JOURNAL OF MATERIALS SCIENCE 38 (2003) 4347–4352

# $MoO_3$ and $WO_3$ based thin film conductimetric sensors for automotive applications

A. K. PRASAD, P. I. GOUMA
*Department of Materials Science and Eng., SUNY at Stony Brook, NY 11794, USA*
*E-mail: k.arunprasad@lycos.com; akapalee@ic.sunysb.edu*

Un-doped semiconducting oxides suitable for automotive gas sensor applications have been studied in this work. Thin films of $MoO_3$ and $WO_3$ were fabricated by ion beam deposition on alumina substrates with gold interdigitated electrodes. The process pressure inside the deposition chamber was $1.6 \times 10^{-4}$ Torr. The oxygen to argon ratio in the secondary plasma was maintained at 5:5 sccm. A stabilization heat treatment of 500°C for 8 h was performed for each set of films that produced nanocrystalline structures. Gas sensing tests were carried out at 450°C with nitrogen dioxide/ammonia with synthetic air background similar to those realized in diesel automotive exhausts. XRD and electron microscopy studies were performed to understand the microstructure of the thin films following the sensing tests. The $MoO_3$ films were selective to ammonia whereas the $WO_3$ films showed high senstitivity towards $NO_2$ with respect to $NH_3$. An attempt is made to correlate the structural characteristics to the sensing behavior of the materials.

## 1. Introduction

The automotive industry is using chemical sensors for emission control and environmental protection. Selectivity to a particular gas has been the key issue of chemical sensor technology that is still lacking. The state of the art in achieving gas selectivity involves the use of metallic or oxide additions as secondary components in sensing elements or the use of multiple sensor arrays. The former approach is only partially effective as aging effects associated with long term use of these detectors allow for the formation of solid solutions and the loss of any gas specificity. The latter approach uses multiple sensors and complex signal processing methods to discriminate between responses to different gases. There is a need for selective chemical sensors for high temperature and harsh environment applications, such as for monitoring emissions from combustion processes. There are several challenges associated with the development of sensor technology for monitoring combustion processes. These include high temperatures, presence of reducing and oxidizing gases, organic vapors (VOCs), high flow rates, etc.

Recently the application of ammonia sensors and $NO_2$ sensors in selective catalytic reduction (SCR) systems has gained importance [1, 2]. SCR systems are employed in the exhaust system of commercial vehicles, combustion systems in power plants and in industrial boilers to monitor the emissions of $NO_2$ and NO. These gases are harmful by-products of combustion processes. In a SCR converter, ammonia serves as a reducing agent for nitrogen oxides converting them into environmentally safe nitrogen and water vapor. An ammonia sensor is required to calculate the amount of un-reacted and excess ammonia, which is fed into the inlet stream. This necessitates the development of a selective ammonia sensor capable of detecting small quantities of ammonia in the presence of interfering gases, such as $NO_x$, CO, and hydrocarbons.

Semiconductor metal-oxide-based gas sensors have been utilized in gas detection in automobiles. This work focuses on two metal oxide systems—Molybdenum oxide, which possesses excellent catalytic, electrochromic and gas sensing properties, and tungsten oxide which has been used to detect various gases due to its excellent semiconducting properties. Mutschall *et al.* [3] first reported the suitability of $MoO_3$ as a potential material for ammonia sensing. Further studies on $MoO_3$ based gas sensors were carried out by various research groups [4–6]. Obermeier's group at the University of Berlin studied $MoO_3$ as gas sensor by depositing the material using RF sputtering on oxidized silicon substrates containing a 30 nm $Al_2O_3$ adhesion layer and interdigitated Pt electrodes on top. The $MoO_3$ films had whisker like grain structures and large grain size. They studied the sensing response of $MoO_3$ to various gases, including CO, $CH_4$, $SO_2$, $NO_2$ and $NH_3$ in the temperature range of 250°C and 475°C, revealing that $MoO_3$ was twice as sensitive to $NH_3$ than to $NO_2$ and $H_2$ at 425°C and that the gas sensitivity dropped with decreasing film thickness ($<300$ nm). Multilayer sputter processing of $MoO_3$ by the same research group resulted in improved $H_2$ sensing properties and low cross-sensitivity towards $NH_3$ [7]. The same group discussed the enhancement of sensitivity and selectivity to $NH_3$ following the addition of Ti overlayers to $MoO_3$, (and to $H_2$, by adding $V_2O_5$ to $MoO_3$ [5]). However, Guidi *et al.* [8] reported sensitivity towards CO for Ti additions to $MoO_3$.

