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Fabrication of thermochromic $SmNiO_3$ film deposited by spin-coating method from aqueous solution

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$SmNiO_3$ (SNO) films were fabricated on quartz substrates by a spin coating method using Sm–Ni based aqueous solution. SNO film annealed at 700°C showed low crystallinity, while film annealed at 800°C showed high crystallinity. The transmittance of these films did not vary above or below the transition temperature of SNO. SNO films were also fabricated on an SNO seeding layer, with crystalline SNO film obtained at an annealing temperature of 700°C. The transmittance of the resulting film changed above and below the transition temperature of SNO.

Key-words : $SmNiO_3$, Film, Thermochromic, Transmittance

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1. Introduction

$SmNiO_3$ (SNO) undergoes a reversible thermally induced metal-semiconductor transition at around 123°C, resulting in great changes in its electrical properties.[1)–4)] The transition temperature of SNO can be controlled by doping with other rare earth cations,[4),5)] thus making it suitable for applications in thermal switches and thermochromic windows.

The electrical properties of SNO films fabricated using vapor phase methods have been evaluated in previous reports.[5)–7)] However, the optical properties of SNO films have not yet been investigated. This investigation aims to fabricate SNO film using chemical solution deposition and evaluate its optical properties, including thermochromic properties.

Previously, perovskite lanthanium nickel oxide (LNO) films, the composition of which is similar to that of SNO, were fabricated by spin coating methods from aqueous or ethanol solutions.[8),9)] In these reports, lanthanum acetate and nickel nitrate were employed as starting materials, furthermore LNO film was fabricated easily. Hence, with reference to the fabrication of such LNO films,[8),9)] aqueous solutions of samarium acetate and nickel nitrate were employed in this investigation to fabricate SNO films using a spin coating method. The optical transmittance of the obtained SNO films was evaluated at various temperatures.

2. Experimental procedure

Nickel nitrate [$Ni(NO_3)_2{\cdot}H_2O$] and samarium acetate [$Sm(CH_3COO)_3$] starting materials were dissolved in distilled water to produce a $0.5\,M\,L^{-1}$ solution with an Sm:Ni elemental ratio of 1:1. 0.1 wt% Poly vinyl alcohol (PVA) was mixed into the precursor solution to increase its viscosity. Precursor $SmNiO_3$ thin films were then fabricated on quartz substrate by a spin-coating method using the above mentioned precursor solution. The films were dried at 150°C for 10 min and then pre-annealed at 400°C for 10 min to remove residual organics. These processes were repeated 10 times, after which the films were annealed at 700–1000°C for 2 h using an electric furnace.

The crystal structure of the specimens was determined using X-ray diffraction (XRD, Miniflex-II; Rigaku Corp., Japan) at room temperature using Cu Kα radiation. The microstructure of the resulting films was observed using scanning electron microscopy (SEM, S-3200N; Hitachi Ltd., Japan), and elemental analysis of the films was carried out by energy dispersive X-ray analysis (EDX) using a JEOL JED-2300. Differential scanning calorimetry (DSC) was performed on SNO powder using a DTG-60 calorimeter (Shimadzu, Kyoto, Japan), at a ramp rate of 5°C/min. The transmittance of the films was measured using a Hitachi UV-3410U spectrophotometer at a wavelength range of 200–2600 nm.

3. Results and discussion

The SNO precursor films were deposited by spin-coating from the prepared Sm–Ni based solution and then annealed at 700 to 1000°C. **Figure 1** shows XRD patterns for the resulting films. Films annealed at 700 and 800°C consisted of SNO as the main phase and Sm_2O_3 as a secondary phase, with the film annealed at 700°C having low crystallinity. Films annealed at 900 and 1000°C showed SNO, Sm_2O_3, and NiO mixed phases, indicating that these annealing temperatures were too high to maintain the SNO phase, which partially decomposed to Sm_2O_3 and NiO. The thickness of the annealed films was about 600 nm, as evaluated by SEM observations. Elemental analysis by EDX revealed that the Sm/Ni ratio was close to 1 (~1.07) in all obtained films.

Figure 2 shows transmittance spectra for the SNO film annealed at 800°C, measured at room temperature and 150°C, above and below the transition temperature, respectively. The observed transmittance of the film did not vary between the two temperatures. This behavior was also observed for the SNO film annealed at 700°C.

