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Sensing characteristics of hematite and barium oxide doped hematite films towards ozone and nitrogen dioxide

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Abstract

Hematite (α-Fe_2O_3) and barium oxide doped hematite (BaO-Fe_2O_3) thin films were investigated as ozone (O_3) and nitrogen dioxide (NO_2) sensing materials. Fe_2O_3 and BaO-Fe_2O_3 films were deposited by radio-frequency sputtering using pure Fe_2O_3, and 1-2% BaO doped Fe_2O_3 targets. The 700°C (1 hour) annealed films showed significant responses to O_3 at temperatures ranging from 150°C to 300°C. Although, hematite is an n-type semiconductor, the Fe_2O_3 and BaO-Fe_2O_3 films exhibit p-type behavior to O_3 and n-type behavior to NO_2 at the studied concentration ranges in this work. The response to oxidizing gases is not strictly an increase in resistance due to a conversion from n-type to p-type depending on gas concentrations. This effect is more visible with increasing Ba concentration.

Keywords: iron oxide; gas sensor; sputtering; O_3; NO_2

1. Introduction

Gas sensors based on metal oxides are studied for many years. The main advantages of metal oxide sensors include simple construction, low cost, small size, high sensitivity and rapid response to low concentration gases [1]. The characteristics of metal oxide gas sensors are determined by the reversible interactions of the gases with the material surface. Although many wide-gap metal oxides (ZnO, WO_3, SnO_2…) were studied as sensing materials [2,3], the use of α-Fe_2O_3 based materials, especially BaO

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doped α-Fe_2O_3 (BaO-Fe_2O_3) is seldom reported in the literature. After studies on alkaline earth oxides doped Fe_2O_3 as humidity [4] and NO_2 sensors [5] in Turin with pellets, ozone (O_3) and nitrogen dioxide (NO_2) sensing characteristics of Fe_2O_3 and BaO-Fe_2O_3 thin-films are presented in this article.

2. Experimental method

The Fe_2O_3 and BaO-Fe_2O_3 films were deposited by radio-frequency (r.f.) sputtering on commercial Al_2O_3 substrates. For this purpose, different targets were prepared. α-Fe_2O_3 powder (Aldrich > 99 %) was ball-milled with or without barium nitrate (Fluka > 99 %) used as precursor. The contents of barium nitrate were equivalent to 1 and 2 wt% of barium oxide. After drying overnight, 3 discs (pure Fe_2O_3, 1 and 2 wt % BaO- Fe_2O_3) were obtained by uniaxially pressing the mixtures and then sintered at 1000°C for 1 hour.

The Fe_2O_3 and BaO-Fe_2O_3 films were deposited on commercial Al_2O_3 substrates equipped with gold electrodes on one side and a platinum heater on the other side, in a r.f. sputtering chamber. More details about the substrates are given elsewhere [3]. The power was 200 W and the deposition pressure in the chamber was 2 Pa with a composition of 90% Ar and 10% O_2. At last, the as-sputtered films were annealed at 700°C for 1 h to get a well-crystallized film structure. The thickness of the films was 500 nm in all cases.

The electrical resistance measurement of the three sensors to O_3 and NO_2 were performed in a Teflon cell. The setup of the test system is described in a previous paper [6]. Briefly, the sensors were connected to a home-made system to measure the electrical resistance variation of the sensors in presence of different target gases. Moist air with 50% relative humidity at 20°C was used as carrier gas for O_3 and NO_2 tests. After the electrical resistance of the sensors was stable in reference air (R_{air}), diluted NO_2 and O_3 mixed with the carrier were introduced into the chamber. O_3 was produced by passing dry air through an ultraviolet lamp. NO_2 was taken from a commercial 100 ppm NO_2 bottle (balance gas is dry air). NO_x and O_3 analyzers (Thermo electron instruments, USA) were used to measure the concentrations of NO_2 and O_3 at the outlet of the Teflon cell. These measurements were carried out at different temperatures ranging from 150 to 300°C.

