

Research Article

Facile Synthesis of Porous-Structured Nickel Oxide Thin Film by Pulsed Laser Deposition

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Porous-structured nickel oxide (PsNiO) was obtained through the oxidization of a nickel thin film. The nickel thin film was deposited using the pulsed laser deposition (PLD) method on a nickel foil as a substrate. The results show uniform PsNiO after the oxidization of the nickel thin film at 750°C for 1 h. X-ray diffraction (XRD) indicates formation of the NiO crystalline structure. Field emission scanning electron microscopy (FESEM) reveals different morphology on the surface of the nickel foil (sample A) and on the nickel thin film (sample B). Comparison of the FESEM results after oxidization shows that the PsNiO on the nickel thin film was more regular and controllable than the NiO layer on the nickel foil. The FESEM images also show that the thickness of the nickel thin film affected the PsNiO size obtained after oxidization. This resulted from the growth of the porous structure at grain boundaries and from the grain sizes. The electrochemical properties of the PsNiO as an electrode are investigated by cyclic voltammetry (CV). These results show the effect of PsNiO size on the current of anodic peak.

1. Introduction

Porous-structured nickel oxide (PsNiO) thin films have numerous applications in a variety of fields, such as electrochemical properties which include charging/discharging mechanism and long life cycles [1], electrochromic display devices [2], gas sensors [3], lithium-ion batteries [4], and catalysts [5]. The porous structure thin film provides a specific surface area and can facilitate a very short diffusion pathway for ions. The control of the surface morphology of the NiO thin film has attracted considerable interest for the development of advanced materials. The large variety of applications for NiO thin films results from its morphology. The PsNiO thin film has been fabricated using several physical and chemical techniques, such as chemical bath deposition [2], sol-gel process [6], anodic electrochemical

deposition [7], hydrothermal method [8], thermal decomposition [9], and pulse laser deposition method (PLD) [10]. Uniform morphology, film thickness, and purity, as well as controllable pore size improve the electrochemical properties of the NiO thin film.

Pulse laser deposition (PLD) is a one method used to fabricate high-quality thin films that is advantageous in tuning the film characteristics [10]. However, there are a few reports on the fabrication of NiO thin film arrays using PLD [11–13]. In contrast, there is a wide range of investigations on high/low temperature oxidization of pure nickel. The two most common methods used to obtain NiO thin film are cathodic precipitation and sol-gel dip coating [14–17]. In the present study, we fabricated PsNiO thin films by combining PLD and oxidization. The advantages of this two-stage method are uniform morphology, purity, controllable

pore size, and lack of template or agent. We aim to determine whether PsNiO is suitable as an electrode by examining its electrochemical properties.

2. Experimental

Two nickel foil substrates (1 cm × 1 cm) were chosen and labeled as samples A and B (purity 99.9%). Sample B was selected as a substrate for the deposition step using the PLD method; a nickel plate (purity 99.98%) was used as a target. Before the deposition process, the substrate and the target were cleaned to eliminate impurities. The thin film was deposited using a Class 4 Laser Nd: YAG with 1064 nm wavelength. The nickel thin film was deposited onto sample B under a vacuum level of 7×10^{-4} Pa. First, deposition took place at 400°C for 10 min. The nickel thin film was then cooled in the chamber by turning off the heater. Next, samples A and B were placed into a horizontal tube furnace (100 cm in length, 5 cm in diameter) for oxidation. High purity O₂ gas was fed at a rate of 30 Sccm into the furnace tube under 1 atm. The furnace was heated from room temperature to 750°C at a rate 10°C/min and then held at 750°C for 1 h. Finally, the furnace was cooled down naturally to room temperature.

X-ray diffraction (XRD) spectra of the samples were recorded on a SIEMENS D5000 X-ray diffractometer (Cu K α X-ray radiation $\lambda = 1.54056 \text{ \AA}$). The morphology of the samples was observed on an FEI Quanta200 FESEM operated at 5.00–20.0 KeV. The cyclic voltammetry (CV) was measured on a CHI 630B electrochemical workstation at a scan rate of 25 mVs⁻¹ between 0.00 V and 0.45 V (versus SCE) in 0.1 M KOH electrolyte.

3. Results and Discussion

Figure 1 shows the XRD patterns of samples A and B. Figures 1(a) and 1(b) show the XRD patterns of the nickel foil and the nickel thin film, respectively, before oxidization. The diffraction peaks at 44.50°, 51.87°, and 76.41° correspond well with the three most intense peaks (111), (200), and (220), respectively, of the face-centered cubic (fcc) metallic nickel (JCPDS Card No. 01-087-0712). Figures 1(c) and 1(d) show the XRD patterns of the nickel foil and the nickel thin film, respectively, after oxidization at 750°C for 1 h under O₂ gas flow. They clearly show diffraction peaks at (111), (200), (220), (311), and (222) of the fcc structured NiO at $2\theta = 37.25^\circ, 43.31^\circ, 62.88^\circ, 75.42^\circ,$ and 79.41° , respectively, which can be indexed to JCPDS File No. 01-089-3493. No impurity peaks are observed in the XRD pattern other than Ni diffraction peaks. The well-defined peaks suggest a well-crystallized structure.

