Preparation of Macroporous Eu-Doped Oxide Thick Films and Their Application to Gas Sensor Materials

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Keywords : gas sensor, photoluminescence, macropore, SnO₂, Eu

Eu³⁺ has been extensively used as a representative and high-effective emission center. And then the addition of Mg²⁺ species into the SnO₂ host can induce a remarkable increase of photoluminescence of Eu³⁺. Meanwhile we have recently reported that macroporous (mp-)SnO₂ sensors with submicron pores showed much higher H₂ and NOₓ responses. If Eu³⁺ could be incorporated at the surface of mp-SnO₂ and then these emission centers would be sensitive to certain gases, we may develop a new sensor utilizing photo-luminescent (PL) properties. The present study has been conducted on the basis of such an idea.

mp-SnO₂ thick films doped with 5 mol% Eu and 0~10 mol% Mg (Lmp-SnO₂(mMg):Eu, L: the size of PMMA microsphere used: 400 or 800 (nm), m: Mg content) were fabricated by a modified sol-gel method that employs PMMA microspheres as a template and constituent metal chlorides as an oxide source. Figure 1 shows variations in PL intensity at 588 nm in air of Lmp-SnO₂(mMg):Eu (L: both 400 and 800) as well as spin-coated (s-)SnO₂(mMg):Eu films prepared for comparative purpose. PL intensities from the most films increased with increasing the Mg-doping amount. This may be due to the increase of absolute Eu³⁺ incorporation as an emission source and oxygen vacancies as a sensitizer for the effective energy transfer in the SnO₂ host by the addition of Mg²⁺, as discussed by Fu et al. Also note that PL intensities of s-SnO₂(mMg):Eu films are comparable to those of Lmp-SnO₂(mMg):Eu, as shown in Fig. 1.

Acetone sensing properties of the Lmp-SnO₂(mMg):Eu thick films in air at 25°C were investigated by monitoring their PL properties at 588 nm. They decreased clearly upon exposure to acetone balanced with air. Here, the magnitude of acetone response was defined by R or ΔI, where R was the ratio (I₀/I) of PL intensity in air (I₀) to that (I) in acetone and ΔI the difference between I₀ and I. Figure 2 shows variations in R (= I₀/I) at 588 nm to 31% acetone in air of these films with the amount of Mg doped. They showed the maximum R at m=1, and beyond that the R value decreased. The s-SnO₂(10Mg):Eu film without macropores showed lower acetone response than Lmp-SnO₂(1Mg):Eu films, although the PL intensities were almost comparable to those of 400mp-SnO₂(10Mg):Eu films. This may be ascribed to the lower amount of sensitive Eu³⁺ near the surface of s-SnO₂(10Mg):Eu than that of Lmp-SnO₂(10Mg):Eu films with well-developed macropores. Variations in ΔI (= I₀ - I) at 588 nm to 31% acetone in air of these films are also shown in Fig. 3. The ΔI increased with increasing the amount of Mg doped, because the increase in Mg content brought the strong PL intensity, as shown in Fig. 1. Lmp-SnO₂(1Mg):Eu showed the highest R, while its S/N ratio was poor. The S/N ratio of acetone response was improved with increasing m, and LmpSnO₂(10Mg):Eu showed the highest ΔI with a good S/N ratio.

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Macroporous (mp-)SnO₂ thick films doped with 5 mol% Eu and 0~10 mol% Mg (Lmp-SnO₂(mMg):Eu, Lₘ: the size of PMMA microsphere used: 400 or 800 nm, m: Mg content) were fabricated by a modified sol-gel method that employs PMMA microspheres as a template and constituent metal chlorides as an oxide source. The photoluminescence (PL) intensity due to Eu³⁺ ions increased with increasing the Mg content in the thick films. These films were subjected to the PL response measurement to acetone, and their PL intensities decreased clearly upon exposure to acetone balanced with air. Among all the films tested, Lmp-SnO₂/(Mg):Eu showed the highest ratio (I₀/I) of PL intensity in air (I₀) to that (I) in acetone, irrespective of the size of macropores, while the signal/noise (S/N) ratio was low. On the other hand, ∆I (= I₀ - I) of Lmp-SnO₂(mMg):Eu was the highest at m = 10 with a high S/N ratio.

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1. Introduction
A series of rare earth metal ions are used as a luminescence center in various matrices. Among them, Eu³⁺ has been extensively used as a representative and highly-effective orange or red emission center. The excitation wavelength above 340 nm (ca. 3.6 eV) yields an efficient energy transfer between the host SnO₂ lattice and Eu⁶⁺. However, due to the large difference of the radius and charge between Eu³⁺ (95 pm) and Sn⁴⁺ ions (74 pm), it is difficult for Eu³⁺ ions to enter the lattice of SnO₂, so that the energy transfer from the host to Eu³⁺ ions is limited, leading to poor luminescence of the phosphor (2)(3). Fu et al. reported that it is difficult for Eu³⁺ ions to enter the lattice of SnO₂, so that the energy transfer from the host to Eu³⁺ ions is limited, leading to poor luminescence of the phosphor (2)(3). By the way, we have recently reported that macroporous (mp-)SnO₂ sensors with well-developed submicron pores showed much higher H₂ and NOx responses, compared with a conventional SnO₂ sensor (4). If Eu³⁺ could be incorporated at the surface of macroporous SnO₂ and then these emission centers would self-assemble into a three dimensional (3-D) array by sedimentation during the drying process.

