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Electrochromic Reaction of InN Thin Films

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Electrochromic (EC) reaction of indium nitride (InN) films prepared by radio frequency (rf) ion plating was studied through their chemical bonding states and crystalline structures as measured by X-ray photoelectron spectroscopy (XPS) and X-ray diffraction (XRD), respectively. In addition, the pH dependence of the EC reaction was characterized. Color of the InN films became darker or lighter when the InN films were polarized anodically or cathodically, respectively, in a Na_2SO_4 solution. Similar color changes were observed when pH of the Na_2SO_4 solution was changed from 4.0 to 11.6. The color change at one unit of pH difference corresponded to the EC color change at a potential difference of 59 mV. From these results, H^+ and OH^- were confirmed to be active reactants in the EC reaction of the InN films. On the other hand, it was revealed from XPS and XRD results that the amount of hydroxides formed at the grain boundaries and the surface of the anodically polarized InN films was greater than that of the film polarized cathodically. Therefore, the electrochromism of the InN films was concluded to be governed by chemisorption of H^+ and OH^- at grain boundaries.

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Electrochromic (EC) materials are able to reversibly change their optical properties when a voltage is applied across them in a solution. They are promising materials for applications to optical switching devices, such as antiglare mirrors, sunglasses, and advanced windows for buildings. Among these EC materials, InN is particularly interesting since there are few nitrides which show electrochromism. Only InN[1] and SnN[2] have been reported as EC nitrides.

EC properties of some EC oxides have been investigated in detail for practical applications. In recent years, their EC responses,[4-6] mechanisms,[7,8] and preparation methods[9-12] are reported continuously. In the case of InN, three works have been reported on EC properties of InN films. Takai reported on fundamental EC response of InN thin films prepared by rf ion plating.[1] Ohkubo et al. prepared amorphous InN films by means of rf sputtering and investigated its EC and photodarkening effects.[3] In our previous paper, we observed the structure of EC InN films and showed the films had columnar structures.[13] Although some EC properties of InN films have been reported, none of the reports have clarified the electrochemical reaction of the electrochromism in InN.

In this paper, we report on reactive ions and their bonding states in the EC reaction of InN thin films prepared by rf ion plating. The pH dependence of the electrochromism was investigated to identify active reactants in the EC reaction. The EC reaction is discussed in terms of chemical bonding states and crystalline structures observed by X-ray photoelectron spectroscopy (XPS) and X-ray diffraction (XRD), respectively.

Experimental

InN thin films were prepared by rf ion plating. The stainless steel ion-plating apparatus had a bell-jar-type vacuum chamber, 340 mm diam and 600 mm high. Prior to evaporation, the vacuum chamber was evacuated to 1×10^{-3} Pa by rotary and oil diffusion pumps. The chamber was then filled with N_2 gas so as to have a pressure of 0.65 Pa. Indium metal shots of 7 N purity were evaporated from an electrically heated alumina crucible. Substrates were placed 140 mm above the crucible. To generate a glow discharge plasma, 100 W rf power was applied to N_2 gas from a 13.56 MHz rf generator through an impedance-matching network terminating in a two-turn coil of 200 mm diam which was placed in the chamber. 500 mm thick InN thin films were deposited onto glass and indium-tin oxide (ITO)-coated glass substrates of $76 \times 26 \times 1$ mm size. The substrate temperature finally reached 50°C after deposition for 60 min.

EC behavior of the films was observed in situ with a double-beam optical spectrometer. Two glass cells filled with a 0.5 M Na_2SO_4 aqueous solution were installed at the positions of the sample holder and the reference one in the spectrometer. In the sample cell, a platinum plate, a saturated calomel electrode (SCE), and a glass plate deposited with the InN thin film were set and used as counter, reference, and working electrodes, respectively. In the reference cell, only a glass plate identical to the sample substrate was placed. Optical transmission spectra of the InN thin films were recorded at the electrode potential of −1.2, 0, and +1.2 V vs. SCE. The EC behavior of the InN films was also studied under various pH conditions. By adding NaOH or H_2SO_4 into 0.5 M Na_2SO_4 solution, pH values were adjusted to be 4.0, 5.9, 6.9, 9.2, and 11.6.

