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Vacuum Evaporated WO_3 Thin Films For Gas Sensing Application

KEYWORDS: WO_3, Thin film, Vacuum evaporation, Gas sensor.

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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, WO3 is an excellent candidate for catalytic, electrochromic and gas sensing applications. WO3 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 WO3 thin films were prepared by vacuum evaporation technique and the gas sensing properties of WO3 thin films was studied.*

INTRODUCTION

There is a considerable interest in the research and development of materials and devices that can be used for optical switching of large-scale glazings. Several potential switching technologies are available for glazings, including those based on the electrochromism, thermochromism and photochromism phenomena. Tungsten oxide (WO_3) has been extensively studied and is reported to have interesting physical properties, which makes it suitable for electrochromic and a variety of potential applications. WO_3 with band gap energy of 2.6 eV is an excellent candidate for catalytic, electrochromic and gas sensing applications.

Among transition metal oxides, WO_3 is one of the most interesting materials exhibiting a wide variety of novel properties particularly in thin film form useful for advanced technological applications. It exhibits structural transformations and sub-stoichiometric phase transitions, which attracted the attention of researchers over the past few years to explore their potential scientific and technological applications in the fields of display systems and microelectronics. It exhibits electrochromic properties which make it suitable for variable reflection mirrors, dazzle free mirrors in automobiles, variable sun protection system usually called smart window and surfaces with tunable emittance of thermal control of satellites. It has been recognized as a significant chromic material that can be colored through electro-, photo-, gas-, laser- and thermochromism processes [1]. There has been a great deal of recent interest in WO_3 thin films for a wide variety of applications in optoelectronics, microelectronics, selective catalysis and environmental engineering [2, 3]. It has been demonstrated that WO_3 films exhibit chemical sensing properties, which will have numerous applications in environmental pollution monitoring. WO_3 thin films show excellent functional activity to various gases, such as H_2S, NO_x, trimethylamine and other organic compound gases. The ability to detect NO_x even at low or elevated temperatures makes WO_3 important for integrated sensors [4, 5].

Tungsten trioxide exhibits a cubic perovskite like structure based on the corner sharing of regular octahedra with the oxygen atoms at the corner and the tungsten atoms at the center of each octahedron. The crystal network is the result of alternating disposition of O and WO_2 planes normally to each main crystallographic direction. Actually, the symmetry of WO_3 is lowered from the ideal ReO_3 structure by two distortions: tilting of WO_6 octahedra and displacement of tungsten from center of its octahedron. Tungsten trioxide thin films have been deposited by a number of deposition techniques such as thermal evaporation, electron beam evaporation, chemical vapor deposition and laser deposition. Each deposition technique produced different properties on different substrates in terms of composition, structure and morphology [6]. Electrochromism in WO_3, which involves ion/electron insertion and extraction, has been studied widely. Intercalation of metal ions (M^+) into tungsten oxide results in a tungsten bronze $MxWO_3$. Usually, the intercalated ions are H^+, Li^+, K^+ and Na^+. Whereas a thin film of WO_3 is a transparent insulator, the tungsten bronze is a conductor and has a deep blue color [7, 8].

An amorphous α–WO_3 film has a definite ionic and electronic conduction. It has large opened pore and it is constituted by clusters. The clusters are built from no more than 3-8 WO_6 –octahedra, linked together by corners or edges and in the complete structure of the film connected with one another by W-O-W bonds, see Fig. 1 and Fig. 2. The voids observed within the film are the result of random packing of the clusters and mostly give the open structure that is normally filled with molecular water taken from the air. The presence of water is necessary to stabilize the microcrystalline structure of an α–WO_3 film with the opened pore structure. The ionic conduction of an α–The most stable WO_3 phase at room temperature has a monoclinic structure, but this phase transforms to an orthorhombic or a tetragonal phase at higher temperatures. Generally WO_3 and related electrochromic materials are divided into three main groups with regard to bulk crystalline structures: (i) Perovskite-like, such as WO_3, MoO_3, $SrTiO_3$; (ii) Rutile-like, TiO_2, MnO_2, VO_2, RuO_2, IrO_2 and RhO_2; (iii) Layer and block structures forming a somewhat undefined group, such as V_2O_5, Nb_2O_5 [9, 10].

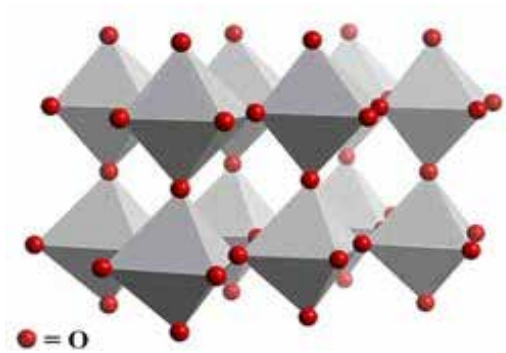

Figure 1: Polyhedral representation of WO_3

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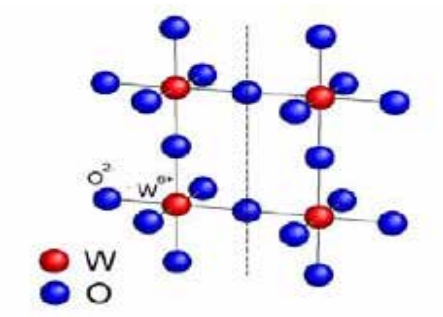

Figure 2: Balls and sticks crystalline structure of WO_3

EXPERIMENTAL

WO_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 [11-14]. 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 WO_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 WO_3 were prepared on Corning 7059 glass substrates keeping all the deposition parameters fixed except the substrate temperature.

The gas sensing mechanism involves the change in the resistance at the surface, leading to the change in the depletion layer in the grain which in turn results in the change in electrical resistance. In order to improve the sensitivity, selectivity and stability, more efforts have been put to investigate the effect of dopants and catalysts on metal oxide semiconductors owing to their potential applications in the field of gas sensors and optoelectronic devices. 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.

Gas sensors based on metal oxide semiconductors may be used in a wide variety of applications including gas monitoring and alarm applications. 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 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.

WO_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 WO_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.

WO_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 (50 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 WO_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 WO_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

Metal oxide semiconducting layers are the most promising conductometric chemical sensors among solid state devices, due to their low dimension, price and power consumption. 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, WO_3 shows good adsorption of ammonia, carbon oxide, nitric oxides and hydrogen. WO_3 films were exposed to different concentrations of NO_2 gas at various temperatures and the sensitivities of the films were recorded at various

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temperatures. 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.

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