The Improvement of the H_2S Sensing Potential for the SnO2 Produced by Mechano-chemical Milling

Ülo Kersen, Helsinki University of Technology, Otakaari 5A, P.O.Box 3000, Fin-02015 HUT, Finland; Tel.: +358-9-4511; Fax: +358-9-451-2991; e-mail: fjsnylkr@netscape.net

Abstract

$SnCl_2$ powder was milled with $Ca(OH)_2$ and K_2CO_3 powder respectively in a ball-mill at room temperature and in an air atmosphere. No X-ray diffraction peaks were observed for the as-milled powder. However, heat treatment above 300 °C causes the appearance of SnO_2, $CaCl_2$ and KCl phases for milled compositions confirming that solid-state displacement reactions have been started during a ball-milling without external heating. Pure SnO_2 was obtained by removal of the $CaCl_2$ or KCl by-product by washing the powder with distilled water using a centrifuge. An initial composition of $SnCl_2$, K_2CO_3 and $Cr(NO_3)_3 \times 9H_2O$ was milled to produce the doped SnO phase with a distributed Cr on the surface. Heat treatment of all milled mixtures at 400 °C for 1h resulted in the formation of tetragonal and orthorhombic phases. Pure SnO_2 powders obtained were impregnated with Ag or La in an aqueous solution of $AgNO_3$ or $La(NO_3)_3 \times 6H_2O$ respectively followed by heat treatment at a low temperature which was still sufficient to decompose the salt and to distribute the surface additive on a fine scale. Higher decomposition temperature over 450°C caused agglomeration of the additive particles for all samples. Surface-doped and undoped SnO_2 powders were then mixed in polyvinyl alcohol (PVA) solution to form pastes and coated onto Al_2O_3 substrates with comb-type Au electrodes and sintered. On exposure to 1 ppm of H_2S gas the La_2O_3-SnO_2 film has higher sensitivity compared to that of the undoped, Ag_2O-SnO_2 or Cr_2O_3-SnO_2. High sensitivity to H_2S gas was gained due to fine crystallites of synthesized tin dioxide powder with unagglomerated surface microstructure. Crystallite sizes ranged from 10 to 25 nm as determined by X-ray diffraction (XRD) analysis. Surface doping by impregnation seemed to be effective since the small SnO_2 crystallite size was maintained which was controlled by varying the concentration of solution and time. The results show that by an appropriate powder synthesis method and control of surface doping, SnO_2 can be modified for use as a H_2S gas sensor in the concentration range below 1 ppm.

Key words: ball-milling, heat treatment, by-product, SnO_2, surface doping, XRD, H_2S adsorption, electronic conductivity.