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Improvement in Photochromic Property of Nickel Oxide-Based Photochromic Composite Films by Cobalt Addition

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Abstract

Nickel oxide (NiO)-based composite films with various Cobalt/Nickel (Co/Ni) ratios were fabricated, and the photochromic properties of the resulting films were evaluated. The NiO particle sizes in the composite films with Co/Ni ratios of 0~0.02 were 40~70 nm. Increase in the Co addition ratio to the composite films caused a decrease in the initial transmittance of the films, and the films with Co/Ni ratio of 0.005 and 0.01 showed a larger transmittance modulation. Co addition caused an increase in the bleaching and coloring rates, which were the largest in the film with Co/Ni ratio of 0.005.

Keywords: NiO, Co, composite film, photochromic

1. Introduction

Nickel oxide (NiO) or nickel oxyhydroxide (Ni-OOH) films show anodic electrochromism; its color changes from brown to transparent on the application of bias (Martini et al., 2001; Granqvist, Niklasson, & Azens, 2007; Abe et al., 2012) due to the redox process between Ni^{3+} and Ni^{2+}.

In our previous investigation, we fabricated NiO nanoparticles-embedded composite films using nickel nitrate methanol solution and transparent urethane resin (Miyazaki, Matsuura, & Ota, 2016). The NiO-based composite films showed a reversible photochromic property by UV irradiation, which was similar to the electrochromic properties of NiO-based thin films. In addition, the bleaching and coloring rate of NiO-based composite films was large while the transmittance modulation was small (Miyazaki, Matsuura, & Ota, 2016).

A previous report showed that the addition of Cobalt (Co) to NiO films affected its electrochromic properties, resulting in large transmittance modulation, high coloration efficiency, fast switching speed, and so on (Zhang et al., 2014). Similarly, Co addition is expected to have similar effects on the optical characteristics of NiO photochromism. In the present investigation, we fabricated Co doped NiO-based composite films according to a previous method (Miyazaki, Matsuura, & Ota, 2016) and evaluated the effects of Co addition on the photochromic properties of NiO.

2. Experimental Procedure

Nickel nitrate hexahydrate ($Ni(NO_3)_2 \cdot 6H_2O$; Wako Pure Chemical Industries Ltd., Japan), cobalt nitrate hexahydrate ($Co(NO_3)_2 \cdot 6H_2O$; Wako Pure Chemical Industries Ltd., Japan) and liquid urethane resin (M-40; Asahi Kasei Chemicals Corp., Japan) were used as starting materials. The liquid urethane resin was cured by UV light irradiation. Nickel nitrate hexahydrate was dissolved in methanol to give a Ni concentration of 5.0 mol/L, and the cobalt nitrate was mixed with the Co/Ni ratio of 0 to 0.02. 0.5 mL of the resulting solution was mixed with 3.3 g (3 cm^3) of the urethane resin. The mixture was kneaded sufficiently, and the precursor slurry was degassed under 1 kPa for 60 min. The degassed precursor slurry was spread between two slide glasses and was cured for 60 min under UV irradiation. A 1 kW high-pressure Hg lamp was used to cure the urethane resin. The cured composite films were then removed from the glass substrates. We controlled the film thickness to about 200 μm. The resulting NiO-based composite films got bleached due to UV irradiation and were, thus, placed in a dark room for 48 h to restore the initial state (the colored film). This resulted in the brown color of the NiO-based composite films.

IR spectra of the films were measured using a Fourier transform infrared spectrometer (Jasco FT-IR 660 plus, Japan). The thickness and microstructure of the films were evaluated by a scanning electron microscope (SEM, JEOL JSM-6510, Japan). The microstructure and electron diffraction of the composite films were observed by transmission electron microscopy (TEM, EM-002B; Topcon Corp., Japan). The photochromic properties of the composite films were measured with a UV-Vis spectrophotometer (UV-1600; Shimadzu Corp., Japan), and the composite films were bleached using the above-mentioned high-pressure Hg lamp.

3. Results and Discussion

In order to confirm the formation of NiO in the composite films, the IR spectra were measured as shown in Figure 1. For all the composite films, the peaks were observed at around 520 cm^{-1} due to Ni-OH bending vibration and around 464 cm^{-1} due to Ni-O stretching vibration (Miyazaki, Matsuura, & Ota, 2016; Ramesh & Kamath, 2006). The other absorption peaks were attributed to the urethane matrix. This result suggested that NiO compounds were formed in all the resulting composite films.

