Structural, morphological and optical properties of sputtered TiO_2/WO_3 bilayers

M. Dobromir, R.P. Apetrei, C.T. Teodorescu-Soare, V. Tiron, and D. Luca

Iasi Plasma Advanced Research Center (IPARC), Faculty of Physics, Alexandru Ioan Cuza University,11 Carol I Blvd., 700506, Iasi, Romania

TiO2/WO3 layered structures were prepared using RF magnetron sputtering and characterized in terms of structure, morphology and optical properties in the as-deposited state and after a heat treatment at 400ºC for 1 hour in air. A significant amount of amorphous materials is evident in the as-deposited state, while upon annealing, the X-ray diffraction patterns depict peaks specific for WO_3 crystalline phases, while the titania films remain amorphous, with no detectable rutile or anatase TiO_2 phases. The optical transmittance of the samples varies between 65% and 85%, making the layered structures a good candidate for photo-catalytic devices with enhanced efficiency. The current results are significant for the design of TiO_2/WO_3 hetero-structures with higher photo-activation duration and oxidation quantum yield.

1. Introduction

TiO_2-based semiconductor materials have been intensively investigated, due to attractive properties, such as high oxidation capacity, low cost, nontoxicity and chemical stability. However, for applications in photo-catalysis, the relatively high rate of recombination of the photo-generated electron-hole pairs in the surface region is an important drawback, since it results in a reduced catalytic quantum yield and, consequently, a poor efficiency device performance [1,2]. To enhance the back-reaction duration, TiO_2/WO_3 hetero-junction structures (HJS) were proposed instead largely known pristine or doped films [3]. In HJS, the increased photo-catalytic performance is ensured *via* spatial separation of the (photo-generated) charge carriers.

The tungsten trioxide (WO_3) thin films were subject for numerous investigations [4-9] since, due to a number of particular electrical and optical properties, they are can be applied in areas, such as electronics, optics and environmental protection. Unless the current study, most papers in the literature deals with the preparation of WO_3 thin films by spray-pyrolysis technique, the magnetron sputtering at low temperatures being scarcely encountered [8,9].

The energy band gap value in the semiconductor materials is one of the key properties of the materials, which should be optimized for efficient conversion of solar energy by photo-catalysis. Coupling a wider band gap semiconductor (in our case - TiO_2, having an E_g value of 3.2 eV) with an other semiconductor with a narrower band gap (here - WO_3, with E_g=2.8 eV) results in effective separation of charge carrier pairs generated in the junction region of the transparent materials by UV light irradiation [10-12], capable to work under low intensity incident flux [13]. This materials' coupling leads to a transfer of an electron from the conduction band of TiO_2 to the conduction band of WO_3, with a considerable lifetime [14]. This transfer is associated with a macroscopically visible change in surface color, which turns blue. Most of the information in on the TiO_2/WO_3 hetero-junctions is related to 1-D structures, where WO_3 nanoparticles were grown on the TiO_2 film surface [13], making a systematic investigation and, possibly, a process model, more difficult.

In this contribution we report on 2-D hetero-structures of a WO_3/TiO_2 device. It was grown by cathodic sputtering of a titania target in a radio frequency reactive discharge. This allowed us to easily control the films thickness and chemical composition on large area samples. The structural, surface morphology and optical properties of the samples were investigated using X-ray diffraction (XRD), atomic force microscopy (AFM) and UV-Vis spectroscopy.

The current results are significant for a potential modeling of the surface processes in non-homogeneous surface regions of the photo-catalytic materials. They are the starting point to future quantitative systematic investigation of the gain in photo-catalytic performance and super-hydrophilicity of titania-based materials.

2. Experimental details

The materials synthesis experiments were carried out using an experimental setup and procedures described in detail elsewhere [15]. The deposition chamber was evacuated up to a pressure of 2.0×10^{-5} mbar. In a first step, WO_3 thin films were grown on borosilicate glass substrates by using a plasma discharge produced in a magnetron arrangement, operated at an RF frequency of 13.56 MHz and an injected RF power of 50W. The discharge was running in a high-purity Ar-O_2 gas mixture. The sputtering source was a 3-inch diameter cathode of WO_3. The substrates were placed at 6 cm in front of the magnetron cathode.

In a second step, TiO_2 thin films were grown on top of the WO_3 films in the same deposition session, using a TiO_2 target and an RF injected power of 150 W, under the same deposition condition, as described above. The total gas pressure in the discharge was set at 2.0×10^{-2} mbar during all deposition runs in the two steps mentioned above. This was ensured, under our pumping speed conditions, by using mass flow controllers and constant mass flow rates of 25 sccm for the Ar gas and 0.5 sccm for the oxygen gas. The later value was chosen to ensure film stoichiometry in the films. During all the deposition runs, the substrates were heated up at 250°C to remove contamination due to residual contaminant species in the processing chamber. The deposition times and film thickness values are shown in the Table 1.