Changes in chemical bonding state and chemical composition due to the electrochromism were determined by XPS (Shimadzu, AXIS), XPS spectra were measured using monochromatized Al Kα radiation. The films were not etched by an Ar^+ ion beam, since nitrogen atoms in the films were preferentially sputtered and the films were denatured due to the sputtering. The films used in the XPS measurement were prepared by the following procedure. After the voltage of −1.2, 0, and +1.2 V vs. SCE was applied to the films for 1 min in the Na_2SO_4 solution, the films were taken out of the solution and rinsed with pure water. They were then dried using a drier and introduced to the XPS analyzing chamber.

XRD patterns of the films were also examined. The samples were treated with the same procedure described previously.

Results and Discussion

InN thin films used in the present experiment had polycrystalline structure with a preferred orientation of 101. Their original color was reddish-brown. Figure 1 shows optical transmission change due to the electrochromism in the wavelength range between 400 and 800 nm. When the InN film is polarized at +1.2 V vs. SCe (+1.2 V in solution), its optical transmission becomes low and the film colors dark reddish-brown. On the other hand, when the film is polarized at −1.2 V vs. SCE (−1.2 V in solution), its optical transmission becomes high and the film colors light reddish-brown. The transmission spectra largely change between 620 and 750 nm. Figure 2 shows the transmission at the wavelength of 633 nm and applied electrode potential. The transmission shows good reversibility and the magnitude of the transmission change is kept constant. The transmission change is almost finished within a few seconds after the potential is stepped. Although the data is not shown, these transmission changes were observed in more than 1000 cycles.

These color changes remained, to some extent, even after the applied voltage was removed and the sample was taken out of the solution. The transmission spectra observed out of the solution are also shown in Fig. 1. In the film polarized at −1.2 V vs. SCE (−1.2 V in air), the color is strongly diminished and only a small spectral change is observed compared to the film polarized at 0 V vs.

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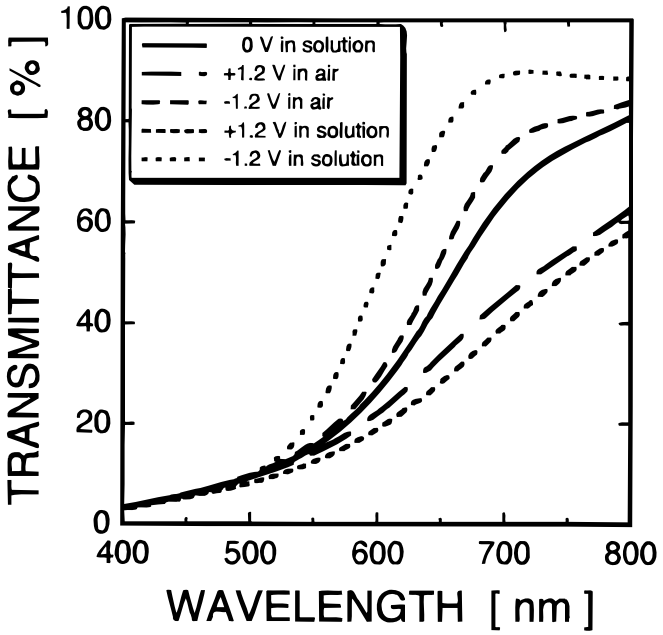

Figure 1. Optical transmission change due to the electrochromism in InN thin films measured in solution and in air.

SCE. On the other hand, the film polarized at +1.2 V vs. SCE (+1.2 V in air) is slightly degraded. These spectra observed in air were measured after XPS measurement (3 h passed after the applied voltage was removed). Therefore, the film polarized at −1.2 V vs. SCE, which was used in the XPS measurement, did not maintain its color change sufficiently.

