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Effect of Ni Interlayer on the Methanol Gas Sensitivity of ITO Thin Films

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Abstract Sn doped In_2O_3 (ITO) and ITO/Ni/ITO (INI) multilayer films were deposited on the glass substrates with a reactive magnetron sputtering system without intentional substrate heating and then the influence of the Ni interlayer on the methanol gas sensitivity of ITO and INI film sensors were investigated. Although both ITO and INI film sensors have the same thickness of 100 nm, INI sensors have a sandwich structure of ITO 50 nm/Ni 5 nm/ITO 45 nm. The changes in the gas sensitivity of the film sensors caused by methanol gas ranging from 100 to 1000 ppm were measured. It is observed that the INI film sensors show the higher sensitivity than that of the ITO single layer sensors. Finally, it can be concluded that the INI film sensor have the potential to be used as improved methanol gas sensors.

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Key words : *ITO, Nickel, Multilayer, Methanol, Gas sensitivity*

1. Introduction

Currently thin film gas sensors for hazard 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. Since most methanol gas sensors operate at relatively high temperatures, a heater is required [2]. But Integration of a heater in gas sensor not only increases the power consumption but also the complexity of the device. Thus, it is very desirable to decrease the operating temperature for viable gas sensors in industrial applications. In this study, Sn doped In_2O_3 (ITO) thin films with 5 nm thick Ni interlayer were prepared to detect methanol gases at a room temperature.

In this study, a sandwich structure of ITO 50 nm/Ni 5 nm/ITO 45 nm (INI) multilayer films and ITO single layer film sensors were prepared by RF and DC magnetron sputtering deposition and then the effects of the Ni interlayer on the electrical, structural properties of the films and methanol gas sensitivity was investigated using X-ray diffraction (XRD), atomic force microscope (AFM), four-point probes and gas sensing measurements, respectively.

2. Experimental procedure

Deposition of ITO and Ni 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 Ni (purity; 99.9%) targets, respectively. ITO and INI films were deposited onto glass (Corning 1747) substrates without intentional substrate heating. Substrate temperature was detected by a K-type thermocouple directly in contact with the substrate. The distance between the target and substrate was 10 cm and the substrate rotation speed was 10 rpm for all depositions. By controlling the deposition time, the thickness of ITO and INI films were kept constantly at 100 nm

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

	ITO	Ni
Deposition pressure (Torr)	8×10^{-4}	2×10^{-3}
Target size	3 inch	3 inch
Power density (W/cm^2)	RF, 3.2	DC, 3.0
Deposition rate (nm/min)	14	12
Gas flow rate (Ar/O_2 sccm)	5 / 0.03	10 / 0

and 50/5/45 nm, respectively.

Table 1 summaries the process conditions used in this study. After deposition, film thickness was confirmed with a surface profilometer. The XRD measurements were perform with Cu-Ka XRD (X'pert Pro MRD, Philips) at the Korea Basic Science Institute (Daegu center). The Auger electron spectroscopy (AES) spectrum and electrical resistivity of the films was measured with Microlab 350 and four point probes (HMS-3000, Ecopia), respectively.

Silver (Ag) electrodes (0.5 cm^2) for measuring sensitivity to methanol vapor were deposited onto the prepared sensors by thermal evaporation. Thin gold wire was attached on the Ag electrode with Ag paste to analysis of the conductivity. The schematic diagram of the static measurement set-up used to measure the sensitivity to methanol vapor was reported in a previous report [3]. The methanol vapors were injected into the test chamber using a calibrated syringe and the gas concentration was varied from 100 to 1000 ppm. Measurement of sensor resistance was carried out using high impedance electrometer. Although the INI 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.

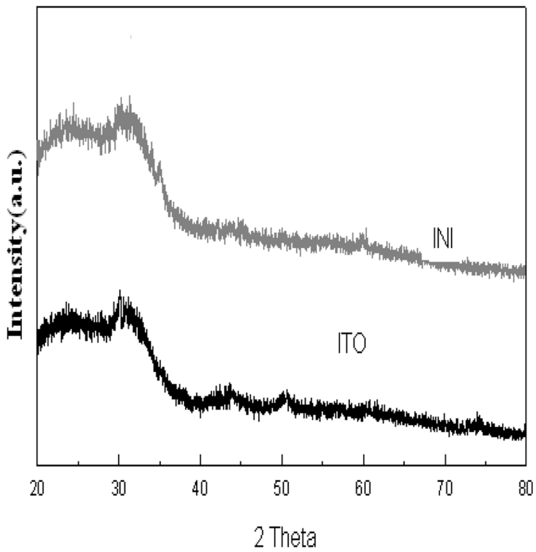

Fig. 1. XRD pattern of as deposited ITO and INI films.

3. Results and discussion

It is well known that ITO films deposited by magnetron sputtering at low temperature are usually amorphous [4]. Fig. 1 shows the XRD pattern of as deposited ITO single layer films and sandwich structure of INI multilayer films. Both ITO and INI 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 [5]. However, the Ni interlayer in INI films did not promote ITO crystallization effectively.

Table 2 shows the carrier density, mobility, and electrical resistivity of the INI and ITO films evaluated with Hall Effect measurements.

