

Growth rate enhancement of liquid phase deposited nickel oxide film on ITO/glass under UV photo-irradiation

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The growth of nickel oxide film grown on indium–tin oxide/ glass substrate by liquid phase deposition is enhanced under ultraviolet photo-irradiation was studied. α -Ni(OH)₂ dominates the composition of as-grown NiO film. After thermal treatment at 300 °C, α -Ni(OH)₂ is transformed into NiO. For thermally treated NiO under ultraviolet photo-irradiation, the recrystallization and the colored and bleached transmittance after 50 times electrochromic test were improved. Both improvements come from fluorine passivation.

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1 Introduction In recent years, nickel oxide (NiO) is an attractive material for its chemical stability, excellent optical, and electrical properties [1]. NiO thin films have been studied for applications in electrochromic device [2, 3], photoelectronic device [4], and MOS gas sensor [5].

There are various methods for the growth of NiO films such as evaporation [6], electrodeposition [7], sputtering [8], sol-gel [9], chemical vapor deposition (CVD) [10], chemical bath deposition (CBD) [11], and liquid phase deposition (LPD) [12]. LPD has many advantages such as low temperature (room temperature is permissible), high uniformity, good selectivity, large area, and low cost [12]. It is especially suitable for the deposition on large area and low melting point window glass. The growth rate of LPD-NiO film was very low (50–75 nm in 16–72 h) using saturated NiF₂ 4H₂O and H₃BO₃ as the aqueous precursors at 30 °C [12]. The very low growth rate has to be improved for practical applications. The growth rate can be enhanced to 25.2 nm/h at the higher growth temperature of 40 °C from the endothermic reaction [13]. However, the growth temperature is limited due to the high vaporization of aqueous solution. The growth is also unstable due to the convention of the aqueous solution. By UV photo-irradiation, the growth rates of CVD, sol-gel process, and LPD- SiO_2 were enhanced [14]. The growth rate is mainly controlled by the formation and dehydration of intermediate species [15]. The high photon energy of UV photoirradiation can enhance the reactions and hence the growth rate. Therefore, the growth temperature can be kept lower to prevent these problems from high growth temperature.

In this study, the growth and the electrochromic characteristics of LPD-NiO films on ITO/glass under UV photo-irradiation (UV-NiO) and thermal treatment were investigated.

2 Experimental details The ITO coated glass with a sheet resistance of $20 \,\Omega$ cm was used as the substrate in this experiment. The growth solution was prepared with saturated NiF₂ 4H₂O and 0.6 M boric acid solutions. The saturated NiF₂ solution was prepared by mixing 10.5 g of NiF₂ 4H₂O with 300 ml deionized (DI) water at room temperature. After filtering NiF₂ 4H₂O precipitate, the saturated NiF₂ solution was obtained. The 0.6 M boric acid solution was prepared by mixing 18.9 g pure boric acid with 500 ml DI water. The growth temperature of LPD-NiO was kept at 30 °C. For UV-NiO growth, a 10 W mercury lamp of 254 nm wavelength was used to irradiate the growth solution. The distance between substrate and lamp is 10 cm. Scanning electron microscope (SEM) was used to measure the film thickness. X-ray was used to examine the crystalline. X-ray photoelectron spectroscopy (XPS) was used to examine the chemical structure.

The UV-NiO and LPD-NiO films were performed using a BRUKER 66v/s for the Fourier-transform infrared spectrometer (FTIR) measurements. The spectra were recorded from 400 to 4000 cm^{-1} which was using the KBr Beam splitter and PE Beam splitter and 80° grazing incident angle reflectance.

For the EC measurement, part of NiO film was removed for probing the ITO electrode. Propylene carbonate solution dissolved with LiClO₄ and a platinum (Pt) foil were used as the electrolyte and the counter electrode. The Li^+ electrode potential is -3.045 V, which is harder reductive than that of K^+ of -2.952 V. The electrolyte with Li^+ ion has better stability for electrochromic device. In addition, the Li⁺ ion with smaller ionic radius (0.78 Å) has higher mobility in metal oxide film than K^+ (1.33 Å). The coloring and bleaching speeds of the Li⁺ ion are faster in device. The LiClO₄ in propylene carbonate solution as the electrolyte is more appropriate than alkaline electrolyte such as KOH. The colored and bleached states of NiO/ITO/glass films were characterized by electrochromic test under ± 5 V for 30 s. The transmittance of NiO/ITO/glass films in the bleached and colored states was determined at the wavelength of 550 nm because it is the strongest intensity of sun radiation. The film thickness of UV-NiO and LPD-NiO films were kept at 100 nm for electrochromic test. A reflecting spectrograph was used to measure the transmittance. The transparency ratio is derived from $\Delta T\% = T_b\% - T_c\%$, where T_b is the transmittance of bleaching state, and $T_{\rm c}$ is the transmittance of coloring state. The optical density change is derived from $\Delta OD = \log(T_b\%/T_c\%)$. The coloration efficiency is derived from $\eta = \Delta OD/q$, where q is intercalated/deintercalated charge per unit area.