Shaver reported the first $WO_3$ gas sensor for the detection of hydrogen [9]. Since then there has been various reports on $WO_3$ sensors for detecting $NO_2$ and $NH_3$ [8, 10–16] and other gases such as ozone and $H_2S$ [17–19]. There has been numerous reports on $WO_3$ sensors for $NO_x$ detection [2, 11–14, 20]. Chung *et al.* [20] discuss the sensing properties for thick film $WO_3$ sensors which are sensitive to $NO_2$ at 100°C. These films showed a very weak response to $NO_2$ above 250°C and the response was found to be *p*-type at higher temperatures (>250°C). Marquis *et al.* [2] discuss the fabrication of sensor arrays for selective detection of $NO_2$ and $NH_3$. These films were found to operate at optimum temperature of 300°C and 350°C for selective detection of $NO_2$ and $NH_3$ respectively. During processing, the substrates were kept at 200°C or higher. Dopants were used to achieve selectivity. Sberveglieri *et al.* [12] reported the sensing properties of sputter deposited $WO_3$ thin films deposited at 350°C. The films showed good response to $NO_x$ at 400°C. They report the presence of triclinic phase being stabilized for the undoped material. Penza *et al.* [11] have reported the presence of tetragonal $WO_3$ films being sensitive to $NO_2$ at 250°C.

This paper focuses on un-doped $MoO_3$ and $WO_3$ thin films prepared by ion beam deposition. There is strong evidence available in the field of catalysis that $MoO_3$ exhibits *structure sensitivity* in some catalytic processes, such as the NO reduction with $NH_3$. That is, the catalytic activity and selectivity of this oxide correlate with the grain morphology as well as with the crystallographic orientation of the surface exposed to the gaseous species. Therefore, it is expected that such structure sensitivity may affect the response of $MoO_3$ (and the related system $WO_3$) with regard to the gas sensing processes, particularly towards ammonia and nitrogen dioxide at temperatures similar to those realized in automotive exhausts.

## 2. Experimental

Thin films of $MoO_3$ were reactively ion beam-deposited onto alumina substrates in a dual ion beam deposition (IBD) system. A 12″ diameter molybdenum target was utilized to sputter Mo using a filamentless radio-frequency inductively coupled plasma (RFICP) primary source, with the film partially oxidized during growth using a RFICP assist source directed at the substrate which is held at room temperature and water cooled. The ratio of oxygen to argon in the secondary plasma was maintained at 5:5 sccm. The overall process pressure was $1.6 \times 10^{-4}$ Torr. A more detailed description of the deposition chamber is given elsewhere [21]. The alumina substrates were pre-patterned with 200 $\mu$m thick interdigitated Au electrodes. Deposition was carried out for half an hour. Following deposition, the films were annealed at 500°C in air for 8 h to complete the oxidation to $MoO_3$. A similar procedure was adopted for preparing $WO_3$ films using tungsten target (6″ diameter).

Sensing tests were carried out with nitrogen dioxide and ammonia gases with synthetic air (10% oxygen and balance nitrogen) in the background. The gases were controlled using 1479 MKS mass flow controllers. The combined flow rate of the gases was maintained at 1000 sccm. A Lindberg/Blue tube furnace is used for programmed heating and the resistance of the sensor monitored using Agilent 34401 digital multimeter. The sensor response is plotted as change in resistance versus time, with varying gas concentration.

Characterization of the films was carried out using Philips CM12 TEM with $LaB_6$ cathode excited at 120 keV and XRD. The films were analyzed after sensing tests.

