Influence of Deposition Parameters on the Optical Properties of Thin Tungsten Oxide Films Prepared By Reactive Dc Magnetron Sputtering

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ABSTRACT
Tungsten oxide thin films are the most investigated because of their possible application in electrochromic devices. Studies have shown that the film properties depend on deposition conditions and preparation techniques. In this work, the optical properties of tungsten oxide thin films prepared in reactive dc magnetron sputtering of tungsten target with argon in oxygen atmosphere have been studied. The optical properties of films prepared at different sputtering power (300 – 400) watts and deposition pressure (0.65 – 0.90) Pa were investigated through the transmittance measurements in the wavelength range 300 - 800 nm. The experimental data were used as an input data for simulations to determine the band gap energy, refractive index, extinction coefficient, and film thickness of tungsten oxide films. From these studies the effects of increasing sputtering power from 300 watts to 400 watts was found to; decreased optical band gap from 3.16 eV to 2.97 eV while refractive index increased from 2.05 to 2.38 respectively. In addition, the deposition rate increased while extinction coefficient decreased with sputtering power. Increasing deposition pressure from 0.65 Pa to 0.90 Pa resulted in the decrease in band gap energy from 2.94 eV to 2.89 eV while refractive index decreased from 2.43 to 2.08 respectively. Further, the X-ray diffraction measurement indicated that tungsten oxide thin films deposited were amorphous. The amorphous nature was confirmed by AFM measurement, which reveals a smooth surface.

Key Words: Tungsten oxide, thin films, optical properties, deposition conditions.

INTRODUCTION
Tungsten oxide thin film is reported to represent the best inorganic electrochromic material for many technological applications, as its optical properties are independent of the viewing angles and has an advantage of high optical contrast (Berggren, 2004).

In architectural engineering, tungsten oxide thin films represent the best working electrode in “smart” (electrochromic) window systems which
can moderate the room temperature through variable reflectance and transmittance of solar and thermal infrared radiation. Lee & DiBartolomeo, 2002; Raul, 1999; Hummel & Guenther, 1995). They can be applied in the making of side mirrors that can control the glare intensity in vehicles (Lampert, 1998; Bange, 1999), in information display (Wei et al., 2001; Lampert, 2003), thermal control of satellite in orbit, (Larsson, 2004; Devries et al., 1999). In addition they yielded the best results in an attempt to produce electrochromic writing medium (Monk et al., 2001).

Although tungsten oxide thin film is one of the most investigated electrochromic materials among the challenges is the need to determine a precise understanding of the intimate relationship between deposition parameters and film properties. This would enable researchers make an intelligent prediction of the film properties from the deposition conditions. Therefore, this study investigated the influence of sputtering power as well as deposition pressure on optical properties of tungsten oxide thin films.

MATERIALS AND METHODS

Tungsten oxide films were prepared using Edwards Auto 306 Magnetron Sputtering System by reactive dc method, from a 99.99% pure metallic tungsten target. The substrate (microscope glass slide) of dimensions 76.2 x 25.4 x1.0 mm were fixed on the rotary work holder, which consist of a 260 mm diameter aluminium plate attached to the chamber top plate by a rotary head through. To ensure uniform deposition of the film on the substrate the dc motor rotates the work holder continuously through 360°. The tungsten target was pre-sputtered in pure argon atmosphere for about 10 minutes before introducing oxygen in order to remove the surface oxide layers on the target prior deposition of each film.
During sputtering the oxygen and argon flow were maintained at constant ratio of 70:30 respectively.

The film thickness during deposition was monitored using the quartz crystal oscillator fixed inside the sputtering chamber and deposition rate was estimated by dividing thickness with the deposition time. However, actual thickness was established through simulation of transmittance data. The thickness of the films deposited ranged from 249 nm to 299 nm as sputtering power varied from 300 watts to 400 watts. In addition, while sputtering power was maintained constant, films of thickness between 250 nm and 283 nm were deposited as deposition pressure varied in the range of 0.65 - 0.90 Pa.

Transmittance spectra for various tungsten oxide thin film samples was recorded using Spectro 320 Optical Analyzer where a 12V, 0.25A dc power lamp powered at 6.75 watts was used as source of radiations for all measurements. The light radiations from the lamp were recorded at normal incidence to the tungsten oxide thin films surface. The lamp to detector separation was maintained at 20 mm while the spectral measurements were recorded in the range of 300 nm to 800 nm.

