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Enhancement of Methanol Gas Sensitivity of Cu Intermediate ITO Film Gas Sensors

Chang-Ho Shin, Joo-Hyun Chae*, Yu-Sung Kim*, Cheol-Woo Jeong and Dae-Il Kim†

School of Materials Science and Engineering, University of Ulsan, San 29, Mugeo Dong, Nam Gu, Ulsan 680-749, Korea
*Technical Institute, New Optics Ltd., Miryang, 627-803, Korea

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Abstract Sn doped In_2O_3 (ITO) and ITO/Cu/ITO (ICI) multilayer films were prepared on glass substrates with a reactive radio frequency (RF) magnetron sputter without intentional substrate heating, and then the influence of the Cu interlayer on the methanol gas sensitivity of the ICI films were considered. Although both ITO and ICI film sensors had the same thickness of 100 nm, the ICI sensors had a sandwich structure of ITO 50 nm/Cu 5 nm/ITO 45 nm. The ICI films showed a ten times higher carrier density than that of the pure ITO films. However, the Cu interlayer may also have caused the decrement of carrier mobility because the interfaces between the ITO and Cu interlayer acted as a barrier to carrier movement. Although the ICI films had two times a lower mobility than that of the pure ITO films, the ICI films had a higher conductivity of $3.6 \cdot 10^{-4}$ Ωcm due to a higher carrier density. The changes in the sensitivity of the film sensors caused by methanol gas ranging from 50 to 500 ppm were measured at room temperature. The ICI sensors showed a higher gas sensitivity than that of the ITO single layer sensors. Finally, it can be concluded that the ICI film sensors have the potential to be used as improved methanol gas sensors.

Key words gas sensor, sensitivity, ITO, Cu, sputtering.

1. Introduction

Currently thin film gas sensors for toxic gases have attracted much attention due to the growing concern of environmental safety. A number of semi-conductive oxides such as SnO_2 have been used for different gas sensors.[1)] Most of these gas sensors are based on a variation in resistance when the film sensors are exposed to target gases.

Recently, Cheng et al. have studied the gas-sensing properties of ZnO thin films to methanol vapor[2)] and methanol gas-sensing properties of CeO_2-Fe_2O_3 thin films have been reported by Neri et al.[3)] They have shown that the addition of Ce to Fe_2O_3 increases the response to methanol at low temperature (< 350°C). In this study, thin film gas sensor using transparent Sn doped In_2O_3 (ITO) semiconductors to detect methanol gases at low operating temperature have been reported. ITO thin films can be fabricated by means of a number of techniques such as sputtering,[4)] and evaporation.[5)] Since most oxide semiconductor gas sensors operate at relatively high temperatures, a heater is required. Integration of a heater not only increases the power consumption but also the complexity of the device. Thus, it is highly desirable to decrease the required operating temperature for viable gas sensors in industrial applications.

In this study, a sandwich structure of ITO 50 nm/Cu 5 nm/ITO 45 nm (ICI) multilayer films and ITO single-layer film sensors were prepared on glass substrates without intentional substrate heating, and then the effects of the Cu interlayer on the sensitivity for detecting methanol vapor was investigated at room temperature.

The purpose of this study is to discuss the enhancement of gas sensor sensitivity through changes in relative sensitivity obtained with magnetron sputtered Cu intermediate ITO film gas sensors.

2. Experimental Procedure

2.1 Film sensor deposition

Deposition of ITO and Cu thin films was performed in a magnetron sputtering system that was equipped with two cathodes. RF (13.56 MHz) and DC powers were applied to ITO (In_2O_3 90% - SnO_2 10%, purity; 99.99%) and Cu (purity; 99%) targets, respectively. ITO and ICI films were deposited onto glass substrates at 70°C without intentional substrate heating. Substrate temperature was detected by a K-type thermocouple directly in contact with the substrate surface. The deposition distance between the target and rotation substrate holder was constant at 10 cm. The substrate rotation speed was set to 10 rpm for all depositions. By controlling deposition time, the thickness

†Corresponding author
E-Mail : dkim84@ulsan.ac.kr (D. -I. Kim)

Table 1. Deposition conditions of ITO and Cu thin films.