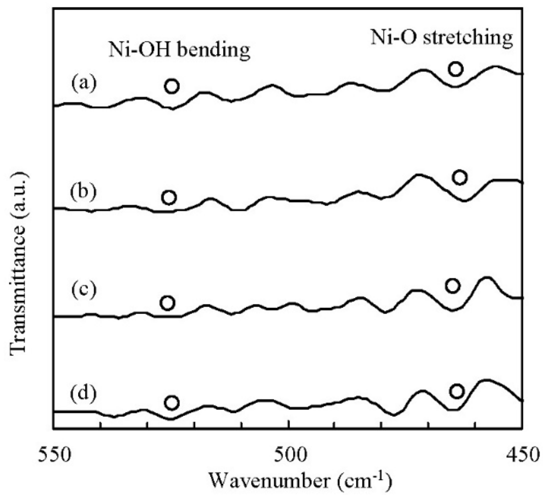

Figure 1. IR transmittance spectra of the composite films with Co/Ni ratio of (a) 0, (b) 0.005, (c) 0.01 and (d) 0.02

Figure 2 depicts the cross-sectional SEM images of the resulting composite films. All the films were dense with flat surfaces. Thus, it was assumed that the microstructure, film thickness and surface morphology of the films did not affect the optical measurements and photochromic properties. The mean thickness of the films with Co/Ni ratios of 0, 0.005, 0.01 and 0.02 were around 200 μm (192, 202, 203, 210 μm, respectively). For evaluation of optical properties of the films, we confirmed that the errors of all the resulting film thickness were within 10%.

We also investigated the fine structures of the composite films by TEM observation. Figure 3 depicts the TEM bright-field images of the composite films with various Co/Ni ratios. The particle sizes of the films with Co/Ni ratios of 0, 0.005, 0.01, and 0.02 were 60~70, 45~60, 40~55, and 40~45 nm, respectively. The particle size of all the composite films decreased slightly with the increase in Co contents. Previous reports have showed that the size of tungsten oxide particles affected the coloring or bleaching speeds of the composite films (Xu et al., 2000; Miyazaki, Inada, Suzuki, & Ota, 2012). In the present study, the particle sizes of the composite films varied slightly with Co addition. Thus, the particle sizes may have an effect on the coloring or bleaching rate of the composite films. We will discuss the relationship between the particle size and the photochromism of the films at the later section.

Using these films, we observed the photochromic properties. Figure 4 illustrates the UV-vis spectra for the composite films before and after 30 min UV irradiation (the bleached film was placed in the dark for 48 h before the measurement). All the films showed bleaching property by UV irradiation; this was because the valence state of Ni in the film was reduced from “+3” to “+2” (Miyazaki, Matsuura, & Ota, 2016). After UV irradiation, the bleached film was placed in the dark; this caused the transmittance to return to values close to that of the initial film. These semi-reversible photochromic properties were similar to the electrochromic properties of NiO films as reported by previous reports (Martini et al., 2001; Granqvist, Niklasson, & Azens, 2007; Abe et al., 2012). The NiO particle sizes of the films were sub-tens nm order (Figure 3); thus, it was inferred that the resulting composite films showed photochromic property.

