The detection of CO$_2$ gas sensor at high temperature by Al-blended TiO$_2$ Semiconductor

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Abstract

Al-blended TiO$_2$ semiconductor layers were investigated as gas sensors detection at temperatures up to 300°C. Thin sensor layers were deposited by screen printing technique from the metallic target of Al on alumina substrate. The layers were characterized by SEM for micro structural constituents. After heating at 300°C for 3 hours in air, the sensor response is measured towards CO$_2$ concentrations up to 20 ppm under dry and humid conditions. Al-blended TiO$_2$ sensor layers exhibited very promising results for sensing CO$_2$ selectively at temperatures exceeding 300°C.

1. Introduction

In the last 10 years, atmospheric pollution in urban areas has achieved to dangerous levels. Processes involving burning in aircrafts, energy and power manufacture and automobile engines as well as through industrial agreement are the main sources of the pollution. Detection and control of the emission relies on the growth of the precious and selective gas sensors [1]. It is known that the transition metal oxides such as SCO$_2$, TiO$_2$, WO$_3$, MoO$_3$, Ga$_2$O$_3$ and Nb$_2$O$_5$ are used as sensing electrodes in such chemical gas sensors due to their semiconducting and electrochemical properties [2]. TiO$_2$ is non-toxic and low cost and has superb chemical stability. It can pose semi-conductive properties on doping, and hence is one of the most important transition metal oxides for this purpose [3, 4]. Nevertheless, TiO$_2$ based gas sensors still need development for the achievement of high-temperature sensitivity, stability or efficiency. One of the methods to improve the performance of the TiO$_2$-based gas sensor devices is the augment of surface area by structuring the sensors. An electrochemical reaction occurs, as a gas species, either oxidizing or sinking, reaches on the semi-conductive metal oxide surface. Thus, the quantity of this reaction relies on the availability of the surface area of the metal oxide. Second solution for higher efficiency or sensitivity and better selectivity at the TiO$_2$-based gas sensor devices is the doping of TiO$_2$ with different valence elements such as Al, Cr, W, etc. It is known that doping of TiO$_2$ with Al causes a change in semi-conductivity, leading to development in CO$_2$-gas sensitivity of TiO$_2$-based gas sensors [5]. In this study, we report the synthesis of highly ordered Al-blended TiO2 nanotubes by anodic oxidation. The sensors produced using these nano-tubular layers are investigated for the sensing properties towards CO$_2$ and CO at the temperature range of 300°C – 500°C.

2. Experimental

The uncontaminated TiO$_2$ nano-tubes were grown on the commercially existing uncontaminated titanium foil (99.6 %) by means of anodic oxidation. First the titanium foil substrates were mirror refined and then washed with the deionized water. Following every shining step, the foils are cleaned in an ultrasonic bath. The anodization process was carried out in two
different solutions; (1) Ethylene Glycol based electrolyte containing 2% vol. H₂O, 98% vol and 0.3% wt. NH⁴F, (2) aqueous electrolyte containing 0.5M H₃PO₄ and 0.14M NaF using an anodization voltage of 20V. Before the sensor measurements, all samples were heated at 450°C. The sensor characterization measurements were carried out under CO₂ or CO after depositing two copper circuits on the Nanotubular-layers at test temperature of 300°C. A constant voltage of 60V was applied and the resistance changes of the sensor devices were recorded upon exposure to CO₂ in the concentrations of 10 ppm to 25 ppm.

3. Results and discussion

The ordered TiO₂ and the metal-blended TiO₂ nano-tubular layers could be obtained after anodization process. The surface and cross-section images of the TiO₂ layer achieved after 1 hour anodic oxidation are shown in Figs. 1a and 1b. In one hour of anodization, nano-tubes lengths of 4-6 µm were achieved. After three hours, the thickness can reach to 16 µm. Figs. 1c and 1d show top view and cross-section images of Al-blended TiO₂ nano-tubular layer.

Fig 1: SEM images of TiO₂ nano-tubular layer after anodic- oxidation. (a) top view (b) cross section of un-blended TiO₂ (c) top view and (d) cross section of Al - blended TiO₂

Fig. 2a shows the sensor response of the unblended TiO₂ nano-tubular layers under CO₂ concentrations of 10, 15 and 20 ppm at 300°C. On release of the 10 ppm CO₂, a sharp increase at resistance value was observed. When the CO₂ run is stopped, the resistance value reduced to the original level. However, under increased CO₂ flow (e.g. 15 ppm), the increase at resistance not reach to a stable state. On contrast, the response of the Al-blended nano-tubular TiO₂-layers was very stable towards the same CO₂-concentrations, compliant very short response times (Fig. 2b). Moreover, the resistivity change showed no drift with and without CO₂ flow. The same base line as well as sensor response were stable.
Fig.2: Sensor response towards CO\textsubscript{2} at 300° C (a) unblended TiO\textsubscript{2} nano-tubular layer (b) Al-blended TiO\textsubscript{2} nano-tubular layer

4. Conclusion

Vertically aligned TiO\textsubscript{2} nano-tube arrays were synthesized in EG-based electrolytes. The sensor measurements were carried out at 300°C with CO\textsubscript{2} concentrations of 10,15 and 20 ppm. The nano structured TiO\textsubscript{2}-gas sensor showed sensibly well response towards CO\textsubscript{2} but the resistivity change was not stable during the CO\textsubscript{2} flow. On Al-doping of the TiO\textsubscript{2} nano-tubes, the gas sensing activity of the sensor towards CO\textsubscript{2} was increased. The resistivity change was stable and fast with and without CO\textsubscript{2} flow. Structuring and doping the TiO\textsubscript{2} layers, and thus increasing the surface area, at the gas sensor electrodes, more sensitive and stable response can be obtained. The response and recovery times of the sensor can be reduced. Al-blended Nano-tubular TiO\textsubscript{2}-electrodes yield very promising sensor devices for stable and sensitive detection of relatively small concentrations of CO\textsubscript{2}.

5. References


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