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Ion-assisted e-beam evaporated gas sensor for environmental monitoring

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Abstract

With increasing air pollution problems, gas sensors for toxic gas detection have recently gained much attention. Among different types of gas sensors, thin film devices have been much of interest because of microelectronic batch-fabricated compatibility, reproducibility, and the ability to form multilayer device structures. In this work, thin film based gas sensors fabricated by electron beam evaporation with ion-assisted deposition (IAD) are developed for immediate applications of CO detection for environmental monitoring and Alcohol testing for drivers. The IAD process offers several advantages for gas sensor fabrication, including reactive deposition for gas-sensitive metal-oxide material optimization and improved thin film adhesion for better device reliability. Gas-sensing performance of ion-assisted electron beam evaporated metal oxide thin film materials, including SnO_2 and WO_3, has been characterized as a function of IAD deposition parameters. The metal oxide layer was deposited on Au/Al interdigitated electrodes on alumina or glass substrates with an unpatterned NiCr thin film heater on the backside. The sensors were tested with reducing gases, including alcohol vapour and CO, in the temperature range between 200 and 350 °C. Experimental results indicate that the SnO_2 thin film has higher sensitivity to both alcohol and CO than the WO_3 thin film under the same IAD deposition parameters. In addition, alcohol and CO sensitivity tends to improve with increased oxygen-ion addition during e-beam evaporation. Our results indicate that ion-assisted e-beam evaporation is a useful and well-controlled process suitable for gas sensor fabrication.

Keywords: Thin film gas sensor; Semiconductor gas sensor; Metal-oxide gas sensor; Ion-assisted e-beam evaporation

1. Introduction

With increasing atmospheric pollution problems, effective monitoring and controlling systems for detection and quantification of pollution sources have become increasingly important. Presently, standard air pollution measurements utilize analytical instruments such as optical spectroscopy, gas chromatography/spectroscopy. These instruments can provide precise analysis, however they are time consuming and expensive. Solid-state gas sensors have been more widely used in many gas-sensing applications due to their low cost, high sensitivity, fast response, and simple electronic interface, however they are less accurate and less selective than analytical instruments. With intense research and development, their performance has been improved dramatically and thus they could soon be effective alternatives for air pollution measurement. Among different types of gas sensors, thin film type semiconductor gas sensors have recently been of much interest because of microelectronic compatibility, ease of control of processing parameters, reproducibility, fast response, and relatively low cost [1–10].

Electron-beam evaporation is one of the preferred techniques for thin film gas sensor fabrication because of the ease of batch fabrication and the ability to form high-quality multilayer thin film structures [4,5]. However, thin film gas sensors prepared by conventional e-beam evaporation tend to suffer from poor gas-sensing sensitivity and selectivity problems because the evaporated metal-oxide material loses the oxygen component due to decomposition at high temperature [5]. With reactive ion addition during e-beam evaporation, the oxygen component can be recomposed in the material by a controllable amount. The properties of the thin film material can be manipulated to enhance the gas-sensing characteristics of e-beam evaporated thin film with ion-assisted deposition (IAD).

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Another significant advantage of this process is that ion-assisted e-beam evaporated thin film might be able to be used for gas sensing with no or low-temperature post-deposition annealing. This benefit would allow easy integration of the gas sensor and microelectronic fabrication processes to produce smart gas sensors with integrated control and signal processing on the same chip. In this work, the gas-sensing performance of ion-assisted electron beam evaporated metal oxide thin film materials, including SnO_2 and WO_3, has been characterized as a function of IAD deposition parameters with no post-deposition annealing. The sensors were tested with reducing gases, including alcohol vapour and CO for immediate applications as Alcohol testing for drivers and CO testing for environmental monitoring.

2. Materials and methods

2.1. Materials for gas sensor fabrication

The starting gas sensitive materials are an industrial grade tin oxide (SnO_2) powder (99.5%) and analytical grade tungsten oxide pellets. For e-beam evaporation, the SnO_2 powder was compressed into a cylindrical lozenge with an approximate size of 2 cm in diameter and a height of 1.5 cm and the compressed powder was sintered in air at 1000 °C for 8 h. The substrates for thin film coating were standard BK7 glass slides and 600 μm-thick Alumina sheet. NiCr (Ni 80% and Cr 20%) is used as the low cost material for the thin film heater.

