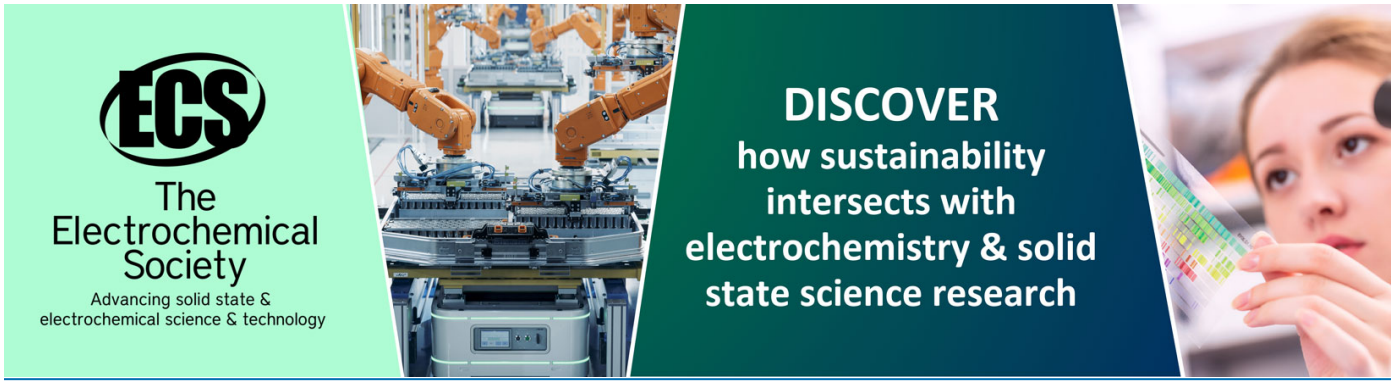
Ag-doped titanium dioxide gas sensor



Ag-doped titanium dioxide gas sensor

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Abstract. Titanium dioxide has been utilized for the fabrication of oxygen sensitive ceramic bodies. In this work, disk-shaped TiO_2 pellets are fabricated by the sintering of the press-formed anatase powder at 1000°C. Two silver contacts are printed on one of the top base of each sample. Silver wire segments are connected to the printed electrodes. It is shown that the gradual diffusion of silver into titanium dioxide from the electrodes profoundly affects the resistive properties of the ceramic samples. SEM, XRD and EDAX analyses are carried out to determine the position of the silver diffused in the structure. At 350°C, before silver diffusion, the electrical resistance of the device decreases ten times in response to the presence of 3000 ppm ethanol contamination. Sensitivity (R_{air}/R_{gas}) to reducing gases is severely affected by the silver doping level in the titanium dioxide. The progress of silver diffusion continuously decreases the sensitivity till it become less than one. Further progress in silver diffusion brings the devices to the condition at which the resistance increases at the presents of reducing gases. In this condition, inverse sensitivities (R_{gas}/R_{air}) as large as 10^3 are demonstrated.
Keywords: Titanium dioxide, Gas sensor, Silver diffusion, Sensitivity, Reducing gas.

1. Introduction

Seiyama found gas sensitivity on metal oxides in 1962, and Taguchi brought metal oxide semiconductor-based gas sensors to the market [1,2]. ZnO, TiO_2 and SnO_2 are the most widely studied metal oxide semiconductors for gas sensing applications [3]. They are all wide-band-gap semiconductors whose charge carrier populations are determined either by doping with aliovalent cations [4] or oxygen nonstoichiometry [5]. In undoped metal oxide materials, oxygen deficient crystals present n-type semiconductivity since the formation of oxygen vacancies accompanies electron generation. In contrast, the p-type semiconductivity can be explained by the deficiency of metal ions in the material [6]. The effect of oxygen vacancy-related defects on gas-sensing properties of n-type metal oxide gas sensors has previously been investigated [7]. In n-type polycrystalline metal oxides the sensing mechanism mainly is related to the change in the barriers which formes between grains by imperfections and oxygen adsorption at working temperature [8]. Moreover, Schottky-type metal contacts can play important role in the sensing mechanism and in comparison to resistive gas sensors, Schottky types can potentially be more sensitive [9]. Although resistive gas sensors are popular owing to their reasonable prices and good durability [10], their selectivity and sensitivity are limited. These deficiencies are the main driving force for developing new materials and methods for superior gas detectors [10]. There are numerous papers focused on optimizing parameters of metal oxides to enhance these properties by controlling the size and the shape of the gas sensor's oxide grains [11] or introducing catalytically active additives in the sensing layer via doping or surface

functionalization [12, 13]. In addition, the selectivity of these sensors have been improved by external methods like thermal modulation [14] and connection to microfluidic channels [15].

