

## Preferred orientations of NiO thin films prepared by RF magnetron sputtering

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NiO thin films are very attractive for use as an anti-ferromagnetic layer [1], *p*-type transparent conducting films [2], in electrochromic devices [3, 4] and functional sensor layer for chemical sensors [5], due to their excellent chemical stability, as well as optical, electrical and magnetic properties. In addition, (100)- and (111)-oriented NiO films can be used as buffer layers to deposit other oriented oxide films on them, such as *c*-axis-oriented perovskite-type ferromagnetic films and superconducting films, because of their chemical stability and the similarity in symmetry of oxygen ion lattice and lattice constants between the NiO films and the oriented oxide films [6]. For using the NiO films as the buffer layers, controlling the crystallographic orientation and surface roughness of the films are very important.

There has been reports on NiO films produced by sputtering [2, 3], by electron beam evaporation [7], by metalorganic chemical vapor deposition (MOCVD) [8], and by dip coating [9]. Among these processes, the sputtering process has been widely used because of its advantages of low substrate temperature, good surface flatness, transparency and dense layer formation. In this study, (100)- and (111)-oriented NiO thin films were grown on Si(100) substrates by RF magnetron sputtering. We describe the effect of the flow ratio of O<sub>2</sub> to Ar for plasma generation on the crystallographic orientation, deposition rate, and surface morphology of the NiO films, and also discuss the growth mechanism and surface roughness of the films.

We prepared NiO thin films on Si(100) substrates in a sputtering unit equipped with an RF generator operating at 13.56 MHz. NiO powders (>99.9%, Aldrich Co.) were used as the raw material for the production of a NiO target with 5 cm diameter by sintering at 1350 °C for 3 h in air atmosphere. The target-to-substrate distance was 10 cm and an incident angle was approximately 55° to the normal of a substrate (off-axis). The sputtering chamber was evacuated down to  $3 \times 10^{-6}$  Torr before introducing the sputtering gas, and the ratios of O<sub>2</sub> to Ar for the sputtering gases were 0%, 50%, and 100%, respectively. The working pressure was kept at 5 mTorr with 80 W (3.95 W/cm<sup>2</sup>) of RF power. After the target was presputtered for 30 min in Ar to clean the target surface, the main sputter-

ing was performed. The substrates were rotated with 25 rpm for the film uniformity and unheated (room temperature).

X-ray diffraction (XRD: Rigaku D/Max-3C, Japan) was used to study the crystallinity and crystal orientation of the films. The cross-sectional view and the surface of the films were observed by field-emission scanning electron microscope (FE-SEM: Hitachi S-4700, Japan). The film thickness was measured by spectroscopy ellipsometry (J. A. Woollam Co., M-2000V, USA). The surface morphologies and roughnesses of NiO films were examined by atomic force microscopy (AFM: Digital Instruments Inc., NanoScope IV, USA), which was operated with the tapping mode.

Fig. 1 shows X-ray diffraction patterns of as-deposited NiO thin films on Si(100) for 30 min with the flow ratio of O<sub>2</sub> to Ar. The crystalline peaks were observed at the ratio of 0% (pure Ar) and 100% O<sub>2</sub>. The film deposited in Ar shows only a sharp (200) peak, which indicates a strong (100)-orientated crystal structure and good quality of crystallinity. The film deposited in the flow of O<sub>2</sub> shows only a (111) peak of weak intensity, which implies that the film has (111)-oriented crystal structure with poor crystallinity. On the other hand, it is difficult to find a crystalline peak of the film deposited in the Ar-O<sub>2</sub> mixture gas (50% Ar + 50% O<sub>2</sub>). Sato *et al.* [2] reported that NiO thin films deposited with the O<sub>2</sub> content above 20% by RF magnetron sputtering exhibited two weak diffraction peaks from the (111) and the (200) planes.

