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NiO films grown epitaxially on MgO substrates by sol–gel method

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ABSTRACT

NiO films were grown epitaxially on MgO (100) substrates by a sol–gel spin-coating technique using a solution of nickel acetate tetrahydrate in 2-methoxyethanol stabilized by monoethanolamine. X-ray diffraction, high-resolution transmission electron microscopy, and selected-area electron diffraction analyses indicated that the NiO films grew epitaxially on the MgO substrates. X-ray reciprocal space maps around the asymmetric 311 diffraction point revealed that the NiO films were in a partially strained state, with the lattice parameter contracted along the direction normal to the surface and expanded along the direction parallel to the surface in each film, caused by a lattice mismatch between NiO and MgO. Strain relaxation was gradually enhanced as the film thickness increased. In addition, the Poisson's ratio of NiO was estimated to be about 0.22 from the lattice parameter changes, which is somewhat lower than the value predicted from the elastic constants of NiO.

1. Introduction

Nickel oxide is a *p*-type semiconductor with a wide band gap of ~3.7 eV [1,2], and has attracted interest as a material for gas sensors [3], electrochromic devices [4], transparent conducting electrodes [5], and nonvolatile resistive switching memories [6]. NiO is also a candidate for potential applications in heterojunction devices with *n*-type oxide semiconductors. UV light emitting diodes [7], UV photodetectors [8], and visible light transparent solar cells [9,10] have been demonstrated using heterojunctions with *p*-type NiO and *n*-type ZnO.

NiO films are prepared by various methods. In particular, NiO epitaxial films have been grown on MgO substrates by rf sputtering [11], molecular beam epitaxy (MBE) [12], pulsed laser deposition (PLD) [13], and atomic layer deposition (ALD) [14]. They have been also grown on sapphire substrates by metalorganic vapor phase epitaxy [15]. MgO is suitable as a substrate in the epitaxial growth of NiO films because it has the same rock salt structure as NiO and the respective lattice constants are very similar: 0.4213 nm for MgO and 0.4177 nm for NiO. The sol–gel method is more convenient and less expensive and provides general advantages such as easier composition control and superior uniformity. However, there have been few reports on the epitaxial growth of NiO films using the sol–gel method.

In this study, we describe the epitaxial growth of NiO films on MgO substrates by the sol–gel method and the characterization of the grown films by X-ray diffraction (XRD) and transmission electron microscopy (TEM) analyses.

2. Experimental

NiO films were prepared on MgO (100) single-crystal substrates by the sol–gel method. As a starting material, nickel acetate tetrahydrate was used. 2-Methoxyethanol and monoethanolamine were used as the solvent and stabilizer, respectively. Nickel acetate tetrahydrate was first dissolved in a mixture of 2-methoxyethanol and monoethanolamine. The molar ratio of monoethanolamine to nickel acetate tetrahydrate was maintained at 1.0 and the concentration of nickel acetate tetrahydrate was 0.4 mol/L. The films were spin-coated on the substrates at 3000 rpm. After spin-coating, the substrates were first heated at 90 °C in air for 10 min to evaporate the solvent and then at 400 °C for 20 min to eliminate the organic component in the film. This procedure was repeated several times to adjust the film thickness. The films were then heat-treated at 700 or 800 °C in air for 1 h. The film thickness was varied from 27 to 320 nm.

The structural properties of the films were studied by XRD in the $2\theta-\omega$ scan, ϕ-scan, and reciprocal space mapping modes using a Bruker D8 Discover X-ray diffraction system with Cu-K_α radiation. The surface and cross-section of the films were observed by a Hitachi S-5500 scanning electron microscope (SEM). High-resolution transmission electron microscopy (HRTEM) measurements using a JEOL JEM-ARM 200F atomic resolution analytical electron microscope with an acceleration voltage of 200 kV and selected-area electron diffraction (SAED) were also performed to study the microstructures.

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3. Results and discussion

3.1. Structural features of NiO films grown on MgO substrates

Fig. 1(a) shows the XRD pattern from the $2\theta-\omega$ scan of a NiO film on a MgO substrate. Only the 200 and 400 diffraction peaks from the NiO film and MgO substrate were observed. This indicated that the NiO film was preferentially oriented along the direction normal to the substrate surface. The in-plane orientation between the film and the substrate was determined by XRD ϕ-scans for (311) NiO and (311) MgO, respectively. As shown in Fig. 1(b), four peaks separated by 90° from each other were observed for both the NiO film and MgO substrate. This suggested that the NiO film was well aligned in-plane with the MgO substrate. Therefore, these results implied that the NiO films grew epitaxially on the MgO substrates.

Fig. 2(a) shows the surface morphology of a NiO film on a MgO substrate observed by SEM. Although small rectangular hollows, with a depth of around 10 nm, exist on the surface, the NiO film continuously covers the whole MgO substrate surface. The cross-section of the film is flat and uniform as shown in Fig. 2(b), indicating that the grains and grain boundaries cannot be recognized.

