PROGRESS REPORT FOR 10P054

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<th>PROJECT TITLE</th>
<th>Thermally evaporated WO$_3$ thin films for gas sensing applications</th>
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**SCIENTIFIC OBJECTIVES**

The scientific objective of this project is to investigate the gas sensing performance of thermally evaporated tungsten oxide (WO$_3$) thin films. This will be achieved through thin film deposition, film characterisation, fabrication of gas sensors and testing the sensing performance of the sensors for different target gases.

The specific aim of this AINSE award is to characterise the composition of thermally evaporated pure and iron-doped tungsten oxide (WO$_3$) thin films and depth profile of the elements by Rutherford Backscattering (RBS) using ANSTO facility. The RBS results will be compared with results obtained from other spectroscopic measurements such as XPS.

**PROGRESS REPORT and RESEARCH OUTCOMES**

(In addition to a discussion of your research results please indicate the value of any other funding generated by AINSE support for this project and the resulting benefits, if any, to the Australian community):

The intrinsic electronic properties of metal oxides in a thin film sensors and any deviation from their stoichiometric chemical properties determine the gas sensing performance of the sensors. As the metal oxides approach stoichiometry, the conductivity of the films becomes extremely low (high resistance) and this is not favourable for gas sensing since conductivity change due to target gas can be very low. Dopants and defects such as interstitial cation or anion vacancies can play an important role in enhancing the gas sensing properties (1-3). Doping with metals or a mixture of metal oxides is used in the high temperature metal oxide gas sensors to modify the electronic structure of the metal oxides and hence enhance sensitivity (4-7).

In this project, pure tungsten oxide (WO$_3$) and iron doped tungsten oxide thin films (WO$_3$:Fe) were prepared using thermal evaporation techniques. The films were deposited at room temperature from powders of WO$_3$ (99.9% purity) and iron (99.9% purity) in high vacuum condition (4x10$^{-5}$ Torr) on silicon substrate at a working distance of 38 cm. For the Fe doped films, 2 g of Fe (99.9% purity) was mixed with 98 g of WO$_3$ for evaporation. The films were deposited at evaporation rate of 5 nm/s as-measured using quartz crystal monitor. The thicknesses of the films during deposition were between 250-300 nm. All the films were annealed at 300°C for 1 hour in air. The films have been characterised using various techniques including RBS, XPS, Raman Spectroscopy, AFM and high resolution SEM.

WO$_3$ films have been studied using Rutherford Backscattered Spectroscopy. The composition and distribution of constituent elements in the film have been determined using RBS. The effect of Fe doping on the film microstructure and stoichiometry have been studied using AFM and XPS,
respectively. The RBS experiments performed at ANSTO have provided insight into the AFM and XPS results performed at QUT. The results from RBS, AFM and XPS suggested that addition of iron into WO₃ did not affect the stoichiometry of the WO₃ film and successive annealing only affected the grain size without imparting any changes in stoichiometry.

This Ph.D. project requires further investigation and analysis of WO₃ films including doping of the films with Iron and Strontium using ion impanation and characterized using RBS, AFM and XPS. In addition, all the WO₃ based films (i.e. pure WO₃ films, WO₃:Fe and WO₃ films implanted with Fe and Sr) will be characterized using high resolution TEM and Raman spectroscopy. The overall results obtained from RBS, AFM, XPS, TEM and Raman Spectroscopy can help us in optimizing the film microstructure and composition to improve the gas sensing properties of WO₃ based gas sensors. Ultimately, the sensing performance of the sensors for different target gases will be investigated.

The sensors that will be developed in this project will be directed for environmental and air-quality monitoring to reduce undesirable gas emissions and create a truly environmentally-aware and healthy society. The sensors could be tailored for a range of applications that require sensing of gases including monitoring of the environmental conditions during the transportation of perishable and sensitive goods, with sensors coupled to radio frequency identification smart tags to enable rapid action to be taken in response to dangerous transport conditions (8), artificial olfaction and electronic noses for medical applications (e.g. examine odours from the human body to identify diseases), food industry applications (e.g. quality assessment in food production), and even security applications (e.g. smart fire detector in remote forests, chemical warfare agents detector) (9). The development of the new sensors is a direct enabler for a range of national economic, environmental and health benefits.

**DATA** (Please summarise the data collected within this Award. You may use tables, graphs or diagrams)

Within this AINSE award, Rutherford Backscattering measurements were carried out at ANSTO on the following thermally evaporated WO₃ based samples:
- As-deposited (300 nm) and annealed (300 nm) WO₃ films,
- As-deposited (300 nm) and annealed (250 nm) WO₃:Fe films.

