Effect of Doping at TiO2-Nanotubular Gas Sensors

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1. Introduction

In the last decades, atmospheric pollution in urban areas has achieved to critical levels. Processes involving combustion in aircrafts, energy and power production and automobile engines as well as through industrial settlement are the main sources of the pollution. Detection and control of the emission relies on the development of the precious and selective gas sensors [1]. It is known that the transition metal oxides such as SnO_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 excellent 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 improvement 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 increase of surface area by structuring the sensors. An electrochemical reaction occurs, as a gas species, either oxidizing or reducing, 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 Cr^{3+}, Al^{3+}, Nb^{5+}, W^{6+}, etc. It is known that doping of TiO_2 with Cr^{3+} causes a change in semi-conductivity, leading to improvement in NO_2-gas sensitivity of TiO_2-based gas sensors [5].

In this study, we report the synthesis of highly ordered Cr- or Al-doped TiO_2 nano-tubes by anodic oxidation. The sensors produced using these nano-tubular layers are investigated for the sensing properties towards NO_2 and CO at the temperature range of 300°C – 500°C.

2. Experimental Process

Highly-ordered pure TiO_2 nano-tubes were grown on the commercially available pure titanium foil (99.6 %) via anodic oxidation. First the titanium foil substrates were mirror polished and then rinsed with the de-ionized water. Following every polishing step, the foils are cleaned in an ultrasonic bath. The anodization process was carried out in two different solutions; (1) Ethylene Glycol (EG) - 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 annealed at 450°C. The sensor characterization measurements were carried out under NO_2 or CO after depositing two platinum circuits on the Nano-tubular-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 NO_2-in the concentrations of 10 ppm to 25 ppm.

3. Results and discussion

Well-ordered TiO_2 and the metal-doped 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 Cr^{3+}-doped TiO_2 nano-tubular layer.

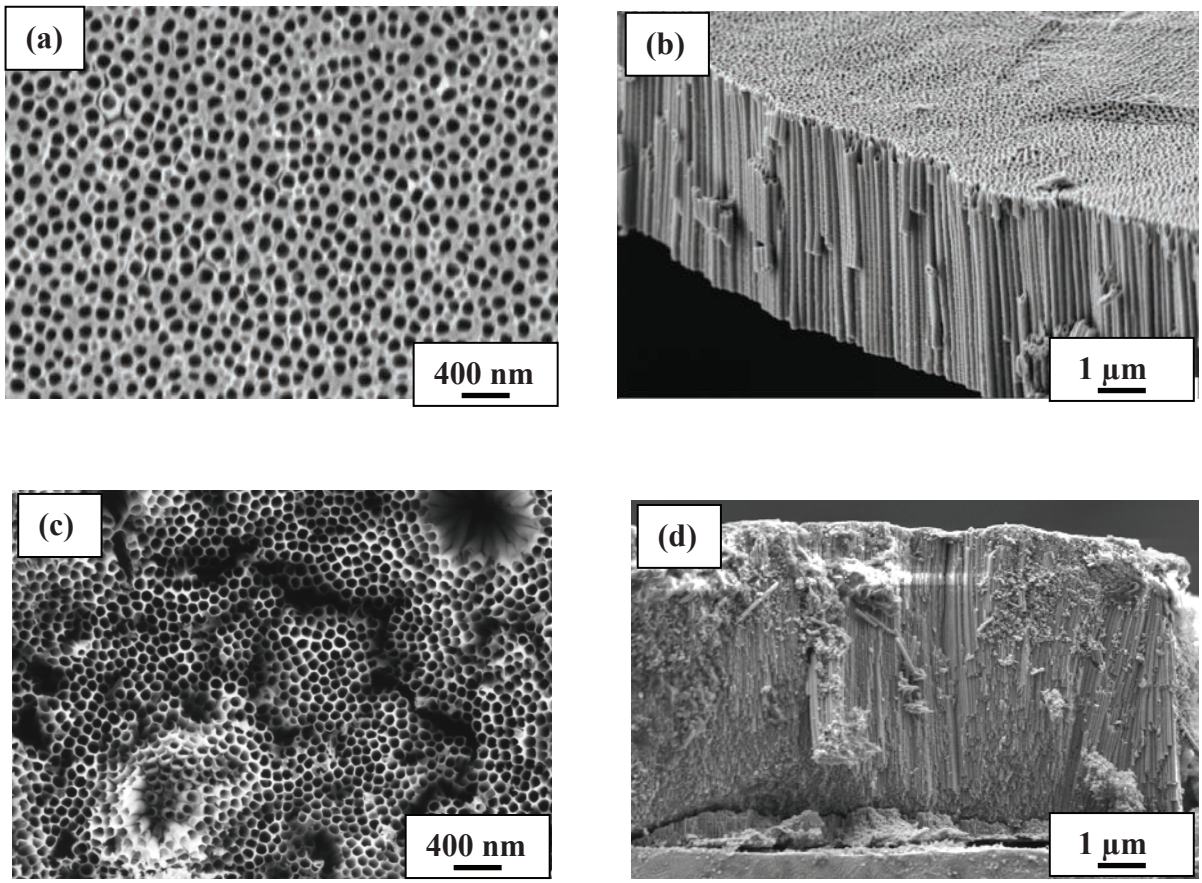

Fig. 1: SEM images of TiO_2 nano-tubular layer after anodic-oxidation at 60V using EG-based electrolyte (a) top view (b) cross-section of undoped TiO_2, (c) top view and (d) cross section of Cr^{3+}-doped TiO_2

