Fabrication and Properties of Porous Ni Thin Films

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ABSTRACT

We have deposited NiO films by RF sputtering on $Al_2O_3/SiO_2/Si$ and 100 nm-thick Gd doped CeO_2 covered $Al_2O_3/SiO_2/Si$ substrates at various Ar/O_2 ratios. The deposited films were reduced to form porous Ni thin films in 4% H_2 at 400°C. For the films deposited in pure Ar, the reduction was retarded due to the thickness and the orientation of the NiO films. On the other hand, the films deposited in oxygen mixed ambient were reduced and formed porous Ni films after 20 min of reduction. We also investigated the possibility of using the films for the single chamber operation by studying the electrical property of the films in the fuel/air mixed environment. It is shown that the resistance of the Ni film increases quickly in the mixed gas environment and thus further improvements of Ni-base anodes are required for using them in the single chamber operation.

Key words : Sputtering, NiO, Porous film, Fuel cell anode, Reduction

1. Introduction

R ecently, there is growing interest of using mini- and micro-SOFCs for portable power generation.[1-4] A micro-SOFC (μ-SOFC) has several distinctive advantages over batteries since it has much higher power density and does not require long recharging times. Therefore, if a micro-fabricated fuel cell could be integrated with other electronic circuits, this would expand the possibility of the operation of portable devices.[1] However, the operation temperature of the conventional SOFC is typically very high (≥800°C), and this constraint imposes several issues such as cell degradation due to interface reactions and thermal expansion mismatches among components such as electrodes, electrolytes, and sealants. Especially for the micro-fabricated cells, this temperature is too high for sustaining the cell structure, thus the operation temperature should be lowered. Furthermore, the cell design that is more resistant to the thermal shock should be studied. In this regard, single chamber SOFCs are particularly attractive since their design can be much simplified without using sealants and this can make single chamber fuel cells more thermal shock resistant.[4]

For the single chamber operation, SOFCs are placed in an air-fuel mixture environment. In this environment, the stability of the electrodes becomes more important for reliable operations. Currently, nickel is the most commonly used material for the anode of SOFCs. This is due to the economical reason and the catalytic activity of Ni anode in the oper-ation temperature range of SOFCs.[5-7] A requirement for Ni anodes is the sufficient porosity for ensuring gas transport to the reaction sites which correspond to the interface between the Ni anode and the electrolyte for increasing the efficiency of the cell operation. The stability of the Ni-based anode in the air-fuel mixed ambient also becomes important for the single chamber operation.

Therefore, in this work, we focused on developing porous Ni thin films for using those in micro-fabricated single chamber μ-SOFCs. The fabrication of porous Ni thin films by reducing NiO films sputter deposited at different O_2/Ar ratios is discussed. Furthermore, the stability of the Ni anodes in the single chamber operation is discussed based on the impedance analysis of Ni films in the air methane mixture environment.

2. Experimental Procedure

$Al_2O_3/SiO_2/Si$ (100) substrates and 100 nm-thick Gd doped CeO_2 (GDC) covered $Al_2O_3/SiO_2/Si$ (100) substrates were used for the experiments. 150 nm-thick Al_2O_3 layers were deposited by using an e-beam evaporation method on thermal SiO_2 (1 μm) covered Si (100) substrates. GDC thin films were sputtered by DC and RF reactive co-sputtering of metal Gd and Ce targets in oxygen/argon ambient. The power of DC (Gd) and RF (Ce) during the deposition was 10 W and 100 W, respectively. The deposition was performed at room temperature and the ambient pressure was 11 mTorr. The measured growth rate of GDC thin film was 1.4 nm/min at an O_2/Ar gas ratio of 0.1 (3 sccm/30 sccm).

NiO thin films were deposited on both Al_2O_3 and GDC covered substrates by using RF sputtering at various O_2/Ar ratios. O_2/Ar ratios were controlled by changing flow rates of each gas at a fixed ambient pressure of 5 mTorr. A 4-inch

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NiO target was sputtered at room temperature with the RF sputtering power of 300 W. After the NiO film deposition, the films were annealed at 400°C up to 20 min in 4% H_2 for reduction.

