ABSTRACT

Semiconducting oxide based gas sensors are widely exploited in gas sensing applications since they are simple in construction, cost effective, user friendly and are also amenable for miniaturization. The gas sensing action of semiconducting metal oxides involves the change of their electrical conductivity in presence of a reducing/oxidizing analyte gas in ambient air, which gets restored to the original value when the trace analyte gas is removed from the ambient. The present thesis deals with the gas sensing properties of trioxides of Mo and W which belong to VI B group of the periodic table. Sensitivity and selectivity of a semiconducting oxide based sensor towards an analyte gas can be enhanced 1) by using the sensor in different geometries viz. porous structures and thin films and 2) by the addition of dopants to the sensor material. Both of these approaches were employed in the present study to improve the sensitivity and selectivity of pure MoO₃ towards ammonia. Since stoichiometric MoO₃ and WO₃ are characterized by high resistivities, effects of dopants such as Ag and V₂O₅ on their gas sensing properties were studied. TiO₂ is thermodynamically stabler than MoO₃ and WO₃ and previous work had shown that its addition to sesquioxide of chromium, which also belongs to VI B group, results in interesting gas sensing properties. Hence, compositions of MoO₃ and WO₃ containing TiO₂ were also explored for their gas sensing characteristics.

As modulation of electrical conductivity of an oxide in the presence or absence of analyte gas is exploited for gas sensing applications, detailed studies on the electrical conductivity of pure MoO₃ was investigated in different gas ambients viz. O₂, air and Ar. Electrical conductivity of MoO₃ was found to be invariant with oxygen partial pressure from 510 to 773 K and the activation energy of this conduction obtained from Arrhenius plot was 0.69±0.08 eV. In humid ambients and at low temperatures, MoO₃ is shown to exhibit a high conductivity mode with an activation energy of 0.27 ± 0.03 eV. This low temperature conductivity mode is attributed to species arising from the reversibly inserted water molecules into MoO₃ lattice. The existence of water molecules in the lattice of MoO₃ were supported by infrared studies and thermogravimetric measurements. Results also indicated that the extent of water insertion to be dependent on initial nonstoichiometry of the trioxide. When O/Mo ratio of the sample was ~ 2.988,
electrical conductivity of the sample was mainly due to these species up to 578 K. Sensing characteristics of porous pellet sensors of MoO₃ towards various analyte gases such as NH₃, LPG and H₂ were investigated in the temperature range of 498 to 673 K. Maximum sensitivity for ammonia was observed at 673 K. Effect of electrode materials on the gas sensing properties of MoO₃ were also investigated. Gold, platinum and graphite electrodes are shown to be compatible with MoO₃ and hence could be used in a practical sensor, while silver is found to be incompatible. Based on results of electrical conductivity measurements, thermogravimetric analysis and studies involving XRD, XPS and SEM ammonia sensing mechanism by MoO₃ was confirmed to involve the formation of molybdenum suboxides and Mo₂N which is contrary to the mechanism postulated in literature invoking involvement of adsorbed oxygen ions. Thin films of MoO₃ were deposited over polycrystalline alumina and quartz substrates by pulsed laser deposition and their gas sensing characteristics were studied. The results indicate that thin film sensors show better gas sensing characteristics than porous pellet sensors. Among thin film sensors, films deposited over quartz substrates have shown higher sensitivity towards ammonia than those on polycrystalline alumina substrate. These results also indicated that pure MoO₃ (as porous structures or thin films) can be used as sensor material for sensing ammonia in air at tens of ppm levels but would have low sensitivity at near threshold limit values (TLV) of ammonia viz. 25 ppm.

MoO₃ rich region of Ag-Mo-O system is characterized by the presence of the compound Ag₆Mo₁₀O₃₃. Electrical conductivity and transport number of Ag⁺ ions (tAg⁺) in this compound were determined and the results show that this compound possesses high conductivity and tAg⁺ values. These data could be correlated to the structure of Ag₆Mo₁₀O₃₃ where planes populated by Ag⁺ ions are flanked by layers consisting of MoO₆ octahedra. Gas sensing studies showed that porous pellets of Ag₆Mo₁₀O₃₃ are capable of sensing ammonia in air below its TLV limits. Based on results of XRD, SEM and XPS studies, mechanism of ammonia sensing is shown to involve the formation of sub oxides of molybdenum, Mo₂N and metallic silver. When equilibrated with air, these reaction products recombine fast to form the original compound.

