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Electrical screening of ternary NiO–Mn_2O_3–Co_3O_4 composition spreads

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Abstract

The compositional optimization of infrared-transparent conducting oxides was performed using high throughput screening of combinatorial libraries. Complete ternary composition spreads of NiO–Mn_2O_3–Co_3O_4 alloys were deposited onto conducting Nb-doped $SrTiO_3$ substrates using the pulsed laser deposition technique. Resistance–temperature relations of each composition in the spread were determined using a custom-designed scanning probe. The binary $NiCo_2O_4$ oxide showed the lowest electrical resistivity of about 0.1 Ω cm but unacceptably large resistance–temperature dependence (3.5%/°C). Electrically conducting ternary alloys along the line $Mn_{0.45}Ni_{0.63}Co_{1.92}O_4$–$Mn_{0.60}Ni_{0.72}Co_{1.68}O_4$–$Mn_{0.69}Ni_{0.81}Co_{1.50}O_4$ exhibited much lower temperature sensitivity (of about 1.5%/°C) as well as electrical resistance comparable to that of $NiCo_2O_4$. From this screening we propose new compounds for the thin-film ITCO sensors.

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Keywords: Infrared-transparent oxide (ITCO); High-throughput combinatorial methods; Composition spreads; PLD; Scanning probe

1. Introduction

Recently Ni–Co oxides with spinel crystal structure AB_2O_4 have attracted attention as infrared-transparent-conducting oxides or ITCOs [1]. Utilization of such IR-transparent conducting oxides includes

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optical coatings for flat panel displays, infrared sensors, and solar cells [2,3].

The ITCO materials must satisfy conflicting requirements of high conductivity and infrared transparency. Infrared transmission of highly conducting n-type oxides is severely limited by free carrier absorption [4]. The p-type hopping semiconductors, such as Co_3O_4 and NiO, typically show excellent infrared transmissivity but markedly lower conductivity when compared to their n-type counterparts. In addition, hopping conductivity follows the relation $\sigma = \sigma_0 \exp(-E_a/kT)$, and due to the relatively large activation energy E_a it exhibits unfavorable temperature dependence [5].

The binary oxides containing Co and Ni give higher conductivities, up to 5 orders of magnitude more than either of the two end members [6]. It was suggested that ternary spinel alloys could provide even higher conductivity and lower temperature dependence, while retaining adequate transmissivity at long wavelengths [7].

Ternary spinel oxides containing manganese, cobalt and nickel exhibit p-type hopping electrical conduction and an optically transparent window from 6 to 14 μm wavelength [8]. Their electrical conductivity and hopping activation energy strongly depend on chemical composition. Therefore, in order to be used for the ITCO devices, these ternary alloys must be screened for the most advantageous electrical transport characteristics.

Performing such materials optimization is a very labor- and time-intensive process. Fortunately, recent advances in the thin film technology made possible simultaneous fabrication and characterization of large libraries of complex oxide alloys in combinatorial manner. This paper describes fabrication and electrical screening of a full ternary Mn_2O_3–NiO–Co_3O_4 oxide system. The composition spread films were deposited onto a conducting Nb-doped $SrTiO_3$ substrate. Electrical conductivity of the oxide films was determined using a conducting scanning probe. The temperature of the substrate was varied, elucidating the conductivity–temperature relations of each composition.

2. Experimental

The continuous ternary composition spread samples were fabricated by pulsed laser deposition (PLD) using a moving shutter and a rotating substrate holder. The sample consists of the three interpenetrating and intermixed strips of elemental oxides rotated with respect to each other by 120° as shown in Fig. 1. Thus the obtained sample contains a full range of ternary oxide compositions (regular triangular area in the center) as well as three separate full binary oxides spreads.

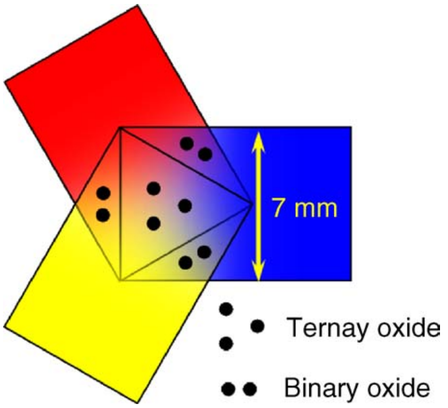

Fig. 1. Schematic drawing of the ternary continuous composition spread sample.

Each strip was deposited in multiple steps to insure atomic mixing of the cations. First a single wedged strip of Mn_2O_3 was deposited with the help of a moving shutter and the pulsed ablation with deposition rate of approximately ~0.05 Å per pulse. The tapered strip had a thickness ranging from 0 to approximately 4 Å. Then the substrate was rotated and the Co_3O_4 strip was deposited in the same way. Finally, the graded-thickness NiO strip was deposited. After all three individual wedged strips were formed the process was repeated to eventually obtain 100 nm thick composition spreads.

The films were deposited onto the 0.8% Nb-doped $SrTiO_3(100)$ substrates purchased from Shinkosha company. The temperature of the substrate was maintained at 400 °C during the course of the deposition (11 h). After deposition the sample was annealed at 600 °C for 30 min. The oxygen pressure during deposition and post-annealing treatment was 10^{-4} Torr.

The deposition rate for each unary oxide was determined prior to fabrication of the ternary maps, and the number of pulses for forming each strip was adjusted to obtain the ternary film of a uniform