Gas-sensing Properties of Photoluminescence-type Macroporous SnO_2-based Sensors

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Abstract

Macroporous (mp-) SnO_2 thick films mixed with 2.5 mol% Eu_2O_3 and 0~50 mol% metal oxide (mp-SnO_2(*m*M):Eu, M: constituent metal element (Mg, Ca, Sr, Ba or Li) of metal oxide (MO) mixed, *m*: the content of metal oxide (mol%)) were fabricated by a modified sol-gel method employing PMMA microspheres as a template. The photoluminescence (PL) intensity of mp-SnO_2(*m*M):Eu due to Eu^{3+} ions increased with mixing MO in the thick films. These films were subjected to the PL response measurements to various gases (acetone, NO_2 and O_2), and their PL intensities changed clearly upon exposure to these gases balanced with air or N_2. Response of PL to these gases tended to increase with an increase in their PL intensities, and the addition of 20 mol% MgO or $LiO_{0.5}$ was more effective in improvig their responses among all films tested.

Keywords: Gas sensor, Photoluminescence, Macropore, SnO_2, Eu

Introduction

Eu^{3+} has been extensively used as a high-effective emission center in various host materials, and the addition of Mg^{2+} species into the hosts has increased the PL intensity of Eu^{3+}. We have recently reported that mp-SnO_2(*m*Mg):Eu is very attractive as a PL-type acetone-sensing material, but the low magnitude of response and poor S/N ratio should be improved for its practical applications. Therefore, we have investigated effects of the addition of various metal oxides to the mp-SnO_2 mixed with Eu_2O_3 (mp-SnO_2:Eu) on the PL intensities and gas-sensing properties in this study.

Experimental

mp-SnO_2(*m*M):Eu were fabricated by a modified sol-gel method which employs PMMA microspheres with a diameter of 800 nm as a template and constituent metal chlorides as an oxide source. Typical PL spectra of the oxide thick films in air were investigated at room temperature (excitation

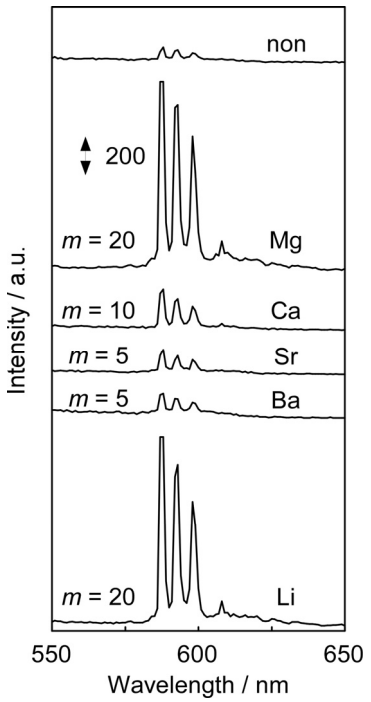

Fig. 1 PL spectra of mp-SnO_2(*m*M):Eu thick films excited by UV (260 nm) irradiation.

wavelength = 260 nm). Sensing properties of these thick films to acetone, NO_2 and O_2 were investigated by monitoring their PL properties at 588 nm in air or N_2. The magnitude of response was evaluated with ΔI, where ΔI was defined as the difference between I_0 and I of PL intensity in air (I_0) to that (I) in gas at 10 minutes after introducing gas.

Results and Discussions

Figure 1 shows PL spectra of mp-SnO_2:Eu and mp-SnO_2(*m*M):Eu thick films in air at an excitation wavelength of 260 nm. All films exhibited three strong peaks derived from $^5D_0 \rightarrow {}^7F_1$ transition at 588, 593 and 599 nm. The PL spectra of mp-SnO_2(*m*M):Eu were larger than that of mp-SnO_2:Eu, probably because the effective incorporation of Eu^{3+} into the host lattice [1] by the substitution of M^{n+} for the Sn^{4+} site. In addition, the substitution of Mg^{2+} or Li^+ may give a rise to the substantial number of oxygen vacancies, which might facilitate charge transfer from conduction band of the SnO_2 to energy state of Eu^{3+}, too [2].

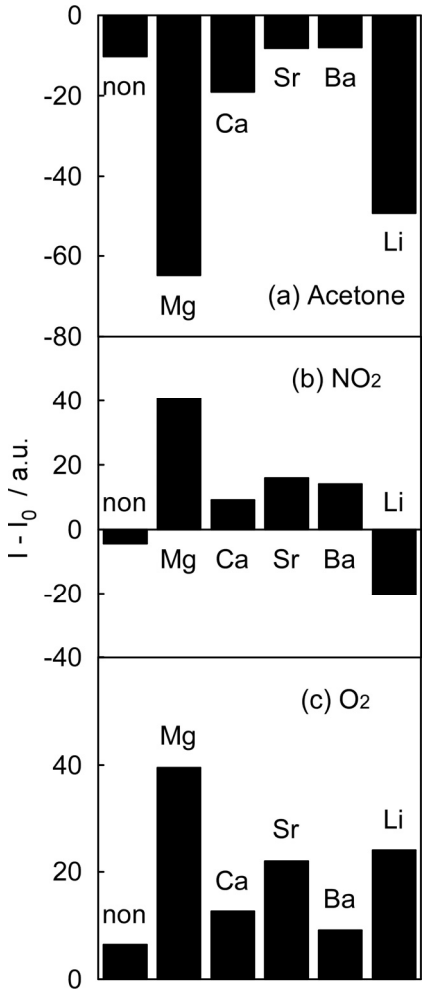

Fig. 2 Variation in ΔI (= I_0 – I) to (a) 30.9% acetone and (b) 29.1 ppm NO_2 in air, and (c) 30% O_2 in N_2 at 588 nm of mp-SnO_2(*m*M):Eu.

Variation in ΔI at 588 nm to various gases in air or N_2 of mp-SnO_2(*m*M):Eu films are shown in Fig. 2. PL responses of all films to these gases tended to increase with an increase in their PL intensity (see Fig. 1). The PL intensity of all films decreased upon exposure to 30.9% acetone in air, while that of all films increased upon exposure to 30% O_2 in N_2. These results show that the PL intensity may be largely dependent on the coverage of oxygen adsorbates on the oxide surface. On the other hand, the PL intensity of mp-SnO_2(*m*M):Eu (M = alkaline-earth metal) films increased and that of mp-SnO_2:Eu and mp-SnO_2(*20*Li):Eu decreased upon exposure to 29.1 ppm NO_2 in air. The chemisorption state of negatively-charged NO_2^- species on the oxide surface may be an important key to control the PL intensity of mp-SnO_2(*m*M):Eu. More detailed investigations on the surface and solid-state chemistry of mp-SnO_2(*m*M):Eu films are our future subjects to clarify their gas-sensing mechanism.

References

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