The dependence of crystallographic orientation on the flow ratio of O<sub>2</sub> for the sputtering gas might be explained as follows. In the deposition of oxide films, the films initially nucleated in a random orientation. Thus, the crystal orientation of the film is determined by the condition for growth of the nuclei. When the film grows from the initial nuclei, the crystal plane of the nuclei with minimum surface free energy may remain parallel to the film surface, because the growth rate of the crystal plane with minimum surface free energy is lower than that of the other crystal planes. In an ionic crystal of NiO with NaCl-type crystal structure, crystallographic orientation of the film is affected by

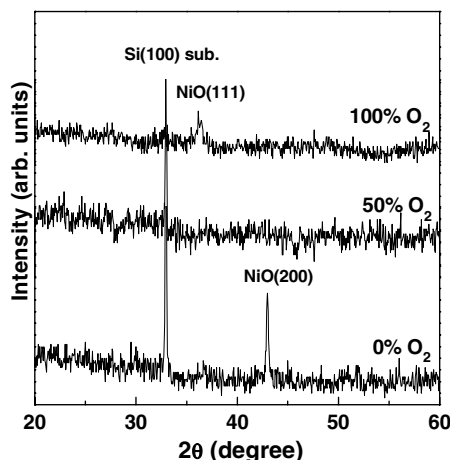


Figure 1 XRD patterns of NiO thin films deposited with different flow ratios of  $O_2$  to Ar.

the arrangement of  $O^{2-}$  when active species of nickel and oxygen, which are produced by sputtering process, collide separately with the growing film surface. This is because NiO has no directivity of combination between  $Ni^{2+}$  and  $O^{2-}$ , and the radius of  $O^{2-}$  (0.140 nm) is larger than that of  $Ni^{2+}$  (0.069 nm). The (111) plane is the most densely packed plane of  $O^{2-}$  for NiO crystal structure, indicating that the (111) orientation minimizes the surface free energy of growing NiO film in this case. When the deposition is conducted in  $O_2$ , the sputtering process may yield far more species of oxygen due to plasma decomposition of  $O_2$  than those of sputtered target atom or molecule. Consequently, crystallographic orientation of the NiO film deposited in  $O_2$  might be controlled by the arrangement of  $O^{2-}$ , resulting in (111) orientation of the NiO films. In NiO with NaCl-type crystal structure, on the other hand, (100) is the most densely packed plane among the planes composed of both  $Ni^{2+}$  and  $O^{2-}$ , indicating that the (100) orientation minimizes the surface free energy of growing NiO films in this case. When Ni atoms or NiO molecules are sputtered more efficiently than oxygen atoms, (111)-oriented NiO film may be difficult to obtain because the growth layer is composed of a mixture

of  $Ni^{2+}$  and  $O^{2-}$  under this condition. In an Ar atmosphere, the sputtering process may sputter preferentially Ni atoms or NiO molecules, rather than oxygen atoms from the NiO target. This is because energy transfer efficiency between argon and metal atoms is larger than that between argon and oxygen atoms [10]. Moreover, there are no active species of oxygen produced by plasma decomposition of  $O_2$ . Therefore, the growth of the film may be affected dominantly by the sputtered Ni atoms or NiO molecules under the above condition, leading to the (100)-oriented NiO film.

The thickness of the NiO films prepared in Ar, Ar- $O_2$  mixture, and  $O_2$  were about 90, 34, and 37 nm, respectively. It might be also reasoned that the deposition rate decreases with the introducing  $O_2$ , because a heavier gas such as argon is more efficient in a momentum transfer process than a lighter gas such as nitrogen and oxygen [11]. Fig. 2 shows the SEM micrographs of the surface and cross-section of the NiO films. Each of the films had a columnar structure with growth perpendicular to the film surface, and was dense, smooth and homogeneous. Also, the films deposited in  $O_2$  and Ar- $O_2$  mixture gas exhibited very small grains, while coarse grains were observed for the films processed in Ar.