## 3. Results

### 3.1. Tungsten trioxide

### *3.1.1. Sensing tests*

The response of the IBD $WO_3$ to ammonia and $NO_2$ at 450°C is as shown in Figs 1 and 2 respectively. As is evident from the graphs, $WO_3$ is highly sensitive to $NO_2$ even at the low concentration of 1 ppm. The response and recovery times are 10 s and 25–50 min respectively. The adsorption of $NO_2$ on the surface of the $WO_3$ and possible slow desorption time may be responsible for the prolonged recovery time. Gas adsorption studies are

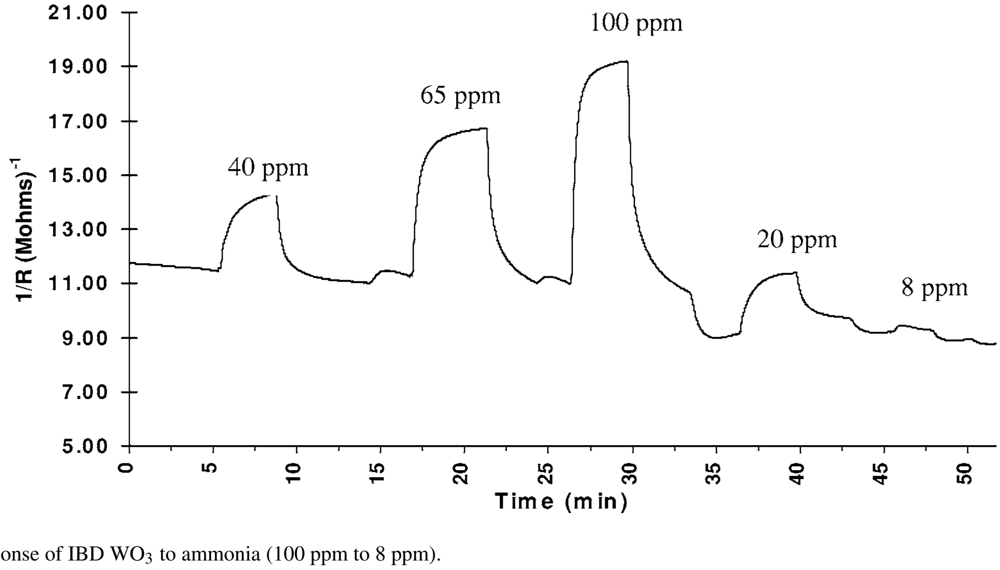

*Figure 1* Response of IBD $WO_3$ to ammonia (100 ppm to 8 ppm).

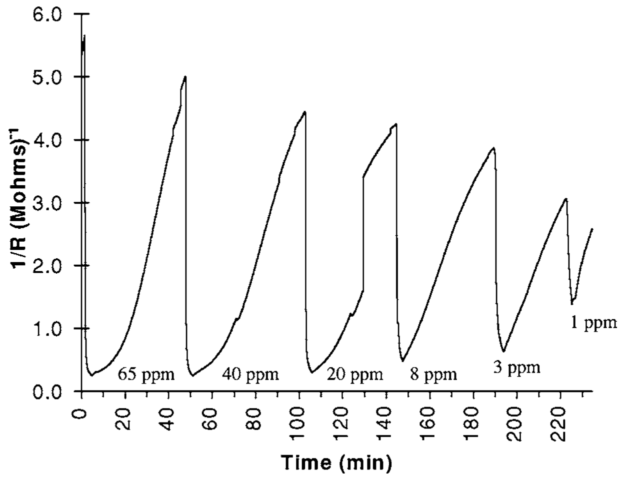

*Figure 2* Response of IBD $WO_3$ to $NO_2$ (65 ppm down to 1 ppm).

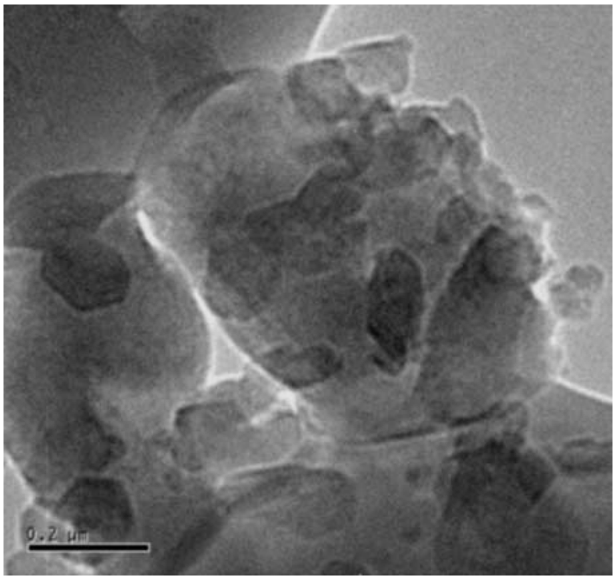

*Figure 3* TEM image of IBD $WO_3$.

