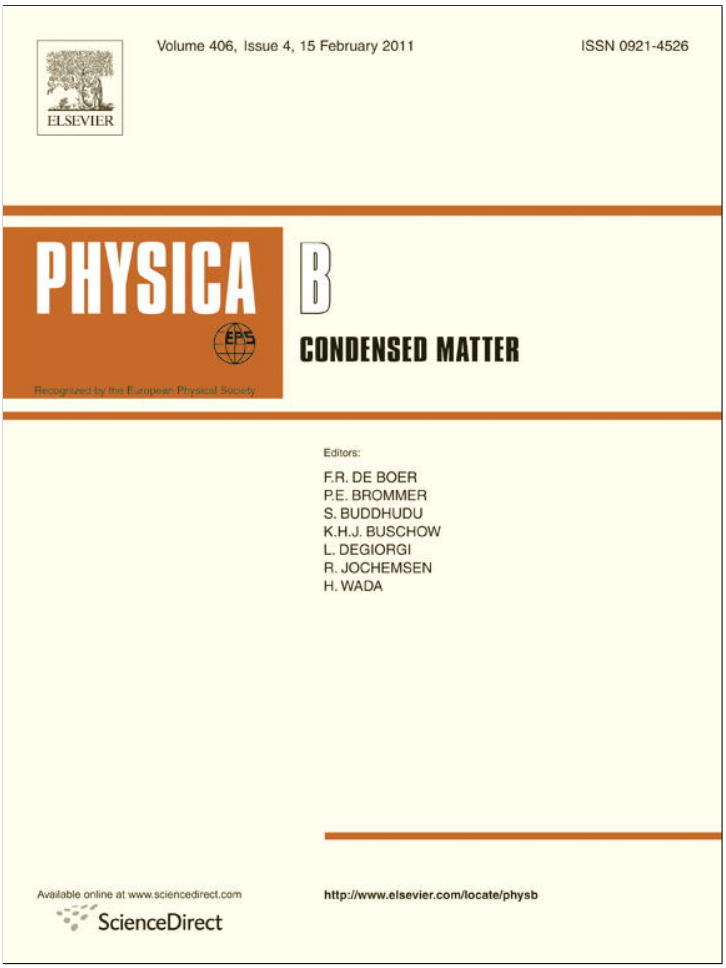

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Development of structural and optical properties of WO_x films upon increasing oxygen partial pressure during reactive sputtering

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ABSTRACT

WO_x films were prepared by reactive dc magnetron sputtering using tungsten target. Sputtering was carried out at a total pressure of 1.2 Pa using a mixture of argon plus oxygen in an effort to determine the influence of the oxygen partial pressure on structural and optical properties of the films. The deposition rate decreases significantly as the surface of the target is oxidized. X-Ray diffraction revealed the amorphous nature of all the films prepared at oxygen partial pressures higher than 1.71×10^{-3} Pa. For higher oxygen partial pressures, fully transparent films were deposited, which showed a slight increase in optical band gap with increasing oxygen partial pressure, while the refractive index was simultaneously decreased.

1. Introduction

WO_x thin films have found enormous applications in different technological areas [1–3]. For example, tungsten trioxide (WO_3) has a high capability to reversibly change its optical properties by insertion or extraction of small (e.g. H, Li) ions and charge-compensating electrons [4]. This makes it suitable for use in a variety of applications such as smart windows, nonemissive display devices, variable reflectance mirrors, and variable emissivity surfaces [4,5]. WO_3 is also used as an active layer in gas sensors since it has the ability to decrease its high resistance when gasses are adsorbed [6,7].

Several preparation techniques can be used to deposit WO_x thin films, including reactive radio-frequency (rf) magnetron sputtering [8], radio-frequency assisted pulsed laser deposition [9], pulsed laser deposition [3], reactive direct current (dc) magnetron sputtering [10], etc. Sputtering is a widely used technique for thin film preparation, and is superior in composition reproducibility and thin film formation on a large-area substrate. However, there are only a few detailed studies on the formation process of WO_x films by reactive sputtering [8,11,12].

Thus, the main purpose of this work is to prepare WO_x films with different stoichiometries, by reactive sputtering, for optoelectronic applications. The effect of oxygen partial pressure on the deposition rate, chemical composition, and structural and optical characteristics of the films was studied.