XPS spectra were measured in order to observe some chemical shifts and determine compositions of the InN thin film as prepared and polarized at −1.2, 0, and +1.2 V vs. SCE in the Na_2SO_4 solution. In wide-scan XPS spectra, In, N, O, and C were detected, whereas Na and S were not detected. The carbon was found to be derived from ambient air, since it was perfectly eliminated after Ar^+ ion bombardment at 2 keV for 15 min. However, preferential sputtering of nitrogen simultaneously occurred during the bombardment as reported previously.[14,15] Hence, in the following XPS measurement, the film surface was not sputtered with Ar^+ ion, since we thought that the surface state was changed by even low-energy or short-time bombardment.

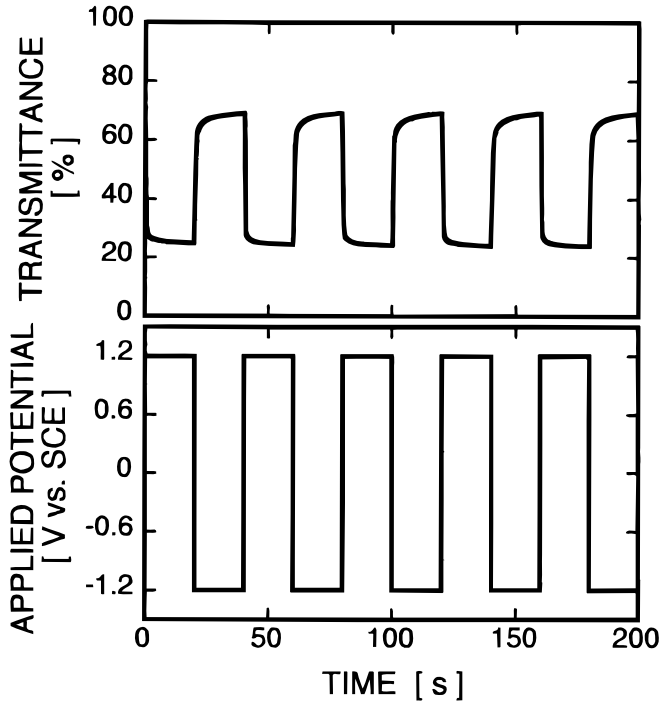

Figure 2. (a) Transmittance at λ = 633 nm of the InN thin film and (b) applied electrode potential.

Figure 3a shows In 3d spectra of the film as prepared and polarized at −1.2, 0, and +1.2 V vs. SCE. The peak of In $3d_{5/2}$ spectra appears at 444.4 eV. Although no distinct chemical shifts are observed, full width of half-maximum (fwhm) of In $3d_{5/2}$ spectra is different. The fwhms of the film as prepared and polarized at +1.2, 0, and −1.2 V vs. SCE are 1.54, 1.74, 1.68, and 1.68 eV, respectively. The difference of the fwhms is based on oxidization during the EC reaction. If In $3d_{5/2}$ spectra can be deconvoluted, this will be made clear. However, it is impossible to distinguish oxidized state from nitrided state since peak positions of In $3d_{5/2}$ for bulk In_2O_3 and bulk InN appear at almost same binding energy.[14] Furthermore, in this case two kinds of oxidized states are considered to exist, indium oxide and indium hydroxide, whose In $3d_{5/2}$ peaks appear at the same binding energy.[16] Therefore, it was impossible to deconvolute the In $3d_{5/2}$ spectra.

Figure 3b shows O 1s spectra of the InN film. Although no chemical shifts are observed, the peak intensity is different in each spectrum. The spectra shown in Fig. 3b are composed of three components. The most intense peak positioned at 531.4 eV is assigned to hydroxyl groups.[16] The others are determined to be indium oxide (529.8 eV) and adsorbed water (533.0 eV). The peak at 531.4 eV becomes more intense in the film polarized at +1.2 V vs. SCE. On the other hand, its peak intensity decreases in the film polarized at −1.2 V vs. SCE, while the peak intensity of 529.8 eV is almost constant. The difference of the peak intensity of 531.4 eV is small between the films polarized at 0 and −1.2 V vs. SCE. This is because the film polarized at −1.2 V vs. SCE did not maintain the color change due to the electrochromism as shown in Fig. 1 (−1.2 V in air). Thus, it was found from the O 1s spectra that hydroxides were excessively formed in the InN film polarized at +1.2 V vs. SCE.

