UV Light Activation of TiO$_2$-Doped SnO$_2$ Thick Film for Sensing Ethanol at Room Temperature

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TiO$_2$-doped SnO$_2$ nanopowder is synthesized via a sol-gel method and characterized by atomic force microscopy and X-ray diffraction. Using this nanopowder, we have fabricated a novel semiconductor gas sensor that is sensitive to UV light illumination. We find that gas-sensing properties of TiO$_2$-doped SnO$_2$ sensor can be enhanced significantly under the exposure of UV light. The sensor exhibits a high sensitivity of 25 and rapid response-recovery times of 8 s and 24 s, respectively, under an ethanol gas of up to 100 ppm at room temperature (323 K). This suggests the possibility of development of a gas sensor for detecting ethanol at room temperature. [doi:10.2320/matertrans.MC200904]

1. Introduction

Semiconductor metal oxide gas sensors have attracted a great deal of attention in the past decade due to their many advantages such as simple manufacture technique, low cost, and rapid response and recovery time. Of these oxides, semiconducting materials, TiO$_2$ and SnO$_2$, are promising for gas sensor applications.[1–4] As far as the sensing mechanism is concerned, they present different behavior. Surface and bulk interactions control gas-sensing mechanism of SnO$_2$ and TiO$_2$-based devices, respectively.[5] This has profound implication in applying these oxides as an ultimate component in gas sensor devices. Due to the slow and insignificant interaction of introduced gas with the surface of sensing materials at room temperature, commercially available semiconductor sensors usually operate at high temperatures. The necessity to use a heating device hinders greatly the widespread applications of semiconductor sensors. For example, it is unlikely to monitor explosive gases because the high temperature could pose an explosion.

It is reported that UV light irradiation is a very useful way to improve the gas-sensing properties and reduce the working temperature of sensor.[6,7] To the best of our knowledge, little is known on the gas-sensing performance of SnO$_2$-TiO$_2$ sensors under the UV light illumination. Therefore, in present study, we prepare SnO$_2$-TiO$_2$ powder by a sol-gel method and measure the sensing properties of the TiO$_2$-doped SnO$_2$ gas sensors under the UV light activation at room temperature (defined as 323 K). We have found that the sensor has good gas-sensing properties at a low working temperature.

2. Experimental

TiO$_2$ colloidal solution was prepared by following procedure. A mix of 10 ml of tetrabutyl titanium (Wako Pure Chemical, 95%) and 4 ml isopropylalcohol were first gradually added to 150 ml deionized water. The solution was amply stirred for several hours until the sol is formed. Next, the sol was transferred to a well sealed autoclave vessel containing 0.5 M teramethy-ammonium hydroxide solution. Peptization process occurred after being heated at 393 K for 6 h. SnO$_2$ colloidal solution was prepared in as similar way. SnCl$_4$·5H$_2$O (Wako Pure Chemical) was dissolved in ethanol (0.4 M). The solution was stirred thoroughly and refluxed for 3 h. A 5.5 M aqueous ammonia solution (Wako Pure Chemical, 25–27.9%) was added dropwise to a refluxed solution and the resultant precipitate was washed thoroughly with deionized water. Finally, SnO$_2$ colloidal solution was prepared by adding deionized water.

The SnO$_2$-TiO$_2$ coating solutions were prepared by mixing the TiO$_2$ with SnO$_2$ colloidal solutions in a Sn/Ti ratio of 5 : 1. The colloidal was then dried and abrasive into powder. Finally, the powder was annealed at 723 K in air for 2 h under a heating rate of 6 K/min. The sensor fabricated in this study was of thick-film type. The obtained powders were mixed with diethanolamine and the formed paste was screen printed on an alumina substrate with a set of comb-like Au electrodes attached (distance between electrodes is 200 μm) and sintered at 773 K for 3 h. The gas sensing properties were characterized using a computer-controlled sensing system. The electric resistance and gas-sensing properties were measured using a static system in a laboratory condition (303 K, 40% relative humidity). In this paper, the response time was defined as the time for reaching 90% of the full response change of sensor when the test gas is in. The recovery time was defined as the time to fall down to 10% of final resistance while the test gas is out. An XD-5A diffractometry with Cu $K\alpha$ operated at 30 kV and 100 mA was used to determine the phase and grain size. The microstructure of thick film was analyzed using a high-speed CSPM4000 atomic force microscopy with contact mode.