required to clarify this issue. The response to ammonia, though fast (10–15 s), is negligible when compared to $NO_2$. Taking the sensitivity into account (10 times increase in resistance for $NO_2$ as opposed to within 0.75 times for $NH_3$), $WO_3$ films prepared by IBD is relatively selective towards $NO_2$ over $NH_3$.

### *3.1.2. Characterization*

Fig. 3 shows the transmission electron micrograph of ion beam deposited $WO_3$ after sensing experiments. It can be observed that the film is composed of tiny grains of 50 nm. XRD studies of the films after sensing revealed the presence of orthorhombic phase (JCPDS 71-0131—Space Group: Pmnb 62, a: 7.341 Å, b: 7.57 Å, c: 7.754 Å) (Fig. 4).

## 3.2. Molybdenum trioxide

### *3.2.1. Sensing tests*

The response of ion beam deposited $MoO_3$ to ammonia and nitrogen dioxide is shown in Figs 5 and 6 respectively. As seen from the graphs, ion beam deposited $MoO_3$ films are selective to ammonia over nitrogen dioxide. In Fig. 5, the conductance is plotted against time for various concentrations of ammonia. The concentration of ammonia is varied from around 490 ppm down to 10 ppm with a background gas containing 10% oxygen and the remainder nitrogen. Ammonia being a reducing gas, the conductance of the film increases when ammonia is passed over it and is proportional to the concentration of ammonia. The response time is rapid (a few seconds) and the recovery time is also fast (in the order of 2–3 min).

The film is then subjected to varying $NO_2$ concentrations from 490 ppm down to 10 ppm. It is found that there is negligible change in conductance upon $NO_2$ exposure.