N 1s spectra are shown in Fig. 3c. The peak at 396.9 eV is ascribed in InN.[15,17] Since no chemical shifts are observed in N 1s spectra, the chemical bonding states of N are not changed. However, the peak intensity of the polarized films decreases. The composition of N to In (N/In) in the polarized film determined by XPS decreased about 20% compared to the film as prepared. However, the decrease of N/In seems to have occurred near the surface of the InN film, since the electron escape depth of the photoelectron is several nanometers.[18] In addition, from the fact that cycle life of the EC coloration was over 1000 times, the N/In decreased near the surface of the InN film.

From the results that the intensity of the O 1s spectrum derived from hydroxyl groups increased in the film polarized at +1.2 V vs. SCE and the N/In decreased about 20% in the polarized film, it was considered that the N atoms of InN near surface were decomposed and replaced by hydroxyl groups. Thus, OH^- ions in the solution were confirmed to play a key role in the electrochromism of InN. This result implied that H^+ also interacted with the InN films in the EC reaction. Because of this hypothesis, a pH dependence of the electrochromism in InN films was investigated in order to confirm this.

Figure 4 shows optical transmission spectra of the InN film at pH 4.0, 5.9, 6.9, 9.2, and 11.6. The minimum pH value was determined to be 4.0, since the film peeled out from the glass substrate less than pH 3. The potential applied to the film was not fixed and the temperature of the solution was kept at 25°C. In Fig. 4, optical transmission in the wavelength range 500-800 nm gradually decreases with the increase in pH value. The similar spectrum at pH 5.9 was able to be obtained when a proper potential was applied to the film in solutions with pH 4.0, 5.9, 6.9, 9.2, and 11.6. These potentials were plotted as a function of the corresponding pH value as shown in Fig. 5. The inclination of an extrapolated line in Fig. 5 was calculated to be 59 mV/pH. It is well known that the pH dependence is

