XPS Characterisation of Vacuum Annealed Nanocrystalline WO$_3$ Films

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X-ray Photoelectron Spectroscopy was conducted on magnetron sputtered WO$_3$ thin films, following a sequence of ultra high vacuum anneals from 100°C to 900°C. Annealing from 100°C to 400°C induced an upward surface band bending of about 0.3 eV, attributed to the oxygen migration from the bulk to the surface, but no changes in the surface topography. Chemical changes occurred from 600°C to 800°C, associated to the formation of secondary oxide species. Ag deposition did not induce any band bending, indicating that the Fermi level is pinned. The Ag was entirely removed from the surface after annealing at 600°C. The implications in terms of gas sensing are discussed.

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I. INTRODUCTION

Tungsten Trioxide (WO$_3$) is an n-type wide band gap metal-oxide semiconductor. It is a promising material for gas sensing devices due to its electrical conductivity and excellent sensitivity and selectivity [1]. Low fabrication costs and low power consumption, together with the promise of sensitive gas sensors tailored towards specific target gases, are the driving force behind the research for this and other metal-oxide semiconductor gas sensors.

The sensing mechanism is based on changes in bulk resistance of the WO$_3$ film induced by reactions between the surface and target gases such as CO, H$_2$S, NO and NH$_3$ [2]. As these gases absorb on to the surface they change the electron concentration and also alter the height of the potential barrier between adjacent grains, which an electron must overcome in order for a current to flow.

The microstructure and morphology of the WO$_3$ films have a significant impact on the sensitivity and stability of the sensor; for example the sensitivity increases when the size of the particles in the sensing film decreases towards the nanometre regime [3]. However the selectivity of semiconducting metal-oxide sensors is generally poor. This is a well-known problem which has been addressed over the years by adding noble metals to the sensing materials in order to tune the selectivity of the sensors towards a particular gas. Yet the optimisation of the performances rely on trial and error rather than a fundamental understanding of the interaction of the metal with the semiconducting oxide.

Additionally, gas sensing devices operate at elevated temperature to promote surface chemical reactions. Typical operating temperatures range from 100°C to 400°C, but could be higher in some cases [4, 5]. Gas sensing are also often annealed or calcinated at high temperature to promote the formation of sintering necks between particles.

It is therefore crucial to understand the effect of elevated temperature and metal deposition on the surface properties of the sensing material. In this article we investigate the effect of vacuum annealing and Ag deposition on the chemical and electronic properties of the surface of nanocrystalline WO$_3$ thin films, using X-ray Photoelectron Spectroscopy (XPS). The implications in terms of gas sensing are discussed.

II. EXPERIMENTAL DETAILS

Tungsten oxide thin films were prepared by reactive magnetron radio frequency sputtering onto silicon substrates. The deposition was performed starting from a metallic target with certified purity at 99.99% in an oxidizing atmosphere with 50% argon and 50% oxygen at a working pressure of $8 \times 10^{-3}$ mbar. The substrate is kept at 300°C, during the deposition, to favor the formation of a stable layer. The films thickness was around 300 nm and STM scans showed a polycrystalline morphology with a grain size of around 35 nm [6]. The samples were loaded into the ultra high vacuum (UHV, base pressure $10^{-10}$ mb) VG Escalab XPS system without any prior surface treatment. Annealing of the sample was done in the XPS chamber in UHV by electron bombardment of the back of the silicon substrate, with a temperature accuracy of 25°C. The samples were annealed for 30 minutes in step of 100°C, from 100°C to 900°C. XPS scans were performed after each annealing step. For the Ag deposition experiment, a second sample was annealed to 300°C prior to thermal evaporation of Ag. The sample was then scanned and subsequently annealed at 600°C and scanned again.
III. RESULTS AND DISCUSSION

The changes in the chemical and electronic properties of the WO₃ surface as a function of annealing temperature are shown in Fig. 1. Figure 1(a) shows the variation of the W 4f XPS spectra line shape, from RT (as loaded sample) to 900°C. The W 4f peakshape gets sharper as a result of annealing from RT to 300°C, but becomes increasingly broader from 400°C to 800°C. A similar trend was observed on the O 1s peakshape, with an obvious shoulder on the high binding energy side at RT. This shoulder decreased significantly after the first annealing step, indicating that it is associated with surface contaminants such as water vapour, which were removed by the anneal. Desorption of surface contaminants could account for the O 1s and W 4f peaks becoming sharper as the surface becomes cleaner. Above 400°C it is likely that the broadening of the peak indicates a change in the stoichiometry of the sample surface, with the formation of different oxide species such as WO₂ or WO.