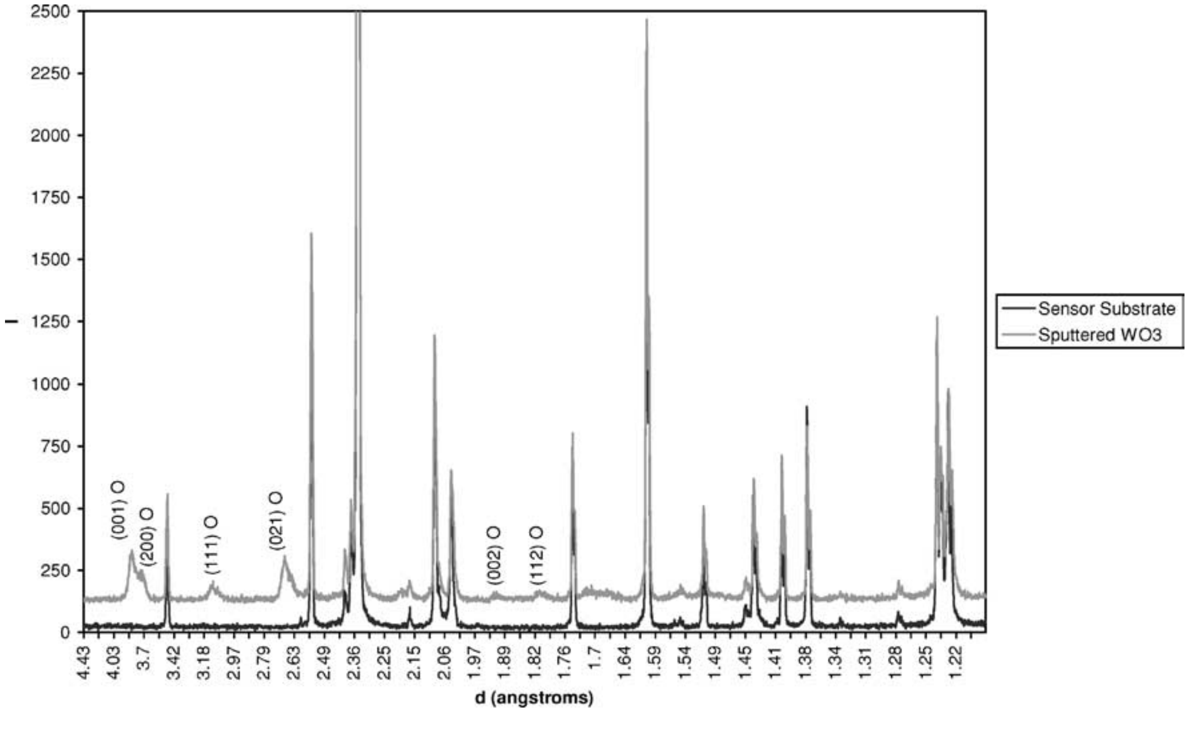

*Figure 4* d vs. I graph for ion beam deposited $WO_3$ after sensing tests.

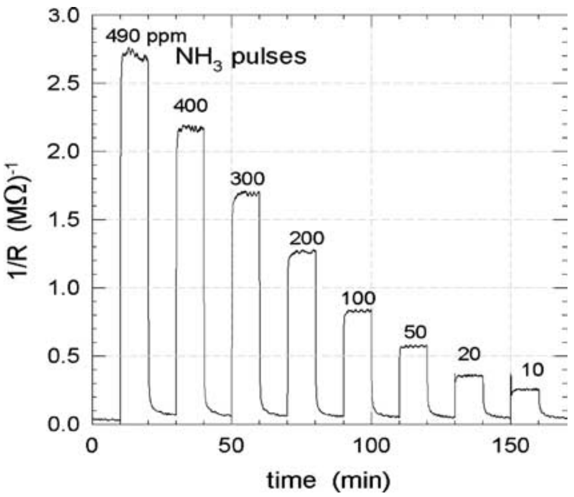

*Figure 5* Response of ion beam deposited MoO$_3$ films to ammonia at 450°C.

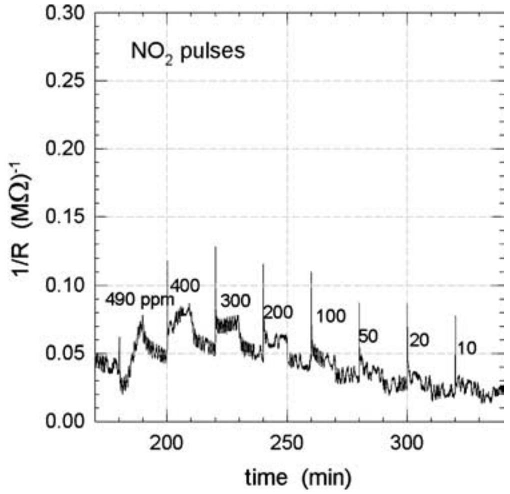

*Figure 6* Response of ion beam deposited MoO$_3$ films to nitrogen dioxide at 450°C.

### *3.2.2. Characterization*

Fig. 7 shows a bright field transmission electron micrograph showing the grain structure of a sputtered and heat-treated MoO$_3$ film. The average grain size is approximately 60 nm. XRD characterization performed on the film after sensing revealed the presence of orthorhombic phase (JCPDS 35-0609—Space Group: Pbnm 62, a: 3.9630 Å, b: 13.856 Å, c: 3.6964 Å) as shown in Fig. 8.

## 4. Discussion

The simple nature of the sensing mechanism of resistive sensors often results in a given oxide system being sensitive to more than one type of gases, which causes undesirable gas interference effects to the sensing behavior of this system.

This paper has focused on the undoped material and has addressed the importance of the polymorph selection for gas sensing. Excellent sensitivity and selectivity to ammonia were obtained when the orthorhombic MoO$_3$ phase was used for sensing. Orthorhombic MoO$_3$ crystallizes in a unique 2D layered structure that is built up of double chains of edge-sharing [MoO$_6$] octahedral connected through vertices.

