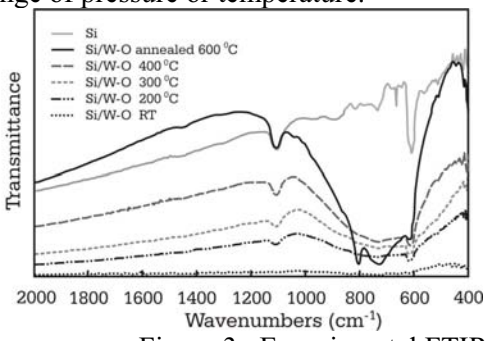

Figure 3. Experimental FTIR spectrum

In order to improve the WO_3 crystallinity, the films were annealed at 600°C in air for 1 hour. For a precise determination of the experimental parameters which are critical in forming of the crystalline phase, the thermal treatment was made in two ways: (a) annealed in high vacuum, 5×10^{-6} Torr, and (b) in air at the same temperature and timing. The study shows that both in high vacuum and in air, at 600°C the films became crystalline (figure 1(c)). This means that the main role in the annealing process stands for temperature. Our analysis (by comparing with ICDD powder diffraction files 20-

1324 and 20-1323) shows that the annealed films present orthorhombic and triclinic phases. We have to mention that first three main peaks (left side) fit very well with orthorhombic phase both angular and as intensity; the other peaks fit very well with triclinic phase.

Furthermore, in order to obtain additional information we used the FTIR technique as well. Thus in figure 3 there are shown the absorption spectra measured in the range 400-2000 cm^{-1} of films deposited at different temperatures and on the silicon substrate. First observation: the amorphous film deposited at RT does not present the typical large peak in the range 600 -800 cm^{-1} [11]. As far as the substrate temperature is increasing, the typical peak from 600 -800 cm^{-1} becomes more proeminent. For a typical crystalline WO_3 film (the film annealed at 600°C), FTIR spectrum is similar to standard tungsten trioxide (wolframite); besides the main band, one can also observe the peak from 1150 cm^{-1} [11]. The microstructure of WO_3 thin films investigated by SEM is illustrated in figure 4 (a) top view, and (b) cross section. The image of the surface shows very smooth without visible grains at 100 nm scale, in contrast with [10]. In the cross section, the material is very compact, without any cracks, or columnar shapes.

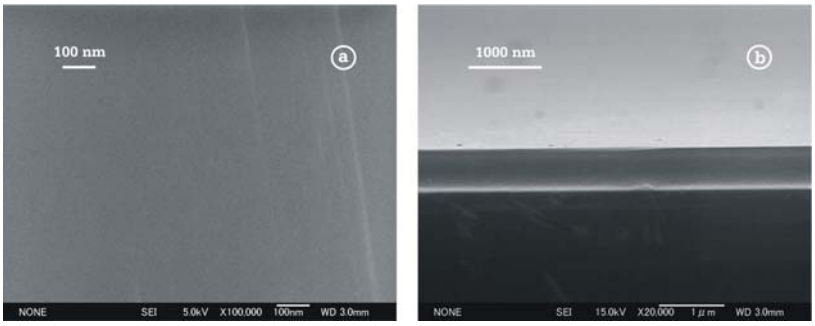

Figure 4. SEM images: (a) top view image of a surface of a WO_3 thin film, (b) cross section.

4. Conclusions

We have successfully deposited tungsten in optimal conditions at 355 nm / 5J/cm^2 / 46 mJ / vacuum with a deposition rate of 0.044 nm/pulse and 17 nm roughness. Tungsten trioxide films deposited at RT to 400°C presented amorphous phase but after annealing at 600°C, are crystalline with orthorhombic and triclinic phases. The amorphous films had the elemental composition (W:O=1:3). The optimal conditions for deposition of compact, smooth and crystalline WO_3 were: 355 nm / 5J/cm^2, 100 mTorr oxygen pressure, any substrate temperature and an annealing temperature of 600°C.

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