Titanium dioxide is known as n-type wide bandgap semiconductor, with 3.1 eV for rutile and 3.3 eV for anatase [16]. There are several methods to produce TiO_2 such as thermal oxidation [17], hydrothermal [18], and sol-gel [19]. Proper phase, morphology, grain size and porosity can be achieved by controlling the fabrication parameters in each method [20]. Both rutile and anatase phases of TiO_2 have been used for gas sensor [9, 17], UV detector [21] and solarcell fabrication [22]. In most of these cases, many noble metal-TiO_2 contacts are utilized for connecting them to the outside circuitry [23]. Besides, it is found that TiO_2 doped with noble metals, such as Ag, Au, Pt, and Pd can enhance device properties. Ag presents numerous interesting properties, such as high efficiency, low cost compared to other noble metals, and high oxygen adsorption reactivity. TiO_2 thin films doped with Ag have shown many attractive characteristics [24]. Moreover, Ag metallic ion is known as a high mobility cation, which has been used in resistive switching devices [25].

In the present study, we report on the electronic properties of the Ag/TiO_2/Ag structure and using the device as gas sensor. We show that silver diffusion into the TiO_2 layer, plays a significant role in determining sensor sensitivity. By gradual silver diffusion, the sensitivity of the device increases slightly, but with further progress of silver diffusion, the sensing mechanism changes and the sample resistance increases at the presence of the reducing gas. The change in the sensing mechanism is describe by TiO_2 acting like a p-type semiconductor when Ag particles present in the open structure of the polycrystalline TiO_2.

2. Experimental

TiO_2 pellets with 5 millimeters in diameter are prepared by addition of 2 milliliters of distilled water into 5 grams of anatase TiO_2 powder. The samples are dried and prepared for sintering at 1000℃. The grains grow during sintering, and this phenomena lead to larger grains which, evidently, reduce the population of the smaller pores. In this process, samples are placed in an electric muffle furnace at definite temperature for 60 minutes. The atmosphere of the furnace is air.

Samples are fabricated by silver electrode deposition on the thermally oxidized titanium foil chips. As shown in figure 1, a microheater is attached beneath the substrate and provides elevated temperatures up to 500℃. Large area ohmic connections to Ag/TiO_2 structure were prepared by silver paste printing. After settling and hardening of the silver paste, the samples are placed at 300℃ for 15 minutes.

As shown in figure 2, the measurement system comprises of a signal generator to provide the input ac voltage, Sanwa PC-5000 multimeter for continuous monitoring of the sensor output, and a fine type-S thermocouple placed on the sample surface to controls the operating temperature of the sensor. For measuring the sample resistance, a sinusoidal voltage with frequency of 80 Hertz is applied to the sample and a series resistor is used for monitoring the output voltage.

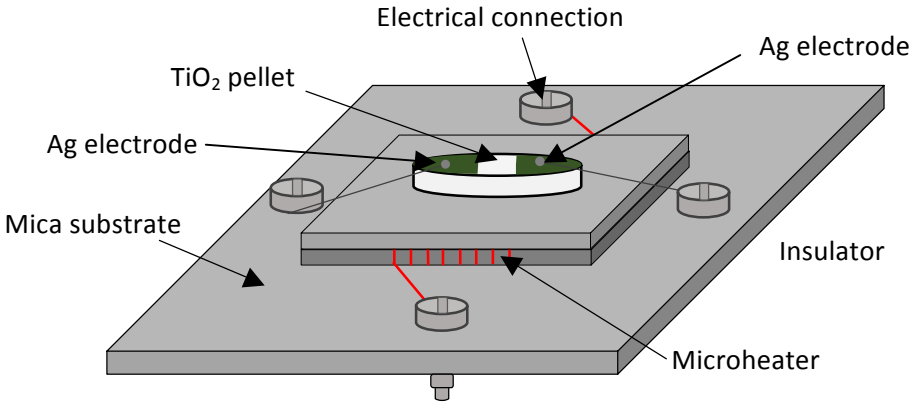

Figure 1. The schematic diagrams fabricated device comprising sensing oxide, silver electrodes on the top surface, and the microheater.