Tungsten trioxide films prepared in our case were stabilized in orthorhombic phase and were found sensitive to NO$_2$ over NH$_3$. We have shown that there is a 10 time decrease in conductance when the films are exposed to NO$_2$ whereas there is only a 0.75 times increase on exposure to ammonia. We also relate the polymorphic dissimilarities between orthorhombic MoO$_3$ and orthorhombic WO$_3$. The crystal structure of WO$_3$ is a distortion of rhenium oxide cubic structure in which tungsten atoms are located in cube corners and the oxygen atoms are located on the cube edges [22]. The

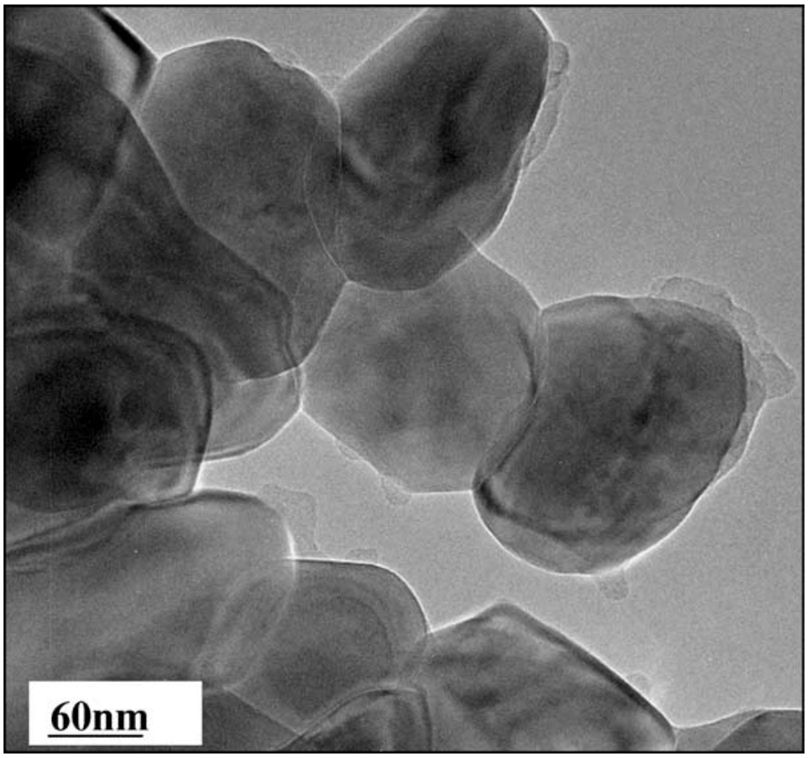

*Figure 7* Microstructure of MoO$_3$ thin films used for sensing.

