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Influence of Deposition Parameters on Optical Properties of Sputtered Tungsten Oxide Films

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Abstract: Thin films of tungsten oxide were deposited on glass substrates at different temperatures and O_2/Ar ratios using DC Magnetron sputtering system. The samples were characterized using x-ray diffractometry and spectrophotometer structurally and optically respectively. Analysis of the results reveals dependence of structure on thickness and temperature. The O_2/Ar ratio is also found to influence the optical properties appreciably for the entire wavelength range studied. Visual inspection of the films show that O_2/Ar ratio influences the coloration of the film which varies from clear to dark blue for high to low O_2/Ar ratios respectively.

Keywords: Tungsten oxide, Optical properties, O_2/Ar ratio

1 Introduction

Tungsten oxide is a wide band gap semiconductor and has been widely studied in relation to its application in electrochromic devices [1,2], gas sensing [3], buffer layer in solar cells [4], and photocatalysis [5] . It has a tendency to form non-stoichiometric oxides giving films with varying colouration albeit stable.

Several thin film deposition techniques can be employed to fabricate tungsten oxide films [6,7,8,9]. Reactive sputtering, which involves sputtering a metallic target of tungsten in a plasma has advantages of easy control of deposition parameters such as the plasma gas, O_2, sputtering power, substrate temperature, pressure among others. The optimization of deposition parameters is key in achieving films with desired stoichiometry hence properties. For instance, Acosta *et al* observed that tungsten oxide films grown with argon pressure pAr≥6 Pa have high transmittance and are transparent but transmittance degrades with reduced pressure to as low as 20% at pAr = 3.33 Pa [10]. In this work, tungsten oxide films were deposited with varying O_2/Ar gas ratios in the plasma, temperatures and thicknesses. The properties were investigated in relation to structure and optical behavior of the film.

2 Experiments

Thin films of thickness between 60nm and 400 nm were deposited by DC magnetron sputtering on microscope glass slides at various substrate temperatures spanning from ambient to 400°C. Before sputtering, the system was pumped down to ~10-7 millibars after baking the chamber for 8 hours. The thickness of the films was determined by profilometry (Tencor Alpha Step) while temperature was monitored by thermocouple probes placed directly below the substrate. Reflectance and transmittance were measured by a Perkin–Elmer Lambda 900 UV/vis/NIR double beam spectrophotometer in the wavelength range 0.3–2.5 mm equipped with an integrating sphere to allow for measurements of rough substrate surfaces. For structural characterization, X-ray diffraction (XRD) was used to determine crystallinity of the produced films. XRD measurements were performed by a Siemens D5000 Diffractometer operating with a grazing incidence angle of 1o in parallel beam geometry using Cu Kα radiation. The diffraction pattern was analyzed between 20° and 60°.

3 Results and Discussion

3.1 Discharge Voltage and Current

During deposition of the films, argon flow rate was maintained constant in the sputtering chamber. It was

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expected that increase in O_2 flow rare would lead to a decline in current. Given that power was fixed, voltage was expected to rise in order to maintain constant power. This is evident from Figure 1. Temperature seemed to correlate with sputter yield resulting to higher currents at elevated temperatures with the converse with regard to voltage.

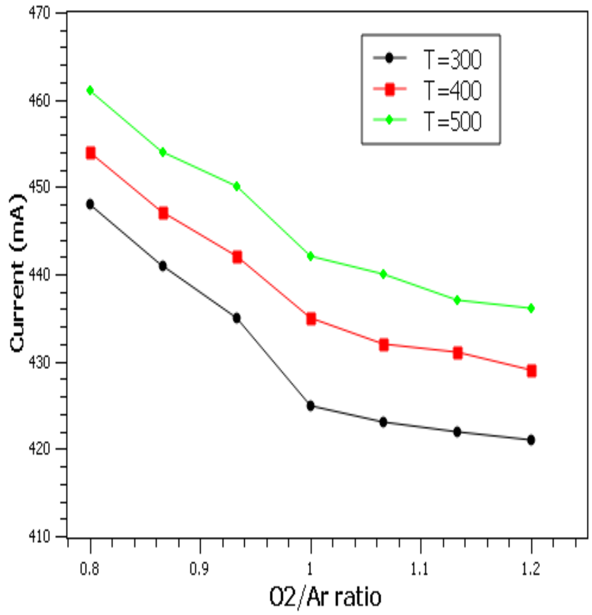

Fig. 1(a): Current dependence on O_2/Ar ratio.