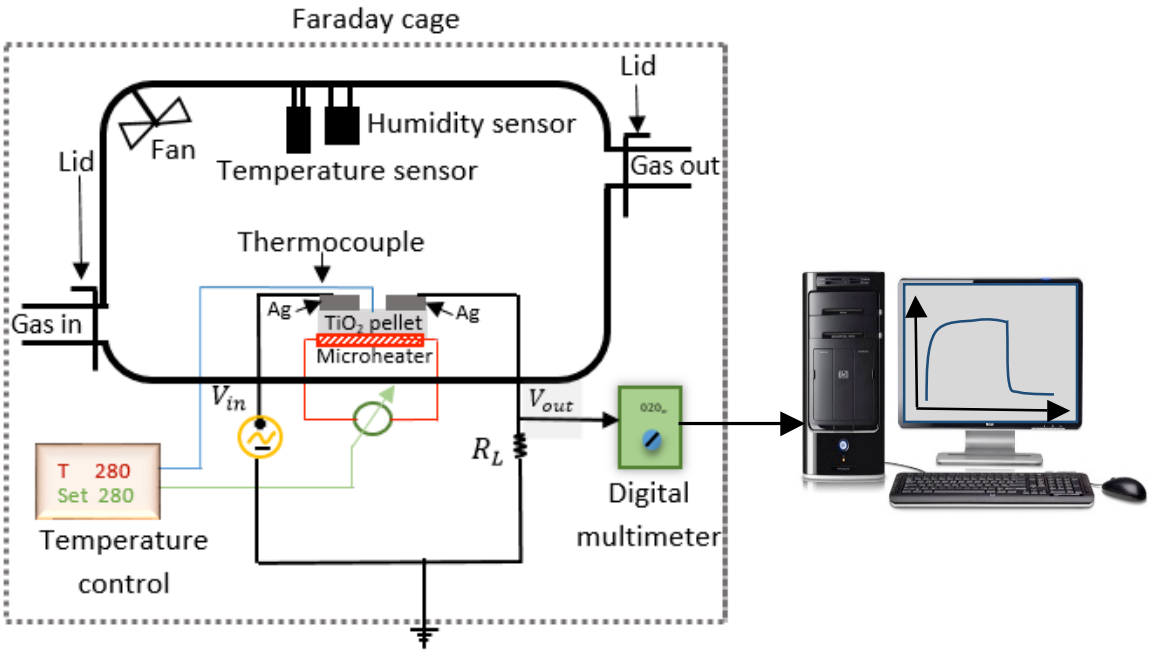

Figure 2. The schematic diagram of the experimental setup used for recording sample resistance at presence of gas contaminant.

Silver paste electrodes are connected to external circuit with silver wire segments (figure 3). XRD pattern shows that the TiO_2 samples sintered at 1000℃ for 60 minutes are totally of anatase phase.
The transient response of the sample to the presence of 1000 ppm ethanol contamination at 320℃ is a 6-fold change in conductance, as shown in figure 4. The transient response of pure TiO_2 shown in figure 4 is consistent with the TiO_2 disk produced being an n-type semiconductor. The increase in conductivity of pure TiO_2 at the presence of reducing gases is due to the increased oxygen vacancy and decreased potential barriers established at the grainboundaries.

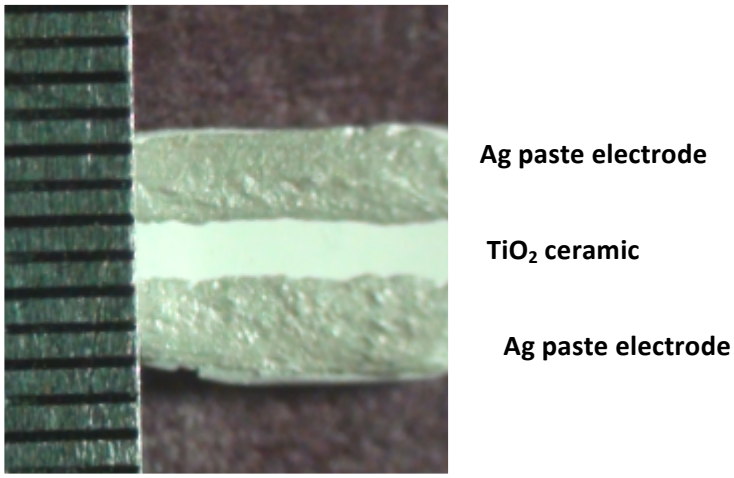

Figure 3. Optical microscope image of the pure titanium dioxide with two parallel silver electrodes deposited on it.