To confirm the crystallinity and phase of the thin films, X-Ray Diffraction (XRD, Rigaku, CuK_α) measurements were carried out and the surface morphologies and thickness of thin films were observed by scanning electron microscopy (SEM, Philips, V_{acc} = 15 kV). The reduction and the re-oxidation behavior of Ni-base films in H_2 and CH_4/O_2 (R_{mix} = 2) mixed ambient were investigated by AC impedance spectrum analysis (SI 1287 and SI 1260, Solartron). The impedance analysis was performed on the NiO films deposited on the Al_2O_3 covered substrates for investigating the property of the films only without the interference of that of the electrolyte (GDC). The measurement frequency range varied from 0.1 Hz to 10 MHz.

3. Results and Discussion

Fig. 1(a) shows θ-2θ XRD measurement results of as-deposited NiO thin films on $Al_2O_3/SiO_2/Si$ at various O_2/Ar
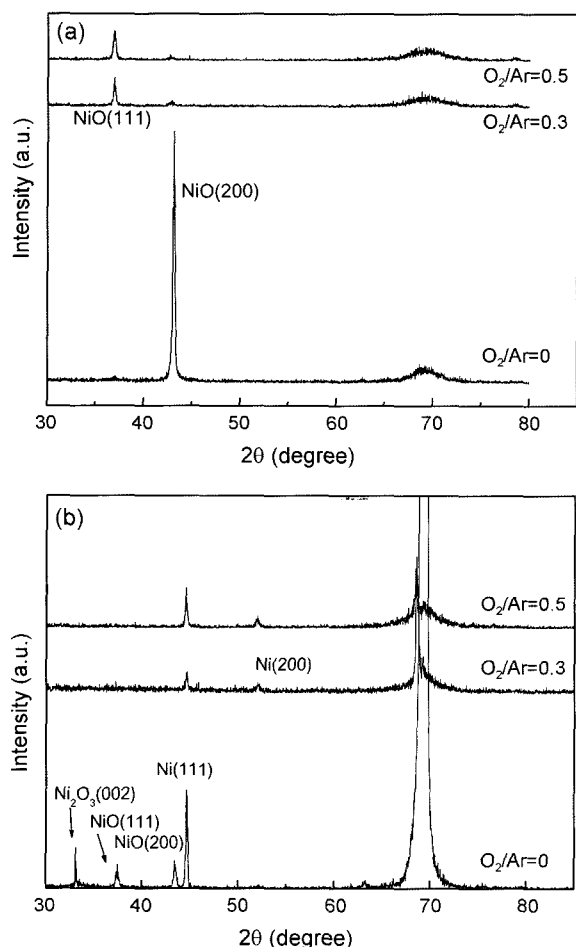

Fig. 1. θ-2θ XRD results of (a) as-dep NiO thin films in various O_2/Ar ratios and (b) films after reduction.

ratios for 1 h. The film deposited in pure Ar ambient exhibits only a sharp (200) peak, which indicates a strong (100) textured structure. On the other hand, the films deposited in O_2/Ar mixed ambient show (111) and weak (200) peaks. Ryu et al.[8] explained this phenomenon with the atomic arrangement and surface free energy of growing NiO films. In oxygen mixed ambient, the sputtering process may yield an oxygen-abundant environment due to the plasma decomposition of O_2, hence the crystallographic orientation of the NiO film is controlled by the arrangement of O^{2-}. This results in the (111)-oriented NiO structure because the (111) plane is the most densely packed plane of O^{2-}. For the films deposited in pure Ar ambient, however, Ni and O ions may exist in similar proportion, thus (100) planes on which both Ni and O are close-packed are preferred.[8]

We postulate that the relatively high intensity of the (200) peak of the film deposited at O_2/Ar = 0 is due to the thicker NiO film layer compared with other specimens deposited at different O_2/Ar ratios. The thicknesses of the NiO films prepared in pure Ar, O_2/Ar = 0.3, O_2/Ar = 0.5 were approximately 540 nm, 203 nm, 207 nm, respectively, which indicates that the deposition rate decreases when O_2 is introduced. This is because Ar is heavier than O_2 and more efficient in a momentum transfer process, thus the sputtering yield increases.[9] Also, the sharpness of the (200) peak of the film deposited in pure Ar suggests that this film has larger grain sizes and better crystallinity compared with other films sputtered in oxygen mixed ambient.