Studies on MoO₃ – TiO₂ system were carried out with compositions having formula Mo₁₋ₓTiₓO₃₋₅ (where x = 0.05 - 0.9). Solubility limit of TiO₂ in MoO₃ is found to be less than 5 mole %. Electrical conductivity of TiO₂ added compositions were lower.
than that of pure MoO$_3$ and this was traced to reduction of Mo$^{5+}$ ions in the MoO$_3$ phase. Addition of TiO$_2$ was found to enhance the sensitivity of MoO$_3$ towards ammonia and the composition with 50 mole % TiO$_2$ in MoO$_3$ was found to exhibit maximum sensitivity. Mechanism of ammonia sensing by this composition was found to involve formation of suboxides of molybdenum and Mo$_2$N, as in the case of pure MoO$_3$.

In case of V$_2$O$_5$ addition to MoO$_3$, formation of solid solution was observed up to 1 mole % of V$_2$O$_5$ and addition of 2.5 mole % of V$_2$O$_5$ resulted in the formation of V$_9$Mo$_6$O$_{40}$. Vanadia doped compositions possess higher electrical conductivities than pure MoO$_3$. They also exhibit higher sensitivities than pure MoO$_3$ towards LPG, H$_2$ and NH$_3$ at all temperatures although selectivity enhancement was not observed towards any of these gases.

Electrical conductivity of pure WO$_3$ was also studied under different gas ambients viz. dry as well as humid O$_2$, air and Ar, in the temperature range of 373 to 773 K. These results showed that the electrical conductivity of WO$_3$ is also independent of oxygen partial pressure. Activation energy for the electrical conduction up to 603 K, where transition of monoclinic phase of WO$_3$ to orthorhombic form takes place, was determined from Arrhenius plot as 0.50±0.02 eV. It was also established that humidity does not play any role in the electrical conduction of WO$_3$. Gas sensing characteristics of porous pellet sensors of WO$_3$ towards LPG, H$_2$ and NH$_3$ were studied in the temperature range of 498 – 623 K. Pure WO$_3$ is found to be highly sensitive and selective to hydrogen at 498 K. Thin films of tungsten oxide were prepared on polycrystalline alumina substrates by pulsed laser deposition and their gas sensing characteristics were compared with those of porous pellet sensors. Thin film sensors showed better retracing characteristics than porous pellet sensors while other characteristics were retained. Effect of Ag, TiO$_2$ and V$_2$O$_5$ as dopants on the gas sensing properties of tungsten oxide were also studied. Attempts to synthesize Ag$_6$W$_{10}$O$_{33}$, a compound similar to that in Ag-Mo-O system, were not successful and a mixture of Ag$_2$W$_4$O$_{13}$ (major phase) and Ag$_2$W$_2$O$_7$ (minor phase) was always obtained. This mixed phase composition exhibited higher sensitivity and selectivity than pure WO$_3$ towards ammonia at all temperatures. Electrical conductivity and gas sensing characteristics of WO$_3$ containing TiO$_2$ (5 to 25 mole %) were similar in case of MoO$_3$ with TiO$_2$ content. Solubility limit of TiO$_2$ in WO$_3$ was also found to be below 5 mole %. Electrical conductivity of TiO$_2$ added samples were also lower than that of pure tungsten oxide and the sensitivity towards ammonia was
found to increase with increase in TiO₂ addition. Similar studies were carried out with WO₃ containing 0.5, 1 and 2.5 mole % of V₂O₅. Results showed the formation of solid solution of V₂O₅ in tungsten oxide up to 2.5 mole %. Gas sensing characteristics of vanadia added compositions showed them to possess no special features when compared to pure WO₃.

This thesis work has brought out the characteristics of electrical conductivities of pure and doped MoO₃ and WO₃. The gas sensing mechanism of oxides such as MoO₃ (which donot chemisorb oxygen) was established to be different from that of other semiconducting metal oxides. Potentials of 1) silver ion conducting Ag₆Mo₁₀O₃₃ and 2) 50 mole % MoO₃ – 50 mole % TiO₂ for sensing trace levels of ammonia in air with the former having capabilities to extend below TLV levels of NH₃ are brought out. Suitability of thin films of WO₃ for sensing very low levels of hydrogen in air is also indicated.