RESEARCH PAPER | Physics | Volume : 3 | Issue : 4 | April 2013 | ISSN - 2249-555X

Vacuum Evaporated MoO_3 Thin Films for Gas Sensing Application

KEYWORDS

M. C. Rao

Department of Physics, Andhra Loyola College, Vijayawada - 520008, India

ABSTRACT *Chemical sensors are becoming a field of increasing popularity and have become a field of much focus in recent years. Chemical sensors are in greater demand than ever in the past due to the increased need to determine the concentrations of toxic and carcinogenic gases in the air. Semiconductor metal oxide thin films have been extensively used for gas sensors as their conductivity changes due to interactions with gas molecules. Such sensors also offer low cost, easy fabrication and consistent performance with respect to other type of gas sensors. Among the semiconductor metal oxides, MoO3 with band gap energy of 2.39 - 2.9 eV is an excellent candidate for catalytic, electrochromic and gas sensing applications. MoO3 thin films have been widely considered as good candidates for their use as environmental gas sensors for detecting pollutant gases like carbon monoxide, carbon dioxide, hydrocarbons, ammonia and nitrogen oxides. Hence in the present investigation MoO3 thin films were prepared by vacuum evaporation technique and the gas sensing properties of MoO3 thin films was studied.*

INTRODUCTION

The growing demand of fast accurate and low cost air quality analysis techniques for environmental monitoring, automotive applications, air conditioning in airplanes, spacecrafts and houses, sensors networks, in domestic and industrial environments, is tailoring the research toward new materials and techniques to solve the problems related to the commercial sensors. Metal oxide semiconducting layers are the most promising conductometric chemical sensors among solid state devices, due to their low dimension, price and power consumption. Considerable research has been carried out on the development of chemical sensors based on semiconductor metal oxides such as SnO_2, ZnO and TiO_2. Among the semiconductor metal oxides, Molybdenum trioxide (MoO_3) with band gap energy of 2.39-2.9 eV is an excellent candidate for catalytic, electrochromic and gas sensing applications. MoO_3 has been well known for its application as a catalyst for the oxidation of hydrocarbons and reduction of NO_x in the chemical and petroleum industry [1]. Semiconductor metal oxide thin films have been extensively used for gas sensors as their conductivity changes due to interactions with gas molecules. Such sensors also offer low cost, easy fabrication and consistent performance with respect to other type of gas sensors. Recently, there is an increasing trend to use specifically engineered structured materials as gas sensing elements. The use of such structured materials such as belts, rods and wires in micro-, meso- or nano-dimensions, offer high surface to volume ratios and unique structural features that are expected to enhance the properties and performance of gas sensors. Such structured oxide based chemical sensors were also found to decrease the device response time due to rapid diffusion of gaseous species into the materials' micro-, meso- and nano-porosities [2]. Among the semiconductor metal oxides, Efforts were also made to examine and improve the gas sensing properties of MoO_3 based devices to detect H_2, CO, NH_3 and LPG [3].

MoO_3 is metal oxide that has excellent photochromic and electrochromic properties. As some other transition metal oxides, MoO_3 shows good adsorption of ammonia, carbon oxide, nitric oxides and hydrogen. It is also sensitive to many organic compounds such as hydro carbonic and aromatic gases, ethanol, gasoline, trimethylamine and many others. However, MoO_3 has a low melting point of 795°C. There has been limited research on MoO_3 for gas sensing applications. Thin films of MoO_3 were prepared by RF sputtering. These films were found to be highly sensitive to ammonia in the temperature range of 400-450°C. The possibility of nanostructured MoO_3 films to build advanced chemical sensors is very perspective [4]. MoO_3 films of various thicknesses (300 nm – 1.5 μm) were deposited by RF reactive sputtering on quartz resonators with silver (Ag) and gold (Au) electrodes. The aim is to use the quartz crystal microbalance (QCM) method for studying gas sensing properties of MoO_3 thin films. QCM is an extremely sensitive mass sensing method, capable of measuring mass changes in the nanogram range. This means that QCM sensors are capable of measuring mass changes as small as a fraction of a monolayer or a single layer of atoms.

