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Facile synthesis of single crystalline SnO_2 nanowires

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Abstract

Single crystalline SnO_2 nanowires with diameter in the range of 10–100 nm and several micrometers in length have been successfully prepared by the combustion technique in air using Al, Cu_2O and SnO as the raw materials. FE–SEM and TEM images showed that the nanowires were single crystalline, growing along the [310] direction. The nanowires' growth mechanism was suggested to follow both VLS and VS mechanisms. The formation of SnO_2 nanowires underwent three steps: tin vapor generation via combustion synthesis, oxidation of the tin vapor and its nucleation and subsequent growth. At the same time, porous Al_2O_3 ceramic and Cu–Sn alloy were obtained during the combustion synthesis process.

Keywords: Nanowires; SnO_2; Combustion synthesis; SHS

1. Introduction

Solid state sensors are one of the most effective tools for the development of devices used for monitoring and controlling of air quality, detecting trace concentration of toxic and combustible gases in air, medical diagnosis, and optimization of combustion [1–3]. It was found that the charge carrier concentration on the surface of metal-oxide semiconductors changes in accordance with the composition of the surrounding atmosphere [4]. Metal-oxide semiconductors such as SnO_2, TiO_2, ZnO, In_2O_3 and WO_3 are popular materials for solid state sensors because of their high response value, fast response, quick recovery, excellent stability and simplicity in fabrication [5–9]. Design and fabrication of metal-oxide semiconductor sensor materials have become one of the most active research fields in recent years.

Tin dioxide (SnO_2), an n-type semiconductor with a band gap of 3.6 eV at 300 K, has been widely utilized in many fields such as dye-sensitized solar cells [10], gas sensors for detecting leakage [1–4,9], transparent conducting electrodes [11], catalyst supports and electrochemical modifiers on electrodes, etc [12–15]. Recently, one-dimensional (1D) nanostructures such as nanobelts, nanofibers and nanowires have attracted much attention because of their high ratio of specific surface area and electronic structural changes due to quantum confinement. SnO_2 with 1D nanostructures can be applied as semiconductor sensors with high performance. Up to now, 1D nanostructured SnO_2 has been synthesized successfully by many methods including chemical vapor deposition (CVD) [16], the sol–gel template method [17], hydrothermal synthesis [14], the reaction sintering method [18], the co-precipitation method [19], the molten-salt method [9], etc. Although SnO_2 with 1D nanostructures were synthesized by many methods, there were no reports on synthesis of SnO_2 nanowires by combustion synthesis.

Combustion synthesis or self-propagating high temperature synthesis (SHS) represents a relatively new technique for the synthesis of inorganic materials [20–23]. The process takes advantage of the high exothermicity of reactions associated with the synthesis of highly stable compounds [24,25]. With low energy consumption and short reaction period, combustion synthesis is a facile technique to prepare SnO_2 nanowires, especially for

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large-scale industrial production. In the present study, novel SnO_2 nanowires were prepared by combustion synthesis using Al, SnO and Cu_2O as the starting powders. Based on the experimental results, the possible formation mechanism of SnO_2 nanowires was discussed.

2. Material and methods

Commercial powders of aluminum (Al, 99.5% purity, 100–200 mesh), stannous oxide (SnO, 99.5% purity, 200–300 mesh) and cuprous oxide (Cu_2O, 90.0% purity, 200～300 mesh) were used as the raw materials. The raw powders were mixed with stoichiometry and manually ground in an agate mortar in dry condition. Then the mixed powders were put in a clay–graphite crucible and placed in a combustion chamber after being dried at 120 °C for 2 h.

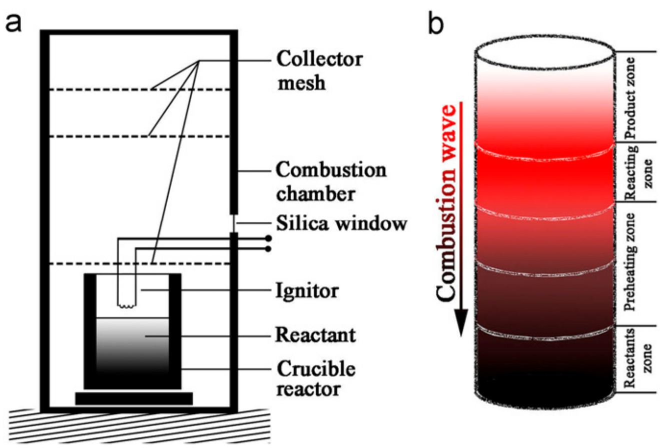

Fig. 1. Schematic diagram of (a) experimental apparatus and (b) combustion process for SHS.