	ITO	Cu
Deposition pressure (Pa)	3×10^{-2}	2.2×10^{-1}
Power density (W/cm^2)	RF, 2.5	DC, 2.8
Deposition rate (nm/min)	14	20
Gas flow rate (Ar/O_2 sccm)	5 / 0.03	5 / 0

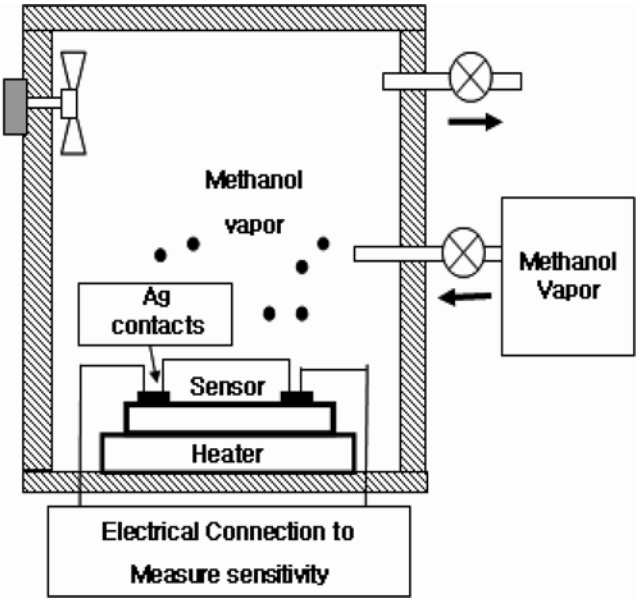

Fig. 1. The schematic diagram of the static measurement set-up.

of ITO and ICI films were kept constant at 100 nm and 50/5/45 nm, respectively. Table 1 summarizes the process conditions used in this study. A Cu-Kα XRD was used to observe the thin film crystalline. Surface average roughness (Ra) was measured on $2 \times 2\ \mu m^2$ areas with tapping mode AFM under ambient conditions. The Ra of the bare glass substrates was 1.5 nm. The electrical conductivity was evaluated with Hall Effect measurement.

2.2 Gas sensing test

All gas sensing measurements were carried out at room temperature. Ag electrodes ($0.5\ cm^2$) for measuring sensitivity to methanol vapor were deposited onto the prepared sensors by thermal evaporation. Thin gold wire attached on the Ag electrode with Ag paste to analysis of the conductivity. Fig. 1 shows the schematic diagram of the static measurement set-up used to measure the sensitivity to methanol vapor. In this study, the methanol vapors were injected into the test chamber using a calibrated syringe and the gas concentration was varied from 100 to 500 ppm. Measurement of sensor resistance was carried out using high impedance electrometer. Although the ICI film sensor can detect the methanol gas in 5 seconds, the gas sensitivity was evaluated after 10 seconds to obtain the equilibrated values. After gas sensing, the film sensors were heated at 80°C for 10 minutes. This enabled the methanol to vaporize and did not allow surface condensation on the film sensor.