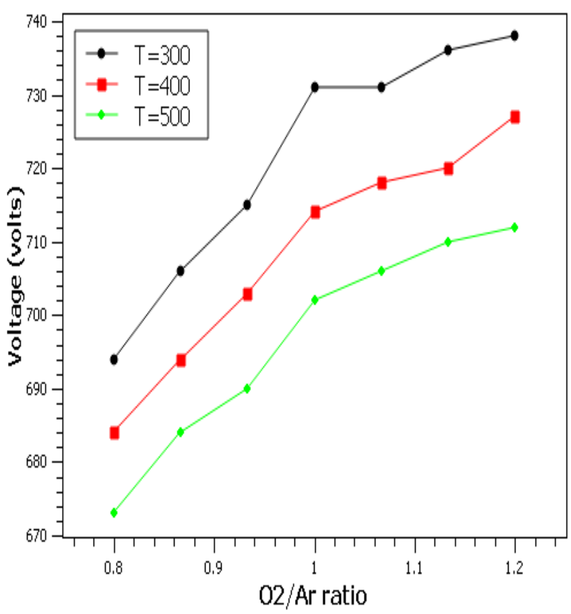

Fig. 1(b): Voltage dependence on O_2/Ar ratio.

3.2 Structure

The structure of the samples was investigated with regard to temperature and thickness. Figure 2 shows how temperature influences the structure of sputtered titanium oxide films at O_2/Ar ratio of 0.87. Films deposited at ambient (50ºC) and 300ºC were amorphous. At higher temperatures, films adopt a crystalline structure. This observation was also made by Hasan *et al* [11] when they investigated the properties of nanostructured tungsten oxide thin films using RF reactive sputtering.

Film crystallinity was also found to increase with thickness as in Figure 3. The peak at 23.37o and 47.82o are seen to evolve as thickness increase.

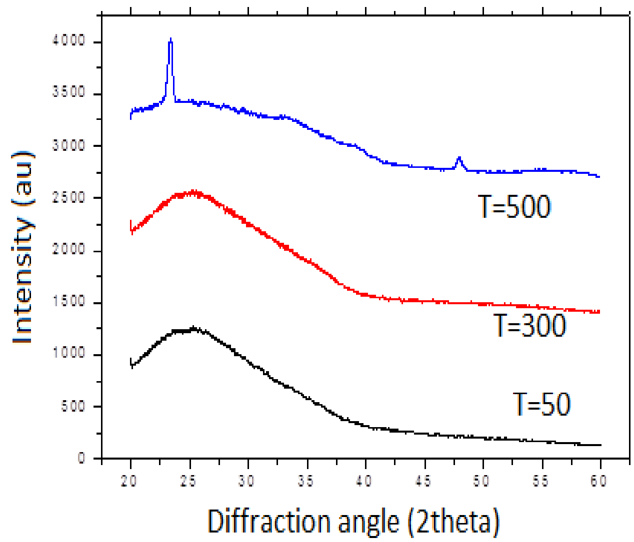

Fig. 2: Effect of Temperature on sputtered tungsten films at fixed thickness (202 nm) and O_2/Ar = 0.87.