3. Results and discussions

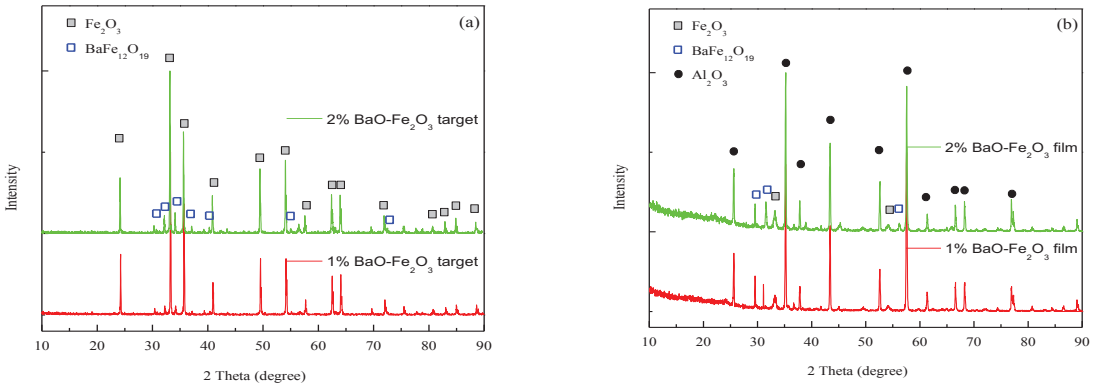

Fig 1: XRD patterns of (a) BaO-Fe_2O_3 targets and (b) annealed BaO-Fe_2O_3 films on Al_2O_3 substrates.

The sputtering targets and the annealed films were characterized by X-ray diffraction. Fig. 1 shows the presence of two phases in the targets and annealed films: Fe_2O_3 (PDF 33-0664) and $BaFe_{12}O_{19}$ (PDF 27-

1029), as well as the Al_2O_3 phase of the substrate. BaO was not observed. It is noticed that the amount of $BaFe_{12}O_{19}$ in 1% BaO-Fe_2O_3 sample is much lower than that in 2% BaO-Fe_2O_3, which should be due to the solubility of most BaO in Fe_2O_3.

The surface morphologies of the annealed film as well as the bare Al_2O_3 substrate were inspected by SEM as shown in Fig. 2. The substrate is covered by a continuous film formed by small grains (<200 nm).

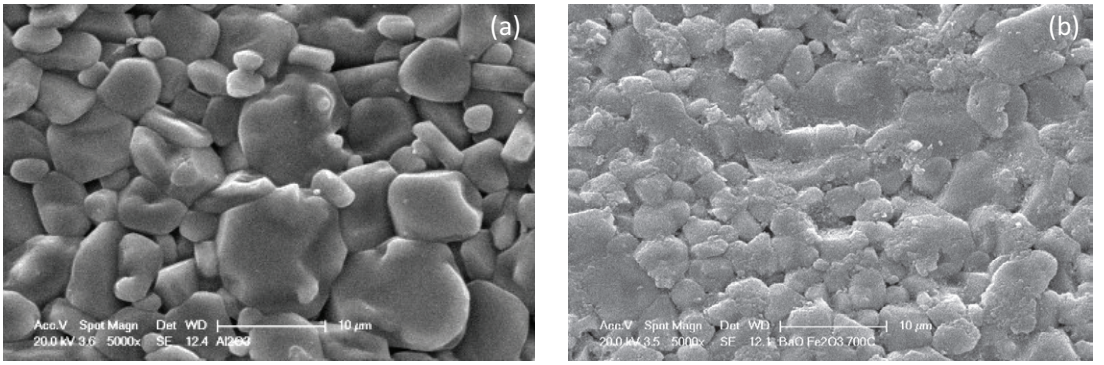

Fig. 2: SEM top-surface morphology of (a) bare Al_2O_3 plate and (b) 1% BaO- Fe_2O_3 film after the heat-treatment at 700°C for 1 h.

The sensing characteristics of the films were studied at temperatures ranging from 150 to 300°C. Fig. 3a and b show the electrical responses of the three sensors submitted to 0.15-1.25 ppm O_3 and 0.62-5.00 ppm NO_2 in moist air (50% RH) respectively. Fig. 4 shows the sensor responses of Fe_2O_3 to O_3 and NO_2 as a function of working temperature (the sensor response is defined as R_{air}/R_{O3} for O_3 injections and R_{NO2}/R_{air} for NO_2 injections). The Fe_2O_3 films showed maximum responses to O_3 at 200 and 225°C while the response to NO_2 is still increasing when reducing the temperature. However, the response time and recovery time increase dramatically at lower temperatures.