2. Experimental details

WO_x films were prepared on microscopic glass slides and Si (1 0 0) substrates by reactive magnetron sputtering of metallic tungsten (W) target in an argon and oxygen gas mixture. Sputtering was carried out from 7.5 cm diameter target at an average power of 800 W and with the substrates starting at room temperature. The W target was sputtered at a total pressure of 1.2 Pa in an oxygen–argon mixture, with the oxygen partial pressure controlled by regulating the oxygen flow. The oxygen partial pressure was varied from 2.99×10^{-4} to 0.52 Pa by variation of the flow rate from 0 to 70 sccm. The distance between the target and the substrate holder was 8.5 cm. The substrate was ultrasonically cleaned in acetone and dried with a flow of pure nitrogen before mounting on the substrate holder.

The cryogenically pumped vacuum system had a base pressure of 1.3×10^{-4} Pa at full pumping speed of 1500 l/s for air. To accommodate the relatively high pressure during sputtering, the pumping speed was throttled to about 25% of its maximum, resulting in a throttled base pressure of about 1.3×10^{-3} Pa. The total pressure during deposition was kept constant at 1.2 Pa as monitored by a Baratron® capacitance manometer. The total pressure was kept constant by adjusting the Ar flow while systematically varying the O_2 partial pressure. A differentially pumped gas

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monitor (PPM 100 by SRS) was used to measure the partial pressures during deposition. This gas monitor was pre-calibrated via the readings of the Baratron.

Glass slide substrates were used for X-ray diffraction (XRD) because of their amorphous structure and for measurements of the optical properties because of their high transparency in the visible range. Si(1 0 0) substrates were used for film thickness measurements (Dektak IIA profilometer) and composition analysis (energy dispersive analysis of X-ray, EDAX). The profilometer had an experimental error of about ± 10 nm in determining the film thickness.

The crystallographic structure of the films was determined by X-ray diffraction using a Siemens D-500 diffractometer with a Cu tube operated at 40 kV and 30 mA. The measurements were carried out using CuK_α radiation with a Ni filter to remove the CuK_β reflections. EDAX bulk composition measurements were performed in a Philips XL 30 scanning electron microscope at 10 kV using only internal absorption values and, therefore, the O content could be higher than the figures obtained.

The spectral transmittance (T) and reflectance (R) were measured at normal incidence using a Perkin-Elmer Lambda-19 spectrophotometer in the wavelength range $\lambda = 300$–2500 nm.

3. Results and discussion

3.1. Deposition characteristics

Fig. 1a shows the variation of oxygen partial pressure (P_{O_2}) with oxygen flow. In regions below 22.5 sccm and above 25 sccm it increases linearly. The slope is very small below 22.5 sccm, as oxygen is gettered by the sputtered metal. For the oxidized target above 25 sccm this mechanism is missing. Hence the oxygen partial pressure increases more rapidly with the oxygen flow in this regime. However, the steepest slope is observed between 22.5 and 25 sccm, as in this region the oxygen gettering breaks down due to the formation of oxide on the target surface.

The actual deposition rate (shown in Fig. 1b) was calculated by dividing the measured film thickness by the sputtering time. When the oxygen partial pressure increases from 2.99×10^{-4} to 0.01 Pa the deposition rate increases due to the incorporation of oxygen into the growing film. A significant drop in deposition rate is seen above 0.01 Pa. According to Meng and Dos Santos [13], this drop is due to the oxidation of the surface of the target causing a sudden reduction in the sputtering yield. For higher oxygen partial pressures, deposition decreases slightly.

3.2. Film composition and structure

The change in chemical composition of WO_x films was detected by EDAX. The peak heights in the EDAX spectra are proportional to the elements concentration. The qualitative EDAX spectra for WO_x prepared at $P_{O_2} = 5.74 \times 10^{-3}$ and 0.52 Pa are shown in Fig. 2a–d. It is seen from the spectra that in addition to O and W peaks there are C and Si peaks that may be ascribed to contamination by hydrocarbons and the contribution of the Si(1 0 0) substrate, respectively. Fig. 3 shows the variation of O/W with P_{O_2}. Initially the O/W atomic ratio increases approximately linearly upon increasing P_{O_2}. At $P_{O_2} = 0.20$ Pa the film is in the oxidic mode and has the stoichiometry of $WO_{3.04}$. Above 0.20 Pa sccm, the film composition remains constant and the oxygen partial pressure does not have any significant influence on the stoichiometry. This variation of stoichiometry with increasing P_{O_2} depends on the chemical reaction on both the target surface and the substrate. At the substrate, at low gas pressures, the formation of the compound is limited by the arrival rate and utilization of the reactive gas and so a substoichiometric (metal-rich) film is formed. As the reactive gas pressure is increased, the arrival of reactive gas increases and the film becomes stoichiometric/overstoichiometric [14]. The measured excess of oxygen found in the films prepared in the oxidic mode lies within the error bar. Another group [15] has reported a similar excess of oxygen and related it to the presence of OH groups on the film [15].