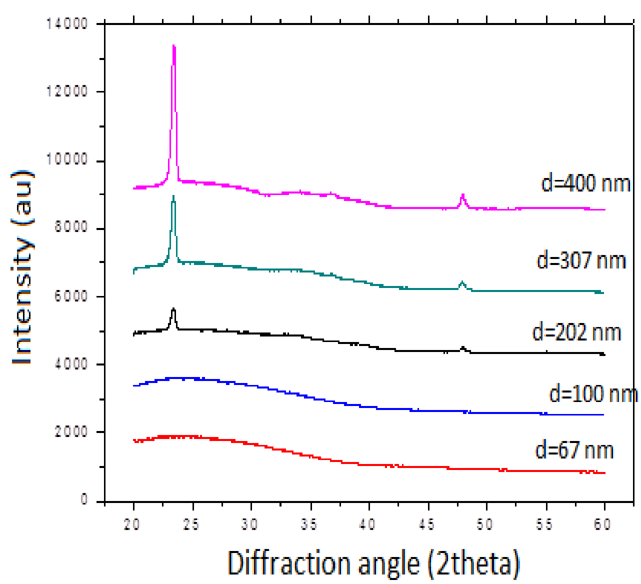

Fig. 3: Evolution of XRD peaks as thickness increase.

3.3 Effect of O_2/Ar Ratio on Sheet Resistance

The dependence of sheet resistance on gas ratio in the chamber is shown in Figure 4(a-d) for four films deposited at 50ºC, 300ºC, 400ºC and 500ºC. At low temperatures (<300ºC), sheet resistance increases almost exponentially with increased in O_2/Ar ratio. The formation of sub-stoichiometric tungsten oxide films could attribute to lower resistivities at lower gas ratios. At elevated temperatures (>300ºC), formation of crystalline films improves film conductivity which deteriorates as O_2/Ar increases due to diminishing oxygen vacancies.

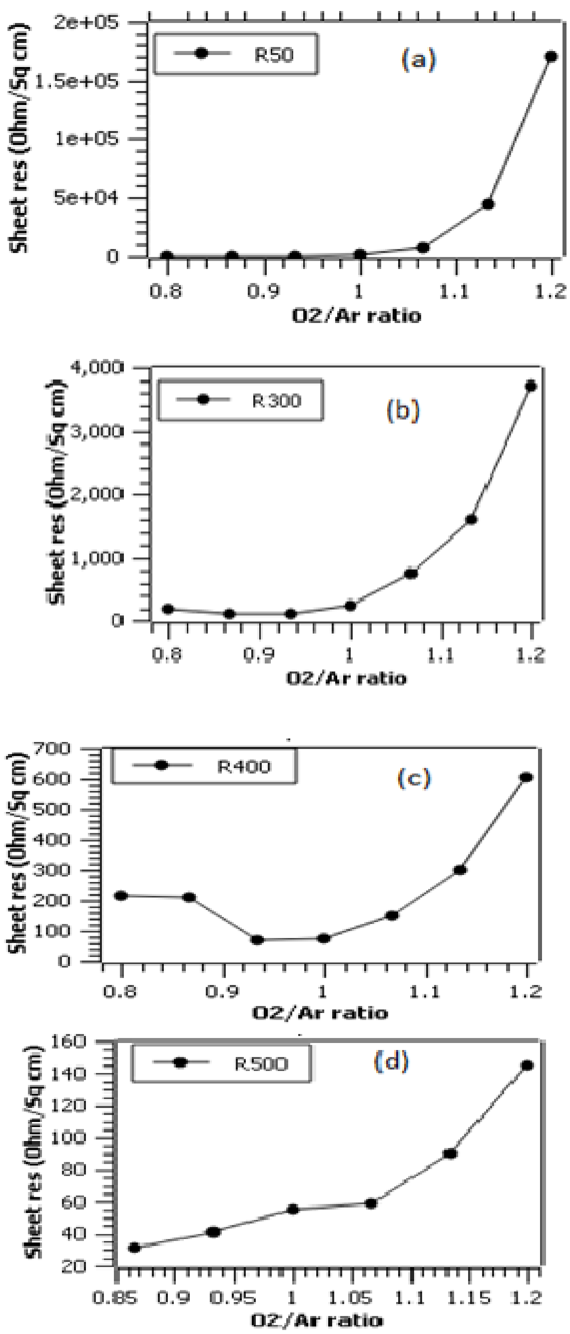

Fig. 4(a-d): Variation of Sheet résistance with O_2/Ar ratio for films deposited at different temperatures.