In general, oxygen gas flow rate during ITO deposition is very effective on the electrical resistivity because each oxygen vacancy on the In_2O_3 matrix donates two electrons. Although a severe oxygen deficiency also cause the high resistivity due to structural disorder and reduced the mobility by oxygen vacancies, moderate

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/Ni/ITO (INI) multilayer films

	ITO	INI
Carrier density	2.1	3.0
Carrier mobility	133	653
Resistivity	22.2	3.3

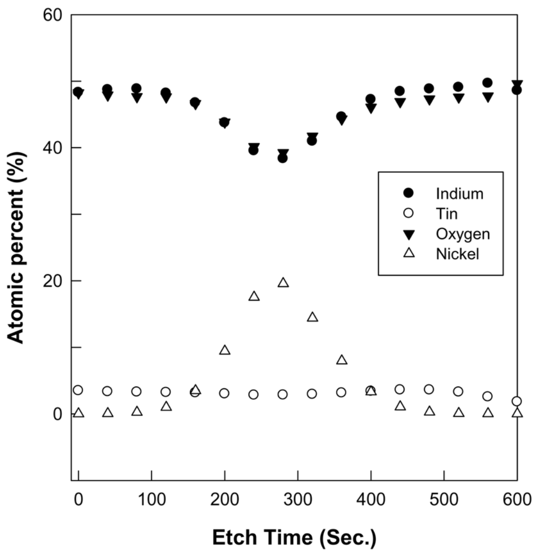

Fig. 2. AES spectrum of INI multilayer film.

deficiency of oxygen in In_2O_3 film is favorable to the electrical conductivity due to increase carrier density [6, 7].

However, in this study ITO films were deposited under constant oxygen flow rate of 0.5 sccm for all deposition but INI films show the lower electrical resistivity than that of the ITO films. From Table 2, it is concluded that the increased carrier density and mobility with Ni interlayer in INI films led in the lower resistivity of 3.3×10^{-4} Wcm.

Fig. 2 shows the AES spectrum of INI multilayer film. Some degree of inter-diffusion between ITO and Ni layer is observed. In Fig. 2, the observed Ni profile shows that Ni's atomic percentage is less than 20% at the etch time of 280 Seconds.

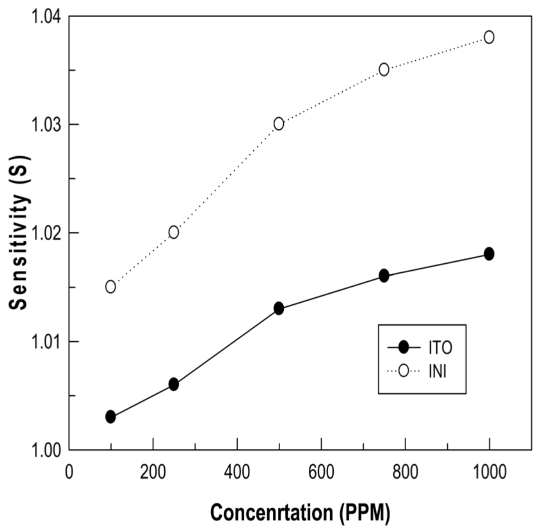

Fig. 3. Variation of gas sensitivity with methanol vapor concentration for ITO and INI film gas sensor.

Fig. 3 shows the variation of the sensitivity with methanol vapor concentration at operation temperature of 50°C. The sensitivity (S) of the film sensor was determined using the following equation :

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

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 [8].

The gas sensitivity increases with gas concentration and the INI multilayer sensors show a higher sensitivity than that of the ITO single layer sensors within observed methanol vapor concentration in this study.

Recently V. S. Vaishnav reported that the influence of a stimulating layer of MgO below the ITO film on the ethanol sensitivity [9]. It is found that the stimulating layer of MgO shows enhancement in the sensitivity relative change in resistance with an improvement of 23 times than the ITO single layer films.

Fig. 4 shows the variation of gas sensitivity of

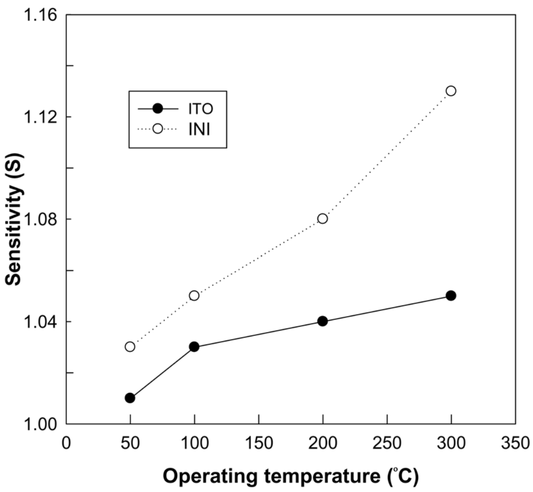

Fig. 4. Variation of gas sensitivity of the ITO and INI sensors to methanol vapors with operating temperature.

the film sensors to methanol vapors with operating temperature. The concentration of methanol was 500 ppm. The observed results are similar with V. S. Vaishnav's study [9]. The Ni layer which is intermediated to enhance the methanol vapors increased the sensitivity with operating temperature proportionally.

4. Conclusion

The fabrication and characterization of ITO/Ni/ITO (INI) multilayer film gas sensors prepared with reactive magnetron sputtering has been reported.

The changes in the sensitivity for methanol gas of INI film sensors were investigated without intentional sensor heating and then compared to those of conventional ITO film sensors. It was demonstrated that the INI film sensor shows the increased sensitivity to methanol gases compared to the ITO film sensor. Finally, it can be concluded that the INI film sensor have the potential to be used as improved methanol gas sensors.

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