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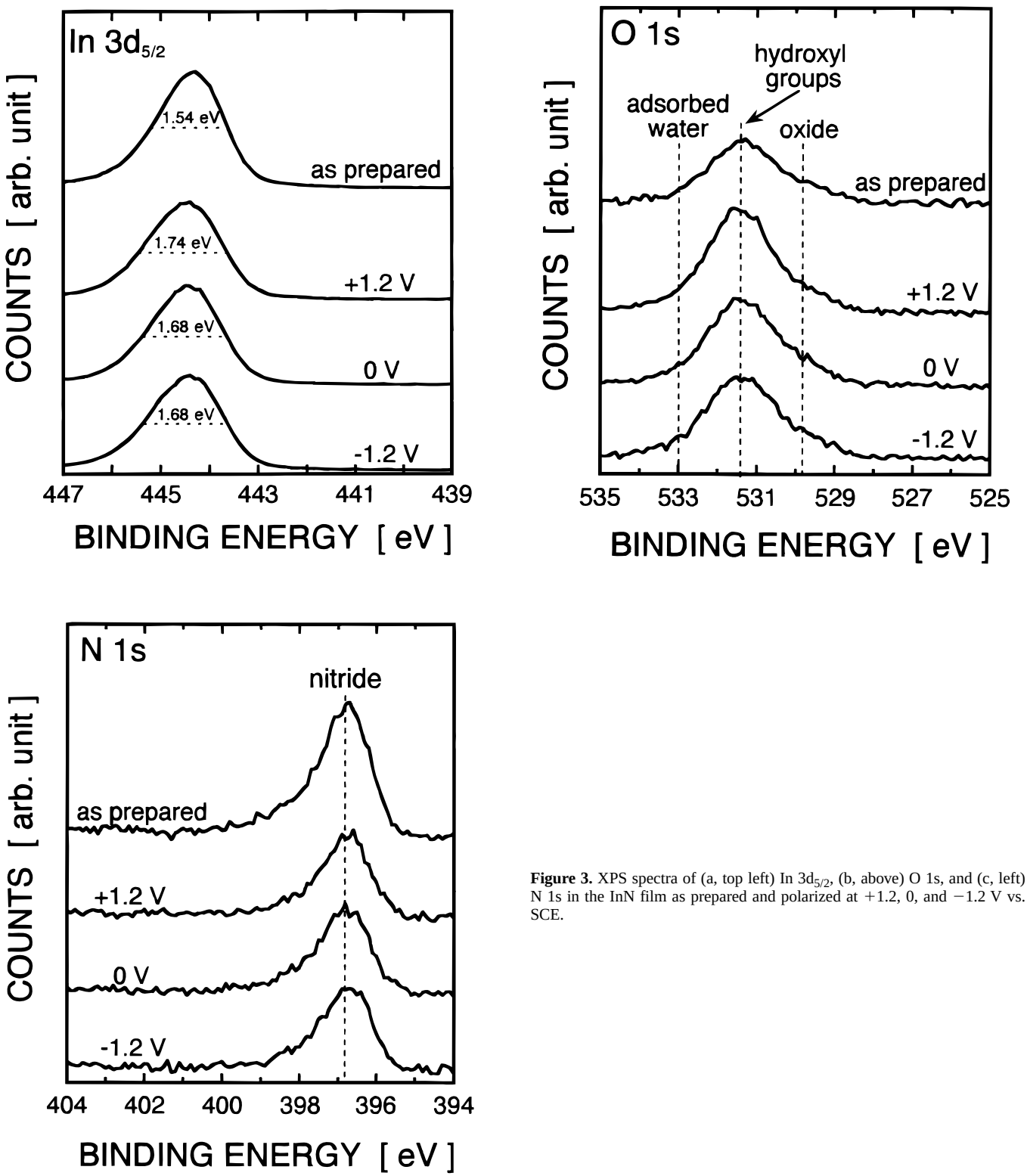

Figure 3. XPS spectra of (a, top left) In $3d_{5/2}$, (b, above) O 1s, and (c, left) N 1s in the InN film as prepared and polarized at +1.2, 0, and −1.2 V vs. SCE.

explained by the acidic or the basic character on the surface of metal or semiconductor which can interact with H^+ or OH^-. [19] When H^+ ions adsorb on the surface of InN films, a potential gap between an electrode and a solution is led by Eq. 1 and 2

$$H^+ + e^- \rightleftarrows H_{(ad)} \qquad [1]$$

$$\Delta\Phi = \Phi_s - \Phi_1 = \text{const} + (RT/F)\ln(a_{H^+}/a_{H_{(ad)}}) \qquad [2]$$

where Φ_s is the potential of the electrode surface, Φ_1 is the potential of the solution, a_{H^+} and $a_{H(ad)}$ are activities of H^+ and $H_{(ad)}$, R is the gas constant, T is temperature, and F is Faraday's constant. Since $a_{H(ad)}$ is nearly independent of pH value of the solution, one can derive the following equation at room temperature

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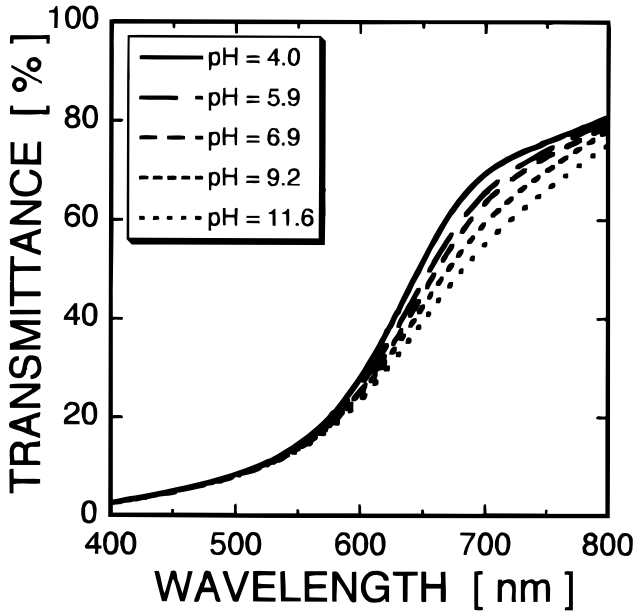

