Structural, optical, and surface properties of WO₃ thin films for solar cells

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Abstract

Transparent back contacts can be used in thin film solar cells facilitating their potential application in tandem cells, bifacial devices and solar windows. In this study, tungsten oxide (WO₃) thin films were deposited by Radio Frequency (RF) reactive sputtering in Ar + O₂ ambient. The effects of post deposition anneals in air on the structural, optical, and surface properties of the deposited films were investigated using x-ray diffraction, UV/Vis/NIR spectrophotometry, and x-ray photoelectron spectroscopy, respectively. As-deposited films exhibited amorphous structures with no change after annealing at 300 °C. Samples annealed at 400 and 500 °C were crystallized and identified as pure monoclinic WO₃ phase with (200) and (002) preferred orientation, respectively, determined by XRD fiber texture analysis. Scherrer analysis of excess broadening indicated a coherency length of 50 and 65 nm for the 400 and 500 °C annealed films, respectively. High resolution XPS studies showed the presence of W⁶⁺ (WO₃) oxidation states at the surface of the as-deposited and the 300 °C annealed films. Annealing at 400-500 °C led to an oxygen deficient surface with a sub-stoichiometric WO_{3-x} phase. UV/Vis/NIR spectrophotometry revealed that post processing decreased the optical bandgap

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from 3.30 eV for the as-deposited films to 3.17 eV for the 500 °C annealed films. Results are compared with MoO₃ films deposited by a similar technique.

Keywords: oxide materials, semiconductors, thin films, energy storage materials, optical properties

1- Introduction

Mo is the most widely used material for the base electrode in Cu(In,Ga)Se₂ thin film solar cells. At typical thicknesses from 200-700 nm, Mo is opaque and is not useful for bifacial or tandem devices. Several groups have reported transparent back contacts for both substrate and superstrate configurations of CuInSe₂-based solar cells [1–3]. However, it was found that the Cu(In,Ga)Se₂ film should be deposited at low temperature (< 500 °C) with these materials to prevent the diffusion of F, in the case of SnO₂:F [4], or the formation of Ga₂O₃ at the interface [4–6], and thus limiting their potential application in Cu(In,Ga)Se₂ based devices.

In another study, Woods, et al. [7] showed that while transparent conductive oxide layers such as ITO can be proper back contact candidates for low band gap devices, non-ideal band alignment and lack of sufficient interface states or mid-gap states in the TCO for tunneling necessitates use of an interface layer for wide band gap ($E_g > 1.35$ eV) CuInSe₂-based devices. An appropriate interface layer can be used to control interface reactivity and to overcome poor band alignment. We have previously shown an example of this approach using a MoO₃ interlayer [8].

Models have shown that the barrier height at the back contact of the absorber should not exceed 0.3 eV in order to not impede cell performance[9]. Using the Schottky model [10] as a guide and assuming no interface reactivity, the barrier height (Φ_b) depends on the band gap (E_g) of the p-type semiconductor, the electron affinity (χ) of the p-type semiconductor, and the band gap (E_g^{SC}) and electron affinity (χ^{SC}) of the primary contact:

$$\Phi_b^p = E_g + \chi - (E_g^{SC} + \chi^{SC}) \quad (1)$$

Therefore, a well-aligned buffer layer is needed to reduce Φ_b .

We have recently demonstrated MoO₃ films as the primary back contact (interlayer) of Cu(In,Ga)Se₂ thin film solar cells [8,11–13]. Solar cell efficiencies of 14% and 12% were achieved for the Mo-MoO₃ and ITO-MoO₃ back contacts, respectively [8].

Analogously, WO₃ films with a work function $\Phi_M > 6$ eV [14] can be considered as a potential candidate for the primary back contact of Cu(In,Ga)Se₂ thin film solar cells. In particular, transparency $> 80\%$ in the visible and near-IR range and wide bandgap, with reports of $E_g = 2.5$ - 3.2 eV [15–17], make WO₃ a good back contact candidate for the bifacial and tandem devices. Its Fermi level and density of states can be potentially tuned by controlling the oxygen stoichiometry during deposition and/or post processing. To do so, we need an in-depth understanding of the structural, optical and surface properties of WO₃ films.