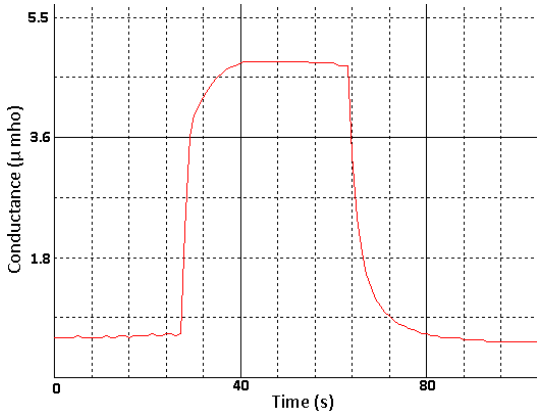

Figure 4. Transient response of the sample to the presence of 1000 ppm ethanol contamination at 320℃.

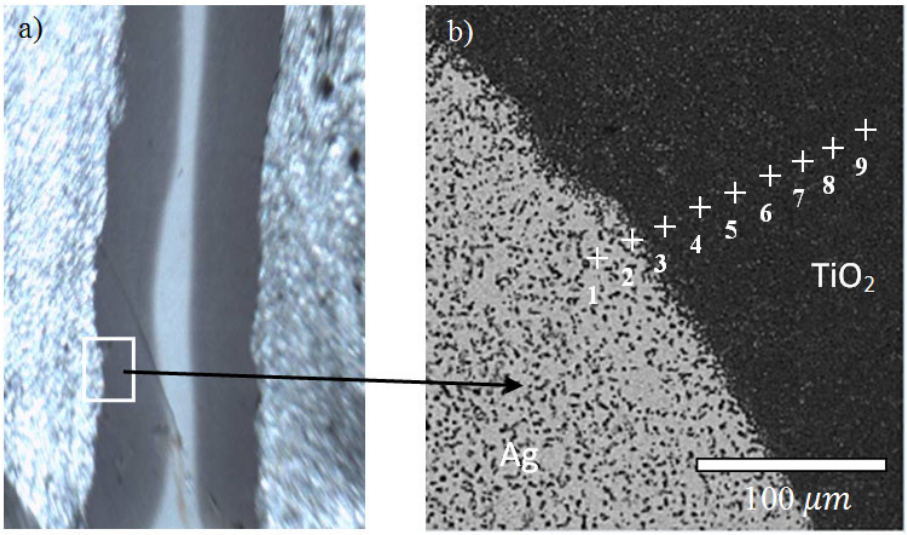

Figure 5. Micrographs illustrating silver diffusion from the silver electrode into the titanium dioxide: a) the silver halo created around the silver electrodes by silver diffusion, b) SEM image of the area selected in (a).

Silver diffusion into TiO_2 body is investigated at elevated temperatures up to 400℃. The established electrical field helps silver diffusion. Microscopic images of an Ag-TiO_2 contact after silver diffusion are given in figure 5.

3. Results and discussion

The concentration of silver in points 2 to 9 shown in figure 5 is analyzed by EDAX surface analyzer. The results are plotted vs. distance in figure 6.

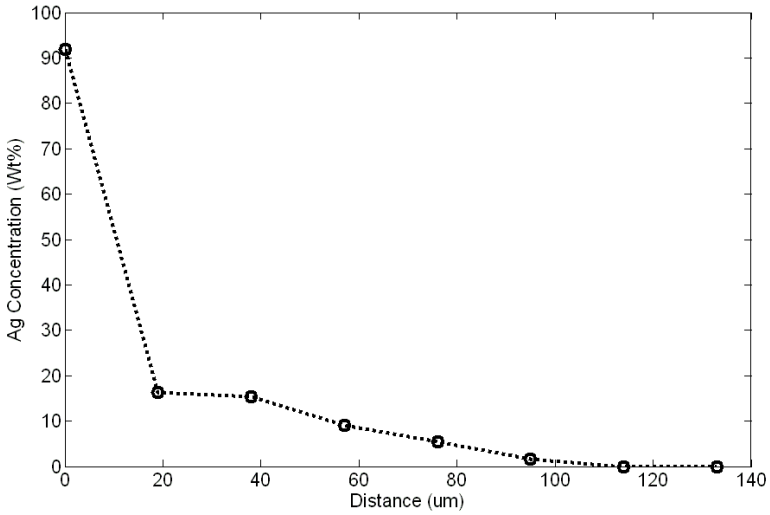

Figure 6. Silver concentration in points marked in figure 5-b.