For the cyclic voltammetry (c-v) measurement, a CHI627C electrochemical gauge was used with a scanning rate of 1 mVs^{-1} in the range from 0.2 to 1.2 V.

3 Results and discussion Figure 1 shows the growth thicknesses of LPD-NiO and UV-NiO films prepared at



Figure 1 (online color at: www.pss-a.com)LPD-NiO and UV-NiO thicknesses as a function of growth time.

30 °C as a function of the growth time. For LPD-NiO film, the growth rate is 1.9 nm/h. For UV-NiO film, the growth rate is much enhanced to 5.9 nm/h. A smooth surface of UV-NiO film with the thickness of 260 nm grown on ITO/glass substrate is shown in Fig. 2(a), and LPD-NiO film cross-section of grown on ITO/glass substrate is shown in Fig. 2(b). Figure 2(c) and (d) are top views of UV-NiO and LPD-NiO film, respectively.

The FTIR spectrum for LPD-NiO film is exhibited in Fig. 3(1). The peaks at 3375 and 1600 cm^{-1} have been assigned to H–O bond vibrations of physisorbed and chemisorbed water linked to NiO film, respectively [16]. The peaks at 1460 and 1250 cm⁻¹ are assigned to C–H bond and C–O stretching vibration from surface contamination [17, 18]. The very weak peaks at around 1000 cm⁻¹ could be ascribed to Si–O and Si–OH [19] from the etching of glass substrate during the LPD-NiO deposition. The peak at



Figure 2 (a) and (b) for SEM cross-section, and (c) and (d) for top views of UV-NiO and LPD-NiO, respectively.





Figure 3 (online color at: www.pss-a.com) FTIR spectra for LPD-NiO and UV-NiO films.



Figure 5 (online color at: www.pss-a.com) X-ray diffraction patterns of LPD-NiO and UV-NiO films.

707 cm⁻¹ corresponds to the vibration of Ni²⁺–OH from α -Ni(OH)₂ [19].

The peak 480 cm^{-1} is attributed to the vibration of Ni²⁺–O from β -Ni(OH)₂. α -Ni(OH)₂ dominates the composition of as-grown LPD-NiO film. It is similar to the result

using Ni(NO₃) $6H_2O$ as the precursor [20]. The FTIR spectrum for UV-NiO film shown in Fig. 3(2) is almost the same as LPD-NiO. But a stronger peak of α -Ni(OH)₂ is observed. It comes from higher fluorine (F) passivation [21] due to higher F incorporation in the film under UV irradiation



Figure 4 (online color at: www.pss-a.com) X-ray photoelectron spectrum of LPD-NiO and UV-NiO films.



Figure 6 (online color at: www.pss-a.com) Atomic force microscopy 2D and 3D pictures of (a) LPD-NiO and (b) UV-NiO films.

[14]. Because α -Ni(OH)₂ has a more disorder structure and larger interlamellar spacing, the peaks of physisorbed water at 3375 cm⁻¹ and carbon surface contamination at 1460 cm⁻¹ are stronger.

From a previous study, NiO film shows the best electrochromic characteristics at the annealing temperature of 300 °C in air [13, 22]. In this study, the thermal treatment temperature is kept at 300 °C. The full ESCA spectra for LPD-NiO and UV-NiO films thermally treated at 300 °C in air are shown in Fig. 4(a). There are Ni, O, F, C, and Si in the UV-NiO and LPD-NiO films. The C is from the surface contamination, and Si is from substrate (ITO/glass). The clear Ni peaks are shown in Fig. 4(b). The peaks at about 857 and 862 eV are from Ni $2p_{3/2}$ and the peaks at about 874 and 882 eV are from Ni $2p_{1/2}$ belong to NiO [23]. The peaks of UV-NiO film are stronger and show red shifts compared with that of LPD-NiO from more F incorporated in UV-NiO film. The decomposed Ni $2p_{3/2}$ shows 854 and 862 eV belongs to Ni^{2+} state in NiO and 858 eV to Ni^{2+} in Ni(OH)_2 as shown in Fig. 4(c). It indicates that the transformation of Ni(OH)₂ to NiO is not complete under 300 °C thermal annealing in air. The Ni-F peak at about 687 eV for UV-NiO and LPD-NiO films are shown in Fig. 4(d). The Ni-F peak intensity of UV-



Figure 7 (online color at: www.pss-a.com) Transmittance spectra of (a) 1st and (b) 50th colored and bleached states for thermally treated UV-NiO and LPD-NiO films.



