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Growth mechanism of single-crystalline NiO thin films grown by metal organic chemical vapor deposition

Teuku Muhammad Roffi*, Shinji Nozaki, Kazuo Uchida

Department of Engineering Science, The University of Electro-Communications, 1-5-1 Chofugaoka, Chofu, Tokyo 182-8585, Japan

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ABSTRACT

Nickel oxide (NiO) thin films were grown by atmospheric-pressure metal organic chemical vapor deposition (APMOCVD). Growth was carried out using various growth parameters, including the growth temperature, the input precursor (O_2/Ni) ratio, and the type of substrate material. Effects of the growth parameters on the structural and electrical properties of the films were investigated. X-ray diffraction analysis revealed that the crystal structure and quality were strongly affected by the growth temperature and the type of substrate material. At an optimized growth temperature, single-crystalline NiO films were grown on MgO(100) and MgO(111) substrates in a cube-on-cube orientation relationship, while on an Al_2O_3(001) substrate, the film was grown in the NiO[111] direction. The use of MgO substrates successfully suppressed the formation of twin defects, which have been frequently reported in the growth of NiO. The difference in the formation of the twin defects on MgO and Al_2O_3 substrates was discussed. It was observed that the resistivity dependence on crystal quality was affected by the choice of substrate material. The effects of the precursor ratio on the transmittance and resistivity of the films were also investigated. Improved transparency in the visible wavelength region and higher conductivity were found in films grown with higher O_2/Ni ratios.

1. Introduction

Nickel oxide (NiO) is a wide-bandgap, p-type semiconductor with unique properties, including high optical transparency and electrical conductivity. It has been studied for various applications, including transparent conducting oxides, light emitting diode (LED), and resistive random access memory (RRAM) [1–3]. In addition, it has been recently studied as a promising material for transparent electronics because most oxides show n-type conductivity. The p-type conduction in NiO was reported to occur by incorporation of native defects, i.e., nickel deficiencies, which generate holes [4]. To realize a functional NiO material, synthesis of high-quality NiO and understanding of its fundamental characteristics are very important. However, growth of NiO has been limited to the formation of polycrystalline NiO on glass substrates [5–8] and single-crystalline NiO with twin defects on Al_2O_3 substrates [5,9,10]. Very few studies have reported the growth of single-crystalline NiO [11] or described the effects of the crystal structure on the film properties [12]. Thus, a study on the effects of various growth parameters followed by characterization of the NiO properties is of significant interest. The capability of growing single-crystalline NiO and its characterization will improve understanding of the fundamental characteristics of NiO.

In this work, NiO thin films were grown by atmospheric pressure metal organic chemical vapor deposition (APMOCVD) under various growth parameters, i.e., the growth temperature, the input precursor (O_2/Ni) ratio, which is the nominal molar ratio of the Ni precursor to the O_2 gas, and the substrate material. Characterization was then carried out on the obtained samples to correlate the effects of the various growth parameters to the film properties, including the crystal structure, resistivity, and optical transmittance.

2. Experimental details

The APMOCVD system used in this study comprised a horizontal reactor with an inclined susceptor made for the growth of oxide thin films. Single-crystalline Al_2O_3(001), MgO(100), and MgO(111) were used as substrates for the growth. Prior to growth, the substrates were degreased in an ultrasonic bath of acetone, ethanol, and deionized water for 10 min each. Allyl (cyclopentadienyl) nickel ($C_8H_{10}Ni$) was used as the nickel precursor and was kept at 30 °C to obtain a vapor pressure of 0.84 Torr. Pure O_2 gas was used as an oxygen source, and N_2 was used as a carrier gas. Substrates were placed on the susceptor inside the reaction

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* Corresponding author.
E-mail address: tmroffi@uec.ac.jp (T.M. Roffi).

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chamber and heated to the desired growth temperature with a constant flow of N_2. The growth temperature was measured using a thermocouple inserted into the susceptor.