WO₃ has been used in various applications such as gas sensors [18], high temperature superconductivity [19,20], electro-chromic devices, windows, and displays [21,22], photo-electrochemical cells for solar energy conversion [15,23], and bulk-hetero-junction solar cells [24–26].

WO₃ is reported to have different crystal structures as a function of temperature: low-temperature monoclinic structure from -140 to -50 °C, triclinic structure from -50 to 17 °C, room temperature monoclinic structure from 17 to 330 °C, orthorhombic structure from 330 to 740 °C and a tetragonal structure above 740 °C [27–30]. The room temperature monoclinic structure is the most stable form of WO₃ with the space group of P21/n [29], however, oxygen deficiency may lead to the formation of sub-stoichiometric phases of W_nO_{3n-1} and W_nO_{3n-2} which are indicated in the W-O phase diagram [31].

This study addresses the properties of WO₃ thin films deposited by reactive RF sputtering in Ar + O₂ ambient. The effects of annealing on the structural, optical, and surface properties of the deposited films were studied. Evaluation of the WO₃ electronic properties and back contact role in Cu(In,Ga)Se₂ thin film solar cells is in progress and not reported here. Results are compared with MoO₃ films deposited by a similar technique.

2- Experimental

Tungsten oxide films were deposited on the soda lime glass substrates with transmittance > 99% over the wavelength of 350-2000 nm by reactive RF sputtering of a 10 cm diameter W target (99.95% purity). The sputter chamber was pumped to a base pressure of ~10⁻⁷ Torr. The

sputtering gases were a mixture of Ar and O₂, with oxygen content O₂/(O₂+Ar) = 50%. The sputtering pressure was fixed at 10 mTorr and RF power was 250 W. For each run, the target was pre-sputtered for 30 minutes to clean and condition the surface. The films were ~ 250 nm thick, as measured using a Dektak mechanical step profilometer. Post-processing of the films was performed by annealing at temperatures of 300-500 °C, for 1 hr in an air atmosphere, in a 6 cm diameter quartz tube furnace.

Structural properties of the films were characterized by symmetric x-ray diffraction (XRD) with Cu K α radiation, and 0.02° step size. High resolution x-ray photoemission spectroscopy (XPS) measurements with 0.05 eV step size were performed to study the core level binding energy and oxidation states of the films using a Physical Electronics Model 5400 instrument with monochromatic Al K α x-ray excitation under an applied voltage of 20 kV. Charging effects, which might be significant for the highly resistive samples, were corrected by calibrating the XPS spectrum based on the C 1s peak position (284.8 eV) [32]. Optical properties of the samples were analyzed using a Perkin-Elmer Lambda 750 UV/Vis/NIR spectrophotometer equipped with an integrating sphere. Total transmittance (T) and reflection (R) data were obtained from 300-1400 nm at 1 nm intervals.

3- Results and Discussion

Fig. 1 shows the XRD patterns of the WO₃ films as-deposited and annealed at different temperatures. The as-deposited film shows a broad peak centered at ~ 24° indicating an amorphous structure with a short range order of the atoms in the crystal lattice. This feature may

contain scattering from both the film and glass substrates. Annealing at 300 °C did not produce any measureable difference in the structure of WO₃ films so it didn't provide sufficient energy for nucleation and growth of WO₃ crystallites.

Samples annealed at 400 °C became crystalline (Fig. 1, and Table 1), with reflections at angles listed in Table 1 which were identified as reflections of the monoclinic WO₃ phase [33], space group P21/n with $a_0 = 0.731$ nm, $b_0 = 0.754$ nm, $c_0 = 0.769$ nm, and $\beta = 90.8$ degrees. These films have a (200) preferred orientation. Fig. 1 and Table 1 show that samples annealed at 500 °C were also identified as WO₃ phase, but with a (002) preferred orientation.