Figure 4. Optical transmission change of the InN thin film at various pH values.

$$\Delta\Phi = \text{const} + 0.059 \log a_{H^+} \quad [3]$$

$$= \text{const} - 0.059\ \text{pH} \quad [4]$$

The pH dependence of 59 mV/pH in the electrochromism, therefore, proves that reactive ions in the present EC reaction are H^+ and OH^-. Hotchandani et al. reported that pH altered the onset of the EC effect in WO_3 thin films.[20] In an n-type oxide semiconductor, the conduction band shifts to more negative potential with increase in pH of a solution. Accordingly, they concluded that the band energy of the WO_3 films controlled its EC effect. This implied that the electrochromism in InN films was controlled by the band energy, since the InN film is also one of the n-type semiconductors.

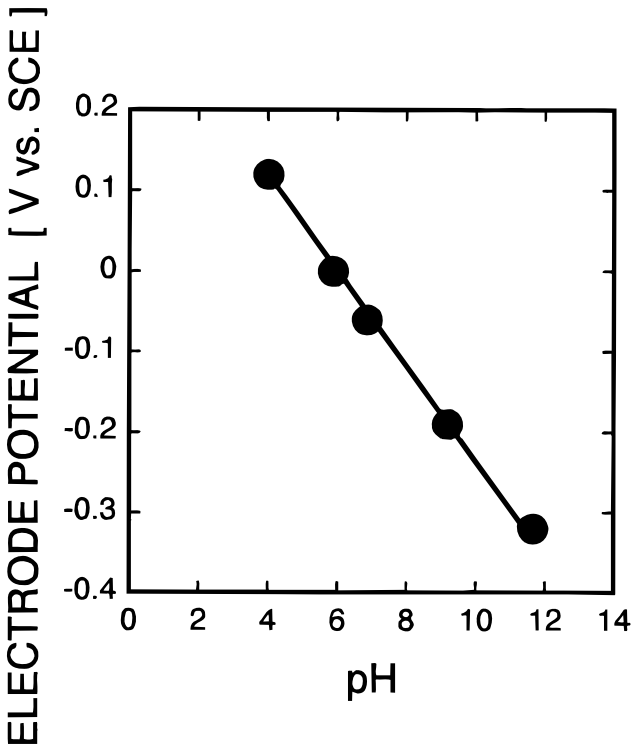

Figure 5. The applied potential to the InN film as a function of pH. The inclination of the extrapolated line is calculated to be 59 mV/pH.

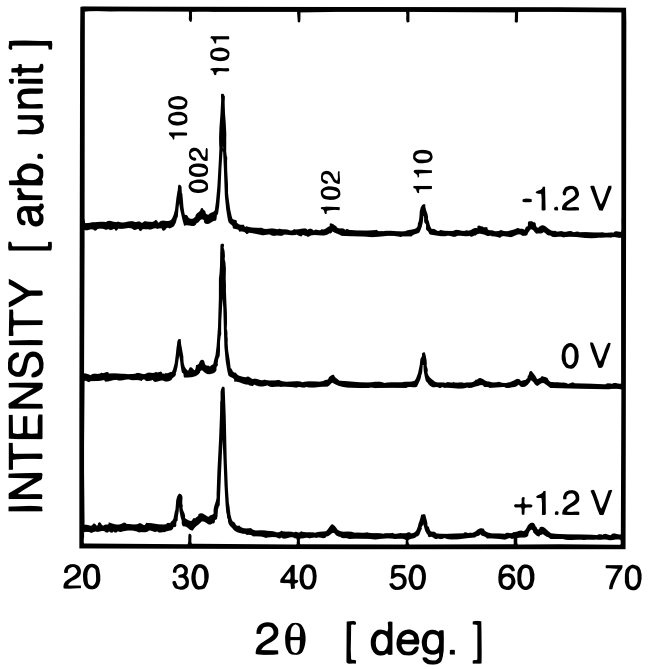

Figure 6. XRD patterns of the InN film polarized at −1.2, 0, and +1.2 V vs. SCE. Diffraction peaks correspond to InN with wurtzite crystal structure.

