Mixed Vanadium/Aluminum Oxide Films for Sensing of Organic Compounds

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Mixed oxides such as Ti-W [1] and Ti-Fe [2] have recently been investigated as thin film semiconducting oxides for gas sensor applications. The rationale is that the film may potentially be composed of a physical mixture of two oxides with two different functions: one that controls the electrical response for gas sensing, and another that may inhibit grain growth and act as a catalyst. Mixed oxides of this type may exhibit enhanced sensing properties compared to binary oxide films.

The ternary oxide ($AlVO_4$) has been reported in literature as an O_2 and NH_3 sensor at elevated working temperatures (>600°C)[3] . In addition, porous Al_2O_3 has been demonstrated to be a humidity sensor [4] and V_2O_5 has been used as an ethanol sensor at lower working temperatures [5] . In this work, we present compositional characterization of vanadium/aluminum oxides grown by RF magnetron sputtering using x-ray photoelectron spectroscopy (XPS) and report electrical sensor response measurements upon exposure to organic compounds.

Thin films were deposited by RF magnetron sputtering at a deposition temperature of 300°C in a reactive atmosphere (50% O_2 - 50% Ar) using an aluminum target with 14 holes filled with either vanadium or aluminum inserts, so as to vary the ratio of aluminum to vanadium. We used 14, 12 and 7 inserts of vanadium. The thickness of the films was approximately 500 nm.

For electrical measurements, films were deposited onto 3x3 mm^2 alumina substrates, with a Pt meandering heater patterned on the backside and Pt interdigitated electrodes contacting the films. For XPS measurements, films were deposited onto polished silicon (100) substrates. Post-deposition annealing treatments were carried out in laboratory air at 600 or 800 °C for 12 h.

Surface compositional analysis was determined by XPS using Mg Kα X-rays with a geometry of normal emission of photoelectrons detected by a hemispherical energy analyzer. For as-grown films, XPS data showed that the V/Al ratio was 11%, 25% and 32% in samples grown with 7, 12 and 14 vanadium inserts, respectively. The film compositions did not change within the resolution of XPS following annealing treatments at 600°C. However, following annealing at 800°C, the V/Al ratio decreased to 5% for all films. Based on these observations, we believe that a physical mixture of Al_2O_3 and V_2O_5 was formed during deposition and that the V_2O_5 component preferentially evaporated during the 800°C treatment (vapour pressure for V is 10^{-4} Torr at 1547 °C but for V_2O_5 is 10^{-4} Torr at 500 °C [6]).

A volt-amperometric technique was used to monitor the change in conductivity when trace gases were fed into the test chamber. Measurements were performed by keeping the test chamber at 20°C at constant relative humidity (RH=20%). The sensor operating temperature was varied between 300 and 500°C.

The sensor response was tested for nitrogen dioxide (up to 15 ppm), carbon monoxide (300 ppm), and organic vapours: ethanol (up to 800 ppm), methanol (800 ppm), ammonia (15 ppm) and toluene (80 ppm). NO_2 showed an oxidising effect while ethanol, CO and other organic vapours showed a reducing effect, indicating n-type conductivity behaviour.

For all vanadium concentrations and annealing temperatures, the relative response towards CO and NO_2 was small. On the contrary, sensors increased their conductance by at least an order of magnitude when ethanol was introduced into the test chamber. A similar effect was observed with methanol and toluene.

The response spectrum towards target gases was tested by varying the vanadium content in the mixed vanadium/aluminium oxide sensors and the operating temperature. A typical dynamic response is shown in figure 1 for a sensor film fabricated with 7 inserts and annealed at 600°C. The best results for ethanol sensing were obtained with as-deposited samples, but the stability of these sensors was poor without an annealing treatment. The best compromise between stability and sensitivity was reached with samples treated at 600°C. Sensors treated at 800°C showed less sensitivity to organic vapours presumable due to the loss of the vanadium oxide component.

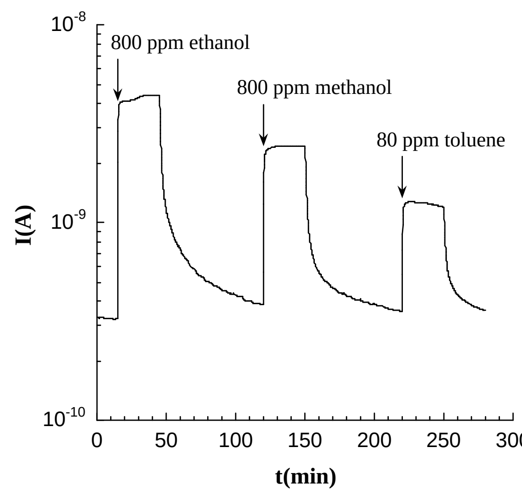

Fig. 1: Dynamical response of a sensor film towards organic vapours at a 300°C working temperature with RH=20%. The sensor film was deposited with 7 inserts of vanadium and annealed at 600°C

Long term stability and reliability of these mixed oxide films for sensing may be dependent on the exact nature of their heterogeneous microstructure, which in turn is directly dependent on deposition and processing conditions as well as microstructural changes during extended time at the operating temperature. Experiments which continue to address these issues are underway.

References

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