An AFM operating in air has been used to investigate the surface morphologies and roughness of the NiO films and a graphical impression of the surface microstructure is obtained by directly viewing the 3-dimensional AFM images of  $0.5 \times 0.5 \mu m^2$ . As can be seen in Fig. 3, NiO films revealed different surface morphologies and roughnesses with the flow ratio of  $O_2$  to Ar. The films deposited in  $O_2$  and Ar- $O_2$  mixture gas have uniform morphologies as well as small surface roughness, and their area RMS (root mean square) roughnesses were 0.64 and 0.47 nm, respectively. For the film prepared in Ar, the individual grains are rather large and abnormal growth of some grains is observed, and accordingly the RMS roughness was increased to 1.99 nm. The differences in morphology of the films indicate that the type of sputtering gases have also influence on the growth of grains in the NiO thin films.

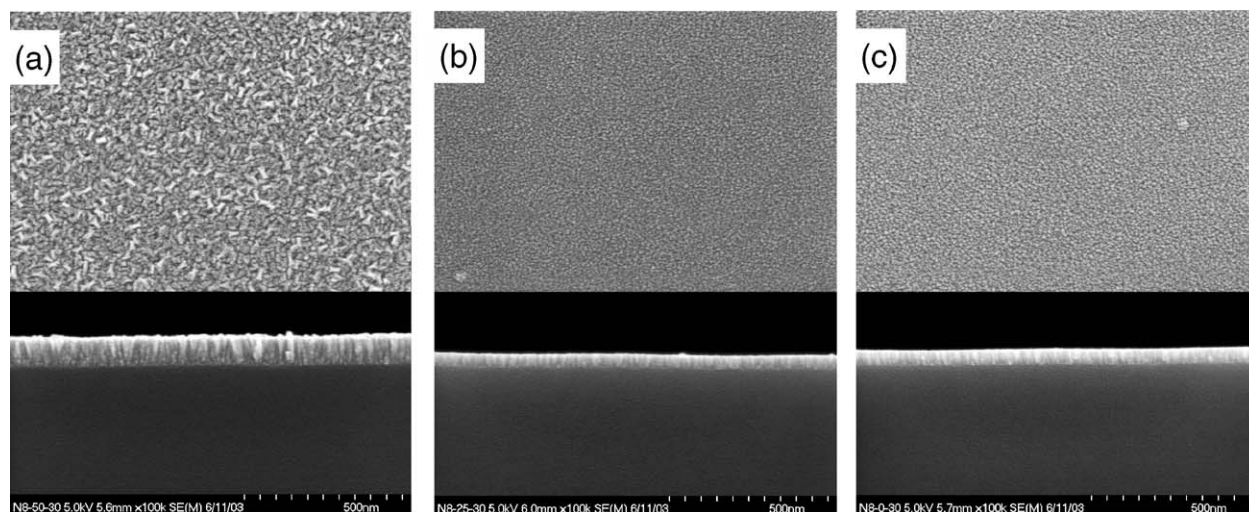


Figure 2 Top surface and cross-sectional images of NiO thin films deposited in: (a) Ar, (b) Ar- $O_2$  mixture (50% Ar + 50%  $O_2$ ) and (c)  $O_2$ .