As mentioned above, monoclinic and orthorhombic structures are stable in the temperature range of 17-330 °C and 330-740 °C, respectively [27–30]. The monoclinic structure observed in this work might be formed because the very thin films did not experience the phase transition at 330 °C or because an orthorhombic structure formed during annealing above 330 °C following a transformation to a monoclinic phase when the temperature decreases down to room temperature. This result is in good agreement with the work done by Mahammad and Gillet [34] who have studied the phase transformation of WO₃ films by TEM and didn't observe any orthorhombic phase for the films annealed above 330 °C in air.

Preferential orientations of the films were determined using the fiber texture method proposed by Harris [35]. In this method, the texture coefficient (TC_{hkl}) of the crystals with the {hkl} orientation compared to a randomly oriented sample can be determined using the following equation [36]:

$$TC_{hkl} = n \frac{I_{hkl}}{I_{r,hkl}} \sum \frac{I_{hkl}}{I_{r,hkl}} \quad (2)$$

where I_{hkl} is the integrated intensity of the hkl reflection, and n is the number of reflections. The r indices refer to the randomly oriented sample, which can be derived from the ICDD card of powders. The volume fraction (V_{hkl}) of crystals oriented along each hkl will then be determined as followed:

$$V_{hkl} = 100 \times \frac{TC_{hkl}}{\sum TC_{hkl}} \quad (3)$$

For totally random samples such as powders, the TC numbers would be all equal to 1 with all the volume fractions (V_{hkl}) equally divided. For this study, the 8 peaks with the highest intensity were considered for the orientation analysis of films using the Harris method. The results for different hkl 's of the monoclinic unit cell are summarized in Table 1. The sum of the TC's for these samples is about 7. It can be seen that films annealed at 400 °C have about 24 vol. % of crystallites oriented in the (200) direction. However, a higher annealing temperature of 500 °C shifts the orientation of WO_3 films, and 27 vol. % of the crystallites are oriented in the (002) direction. For both cases, (-121) is the second preferred orientation of the annealed films.

The preferred (h00) orientation in the 400 °C annealed films suggests a coordination between the WO_3 planes containing a maximum W atomic density in WO_3 and the terminating O atoms in SiO_2 . In this closest-packing configuration, the W atoms lie exactly within planes parallel to the substrate (Fig. 2a). Line profile analysis of the (200) reflection profile indicates a Pearson VII

distribution with extended tail. Scherrer analysis [37] of excess broadening indicates a coherency length of 50 nm.

For the 500 °C annealed films, (h00) texture is vanished, with a lower (200) intensity and the elimination of the (400) reflection. Preferred orientation shifts to (001) suggesting a loss of coordination with the substrate O atoms. In this c-axis configuration, W atoms lie in 2 sets of parallel planes within the unit cell (Fig. 2b). Line profile analysis of the (002) reflection indicates a Pearson VII distribution with low nanocrystalline tail broadening and a coherency length of 65 nm.

Besides, the impact of impurity diffusion from the glass cannot be ruled out as a factor influencing film recrystallization and orientation at high temperature annealing [38].

Fig. 3 shows the optical T and R plots of the WO₃ films. All films show high transmittance in the visible range, indicating a low concentration of oxygen ion vacancies [39],[40]. The transmittance values drop steeply below the $\lambda \approx 400$ nm indicating a strong band-to-band absorption [41]. Increasing the annealing temperature did not significantly change the total transmittance of films but did cause a shift in the absorption edges to lower energy ranges, thus decreasing bandgaps.

The total absorption coefficient α was calculated from the T-R measurements using the following equation [41]:

$$\alpha = \frac{1}{d} \ln \frac{(1-R)^2}{T} \quad (4)$$

where d is the thickness, T the transmittance, and R the reflectance of WO_3 films. For photon energies slightly larger than E_g the absorption coefficient α can be described by the following equation:

$$\alpha E \sim (E - E_g)^n \quad (5)$$

where E is the photon energy and the exponent n depends on the type of optical transition in the gap region. Specifically, n equals $1/2$, $3/2$, and 2 for transitions being direct allowed, direct forbidden, and indirect allowed, respectively [41].

