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OPTICAL PROPERTIES OF TUNGSTEN OXIDE (WO_x) THIN FILM PREPARED BY PULSED LASER DEPOSITION (PLD)

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Abstract. The enormous interest of this material is their optical and electrical properties which are useful for development of advanced technological applications (sensors, photovoltaic cells). The aim of this study is the control of the optical properties of the WO_x thin films prepared by PLD with variation of the deposition parameters.

Key words: thin film, spectro-ellipsometry, tungsten oxide.

1. INTRODUCTION

Metal oxides semiconductors thin films have attracted attention due their great properties which are useful into advanced technological applications [1]. Also, high sensitivity, low-cost production and simplicity of fabrication technology and its high compatibility with micro-fabrication [2] making them make them accessible on a large scale in the technology development.

Among the available metal oxide, tungsten oxide (WO_x) is one of the most important and used metal oxide semiconductors (MOS) [3] that have been rigorously studied [2] due their essential properties for photocatalyst, electrochromic devices, gas sensors, photovoltaics and to their small size with high surface-to-volume ratio [4].

Tungsten oxide thin films is an *n*-type semiconductor [5–6] and can be fabricated with various deposition methods (with its limitations) a fact that contributes to its unique properties that do not exist in its bulk form [7]. WO_x nanostructures can be manufactured in different forms such as nanoparticles, nanorods, nanowires and nanosheet [4], nano powders [8] and thin films involving a compatible deposition technique.

For the deposition of tungsten oxide WO_x with different structures at the nanoscale level, can be used, such as Chemical Vapor Deposition (CVD) (with technique like spin coating [9], sol gel [8] and electrodeposition [10–11] and physical vapor deposition (PVD), pulsed laser deposition (PLD) [12–14, 6], magnetron sputtering [15] or thermal evaporation (TVE) [16, 5]. In this paper we present the optical properties of the WO_x thin films deposited by PLD technique. The properties and the quality of the film depend exclusively on the deposition parameters: spot area, laser energy, target-substrate distance, high vacuum, substrate temperature and the carrier gas in the chamber [17]. For this material another important controlling parameter is the introduction of the oxygen vacancy which can affect the photocatalytic decomposition [18], can lead to lowering the band gap of the material [19], impacts suppress recombination of photo-induced carriers [20] and induces the large absorption into the near-infrared (NIR) and visible (VIS) range [21]. The absorbance of the WO_x in the vis-NIR region depends on the degree of reduction or ion insertion coefficient [22]. The optical properties of WO_{3-x} ($0 < x < 1$) can be adjusted by tuning the oxygen ratio during the deposition process. WO_x has high transmittance in the visible range, but absorbs in the UV and IR range spectrum. The intrinsic defects, such as oxygen vacancy determine the main optical properties of WO_x. This property leads to development of the NIR sensors and heterojunction photovoltaic cells. The aim of this work is to obtain the tungsten oxide thin films, using PLD deposition technique with different optical properties, which are indispensable for the development of the NIR- sensors or other devices, such as photovoltaic cells. In this work, we present a parametric study on the influence of deposition parameters on the properties of WO_x thin films. The optical properties were investigated by spectroscopic ellipsometry (SE) technique.

2. EXPERIMENTAL SET-UP

For the fabricated the Tungsten Oxide (WO_x) thin films, the Pulsed Laser Deposition (PLD) and RF discharge plasma assisted PLD method was used, which consisted in a vacuum chamber, a pumping system, a heater acting as substrate holder, a rotation-translation system of the target, mass flow controller for gas admission and a laser source (Surelite pulsed YAG-Nd solid laser and ArF excimer laser) [23]. A ceramic target of WO_3 was ablated by a laser source at different wavelengths (193 nm and 532 nm) and a repetition rate of 10 Hz. The deposition material was transferred on the Si (100) substrate at the laser fluence of 3 J/cm^2 and at 4 cm substrate-target distance for all the samples. The working gas pressure was set at 10 Pa, in equal proportion of O_2 and Ar. The discharge RF plasma was oriented at an angle of 45 degree reported at plane of substrate surface. For obtaining different optical properties of tungsten oxide thin films, the following deposition parameters were varied: the laser wavelength, the substrate temperature

(600°C and room temperature (RT)) and the Radio Frequency (RF) power (0 W or 150 W), generated by RF discharge generator working at 13.56 MHz and a maximum power of 1000 W.