3. Results and Discussion

3.1 Characterization of sensing materials

To determine chemical composition of the prepared powder, we performed XRD analysis, as shown in Fig. 1, where textural orientations of detected matters are given as well for easy reference. From this figure, one can clearly

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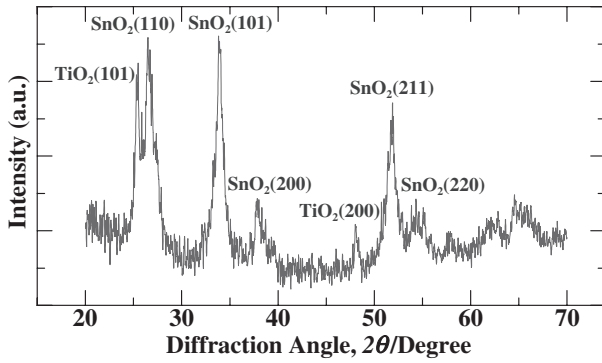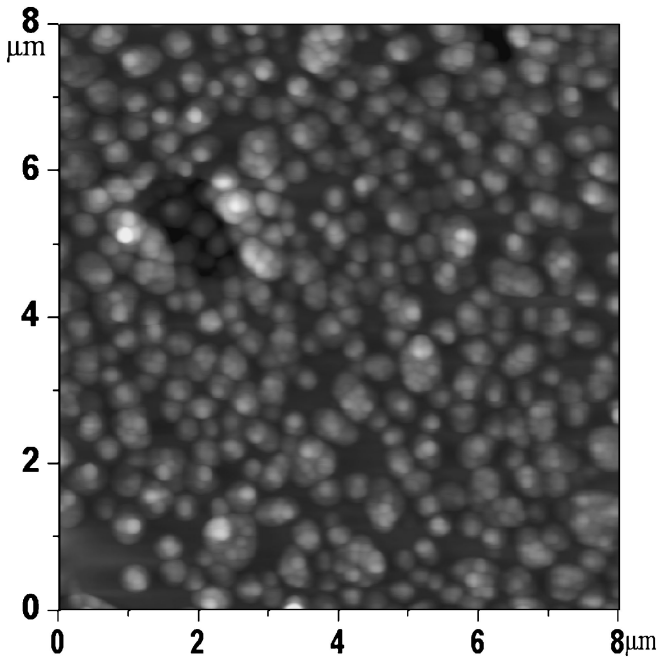
Fig. 1   XRD spectrum of the SnO$_2$-TiO$_2$ powder.

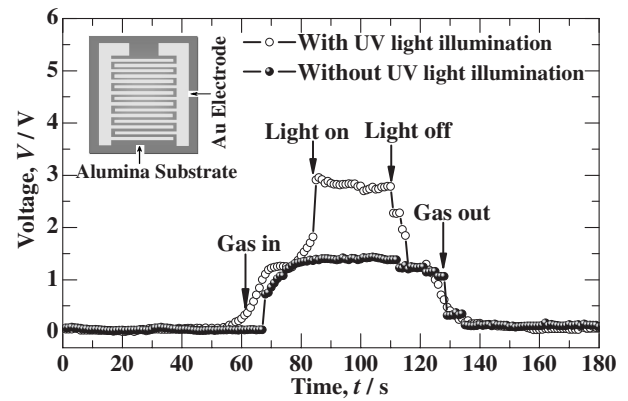Fig. 2   AFM image of the SnO$_2$-TiO$_2$ thick film.



Fig. 3   Response-recovery properties of the sensor operating under the ethanol gas of 100 ppm. The inset shows a schematic diagram of the gas sensor.

observed that the sample has an anatase TiO$_2$ phase and a rutile SnO$_2$ phase, as expected from the preparation process describe above. The particle size is calculated to be about 20 nm in terms of the Scherrer formula. The surface morphology of the SnO$_2$-TiO$_2$ thick film was observed from the AFM micrographs shown in Fig. 2, where one can see that the grains are uniformly distributed within the scanning area (8 μm × 8 μm). The mean particle size in the thick film is determined to be 38 nm by quantitatively characterizing the AFM images. This value is somewhat larger than the data obtained from the XRD pattern. This is mainly because grain size may be falsely imaged due to the magnification effect of AFM.