Semiconductor metal oxides are being used as gas sensors in monitoring environmentally pollutant gases coming from automobile exhaust, toxic gases from chemical industries and explosive gases. The operation of most of gas sensors is based on the reversible changes of the resistivity of specific materials, caused by the presence of a gas in its environment. The resistance change originates from an interaction between the gas and the metal oxide. The interaction takes place through mediation of adsorbed oxygen of the metal oxide not only through the adsorption of the gas itself. That is, the analyzed gas reacts with the adsorbed oxygen, causing its decrease from an equilibrium concentration level in air. In other words, catalytic oxidation of the gases takes place on the metal oxide and the resulting decrease of the adsorbed oxygen is eventually monitored as a change in the electrical resistance of the sensor element. The focus of sensor development concerns the modification of surface structure of materials that provide increased sensitivity, selectivity and stability.

Chemical sensors are in greater demand than ever in the past due to the increased need to determine the concentrations of toxic and carcinogenic gases in the air. Chemical sensors that are small, portable, cost efficient and able to detect low concentrations of gases are needed for this application. If a sensor exhibits a specialized response to one gas only, then it can be used to detect that gas since there will be no interference by other gases. The ultimate goal is to create a useful chemical gas sensor that can be used to determine the concentration of one gas in air at the lowest concentration possible before it becomes dangerous to human health. Metal oxide sensors often show a great response to volatile gases. Their response to gases occurs due to reactions that occur with oxygen adsorbed to the surface of the metal oxide. Work has been done using metal oxides, polymers, and various layered mixtures of the two. Metal oxide-polymer sensors often show a response that is markedly different than either of its constituents [5].

Volume : 3 | Issue : 4 | April 2013 | ISSN - 2249-555X

EXPERIMENTAL

MoO_3 thin films were prepared on to Corning 7059 glass substrates by thermal evaporation of pure MoO_3 Powder (purity 99.99% obtained from MERCK) from an electrical heated molybdenum boat kept at ~ 1823 K in a vacuum better than 8 x 10^{-6} Torr. A Hind High Vacuum 12A4 Coating unit was used for the deposition of the experimental films. A diffusion pump backed by a rotary pump was employed to produce the ultimate pressure of 3 x 10^{-6} Torr. Well cleaned Corning 7059 glass substrate along with suitable masks were mounted on a copper holder which was fixed on a tripod in the beljar. The source to substrate distance was fixed at 15 cm. After getting the ultimate vacuum of 5 x 10^{-6} Torr and the desired substrate temperature in the chamber, the glow discharge was initiated further ionically clean the substrates in the vacuum chamber. This was done for about two minutes. The system was allowed to reach the ultimate vacuum. When the power was fed to the boat, the material in the boat evaporated and the vapors reacted with the oxygen gas leading to film deposition on the substrate [6-9]. The deposition temperature was in the range of 303 - 603 K and it was measured by a Chromel- Alumel thermocouple attached to the substrate and precisely controlled by a temperature controller. The temperature of the boat during deposition was monitored by means of an optical pyrometer. The substrates were maintained at the required deposition temperature and then, the molybdenum boat in which MoO_3 powder was kept and heated slowly. The shutter covering the substrates was opened when the temperature of the boat reached about 1823 K and it was maintained during the deposition of the films. The deposition rate observed by a quartz crystal thickness monitor was 10 A^0/sec. The thickness of the films investigated was about 4000 A^0.

RESULTS AND DISCUSSION

The deposition parameters such as substrate temperature, deposition rate, film –substrate combination, vacuum during the film deposition etc. greatly influence the physical and chemical properties of the oxide thin films. In the present investigation thin films of MoO_3 were prepared on Corning 7059 glass substrates keeping all the deposition parameters fixed except the substrate temperature.