The electronic structure calculation of WO_3 indicate that the valence band and conduction band are comprised of the $2p$ orbitals of oxygen ions and $5d$ orbital of the tungsten cation, respectively [42,43]. Previous studies have reported both direct allowed [15,16,42] and indirect allowed [17,44] transition for the bandgap of WO_3 . Therefore, both conditions were examined here and the optical bandgaps (E_g) of the films were determined by plotting $(\alpha E)^2$ or $(\alpha E)^{1/2}$ versus $h\nu$ and by performing a linear fit to the data, extrapolating to the x-axis (E), as shown in Figure 3.

Linear fitting was performed for the data above the principal inflection point. Then, a series of fits were considered to perform the linear fit. The best fit was determined based on the shape of the curves, statistical absolute error (ΔE_g), and the coefficient of determination (r^2). As Figure 4a shows, none of the plots are well-matched with a linear fit. However, the indirect allowed transition gives a much better coefficient of determination (r^2), and is considered as the primary transition for the bandgap evaluation (Fig. 4b).

The bandgap values determined from the linear fit of the data above (for the same α range of 10^5 to 2×10^5) for the as-deposited, 300 °C annealed, 400 °C annealed, and 500 °C annealed films are shown in Figure 5. One can see that the annealing has reduced the bandgap values of reactive-sputtered WO₃ films. This is in agreement with the work of previous studies in which a drop in bandgap value was observed for the films annealed at high temperature, due to oxygen deficiency that occurs in WO₃ at higher annealing temperatures [45–47].

Fig. 6 shows the XPS survey scan of the WO₃ film deposited at room temperature with the major core level binding states indicated in the graph. This is a typical spectrum for all the WO₃ films independent of post treatment conditions. The carbon peak (C 1s) observed at ~284 eV is due to the surface contamination of the film as they were exposed to atmosphere.

High resolution scans of W 4f doublet core levels of all the WO₃ films are shown in Fig. 7. The peaks were fitted by Gaussian-Lorentzian curves satisfying the following constraints: a) the 3f_{7/2} to 3f_{5/2} ratio is 4:3; b) each doublet has equal FWHM; and c) the spin orbit splitting of the W 3d doublets is 2.18 eV [32,48]. The as-deposited film produces a symmetric line shape with no indication of mixed oxidation states. Peaks located at energies of 35.55 eV and 37.73 eV were identified as 3f_{7/2} and 3f_{5/2} peaks of WO₃ phase, respectively. The film annealed at 300 °C was also identified as the pure WO₃ phase with peaks positioned at 35.64 eV and 37.76 eV, respectively. However, annealing at 400 °C resulted in a shift to lower binding energies of 35.11 eV (3f_{7/2}) and 37.29 eV (3f_{5/2}) due to the presence of single phase WO_{3-x} at the film surface.

Annealing at 500 °C leads to the formation of another set of peaks at 33.69 eV and 35.87 eV, probably corresponding to more oxygen deficient phases (such as $W_{18}O_{49}$, $W_{24}O_{68}$, and/or WO_2) [31,48] besides the main WO_{3-x} doublet of 35.04 eV and 37.22 eV. The shift to a lower oxidation state indicates a loss of more oxygen atoms at the surface after the 500 °C anneal. This result is in good agreement with the work done by Mahammad et al. [34] in which a WO_{3-x} phase (Magneli phase) in variable proportions was observed by a TEM study of WO_3 films annealed at 300-450 °C in air.

The change in the surface oxidation can be compared to the free energy (ΔG) and equilibrium constant (k) for the following reversible reaction at different temperatures [49]:

While the reaction free energies to form the sub-oxide are positive in all cases the equilibrium constants give finite and relatively large product quantities. The addition of oxygen via air to the treatment environment will, through le Chatelier's principle, reduce these quantities such that 'at air' concentration, $[O_2] = 20\%$, the equilibrium constants are reduced to 0.03 at 400 °C and 0.11 at 500 °C. Since we do not know about the mass transfer limitation from the bulk to the surface region, this argument suggests that surface reduction can occur, even in the presence of air. The

WO_{3-x} phase is not seen in the XRD analysis above indicating that it is confined to the film surface and below the XRD detection limit.