2.2. Gas sensor fabrication

The gas sensors were fabricated from a series of thin film deposition using Denton's ion-assisted e-beam evaporator system. This system consists of a high vacuum chamber equipped with electron gun, ion gun, quartz lamp, quartz crystal monitor, and optical monitor. The electron gun is a tungsten filament biased and controlled by electric and magnetic field. The ion gun is a cold cathode ion source. The material holder is a four-pocket crucible and the substrate holders are machined flat plates with a motor drive.

The gas sensor fabrication process started with the deposition of Al/Au interdigitated electrodes on a glass or alumina substrate. Prior to deposition, the glass or alumina substrates were pre-cleaned by isopropyl alcohol and then loaded into the e-beam evaporator. Next, the substrates were cleaned by oxygen-ion bombardment in a vacuum pressure of $\sim 10^{-4}$ Torr. This cleaning is to improve adhesion of the film to the substrates by removing moisture and any organic contaminants on the surface. Aluminium (Al) and gold (Au) layers were then successively e-beam evaporated over the glass substrate through electroplated-Ni shadow masks having an interdigitated pattern. The width, spacing, and length of the interdigitated electrode were ~ 100, ~ 100, and ~ 1 mm, respectively. The thickness of Al and Au layers were ~ 200 and ~ 80 nm, respectively. The film thickness was measured by the quartz crystal monitor and calibrated by a Detak profiler.

Next, a metal oxide layer was evaporated over inter-digitated electrode through another electroplate shadow mask with square window pattern aligned to interdigitated area. For metal oxide deposition, substrates were heated to the desired temperature with quartz lamp radiation. The metal oxide evaporation was then started in oxygen-ion environment under vacuum of $\sim 10^{-4}$ Torr. For this study, the depositions were conducted with different oxygen flow rates. The oxygen flow rate was varied from 25 to 30 sccm. The deposition rate, film thickness, substrate temperature, and ion source parameters including ion driving voltage, and ion flux current were kept constant for all experiments. The deposition rate, film thickness, and substrate temperature were approximately 0.2 nm/s, 200 nm, and 130 °C, respectively. The ion driving voltage and ion flux current are ~ 400 V and ~ 0.13 A. There was no post-deposition annealing for these metal oxide thin films.

After the metal oxide coating, a NiCr (Ni 80% and Cr 20%) layer were then blanket e-beam evaporated over the backside of substrate. If glass substrate is used, a thin Cr layer must be evaporated before NiCr layer. The Cr layer is required as an adhesive layer between the NiCr film and the glass substrate. The thickness of Cr and NiCr layers were ~ 80 and 400 nm, respectively. The thickness of NiCr layer is suitably chosen for gas sensor heating up to 350 °C. The structure and typical optical photograph of the gas sensor are shown in Fig. 1. The morphology of e-beam evaporated metal oxide thin films were imaged using a scanning tunnelling microscope (STM). A typical STM micrograph is shown in Fig. 2. It can be seen that the surface of e-beam evaporated metal oxide thin film contains numerous sharp nano-protrusions with the average size at the base of the tip of ~ 5–10 nm. The root mean square (rms) surface roughness of this film was estimated to be ~ 5.6 nm from the STM data by the WSxM software. Thus, the e-beam evaporated surface is macroscopically smooth with very fine nanoprotrusions.

2.3. Gas sensing measurements

The gas-sensing characteristics of metal oxide thin films were characterized with two reducing gases, ethanol (C_2H_5OH) and carbon monoxide (CO). For electrical testing, the sensor electrodes were gold-ball bonded for electrical connection and the NiCr heaters were bonded to solid wires with silver conductive epoxy. The gas sensors were then mounted in a stainless steel gas-testing chamber. The NiCr-heater was heated by a regulated dc power supply to different operating temperatures. The resistances of various sensors were continuously monitored with a Lab-View based software from the computer through the measuring circuit. The measuring circuit was a current to

