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Resistivity Variation of Nickel Oxide by Substrate Heating in RF Sputter for Microbolometer

Yong Soo Lee[+]

Abstract

Thin nickel oxide films formed on uncooled and cooled SiO_2/Si substrates using a radio frequency (RF) magnetron sputter powered by 200 W in a mixed atmosphere of argon and oxygen. Grazing-incidence X-ray diffraction and field emission scanning electron microscopy are used for the structural analysis of nickel oxide films. The electrical conductivity required for better bolometric performance is estimated by means of a four-point probe system. Columnar and (200) preferred orientations are discovered in both films regardless of substrate cooling. Electric resistivity, however, is greatly influenced by the substrate cooling. Oxygen partial pressure increase during the nickel oxide deposition leads to a rapid decrease in resistivity, and the resistivity is higher in the cooled nickel oxide samples. Even when small microstructure variations are applied, lower resistivity in favor of low noise performance is acquired in the uncooled samples.

Keywords: Microbolometer, Nickel oxide, Substrate heating effect, Cooled and uncooled, Resistivity

1. INTRODUCTION

Nickel oxide (NiO) films with an NaCl-type structure have attracted attention when used in antiferromagnetic layers [1], *p*-type transparent conducting films [2], electrochromic devices [3, 4], and functional sensing layers for chemical sensors [5], owing to their excellent chemical stability as well as optical and electrical properties [6]. A variety of growth techniques to form nickel oxide films has been developed for based on sol-gel deposition, spray pyrolysis, electron beam evaporation, plasma-enhanced chemical vapor deposition, reactive sputtering, molecular beam epitaxy, etc. [7]. Because reactive sputtering has the potential advantages of a high deposition rate, a low temperature process, a high degree of uniformity in a large substrate area, and excellent controllability of compositions in deposited films, it has been widely adapted for nickel oxide growth technology [8].

The sputtered nickel oxide films are prominently studied in physical properties dependent on the changing of reaction gas, partial pressure, and substrate temperature [6-10]. Many previous studies have mentioned good consequences in electric conductivity and optical properties of NiO films. They were grown in a pure oxygen atmosphere on a heated substrate (200-600°C) with a reactive sputtering system at a sputtering pressure of 0.1 to 1Pa [6-10]. A few of experimental studies considering room temperature deposition of nickel oxide were recently published [6,14,15]. Even in reports describing room temperature deposition, the natural heating of substrate is an important issue that not be ignored. Thus, we have investigated the effects of substrate heating.

Sputtering gas ratio, sputtering pressure, RF power, and substrate temperature are well known process parameters influencing the characteristics of deposited films. An increase in substrate temperature increase during deposition or post-growth annealing can lead to the transition of the crystal structure from a disordered nanocrystalline phase to a more ordered crystalline structure [16]. The surface of the substrate can be heated during the sputtering process by the heat radiated from the target and the collisions of ions and secondary electrons at the substrate. Thus, there is always the possibility of crystal phase change during NiO film growth. One report mentioning the substrate heating effect describes the possibility of temperature increase up to at least 140°C if the NiO film was deposited on the uncooled substrate during the sputtering process [2].

Institute of Semiconductor Fusion Technology, College of Engineering, Kyungpook National Unversity
80 Daeharo, Bukgu, Daegu, 41566, Korea
[+]Corresponding author: leesoo@femtoline.com
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Chen et al. reported that the crystallographic orientations of NiO films have strong dependence on the substrate temperature [17]. Bruckner et al. mentioned that high irreversible stress changes formed at 100°C were found in thin films sputtered using a stoichiometric NiO target in an Ar plasma atmosphere [18]. However, research groups, have not paid much attention to monitoring unintentionally heated substrates, which can change NiO film characteristics through the sputtering deposition process.

In this study, we investigated the influence of surface heating on the physical properties and electric conductivity of nickel oxide films. NiO films about 100-nm-thick were formed on uncooled and cooled SiO_2/Si substrates for the investigation of the substrate heating effect, and then, their potentially affected crystalline and electric conductance were investigated in detail. By comparing each X-ray diffraction (XRD) and resistivity result obtained from the cooled and uncooled substrates, temperature-dependent microstructural and electrical characteristics analyzed. The oxygen partial pressure influences on the properties of the NiO films grown on the cooled and uncooled substrates were investigated.