Using the transmittance spectra measurement as input, a simulation approach using Scout-98 software and applying OJL model by O'Leary et al. (1997) and adapted by Thesis (2000), produced simulated transmittance spectra that can be compared directly to the measured data. The model is adapted for computer simulation as it adequately covers electronic transition between valence and conduction bands. In addition, it describes both amorphous material and crystalline phases with high defect density quite well. Further, OJL model gives expressions for joint density of states for optical transitions from the valence band to the conduction band. From the
RESULTS AND DISCUSSION

A: Influence of Sputtering Power

Figure 1 show the rate of deposition of tungsten oxide film as a function of sputtering power where deposition rate increases with sputtering power. This can be attributed to the fact that, increase in sputtering power results to an increase in momentum of the argon ions, which are responsible for knocking out the tungsten atoms from the target. Hence, the sputtering yield increases (Swann, 1988) resulting to higher rate of deposition as compared to lower sputtering power.

expression for the density of states, the imaginary part of the dielectric function is modelled and then the real part is calculated by fast Fourier transformation to satisfy causality (Kramer-Kronig relations). The optical constants and other model parameters are then determined. XRD measurements were performed in order to determine the structure of the film. The samples were fixed at a grazing incidence angle (\( \omega \)) of 0.75° and the detector scan performed using RINT2000 Vertical goniometer. In addition, Atomic Force Microscopy (AFM) was performed on the surface of these films to examine the topology of the film surface and produce a topological image of the surface from which the nature of the material (amorphous or crystalline) can be detected.

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Figure 1: Deposition rate as a function of sputtering power.

Figure 2 shows the superimposed spectra of the optical transmittance as a function of wavelength. It's observed that the films formed are all transparent with their transmittance in the range of (60-87) % in the visible regions of the electromagnetic spectrum. This observation is supported by Gordon et al (2001) who reported that in its' fully oxidized state WO$_3$ is transparent throughout the visible region of the spectrum.

Figure 2: Optical transmittance as a function of wavelength for varying sputtering power.
Figure 3 illustrates a typical fit of experimental data for a sample prepared at 375 watts. The fit between the measured data and simulation indicates that the model used for this simulation adequately describes the optical behaviour of the deposited films.

The refractive index of tungsten oxide thin film was found to increase with sputtering power but decreased with wavelength as shown in figure 4. Increase in refractive index can be associated with physical and compositional changes (Smith, 1995) at higher sputtering power resulting to a higher packing density of the deposited film. The refractive index for film deposited at 400 watts was found to be more than 2.3 for wavelengths less than 500 nm. Hence from report by Kaneko et al. (1982) that films of refractive index around (2.3 – 2.4) are electrochromic, then films deposited at 400 watts are likely to be electrochromic.
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Figure 4: Refractive index as a function of wavelength for films deposited at different sputtering power.

The band gap energy for the films deposited decreases with increasing sputtering power as shown in figure 5. At high sputtering power, changes in composition of tungsten and oxygen atoms results to substochiometric oxide, (WO$_3$-x), where (x>0), with pseudo bands due to incomplete bonds. Such defects produced localized states in the amorphous solids. The presence of these bands is associated with lower band gap energy (Theye, 1974). The general decrease in the band gap energy with sputtering power can be attributed to presence of these localized states. The band gap values in this study (2.97 –3.16) eV compares well with report by Daniel et al. (1988) that the band gap energy for reactively sputtered amorphous tungsten oxide from tungsten target is around 3.1eV.
From figure 6, the extinction coefficient is found to increase exponentially with wavelength within the visible region of the spectrum. A general decrease in extinction coefficient with sputtering power is observed in the range of 300 - 375 watts. Increase in extinction coefficient for films deposited at 400 watts can be attributed to compositional changes in the $\text{WO}_3-x$ film resulting from increased $x$. In addition, Ong et al. (2001) reported that for large non-stoichiometry $\text{WO}_3-x$ where ($x>0.4$), the absorption goes up. From the equation $\alpha = 4\pi k/\lambda$ the extinction coefficient is proportional to absorption coefficient and hence the extinction coefficient is found to increase at 400 watts.
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Figure 6: Extinction coefficient as a function of wavelength for films deposited at different sputtering power.

Figure 7 (a, & b) shows the XRD pattern for tungsten oxide thin film deposited at sputtering power of 300 watts and 400 watts respectively. The X-ray diffraction pattern reveals two broad peaks. This suggests that the films are amorphous.
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Figure 7 (a) XRD spectrum for film deposited at 300 watts

Figure 7 (b): XRD spectrum for film deposited at 400 watts.

B: Influence of deposition pressure

Figure 8 shows deposition rate obtained through simulation of transmittance data on deposited films. An increase in deposition rate is
observed from 0.65 Pa to 0.75 Pa followed by a pronounced decrease from 0.80 Pa to 0.90 Pa. The initial increase in sputtering rate from 0.65 Pa to 0.75 Pa can be associated with resputtering at low pressures (Ohring, 1992). The decreased deposition rate from 0.8 Pa can be attributed to a reduction in the mean free path due to increased pressure resulting to an increased particle scattering. Therefore, few sputtered atoms reach the substrate resulting to low deposition rate. Decrease in deposition rate as deposition pressure increases during sputtering is also reported by Kaneko et al. (1982), Berggren (2004) and Deneuville and Gerard (1978).