Previous reports have shown that oxygen defects in the SNO lattice are generated by high temperature heat-treatment at a low oxygen pressure.[10)] In order to confirm oxygen defects in the

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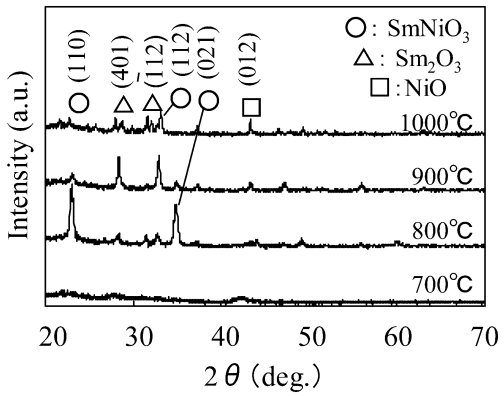

Fig. 1. XRD patterns for SNO films annealed at 700–1000°C.

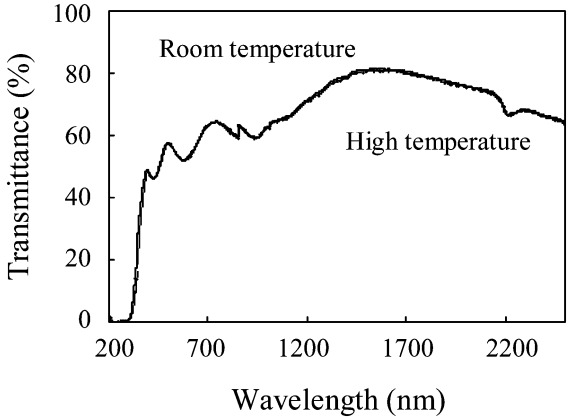

Fig. 2. Transmittance spectra for SNO film annealed at 800°C, measured at RT (25°C) and 150°C.

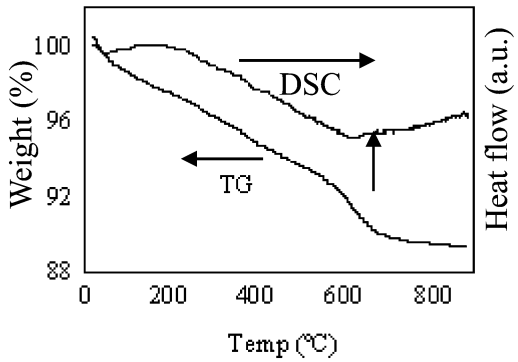

Fig. 3. DSC curve for SNO precursor powder.

SNO produced in this investigation, TG-DSC measurement was carried out on sample powder prepared by treating precursor solution at 400°C. **Figure 3** presents DSC curves for this precursor SNO powder. From the TG curve, a drastic decrease in sample weight was observed above 650°C. This result suggested that oxygen defects were generated in the SNO lattice above 650°C. The DSC curve revealed a slight exothermic peak at 680°C, attributed to crystallization of SNO at this temperature. The present crystalline SNO film was fabricated at 800°C, and thus it was assumed that this annealing temperature had been too high to produce a SNO film without oxygen defects.

To lower the annealing temperature, SNO films were also fabricated on an SNO seeding layer as a self-crystallization layer.

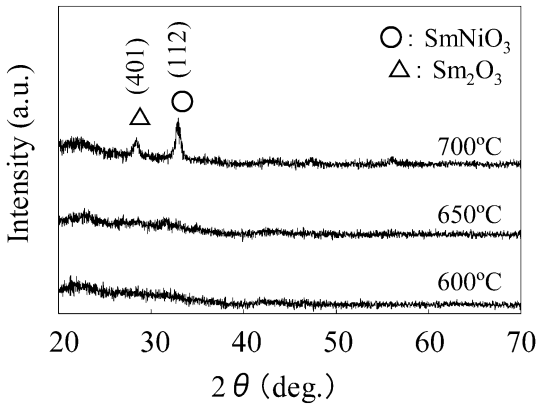

Fig. 4. XRD patterns for SNO films deposited on SNO seeding layer and annealed at 600–700°C.

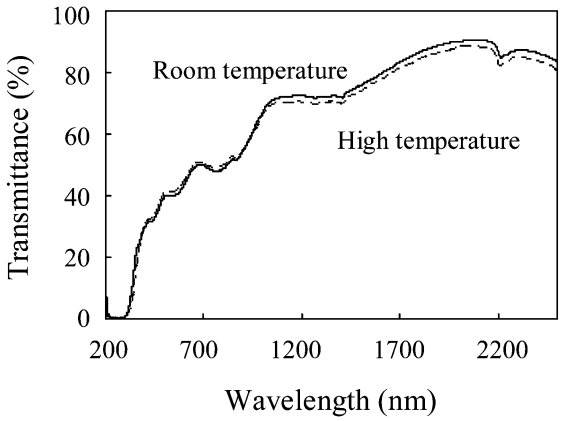

Fig. 5. Transmittance spectra for SNO film on SNO seeding layer annealed at 700°C, measured at RT (25°C) and 150°C.