Nevertheless, XPS results do support the optical properties where a shift in the absorption edge to lower energy ranges (decreasing bandgaps) is observed in the films annealed at 400-500 °C. Therefore, oxygen deficiency and the presence of lower oxidation states resulted in decreasing bandgaps of tungsten oxide films annealed at 400-500 °C. The optical modeling of the room temperature γ -WO₃ phase suggests a 0.50 eV drop in the energy gap if an oxygen vacancy is formed [45]. In another work, Gillet et.al [44] have also reported the lower bandgap of oxygen deficient WO₃ films due to the presence of donor levels caused by oxygen vacancies at the surface. When the surface oxygen vacancy concentration increases, the donor orbitals overlap and lead to the formation of a band which lessens the gap [44]. The impurity energy state induced by oxygen deficiency might also lead to a decrease in the bandgap of WO₃, similar to what has been reported for the MoO₃ films [50,51].

Discussion: Comparison to MoO₃

Since Mo and W both belong to the group VI of transition metals, with the same number of electrons on the outer shell, analogous properties of their compounds is expected. However, we find differences in the structural, optical, and surface properties of reactively-sputtered and air-annealed MoO₃ and WO₃ films.

As-deposited MoO₃ films have an amorphous structure. Annealing at 300 °C in air resulted in a crystallization of the molybdenum oxide films in the monoclinic β -MoO₃ phase. Samples

annealed at 400 and 500 °C were both identified as pure orthorhombic α -MoO₃ phases with (020) preferred orientation [11]. For the WO₃ films, as-deposited films exhibit amorphous structure with no change detected after annealing at 300 °C. Samples annealed at 400 and 500 °C were crystalized and identified as pure monoclinic WO₃ phase with (200) and (002) preferred orientation, respectively.

UV/Vis/NIR spectrophotometry revealed a high optical transmittance (> 80%) in the visible range, with bandgaps in the range of 2.6 eV to 2.9 eV for the as-deposited MoO₃ films.

Annealing at 300 °C had a negligible effect on the optical properties of the MoO₃ films, but samples annealed at 400 °C and 500 °C exhibited wider bandgaps within the range of 3.1-3.4 eV.

In the case of WO₃ films, post processing had no significant effect on optical transmittance of the films, but it decreased the optical bandgap from ~3.30 eV for the as-deposited films to the ~3.15 eV for the films annealed at 400-500 °C.

High resolution XPS studies showed the presence of Mo⁶⁺ (MoO₃) and Mo⁵⁺ (Mo₄O₁₁) oxidation states at the surface of as-deposited and low temperature (300 °C) annealed films. Annealing at 400-500 °C suppressed the oxygen deficiency at the surface, resulting in films with a composition close to the stoichiometric phase. On the other hand, XPS studies of WO₃ films showed the presence of W⁶⁺ (WO₃) oxidation states at the surface of as-deposited films and of films annealed at 300 °C. Annealing at 400-500 °C led to an oxygen deficient surface, resulting in films with higher sub-stoichiometric (WO_{3-x}) phases.

The inconsistencies observed in the properties of reactively-sputtered and air-annealed MoO₃ and WO₃ films can be explained by the difference in structural characteristics of these materials. For both MoO₃ and WO₃, the metal atoms have occupied the distorted octahedral sites, but difference in the connectivity of the octahedrons resulted in dissimilar structures. Consequently, the α -MoO₃ crystallizes with a layered structure (orthorhombic with space group Pbnm, see Fig. 8a), while the γ -WO₃ forms a ReO₃-related structure (monoclinic with space group P21/c, see Fig. 8b) with a very different π -type overlap between the metal (d) and oxygen (2p) orbitals, similar to metastable β -MoO₃ phase with monoclinic structure [52,53]. Therefore, γ -WO₃ phase has properties similar to the metastable β -MoO₃ phase than that of α -MoO₃ phase.