3.4 Transmittance and Reflectance

Sub-stoichiometric tungsten oxide arising from oxygen deficiency has low transparency. As seen in Figure 5(a&b), films with relatively higher O_2/Ar exhibit maximum transmittance close to 70% at 500 nm. Elevated temperatures lead to possible increased oxygen vacancies hence reduced transmittance. This is demonstrated by films deposited at 300 and 500 with maximum transmittance of 55% and 45% respectively. The films registering higher transmittance are those with higher O_2/Ar ratio in all the cases. The films exhibit varying coloration depending on O_2/Ar ratio as shown in Figure 5 ranging from dark for low O_2/Ar to almost clear (inset in Figure 5(b)). According literature [12], there are various forms of tungsten oxides depending on W:O ratio examples being WO_3 (Yellow), $WO_{2.9}$ (dark blue), $WO_{2.72}$) violet and the WO_2 (chocolate brown).

The films reflectivity increase sharply at wavelengths > 600 nm for films deposited at 500ºC (Figure 6(a)). This behavior is not surprising given that the films deposited at high temperatures exhibited lower resistivity.

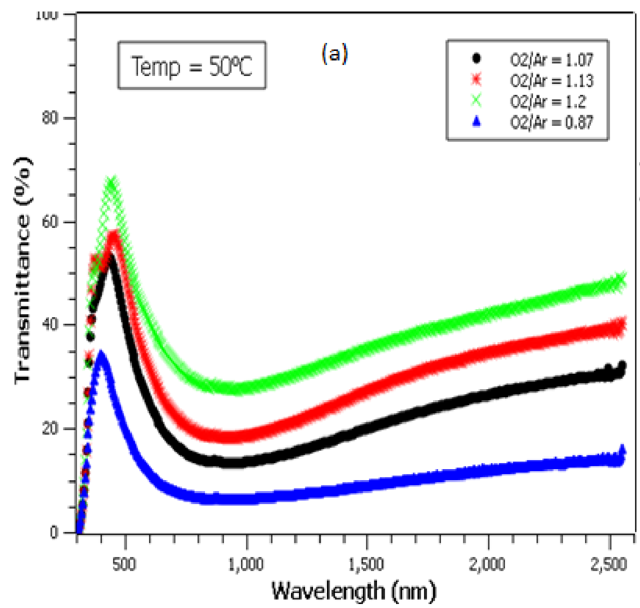

Fig. 5(a): Transmittance of 202 nm thick tungsten oxide films deposited at 50ºC for varying O_2/Ar ratios.

The films also show a remarkable change in transmittance with thickness. 300 nm thick films deposited at 500ºC is hardly transmitting while a 67 nm thick film exhibits close to 50% transmittance at 500 nm (Figure 6(b)). This demonstrates the influence of the gas ratios in the plasma to the optical properties of the tungsten oxide films.

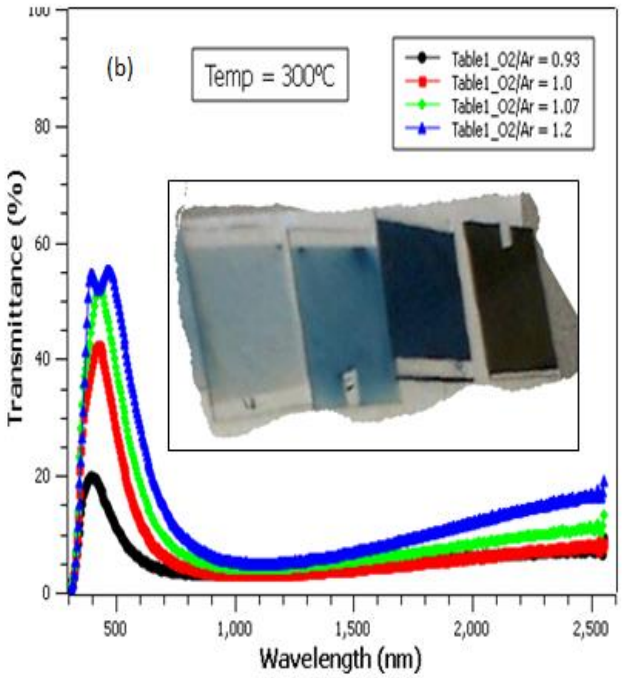

Fig. 5(b): Transmittance of 202 nm thick tungsten oxide films deposited at 300ºC for varying O_2/Ar ratios.. Inset on the lower panel are tungsten films showing some of the actual films.