Fig. 2a shows the sensor response of the undoped TiO_2- nano-tubular layers under NO_2 concentrations of 10, 15 and 20 ppm at 300°C. On release of the 10 ppm NO_2, a sharp increase at resistance value was observed. When the NO_2 flow is stopped, the resistance value decreased to the original level. However, under increased NO_2 flow (e.g. 15 ppm), the increase at resistance can not reach to a steady state. On contrast, the response of the Cr-doped nano-tubular TiO_2-layers was very stable towards the same NO_2-concentrations, yielding very short response times (Fig. 2b). Moreover, the resistivity change showed no drift with and without NO_2 flow.The same baseline as well as sensor response were stable.

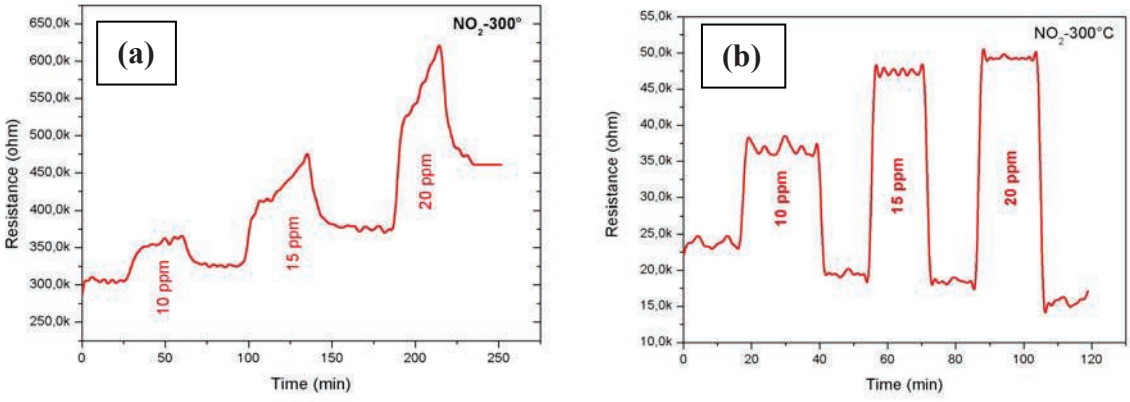

Fig. 2: Sensor response towards NO_2 at 300° C (a) undoped TiO_2 nano-tubular layer (b) Cr^{3+}-doped TiO_2 nano-tubular layer

3. Conclusion

Vertically aligned TiO_2 nano-tube arrays were synthesized in EG-based electrolytes. The sensor measurements were carried out at 300°C with NO_2 concentrations of 10,15 and 20 ppm. The nano-structured TiO_2-gas sensor showed reasonably well response towards NO_2 but the resistivity change was not stable during the NO_2 flow. On Cr-doping of the TiO_2 nano-tubes, the gas sensing activity of the sensor towards NO_2 was increased. The resistivity change was stable and fast with and without NO_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. Cr^{3+}-doped Nano-tubular TiO_2-electrodes yield very promising sensor devices for stable and sensitive detection of relatively small concentrations of NO_2.

References

[1] Y. Jun, H.S. Kim, J.H. Lee and S. H. Hong, CO Sensing performance in micro-arc oxidation TiO_2 films for air quality, *Sens. Actuators B*, (2006), 69-73.

[2] A. M. Ruiz, G. Sakai, A. Cornet, K. Shimanoe, J. R. Morante and N. Yamazoe, Cr-doped TiO_2 gas sensor for exhaust NO_2 monitoring, *Sens. Actuators B* (2003), 509-518.

[3] K. Zakrzewska, Mixed oxides as gas sensors, Thin Solid Films 391 (2001) 229–238.

[4]Y. Xu, K. Yao, X. Zhou, Q. Cao, Platinum–titania oxygen sensors and their sensing mechanisms, *Sens. Actuators B: Chem.* 13–14 (1993) 492–494.

[5] A.M. Ruiz, J. Arbiol, A. Cirera, A. Cornet, J.R. Morante, Surface activation by Pt-nanoclusters on titania for gas sensing applications, *Mater. Sci. Eng. C* 19 (2002) 105–109.