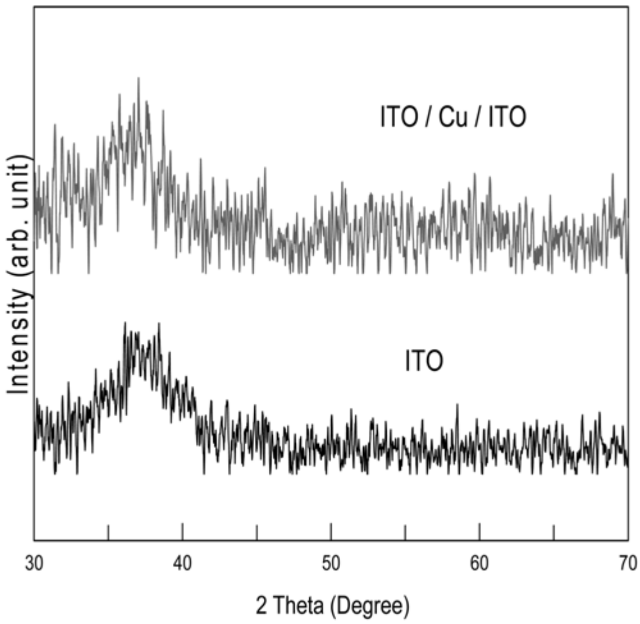

Fig. 2. The XRD pattern of ITO and ICI films.

Table 2. Comparison of carrier density ($\times 10^{20}/cm^3$), carrier mobility (cm^2/Vs) and electrical resistivity ($\times 10^{-4}\ \Omega$ cm) of ITO single layer and ITO/Cu/ITO multilayer films.

	ITO	ICI
Carrier density	0.26	2.70
Mobility	136	65
Resistivity	31.2	3.6

3. Results and Discussion

It is well known that ITO films deposited by magnetron sputtering at low temperature are usually amorphous.[4] Fig. 2 shows the XRD pattern of as deposited ITO single layer films and sandwich structure of ICI multilayer films. The ITO films did not show any diffraction peaks on the XRD pattern. Recently, Y. Kim et al reported that ITO films deposited on Au coated polymer substrates crystallized without intentional substrate heating.[6] However, the Cu intermediate ICI films did not show any diffraction peaks. This means that the Cu interlayer is not effective in crystallizing the ITO films.

Table 2 shows the electrical properties of the ICI and ITO films evaluated with Hall Effect measurements. In general, the resistivity of ITO films depends on carrier mobility and carrier density. Since the ICI films contain Cu interlayer which has many electrons, ICI films have the 10 times higher carrier density than that of the pure ITO films. But the Cu interlayer may cause the decrement

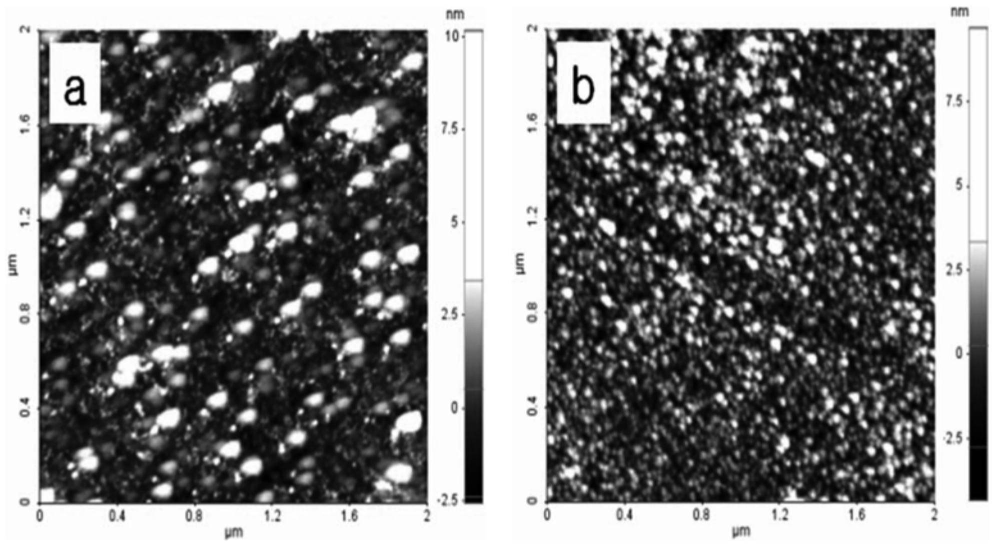

Fig. 3. The three-dimensional AFM images of ICI (a) and ITO films (b).