The RBS data measured with 1.8 MeV ⁴He have been discussed and the results are explained by comparing with XPS and AFM results performed at QUT. Figure 1 shows RBS spectrum and corresponding depth profile of as-deposited WO₃ film. The spectrum (Figure 1a), exhibits a typical staircase structure with each step associated with an element in the sample. The flat part between different steps indicates a constant concentration for each element throughout the surface.

![Figure 1: RBS spectrum (a) and depth profile (b) of as-deposited WO₃ film.](image)

Well separated and high intensity of W peak from the film is due to the higher mass (atomic weight) of W compared to O or other trace elements such as N. Also the He particles are scattered with
much higher recoil energy in the film than from the substrate (Si) in this elastic scattering process. Figure 1b shows the depth profile of WO$_3$ film indicating the presence of O, N and W. RBS is limited by resolution for light elements such as B, C, O, N and poor resolution of elements with similar masses. XPS analysis performed on these films has shown C and N as impurities present in the near surface region. Presence of oxygen can be attributed to adsorbed oxygen from the environment in addition to the lattice oxygen created within the film.

![Image of RBS spectrum and depth profile](image1)

**Figure 2:** RBS spectrum (a) and depth profile (b) of annealed WO$_3$ film. Upon annealing the WO$_3$ film in air at 300°C for 1 hour, the W peak becomes slightly sharper and intense (Figure 2a) compared to the peak of the as-deposited film (Figure 1a). The depth profile (Figure 2b) shows a significant decrease in the amount of O and increase in the amount of W as compared to the corresponding values of the as-deposited film (Figure 1b). This reduced amount of oxygen can be due to desorption of surface contaminants and creation of oxygen vacancies after annealing the films. This is also confirmed by XPS analysis which showed that upon annealing, the O 1s and W 4f peaks slightly shifted to lower binding energy side, indicating desorption of surface contaminants.

![Image of RBS spectrum and depth profile](image2)

**Figure 3:** RBS spectrum (a) and depth profile (b) of as-deposited WO$_3$:Fe film.
Figure 3 shows the RBS spectrum and depth profile of as-deposited WO$_3$:Fe film. The W peak shows same intensity as that in pure WO$_3$ film (Figure 3a). The depth profile shows O, W, N and Fe (Figure 3b). The RBS depth profile shows that the amount of Fe in the films is only about 0.5 at% (Table 1). However, Fe was not detected in this film when analysed using XPS. AFM results show that addition of Fe resulted in slight grain size increase from 14 nm to 15 nm (Table 1). Addition of Fe appears to have slightly changed the stoichiometry of the film (change in amount of O and W).

| Table 1 Film composition, grain size and binding energy of WO$_3$ and WO$_3$:Fe thin films. |
|----------------|----------------|----------------|----------------|----------------|
|                | RBS            | AFM            | XPS            |                |
|                | W (at%)        | O (at%)        | N (at%)        | Fe (at%)       |
| WO$_3$         | 22             | 50             | 28             | -              |
| WO$_3$ annealed| 36             | 34             | 30             | -              |
| WO$_3$:Fe      | 26             | 38             | 35.5           | 0.5            |
| WO$_3$:Fe annealed | 36         | 38             | 25.5           | 0.5            |

Figure 4 shows the RBS spectrum and corresponding depth profile of WO$_3$:Fe film after heat treatment. The intensity of W peak (Figure 4a) is similar to that observed in annealed WO$_3$ film. Moreover, the depth profile (Figure 4b) also shows that amount of W and O is similar to that in annealed WO$_3$ film. This observation is in agreement with XPS analysis which shows similar O 1s and W 4f peak positions in both the annealed WO$_3$ and annealed WO$_3$:Fe films. AFM analysis also shows same grain size of 10 nm in both the annealed WO$_3$ and annealed WO$_3$:Fe films (Table 1). This finding indicates that the change in stoichiometry and grain size of WO$_3$ due to addition of Fe is restored by annealing and the film is similar to annealed WO$_3$ film.

References:
5. N. Han et al., Sensors and Actuators B: Chemical 147, 525 (2010).
The gas sensing performance of the thermally evaporated WO$_3$ and WO$_3$:Fe films for different target gases is underway. Once these tests are done, we should be able to produce a number of high quality journal articles.

PhD STUDENTS For each student involved with the project, please indicate the date or anticipated date of conferment of a PhD or other award, and give the title of the thesis.

PhD Student Name: Mohammed Ahsan
Anticipated PhD Conferment date: July 2011
Thesis title: Thermally evaporated tungsten trioxide (WO3) thin films for gas sensing applications