Effect of crystallographic orientations on electrical properties of sputter-deposited nickel oxide thin films

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Available online 13 July 2007

Abstract

Nickel oxide thin films of various preferred orientations were deposited by radio-frequency (RF) magnetron sputtering process in different gas ratios of oxygen atmosphere at RF power 200 W on unheated and heated for (673 K) substrates. The relationships among substrate temperature, preferred orientation and electrical properties of the NiO films were investigated. The resulting films were analyzed by grazing-incidence X-ray diffraction, high-resolution transmission electron microscopy (HR-TEM), and ultrahigh resolution scanning electron microscopy (HR-SEM). The electrical properties were measured using four probe and Hall effects measurements. The results show that films deposited at room temperature with the ratio of oxygen varying from 0 to 100% develop a (111) preferred orientation. At temperature of 673 K, while the (111)-orientated film was obtained under a low ratio of oxygen (<50% O2), a (200) preferred orientation was developed under 100% oxygen. The lowest sheet resistance 0.01 MΩ, resistivity 0.83 Ω-cm and higher carrier density 7.35×10^18 cm^-3 could be obtained on (111) preferred orientation samples prepared on unheated substrates in pure oxygen atmosphere. The relationship between preferred orientation and electrical properties was proposed in this paper.

Keywords: Nickel oxide; Reactive sputtering; Preferred orientation; Electrical properties

1. Introduction

Nickel oxide (NiO) thin films with NaCl-type structure have recently drawn considerable attention because they are important in several scientific and technological applications. They exhibit excellent chemical stability, as well as optical, electrical and magnetic properties. They have been employed as an antiferromagnetic material [1], p-type transparent conducting films [2], a material for electrochromic display devices [3], and a part of functional sensor layers in chemical sensors [4]. Furthermore, (100)- and (111)-oriented NiO films can be used as buffer layers that are deposited on oxide films with other orientations, such as c-axis-oriented perovskite-type ferromagnetic films and superconducting films [5–7]. Such films have been fabricated using various physical and chemical vapor deposition techniques, including spray pyrolysis [8,9], electron beam evaporation [10], pulsed laser deposition [11], plasma-enhanced chemical vapor deposition [1,12] and reactive sputtering [3,13,14]. Reactive sputtering is the most widely used among these methods. The dependence of film properties on sputtering parameters has been studied extensively [12,15–23]. Many reference data and studies [12,15–23] have indicated that superior electric and optical properties of NiO films can be obtained by reactive sputtering in a pure oxygen atmosphere in the range 0.1–1 Pa and using a heated substrate. Previous studies indicated the electrical properties of NiO films depending on Ni-defective, structure and thickness [15–18,20–23]. Also, the gas ratio of O2 and substrate temperature influence crystallographic orientations and microstructure of the NiO films in sputtering process have been discussed [22]. The relationships between electrical properties and crystallographic orientations of NiO films were not to be discussed. Therefore, this paper tried to explain about the effect of crystallographic orientations on electrical properties of NiO films.

2. Experimental methods

Nickel oxide films were deposited on the 0.7-mm thick Corning 1737 glass substrate by a radio-frequency (RF) magnetron sputtering system from an NiO target of 99.99% purity in an oxygen (99.99%) atmosphere. The distance between the target and the substrate was approximately 80–85 mm. The chamber was evacuated to a pressure below 3×10^-4 Pa before deposition. Sputtering deposition was performed under a gas
pressure of 1 Pa. The power of target was kept at a constant RF power of 200 W. The substrates were used without intentional heating (room temperature) or heated at 673 K using quartz heating lamp. The thickness of the films was about 200 nm.

A conventional profilometer (Alpha-step 200) was used to measure the thickness of the films. The electrical properties of nickel oxide films, including resistivity, carrier concentration, mobility and Hall coefficient were measured with a Hall measurement system ("Lake Shore" model 7604 Hall effect measurement systems). The sheet resistance of the films was measured with a four-point probe system (Napson, RT-7) in the air atmosphere. Then the crystal structure of the deposited films was identified by grazing-incidence X-ray diffraction (GIXRD) using a Rigaku D/MAX 2500 multipurpose X-ray thin film diffractometer with monochromatic high-intensity CuKα radiation (λ = 0.15418 nm). The microstructure was observed using ultrahigh resolution transmission electron microscope (HR-AEM, Hitachi model HF-2000 field-emission transmission electron microscope) and FEG-TEM (Philips Tecnai F30 Field Emission Gun Transmission Microscope). The surface morphology was observed with ultrahigh resolution scanning electron microscopy (HR-SEM, Hitachi S4100, Japan) operated at 30 kV.