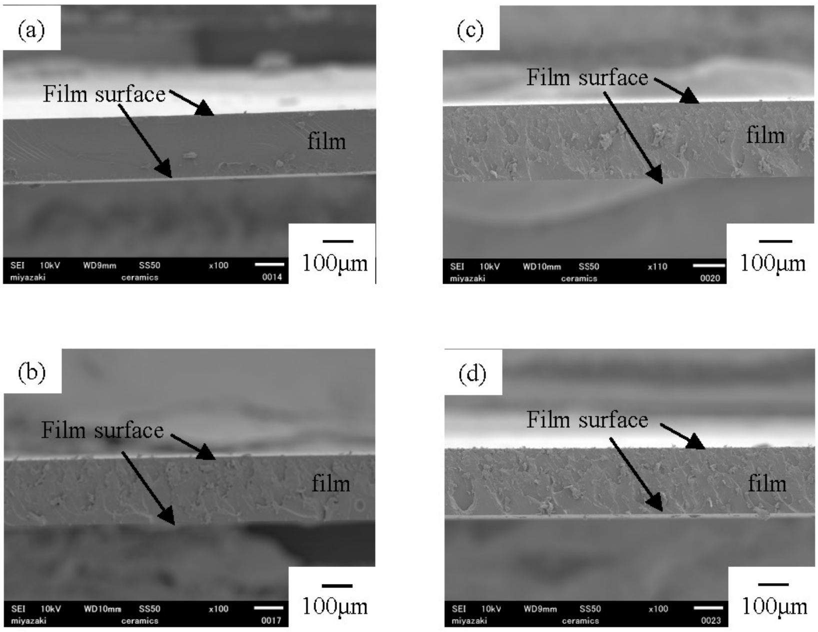

Figure 2. The cross-sectional SEM images of the NiO-based composite films with Co/Ni ratio of (a) 0, (b) 0.005, (c) 0.01 and (d) 0.02

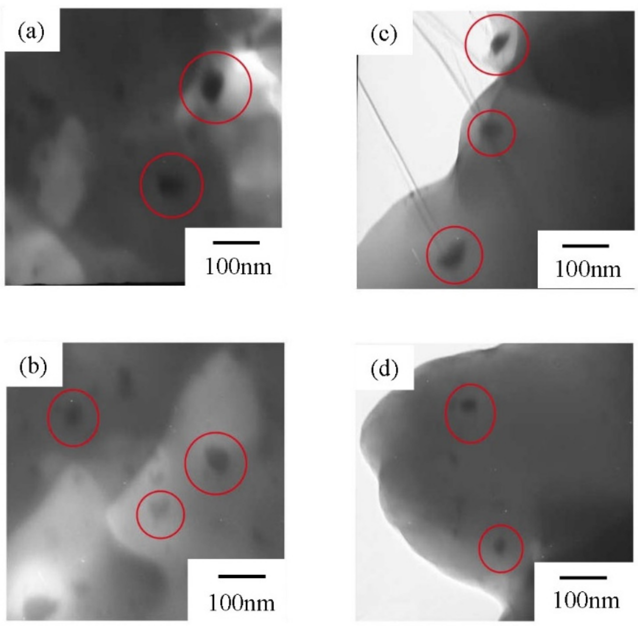

Figure 3. The TEM images of the NiO-based composite films with Co/Ni ratio of (a) 0, (b) 0.005, (c) 0.01 and (d) 0.02.

