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Gas-Sensing Characterization of TiO_2 -ZnO Based Thin Film

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Abstract—In this work, we investigate gas sensing characteristics of a new composite material, ZnO doped TiO_2 . TiO_2 /ZnO layers have been deposited by ion-assisted e-beam evaporation with different doping concentrations. Structural and morphological characterization has been carried out by means of SEM, XRD and EDX in order to correlate structural properties with gas sensing behavior. Gas-sensing characterizations toward acetone, ammonia, ethanol, CO, and NO_2 highlight interesting behavior for the layers tested. Low ZnO concentration (1%) increase responses toward acetone and ethanol while response toward CO, NO_2 , and ammonia are still low. However, high ZnO concentration (5-10%) decreases acetone and ethanol responses while CO, NO, and ammonia is almost diminished. In addition, ZnO: TiO_2 exhibit good response at medium operating temperature of 300 °C.

I. INTRODUCTION

Titanium dioxide (TiO_2) and Zinc oxide (ZnO) are well-known metal-oxide materials that have promising gas-sensing properties. TiO_2 is a versatile material, which has been used in many applications such as gas sensor, solar cell, photocatalytic layer for self-cleaning glass, optical coating for filters and waveguides, etc. TiO_2 is one of the most promising gas-sensing materials due to its high temperature stability, harsh environment tolerance, and catalytic properties. For gas sensing applications, TiO_2 is used in anatase phase that has lower resistance and higher response to gas adsorbents than the rutile phase, which is stable at higher temperature. TiO_2 nanocrystalline thin films were preferred because of their stable and good gas-sensing characteristics at operating temperatures below 400 °C. However, its low electrical n-type conductivity inhibits its practical implementation as a conductometric sensor. The addition of foreign atoms, such as Sn, Cr, Nb, W, Mo, into TiO_2 host has been widely studied to improve its gas sensing behaviors [1-7].

ZnO is another widely studied gas-sensing and piezoelectric material with interesting behaviors including fast response to a wide variety of gases [8-10]. Nevertheless, its very high working temperature and poor selectivity made ZnO an unpopular gas sensor. ZnO- TiO_2 should be an interesting mixture for gas sensing material because their useful properties may be collective. However, there is no report on gas sensing study of this combined material.

It is well known that preparation technique can considerably affect the structural and gas sensing properties of the mixed oxide sensors because these peculiarities rely on the essential surface activity of the layers. Electron-beam evaporation is one of preferred techniques for thin film gas sensor fabrication because of doping flexibility, ease of batch fabrication and ability to form high-quality multilayer thin film structures [11-13]. In this work, we investigate gas sensing behaviors of ZnO- TiO_2 thin films prepared by ion-assisted electron-beam evaporation with different compositions and the sensors were tested toward various gases, including Ethanol, Ammonia, Acetone, Carbon Monoxide and Nitrogen Dioxide.

II. MATERIALS AND METHODS

A. Materials for gas sensor fabrication

The oxide materials used for the deposition are analytical grade (99.9%) TiO_2 and ZnO powders. In this study, they were thoroughly mixed by the weight ratio of 0.9:0.1, 0.95:0.05, and 0.99:0.01, respectively. The prepared materials are listed as shown in Table I. For e-beam evaporation, the mixed powder was compressed into cylindrical pellets. The substrates for thin film coating were 200 μm -thick alumina substrate. Platinum (Pt) is used as the inert material for sensor electrode and thin film heater.

TABLE I. LIST OF THE DIFFERENT MATERIALS PREPARED.

TiO ₂	ZnO	Elemental comp. by EDS (at. %)			
		Ti	Zn	O	Ti:Zn
99%	1%	11.79	0.8	87.41	14.73
95%	5%	10.65	3.94	85.41	2.70
90%	10%	9.77	6.86	83.37	1.42