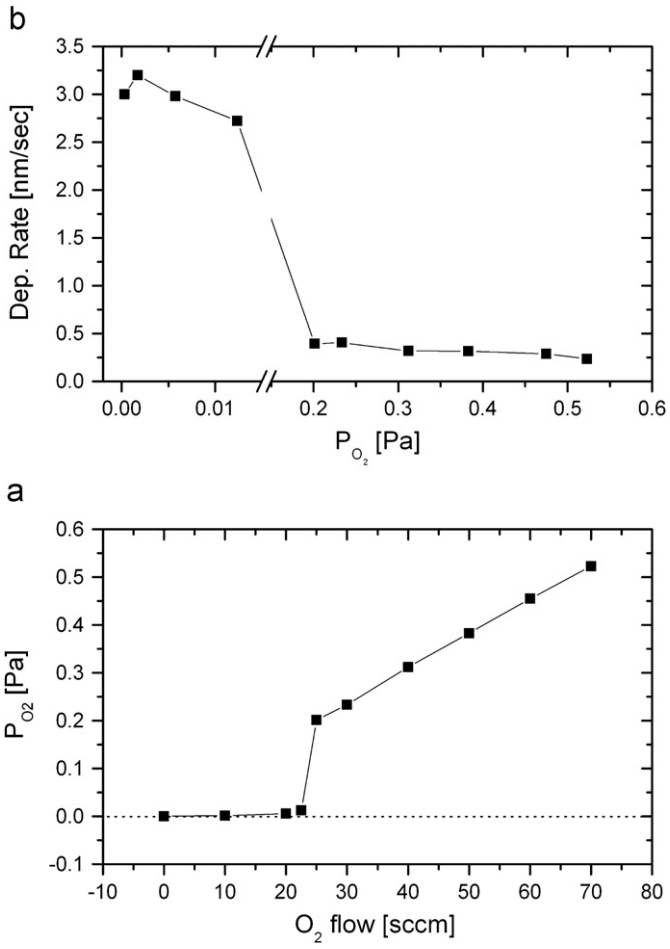

Fig. 1. (a) Oxygen partial pressure as a function of oxygen flow during reactive sputtering of tungsten and (b) deposition rate of WO_x films as a function of oxygen partial pressure.

The change in stoichiometry should also be reflected in a steady change of film structure with composition, i.e. oxygen partial pressure. Therefore, X-ray diffraction was employed to study the film structure. Fig. 4a–e displays the X-ray diffraction results of the as-deposited WO_x films formed at different oxygen partial pressures. At $P_{O_2} = 2.99 \times 10^{-4}$ Pa (0 sccm O_2 flow) the film is crystalline and the observed peaks are characteristic for the highly textured β-W (JCPDS card no. 47-1319). On addition of a small amount of oxygen, $P_{O_2} = 1.71 \times 10^{-3}$ Pa, the crystalline phase will still have the same general characteristics. Even though the pattern in Fig. 4b shows quite a few similarities to Fig. 4a, changes in composition are also evident: the preferred orientation changed, the intensity of the peaks decreased and new peak immerged (the (2 1 1) peak). As the oxygen partial pressure increased to $P_{O_2} = 5.74 \times 10^{-3}$ Pa, the long-range order is lost and an amorphous structure is dominant. All data depicted for the films formed at P_{O_2} higher than 5.74×10^{-3} Pa are characteristic for amorphous films. This type of structure has already been observed by several authors using the deposition methods with a low substrate temperature