Fig. 1(b) shows XRD patterns of reduced NiO thin films in 4% H_2 atmosphere at 400°C for 20 min. It is shown that the films fabricated in the O_2/Ar ambient are completely reduced to Ni after the reduction. On the contrary, the film deposited in pure Ar exhibits remaining NiO peaks even after the reduction, which means the reduction of the film is sluggish. Such sluggish oxygen removal kinetics is also supposed to explain the existence of extraordinary peak at 32°, which corresponds to (002) peak of Ni_2O_3. We believe that the thickness of the film contributes to this result. In addition, the removal of oxygen from this film may be retarded since the oxygen close-packed plane, i.e. (111), is not parallel to the film surface due to its strong (100) texture.
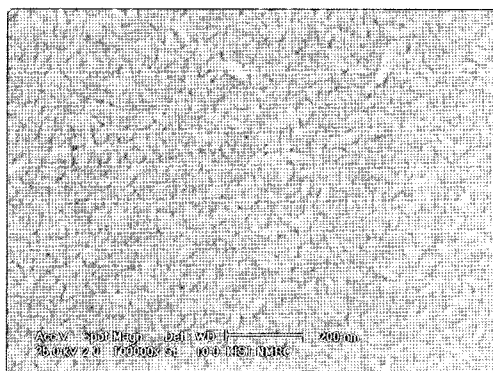
Fig. 2(a), (b), and (c) show the SEM micrographs of the surface of the as-deposited NiO films on GDC thin films in pure Ar, O_2/Ar = 0.3, and O_2/Ar = 0.5, respectively. Each of the films displays continuous and homogeneous surface morphologies. The films deposited in the Ar-O_2 gas mixture consist of small grains, while coarse grains are observed for the films fabricated in Ar. We believe that the difference of grain size is caused by the difference of the film thicknesses and excess O atoms. The grain size of the film increases as the thickness of thin film increases. In addition, oxygen incorporation during the growth can contribute to the grain size difference. As O_2 in the ambient increases, the oxygen content of thin films could increase. These excess O atoms may segregate at grain boundaries and impede grain growth. This phenomenon is in good agreement with the
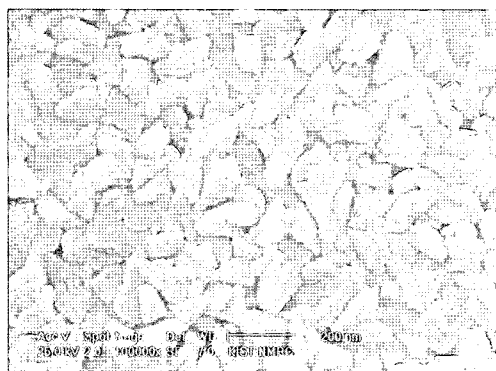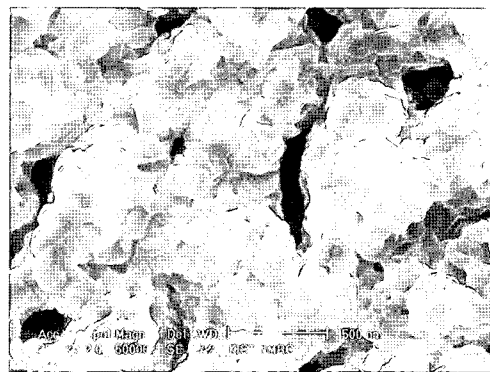
(a)
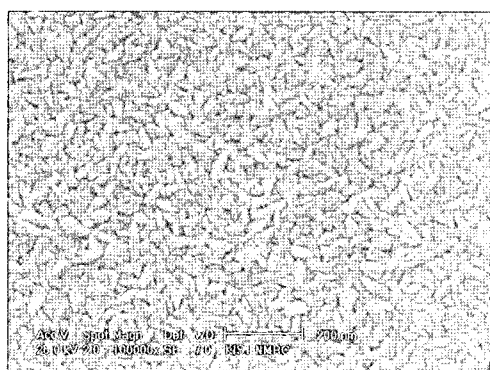
(b)

(c)

Fig. 2. SEM micrographs of as-dep NiO thin film surfaces deposited in (a) pure Ar, (b) O_2/Ar=0.3, and (c) $O_2/$Ar=0.5.