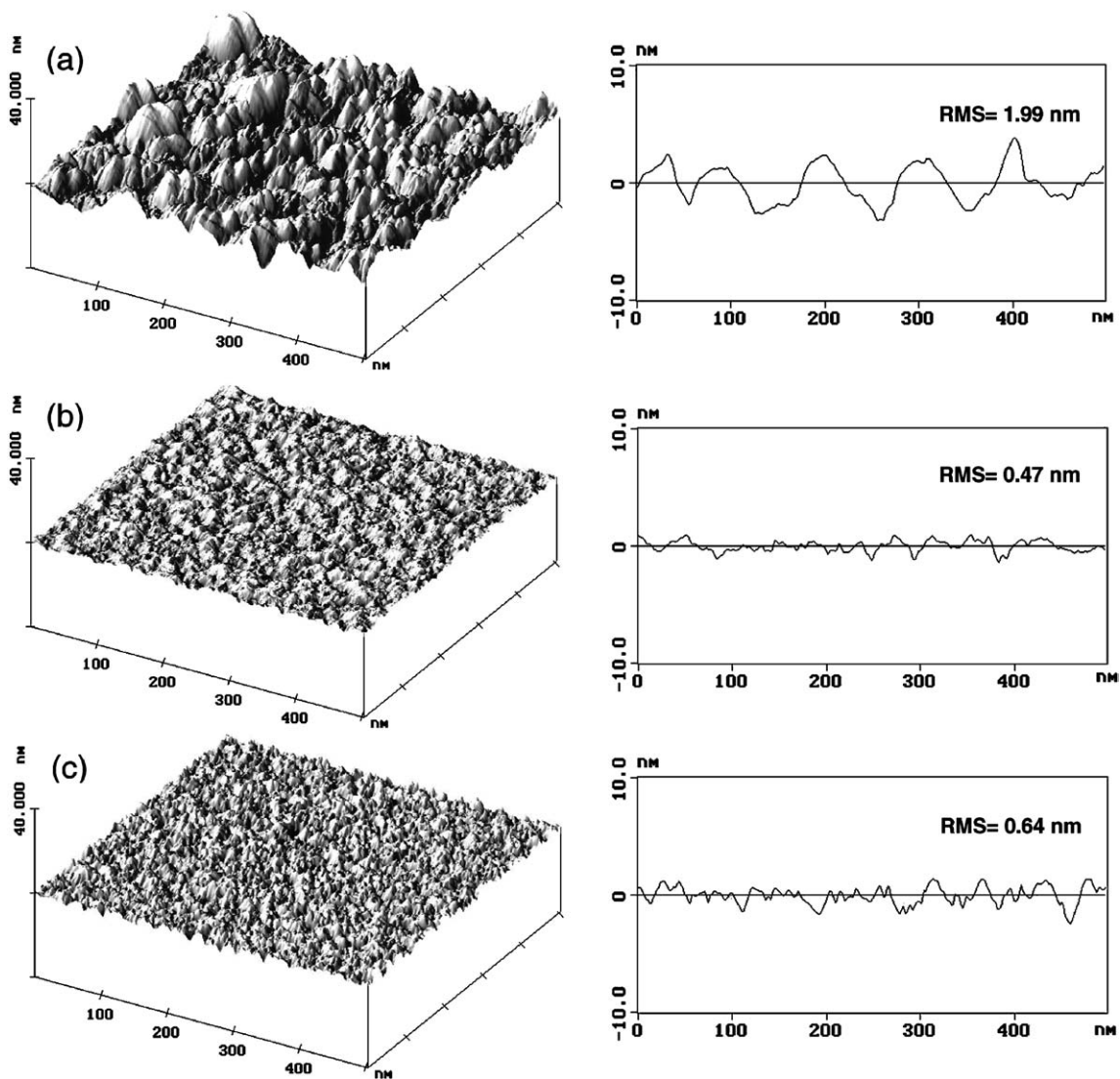


Figure 3 Surface morphologies and cross-sectional profiles of NiO thin films deposited in: (a) Ar, (b) Ar-O<sub>2</sub> mixture (50% Ar + 50% O<sub>2</sub>) and (c) O<sub>2</sub>.

In summary, NiO films on Si(100) substrates with different crystallographic properties depending on the type of sputtering gases, were deposited by RF magnetron sputtering from a NiO target at room temperature; (100)-oriented NiO film with good crystallinity was obtained in an Ar atmosphere, and (111)-orientated film was obtained in an O<sub>2</sub> atmosphere, whereas the film deposited in Ar-O<sub>2</sub> mixture gas (50% Ar + 50% O<sub>2</sub>) was not crystallized. The respective thicknesses of the films were 1.99 nm, 0.64 nm and 0.47 nm, respectively, and the deposition rate of the film decreased when it was processed in O<sub>2</sub> or Ar-O<sub>2</sub> mixture gas. Also, NiO films exhibited different surface morphologies and roughnesses with the flow ratio of O<sub>2</sub> to Ar. Surface morphologies of NiO films deposited in O<sub>2</sub> and Ar-O<sub>2</sub> mixture gas were similar and smoother, and showed very small grains compared with the film deposited in Ar. Their RMS roughness was 0.64, 0.47, and 1.99 nm, respectively.

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