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Structural phototransformation of WO_3 thin films detected by photoacoustic analysis

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ABSTRACT

The photoacoustic technique (PA) was used to detect the phase transformation from amorphous to crystalline state of tungsten oxide (WO_3) thin films induced by UV pulsed laser radiation at low energy (<1.5 mJ). The evolution of photoacoustic signal was studied by a correlation analysis, comparing successive signals at fluences ranging from 0 to 20 mJ/cm^2. In this interval, it was possible to observe structural changes and the ablation threshold in films due to incident laser fluence effect. Thin films of WO_3 were deposited by DC reactive magnetron sputtering over glass substrates at different deposition times. The results obtained by correlation analysis were compared with Raman spectroscopy data.

1. Introduction

Transition metal oxides are materials with a high degree of application in the field of information storage. Many of these oxides show interesting phase transitions from one crystal structure to another accompanied by changes in its magnetic, electrical and other properties [1].

Tungsten oxide (WO_3) belongs to the electrochromic materials group, which were discovered in 1969 by Deb [2]. These materials are capable to change their optical properties in a persistent and reversible way when subjected to a voltage excitation [3]. Tungsten oxide has been intensively studied in the last decades due to their wide variety of applications; particularly, in thin film form has been used in optoelectronics, microelectronics, selective catalysis, environmental engineering, electrochromic devices, etc. [4–6].

WO_3 is a very complex material in regarding to its crystal structure and thermal stability due to its purity and oxygen deficiencies. Several structures have been reported in the 0–1220 K range for this semiconductor, among which are: the monoclinic, triclinic, tetragonal, orthorhombic, cubic and hexagonal [7–9].

In this paper, the amorphous to crystalline phase of tungsten oxide thin films (WO_3) was monitored "in situ" through the pulsed laser photoacoustic technique. This technique involves the generation of sound waves (mechanical waves) produced within the material due to thermal processes response of the absorption of pulsed light.

The physical mechanisms involved in the generation of the photoacoustic effect to determine structural changes in samples, are given as follows.

The acoustic signal generated by a pressure wave traveling inside of material induced by the incidence of the laser beam. The mechanically stressed state in the material, created by the pressure wave, changes the volume as a function of the pressure. The compliance of the system's volume with respect to the pressure is what characterizes the volume compressibility. This physical parameter is relatively small in solids. However, as microscopic characteristics of the illuminated laser beam material determine the temporal profile of the acoustic pressure, a microscopic change in the material would then be reflected by some appropriately constructed correlation curve, via the out-coming photoacoustic signal. Consequently, if in a material, a photoacoustic experiment is carried out as a function of fluence, and the out-coming response can be used to evaluate changes in a physical parameter. Therefore, the photoacoustic experiments can be appropriate to determine structural changes due to fluence and also to detect different types of phenomena such as the presence of phase transitions.

The photoacoustic signals generated in the sample while increased the fluence were detected using a piezoelectric transducer and visualized on a digital oscilloscope as voltage vs. time curves (Fig. 1). These signals were analyzed by means of correlation functions, which allow determining the stability of the sample. In this way, it was possible to detect both phase changes in the material caused by the laser irradiation and also the threshold ablation.

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The photoacoustic signal PA(t, X_i) is a function that represents the interaction between laser beam and the sample, where t indicates temporal signal range and X_i is the changing parameter, in this case the different energy fluences. The correlation, R, between successive functions [PA(t, X_i), PA(t, X_{i+1})], proves any change in the physical system [10,11]; if $R = 1$, the functions are identical and changes do not exist in the sample, but $R < 1$ is located on the curve peaks showing that there are significant structural instabilities. The photoacoustic analysis has proved to be a powerful tool in the characterization of a variety of materials in bulk or thin film [12–14].

WO_3 thin films were prepared by the sputtering technique at room temperature in amorphous state. The results obtained by photoacoustic analysis were compared and discussed with Raman spectroscopy data.

2. Experimental details

Tungsten trioxide (WO_3) thin films were deposited by DC reactive magnetron sputtering on glass slides (soda-lime type) substrates. Substrates were placed parallel to the target surface and the temperature was kept at room temperature. Working pressure was 1.13×10^{-3} mbar, as a mixture of argon and oxygen 2:1. It was used a tungsten target 99.995% purity. All samples were deposited at 250 W and at different deposition time intervals (2–6 min), which lead to obtain the next thickness: WO_3(I) 412.9 nm, WO_3(II) 522.4 nm, and WO_3(III) 1085.5 nm. An Advanced Energy DC power supply was used in order to generate the plasma discharge, and a Sloan Dektak IIA profilometer to measure thin film thickness. It was observed that the aspect of films was transparent, but when viewed from different angles, a number of colors become apparent, this was attributed to film thickness non-uniformed.