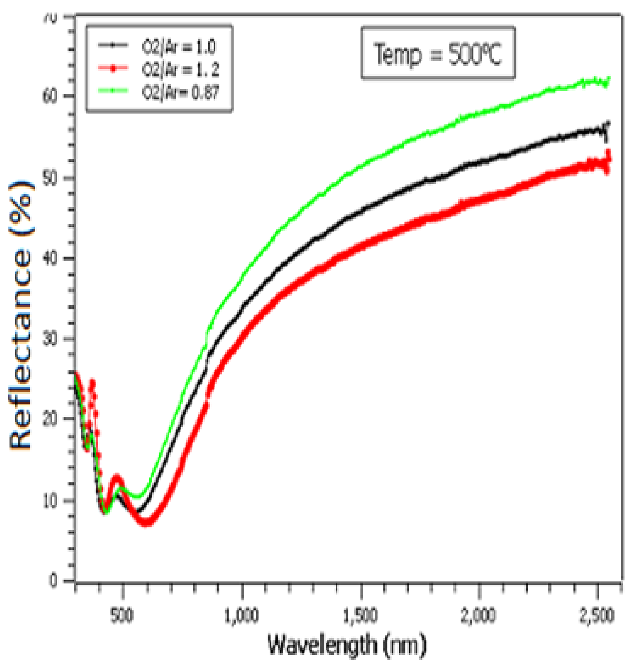

Fig. 6(a): Tungsten oxide films deposited at 500ºC: Reflectance of 202 nm thick films for varying O_2/Ar.

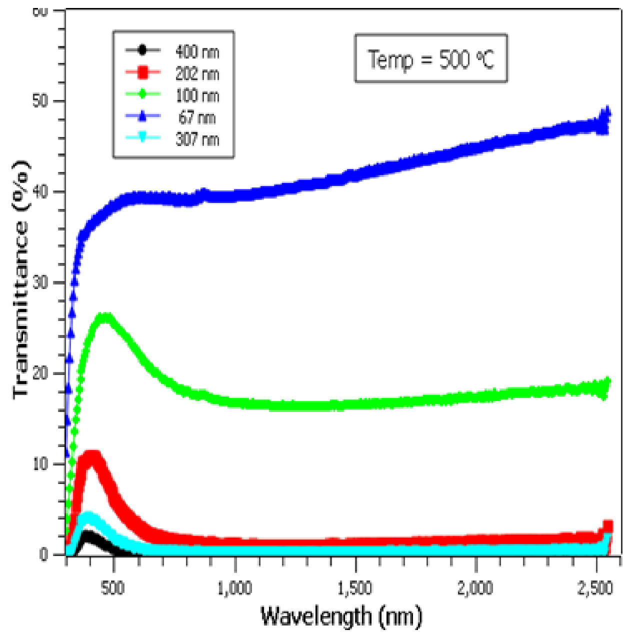

Fig. 6(b): Tungsten oxide films deposited at 500ºC illustrating transmittance dependence on thickness of the films.

4 Conclusions

The aim of this work was to investigate the role of O_2/Ar ratio, temperature and thickness on the structural and optical properties of sputtered tungsten oxide films. The study reveals that thickness and temperature influence the structure. Deposition of the films at temperatures below 300 led to amorphous films and even at elevated temperatures, thickness would still play a role in determining the structure. It has also been shown slight variation in O_2/Ar ratio affects the optical properties significantly.

Acknowledgement

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