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Impedancemetric acetylene gas sensing properties of Sm–Fe-based perovskite-type oxide-based thick-film device

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ABSTRACT

Perovskite-type $Sm_{1-x}Ca_xFeO_3$ (x = 0, 0.05, 0.20, 0.50, 0.75, 1.0) powders as sensor materials were prepared by a wet-chemical route using a polymer precursor method at 750 °C. A perovskite-type oxide thick-film device prepared by a screen-printing method was used for an acetylene (C_2H_2) sensor for which outputs were measured by AC impedance spectroscopy at 400 °C. Although sensitivities of the devices using oxides with Ca^{2+} substitution were decreased because of reduction in the amount of impedance change between air and sample gas, the device without Ca^{2+} substitution showed extremely high response at a low frequency. According to Nyquist's plots of the $SmFeO_3$ device, this is attributed to the fact that impedance of charge transfer from the surface reaction was taken at a low frequency. It was also found that the sensor devices showed good selectivity to interference gases.

1. Introduction

Perovskite-type oxides are functional inorganic materials that have a wide range of applications and various interesting properties including catalytic activity [1], ion conductivity [2–4,8], dielectric [5] and photoluminescence [6]. Their properties are further improved by substituting another metal in the A- and/or B-site, and such materials can be used in many fields as oxidation catalysts [7–10], photocatalysts [11,12], electrode catalysts [13], and electrolytes [14–16]. The materials can also be used as sensing materials for detection of CO [17], NO_x [18], NH_3 [19], hydrocarbon [20], and VOC [21]. Mixed metal oxides such as perovskite-type oxides have so far been prepared by a solid reaction method; however, high temperature sintering and homogenous crushing method have been required in this method. Thermal decomposition such as cyano-complex decomposition reported by Travelsa et al. enabled homogenous nano-powder to be prepared at a lower temperature [22]. Moreover, other wet methods such as methods using a polymer precursor [23], a reverse micelle [24] and a reverse coprecipitation [25] enabled synthesis at a low temperature for the thermal decomposition route. Also, Mori et al. reported that catalyst properties of $SmFeO_3$ were affected by the synthesis method and sintering temperature [26].

Recently, development of a hydrocarbon sensor has been accelerating due to tightening regulations for hydrocarbon gases, such as Euro 6. Also, rules for gases generated from industry and building products have become stricter. C_2H_2, the detection gas in this study, is an important industry gas as it can be used for many fields such a starting material of benzene and poly-acetylene and as a fuel for metal welding. Moreover, C_2H_2 is generated from insulating oils of oil-immersed transformers, and a C_2H_2 sensor could therefore be utilized as a maintenance marker of the transformer. However, there have been few studies on a C_2H_2 sensor [27–30].

We have reported that an $SmFeO_3$ thin-film device showed the highest sensitivity to C_2H_2 among the perovskite $SmMeO_3$ (Me = Cr, Mn, Fe, Co) thin-films prepared in our previous study [31]. Although $SmFeO_3$ is a good sensor material, it has low conductivity, which is a disadvantage for application. In this study, we prepared $Sm_{1-x}Ca_xFeO_3$ with an oxygen defect to improve its conductivity. An oxide thick-film device using perovskite-type oxide powder synthesized by a polymer precursor was prepared by screen-printing, and then the sensing properties to C_2H_2 of the devices were investigated. We found that the $SmFeO_3$ device had high response in resistance and that $SmFeO_3$ with Ca^{2+} substitution showed response in capacitance.

2. Experimental

Fig. 1 shows the process for preparation of the perovskite-type oxide $Sm_{1-x}Ca_xFeO_3$ (x = 0, 0.05, 0.20, 0.50, 0.75, 1.0) powders by a polymer precursor method in which stoichiometric metal nitrates were dissolved in ethylene glycol (EG) solution. Then acetyl acetone (AcAc; 4A mol) and polyvinylpyrrolidone (PVP; 3.75 wt.% of total materials) as a coordination agent and a polymer additive, respectively, were added to this solution. The prepared polymer precursor solution was evaporated at 120 °C, pre-calcinated at