2. EXPERIMENTAL

2.1 Fabrication of Nickel Oxide Films

Transparent p-type NiO thin films were grown on SiO_2/Si (p-type) substrates with a radio frequency (RF) sputtering system using the reactive method with an Ni (99.99 %) target in mixed atmosphere with argon and oxygen under different oxygen partial pressure. The distance between the target and the substrate was approximately 140 mm. Before deposition of the sputtering gas mixture, the chamber was evacuated to a base pressure below 5×10^{-6} torr with a rotary pump and a turbo molecular pumping system. A pre-sputtering process was conducted for 15 min to clean the target surface and then a shutter was removed to expose the substrate in a sputtering gas plasma.

The working pressure was 10 mTorr and the target was sputtered at a constant RF power of 200 W. The thickness of grown films in this study was approximately 100 nm. The substrates were partly installed on a holder with a water cooling system and the rest were on a holder without cooling system. The different mixed gases of $O_2/(Ar+O_2)$ for Ni target sputtering and NiO film formation were used, keeping other deposition conditions such as substrate temperature, sputtering power and sputtering pressure constant.

2.2 Measurement of Nickel Oxide Films

The crystal structures of the NiO films deposited at various $O_2/(Ar+O_2)$ ratio were examined by grazing-incidence XRD using monochromatic high-intensity Cu-Kα radiation (λ = 0.15406 nm). The surface morphology and cross-sectional image were observed with field emission scanning electron microscopy (FE-SEM). The sheet resistance of NiO films was estimated with a four-point probe, and the resistivity of the film was calculated.

3. RESULTS AND DISCUSSIONS

3.1 XRD results

Fig. 1(a) shows the XRD diffraction patterns of NiO films grown at various $O_2/(Ar+O_2)$ ratios without any intentional substrate heating equipment. The prominent diffraction peaks of NiO films are observed at 36.54°, 42.78° and 64.02° correspond to (111), (200), and (220) planes of NiO film. The crystal structure of as-deposited NiO films appeared on the XRD spectrum as polycrystalline, and it existed in a simple NiO molecular form without any other molecules such as Ni_2O_3 and $Ni_{15}O_{16}$. There are three peaks of NiO, including the (200) preferred orientation with the (111) and the (220) minor orientations. Some other groups presented slightly different crystalline orientations of NiO film. Pater *et al*. reported that the NiO films deposited on a glass at room temperature showed the (111) preferred orientation with the (200) and (220) minor orientations. However, the preferred orientation, which was described by Fujji et al., changed from (111) to (200) directions with the increase of the substrate temperatures [1,19]. Chen *et al* observed that the NiO films deposited at a substrate temperature of 303 K, with a ratio of oxygen ranging from 0 to 100%, displayed a (111) preferred orientations [14]. The NiO films deposited at the substrate temperature of 673 K showed the (111) orientation, when the oxygen ratio was low, which changed to the (200) preferred orientation at ratio of 100% oxygen. We investigated the (200) preferred orientation (shown in Fig 1(a)) is due to the substrate temperature increase or if it is related to the oxygen pressure. An effective cooling system was installed to maintain the substrate at room temperature to avoid unintentional heating. And then the influence of oxygen pressure was studied.