In previous studies, seeding layers have been used to lower crystallization temperature during deposition of thin films.[11),12)] The SNO seeding layer was obtained by annealing a single spin-coated layer of precursor film at 800°C. Ten layers of SNO precursor film were then spin-coated onto the seeding layer and annealed at 600–700°C. **Figure 4** depicts XRD patterns for the obtained films. No diffraction peaks were observed for films annealed at or below 650°C, while the film annealed at 700°C consisted of a SNO main phase and a Sm_2O_3 secondary phase. The crystallinity of this SNO film with seeding layer was higher than that of the film without the seeding layer also annealed at 700°C (see Fig. 1). Thus, SNO film with high crystallinity was obtained at a low annealing temperature of 700°C using a seeding layer.

Figure 5 shows transmittance spectra for the SNO film deposited onto a seeding layer and annealed at 700°C measured at room temperature and 150°C, above and below the SNO transition temperature, respectively. Transmittance of the film varied within the measured wavelength range of 1200–2600 nm between RT and 150°C, exhibiting a 1.5% change in transmittance at 2000 nm. This thermochromic property of the SNO film was attributed to its low fabrication temperature creating fewer oxygen lattice defects. Furthermore, the thermochromic property was found to be reversible.

Figure 6(b) shows an SEM image of the surface of the SNO film deposited onto a seeding layer and annealed at 700°C. In order to confirm the seeding layer effect, SEM was carried out on

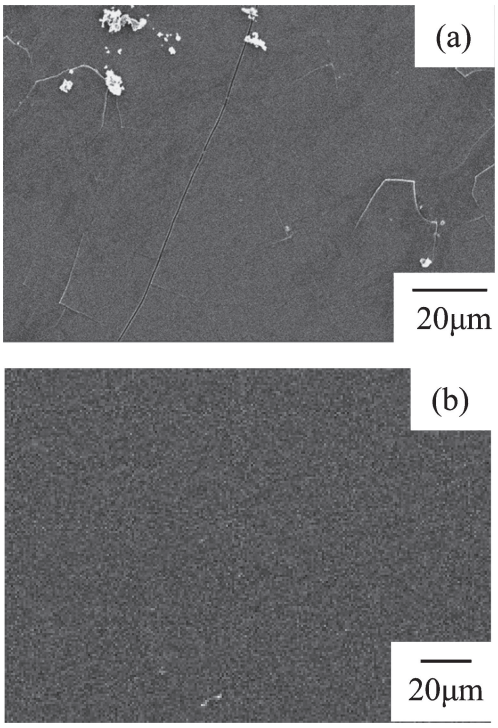

Fig. 6. SEM images of SNO film annealed at 700°C with SNO seeding layer, and SNO film annealed at 700°C without SNO seeding layer.

the SNO film annealed at 700°C without a seeding layer, shown in Fig. 6(a). The SNO film with seeding layer showed a flat surface and high density, while the SNO film without seeding layer had many visible cracks and pores. These results revealed that the seeding layer not only lowered the crystallization temperature of the fabricated SNO films, but also caused them to form a flat and crack-free surface.

We also fabricated an SNO film with seeding layer in oxygen atmosphere at 700°C. The photochromic properties of this SNO film were similar to those of SNO film with seeding layer annealed in air. Typically, $SmNiO_3$ powder has few oxygen defects when synthesized under a high oxygen pressure (5.0 MPa).[10] This pressure is much higher than the 101.3 kPa (atmospheric pressure) used to fabricate the present SNO films, which had a large amount of oxygen defects. Oxygen defects in SNO causes low electron conductivity at the high temperature phase of the SNO,[13] which assumes to be attributed to low carrier density. Low carrier density causes low reflectivity of near-IR to IR region light. Thus, SNO film should be fabricated under high oxygen pressure to form a SNO lattice without oxygen defects.

4. Conclusion

Polycrystalline $SmNiO_3$ films were fabricated by spin coating of a Sm–Ni based aqueous solution. Films fabricated on quartz substrate at annealing temperatures of 700 and 800°C consisted of a SNO main phase and Sm_2O_3 secondary phase. The transmittance of these films did not vary between temperatures above and below the transition temperature because of oxygen defects in the SNO lattice. To decrease the annealing temperature, SNO films were fabricated on an SNO seeding layer. As a result, crystalline SNO film was obtained at an annealing temperature of 700°C, a much lower crystallization temperature than that obtained without the seeding layer. The SNO film with a seeding layer annealed at 700°C exhibited optically thermochromic properties, and showed a flat surface with high density.

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