3. Results and discussion

3.1. Crystallographic orientations

The crystal structure of the as-deposited NiO film was identified to be polycrystalline. The thicknesses of the films...
under investigation were consistently around 200 nm. The X-ray diffraction patterns of the films deposited at the substrate temperature from 303 K to 673 K with different ratios of oxygen to argon are shown in Fig. 1. The diffraction peaks were identified and compared with those of the standard 2 theta peaks on a JCPDS card (Bunsenite, NaCl-type structure, 2003 JCPDS database No: 89-7130). Fig. 1 (a) shows X-ray diffraction patterns of the films deposited at the substrate temperature of 303 K with different ratios of oxygen to argon. The film deposited in pure argon atmosphere shows (111) and (200) peaks while the films deposited in different fractions of oxygen show (111), (220) and (311) peaks. The peak intensity of (111) increases with an increasing ratio of oxygen. Fig. 1 (b) shows patterns from films deposited at a substrate temperature of 673 K with different fractions of oxygen to argon. The films deposited in Ar (0% O2) and 50% O2 show dominating (111) peak. However, as the fraction of oxygen increases to 100%, the preferred orientation is changed from (111) to (200). Fig. 2 shows the preferred orientation gradually changed from (111) to (200) while the ratios of oxygen to argon increased from 60% O2 to 100% O2 at substrate temperature of 673 K.

Fig. 3 shows SEM micrographs of NiO films deposited at substrate temperatures of 303 K and 673 K with 100% O2. Fig. 4 shows TEM images of plane view and transmission electron diffraction patterns of NiO films prepared at different substrate temperatures with 100% O2. Fig. 5 shows TEM micrographs of the cross sections. All the films exhibit a columnar structure with the growth direction perpendicular to the surface. Figs. 6 and 7 show HR-TEM lattice images and diffraction pattern of NiO films prepared at substrate temperature of 303 K and 673 K under pure oxygen atmosphere.

NiO film texture depends on both the oxygen content in the film and the deposition temperature [1,2,9,14,19,20]. The crystal orientation of the film is controlled by the nucleation and growth of the grains [23]. The crystallographic orientations of NiO films are affected by the arrangement of O2− under the pure oxygen atmosphere at low substrate temperatures (303 K) and the low ratio of oxygen (<50% O2) at a deposition temperature.
temperature of 673 K. Ni$^{2+}$ and O$^{2-}$, which are produced by sputtering process, collide separately onto the growing film surface [1]. The radius of O$^{2-}$ (0.140 nm) is larger than that of Ni$^{2+}$ (0.069 nm). In order to minimize the surface energy of the growing NiO film, O$^{2-}$ must be arranged in the most densely packed plane; (111), as shown in Figs. 6 and 8(b). Therefore, the preferred orientation is (111) under pure oxygen atmosphere at a high substrate temperature of 673 K.

Ventricre Jr. proposed that repulsive forces exerted between oxygen ions and electrostatic energy of Ni–O pairs significantly contributes to the formation of NiO [24]. The surfaces of any ionic or partly ionic crystal have been identified by Tasker [25] as types I, II, or III. In type I surfaces, the stacking plane is neutral and composed of both anions and cations at a stoichiometric ratio, resulting in no dipole perpendicular to the surface. Type II surfaces contain a series of charged planes. They make a symmetric repeat unit that has no net dipole plane in order to minimize the surface energy as shown in Figs. 7 and 8(c). Therefore, the preferred orientation is (200) under pure oxygen atmosphere at a high substrate temperature of 673 K.

Fig. 5. TEM micrographs of cross-sectional view of NiO films deposited at substrate temperatures of (a) 303 K and (b) 673 K with 100% O$_2$.

Fig. 6. HR-TEM lattice image and diffraction pattern of NiO films prepared at substrate temperature of 303 K under pure oxygen atmosphere.
perpendicular to the surface. Type III charged surfaces have a dipole moment in the repeat unit perpendicular to the surface.

When the NiO film is deposited under the low temperature or the low ratio of oxygen at high temperature, Ni\textsuperscript{2+} and O\textsuperscript{2−} collide separately onto the growing film surface and not enough energy or oxygen is provided for the Ni\textsuperscript{2+} and O\textsuperscript{2−} to recombine. It is more likely for the film to be formed with non-stoichiometric ratio, which is electrostatically polar. According to Fisher [26], the surface of the (111) crystal plane of NiO is a Type III surface in Tasker’s scheme [25]. It can then be understood that (111) will be the preferred orientation under the low sputtering temperature or the low ratio of oxygen at high temperature.

When the NiO film is deposited under high temperature, Ni\textsuperscript{2+} and O\textsuperscript{2−} collide onto the growing NiO film at the same time. It is more likely for the film to be formed with stoichiometric ratio.

Fig. 7. HR-TEM lattice image and diffraction pattern of NiO films prepared at substrate temperature of 673 K under pure oxygen atmosphere.