(a)

(b)

(c)

Fig. 3. SEM micrographs of NiO films deposited in (a) pure Ar, (b) O_2/Ar=0.3, and (c) O_2/Ar=0.5 after reduction in 4% H_2 at 400°C.

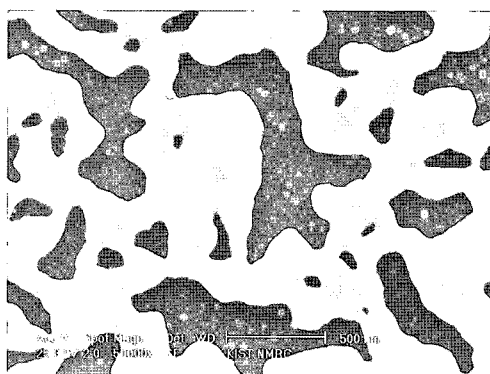results that Yoon et al.[10] have reported.

Fig. 3(a), (b), and (c) show the SEM micrographs of the surface morphologies of the films deposited on GDC covered substrates in pure Ar, O_2/Ar = 0.3, and O_2/Ar = 0.5, respectively, after reducing in 4% H_2. The surface morphology of the film deposited in pure Ar is dissimilar to that of others. The films grown in oxygen mixed ambient became substantially porous because of the complete reduction of NiO to Ni, while the porosity of the film deposited in pure Ar is much less than that of other films due to the sluggish reduction. This result is also consistent with the XRD results shown in Fig. 1.

From these results, we believe that the oxygen mixed ambient during the sputtering process is more beneficial for fabricating porous Ni thin film, even though that the crystallinity of as-deposited films in pure Ar appears to be better. This porous structure is essential for SOFC electrode applications for increasing triple phase boundaries. However, when O_2/Ar proportion increases to 0.5, the adhesion of the film deteriorates significantly due to high porosity. Thus, we chose the condition for depositing NiO films as $O_2/$Ar = 0.3 for further experiments.

For observing the reduction behavior of NiO films, we performed impedance analysis on the NiO film in 4% H_2 at
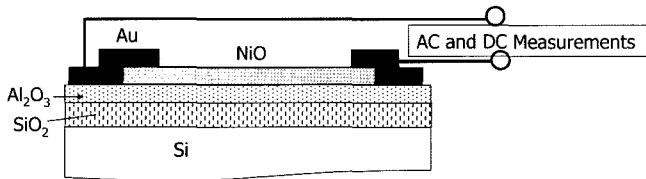
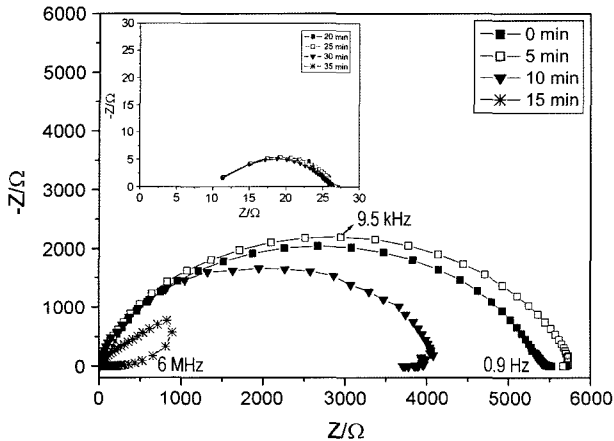**Fig. 4.** Impedance measurement configuration of NiO thin films.