It is crucial to know the change of crystalline structure due to the EC reaction of InN, since XRD patterns of a polycrystalline WO_3 film, which is one of the typical EC materials, are changed due to its EC coloration.[21] This is because ions are intercalated into the WO_3 film, especially into crystal grains of WO_3. In contrast, XRD patterns of the InN film showed similar XRD profiles even after the film was polarized at +1.2, 0, and −1.2 V vs. SCE (Fig. 6). The prepared InN film had a columnar structure which was porous enough for ions to be able to diffuse through voids formed at grain boundaries of the columnar grains. This was observed by transmission electron microscopy.[13] These results support that the EC reaction occurs at the grain boundaries and the surface of the InN film, that is, the ions are not intercalated into the crystal grains of InN.

From the results of pH dependence, the InN film was confirmed to interact with H^+ and OH^- ions in the EC reaction. It should be mentioned that the EC reaction occurs at the grain boundaries and the surface. In addition to them, it was considered that the N atoms of InN near the surface were decomposed and replaced into H or OH during the EC reaction, since the XPS measurement revealed that the N/In of the polarized films decreased about 20% compared to the film as prepared. Although this was observed on the surface of the InN films, the same reaction was also considered to occur at the grain boundaries. XPS measurement also indicated that the hydroxides were formed in the film polarized at +1.2 V vs. SCE more than in the film polarized at 0 and −1.2 V vs. SCE. Taking into account these experimental results, the EC reaction of InN is considered as follows (Fig. 7). When the InN film is polarized anodically in the solution, supplied holes combine with OH^- to compensate the charge. As a result, H^+ ions chemisorbed on the InN are replaced with OH, and the film colors dark reddish-brown. On the contrary, when the InN film is polarized cathodically, supplied electrons combine with H^+ to compensate exceeded electrons. These H^+ ions chemisorb on the InN instead of the hydroxyl groups, resulting in a color change of the InN films to light reddish-brown. In the process of these EC reactions, the valence number of indium does not change.

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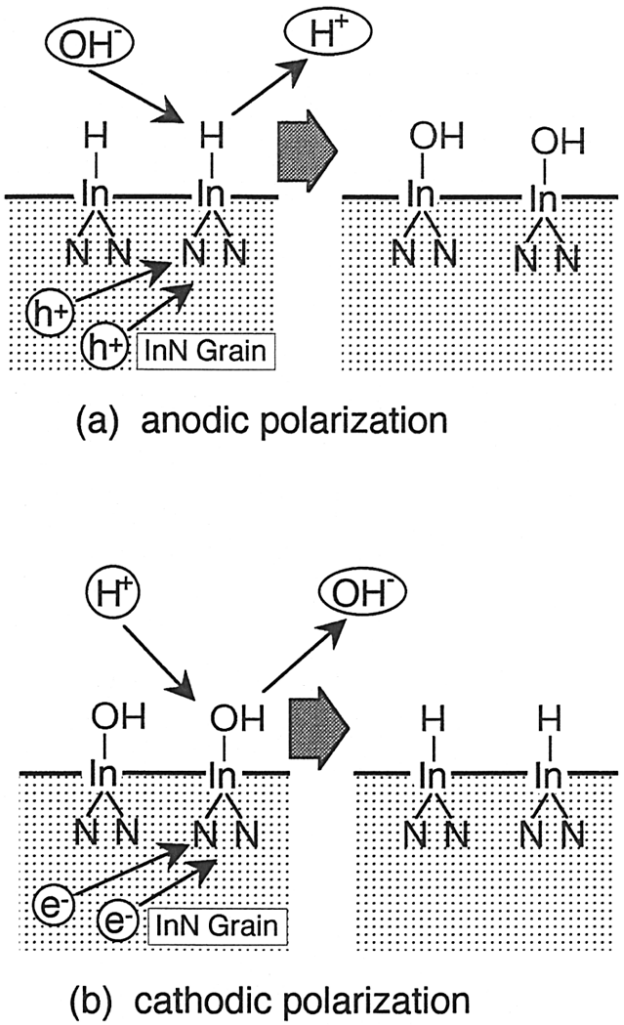