Figure 1(b) shows the variation of the binding energy of the W 4f and O 1s core level. Up to 400°C both W 4f and O 1s core level binding energies follow the same trend. First, there is a slight increase from RT to 100°C, of 0.12 eV and 0.05 eV for the W 4f and O 1s core levels, respectively. This small shift corresponds to downward band bending and might be caused by desorption of surface contaminants. This is followed by a drop in binding energy from 100°C to 400°C, of 0.49 eV and 0.38 eV for the W 4f and O 1s core levels, respectively. As both core level binding energies vary by nearly the same amount it is likely that these shifts are mostly rigid Fermi shifts, corresponding to surface band bending. This is in good agreement with previous XPS work by Stankova et al. who report very little chemical changes up to 450°C vacuum annealing for their WO₃ samples, also grown by magnetron sputtering [7]. The upward surface band bending observed after annealing between 100°C and 400°C could be attributed to the migration of oxygen from the bulk to the surface as previously reported by Ottaviano et al. when annealing WO₃ films in vacuum [8]. This oxygen segregation has the effect of neutralising surface oxygen vacancies, which act as donors [9], therefore rendering the surface less n-type. This would result in the Fermi level moving towards the middle of the gap from near the conduction band edge.

FIG. 1: Influence of annealing temperature on (a) the W 4f core level spectra, (b) the relative binding energy of the W 4f and O 1s core levels (relative to the binding energy at RT) and (c) the relative intensity of the O 1s and C 1s core level with respect to the W 4f core level. In (a), the spectra have been shifted vertically for clarity.

FIG. 2: Ag 3d core level spectra taken before Ag deposition, after Ag deposition and after annealing the Ag covered surface at 600°C.
(upward band binding). Oxygen migration to the surface is widely considered detrimental to gas sensing as oxygen vacancies are active sites for surface reactions. It should be noted that more than half of the band bending occurs between 300°C to 400°C, suggesting that operating the sensor at 300°C would avoid most of the oxygen migration. The slight deviations between the W 4f and O 1s core levels, and the observed sharpening of the W 4f core level lineshape (Fig. 1(a)), can be explained by small chemical changes of the surface induced by the desorption of surface contamination.

From 400°C to 600°C, Fig. 1(b) shows that the binding energy of the W 4f and O 1s core level do not change significantly, even though the broadening of the W 4f lineshape suggests chemical changes. It is likely that these changes, i.e. the formation of secondary oxide species, are not important enough up to 600°C to cause a shift in the binding energy of the W 4f core level. However, after annealing at 700°C and 800°C, the binding energy of the W 4f/2 line increases by 0.25 eV while that of the W 4f/2 line decreases by 0.15 eV. This 0.4 eV decrease in the energy separation of the W 4f doublet (from 2.1 eV at 600°C to 1.70 eV at 800°C) is a clear indication that new chemical species have been formed, possibly WO₃ or WO₂ with x < 3.

After annealing at 900°C, the W 4f peak energy position shifted 4.6 eV from 35.5 eV to 30.9 eV, indicating that the tungsten oxide species have totally dissociated, leaving only metallic tungsten on the surface. This is supported by Fig. 1(c), which shows the change in core level intensity for O 1s and C 1s compared to that of the W 4f core level. The O 1s to W 4f intensity ratio drops from 3.3 to 1 after annealing at 900°C indicating a drastic loss of oxygen. In fact, the Si core level peaks from the substrate became apparent after 900°C confirming the complete dissociation of the WO₃ film, leaving only some metallic tungsten on the silicon substrate.

The O 1s to W 4f ratio is 3.6 on the as loaded sample (before annealing), somewhat larger than stoichiometry, possibly because of the presence of water vapour and oxygen surface contamination. Figure 1(c) shows that the O 1s to W 4f ratio decreases steadily with annealing temperature, because of the contaminants desorption and also loss of oxygen from the WO₃ at higher temperatures (above 600°C), resulting in the formation of secondary oxide species. The fact that the ratio remains above 3 is probably due to the error induced by background removal when measuring the core level intensity, leading to an overestimate of the O 1s intensity. However, as the background removal was kept the same for all spectra, the decreasing trend can be confidently attributed to surface oxygen loss.

Figure 2 shows the Ag core level spectrum, before and after Ag deposition, indicating that the position of the Fermi level relative to the band edges is not affected by Ag deposition. This suggests that the Fermi level is firmly pinned, possibly by a large density of defects. This Fermi level pinning could be detrimental to the sensitivity of gas sensing devices as the height of the potential barrier at grain boundaries would not be affected by surface reactions. The O 1s spectrum after Ag deposition also shows a high binding energy shoulder which can be attributed to the formation of Ag–O species. This shoulder was removed after annealing at 600°C.

IV. CONCLUSION

We investigated the effect of vacuum annealing thin WO₃ nanocrystalline films using XPS to probe the chemical and electronic surface properties. Annealing from 100°C to 400°C induced an upward surface band bending of about 0.3 eV, attributed to the oxygen migration from the bulk to the surface. Annealing from 600°C to 800°C caused significant chemical changes, linked to oxygen loss. After annealing at 900°C the WO₃ films completely dissociated. Ag deposition did not induce any band bending, indicating that the Fermi level is pinned. The Ag was en-
tirely removed from the surface after annealing at 600°C. These results indicate that the WO$_3$ films grown by magnetron sputtering remains chemically and after annealing at up to 400°C in UHV but that annealing at higher temperatures leads to irreversible chemical changes.