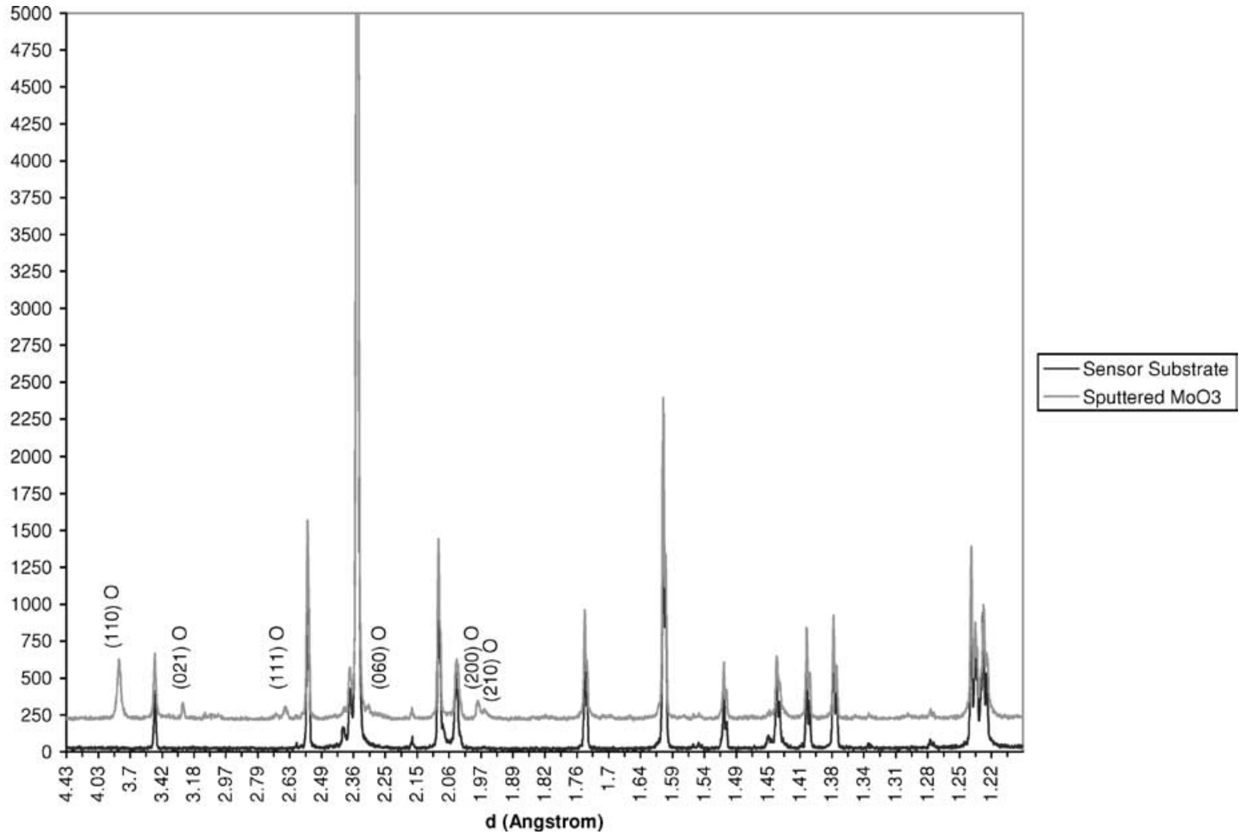

*Figure 8* d vs. I graph of ion beam deposited $MoO_3$ after sensing tests.

distorted structure is stable in several forms giving rise to different phases depending on the temperature; in this case studied the orthorhombic polymorph was stabilized.

Earlier studies by the authors of this paper [21] has shown that when the $MoO_3$ sensing film consists of both $\alpha$- and $\beta$-polymorphs its sensitivity to ammonia is reduced. This may be explained by the fact that the $\beta$-$MoO_3$ structure is closely related to that of $WO_3$, which is not sensitive to $NH_3$. Moreover, a chemical reaction between $MoO_3$ and ammonia is expected to occur during sensing [23] whereas in the case of $WO_3$, only adsorption is anticipated to be the underlying sensing mechanism against $NO_2$. Further investigations are currently under way to elucidate the sensing mechanism for the two oxides relative to the gases examined here.

In summary, it is important to note that the microstructure and crystallographic characteristics of the oxide used for sensing are key parameters controlling the gas sensing response. The discrepancy in the reported sensing properties for the same oxide system (as discussed for $MoO_3$ and $WO_3$ above) by several workers is expected to be strongly related to the differences in the (micro-) structural configuration of the sensing elements.

## 5. Conclusions

Thin films of $MoO_3$ and $WO_3$ were prepared by ion beam deposition and subjected to similar annealing conditions of 500°C for 8 h. $MoO_3$ films are found to be sensitive to ammonia whereas $WO_3$ films are found to be selective to $NO_2$. The longer recovery times as observed in latter films might be attributed to lower gas desorption rate. The importance of the oxide polymorph used for sensing has been discussed in the light of the present and earlier results. Microstructural control of the oxide films is expected to be critical for achieving selectivity in gas sensing.

## Acknowledgements

The authors wish to acknowledge the support of Drs. D. Kubinski and J. Visser, Ford R&A, and Prof. Richard Gambino, Magneto-Optics Group MSE dept, SUNY Stony Brook. This project has been supported by NSF award #DMR0224642 with Dr. L. Madsen as the program manager.