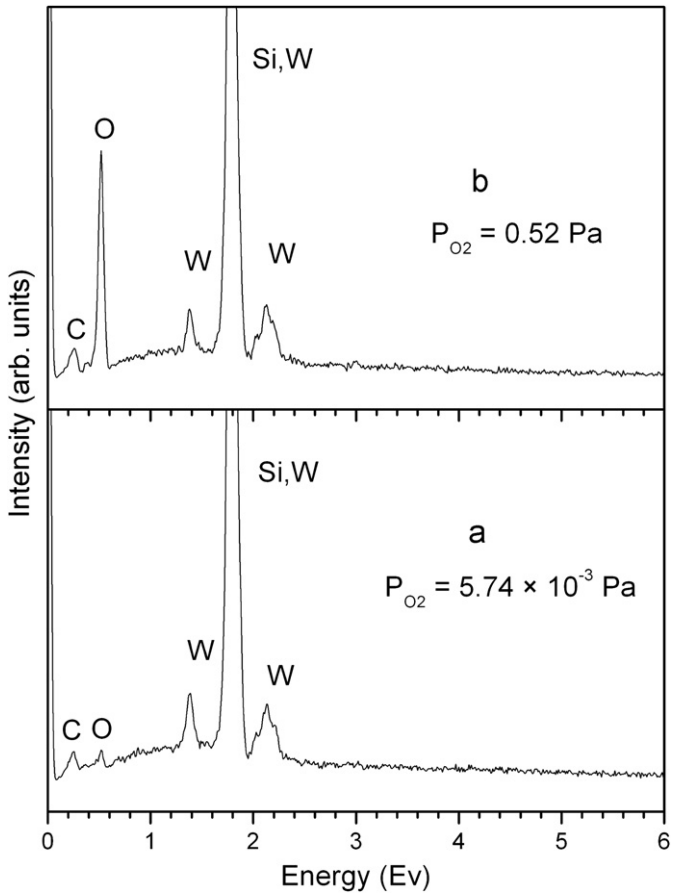

Fig. 2. EDAX spectra of WO_x films deposited at different P_{O_2}.

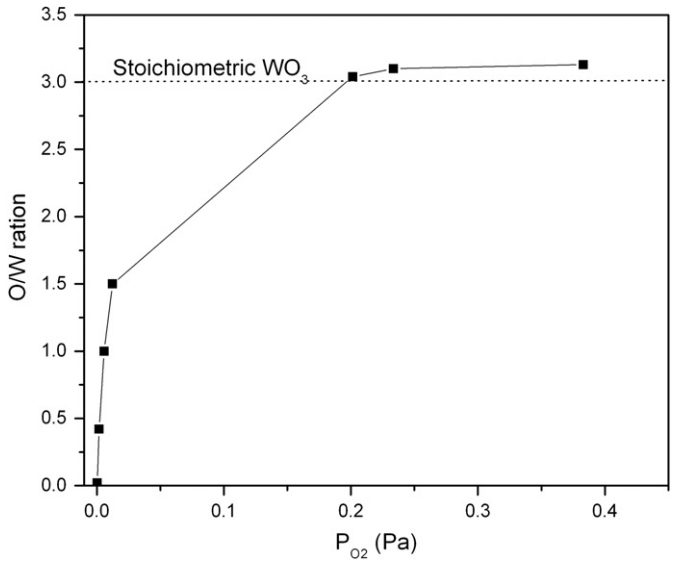

Fig. 3. O/W ratio of the as-deposited WO_x films prepared at 1.2 Pa vs. oxygen partial pressure. The solid line is a guide to the eye only.

[15]. One can suppose that the films are amorphous due to the low energy of particles impinging on the "cold" substrates.

3.3. Optical properties

Fig. 5 shows the spectral transmittance of WO_x films prepared at different oxygen partial pressures and total pressure of 1.2 Pa. A