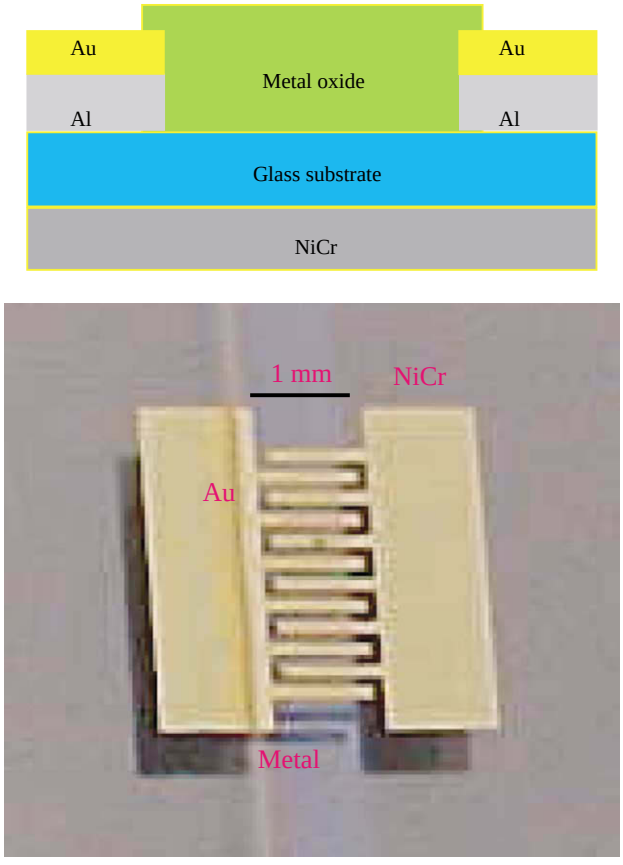

Fig. 1. The structure and typical optical photograph of e-beam evaporated metal-oxide gas sensor.

voltage converter, which gives the output voltage that is inversely proportional to the resistance of the gas sensor [10].

For gas testing, purified air (99.99% Air Zero) and nitrogen containing gas sample (Et or CO) were mixed in different ratios and made to flow through the testing chamber. The gas flow rate were precisely manipulated using a computer controlled multi-channel mass flow controller. Purified air was used at a constant flow rate of 0.100 litres per minute. The CO source was a certified gas balanced in nitrogen with a calibrated concentration of 1000 ppm. The ethanol gas source was obtained by passing nitrogen through 99.9% ethanol. The sensor was exposed to the gas sample for ~5 s for each gas response tested and the sensor was recovered by exposure to purified air. The operating temperature was varied from 200 to 350 °C.

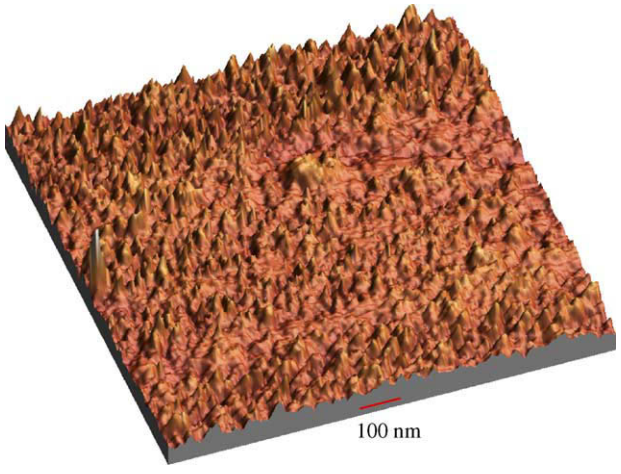

Fig. 2. Typical STM micrograph of surface morphology of e-beam evaporated metal oxide thin film.

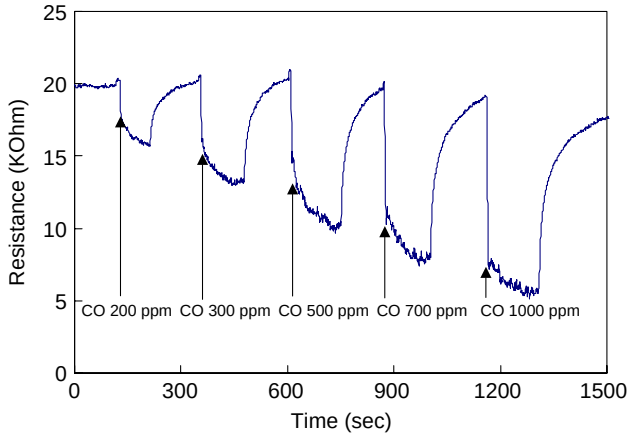

Fig. 3. Typical time responses to CO at 300 °C of tin oxide thin film with an oxygen flow rate of 30 sccm.