Table 1: The deposition times and the mass flow rates for Ar and O_2 gases

Sample	**WO_3**	**TiO_2**	**Film thickness (nm)**
S1	15 min	60 min	46
S2	30 min	120 min	90
S3	60 min	240 min	115

To increase film crystallinity, the samples were post-annealed in air at 400°C for 1 hour. The information on films crystallinity was derived from X-ray diffraction data, acquired with a Shimadzu LabX XRD-6000 diffractometer (Cu Kα radiation, λ=1.54182 Å). The surface morphology Films was investigated using an NT-MDT Solver Pro-M atomic force microscope, operated in tapping mode. The AFM images were analyzed with Gwyddion software. The optical transmittance spectra of films within the 190 - 1100 nm range were recorded using an Evolution 300 UV-Vis Thermo Scientific spectrometer. An AvaSpec-2048 equipment and the Avasoft thin film software package was used for film thickness measurements.

3. Results and discussions

The XRD patterns (Fig. 1) of the investigated annealed samples show low index peaks, specific for the triclinic crystal structure of WO_3 material [16]. No TiO_2 peaks could be detected in the diffraction patterns, even after the annealing at 400°C. Triggering the crystallization processes in the TiO_2 film involves a careful choice of the deposition parameters of this material, as long as increasing the annealing temperature may result in diffusion across the films' interface, with adverse consequences in terms of junction profile.

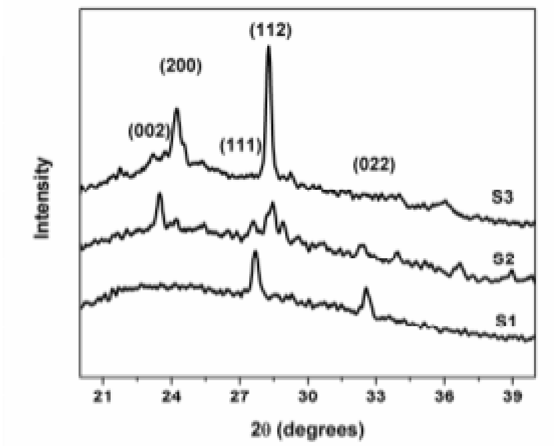

Fig. 1: XRD patterns of the TiO_2/WO_3 layers.

As revealed by AFM imagery (a typical example is shown in Fig. 2), the surface of the investigated samples with the titanium dioxide films on top of the bilayer is fairly compact, with no porosities and a relatively flat surface profile. The RMS roughness values were situated within the 8 - 9 nm range.

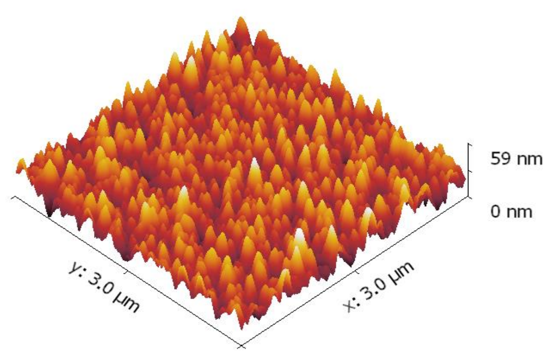

Fig. 2: A typical example of 3-D AFM images, showing the surface topography of the thickest sample (S3).

The transmittance spectrum of the samples within the 350 - 1100 nm wavelength range is shown in Fig. 3. A sharp decrease in the film transmittance below 350 nm is noticeable for all the samples, with a special remark for the lowest thickness sample (S1), there where the transmittance in the higher wavelength region is missing, as expected.

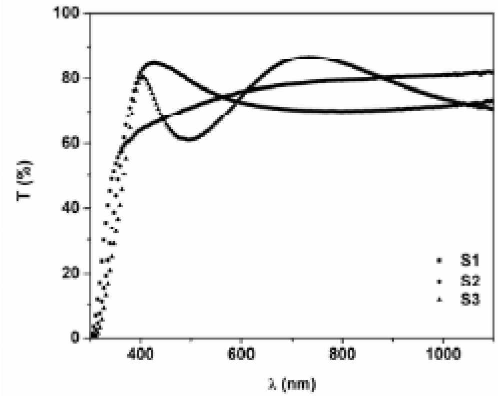

Fig. 3: Transmittance spectra of the 3 samples.

The differences in the shape of the transmittance envelope are related to interference effects and have been, therefore, used to calculate the samples thickness values, according to the Sreemany procedure [17]. The transmittance data can be used as a main part of the input for the calculation of the band gap of the investigated materials.

4. Conclusion

TiO_2/WO_3 thin layers were synthesized on heated glass substrates by RF magnetron sputtering. Upon annealing at 400°C for 1 hour in air, the XRD analysis of deposited samples revealed the presence of triclinic crystalline phase of the WO_3 film, but no structural ordering in the TiO_2 film. The samples were transparent and fairly flat at surface, with a RMS roughness value of approx. 8-9 nm. Experiments are currently carried out to complete the reported results with data on elemental sputter depth profile, electrical properties, photo-catalytic activity and surface hydrophilicity. The results may serve to design new devices for photo-catalytic application in environment and energy-related applications and as an input for a comprehensive model of the interface processes in oxide hetero-junctions.

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