4- Conclusion

Tungsten oxide thin films were prepared via reactive sputtering at O₂/(O₂+Ar) = 50%. The effects of post-deposition annealing on the structural, optical, and surface properties of the deposited films were investigated. XRD analysis showed that as-deposited and 300 °C annealed films are amorphous while the 400-500 °C annealed samples have the crystallized monoclinic structure. Studying the preferential orientations of the films using the method proposed by Harris revealed that the films annealed at 400 °C have 24.5 vol. % of crystallites oriented in the (200) direction. However, a higher annealing temperature of 500 °C shifts the orientation of WO₃ films, and 27 vol.% of crystallites are oriented in the (002) direction. High resolution XPS studies showed that W⁶⁺ (WO₃) are the dominant oxidation states present at the surface of the as-deposited and 300 °C annealed films. No contribution from any of the lower oxidation states, such as W⁵⁺ and or W⁴⁺ was identified in either case. However, annealing at 500 °C resulted in

an oxygen deficiency and the presence of WO_{3-x} phase at the film surface. UV/Vis/NIR spectrophotometry revealed similar bandgap values of 3.30 eV to 3.26 eV for as-deposited and 300 °C annealed samples. However, samples annealed at 400 °C and 500 °C exhibited lower bandgaps of ~3.15 eV. All films have a high regular transmittance (> 80%) in the visible range indicating low concentration of oxygen ion vacancies.

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Captions of tables

Table 1- The peak positions (2θ), d-spacing (D), relative intensity (I), texture coefficient (TC), and volume fraction (V) of WO_3 films and annealed at 400 and 500°C, in comparison with ICDD card 01-072-0677 [33].

Captions of figures

Figure 1- XRD pattern of WO₃ films annealed at different temperatures. Peak position and planes indices are also shown based on ICDD card 01-072-0677 [33].

Figure 2. WO₃ monoclinic unit cell b-axis projection with (a) (h00) planes horizontal and (b) with (001) planes horizontal. Drawings made using VESTA [54].

Figure 3- Transmittance and reflectance plots of the WO₃ films deposited at O₂/(O₂+Ar) = 50% and annealed at different temperatures.

Figure 4- $(\alpha E)^2$ vs. E for WO₃ films deposited at O₂/(O₂+Ar) = 50% and annealed at different temperatures.

Figure 5- Variation of optical bandgap as a function of annealing temperature.

Figure 6- XPS spectrum of the WO₃ film deposited at room temperature.

Figure 7- XPS core level binding energy of W 4f doublets of WO₃ films deposited at O₂/(O₂+Ar) = 50% and annealed at different temperatures. The 3f_{7/2} and 3f_{5/2} peaks of WO₃ phase are shown by red and blue colors, respectively.

Figure 8- The structures of (a) orthorhombic α -MoO₃ and (b) monoclinic γ -WO₃ phases. Drawings made using VESTA [54].

Table

Table 1

Measured						ICDD		
(2θ)	D (Å)	I	(hkl)	TC	V (%)	(2θ)	D (Å)	I
Annealed at 400 °C								
23.18	3.81	67	002	1.08	16.6	23.11	3.85	99.0
23.58	3.74	25	020	0.42	6.4	23.58	3.77	96.0
24.38	3.62	100	200	1.59	24.5	24.35	3.65	100.0
26.60	3.32	13	120	1.07	16.4	26.59	3.35	19.0
28.94	3.05	14	-121	1.38	21.1	28.91	3.08	16.0
34.20	2.58	35	202	0.98	15.1	34.15	2.62	56.0
49.88	1.77	8	400	0.88	13.5	49.89	1.83	22.0
55.90	1.58	8	420	1.08	16.6	55.89	1.64	15.0
Annealed at 500 °C								
23.16	3.81	100	002	1.92	27.1	23.11	3.85	99.0
23.58	3.74	32	020	0.62	8.8	23.58	3.77	96.0
24.32	3.63	63	200	1.19	16.8	24.35	3.65	100.0
26.86	3.29	8	120	0.80	11.3	26.59	3.35	19.0
28.90	3.05	12	-121	1.45	20.5	28.91	3.08	16.0
33.26	2.65	9	022	0.44	6.2	34.15	2.69	56.0
34.16	2.58	20	202	0.66	9.4	49.89	2.62	22.0
55.88	1.58	7	420	0.93	13.1	55.89	1.64	15.0

Figure 1

Figure 2a

(a)

Figure 2b

(b)

Figure 3a

Figure 3b

Figure 4a

Figure 4b

Figure 5

Figure 6

Figure 7

Figure 8a

Figure 8b

(b)