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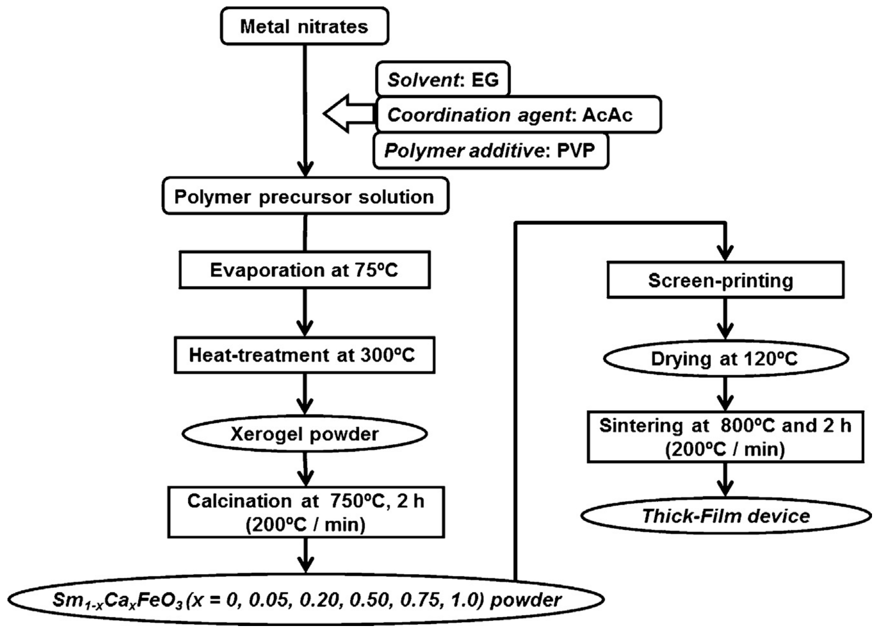

Fig. 1. Preparation and characterization processes of $Sm_{1-x}Ca_xFeO_3$ ($x = 0, 0.05, 0.20, 0.50, 0.75, 1.0$) thick-film devices.

300 °C, and finally calcinated at 750 °C to form oxide powder. The heat-treatment temperatures were determined by TG-DTA. Crystalline structures of the powders were elucidated using XRD (JEOL JDX3500K) and chemical states of the oxide surfaces were characterized by XPS (SHIMADZU KRATOS AXIS-NOVA). The XPS spectra were measured under the follow conditions: X-ray source (monochrome Al Kα) and all binding energy values were referenced by the C 1s line at 284.5 eV. To prepare a thick film, the obtained oxide powder was mixed with PVP and α-turpentine and was screen-printed on a gold interdigitated Al_2O_3 substrate (10 mm × 5 mm × 1 mm). Finally, the as-printed film was sintered at 800 °C for 1 h in air.

The measurement apparatus and an image of the actual device are shown in Fig. 2. The prepared device was attached to a gold wire (φ = 30 μm) with gold paste and it was connected with an LCR meter (HIOKI 3532-50). Gas sensing properties of the device were investigated by the AC impedance method with applied voltage of 0.5 V under the follow conditions. Measurement temperature was set at 400 °C after heat cleaning at 600 °C in air to remove contaminates from the surface. Gas sensing properties of the device were investigated by the AC impedance method between 50 Hz and 5 MHz at

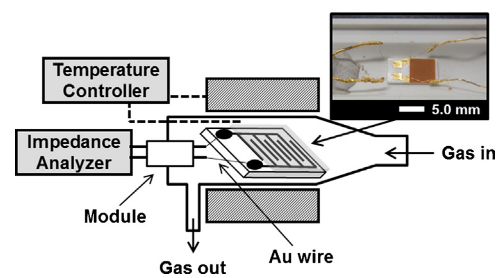

Fig. 2. Schematic diagrams of measurement apparatus and image of the actual device.

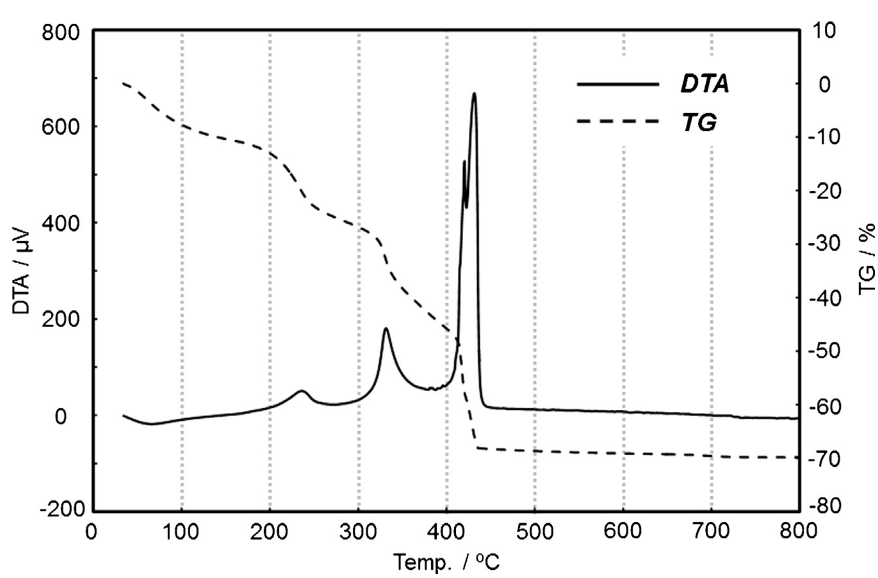

Fig. 3. TG-DTA curves of Sm–Fe precursor in air.