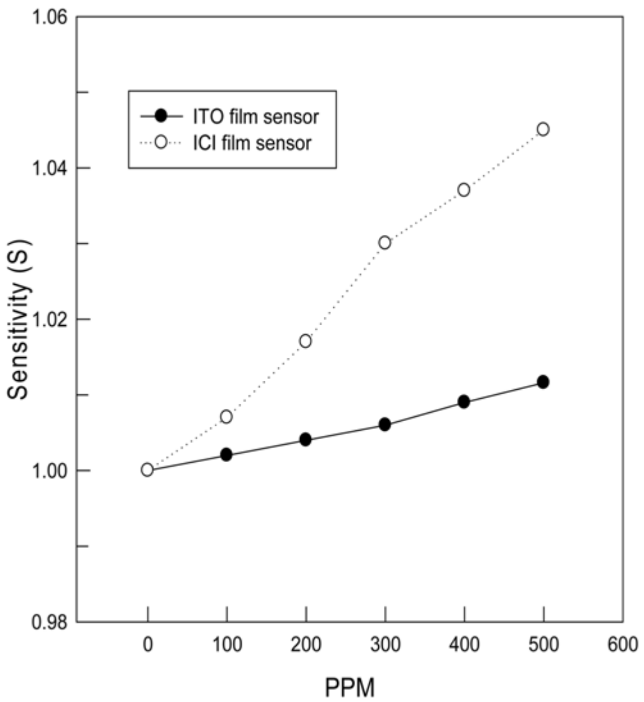

Fig. 4. The variation of sensitivity with methanol vapor concentration for ITO and ICI film gas sensor.

of carrier mobility because the interfaces between the ITO and Cu interlayer act as a barrier to carrier movement. However, although ICI films have the 2 times lower mobility than that of the pure ITO films, ICI films have the higher conductivity of 3.6×10^{-4} Ωcm due to higher carrier density.

Fig. 3 shows the AFM images of the ITO and ICI film gas sensors. The ITO sensor shows the relatively flat surface, which have the Ra of 1.5 nm, whereas ICI films show the some hills on the surface and the Ra of 2.1 nm. In this study, the major factor of gas sensitivity of ICI sensor is the low resistivity due to the presence of Cu interlayer in ICI films and the rougher surface of ICI films than that of the ITO films is also important factor because it results in the more adhering chance of methanol gases to the sensor surface.

Fig. 4 shows the variation in sensitivity with methanol vapor concentration. The sensitivity (S) of the film sensor was determined using the following equation[7]:

$$S = (R_{vap} - R_{air}) / R_{vap} \quad (1)$$

where R_{vap} is the resistance of the film sensor in presence of methanol vapors and R_{air} the resistance in air, which should be constant for a given test temperature. Recently N. G. Partel also shows the similar results in his study.[7] The sensitivity increases with gas concentration and the ICI sensors show a higher sensitivity than that of the ITO film sensors. In order to consider the durability of ICI sensor, the exposure test for long term in methanol was conducted. The sensitivity of ITO film sensors decayed about 13% from 1.012% measured at 500 PPM over a time period of 600 hours, while the sensitivity of the ICI film sensors decayed only 7% from 1.045% measured at same methanol vapor concentration. The sensitivity of ICI film sensor decayed more slowly than that of the ITO film sensor. It is supposed that the Cu interlayer in ICI films that acts as a catalyst to sense methanol gas may prolong the durability and Reproducibility of the films. Therefore, it is concluded that the Cu intermediate ITO films (ICI) showed the improved methanol gas sensing stability because the ICI multilayer films have the higher carrier density and rougher surface morphology than those of the ITO single layer films, simultaneously.

4. Conclusion

The fabrication and characterization of ITO/Cu/ITO (ICI) multilayer film gas sensors prepared with reactive magnetron sputtering has been reported. The changes in the sensitivity for methanol gas of ICI film sensors were investigated without intentional sensor heating and then compared to those of conventional ITO film sensors. It was demonstrated that the ICI film sensor shows significant increase in sensitivity to methanol gases compared to the ITO film sensor. Finally, it can be concluded that the ICI film sensor have the potential to be used as improved methanol gas sensors.

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