



Preparation and characterization of tungsten oxide thin films

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ABSTRACT

The present review article deals with the deposition technique for the preparation of tungsten oxide films. There are several different methods of deposition were widely used including screen printing method, electrophoretic deposition, thermal evaporation, pulsed laser deposition method, sol gel spin coating deposition, radio frequency reactive magnetron sputter deposition and chemical bath deposition technique as described by many researchers. X-ray diffraction was used to determine the structure of obtained films. The X-ray diffraction patterns indicate that the as-deposited films and annealed films are amorphous and crystallite, respectively.

Keywords: Tungsten oxide, thin films, semiconductor, deposition, film thickness.

INTRODUCTION

There are some allotropic modifications such as tetragonal, monoclinic and orthorhombic structure could be seen for tungsten oxide thin films. Researchers point out that these structures are affected by many factors including temperature, impurity and substrate material. Tungsten oxide thin films are *n*-type semiconductors with a band gap of 2.8 eV [1] having a strong absorption within the solar spectrum (440 nm). These films have been widely studied for various applications such as photocatalysis [2], high density memory devices, smart windows [3], gas sensor [4, 5], photoelectrochemical water splitting, and electrochromism [6-8].

Generally, characterization of thin films will be carried out by using different tools such as x-ray diffraction [9-14], scanning electron microscopy [15-20], atomic force microscopy [21-29], energy dispersive analysis x-ray [30-34], and UV visible spectrophotometer [35-40] as described by many researchers. So that, the general properties such as structure, composition, surface morphology and band gap of thin films can be investigated. In this work, the synthesis of tungsten oxide thin films by using various deposition methods will be discussed. The obtained films will be characterized and analyzed by using different characterization tools.

LITERATURE SURVEY

Gullapalli et al., 2010 [41] have successfully prepared WO₃ thin films using radio frequency reactive magnetron sputter deposition. Finally, they conclude that the obtained films prepared at 100-300 °C could be the best candidate for hydrogen sulfide sensor for application in coal gasification system. Sulfur is highly toxic and it is a natural contaminant in fossil fuel supplied. They aware that the amount of hydrogen sulfide produced from coal gasification plant must be effectively controlled and monitored.

Nishchay et al., 2016 [42] prepared tungsten oxide films using spark ablation and focused inertial deposition technique. The various crystal structures of the resulting materials were produced by controlling the experimental conditions. For example, the as-deposited films and annealed films (at 500 °C) are amorphous and crystallite, respectively. Lastly, they conclude that the obtained films provide high sensitivity and high accuracy in application for NO₂ sensing.

Hiroharu et al., 2004 [43] have proposed that the preparation of tungsten oxide thin films by using pulsed laser deposition method. They choose this deposition method due to many advantages such as fast, cost effective and versatile. The films were doped with various amounts of gold and palladium. The obtained results show that the maximum sensitivities for 200 pm NO₂ gas were 69 for the films doped with gold and 24 for the films doped with palladium, at the temperature of 300 °C. Lastly, they figure out that these maximum sensitivities are higher than that of the non-doped tungsten oxide films which sensitivity is estimate about 17.

Thermal conductivity of sputtered tungsten oxide films with thickness of 100 to 300 nm was investigated by Wang et al., 2006 [44]. X-ray diffraction patterns of thin films of 10 % oxygen and 100 % oxygen show a mixture of WO₂ & WO₃ and WO₃ only, respectively. They further explain that the oxidation reaction is incomplete. These films produced two strong peaks which contributed to trigonal WO₂ and monoclinic WO₃, respectively. In terms of thermal conductivity studies, the films of 100 % oxygen (1.6 Wm⁻¹K⁻¹) have a higher thermal conductivity than those of 10 % oxygen (1.3 Wm⁻¹K⁻¹). This fact is due to mismatch of phonon state between the WO₂ and WO₃ phases.

Tungsten oxide thin films were grown onto substrate by using a sol gel spin coating deposition method as proposed by Riech et al., 2013 [45]. XRD data analysis show that the intensity of the monoclinic WO₃ peaks increased as the sample was heated at 500 °C. They have shown that the band gap was 3.17 eV as an indirect transition. Finally, the photoluminescence spectra of obtained films indicate broad band in the blue region.

Geun et al., 2016 [46] have proposed the synthesis of WO₃ films by using spin coating and screen printing method in the presence of organic additive such as polyvinylpyrrolidone. Scanning electron microscopy results show that the screen printed films and spin coated films have thickness of 1.8 μm and 1.2 μm, respectively. Furthermore, the obtained morphology results reflect that the screen printed films contain much larger irregular particles. In terms of optical transmission study, they found that the screen printed films show higher optical transmittance at 630 nm. Further, they conclude that these films could be used in an-assisted tandem PEC/DSSC cell configuration for un-assisted water splitting.

Thermal evaporation method was used to prepare WO₃ thin films as suggested by Saleem et al., 2015 [47]. They observe that the optoelectronic properties were significantly changes before and after hydrogen annealing treatment. For example, as-deposited films show stoichiometric, amorphous and electrical insulator. However, they conclude that the change in electrical resistivity and carrier concentration of the annealed films are due to some reasons including formation of intrinsic defects and improvement in crystallinity. For example, resistivity of 0.048 Ωcm with carrier concentration of 2.8 X 10²¹ cm⁻³ was detected for the films heated at 550 °C.

Electrophoretic deposition method was employed to prepare WO₃ films for the application of photoelectrochemical water splitting as proposed by Fang et al., 2015 [48]. They explain that control the films thickness is needed in order to maximize the light absorption. They also comment that thick films can improve the light absorption, but can also shorten the excited charge lifetime. For example, it was clearly observed that the photo conversion efficiency increased with an increase in the film thickness up to 18 μm (0.924%). However, the photo conversion efficiency drops gradually when the film thickness was increased further, such as 22 μm (0.316 %) and 36 μm (0.175 %). A similar trend has been detected for the visible efficiency and UV-efficiency as well.

A low cost, simple chemical bath deposition technique has been selected to prepare WO₃ films as described by Metodija & Toni, 2007 [49]. Fluoride doped tin oxide substrates were used as substrate and they were cleaned with detergent and distilled water. The deposition process was carried out at 90 °C in acidic conditions in the presence of diethyl sulfate and Na₂WO₄.2H₂O solutions. They found that optical transmittance spectra of colored and bleached states indicated significant change in the transmittance. Further, they suggest that these films could be used in electrochromic devices.

CONCLUSION

This work has confirmed that WO₃ thin films have been successfully deposited by using a variety of methods. Researchers point out that as-deposited films and annealed films are amorphous and crystallite, respectively based on X-ray diffraction data. The experimental findings reflect that WO₃ films could be used in gas sensor, photoelectrochemical water splitting and electrochromic devices.

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