Microstructural design of gas-sensing materials by utilizing various templates

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Strict meso- and macro-structural controls of gas-sensing materials are essential for developing the sophisticated gas sensors. However, bottom-up fabrication techniques for gas sensors have not so far been established sufficiently. Therefore, our recent studies have focused on the development of mesoporous and/or macroporous materials with different kinds of templates and the improvements of the gas-sensing properties.

Mesoporous oxides

Mesoporous (m-) SnO_2 powders have been prepared from sodium stannate by utilizing a self-assembly of different surfactants such as *n*-cetylpyridinium chloride and blockcopolymers in an aqueous solution as a mesopore template. The most important key to the drastic improvement of their thermal stability is to immerse the m-SnO_2 powders in a phosphoric acid aqueous solution before calcination and consequently loading of phosphorous-components on the surface of m-SnO_2 crystallites. The treatment enables us to prepare the m-SnO_2 powders with small crystallite size (2~3 nm in diameter) and large specific surface area (>300 m^2 g^{-1}) even after calcination at 600ºC. The semiconductor gas sensors fabricated with m-SnO_2 by screen printing showed relatively large responses to H_2 and NOx in air. The surface modification of conventional large oxide particles with m-SnO_2 was very effective in the improvement of gas-sensing properties. In addition, the loading of Pd or Au to m-SnO_2 resulted in the interesting electrical properties and gas-sensing properties. Recently, we have also attempted to fabricate the high qualitative m-SnO_2 films by electrophoresis of m-SnO_2 nanoparticles or direct-deposition of m-SnO_2 by utilizing electrochemical pH changes at near-electrode surface in an aqueous solution.

Macroporous materials

Macroporous (mp-) films have been fabricated by a modified sol-gel technique or a physical vapor deposition process employing a polymetheylmethacrylate (PMMA) microsphere film as a macropore template. Different kinds of gas sensors fabricated with the mp-semiconductor films (SnO_2 and In_2O_3 to detect H_2, NOx and H_2S), solid-electrolyte-type (Li_2CO_3-$BaCO_3$ to detect CO_2), photoluminescence-type (SnO_2 mixed with Eu_2O_3 to detect H_2 and NO_2) and quartz crystal microbalance-type ($BaCO_3$ to detect NO_2) showed larger gas responses as well as fast response and recovery speeds in comparison with those fabricated with a conventional film. In addition, mp-oxide powders have been prepared by pyrolysis of an atomized aqueous precursor solution containing an appropriate amount of PMMA microspheres. The semiconductor gas sensors fabricated with the well-developed mp-oxide powders by screen printing showed excellent gas-sensing properties in comparison with those fabricated with conventional powders without macropores. Recently, we have attempted the introduction of mesopores into the frameworks of the macroporous structures to improve the gas-sensing properties drastically.