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Microstructural characterization of nickel hydroxide films deposited using an ammonia-induced method and subsequently calcined nickel oxide films

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ABSTRACT

Nickel hydroxide films were deposited using a facile ammonia-induced method. The deposited films were composed of stacking structures without using templates or surfactants. The microstructures of the deposited films and subsequently calcined NiO films were characterized using X-ray diffraction, scanning electron microscopy and transmission electron microscopy. The electrical properties were also investigated. The deposited films consisted of triangular stacks of single crystal hexagonal $Ni(OH)_2$ and their microstructures were highly affected by the substrate type. A preference for orientation along the (001) plane was observed in the $Ni(OH)_2$ films deposited onto indium tin oxide (ITO) substrates with a high texture coefficient of 4.5. These characteristics were not found in $Ni(OH)_2$ films deposited onto glass and silicon substrates. Calcined films did not show a strong preference in orientation and were found to be n-type NiO.

1. Introduction

Nanostructured inorganic materials have attracted considerable attention in recent years because of their superior structural features. One such feature is a high surface area that promotes surface activity. This feature is important in various applications, such as fuel cells [1] and electrochemical capacitors [2]. Nickel hydroxide ($Ni(OH)_2$) and nickel oxide (NiO) films have been extensively studied for a variety of applications. The $Ni(OH)_2$ films can be used as electrodes in battery applications as well as fuel cells. The NiO films, which can be achieved through calcination of $Ni(OH)_2$ films, are applicable to electrochromic devices [3,4], gas sensors [5], and electrochemical supercapacitors [6].

$Ni(OH)_2$ film deposition can be achieved using various methods, such as spray pyrolysis [7], sputtering [8], electrodeposition [9], and chemical bath deposition [10]. The chemical bath deposition (CBD) is one of the simplest film deposition techniques. Films formed using CBD also have the advantage of having a porous structure. Various nanostructured $Ni(OH)_2$ films have been reported [11–13]. However, conventional CBD film microstructures without surfactants [10–12] are difficult to control because of their fast reaction rates.

In 2008, Li et al. [14] reported the formation of nanostructured particles of $Ni(OH)_2$ synthesized using ammonia-evaporation-induced synthetic method. This technique allowed some control over the microstructures of the formed particles. In this study, we use a facile, template-free ammonia-induced technique to form $Ni(OH)_2$ films on the glass and indium tin oxide (ITO) substrates. This allowed us to investigate the microstructures of these films and the properties of

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the CBD films formed by the ammonia-induced technique. The morphologies and crystallography of the deposited Ni $(OH)_2$ films and the subsequently calcined NiO films were characterized using X-ray diffraction (XRD), scanning electron microscopy (SEM) and transmission electron microscopy (TEM). The electrical characteristics were also measured and discussed.

2. Materials and methods

The chemicals used in this study were nickel (II) nitrate hexahydrate and 28–30% ammonium solution obtained from Sigma-Aldrich. All chemicals were used without further purification. Glass slides, commercially available ITO glass and silicon served as the substrates for deposition. They were cleaned thoroughly, dried and put in a Petri dish with the deposition side up. The deposition of $Ni(OH)_2$ using an ammonia-induced method was conducted by mixing 20 ml of 1 M nickel nitrate solution and 40 ml of ammonium solution. The mixed solution was poured into a Petri dish and covered. The Petri dish was put inside an oven and set to 90 °C for 3 h. Calcination was conducted at 400 °C in the air for 2 h. The heating and cooling rates were 5 °C min^{-1}.

Deposited films both before and after calcination were investigated using parallel beam XRD (Rigaku, TTRAX III) with CuKα radiation at 50 kV, a current of 300 mA, and a scanning speed of 5° min^{-1} at 2θ steps of 0.02°. The parallel beam method was applied to eliminate the effect of surface roughness of the sample. A scanning electron microscope (SEM, JEOL JSM-5410) operated at an accelerating voltage of 20 kV and a transmission electron microscope (TEM, JEOL JEM-2010) operated at 200 kV were used to investigate the phases and microstructures of the deposited samples. Cross-sectional TEM specimens were prepared using a focused ion beam. Electrical properties of the calcined samples were investigated by a 4-probe method using a home-made device.