Fig. 8. Schematic illustrations of nickel and oxygen atoms arrange in the unit cell of NiO.
which is electrostatically neutral. According to Fisher [26], the surface of the (200) crystal plane of NiO is a Type I surface in Tasker’s scheme [25]. It can then be understood that (200) will be the preferred orientation under the high sputtering temperature.

3.2. Electrical properties

The sheet resistance and resistivity of NiO films were measured using four probe and Hall effect measurements, respectively. Fig. 9 shows that the sheet resistances of the as-deposited films prepared on unheated substrates with different ratios of oxygen to argon were between 1.5 and 0.01 MΩ. While for samples grown on 673 K substrates, the sheet resistances of the films prepared on the unheated substrate of 303 K that are seen to decrease from 1.5 to 0.01 MΩ as the ratios of oxygen to argon are increased from 0 to 100% O₂. Comparatively, the sheet resistances of the films prepared on the heated substrate of 673 K that are seen to increase from 0.05 to 1.4 MΩ as the ratios of oxygen to argon are increased from 0 to 100% O₂. Hall effect data for different preferred orientation of NiO films prepared on different substrate temperatures under pure oxygen atmosphere are shown in Table 1. The films exhibited a (111) preferred orientation at a low substrate temperature (303 K). The preferred orientation gradually changed from (111) to (200) as the substrate temperature (473 K) increased. Finally, the films exhibited a (200) preferred orientation when the substrate temperature reached 673 K [22]. The resistivity and carrier density of the as-deposited films prepared on unheated substrate under pure oxygen atmosphere was 0.83 Ω·cm and 7.35×10¹⁸ cm⁻³, and 0.94 Ω·cm and 1.90×10¹⁸ cm⁻³ for the sample prepared on 473 K, and 14.70 Ω·cm and 6.01×10¹⁶ cm⁻³ for the sample prepared on 673 K under pure oxygen atmosphere.

The conduction mechanism of the NiO film is believed to relate to the vacancies existing in the structure. The electrical properties of NiO films are associated with their microstructure and composition, and consequently, on the deposition environment [15–18,20–23]. The NiO films with (111) preferred orientation that composes were non-stoichiometric ratio [17,22]. Non-stoichiometric nickel oxide (Ni₁₋ₓO) is known as a p-type extrinsic semiconductor [2]. The defects that are the causes of holes conductivity are Ni⁺² ion vacancy. Each vacancy is replaced by two Ni⁺³ ions which act as electron acceptors. However, crystalline NiO film with (200) orientation is formed near stoichiometric ratio. Pure stoichiometric nickel oxide is an insulator with high resistivity (ρ>10¹³ Ω·cm) at room temperature. In this study, the (111) oriented NiO films were developed at different deposition temperatures with different ratios of oxygen to argon. As an exception, the (200)-oriented NiO films were formed at the deposition temperature of 673 K and under the ratio of 100% O₂. These results show that the values of sheet resistance and resistivity of the (200)-orientated NiO films are higher than those (111)-orientated NiO films.

4. Conclusion

The relation between the crystallographic orientations of NiO films and electrical properties is discussed. Those films deposited at a substrate temperature of 303 K, with a ratio of oxygen ranging from 0% to 100%, have displayed a (111) preferred orientation. For films deposited at substrate temperature of 673 K, the (111)-orientated NiO film was obtained under a low ratio of oxygen (<50% O₂), the (200) preferred orientation was developed under a ratio of 100% oxygen. The NiO films with (111) preferred orientation that composes were non-stoichiometric ratio. The NiO films with (200) orientation are formed near stoichiometric ratio. The defects that are the causes of holes conductivity are Ni⁺² ion vacancy. Consequently, the values of sheet resistance and resistivity of the (200)-orientated NiO films are higher than those (111)-orientated NiO films.

Table 1

<table>
<thead>
<tr>
<th>Substrate temperature [K]</th>
<th>Preferred orientation</th>
<th>Resistivity [Ω·cm]</th>
<th>Carrier density [1/cm³]</th>
<th>Hall mobility [cm²/Vs]</th>
<th>Hall coefficient [cm²/C]</th>
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<tr>
<td>303</td>
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<td>0.83</td>
<td>7.35E+18</td>
<td>1.03</td>
<td>0.85</td>
</tr>
<tr>
<td>473</td>
<td>(111)/(200)</td>
<td>0.94</td>
<td>1.90E+18</td>
<td>3.50</td>
<td>3.29</td>
</tr>
<tr>
<td>673</td>
<td>(200)</td>
<td>14.70</td>
<td>6.01E+16</td>
<td>7.07</td>
<td>103.8</td>
</tr>
</tbody>
</table>

Fig. 9. Sheet resistances of NiO films with different ratios of oxygen to argon prepared on unheated (303 K) and heated (673 K) substrates.

References