The electrical conductance of a semiconducting oxide-based gas sensor depends on the chemisorbed oxygen ions, oxygen vacancies and the interstitial ions. The target gases change the oxygen balance of the oxide sensor, leading to a variation in its conductance. It is believed that in most of semiconducting oxide-based devices, the electrical conductance of a semiconducting oxide-based gas sensor depends on the chemisorbed oxygen ions, oxygen vacancies and the interstitial ions. The target gases change the oxygen balance of the oxide sensor, leading to a variation in its conductance.

The conductance of the sensor in dry air was measured by means of conventional circuitary by applying constant voltage and measuring the current by picoammeter. The conductance was measured both in the presence and absence of test gas. The gas response (s) is defined as the ratio of change in conductance in gas to air to the original conductance in air

$$S = (G_g - G_a) / G_a$$

The selectivity is defined as the ability of a sensor to respond to certain gas in the presence of other gases.

MoO_3 conductometric sensors were mounted on an electric heater. Gas response measurements of the devices were performed in a stainless steel test chamber made from Teflon, which was sealed in a quartz lid. The heater was controlled by a regulated DC power supply providing different operating temperatures. The total flow rate was kept constant at 50 sccm and dry synthetic air was used as the reference gas. Subsequently, the device was exposed to sequences of different concentrations of NO_2 for several hours. In the MoO_3 sensor, change in the oxygen balance of the oxide layer leads to a variation in its conductance. In the case of an oxidizing gas (NO_2), reactions directly take place on the oxide surface. During the interaction process, molecules consume conduction electrons and subsequently increase the depletion region at the surface and the resistivity of the sensor increases as presented below.

MoO_3 films were exposed to different concentrations of NO_2 gas at various temperatures. The sensor was placed in a stainless steel test chamber. A continuous flow of gas (100 sccm) passes through the chamber, which makes the pressure in the test chamber to be nearly atmospheric. The desired gas concentration is obtained by mixing the appropriate flows of gases by means of mass flow controllers. The films are generally heat treated before exposure to different gasses because it produces contacts between grains, many of which are between grains having different crystal structures. When both the films are exposed to NO_2 gas, the dc electrical resistance of the film dramatically increased. Since MoO_3 is an n type semiconductor, its electrical behavior upon exposure of NO_2 oxidizing gas can be explained by a decrease of conduction carrier density. The amount of oxygen ions available on the MoO_3 surface increases at the operating temperature. The adsorbing NO_2 molecules interact directly with the adsoption sites at the oxide surface. Therefore the interaction between the film and NO_2 is as follows;

$$NO_2 + e^- \rightarrow NO^{2-}(ad)$$

The interaction with NO_2 results in a decrease in the free electron concentration. The decrease in free carrier concentration causes a rise in the film resistance. The sensitivities for both the films were recorded at various temperatures.

CONCLUSIONS

Gas sensors based on metal oxide semiconductors may be used in a wide variety of applications including gas monitoring and alarm applications. As some other transition metal oxides, MoO_3 shows good adsorption of ammonia, carbon oxide, nitric oxides and hydrogen. It is also sensitive to many organic compounds such as hydro carbonic and aromatic gases, ethanol, gasoline, trimethylamine and many others. Chemical sensors that are small, portable, cost efficient and able to detect low concentrations of gases are needed for this application. MoO_3 films were exposed to different concentrations of NO_2 gas at various temperatures and the sensitivities of the films were recorded at various temperatures. If a sensor exhibits a specialized response to one gas only, then it can be used to detect that gas since there will be no interference by other gases. The ultimate goal is to create a useful chemical gas sensor that can be used to determine the concentration of one gas in air at the lowest concentration possible before it becomes dangerous to human health.

ACKNOWLEDGEMENTS

The author (M. C. Rao) is thankful to UGC for providing the financial assistance through Major Research Project (Link No. F. No. 40-24/2011(SR))

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