To investigate the effects of growth temperature on the properties of NiO, growth temperatures of 300 °C, 400 °C, 500 °C, and 600 °C were employed, with a typical growth time of 5 h. The flow of precursors was fixed to ensure the same amount of materials flowed onto the substrate in all growth processes. Note that the samples discussed in Sections 3.1–3.5 were grown at an input O_2/Ni ratio of 4513. The obtained films were subjected to structural characterization and electrical resistivity measurements.

To investigate the structural properties of the samples, various configurations of X-ray diffraction (XRD) measurements with Cu Kα radiation ($\lambda = 1.54$ Å) were performed. The crystal structure was investigated by grazing incidence X-ray diffraction (GI-XRD) and $\theta-2\theta$ scans. Rocking curves and ϕ scans were performed to analyze the crystal quality and the crystallographic orientation relationship (COR) between the film and the substrate. In samples grown on Al_2O_3 substrates, the ϕ scan was performed at a tilt of 54.73° from the NiO(111)/Al_2O_3(001) plane with the Bragg condition satisfying the orientation of the NiO(200) plane (θ and 2θ of 21.64° and 43.28°, respectively). Then, another ϕ scan was performed at a tilt of 42.31° from the NiO(111)/Al_2O_3(001) plane with the Bragg condition satisfying the orientation of the Al_2O_3(116) plane (θ and 2θ of 28.75° and 57.50°, respectively). In samples grown on MgO(100) substrates, ϕ scans were performed on the NiO sample at a tilt of 45.00° from the NiO(100)/MgO(100) plane with the Bragg condition satisfying the orientation of the NiO(220) and MgO(220) planes ($\theta-2\theta$ of 31.44°–62.88° and 31.15°–62.30°, respectively). Finally, in samples grown on MgO(111) substrates, ϕ scans were performed on the NiO sample at a tilt of 35.26° from the NiO(111)/MgO(111) plane with the Bragg condition satisfying the orientation of the NiO(220) and MgO(220) planes.

To investigate the effects of the precursor ratio on the NiO properties, O_2/Ni ratios of 542, 1354, 2617, and 5641 were employed during the growth using an $\mathbf{Al_2O_3}$(001) substrate at 500 °C. These ratio were obtained by adjusting the flow rates of Ni precursor and O_2 gas. The values indicate the nominal molar ratios of the Ni precursor to the O_2 gas and are represented as 0.5k, 1k, 2k, and 5k, respectively. Surface images obtained from field-emission scanning electron microscopy (FE-SEM) were used to study the morphology of these samples. The effects of the O_2/Ni ratio on the transparency at visible range were studied by optical transmittance measurement in a UV–vis–NIR spectroscopy system. The resistivity of all samples was measured by the four-point-probe and van der Pauw method. All of the measurements were carried out at room temperature.

3. Results and discussions

3.1. Crystal structure and epitaxial relationship

The XRD $\theta-2\theta$ scan of NiO grown on the Al_2O_3 substrate in Fig. 1(a) indicates that NiO was grown in the NiO[111] direction. Peaks of NiO(111) and Al_2O_3(006) were determined based on the powder diffraction files (PDF) from the International Centre for Diffraction Data (ICDD #47-1049 and #46-1212 for NiO and Al_2O_3, respectively). The higher NiO(111) peak intensity at higher growth temperatures indicates that the films are better crystallized. Although the XRD $\theta-2\theta$ only showed the NiO(111) peak, the GI-XRD pattern (not shown) reveals that films grown at 300 °C and 400 °C were polycrystalline, with the presence of peaks from NiO(200) and NiO(220), and single crystalline films were obtained at 500 °C and 600 °C.

The XRD ϕ scans were carried out to evaluate the in-plane COR (not shown). In all samples, six NiO(200) peaks appeared at the same ϕ angle as the Al_2O_3(116) peaks, indicative of a twinned structure. As previously discussed [13,14], the CORs for NiO grown on an Al_2O_3 substrate are $[111]_{NiO} \| [006]_{Al_2O_3}$ (out-of-plane) and $[\bar{1}12]_{NiO} \| [\bar{1}10]_{Al_2O_3}$ & $[21\bar{1}]_{twinned-NiO} \| [110]_{Al_2O_3}$ (in-plane). Twinned NiO on sapphire substrates has also been reported using other deposition methods, such as pulsed laser deposition (PLD), [15] Atomic layer deposition (ALD), [16] and radio frequency sputtering [17].