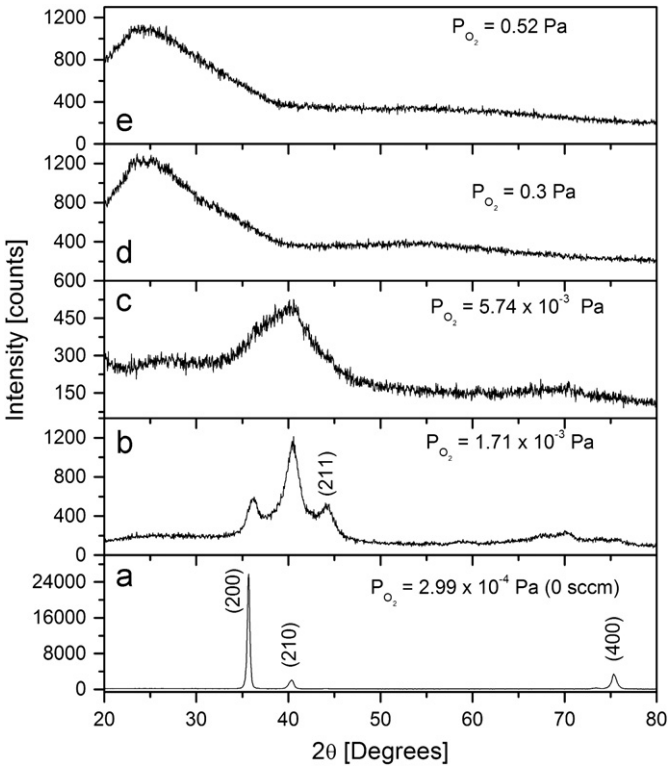

Fig. 4. XRD patterns of WO_x films produced at different oxygen partial pressures.

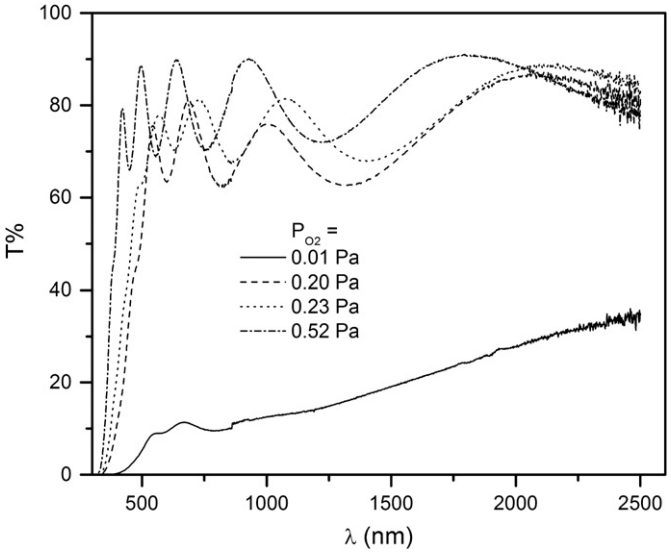

Fig. 5. Transmittance spectra of WO_x deposited at different oxygen partial pressures as a function of wavelength.

jump in transmittance values is observed between 0.01 and 0.20 Pa. This is due to target oxidation. All films prepared at P_{O_2} below 0.01 Pa are highly reflective. The transmittance of the films deposited at P_{O_2} above 0.20 Pa is very high and increases slightly with increasing P_{O_2}. This indicates that the films are completely oxidized in accordance with the measured stoichiometry.

The film refractive index (n), the extinction coefficient (k), and the film thickness (d) were calculated according to the transmission maxima and minima using the method described by Swanepoel [16]. The optical energy gap (E_g) of the films was deduced according to the Tauc relation [17]. The thicknesses determined from

Table 1
Optical band gap and film thickness determined at different oxygen partial pressures.

P_{O_2} (Pa)	E_g (eV)	Thickness, d (nm)	
		Thickness determined using profilometer	Thickness determined using Swanepoel method
0.01	1.56	251	–
0.20	2.90	486	478
0.23	3.00	495	510
0.52	3.18	461	452

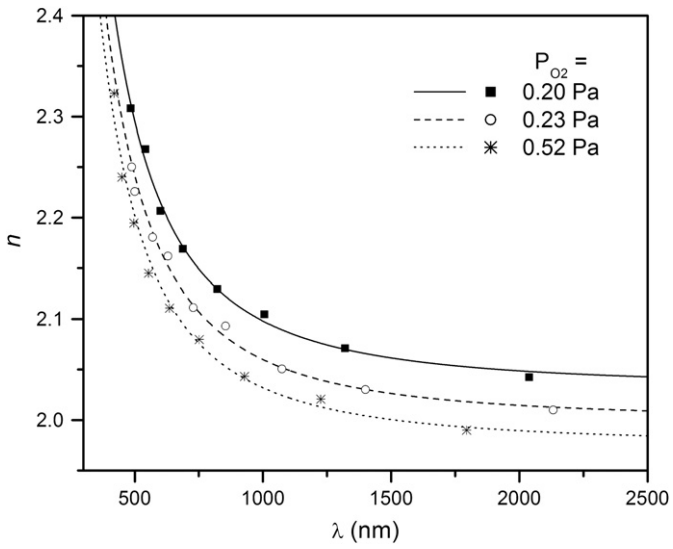

Fig. 6. Variation in refractive index of WO_x films formed under various oxygen partial pressures as a function of wavelength.