Figure 8 (online color at: www.pss-a.com) Cyclic voltammograms (c-v) of (a) LPD-NiO and (b) UV-NiO films after 1st and 50th the cyclic test.



NiO film is higher than that of LPD-NiO film. The higher F concentration has better passivation on defects and traps in UV-NiO film. The mass fractions of F in LPD-NiO and UV-NiO films are 1.93 and 3.42%, respectively.

From X-ray diffraction examination, the structure of asgrown LPD-NiO and UV-NiO are amorphous. After thermal treatment, weak (200) and (220) planes were observed for the structure of LPD-NiO and stronger (220) and (200) planes can be obtained for UV-NiO as shown in Fig. 5. They indicate polycrystalline LPD-NiO and UV-NiO are obtained after thermal treatment. The high crystalline quality of UV-NiO also comes from higher F concentration and better passivation of defects and traps on UV-NiO film.

The surface smoothness of thermally annealed LPD-NiO and UV-NiO films were characterized by AFM measurement as shown in Fig. 6. The root mean squared (rms) roughness of LPD-NiO and UV-NiO films are 52.1 and 3.9 nm, respectively. The much smoother UV-NiO film could be from the scission of clusters of precursors in the solution by the high photon energy under UV photo-irradiation [24].

The transmittance of thermally treated LPD-NiO/ITO/ glass and UV-NiO/ITO/glass are 80 and 86% at the wavelength of 550 nm before electrochromic test. The higher transmittance of UV-NiO/ITO/glass is from the F passivation of defect and traps. Normally, the lifetime of electrochromic device is associated with the Li⁺ ions residual quantity in NiO films. For the 1st and 50th electrochromic tests, the transmittance spectra of colored



Figure 9 (online color at: www.pss-a.com) Curves of (a) LPD-NiO and (b) UV-NiO after 200 times cyclic test.

and bleached states are shown in Fig. 7(a) and (b). The colored and bleached transmittance for LPD-NiO is lower than that of UV-NiO. It also comes from UV-NiO with fewer traps by F passivation.

Figure 8 shows cyclic voltammograms (c-v) of (a) LPD-NiO and (b) UV-NiO films after 1st and 50th the cyclic test. After 50th cyclic test, the area of c-v curve for LPD-NiO decreases significantly and that for UV-NiO almost keeps the same. The UV-NiO film shows highly stable is also from higher F concentration and better passivation.

The coloration efficiencies (η) of UV-NiO and LPD-NiO are 60.5 and 19.07 cm²/C after 50 cyclic test at a wavelength of 550 nm. The durabilities of LPD-NiO and UV-NiO films after 200 times cyclic test are shown in Fig. 9(a) and (b), respectively. The durability of UV-NiO is better than that of LPD-NiO. Figure 10(a) and (b) shows the transmittance as a function of the coloring and bleaching time for LPD-NiO and UV-NiO films. The coloring and bleaching speeds of UV-NiO film are faster than that of LPD-NiO film from higher F concentration and better passivation. Compared with sputtering, CBD and CVD, they show better durability but worse transparency ratio, coloring, and bleaching speed.



Figure 10 (online color at: www.pss-a.com) Transmittance as a function of the (a) coloring and (b) bleaching time for LPD-NiO and UV-NiO films.

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The evaporation, electrodeposition, and sol-gel NiO does not show better electrochromic characteristics.

4 Conclusions The growth rate of LPD-NiO film on ITO/glass is improved to 5.9 nm/h by high photon energy under UV photo-irradation. The thermal treatment can transform α -Ni(OH)₂ into NiO. For thermally treated NiO under ultraviolet photo-irradiation, the rms value of surface roughness is improved to 3.9 nm. The transmittance of thermally treated LPD-NiO/ITO/glass and UV-NiO/ITO/glass are 80 and 86% at the wavelength of 550 nm before electrochromic test. After 50 times electrochromic test, the colored and bleached transmittance for LPD-NiO are lower than that of UV-NiO. The electrochromic properties of the UV-NiO film are better than that of LPD-NiO. These improvements come from UV-NiO with fewer traps by F passivation.

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