Optimal doping for enhanced SnO₂ sensitivity and thermal stability

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In metal-oxide gas sensors the relationship between nano-size and thermal stability is very challenging. Miniaturization of the sensitive material down to nano-scale and doping with noble metals has led to successful detection of analytes in ppb concentrations, but long term stability, which may be related to crystal growth, is still unresolved (Korotcenkov, 2004). The sensitivity of SnO₂, the most widely used metal-oxide for gas sensors, increases drastically with decreasing grain size from 20 to 5 nm (Rothschild et al., 2004). Preserving these sizes during sensor fabrication and operation is difficult since high process and operation temperatures (≈ 200 – 900 °C) are applied. A common practice to improve thermal stability is the use of dopants or additives. In fact, nanocomposite films of SnO₂ containing SiO₂ up to 74 wt% increased the sensor response to 500 ppm CO from 1.8 to 90 at 20 °C in air (Wu et al., 1999).

Here one-step synthesis of thermally stable and highly sensitive SiO₂-doped SnO₂ films is explored by FSP. Control and stabilization of the SnO₂ particle and neck size is obtained by varying the SiO₂ content during synthesis and direct deposition of these SnO₂-based films. Detailed film characterization is carried out to understand the role of SiO₂ for inhibiting SnO₂ grain and crystal growth as well as the role of primary particle and neck size on film sensitivity of EtOH, a common analyte in sensor development.

Figure 1 shows images and electron diffraction (ED) patterns of pure (insets a-c) and 15 wt% SiO₂-doped (insets d-f) SnO₂ particles collected downstream of the sensor substrate. Pure SnO₂ (Fig. 2a,b) consist of polyhedral nanoparticles while SiO₂-doped SnO₂ (Fig. 2d,e) has a finer grain texture (dTEM ≈ 5 nm) with a narrower size distribution. Despite the high SiO₂ content, its ED pattern (Fig. 2f) confirms the presence of ultrafine crystalline material. The crystal planes of pure SnO₂ (Fig. 2b) extend continuously and regularly through the particle.

In contrast, the SiO₂-doped exhibits crystalline (SnO₂) and amorphous (SiO₂) regions (Fig. 2e).

Rapid synthesis of highly sensitive SnO₂ layers doped with 0 – 15 wt% SiO₂ by direct flame aerosol deposition and in-situ annealing on sensor substrates was achieved. Doping with SiO₂ prevented SnO₂ grain and crystal growth leading to nanostructured and thermally stable sensor layers.

An optimal sensor performance with respect to EtOH sensing was discovered at about 2.5 wt% SiO₂-doping of SnO₂. There small monocrystalline SnO₂ primary particles were connected by small sintering necks.

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