## References

1. R. MOOS, R. MULLER, C. PLOG, A. KNEZEVIC, H. LEYE, E. IRION, T. BRAUN, K. MARQUARDT and K. BINDER, *Sensor Actuat B-Chem* **83** (2002) 181.
2. B. T. MARQUIS and J. F. VETELINO, *ibid.* **77** (2001) 100.
3. D. MUTSCHALL, K. HOLZNER and E. OBERMEIER, *ibid.* **36** (1996) 320.
4. E. COMINI, G. FAGLIA, G. SBERVEGLIERI, C. CANTALINI, M. PASSACANTANDO, S. SANTUCCI, Y. LI, W. WLODARSKI and W. QU, *ibid.* **68** (2000) 168.
5. C. IMAWAN, F. SOLZBACHER, H. STEFFES and E. OBERMEIER, *ibid.* **64** (2000) 193.
6. M. FERRONI, V. GUIDI, G. MARTINELLI, P. NELLI, M. SACERDOTI and G. SBERVEGLIERI, *Thin Solid Films* **307** (1997) 148.
7. C. IMAWAN, H. STEFFES, F. SOLZBACHER and E. OBERMEIER, *Sensor Actuat B-Chem* **78** (2001) 119.
8. M. FERRONI, D. BOSCARINO, E. COMINI, D. GNANI, V. GUIDI, G. MARTINELLI, P. NELLI, V. RIGATO and G. SBERVEGLIERI, *ibid.* **58** (1999) 289.
9. P. J. SHAVER, *Appl. Phys. Lett.* **11** (1967) 255.

10. T. MAEKAWA, J. TAMAKI, N. MIURA and N. YAMAZOE, *Chem. Lett.* (1992) 639.
11. M. PENZA, M. A. TAGLIENTE, L. MIRENGHI, C. GERARDI, C. MARTUCCI and G. CASSANO, *Sensor Actuat B-Chem* **50** (1998) 9.
12. G. SBERVEGLIERI, L. DEPERO, S. GROPPELLI and P. NELLI, *ibid.* **26** (1995) 89.
13. X. S. WANG, N. MIURA and N. YAMAZOE, *ibid.* **66** (2000) 74.
14. C. N. XU, N. MIURA, Y. ISHIDA, K. MATSUDA and N. YAMAZOE, *ibid.* **65** (2000) 163.
15. E. LLOBET, G. MOLAS, P. MOLINAS, J. CALDERER, X. VILANOVA, J. BREZMES, J. E. SUEIRAS and X. CORREIG, *J. Electrochem. Soc.* **147** (2000) 776.
16. J. TAMAKI, Z. ZHANG, K. FUJIMORI, M. AKIYAMA, T. HARADA, N. MIURA and N. YAMAZOE, *ibid.* **141** (1994) 2207.
17. C. CANTALINI, M. Z. ATASHBAR, Y. LI, M. K. GHANTASALA, S. SANTUCCI, W. WLODARSKI and M. PASSACANTANDO, *J. Vac. Sci. Technol.* A **17** (1999) 1873.
18. C. CANTALINI, W. WLODARSKI, Y. LI, M. PASSACANTANDO, S. SANTUCCI, E. COMINI, G. FAGLIA and G. SBERVEGLIERI, *Sensor Actuat B-Chem* **64** (2000) 182.
19. J. L. SOLIS, S. SAUKKO, L. B. KISH, C. G. GRANQVIST and V. LANTTO, *ibid.* **77** (2001) 316.
20. Y. K. CHUNG, M. H. KIM, W. S. UM, H. S. LEE, J. K. SONG, S. C. CHOI, K. M. YI, M. J. LEE and K. W. CHUNG, *ibid.* **60** (1999) 49.
21. A. K. PRASAD, D. KUBINSKI and P. I. GOUMA, *ibid.* **93** (2003) 25.
22. L. J. LEGORE, R. J. LAD, S. C. MOULZOLF, J. F. VETELINO, B. G. FREDERICK and E. A. KENIK, *Thin Solid Films* **406** (2002) 79.
23. A. K. PRASAD, P. I. GOUMA, D. J. KUBINSKI, J. H. VISSER, R. E. SOLTIS and P. J. SCHMITZ, *ibid.* **436** (2003) 46.

*Received 3 April*
*and accepted 1 August 2003*