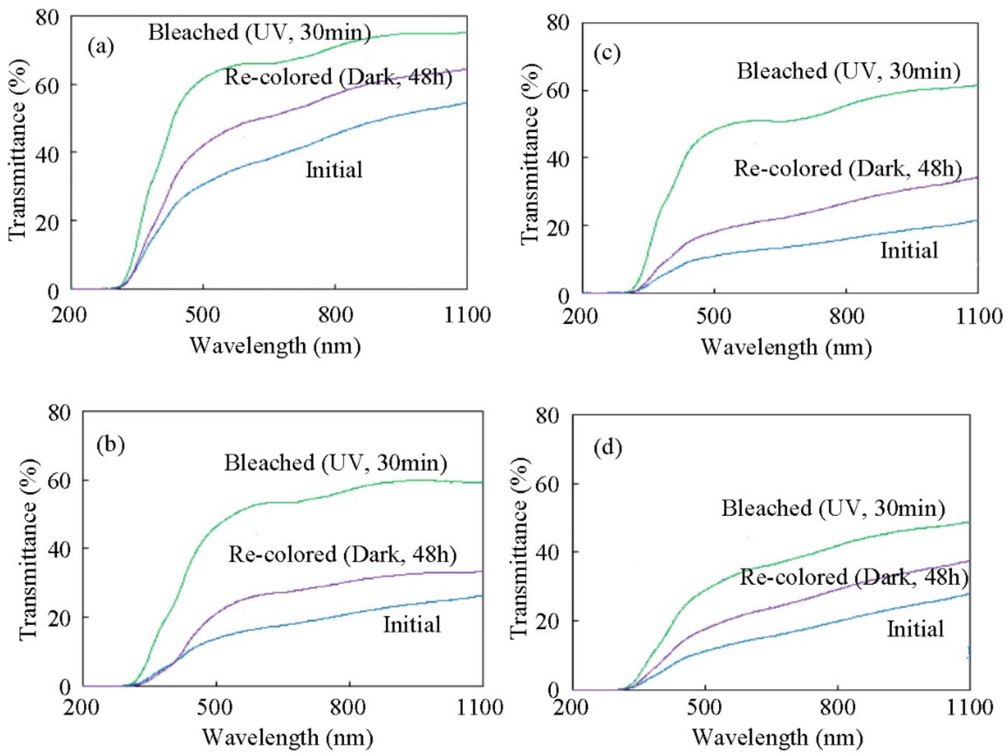

Figure 4. The UV-vis spectra of the composite films initial, after 30 min UV irradiation, and after 48 h in a dark room of the NiO-based composite films with Co/Ni ratio of (a) 0, (b) 0.005, (c) 0.01 and (d) 0.02

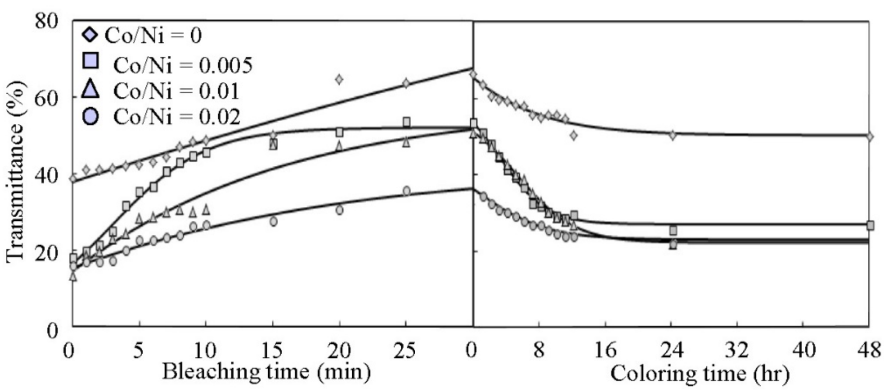

Figure 5. The time dependences of transmittance change on (a) bleaching (UV irradiation) and (b) coloring (placed in a dark room) for the composite films. The employed wavelength was 680 nm

Co addition decreased the initial transmittance of the films; this result was assumed to have improved p-type conductivity of NiO particle in composites by appropriate Co doping (Zhang et al., 2014). The films with Co/Ni ratios of 0.005 and 0.01 showed a large transmittance modulation, and the film with Co/Ni ratio of 0.02 showed a small transmittance modulation. When the cobalt addition amount was more than Co/Ni ratio of 0.02, NiO based composite films were not bleached by UV irradiation because of excess cobalt addition.

Figure 5 presents the time dependences of transmittance change on (a) bleaching and (b) coloring for composite films. The employed wavelength was 680 nm. Co addition was found to increase the bleaching and coloring rates of the films. The bleaching and coloring rates were the largest in the film with Co/Ni ratio of 0.005. From TEM observation, NiO particle size was found to decrease with the increase in Co/Ni ratio in the films, but the bleaching and coloring ratio were independent on the particle sizes (Figure 3).

From the results in Figures 4 and 5, Co addition to films having a Co/Ni ratio of 0.005 caused a high coloring degree, large transmittance modulation, and high bleaching and coloring rates. Thus, Co addition is effective for improving photochromic characteristics of NiO composite films.

4. Conclusion

NiO-based photochromic composite films were fabricated with various Co contents, and the effect of Co addition on the photochromic properties was evaluated. The NiO particle sizes in the composite films with Co/Ni ratios of 0~0.02 were 40~70 nm, and the photochromic characteristics were exhibited due to the small particle size. Co addition caused a decrease in the initial transmittance of the films, and the films with Co/Ni ratios of 0.005 and 0.01 showed larger transmittance modulation. Co addition caused an increase in the bleaching and coloring rates, which were the largest in the film with Co/Ni ratio of 0.005. From the perspectives of coloring degree of an initial state, transmittance modulation, bleaching and coloring rate, it was inferred that the optimum amount of Co/Ni rate in the NiO-based composite film was 0.005 required to improve the photochromic properties in this investigation.

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