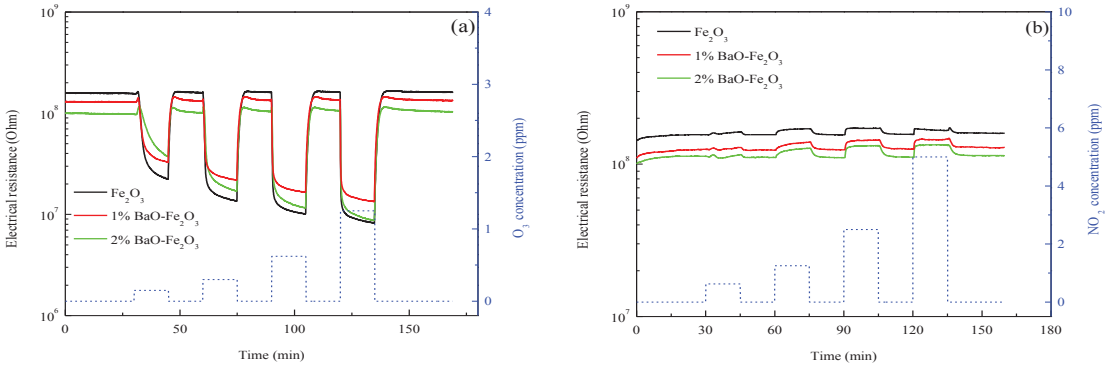

Fig. 3: Electrical response to (a) O_3 and (b) NO_2 in moist air at 275°C.

The sensors show different sensing behaviors when O_3 and NO_2 are introduced. In Fig 3(a), the electrical resistances decrease instead of increase as expected for BaO-Fe_2O_3 films (n-type semiconductors) to O_3 (an oxidizing gas). This phenomenon is due to a conversion of the semiconductors at an oxidizing atmosphere. For lower gas concentrations, low surface doping by the adsorbed gas, the semiconductor acts as an n-type, the oxidizing gas captures free electrons of semiconductor and the conductivity of semiconductor decreases. In the case of higher concentrations, higher surface doping, the

oxidizing gas captures electrons from the valence band and creates holes in semiconductor. In this case, the charge carrier increases. The material acts as a p-type semiconductor. In this regime, the resistance decreases with increasing the gas concentration. This hypothesis was supported by the response to high NO_2 concentrations (Fig. 5). As O_3 is a stronger electron acceptor than NO_2, this phenomenon takes place at lower O_3concentrations. This explains why the behaviors to O_3 and NO_2 are opposite. Moreover, this effect is more visible for the sample with higher Ba content.

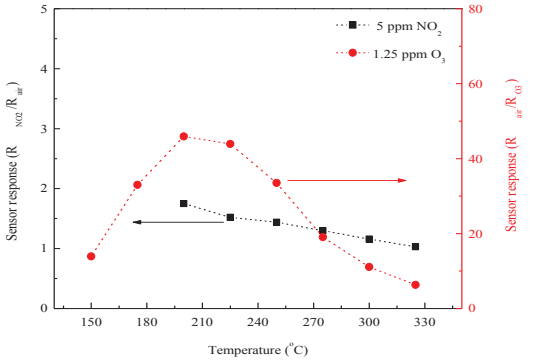

Fig. 4: Sensor response of Fe_2O_3 to NO_2 and O_3 in function of working temperature.

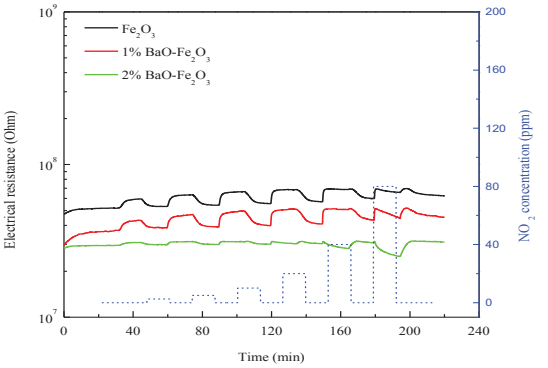

Fig. 5: Response of the three sensors to high concentrations (2.5-80 ppm) of NO_2 at 300°C.

4. Conclusion

This work investigated the response of Fe_2O_3 and BaO-Fe_2O_3 films to O_3 and NO_2. The sensors showed a significant response to O_3 and a weak response to NO_2 in the opposite direction. The Fe_2O_3 and BaO-Fe_2O_3 films converted from n-type to p-type by the adsorption of strong oxidizing gases like O_3 and NO_2 at high concentrations. As O_3 is a stronger oxidizing gas, this phenomenon can happen at lower concentration than that needed for NO_2. This effect is more visible with increasing Ba doping content.

Acknowledgements

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