The experimental measurements were done in the 400–1700 nm range of wavelength by a Woollam V-VASE ellipsometer equipped with HS-190 monochromator.

Spectroscopic Ellipsometry (SE) is a non-destructive technique used to investigate film thickness and optical constants (refractive index *n*, and extinction coefficient *k*). However, it is also applied to characterize composition, crystallinity, roughness and doping concentration.

The main principle of ellipsometry is the measurement of changes in polarization when the light reflects or transmits from a material structure (the variation of light reflection with p- and s-polarizations) [24]. The polarization change, represented as an amplitude ratio, Ψ, and the phase difference, Δ was performed using the J.A. Wollam Spectroscopic Ellipsometer. The measurements were realized by varying the incidence angle from 60 to 70 degrees, from 5 to 5 degrees, on a spectral range between 400 nm and 1700 nm. Choice of the angle of incidence is oblique to the sample surface near the Brewster angle [25].

For the modeling and interpretation of ellipsometry measured data, dedicated software V-Vase 32 was used, which allows the use of different mathematical models for fitting the data and also enables the extraction of optical constants and thickness, together with roughness of the deposited layer.

3. RESULTS AND DISCUSSIONS

The influence of the PLD deposition parameters such as substrate temperature, RF oxygen plasma discharge addition or the used laser wavelength on the optical properties of WO_x thin films is the main purpose of this study and spectro-ellipsometry technique was employed for this task.

For the WO_{3-x} thin films growth by PLD in different experimental conditions, the optical model consisted by a stack of different material layers: the substrate, the thin film and the top rough layer. Each material layer is characterized by its own dielectric function. In our optical model the silicon (Si) substrate is covered by thin native oxide. The dielectric function of Si and SiO_2 layer was taken from literature. In case of WO_{3-x} layer, the dielectric function was obtained using different dispersion formula. The top rough layer was approximated to be a mix layer in B-EMA approximation, with 50% air mixed with 50% WO_{3-x}.

For the WO_{3-x} thin films, in order to find the best-fit, the different dispersion equation was used. The best fit was considered to be a fit with the smallest value of MSE. The mean squared error (MSE) is the most used complex function and it is proportional to the total difference between measured data (Exp) and model calculations (Mod) [24].

Using the proposed optical model, we fitted the registered data in two steps procedure. First, we used a simple Cauchy dispersion equation to calculate the thickness of WO_{3-x} layer and the thickness of the rough layer.

Because the Cauchy equation provides just the real part of dielectric function (n) we used this equation in the range of wavelength, where the WO_{3-x} layer was supposed to be optical transparent. For example, in case of thin films growth by PLD with an excimer laser work at 193 nm, we used the Cauchy dispersion formula for the entire measured spectra (400–1700 nm). Figure 1 shows the results of this fit and it is easy to observe that the generated Ψ and Δ parameters match very well the measured spectra. For the sample deposited at 532 nm laser wavelength, it was necessary to use the Cauchy with Urbach tail in a much smaller wavelength range (500–800 nm). For those samples, in order to extend the fit and calculate the optical constants (*n* and *k*), on the entire measured spectrum, after the thickness of layers was approximated, we replaced Cauchy dispersion with two oscillators: Gauss and Drude oscillators. In this way, we extracted the final optical constants dispersion for the WO_x layers grown in different experimental conditions. As a final step, all parameters used in the fitting procedure, were slightly adjusted to obtain the smaller value of MSE.