3. Results and discussion

Fig. 1 shows XRD peaks of as-deposited $Ni(OH)_2$ films on (a) glass and (b) ITO substrates, with 3 h deposition times. The deposited films were found to match JCPDS card number 04-016-2986 and can be identified as hexagonal $Ni(OH)_2$. It can be clearly seen that the peak intensity at 19.2° of the (001) plane of $Ni(OH)_2$ sample deposited onto the ITO substrate was very high compared to other peaks. The other peaks were indexed as ITO substate and (100), (002) and (012) of $Ni(OH)_2$. This indicated that there was a preferred orientation for films deposited onto ITO substrates. The XRD results of the film deposited onto the glass substrate did not exhibit the same orientation preference. Fig. 2 shows the XRD peaks of calcined films on (a) glass and (b) ITO substrates. The deposited films were found to match JCPDS card number 04-005-9695 and were identified as cubic NiO.

In order to identify the texture of the deposited films, texture coefficients (TC) were calculated using the TC formula shown in Eq. (1):

$$TC(hkl) = \frac{I(hkl)/I_0(hkl)}{N^{-1}\sum I(hkl)/I_0(hkl)} \quad (1)$$

I is the relative intensity of the measured (hkl), I_0 is the standard relative intensity of the reference, and N is the number of peaks used in the calculation. The planes used for the TC calculation of the $Ni(OH)_2$ films were (001), (100), (011), (012) and (110). The planes used for TC calculation of the NiO films were (111), (200) and (220). The TC values of the films deposited onto ITO and glass substrates, both before and after calcination, are shown in Table 1. The high TC value of the (001) plane of the as-deposited film on the ITO substrate indicated that the Ni $(OH)_2$ film was highly textured with a preferred orientation along (001) plane. The calcined NiO film on ITO substrate showed a preferred orientation along the (111) plane, which is an equivalent plane to (001) in hexagonal $Ni(OH)_2$. However, the degree of texture decreased compared to that of the film before calcination. For the glass substrates, TC values of as-deposited and calcined films were below 2, suggesting that there was no specific preferred orientation.

Fig. 3(a) and (b) shows secondary electron SEM images of the as-deposited films on glass and ITO respectively.

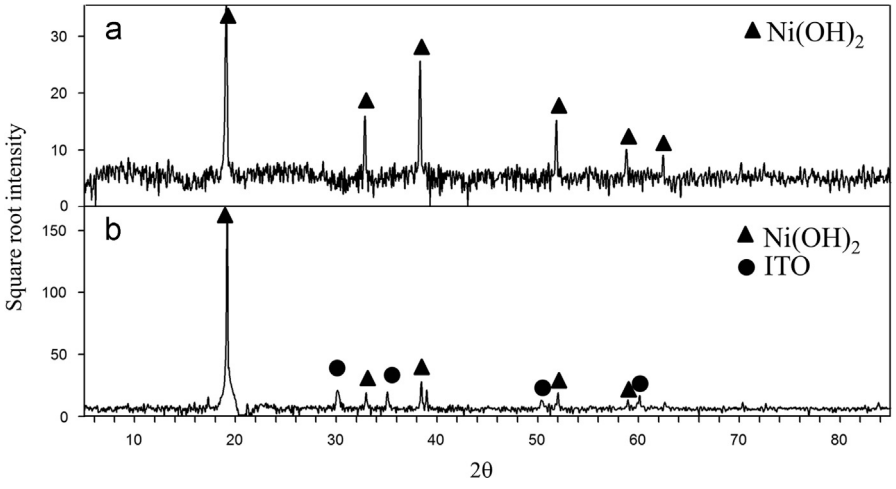

Fig. 1. X-ray diffraction (XRD) results of $Ni(OH)_2$ films deposited onto (a) glass and (b) indium tin oxide (ITO) substrates.