3.2   Gas-sensing properties

Since the goal of this study is to develop a new gas sensor capable of operating at low temperature, we further investigated gas-sensing properties of the thick-film sensor with and without UV light illumination. Here, the sensitivity is defined as the change of conductance in the ethanol gas with respect to that in air. Moreover, the total sensitivity (S_T), which is defined as the sum of sensitivities in air and gas

cases (S_0) and under UV light illumination (S_L), can be expressed by $S_T = S_L + S_0$. As shown in Fig. 3, there appear adsorption of ionic oxygen, O^{2-} and O$^-$, on the surface of SnO$_2$-TiO$_2$, as the surface is exposed in air. Clearly, the sensor exhibits a small response to ethanol without UV light irradiation, which can be ascribed to the low voltage through the sensor at room temperature. The sensitivity of the gas sensor (S_0) is estimated to be about 7 under the ethanol gas of 100 ppm.
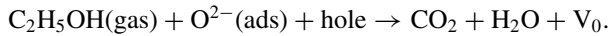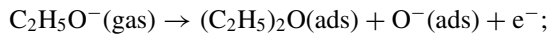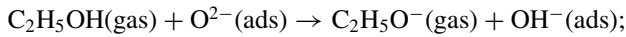
When the sample is irradiated under UV light, the voltage increases sharply and the sensitivity (S_L) has a value of 18. This, together with the total sensitivity (S_T) of 25, is found to meet the industrial needs. The abrupt increase of voltage can be understood by considering that as the light is absorbed by the semiconductor, a hole-electron pair is created. The formed hole is pulled to the surface by electric field and recombines with the adsorbed oxygen. The effect of light relies on the enhancement of interaction between the semiconductor surface and the introduced gas, thereby shifting the equilibrium of reactions as well as speeding up the reactions. For this reason, the voltage through the thick film increases when the light is on. Further, the time needed to reach a stable conductance after irradiation is evaluated to be 8 s and the recovery time 24 s as the irradiation is halted.

3.3   Gas-sensing mechanism

When the sensor is exposed in air, pre-adsorbed oxygen on the surface would trap electrons due to the strong electron negativity of oxygen, thereby producing adsorbed oxygen ions O^{2-}. With the rise of operating temperature, the atmospheric oxygen is first adsorbed on the surface or grain boundaries and then dissociates into ions of various forms, namely, O^{2-}, O$^-$, O^{2-}, as shown in the following:

$$O_2(gas) \rightarrow O_2(ads);$$

$$O_2(ads) + e^- \rightarrow O_2^-(ads);$$

$$O_2^-(ads) + e^- \rightarrow 2O^-(ads).$$
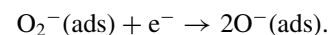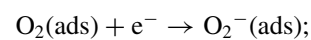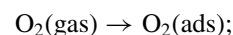
Therefore, the concentration of electrons decreases and the resistance through the material increases. As reductive gas such as ethanol is introduced, chemical reactions may take place between C$_2$H$_5$OH and O^{2-}(ads) on the surface of SnO$_2$-TiO$_2$ film, which can be described as follows:

$$C_2H_5OH(gas) + O^{2-}(ads) \rightarrow C_2H_5O^-(gas) + OH^-(ads);$$

$$C_2H_5O^-(gas) \rightarrow (C_2H_5)_2O(ads) + O^-(ads) + e^-;$$

$$C_2H_5OH(gas) + O^{2-}(ads) + hole \rightarrow CO_2 + H_2O + V_0.$$

Here the V_0 is the doubly charged oxygen vacancy. These reaction-produced electrons may decrease the resistance, which results in the rise of output voltage when sensor is exposed in the gas.[8–10]

On the other hand, the electron-hole pairs, which are generated by the UV light, can increase the conductivity of both bulk and grain interior, which consequently modifies the surface potential. In addition, the free electrons generated by the oxygen adsorption give rise to the broadening of inversion region, which correspondingly increases sample resistance. Our observations show light-induced decrease of resistance, which can be explained by assuming that the reverse spatial charge field pulls the photo-generated holes towards the surface. These holes can recombine with the chemisorbed oxygen, which forms a neutral atom and simultaneously reducing the surface field. The recombination might be hindered by the Ti^{4+} that is diffused into the SnO_2 grains when a small amount of TiO_2 is doped and the $TiSnO_4$ is formed in grain boundaries. Since photo-generated electron determines photosensitivity, the UV light illumination is key to enable SnO_2-TiO_2 sensor to operate at room temperature.

4. Conclusions

We demonstrate that the development of semiconducting thick-film sensors capable of working at room temperature is possible via a photo-assisted technique. Under the UV light illumination, the SnO_2-TiO_2 sensor is found to exhibit high sensitivity and rapid response-recovery time under the ethanol of 100 ppm at room temperature. The enhanced sensing properties make the SnO_2-TiO_2 thick films promising as a sensing material for new gas sensor application.

Acknowledgements

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