Epitaxial growth of NiO on an Al_2O_3 substrate can be explained using the domain matching epitaxy (DME) framework, which employs matching of domains rather than lattice parameters [15,17,18]. In the current system, a 7% mismatch between the in-plane spacings of $\sqrt{2}.d_{NiO(200)}.\sin 60°$ and $d_{Al_2O_3(110)}$ would occur based on the bulk parameters. However, the NiO(200) peak position obtained from the XRD rocking curve scan indicates that the film was not fully relaxed to its bulk parameters, such that the misfit strain between NiO and Al_2O_3 was 6.2% ($\varepsilon = \frac{2.526}{2.379} - 1$). The DME framework suggests that this mismatch can be

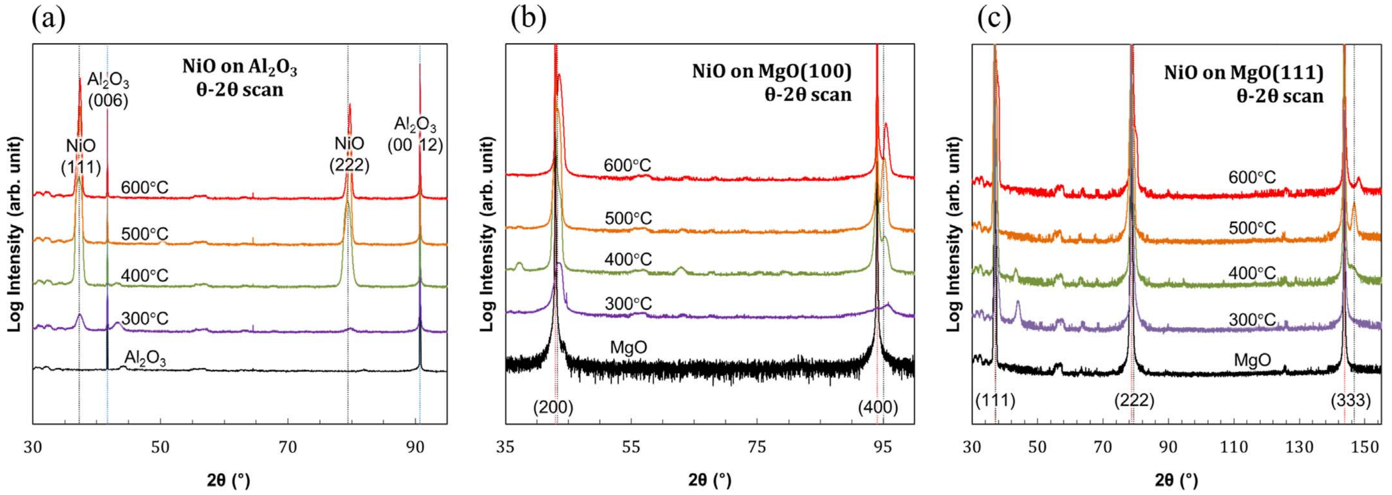

Fig. 1. XRD $\theta-2\theta$ patterns of the NiO films grown at various growth temperatures. (a) On Al_2O_3 substrates, the peaks at 37° and 79° for NiO(111) and NiO(222), respectively, indicate growth toward NiO[111]; (b) On MgO(100), the peaks near 43° and 94° for NiO(100) and NiO(200), respectively, indicate cube-on-cube orientation relationship; (c) On MgO(111), overlaps of NiO and MgO diffraction peaks were observed near 37° and 79°, which belong to NiO(111) and NiO(222), respectively. The diffraction peaks of MgO(333) and NiO(333) were more widely separated and can be observed at 144° and 147°, respectively.