B. Gas sensor fabrication

The gas sensor fabrication process started with the deposition of metal oxide thin film. Prior to deposition, the alumina substrates were cleaned by oxygen-ion bombardment in a vacuum pressure of $\sim 10^{-4}$ Torr. This cleaning was performed to improve adhesion of the film to the substrates by removing moisture and any organic contaminants on the surface. The metal oxide layer was then e-beam evaporated under oxygen-ion beam with an oxygen flow of 25 sccm at a vacuum of 10^{-4} Torr. Alumina substrate temperature, deposition rate, and film thickness were 200 °C, 2 Å/s, and 300 nm, respectively. For this study, the depositions were conducted with different TiO₂-ZnO compositions (Table 1). The films were then annealed inside a furnace under controlled flux of humid synthetic air at 500 °C. At this stage, a group of samples was selected in order to examine surface morphology, microstructure, and crystal structure by means of scanning electron microscope (SEM) Energy dispersive X-ray spectroscopy (EDX), and X-ray diffraction (XRD). For the other group of samples, Pt electrodes were sputtered over the metal oxide layer and substrate through interdigitated shadow masks. Finally, a Pt heater was deposited by sputtering on the backside through shadow masking. For electrical testing, the sensor electrodes and Pt heaters were gold-wire bonded for electrical connection and mounted on a TO8 case.

C. Gas Sensing Measurements

The gas-sensing characteristics of metal oxide thin films were characterized toward Ethanol, Ammonia, Acetone, and CO and NO₂. The flow through technique was used to test the gas-sensing properties of thin films. A constant flux of synthetic air of 0.5 l/min was as gas carrier into which the desired concentration of pollutants—dispersed in synthetic air—was mixed. All measurements were conducted in a temperature-stabilized sealed chamber at 20 °C under controlled humidity. The Pt-heater was heated by a regulated dc power supply to different operating temperatures. The operating temperature was varied from 200° C to 500° C. The resistances of various sensors were continuously monitored with a computer-controlled system by voltage-amperometric technique with 1 V dc bias and current measurement through a picoammeter. The sensor was exposed to a gas sample for ~ 20 minutes for each gas response testing and then the air flux was restored.

III. RESULTS AND DISCUSSION

A. Microstructural Characteristics

The chemical compositions of the TiO₂/ZnO thin films are demonstrated via EDX spectra as shown in Fig. 1. The EDX spectra has been taken on the film deposited on clean Si substrates. The spectra indicate the presence of Ti, Zn, and O elements as expected. The atomic contents of Ti, Zn, and O in the thin film have been calculated based on library standard and listed in Table 1. It can be seen that the atomic contents of Ti:Ni in the thin film is in accordance with the content of the source materials prepared from powder mixing. In addition, it can be seen that oxygen content of the film is slightly decrease as ZnO content increases. However, the oxygen content is far higher than the theoretical values. In fact, this is expected because EDX measurement based on SEM can not provide accurate quantification of light elements such as oxygen, carbon, etc.

Figure 1. Typical EDX spectra of TiO₂/ZnO e-beam evaporated thin film after annealing.

Figure 2. SEM images of TiO₂/ZnO e-beam evaporated thin film after annealing.

Typical SEM micrographs of TiO₂/ZnO e-beam evaporated thin films are shown in Fig. 2. It can be seen that the films have sub-micrometer grain-size and the grain size tends to increase with ZnO content. In addition, there are

brighter particles scattered on the surface. Furthermore, the spotted EDX analysis indicates that these brighter particles have higher Zn composition. However, EDX spectra can not clearly identify if these particles are ZnO crystals.

The information on the crystal structure of the mixed oxide thin films are revealed in X-Ray diffractograms as shown in Fig. 3. It can be seen that crystal structure of the films contain the anatase phase of TiO_2 with the expected anatase: tetragonal peaks at 25.8° , 38.2° , 48.5° , and 54.2° . As the ZnO content increases, the anatase peaks are distorted and reduced in magnitude and a secondary broad peak at around 27.5° is observed. This unknown peak was found not to match with any forms of ZnO or Ti-Zn-O compounds. Thus, ZnO component in the film seems not to form a secondary metal oxide phase in the TiO_2 thin film. As a result, the chemical state of Zn element in the films can not yet be identified.

Figure 3. Typical X-Ray diffractograms of e-beam evaporated TiO_2 -ZnO with different ZnO contents.