3. Results and discussion

The gas-sensing characteristics of oxygen-ion assisted e-beam evaporated metal oxide thin films deposited with different oxygen flow rates at various temperatures were measured. The gas-sensing characteristics of the metal oxide thin film deposited with no oxygen-ion were also measured as a base line. Typical time response to ethanol and CO of the tin oxide and tungsten oxide sensors are shown in Figs. 3 and 4, respectively. Both metal oxide thin films were oxygen-ion assisted e-beam evaporated with oxygen flow rate of 30 sccm and were tested at 300 °C.

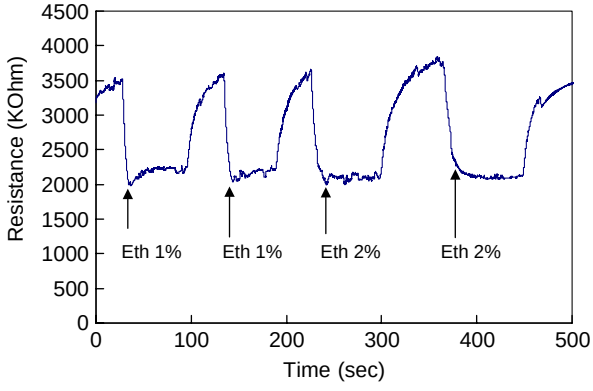

Fig. 4. Time responses to ethanol at 300 °C of tugnsten oxide thin film with oxygen flow rate of 30 sccm.

The concentration of the gas sample is indicated in the figures. From the figures, it is clear that there is an abrupt decrease in the sensor's resistance due to gas adsorption after each injection of gas sample. The abrupt decrease in resistance confirms that the adsorption is chemical adsorption with reducing reaction, which results in electron transfer from the gas sample to the semiconductor surface. The increase of electron concentration on the surface causes the surface resistance to decrease. The typical response and recovery times of the SnO_2 gas sensor to CO are ~5 and ~60 s, respectively; the typical response and recovery times of the WO_3 gas sensor to ethanol are ~4 and ~40 s, respectively. The overall time responses demonstrate that both thin films have a satisfactorily fast response, with good response and recovery rates, to ethanol and CO.

Gas-sensing sensitivity for a reducing gas of a semiconductor gas sensor is normally defined as the ratio of resistance with no gas sample to that with a gas sample. From the time response data, gas-sensing sensitivity was calculated and plotted versus various parameters including oxygen flow rate, gas concentration, and temperature. Fig. 5 shows the sensitivity to alcohol and CO of tin and tungsten oxide thin films with different oxygen flow rates at 300 °C operating temperature. It should be noted that 0 sccm oxygen flow rate means the metal oxide thin film with no oxygen-ion addition. From Fig. 5, it is clear that the tin oxide thin film has higher sensitivity to ethanol and CO than the tungsten oxide thin film. In addition, it can be seen that the sensitivity to ethanol and CO of the e-beam evaporated tin and tungsten oxide thin films tends to improve as oxygen flow rate increases. It should be noted that similar trends are found from the data with other gas concentrations and temperatures.

The results indicate that the oxygen-ion addition improves the gas sensing sensitivity of e-beam evaporated metal oxide thin films. A possible explanation for the observed effect is that the addition of oxygen-ions and the increase of the oxygen flow rate enhance the reducing reaction at the surface of the thin film because the number of oxygen vacancies in and on the surface of the thin film is reduced. It is well known that e-beam evaporated metal-oxide thin film tends to have high amount of oxygen vacancies due to oxide decomposition at very high temperature. Since the reducing reaction with organic gases would result in the increase of oxygen vacancies, the thin film would have poor response to reducing gases if it already has a high oxygen-vacancy density. The addition of oxygen-ion during deposition directly reoxidizes the thin film and hence reduces the number of oxygen vacancies. The advantages of reoxidizing the thin film by oxygen-ions over conventional annealing are the much lower process temperature and higher thin film quality. An additional explanation is that the ion-assisted deposition produces the film with higher surface roughness and porosity. It was found primarily from STM measurements that the surface roughness of the films tends to increase with IAD. The increased roughness and porosity results in a larger surface area for gas adsorption and hence higher gas sensing sensitivity.