Swanepoel method, for all the films presenting interference fringes, are listed in Table 1, and they will be used in the remainder of this paper. The refractive index and the extinction coefficient for WO_x films formed at different oxygen partial pressures are shown in Figs. 6 and 7, respectively. For each P_{O_2} the refractive index decreases significantly with wavelength. The refractive index decreases with increasing P_{O_2}. This may be ascribed to the decrease in density of the films with increasing oxygen partial pressure. The extinction coefficient (Fig. 7) for the film prepared at 0.01 Pa has very high values due to the high absorption observed for this film. The k values for all the films prepared between 0.20 and 0.52 Pa are close to zero between 500 and 2500 nm. The k values decrease with increasing P_{O_2} as the stoichiometry of the films improves and the number of defects that cause absorption decreases.

Using the measured spectral transmittance, reflectance, and the film thickness, d, the absorption coefficient α was calculated according to the following equation:

$$\alpha = \frac{1}{d}\ln\left(\frac{1-R}{T}\right). \quad (1)$$

The optical band gap, E_g, was determined by [17]

$$\alpha h\nu = \beta(h\nu - E_g)^r \quad (2)$$

where β is a constant and r is equal to 2 or ½ for allowed indirect or direct transitions, respectively. The E_g values were extracted from the $(\alpha h\nu)^{1/2}$ vs. $h\nu$ plot, indicating an indirect band gap for all of the films prepared at different P_{O_2}. The obtained E_g values are listed in Table 1. It is found that the optical band gap derived depends slightly on oxygen partial pressure. The E_g value for the film

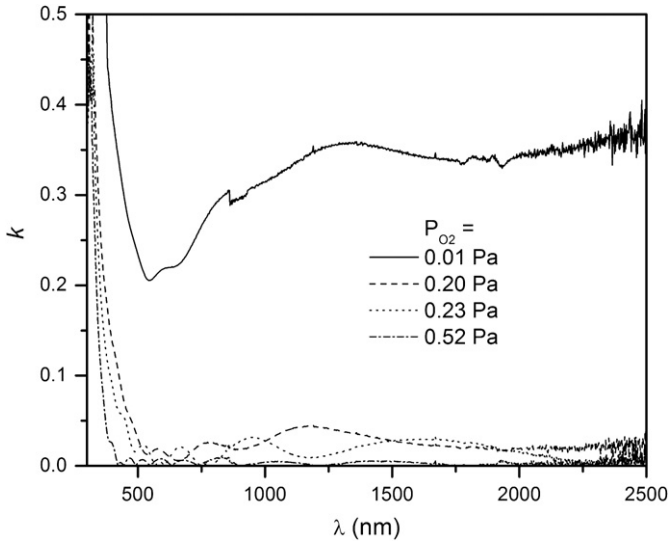

Fig. 7. Variation in extinction coefficient of WO_x films formed under various oxygen partial pressures as a function of wavelength.

prepared at $P_{O_2} = 0.01$ Pa is equals 1.56 eV. This particular film has a metallic-like behavior. The values of the optical band gap increases from 2.90 to 3.18 eV with the increase in oxygen partial pressure from 0.20 to 0.52 Pa. This increase in the optical band gap can be ascribed to the decrease in defect centers as the stoichiometry is improved. The obtained values are close to the values 3.17 – 3.23 eV obtained by Mohamed and Anders [18] for as-prepared amorphous and partially crystalline dc-sputtered molybdenum oxide films.

4. Conclusion

WO_x films were deposited by reactive dc magnetron sputtering in an atmosphere of Ar plus O_2. Sputtering was carried out on glass and Si(1 0 0) substrates held at room temperature. The oxidation of the surface of the target caused a sudden reduction in deposition rate. The films prepared at low oxygen partial pressure were substoichiometric, while a slight excess of oxygen was found in films prepared at higher oxygen partial pressures. The properties of the sputtered WO_x films were strongly affected by the oxygen partial pressure. Crystalline films were obtained only at very low oxygen partial pressures while amorphous films with different stoichiometries were obtained at moderate and higher oxygen partial pressures. The films prepared at oxygen partial pressure below 0.01 Pa were opaque. Above 0.01 Pa the transparency of the films improved. The refractive index, extinction coefficient, and optical band gap were found to change with oxygen partial pressure. The optical band gap increased from 2.90 to 3.18 eV. On the other hand the refractive index decreased slightly with increasing oxygen partial pressure due to the small decrease in density.

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