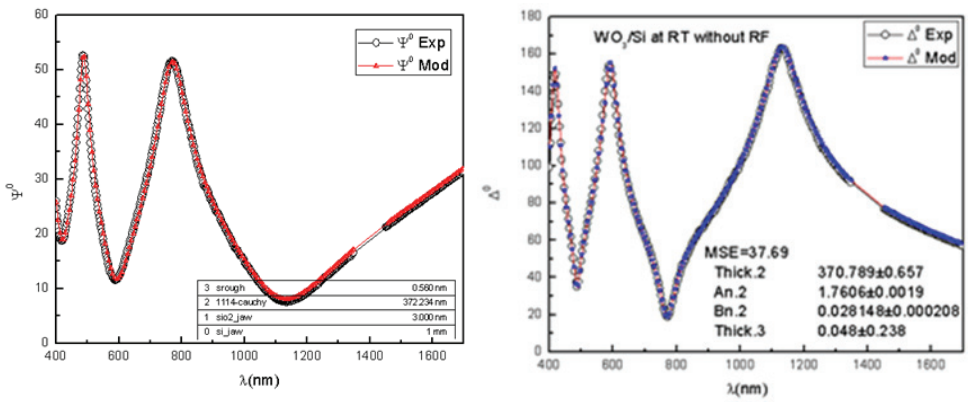

Fig. 1 – Ψ and Δ experimental data and the corresponding generated curves (model fit) obtained from Cauchy fit for the WO_x thin films grown on Si substrate at RT without RF discharge.

From this data we extracted the thickness and the rougness values – presented into Table 1. Figure 2 presents the refractive index dispersion for the WO_x samples obtained by using an excimer laser working at λ = 193 on Si substrate at P = 10 Pa ($O_2 + Ar_2$). The high temperature value of the substrate during deposition of the films has a significant influence on the density of the WO_3 thin films, in the sense that the values of the refractive index are higher than the values of the films grown at room temperature.

Table 1

The values of the thickness and roughness for the WO_x thin films grown on Si substrate at a laser wavelenght of 193 nm at RT without RF discharge measured with SE

Samples number	**$P(O_2 + Ar_2)$ [Pa]**	**T_{sub} [°C]**	**P_{RF} [W]**	**λ [nm]**	**Thickness [nm]**	**Roughness [nm]**	**MSE**
1095	10	600	–	193	540	17	29.3
1105	10	600	150	193	295	7	24.3
1114	10	RT	–	193	370	1	38
1126	10	RT	150	193	526	7	42.2

By adding a RF discharge plasma in the deposition process, the values of *n* can be increased for low *t* deposition temperature values. In order to explain this behaviour, a supposition can be made. In case of low temperature, the addition of reactive oxygen species by RF discharge, in ablation plasma plume can favour the reaction of tungsten atoms with oxygen ones and on the substrate can arrive very small clusters of WO_x with low crystalline ordering.

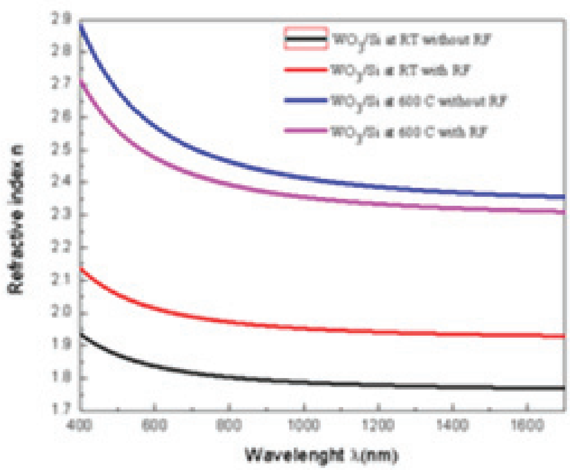

Fig. 2 – Dispersion of the refractive indices for WO_x grown on Si substrate at P = 10 Pa O_2, 193 nm laser walenght.

