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Design of Low Cost Gas Sensor Based on $SrTiO_3$ and $BaTiO_3$ Films

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We have prepared $SrTiO_3/BaTiO_3$ multilayer film on alumina substrates by a sol–gel technique and investigated their response for sensing ethanol vapor. The surface morphology of the films were characterized by atomic force microscope (AFM) showing that the grain size of the films increase up to 40 nm as the annealing temperature increased to 1000 °C. The ethanol sensors based on $SrTiO_3/BaTiO_3$ thin films were fabricated by applying interdigitated gold electrodes by sputtering technique. The ethanol sensing characteristics of $SrTiO_3/BaTiO_3$ thin films were quantified by the change in resistance of the sensors when they were exposed to ethanol. The optimum operating tempearature of these sensors was found to be 350 °C. In addition, the film annealed at 1000 °C exhibited *p*-type gas sensing behavior with the best sensitivity of 30–100 for low ethanol concentration in the range of 100–1000 ppm.

Keywords: $SrTiO_3/BaTiO_3$, Gas Sensor, Sol–Gel Method.

RESEARCH ARTICLE

1. INTRODUCTION

In the past decades, researchers have placed increasing interest in gas sensor fabrication by various techniques to detect wider variety of gases. The metal oxide materials commonly studied in such sensors are TiO_2,[1] SnO_2,[2] and WO_3.[3] Recently, semiconductor-based gas sensors made of the peroskite oxides (ABO_3) received interest due to the the feasibility of doping with different metals to tailor their particular sensitivity.[4] There are two cations (A and B) with different sizes in the perovskite structure that can be replaced by the various dopants. Furthermore, perovskite oxides are suitable for detecting gas in high temperature environment due to high melting temperature and high stability in microstructure and surface morphology. Many research groups have investigated barium titanate for the detection of CO and CO_2,[5] and strontium titanate for the detection of O_2 [6] but not much on solvent vapors such as ethanol, methanol and acetone. In this work, we report the ethanol sensing of amorphous $SrTiO_3$ thin film and $SrTiO_3/BaTiO_3$ multilayer thin film prepared by a sol–gel method. The advantage of such sol–gel coating is that uniform films in large area can be readily produced. It is also cost effective and industrially scalable. The gas sensing characteristics of the films with two distinctively different phase structures, amorphous and polycrystalline, were studied in terms of the sensitivity, the type of the sensors, and the optimum temperature to operate the sensors.

2. EXPERIMENTAL DETAILS

In this work, $BaTiO_3$ (BTO) and $SrTiO_3$ (STO) thin films were prepared on clean alumina substrates by sol–gel spin coating technique. Alumina is an electrical insulator material which is commonly used as a substrate for heating metal oxide gas sensor. It has several advantages among other types of commercial substrates such as low cost, availability and high thermal conductivity resulting in uniform temperature across the device. We dissolved barium acetate and strontium acetate in acetic acid in separate beakers. Then we added titanium butoxide and methanol as a stabilizer in BTO and STO precursors. This process was done near 60 °C with stirring on a hot plate. Then the solution was spincast onto clean substrates at 2000 rpm for 45 seconds. After preheating at 120 °C for 20 min, the films were annealed at two different temperatures, 300 °C and 1000 °C. We observed that it is important to

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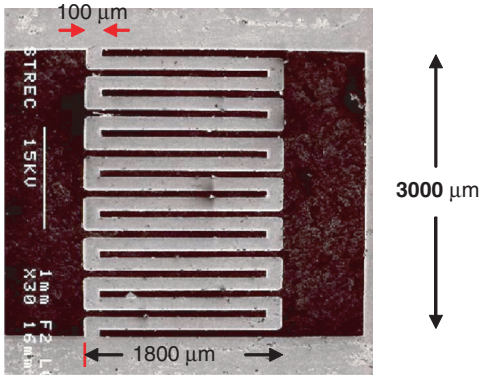

Fig. 1. Top view of scanning electron microscopy (SEM) image of the gas sensor.