Fig. 5. Impedance spectra of NiO thin film during reduction in H_2.

Fig. 6. Resistance change of NiO thin film in CH_4/Air mixed gas.

400°C with increasing reduction time. The film was deposited on an $Al_2O_3/SiO_2/Si$ substrate and the Au electrodes for the measurement were formed on-plane. The measurement configuration is shown in Fig. 4. Fig. 5 shows impedance analysis results of the NiO thin film during the reduction. The resistance of NiO thin film was 5.5 kΩ before the reduction started. The resistance of NiO thin film slightly increased after 5 min of reduction. We postulate that this is because the pores start to appear while the main matrix remains as NiO at the initial stage of the reduction. At this stage, the reduction of NiO to Ni is insignificant and/or the amount of the Ni phase is insufficient to ensure the connectivity that will contribute to the conductivity. After 10 min, we could observe that the resistance of the film started to decrease and then the resistance abruptly decreased around 15 min of reduction. In the inset of the Fig. 5, we present the impedance spectra after 20 min and it is shown that the resistance of the film does not change further from the value less than 30 Ω. This indicates that the significant amount of the NiO phase is reduced during 15 to 20 min and after 20 min the reduction is sufficient to produce the Ni phase over the percolation limit. This is also a consistent result with XRD measurements. The calculated conductivity of the reduced film with the film dimensions was ~ 840 $(\Omega cm)^{-1}$ which is a relatively lower value compared with bulk Ni and this is because the connectivity of the reduced film is poorer than continuous bulk Ni due to the pore formation.

For investigating the possibility of using the porous Ni film in a single chamber SOFC application, we performed
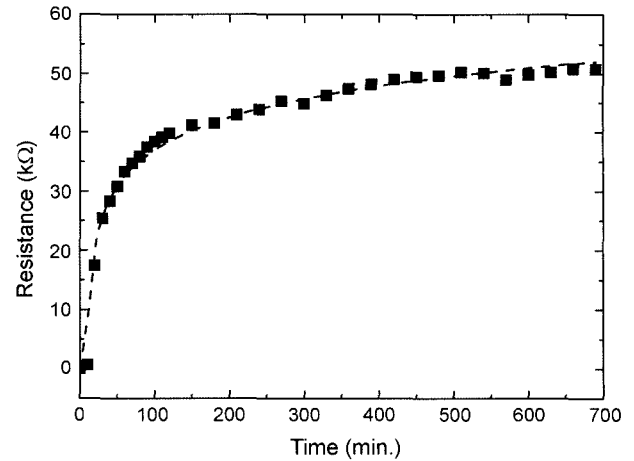
impedance analysis on porous Ni film in a CH_4/Air (R_{mix} = 2) mixed gas environment at 400°C. It is shown in Fig. 6 that the resistance of the Ni film increased during a short duration of the time in the mixed gas environment. We postulate that this indicates that part of the Ni films re-oxidizes quickly in the air/fuel mixture and/or the adhesion of the film is impaired. This sudden decay of the electrical property can deteriorate the overall cell performance during the single chamber operation. Hence, we need to improve Ni-base anodes by using additives or cermets for preventing re-oxidation. Moreover, these attempts may improve the adhesion of the Ni-base anodes. Further investigations based on these ideas are under progress and following results will be presented shortly.

4. Conclusions

We have successfully fabricated porous Ni thin films by reducing NiO thin films. The NiO films were deposited by RF reactive sputtering in various O_2/Ar ratios and reduced by annealing in H_2 atmosphere at 400°C. For the films deposited in pure Ar, the reduction was retarded due to the thickness and possibly the orientation of the NiO films. On the other hand, the films deposited in oxygen mixed ambient were reduced and formed porous Ni films after 20 min of reduction, which is confirmed by using impedance analysis and XRD. The possibility of using the films for the anodes of single chamber micro-SOFCs was investigated by using an air/fuel mixed environment. It is shown that the electrical property of the Ni film deteriorates quickly in the mixed gas environment. Hence, we think that further modifications of Ni-base thin film anodes are required to prevent degradation for using them for the single chamber operation.

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