A cross-sectional low magnification TEM image of a NiO film on a MgO substrate is shown in Fig. 3(a). The interfaces originated from the repetition of spin-coating process cannot be identified despite the film prepared by repeating six times. In addition, the image also indicates the absence of the grains and the grain boundaries. Fig. 3(b) shows a cross-sectional HRTEM image of a region near the interface between the NiO film and MgO substrate. The atomic arrangement in the lattice images of the NiO film is identical to that of the MgO substrate. The roughness of the interface might be caused by the inter-diffusion of Ni and Mg atoms which was confirmed by secondary ion mass spectroscopy analysis. The detail of the inter-diffusion will be reported elsewhere. Moreover, diffraction patterns in the corresponding SAED along the [001] axis showed the 200, 020, and 220 reflections in both the NiO film and MgO substrate, as shown in Fig. 3(c) and (d), meaning that the orientation relationship between the NiO film and MgO substrate can be described as (100)[010]NiO‖(100)[010]MgO. These results also clarified the epitaxial growth of NiO films on the MgO substrates. Thus, the NiO films grew epitaxially on the MgO substrates as a whole film in the sol–gel process as reported in the film grown by PLD [13], but it stands in contrast to the films grown by ALD, in which columnar grains run throughout the whole film [14].

In addition, the NiO films were semi-insulators with a resistivity of 10^5 Ω cm. It is well known that stoichiometric NiO is an insulator and the resistivity is decreased by increasing the concentration of Ni^{2+} vacancy. Therefore, the composition in the NiO films prepared by the sol–gel method would not deviate so much from stoichiometry.

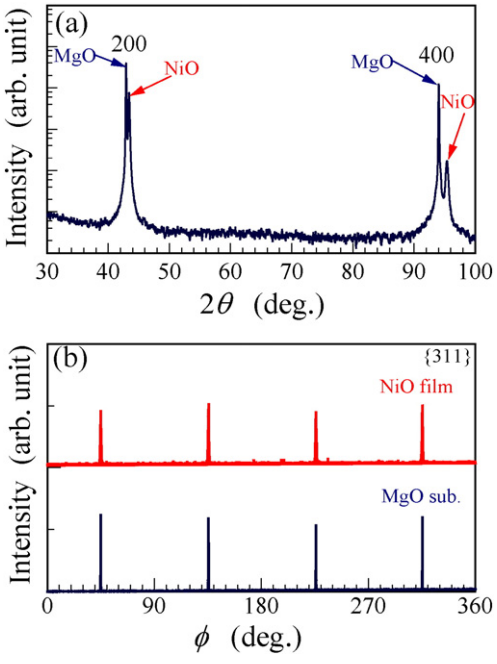

Fig. 1. XRD patterns of a NiO thin film grown on a MgO (100) substrate: (a) $2\theta-\omega$ scan and (b) ϕ-scans for 311 reflection of NiO and MgO.

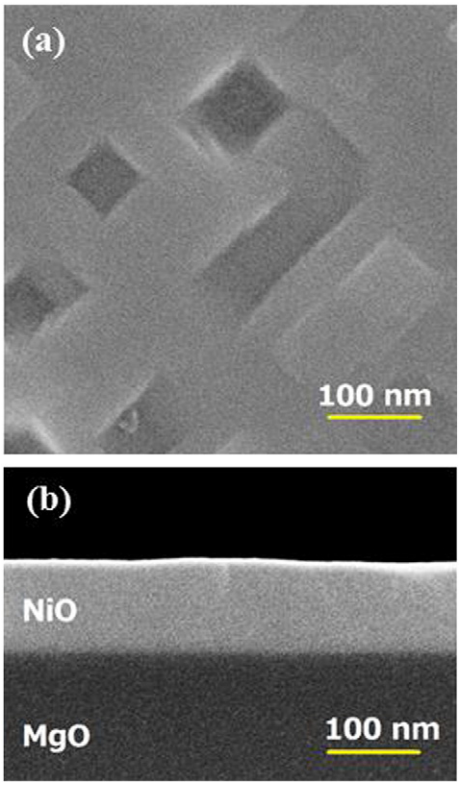

Fig. 2. SEM images of a NiO thin film grown on a MgO substrate: (a) surface and (b) cross-section.

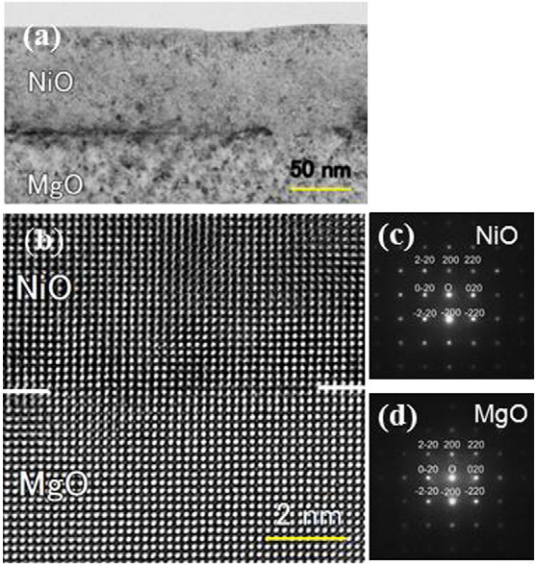

Fig. 3. (a) Low magnification cross-sectional TEM image of a NiO thin film grown on a MgO substrate. (b) Cross-sectional HRTEM image of a region near the interface between the NiO film and MgO substrate. (c) and (d) Corresponding SAED patterns of NiO and MgO, respectively.