Fig. 1(b) presents the XRD diffraction patterns of the films that

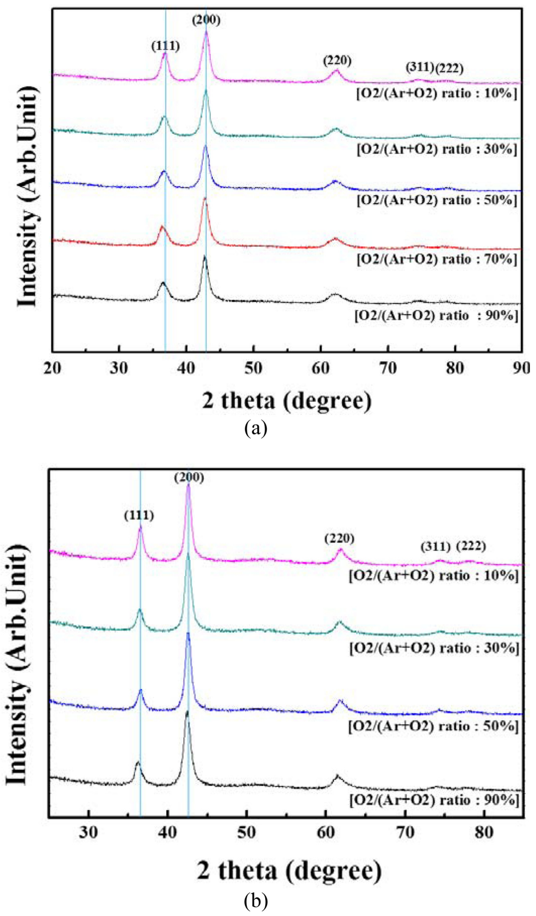

Fig. 1. XRD diffraction patterns of the NiO films deposited at various $O_2/(Ar+O_2)$ ratios; (a) without intentional heating, (b) with intentional substrate cooling.

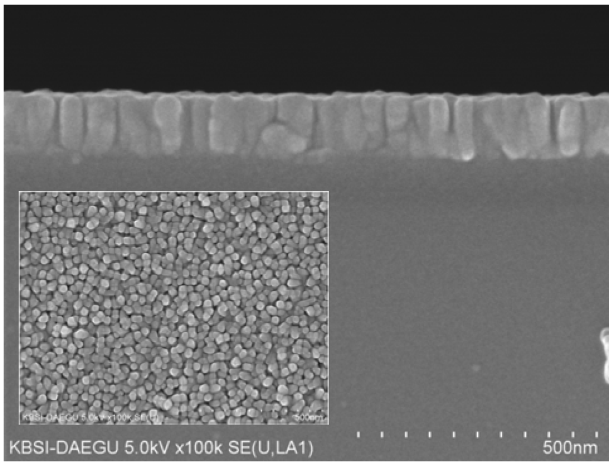

Fig. 2. FE-SEM photographs of the surface and cross-section of the NiO film deposited in 50% $O_2/(Ar+O_2)$ gas mixture.

were acquired at various $O_2/(Ar+O_2)$ ratios with intentional substrate cooling. The grown NiO films deposited with substrate cooling showed NiO(111), NiO(200) and NiO(220) peaks, and the intensity of the NiO(200) peaks are higher than those of both NiO(111) and NiO(220). Thus the preferred orientation does not seem to change if the film is deposited under intentional substrate cooling. However, the peak intensity of NiO(111) decreases gradually when the $O_2/(Ar+O_2)$ ratio increases, which means that the O_2 partial pressure in a reactant gas can cause a slight decrease of (111) orientation in the NiO films. However, the NiO peaks in Fig. 1 shift to a low angle when the $O_2/(Ar+O_2)$ ratio decreases. This indicates that the lattice constant of the NiO film is enlarged while depositing the NiO film in higher $O_2/(Ar+O_2)$ ratio [20].

The FE-SEM photographs of the surface and the cross-section of NiO film deposited in a 50% $O_2/(Ar+O_2)$ gas mixture are shown in Fig. 2. The surface grains are homogeneous and uniform in size and distribution with grain sizes of 50-70 nm.

The cross-sectional view shows columnar structures grown perpendicularly to the SiO_2/Si surface, and dense, smooth and homogeneous features. In the different oxygen rations, all grown films also have structures similar to that shown in Fig. 2. Previous reports have suggested that the NiO film surface depends on both the oxygen content in the film and the deposition temperature [1, 2,6,7,13,21]. However, there was no grain size or direction change in the acquired SEM images, regardless of the substrate cooling. As shown in Fig. 2, the grains grew continuously from the bottom of each grain, and the orientation of each grain did not change during the film growth.