The FESEM images of samples A and B are given in Figure 2. The images show the differences in surface morphology between the nickel foil and the nickel thin film. The surface of the nickel foil before oxidization shows a smooth texture (Figure 2(a)). The ridge-like morphology of the NiO structure can be seen on nickel foil after oxidization (sample A in Figure 2(b)). The cross-section

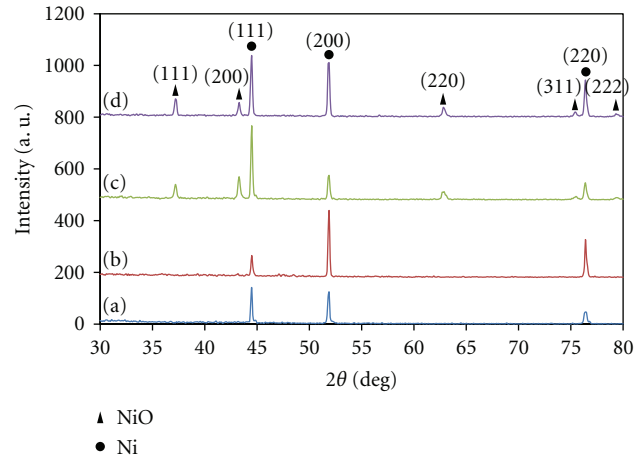


FIGURE 1: XRD patterns of (a) nickel foil, (b) nickel thin film deposited by PLD, (c) nickel foil, (d) nickel thin film after oxidization.

image (Figure 2(c)) shows the oxide layer with a thickness of around 1600 nm. The NiO inner layer is not porous in nature, as the ridge-like morphology was only visible on the surface of the NiO layer. The results of the FESEM images are in agreement with several studies that reported the growth mechanism of the NiO layer in oxidization of nickel [14, 18]. Also, in the low temperature range (700°C to 900°C) ridge-like morphologies are often observed on the surface of nickel foil. These morphologies follow the shapes of the grain boundaries and result from rapid outward grain boundary diffusion. Previous studies have suggested several mechanisms to explain the formation of the NiO inner layer [19].

The FESEM images of sample B clearly show the behavior of the nickel thin film during oxidization. Figure 2(d) shows a smooth texture of the nickel thin film after deposition. The surface morphology considerably changed after oxidization of the nickel thin film at 750°C for 1 h (Figure 2(e)). A relatively uniform pore structure was created on the entire thin film surface deposited on the substrate. The porous structure consisted of an interconnected network of NiO flakes with pore sizes in the range of 100 to 200 nm. The cross-section image shows a uniform coarse columnar morphology oxide layer with a thickness of around 600 nm (Figure 2(f)). The nickel thin film appears to prevent oxidization of the nickel substrate. In addition, oxygen has a stronger interaction with the thin film than with the substrate. Therefore, the formation of a continuous network of porosity during oxidization can be controlled using the film characteristics. Comparison of the FESEM images for samples A and B clearly show that the oxide morphology changed with deposition of the nickel thin film on the nickel foil as a substrate. This can be explained by the uniform pore structure resulting from the growth of the NiO flakes at the grain boundaries and the uniform grain size of the thin film scale. Also, the plastic deformation of the flakes is a consequence of rapid growth [19].