B. Gas sensing characteristics

The gas sensing properties are characterized in term of resistance and gas-sensing response. The resistance of the TiO_2 -ZnO thin films were reduced upon the exposure to reducing gas and increased upon exposure to oxidizing gas, indicating that they are n-type semiconductor. In addition, the resistance of the TiO_2 -ZnO thin films is increased as ZnO content increases. The gas sensing response of n-type semiconductor gas sensor to a reducing gas is normally defined as the ratio of the resistance change to the resistance with gas sample, $(R_0 - R_g)/R_0$, while the response to an oxidizing gas is defined as the ratio of the resistance change to the resistance with no gas sample, $(R_g - R_0)/R_0$. The gas-sensing response was calculated from time response data and plotted versus various parameters including gas concentration and temperature. The selected results of gas-sensing responses of TiO_2 -ZnO e-beam evaporated thin films toward acetone and ethanol are shown in Figs. 4-6.

Fig. 4 shows the acetone response as a function of gas concentration of TiO_2 thin film with different ZnO concentration at 300°C operating temperatures. From Fig. 4, it is clear that the inclusion of ZnO in TiO_2 e-beam evaporated thin film leads to considerable deterioration of response to acetone although the resistance of the film is increased. However, it should be noted that low ZnO concentration (1%) actually increase responses toward acetone compared to the undoped film.

Figure 4. Dynamic response of TiO_2 /ZnO vs. acetone square pulses at an operating temperature of 300°C and 40%RH.

The response to 100 ppm acetone as a function of operating temperature of TiO_2 thin film with different ZnO concentration is shown in Fig. 5. It can be seen that the response to acetone of TiO_2 e-beam evaporated thin film is reduced particularly at high operating temperature as the ZnO content increases. The acetone response is decreased by about an order of magnitude.

Figure 5. Response to acetone of TiO_2 /ZnO vs. operating temperature at 100 ppm concentration.

Fig. 6 illustrates the ethanol response of TiO_2 thin film with different ZnO concentration at 400°C . From Fig. 6, it is obvious that the response to ethanol of TiO_2 e-beam

evaporated thin film is also degraded considerably as ZnO content increases. The response as a function of the concentration follows the well-known power law behavior and the power is decreased by ZnO addition. Similar to acetone cases, ethanol responses of TiO₂ e-beam evaporated thin film is reduced particularly at high operating temperature as ZnO content increases. In addition, low ZnO content TiO₂ thin film exhibits a maximized response to acetone and ethanol at an operating temperature of ~400°C.

Figure 6. Ethanol response of TiO₂/ZnO vs. concentration at 400 °C operating temperature.

On the contrary, the response toward CO, NO₂, and ammonia are found to be very low (less than one) for all TiO₂/ZnO thin films. In addition, high ZnO concentration (5-10%) nearly diminish the response to these gases. Thus, small ZnO doping made TiO₂ sensor selective to acetone and alcohol vapors while high concentrations of ZnO seem to be undesirable for gas sensing applications.

The gas-sensing behaviors of ZnO doped TiO₂ thin films should be mainly attributed to the combined changes in surface morphology, chemical composition, and crystal structure modified due to Zn inclusion. The degradation of gas sensing due to ZnO addition is unexpected because ZnO also has good response toward these gases. A possible cause of gas-sensing deterioration may be the increased grain size and distorted TiO₂ crystal structure of the combined material. Further study still needs to be done to understand the degradation mechanisms of the ZnO doped TiO₂ thin film.

IV. CONCLUSIONS

In conclusion, the gas sensing properties of TiO₂-ZnO composite thin film gas sensor prepared by E-beam

evaporation has been investigated toward various gases including acetone, ethanol, ammonia, CO, and NO₂. It was found that the sensor's conductance increases as the Zn content increases. Low ZnO concentration (1%) increase responses toward acetone and ethanol while response toward CO, NO₂, and ammonia are very low. However, high ZnO concentration (5-10%) decreases the response to all the tested gases. ZnO:TiO₂ exhibit a maximized response to acetone and ethanol at an operating temperature of ~400°C. Thus, small ZnO doping made TiO₂ sensor selective to acetone and alcohol vapors while high concentrations of ZnO seem to be undesirable for gas sensing applications.

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