2. Experimental
2.1 Preparation of PMMA Thick Films Eu-doped mp-SnO₂ films were fabricated by the following procedure. Non-crosslinked polymethylmethacrylate (PMMA) microspheres with a nominal uniform particle size of 400 and 800 nm (Soken Chem. & Eng. Co., Ltd., MP1000 and MP1600, respectively) and a triblockcopolymer (BASF Corp., P123: (EO)₂₀(PO)₇₀(EO)₂₀, MW = 5800) were used as a template and a dispersant, respectively. The PMMA microspheres and triblockcopolymer (0.15 g of P123 for MP1000 (2.0 g) and 0.05 g of P123 for MP1600 (3.0 g)) were dispersed in 5.0 g ultrapure water (resistivity higher than 18.2 MΩ cm). To ensure dispersing of PMMA microspheres, the suspension was sonicated by an ultrasonic device for 30 min. After the suspension was dip-coated onto an alumina substrate, they were dried in ambient air at room temperature (ca. 25°C). PMMA microspheres could self-assemble into a three dimensional (3-D) array by sedimentation during the drying process.

2.2 Fabrication of Oxide Thick Films with and without Macropores The oxide precursor solution was prepared by dissolving 4.5 g SnCl₂·2H₂O (97.0 vol%) in 10 ml methanol (99.8 vol%) with an appropriate amount of EuCl₃·6H₂O (99.9 vol%) and MgCl₂·6H₂O (98.0 mol%). All of them were provided by Kishida Chemical Co., Ltd. The precursor solution was permeated into the openings of the 3-D array of PMMA microspheres in vacuo. And they were subjected to heat treatment (1000°C for 2 h after 400°C for 2 h, heating rate: 5°C min⁻¹) in flowing air to decompose the core PMMA microspheres and then to form ordered macroporous oxide frameworks. As a result, we obtained Lmp-SnO₂:Eu and Lmp-SnO₂(mMg):Eu thick films (Lₘ: PMMA particle size: 400 or 800 nm, the amount of doped Eu: 5 mol%, m: the amount of doped Mg: 0~10 mol%). For comparative purpose, spin-coated (s-) SnO₂:Eu and s-SnO₂(10Mg):Eu (m = 0

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and $m = 10$, respectively) thick films without macropores were fabricated with fine powders prepared by thermal decomposition of precursor solution without PMMA, followed by heat treatment at 1000°C for 2 h.

2.3 Characterization of Oxide Thick Films Morphology of oxide thick films were observed by a scanning electron microscope (SEM, Hitachi, S-2250N). PL spectra of the oxide thick films in air and 31% acetone balanced with air and these responses to 31% acetone balanced with air were measured with a fluorescence spectrometer equipped with a 450 W xenon lamp as the excitation source (JASCO, FP-6500) at room temperature. The magnitude of acetone response was defined by $R$ or $\Delta I$, where $R$ was defined as the ratio ($I_0/I$) of PL intensity in air ($I_0$) to that ($I$) in acetone at 10 minutes after introducing acetone and $\Delta I$ the difference between $I_0$ and $I$.

3. Results and Discussion

Figure 1 shows SEM photographs of representative $L\text{mp-SnO}_2(m\text{Mg}):\text{Eu}$ ($L = 400$ and 800, $m = 5$ and 9) thick films. Well-developed 3D-spherical macropores were confirmed in the films\(^{3(6)}\). The morphology of macropores reflected that of PMMA microspheres used, while the size of macropores was slightly reduced. In addition, the thickness of $400\text{mp-SnO}_2(m\text{Mg}):\text{Eu}$ (9–11 µm) was slightly thinner than that of $800\text{mp-SnO}_2(m\text{Mg}):\text{Eu}$ (18–21 µm). Other films also showed macroporous morphology similar to them, while the shell of spherical macropores tended to be closed, i.e. hollow microsphere likely formed, with increasing the amount of Mg doped, especially for $400\text{mp-SnO}_2(m\text{Mg}):\text{Eu}$ series.