Figure 8: Deposition rate as a function deposition pressure. This data is obtained through simulation of transmittance spectra.

Figure 9 shows the optical transmittance spectra for tungsten oxide films deposited at different deposition pressure. The recorded spectra show that tungsten oxide thin films deposited at deposition pressures ranging from
Figure 10 shows refractive index as a function of wavelength. Refractive index decreases with increase in wavelength. Similar findings were reported by Green (1990), which indicate that refractive index for films made by reactive dc magnetron sputtering is about 2.0 with a tendency to decrease with wavelength. In this study the value of refractive index at lower deposition pressure (below 400 nm) is between 2.3 and 2.4. Figure 10 shows that the refractive index of tungsten oxide thin film is found to decrease with increase in deposition pressure. At high deposition pressure, the mean free path is small and there are many collisions, which reduces the number and the energy of the sputtered atoms that are deposited on the substrate. This may lead to formation of pores in the film hence low packing density resulting in films of low refractive index. The observation made in this work is supported by report on density variation of tungsten oxide with decreasing pressure by Miyake et al. (1983). The report indicates that the density for sputtered amorphous tungsten oxide is about 6.1 g/cm$^3$ and is found to increase to 6.7 g/cm$^3$ with decreasing deposition pressure. The results obtained suggests that low deposition pressure are likely to produce better electrochromic films as their refractive index values range from 2.3 – 2.4 (Kaneko et al., 1982).
From figure 11, the extinction coefficient (k) is found to increase exponentially with wavelength within the visible region of the spectrum. The coefficient is also found to increase with deposition pressure in the range of 7.5 - 9.0 Pa. However, film deposited at 0.65 Pa was found to have greater extinction coefficient contrary to the trend exhibited by the others. This can be associated with various processes that take place during film deposition, such as resputtering, which affects the tungsten to oxygen atoms ratio, in addition to presence of impurities and defects in the resulting film. In general the extinction coefficient is low suggesting that the material hardly absorbs light in the visible region as it is transparent.
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Figure 11: Extinction coefficient as a function of wavelength for films deposited at different deposition pressure.

Figure 12 shows a decrease of the optical band gap with increase in deposition pressure. This can be attributed to deposition of tungsten oxide that has a stochiometry with less oxygen deficiency in comparison with those deposited at lower deposition pressure. Although these films are amorphous and disorderly, the grain sizes are considered wider than for those at lower pressures resulting to reduce band gap. This was pointed out by Green and Hussain (1991) in their explanation for band gap widening in disordered film. The variation of band gap energy with sputtering pressure as shown in this study is supported by research finding reported by Kaneko et al. (1988), Kitao et al. (1992), and Miyake et al. (1983). They reported $3.0 < E_g < 3.4$ eV for tungsten oxide thin film with a tendency that at high pressure of the sputter gas and a high O$_2$ admixture (total deposition pressure) in reactive sputtering giving a low E$_g$. 
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Figure 12: Shows the variation of band gap energy with deposition pressure.

Figure 13 shows a typical X-ray diffraction pattern for films deposited at deposition pressures of 0.75 Pa while the sputtering power was maintained constant at 350 watts. The presence of two broad peaks and absence of intensive peaks suggests that the films are amorphous.
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Figure 13: XRD spectrum for film deposited at 0.75 Pa

Figure 14 shows an AFM image of a sample of the tungsten oxide films deposited in this study.

Figure 14: Atomic force micrograph of the surface of tungsten oxide thin film. The image displays a 1000 x 1000 nm scan range revealing a rather smooth film that is characteristic of amorphous material.

The image reveals very few white protrusions that are sparsely populated. Hence, the film is generally smooth. This implies that the deposited tungsten oxide thin films are amorphous and confirms the results of XRD measurements.

CONCLUSION

In this study a correlation between the deposition parameters and optical properties of the deposited films has been established. An increase in
deposition power resulted to an increase deposition rate and refractive index while band gap energy and extinction coefficient decreases. It was also established that the refractive index and optical band gap decreases as the deposition pressure increased while the extinction coefficient increases with increase in deposition pressure. Variation of refractive index among films deposited at different sputtering power and deposition pressure suggest compositional differences. Therefore, deposition parameters used in this study influenced the optical properties of the deposited films. The as-deposited films are amorphous as evidenced by their X-ray diffraction spectra and the AFM images. In addition, the transmittance spectra reveal highly transparent films within the visible range. We can conclude that the optical properties of tungsten oxide thin films are highly influenced by the sputtering power and the prevailing deposition pressure.

ACKNOWLEDGEMENT

We appreciate the university assistance in sending my samples to Japan for X-Ray Diffraction (XRD) and Atomic Force Microcopy (AFM) measurement. We are grateful to Dr. S. Venkataraj of Advanced Material Laboratory, National Institute for Material Science, Ibaraki, Japan for his assistant in structural measurement that is, the XRD and AFM on the tungsten oxide thin films.

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