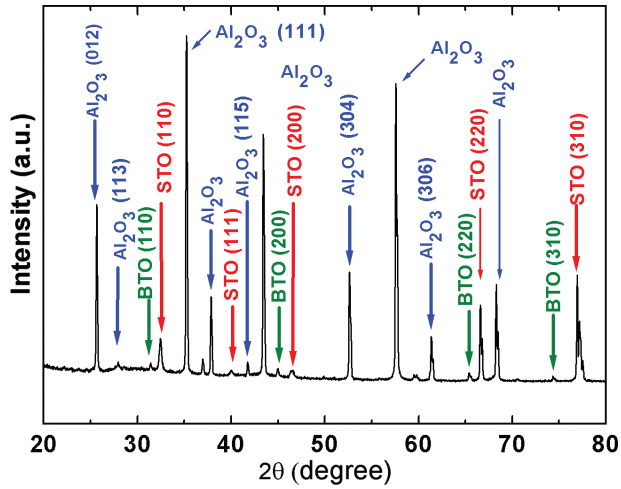

Fig. 2. X-ray diffraction pattern of $SrTiO_3/BaTiO_3$ multilayer thin film on alumina substrate.

deposit one layer at a time through this process to produce dense films. The obtained film deposited for four layers was about 400 nm. We focused on two films, pure STO/STO/STO/STO film annealed at 300 °C and STO/BTO/STO/BTO film annealed at 1000 °C. The gold/cromium (Au/Cr) interdigitated electrode was patterned on the film through an electroplated shadow mask with gap width about 100 microns using DC sputtering. Figure 1 shows a miniature sensor with the gap width of 100 microns, with the finger length of 14 mm and the overall size is 2×3 mm. The gas sensing characteristics of BTO and STO thin films were characterized with ethanol vapor (C_2H_5OH) which is a reducing gas. To test the sensors, we fed purified air into the chamber to generate the base line and than the ethanol vapor with the desired concentrations was introduced for 5 min through mass flow controller. Ethanol vapor was generated by passing nitrogen gas through 99.99% ethanol. The sensors were heated to different temperatures and the resistances of sensor in the presence of air and in ethanol vapor were recorded. The crystal structure of the resulting films were characterized by X-ray diffraction (XRD: Model D8 Bruker diffractrometer) using the wavelength of CuKα1 (1.5406 Å). The surface morphology of the films was examined by atomic force microscopy (AFM: Model Veeco Nanoscope V).

3. RESULTS AND DISCUSSION

Figure 2 shows the X-ray diffraction pattern of the STO/BTO multilayer film prepared at 1000 °C on alumina substrate. This film exhibited a polycrystalline structure. There were no STO characteristic diffraction peaks for the STO film annealed at 300 °C. There are no big grains developed for the film annealed at low temperature as seen from AFM images (data not shown). The film annealed at 1000 °C exhibited large grain with the size of 40 nm due to the increasing of atom mobility at higher temperature. The time responses of two sensors toward ethanol vapor at 100–1000 ppm concentrations are shown in Figure 3.

Figures 3(a) and (b) show the response of amorphous STO film and the polycrystalline STO/BTO multilayer film, respectively. The response time of the polycrystalline film is quicker than that of the amorphous film while the

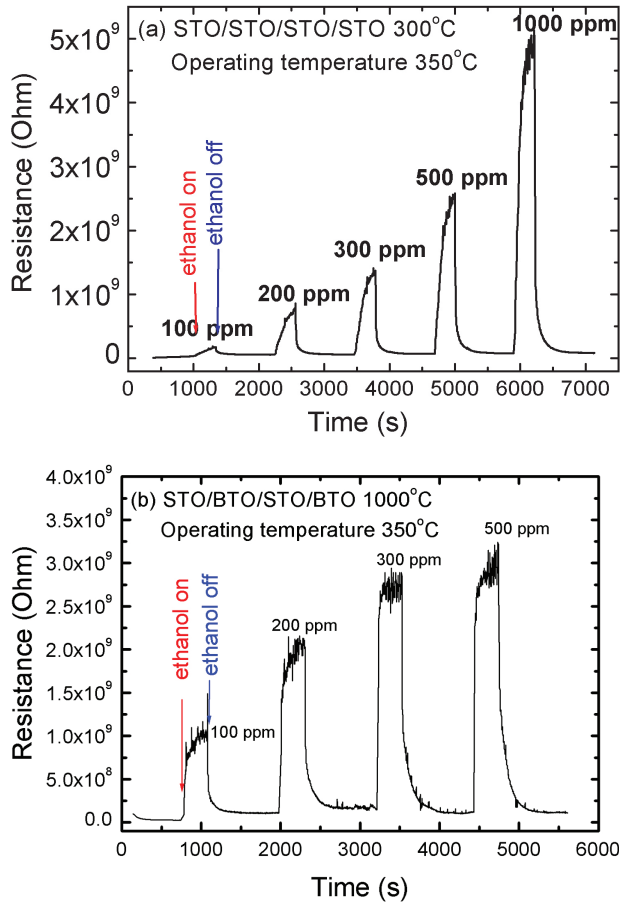

Fig. 3. Time response to ethanol vapor at 350 °C of (a) $SrTiO_3$ film annealed at 300 °C and (b) $SrTiO_3/BaTiO_3$ multilayer thin film annealed at 1000 °C on alumina substrate.