Figure 2 shows PL spectra of $400\text{mp-SnO}_2(m\text{Mg}):\text{Eu}$ ($m = 1$ and 10) thick films exited by UV (260 nm) irradiation. PL spectra from Mg-undoped $L\text{mp-SnO}_2(m\text{Mg}):\text{Eu}$ are not much different from those from $L\text{mp-SnO}_2(m\text{Mg}):\text{Eu}$, while PL intensities from the most films increased with increasing the Mg-doping amount, irrespective of the particle size of PMMA microspheres used. This may be due to the increase of absolute Eu\(^{3+}\) incorporation as an emission source and oxygen vacancies as a sensitizer for the effective energy transfer in the SnO\(_2\) host by the addition of Mg\(^{2+}\), as discussed by Fu et al.\(^{(2)}\). Also note that the PL intensities of s-SnO\(_2(m\text{Mg}):\text{Eu}\) films are comparable with...
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Figure 4 shows response transients of (a) $\text{mp-SnO}_2(1\text{Mg})$:Eu, (b) $\text{mp-SnO}_2(10\text{Mg})$:Eu and (c) $\text{s-SnO}_2(10\text{Mg})$:Eu to 31% acetone in air at 25°C (excitation wavelength = 260 nm, measurement wavelength = 588 nm). Those of $\text{Lmp-SnO}_2(m\text{Mg})$:Eu, as shown in Fig. 3.

Figure 4 shows response transients of $\text{Lmp-SnO}_2(m\text{Mg})$:Eu ($m = 1$ and $m = 10$) and $\text{s-SnO}_2(m\text{Mg})$:Eu ($m = 10$) thick films to 31% acetone in air at 25°C (excitation wavelength: 260 nm, measurement wavelength: 588 nm). Upon exposure to acetone balanced with air, the PL intensities decreased clearly, and the PL intensities recovered to the original intensities just after the flowing gas was changed to air. Such response behavior was observed with all the films. The exact sensing mechanism is not clear at present, but the PL properties of $\text{Eu}^{3+}$ ions at the surface of $\text{SnO}_2$ may be deactivated when the acetone molecules were adsorbed on the ions and/or the $\text{SnO}_2$ matrix. However, the signal/noise (S/N) ratio increased with increasing $m$ and the difference in the emission intensity between in air and in acetone increased with increasing $m$, because their PL intensities tended to increase with increasing the Mg content, as shown in Fig. 3. On the other hand, their spherical macropore size reflecting the diameter of PMMA microspheres did not have a significant influence on the S/N ratio and response/recovery speeds. However, it was obvious that the introduction of macroporous structure resulted in improvements in both the response speed and the magnitude of the response (compare among the response transients of three sensors shown in Fig. 4).

Figure 5 shows variations in $R (= \frac{I_0}{I})$ to 31% acetone in air of $\text{Lmp-SnO}_2(m\text{Mg})$:Eu and $\text{s-SnO}_2(m\text{Mg})$:Eu thick films with the amount of Mg doped.

Figure 6 shows variations in $\Delta I (= I_0 - I)$ at 588 nm to 31% acetone in air of $\text{Lmp-SnO}_2(m\text{Mg})$:Eu and $\text{s-SnO}_2(m\text{Mg})$:Eu thick films with the amount of Mg doped.

Figure 7 shows variations in response at 588 nm in air of $\text{800mp-SnO}_2(10\text{Mg})$:Eu thick films with acetone concentration.
the PL intensity at \( m = 10 \) was the highest among all the films. And then the s-SnO\(_2\):(10Mg):Eu thick film without macropores showed lower acetone response than Lmp-SnO\(_2\):(10Mg):Eu films, although the PL intensities were almost comparable to those of 400mp-SnO\(_2\):(10Mg):Eu films. This may be ascribed to a lower amount of sensitive Eu\(^{3+}\) near the surface of s-SnO\(_2\):(10Mg):Eu than that of Lmp-SnO\(_2\):(10Mg):Eu films with well-developed macropores, as shown in Fig. 1. Variations in \( \Delta I (= I_0 – I) \) at 588 nm to 31% acetone in air of these films are also shown in Fig. 6. The \( \Delta I \) increased with increasing the amount of Mg doped, because the increase in Mg content brought the strong PL intensity, as shown in Fig. 3. The S/N ratio of Lmp-SnO\(_2\):(10Mg):Eu films was the highest among all the films tested. Therefore, acetone concentration dependence of the response at 588 nm in air of the 800mp-SnO\(_2\):(10Mg):Eu thick film was further investigated. As shown in Fig. 7, both R and \( \Delta I \) are proportional to acetone concentration in air in the range of 5–31%, but their responses to acetone of lower concentrations in air seems to be insufficient. Therefore, further efforts should be directed to improving the S/N ratio and the magnitude of response of Lmp-SnO\(_2\):(mMg):Eu, by optimizing the composition as well as macroporous structure.

4. Conclusion

Acetone sensing properties of Lmp-SnO\(_2\):(mMg):Eu thick films in air at 25°C were investigated by monitoring their PL properties at 588 nm (excitation wavelength = 260 nm). Their PL intensities increased with increasing the amount of Mg, \( m \), in Lmp-SnO\(_2\):(mMg):Eu, probably due to the increases of both the amounts of Eu\(^{3+}\) incorporated and oxygen vacancies in the SnO\(_2\) host by the addition of Mg\(^{2+}\): Lmp-SnO\(_2\):(1Mg):Eu showed the highest R, while its S/N ratio was poor. The S/N ratio of acetone response was augmented with increasing \( m \), and Lmp-SnO\(_2\):(10Mg):Eu showed the highest \( \Delta I \) with a good S/N ratio.

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References


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