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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_2O_3 and Nb_2O_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 nano-tubes 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. H_2O, 98% voland 0.3% wt. NH_4F, (2) aqueous electrolyte containing 0.5M H_3PO_4 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 CO_2 or CO after depositing two cupper 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 ®-in the concentrations of 10 ppm to 25 ppm.

3. Results and discussion

The ordered TiO_2 and the metal-blended TiO_2 nano-tubular layers could be obtained after anodization process. The surface and cross-section images of the TiO_2 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 TiO_2 nano-tubular layer.

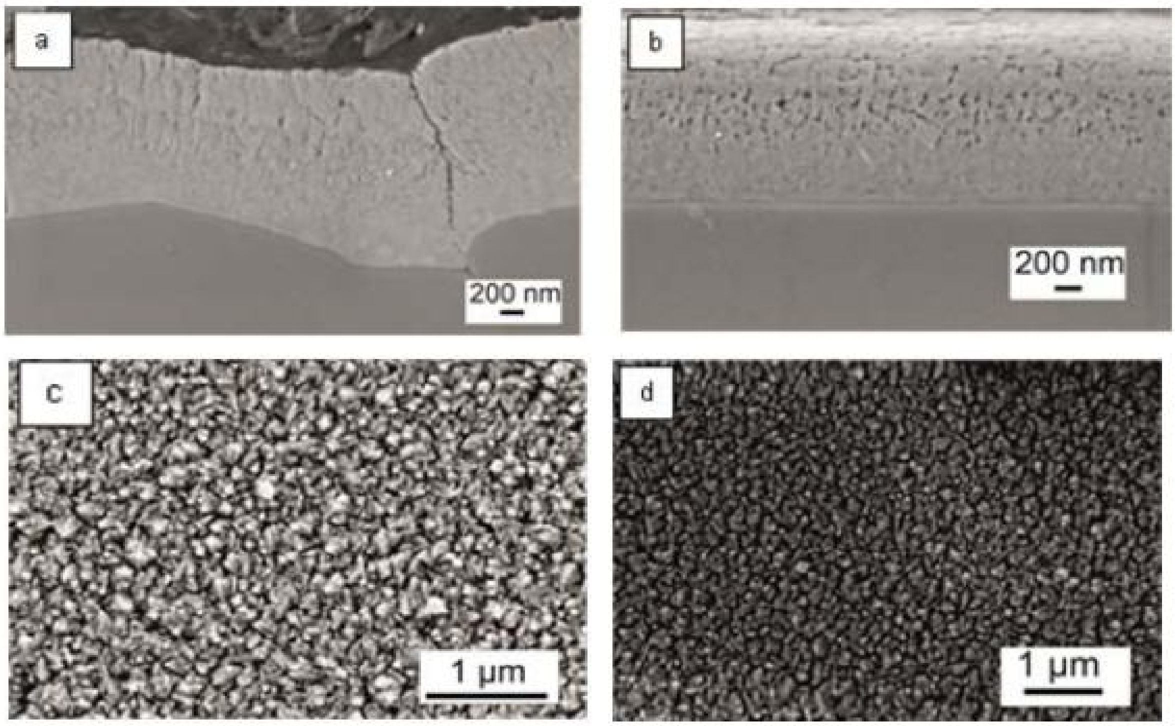

Fig 1: SEM images of TiO_2 nano-tubular layer after anodic- oxidation. (a) top view (b) cross section of un-blended TiO_2 (c) top view and (d) cross section of Al - blended TiO_2

Fig. 2a shows the sensor response of the unblended TiO_2- nano-tubular layers under CO_2 concentrations of 10, 15 and 20 ppm at 300°C. On release of the 10 ppm CO_2, a sharp increase at resistance value was observed. When the CO_2 run is stopped, the resistance value reduced to the original level. However, under increased CO_2 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 TiO_2-layers was very stable towards the same CO_2-concentrations, compliant very short response times (Fig. 2b). Moreover, the resistivity change showed no drift with and without CO_2 flow. The same base line as well as sensor response were stable.

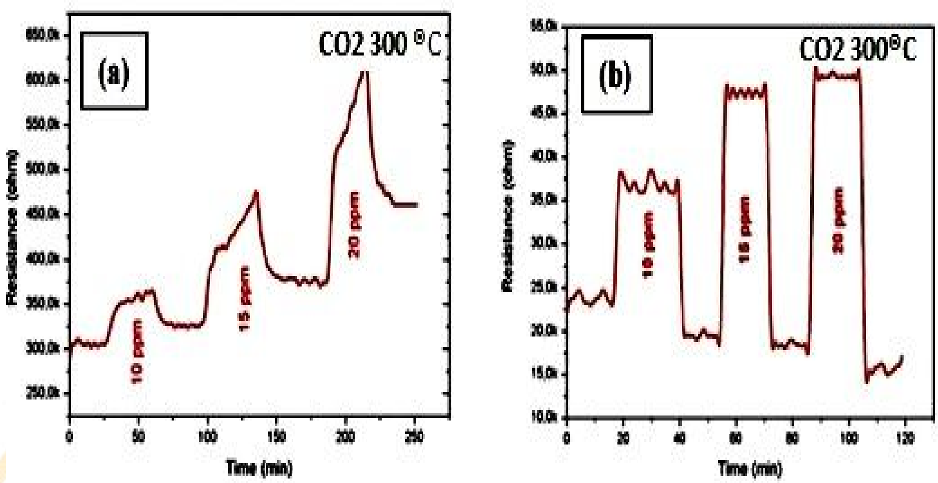

Fig.2: Sensor response towards CO_2 at 300° C (a) unblended TiO_2 nano-tubular layer (b) Al-blended TiO_2 nano-tubular layer

4. Conclusion

Vertically aligned TiO_2 nano-tube arrays were synthesized in EG-based electrolytes. The sensor measurements were carried out at 300°C with CO_2 concentrations of 10,15 and 20 ppm. The nano structured TiO_2-gas sensor showed sensibly well response towards CO_2 but the resistivity change was not stable during the CO_2 flow. On Al-doping of the TiO_2 nano-tubes, the gas sensing activity of the sensor towards CO_2 was increased. The resistivity change was stable and fast with and without CO_2 flow. Structuring and doping the TiO_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_2-electrodes yield very promising sensor devices for stable and sensitive detection of relatively small concentrations of CO_2.

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