The low value of refractive index indicates an amorphous thin film, which contain a higher number of micro voids. When the RF plasma is added, the refractive index value, as well as the value of thickness is increased because during the grown process the small crystalline clusters start to stack each other and thin layer is composed by a mix of nanocrystalline cluster with voids.

When substrate temperature was increased at 600°C, we obtained the opposite results. The higher refractive index n and thickness values are obtained without the presence of RF discharge plasma. Combining high energy on substrate surface (when heated at high temperature) with the RF discharge plasma, the re-sputtering process appears and that can explain a lower value of thickness for this sample.

Figure 3 shows the Ψ and Δ experimental data and the corresponding generated curves (model) obtained from Gauss-Drude fit for the WO_x thin films grown on Si substrate at 600°C, P = 10 Pa O_2, λ = 532 nm, a) with and b) without RF discharge.

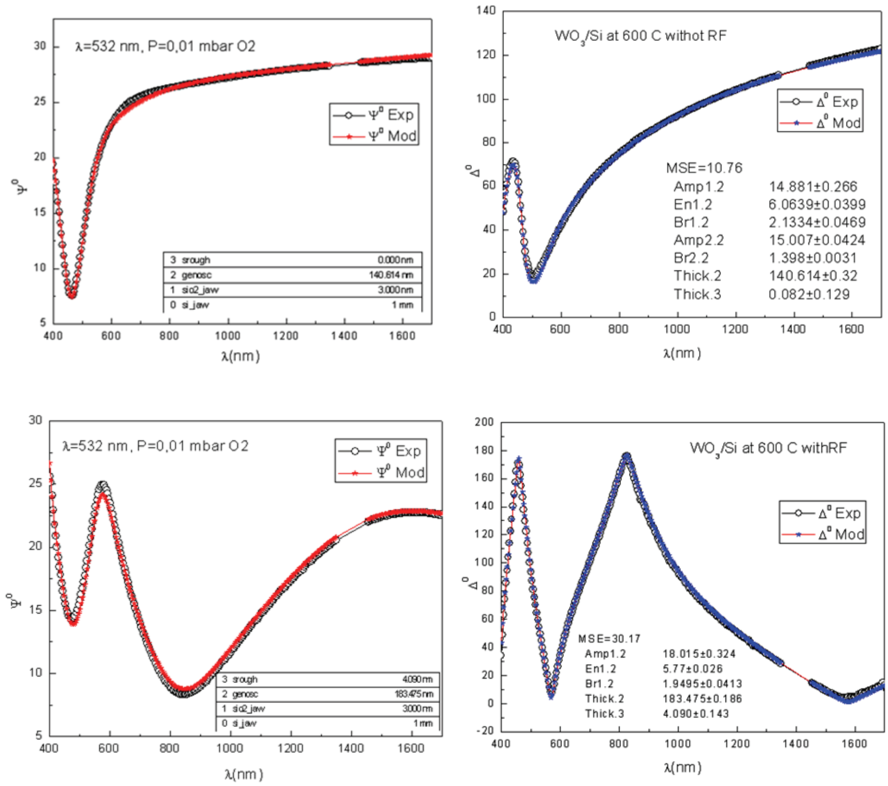

Fig. 3 – Ψ and Δ experimental data and the corresponding generated curves (model) obtained from Gauss-Drude fit for the WO_x thin films grown on Si substrate at 600°C, P = 10 Pa O_2, λ = 532 nm: a) with and b) without RF discharge.

In Fig. 3, the thickness and roughness were extracted and are presented in Table 2.