The XRD analysis is carried out on the TiO_2 body after sintering. The pure TiO_2 body is provided and sintered in 1000℃ for 60 minutes. The surface of a sintered body is completely covered with the silver paste. It is, then, placed in an electric muffle furnace and annealed for 30 minutes at 500℃. After extraction from the furnace, silver layer is removed from the surface of the sample body. XRD was, subsequently, carried out on this sample. As shown in figure 7, in addition to picks of anatase phase, there are 2 little picks related to rutile phase. With respect to this reality, pure TiO_2 is in anatase phase, it is evident from patterns that presence of Ag in pure TiO_2 even in 500℃ converts anatase phase to rutile.

The XRD pattern in figure 7 shows that our TiO_2 sample is a mixture of anatase, and rutile phases. Ag and Ag_2O are present in the sample and there is no sign of possible alloy phases between AgO and TiO_2. Although the XRD analysis system used, claims 5% accuracy, it appears that Ag has not diffused into the TiO_2 crystal structure significantly. The silver particles appear to be mostly metallic residing within the pores and grainboundaries.

Silver diffusion into TiO_2 body severely affects the conductance and response of the sample to the presence of reducing gases. Experiment of silver diffusion from contacts is carried out on several samples and all of them have the same pattern in changing conductance and respond to reducing gas.

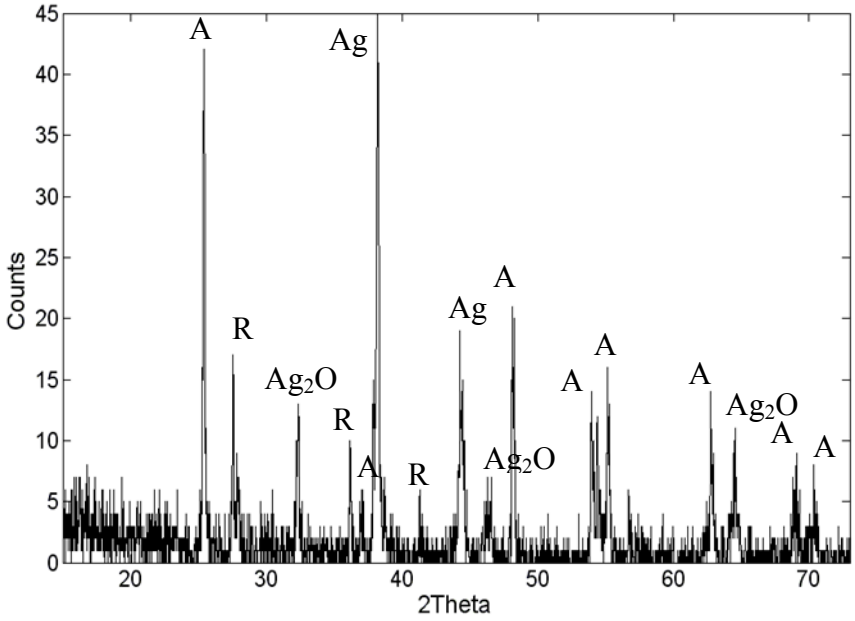

Figure 7. XRD pattern for titanium dioxide after silver diffusion shows peaks of anatase, rutile, Ag and Ag_2O.

4. Conclusion

The Effect of silver diffusion from the electrodes into the TiO_2 pellet of a gas sensor on the responses of the gas sensing properties of the device was experimentally investigated. It was concluded that the sensitivity can increase significantly by diffusing silver to the titanium dioxide body. Before silver diffusion, sensor's response to 3000 ppm ethanol contamination was conductance increase of 10-fold, but after silver diffusion the sensor showed conductance decrease as response to ethanol presence. Silver diffusion into the TiO_2 ceramic body and the sensitivity changes before and after silver diffusion at different conditions requires further studies. The attractions of Ag-TiO_2-Ag structure as a potentially high sensitivity and low cost gas sensing device are clear and make it a good candidate for more investigations.

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