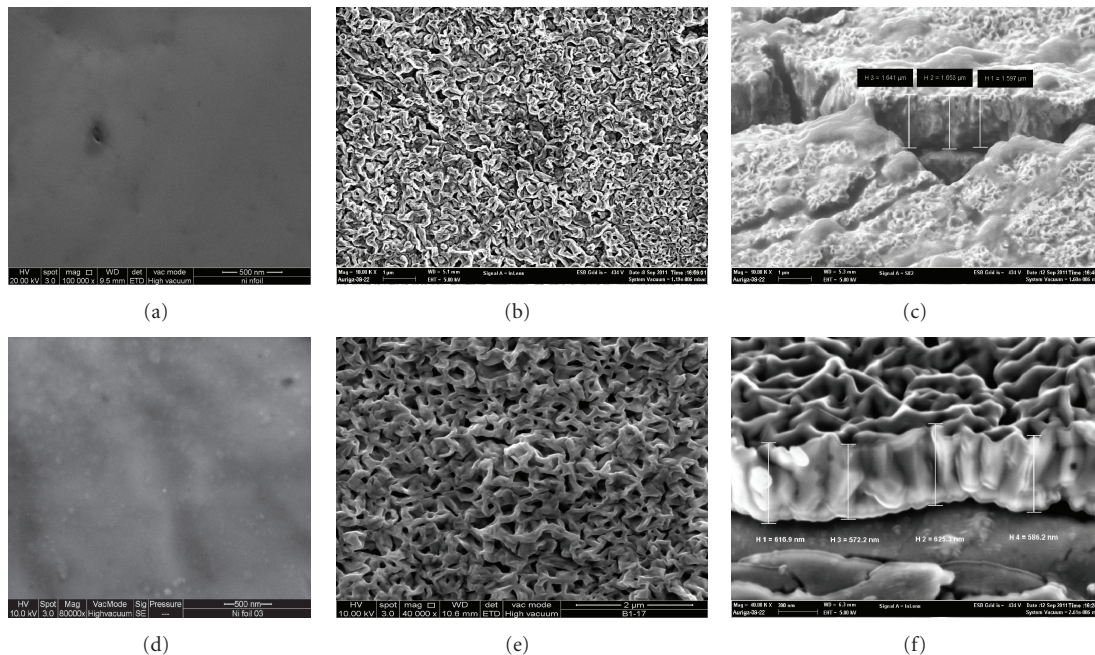


FIGURE 2: FESEM images of samples A and B, for (a) nickel foil, nickel foil after oxidization (b-c), nickel thin film after deposition by PLD (d), and nickel thin film after oxidization (e-f).

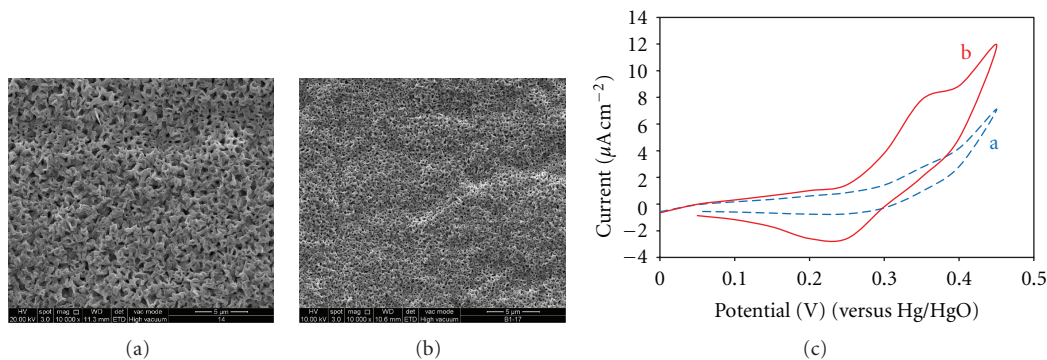


FIGURE 3: FESEM images of porous-structured NiO formed on nickel thin film with deposition of 30 min (a) and 10 min (b). (c) Cyclic voltammograms recorded for (a) and (b).

Figures 3(a) and 3(b) present the FESEM images of the PsNiO thin film obtained from nickel thin films oxidized at 750°C for 1 h. Deposition took place at 400°C for 30 min and 10 min, respectively, for samples a and b; average thickness was calculated as 430 and 170 nm, respectively. The FESEM results confirm that the morphology of both samples was similar but with different porosity. The pore size of the PsNiO increased with the increase in thickness of the nickel thin film. Thus, pore size strongly depends on the shape of the grain boundaries and on the grain size of the thin film. Note that the grain size is proportional to the thickness of the thin film [20]. Thus, the thickness of the deposited thin film can be used to control the pore size.

A cyclic voltammetric test was conducted to determine the ability of the fabricated PsNiO thin film to act as an electrode. Figure 3(c) shows the cyclic voltammograms of

samples (a) and (b) carried out in 0.1 M of KOH aqueous electrolyte. The results clearly show an anodic peak around 0.35 V and a cathodic peak at 0.24 V, in accordance with the results of Wu and Yang [21]. The current of redox reaction in sample (b) increased significantly. The results show that increasing surface area is a consequence of decreasing pore size of the NiO thin film, which facilitates electrolyte penetration. Therefore, the PsNiO thin film with a highly porous-structured morphology obtained by PLD is able to produce thin films to be used as electrodes with advantageous electrochemical behavior.

4. Conclusion

In this study, the PsNiO thin film was successfully prepared on a nickel foil substrate by combining PLD and oxidization;

this two-stage process modified the morphology of the NiO thin film on nickel foil. This method resulted in PsNiO with a high degree of uniformity. The FESEM images show that the highly PsNiO thin films possess an interconnected network structure. The method presented here also reveals that the PsNiO thin film with improved morphology can be used for electrochemical applications.

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