The effect of operating temperature was also investigated. The operating temperature was varied from 150 to 350 °C. Fig. 6 shows the effect of temperature on tin oxide and tungsten oxide thin film sensitivity to ethanol and CO. The oxygen flow rate for IAD deposition of the tin oxide thin film was 30 sccm. For temperatures below 200 °C, the tin oxide thin film gave low to negligible response to alcohol or CO gases and hence the sensitivity is ~1. From Fig. 6, it can be seen that the tin oxide thin films have high sensitivity at moderate temperatures of 300–350 °C and the sensitivity tends to decreases as temperature decreases. It should be noted again that

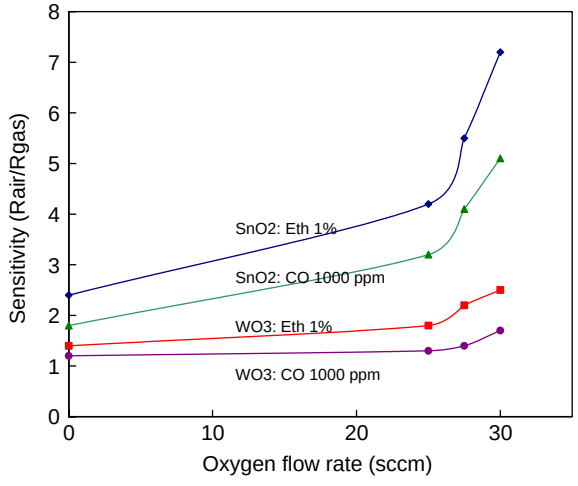

Fig. 5. Typical sensitivity to ethanol and CO vs. oxygen flow rate of tin oxide and tungsten oxide thin films.

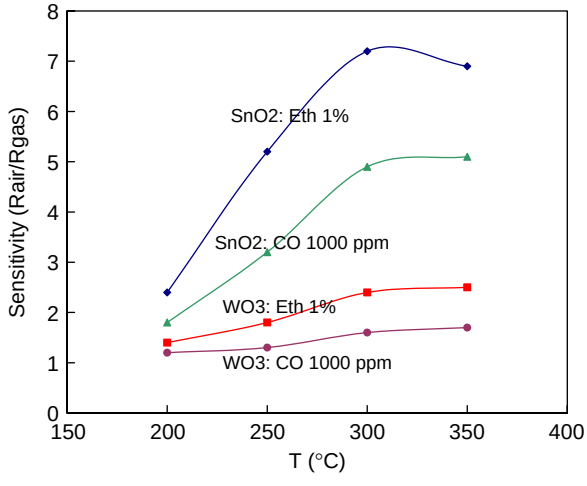

Fig. 6. Typical tin oxide and tungsten oxide thin film's sensitivity to alcohol and CO vs. temperature.

similar trends could be seen for other cases with different oxygen flow rates and gas concentrations.

4. Conclusions

In conclusion, thin film based metal-oxide gas sensors have been fabricated based on an ion-assisted e-beam evaporation process. The gas-sensing characteristics of ion-assisted electron beam evaporated metal oxide thin films with no post-deposition annealing have been studied. The effect of oxygen-ion incorporation during e-beam evaporation on the gas-sensing characteristic of tin oxide thin film has been investigated by varying oxygen flow rate. Experimental results indicate that the SnO_2 thin film has higher sensitivity to both alcohol and CO than WO_3 thin films produced under the same IAD deposition parameters. In addition, the sensitivity to alcohol and CO of metal oxide thin film are improved by oxygen-ion addition during e-beam evaporation and the sensitivity also tends to increase as the oxygen flow rate increases. From the results, it may be principally concluded that ion-assisted e-beam evaporation is a useful and well-control process for thin film gas sensor fabrication because it could produce gas sensors having good response at moderate temperatures with no post-deposition annealing.

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