Table 2

The values of the thickness and roughness for the WO_x thin films grown on Si substrate at a laser wavelenght of 532 nm

Samples number	**$P(O_2 + Ar_2)$ [Pa]**	**T_{sub}**	**RF [W]**	**λ [nm]**	**Thickness [nm]**	**Roughness [nm]**	**MSE**
1207	10	600	–	532	140	1	10.76
1208	10	600	150	532	184	4	30.7

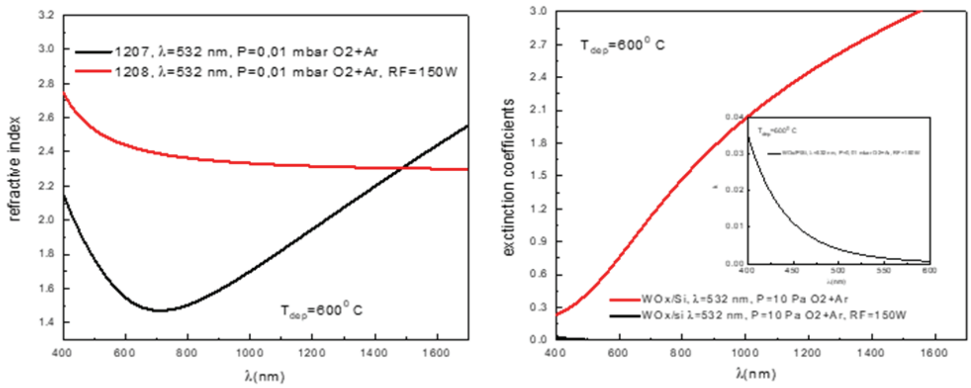

Fig. 4 – Dispersion of the refractive indices for WO_x grown on Si substrate at P = 10 Pa O_2, 532 nm laser wavelength, at 600°C substrate temperature.

The values of thickness were found to be 140–180 nm, much smaller than the thicknesses obtained with ArF laser. If we take into consideration the optical absorption of WO_3 ($E_g > 2.6$ eV), the amount of ablated material is much smaller when we use a higher laser wavelength and this can explain this difference. As we mentioned before, the temperature of the substrate has a high influence on the crystalline state of WO_x, at RT the values of refractive index n, even with addition of RF discharge plasma, are much lower than the reported value for this material. The way to increase the refractive index value is to increase temperature during deposition. In that situation, we grew the WO_x thin film using a laser wavelength of λ = 532 nm, at higher temperature with and without the presence of RF plasma.

From Fig. 4 it can be observed that the higher refractive index values for WO_x thin films deposited on Si at 600°C, are obtained with addition of RF plasma and the values are comparable with those obtained for the sample growth at RT and 193 nm laser wavelengths with RF plasma. A very weak optical absorption is obtained in this case. The value of extinction coefficient k starts to increase below 600 nm. When the deposition process is not assisted by the addition of RF, we obtain a very high variation of the refractive index (between 1.5 and 2,6 in NIR range). Moreover, there is a strong optical absorption in NIR range of wavelength. The NIR absorption is induced when free electrons are introduced into crystals by decreasing the oxygen contents, which will lead to a complex-ordered structure known as the Magneli structure [26].

When the WO_x target was ablated using a higher laser wavelength than 193 nm, the presence of RF plasma is very important if one need to tailor the optical behavior for WO_x.

4. CONCLUSIONS

In summary, we studied the control of the optical properties of thin films of WO_x obtained by PLD. The effects of the laser wavelength, RF discharge plasma or substrate temperature on the optical properties have been revealed and discussed. The high values of refractive index was obtained at $T_{substrates} = 600°C$, $P = 10$ Pa gas pressure and 193 nm laser wavelength. Laser wavelength is the most important parameter in PLD of tungsten oxide using ceramic tungsten oxide target. The addition of RF at room temperature favored the formation of transparent WO_x thin film with higher refractive index. The addition of RF discharge plasma plays an important role when the WO_x layer is grown a higher laser wavelength (532 nm). In this way, it was demonstrated that using the PLD and RF assited PLD deposition techniques WO_x thin films with different optical properties can be obtained, as the ellipsometry results have shown.

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