The self-made experimental apparatus used for the synthesis of the nanowires was shown in Fig. 1(a). The powders of the mixed reactants were ignited in an air atmosphere using an electrically heated Alchrome wire coil in the stainless steel combustion chamber. The reaction was initiated at the top of the reactants and propagated through the whole unburned powders by means of combustion wave movement. The combustion process is shown in Fig. 1(b). Once the combustion mixture was ignited and the igniter turned off, the combustion reaction took place drastically and the reaction temperature reached a relatively high level (1500 °C $< T <$ 3500 °C) [23]. The high temperature needed for further synthesis was supplied by the self-sustained exothermic chemical reaction. During the short reaction period, the reactants were transformed into loosed flocculent products, which were sputtered and collected on the collector sieves with different meshes.

The X-ray diffraction (XRD) experiment was carried out on an X-ray diffractometer (MXP21VAHF, Mac Sci., Yokohama, Japan) using Cu Kα radiation to characterize the phase structure and composition. The microstructure and chemical composition of the as-prepared products on the collectors were investigated by using field emission scanning electron microscopy (FE–SEM, JSM-6700F, JEOL, Tokyo, Japan) equipped with energy dispersive X-ray spectroscopy (EDS, INCA, Oxford Instrument, England). Transmission electron microscopy (TEM, JEM-2010, JEOL, Tokyo, Japan) was applied to perform further observations and acquire the selected area electron diffraction (SAED) patterns and high resolution transmission electron microscopy (HRTEM).

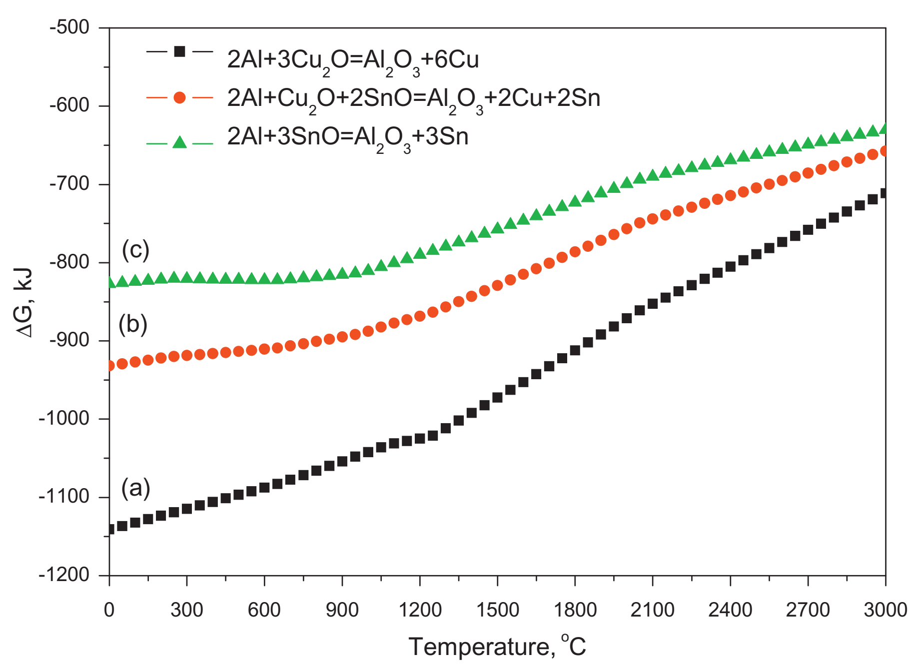

Fig. 2. Gibbs free energies for different aluminothermic reactions in the SnO–Cu_2O–Al system.