In experimental setup for photoacoustic signal detection a pulsed laser was used Nd:YAG ($\lambda = 355$ nm, 10 Hz, with a pulse width of 7 ns). The laser beam diameter was 2–4 mm, which was manipulated by a shutter. The laser energy was controlled using a high power attenuator (Newport Model 934-10) and was measured with a RJ 7620 radiometer (Laser Precision Corp.) in the interval of nano-Joules to Joules. The sample was attached with commercial glue to a piezoelectric microphone which has a 240 kHz bandwidth. Photoacoustic signals were recorded on a 500 MHz digital Tektronix oscilloscope, TD5052B model, and shot was achieved through a fast photodiode placed near the laser beam. In this paper, for the analysis, the whole photoacoustic signal of the first 100 ms was used, as viewed in Fig. 1.

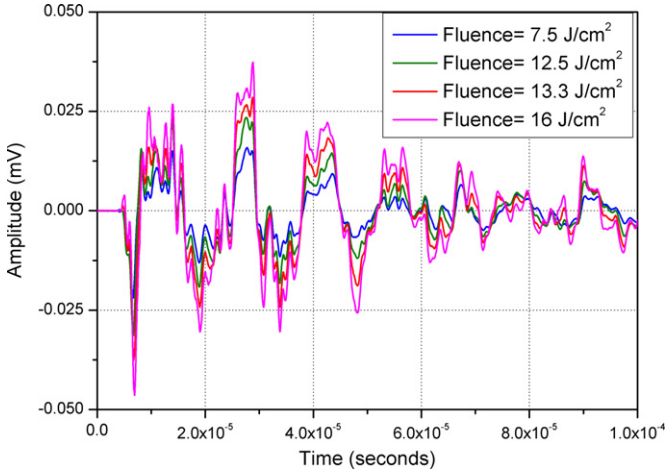

Fig. 1. Photoacoustic signals of WO_3 thin film for different energy fluence values.

The optical absorption spectra of WO_3 thin films were obtained using a UV–vis spectrophotometer (UV160U, Shimadzu) with a spectral range of 200–1100 nm.

The structural changes were characterized by Raman spectroscopy. An Almega XR Dispersive Raman spectrometer equipped with an Olympus BX51 microscope and a double Czerny–Tuner monochromator type, brand Spex model 1403, controlled by a computerized system was used. The monochromator is equipped with two holographic diffraction gratings 1800 lines/mm. Signal was detected with a photomultiplier tube Hamamatsu, model 2761, and a system of data collection and analysis. The excitation of the sample was carried out with argon ion laser (laser LESKEL) using the 514.5 nm line at power levels of 100 mW.

3. Results and discussion

3.1. Absorption spectral

Fig. 2 shows the absorption spectra of WO_3 thin films. Taking into account that the photoacoustic effect is produced by light absorption in the material, these spectra determined the optimum wavelength to irradiate the films. The absorption bands range is between 275 and 375 nm.

It was observed from experiment that photoacoustic signals can be obtained without amplification by using a 355 nm wavelength, despite the sample 22.89 absorption percentage.

As seen in Fig. 2, the absorption bands are shifted to higher wavelengths with increasing thickness of the films. This change in the absorption edge is probably related to particles size, grain boundaries and structural defects in the samples [15]. It is known that the amorphous tungsten oxide thin films, typically contains less oxygen than the stoichiometrically balanced WO_3, which causes slight changes of color in films and therefore in the optical absorption spectra. The optical absorption is caused by small polaron transition between two nonequivalent tungsten sites (W^{5+} and W^{6+}) [16].

3.2. Photoacoustic results

The photoacoustic analysis was performed on 3 oxide tungsten thin films samples: WO_3(I), (II) and (III). Note that, in all samples, the early data from the correlation analysis of the photoacoustic signal are consistent with a natural decay due to instability of laser

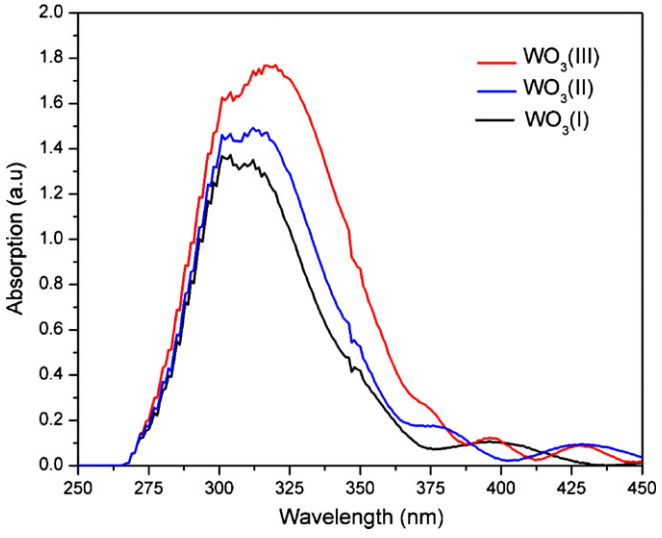

Fig. 2. Absorption spectra of the WO_3 thin films with different thicknesses: 412.9, 522.4 and 1028.5 nm of the sample WO_3(I), WO_3(II) and WO_3(III), respectively.