The thin films of a columnar structure are known for the preferred generation of the micro-crystal orientation due to the different growth rate in each grain [22]. This is based on the hardly movable deposited atoms [22].Thus, each grain generated at the early stage of NiO growth can be easily maintained the initial crystallographic orientation because of a reduced secondary nucleation.

The sheet resistance of NiO were measured with a four-point probe system at as-deposited status. The resistivity of NiO thin film was calculated by the multiplying the sheet resistance by the film thickness.

Fig. 3 shows the resistivity of NiO films formed at different $O_2/(Ar+O_2)$ gas mixtures. The resistivity decreased with increasing O_2 percentage in the $O_2/(Ar+O_2)$ mixture. The conduction mechanism of NiO film is seem to be related to the vacancies existing inside the material. These electrical properties of NiO films are associated with their microstructure and composition which are usually dependent on the deposition environment [17].

The resistivity of stoichiometric NiO is as high as $10^{13}\Omega\cdot cm$ [14]. However, the acquired resistivity of the NiO film

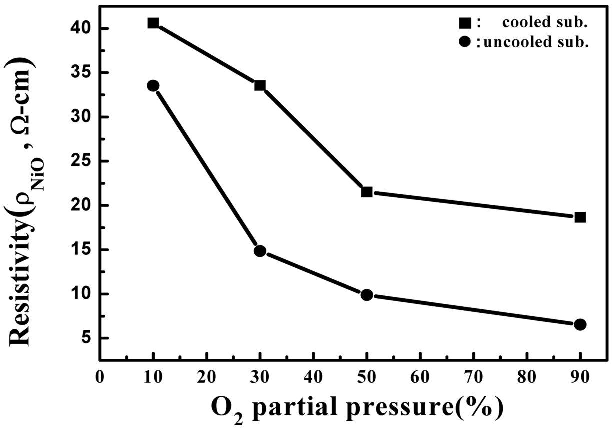

Fig. 3. Resistivities of NiO films deposited at different $O_2/(Ar+O_2)$ gas mixtures: with and without intentional substrate cooling.

deposited in the $O_2/(Ar+O_2)$ gas mixture decreased to a few ┬cm owing to the expected non-stoichiometric NiO films. Excess oxygen in the non-stoichiometric NiO films can create vacancies to occupy Ni^{2+} sites [23]. When two Ni^{2+} ions are replaced by two Ni^{3+} ions, a vacancy can be formed at an Ni^{2+} site. Thus, the increased numbers of holes act as carriers in the NiO films which lead the resistivity to decrease as the $O_2/(Ar+O_2)$ ratio increases [24,25]. At each O_2 partial pressure, the resistivity of NiO films deposited under the cooling is higher than that of the NiO film deposited without intentional cooling.

Chen et al reported that the value of resistivity decreased according to increasing substrate temperature [7]. The results shown in this study are without substrate heating. Thus the change of resistivity was caused by natural heating of the substrate. A comparison between Chen *et al*'s study and these results indicates that the heated substrate lowers the electric resistivity of NiO films. For better resistivity control of NiO film, adapting the cooling system is necessary because the substrate temperature varies greatly. For the lower resistivity of NiO films, precisely controlled high temperature is required.

4. CONCLUSIONS

NiO films were deposited on the SiO_2/Si substrate using no additional heater and an effectively designed substrate cooling system at oxygen ratios ranging from 10% to 90%. The grown films displayed the (200) preferred orientation. The intensity of XRD at the (111) and (200) preferred orientations of NiO films are affected by changing the $O_2/(Ar+O_2)$ ratio. The cross-sectional FE-SEM photographs showed that the NiO film had a columnar structure perpendicular to the surface of the SiO_2/Si substrate. Resistivity decreased according to the increase of the O_2 percentage in the $O_2/(Ar+O_2)$ mixture. At each O_2 partial pressure variation, the resistivity in NiO films deposited when using the intentional cooling system was larger than that of the NiO film deposited without any intentional cooling procedures. Thus, the temperature increase of the SiO_2/Si substrate could change the resistivity even in case with the same oxygen partial pressure. Thus, it can be concluded that the resistivity variation of NiO thin films is dependent on the oxygen content as well as the deposition temperature.

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