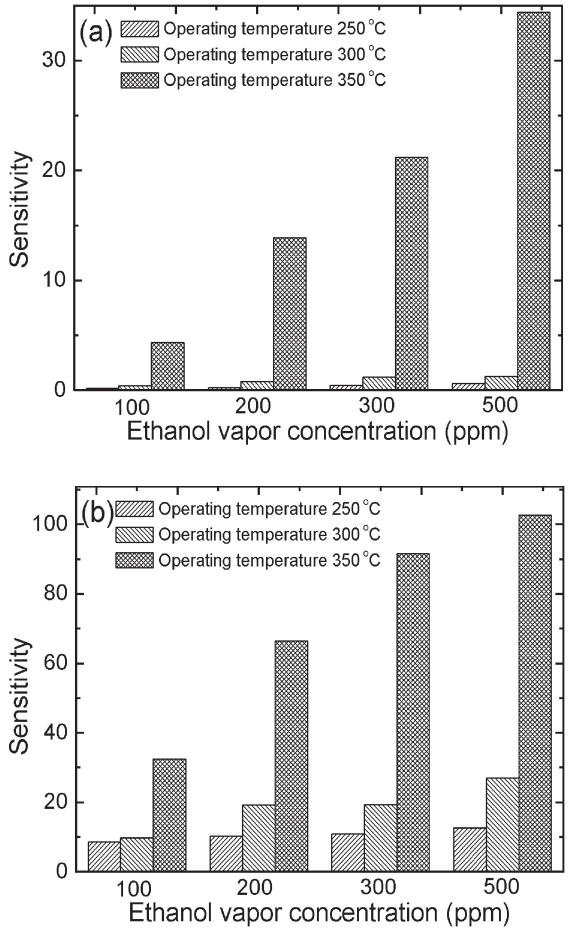

Fig. 4. Sensitivity to ethanol vapor at 100–500 ppm concentrations (a) $SrTiO_3$ film annealed at 300 °C and (b) $SrTiO_3/BaTiO_3$ multilayer thin film annealed at 1000 °C on alumina substrate.

recovery time is quite comparable. The film sensing properties are based on reactions between the film surface and gases. Many possible reactions can occur on the surface depending on the gas used and the type of semiconductor sensor. Ethanol vapor is a reducing gas in which acts as electron donors. For a *p*-type semiconductors, the oxidation of ethanol at the surface transfer electrons to the film surface and the resistance of the film increases with ethanol concentrations in the gas. Our results are consistent with a *p*-type active film. Normally, the gas sensitivity is difined as the ratio of the changes of resistance after the sensor exposed to gas and the resistance of the sensor in the presence of air.

$$\text{gas sensitivity} = \frac{|R_{\text{gas}} - R_{\text{air}}|}{R_{\text{air}}} \quad (1)$$

To determine the optimum operating temperature of the sensor, we plotted the sensitivity as a function of ethanol vapor concentrations at 250 °C, 300 °C and 350 °C, respectively (see Fig. 4). Notice that the optimum temperature of both films was found to be the same, at 350 °C regardless of their crystallinity. This can be explained that the ethanol vapor give electrons to the film surface the most at a certain temperature. The abrupt increase in the sensitivity at 350 °C of the film annealed at 1000 °C, which is higher than that of the film annealed at 300 °C, was observed. The sensitivity of crystalline film annealed at 1000 °C is 2–3 times larger than that of amorphous film annealed at 300 °C. It is possible that the surface area of polycrystalline film which was larger than that of the amorphous film increase the area of reaction. The film annealed at 1000 °C exhibited *p*-type gas sensing behavior with the best sensitivity of 30–100 for low ethanol concentration in the range of 100–1000 ppm. The sensitivity to ethanol vapor of SnO_2 and WO_3 reported by Wisitsoraat et al. was less than 10.[1] The best sensitivity for these perovskite films are higher than those obtained from other metal oxides.

4. CONCLUSIONS

In conclusion, we have developed a *p*-type gas-sensitive material using BTO and STO thin films prepared by a sol gel method. The sensitivity of crystalline film annealed at 1000 °C is larger than that of amorphous film annealed at 300 °C. The obtained sensitivity to low ethanol concentration of the crystalline film is about ∼30–100 which is quite competitive to other sensors based on other metal oxides. The optimum operating temperature of both films is the same at 350 °C.

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