Figure 7. Models of EC reaction in InN thin films: (a) anodic polarization and (b) cathodic polarization. H^+ and OH^- react at the grain boundaries and the surface of the InN thin films.

Conclusion

The chemical bonding states and compositions of the InN films colored due to the electrochromism were investigated. The pH dependence of the electrochromism was also characterized using electrochemical measurement. XPS measurement indicated that the hydroxides were excessively formed in the film polarized at +1.2 V vs. SCE, whereas the hydroxides were reduced in the film polarized at 0 and −1.2 V vs. SCE. On the other hand, the pH dependence revealed that H^+ and OH^- in the solution acted as reactants in the EC reaction. In addition to them, it was proved from XRD measurement that these reaction occurred at the grain boundaries and the surface of the InN films. Therefore, it was concluded that the electrochromism in InN films was governed by chemisorption of H^+ and OH^- at the grain boundaries and the surface.

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References

1. O. Takai, in *Proceedings of the S.I.D.*, **25**, 305 (1984).
2. O. Takai, in *Proceedings of the S.I.D.*, **28**, 243 (1986).
3. M. Ohkubo, S. Nonomura, H. Watanabe, K. Yamamoto, and S. Nitta, *Appl. Surf. Sci.*, **113-114**, 476 (1997).
4. K. Yoshimura, T. Miki, and S. Tanemura, *J. Electrochem. Soc.*, **144**, 2982 (1997).
5. E. Masetti, D. Dini, and F. Decker, *Sol. Energy Mater. Sol. Cells.*, **39**, 301 (1995).
6. M. Denesuk, J. P. Cronin, S. R. Kennedy, and D. R. Uhlmann, *J. Electrochem. Soc.*, **144**, 1971 (1997).
7. S. Hashimoto and H. Matsuoka, *J. Appl. Phys.*, **69**, 933 (1991).
8. X. G. Wang, Y. S. Jang, and S. J. Pang, *Surf. Coat. Technol.*, **99**, 82 (1998).
9. M. Green and K. Pita, *J. Appl. Phys.*, **81**, 3592 (1997).
10. K. Yoshimura, T. Miki, and S. Tanemura, *Mater. Res. Bull.*, **32**, 839 (1997).
11. N. Ozer, D. G. Chen, and C. M. Lampert, *Thin Solid Films*, **277**, 162 (1996).
12. M. Chigane and M. Ishikawa, *J. Chem. Soc.*, **94**, 3665 (1998).
13. N. Asai, Y. Inoue, H. Sugimura, and O. Takai, *Thin Solid Films*, **332**, 267 (1998).
14. B. R. Natarajan, A. H. Elthukhy, and J. E. Greene, *Thin Solid Films*, **69**, 201 (1980).
15. I. Bello and W. H. Lau, *J. Vac. Sci. Technol. A*, **10**, 1642 (1992).
16. S. M. Thurgate and N. E. Erickson, *J. Vac. Sci. Technol. A*, **8**, 3669 (1990).
17. S. Kumar, L. M. Motlan, and T. L. Tansley, *Jpn. J. Appl. Phys.*, **35**, 2261 (1996).
18. D. Briggs and M. P. Seah, *Practical Surface Analysis*, 2nd ed., Vol. 1, Wiley & Sons, New York (1990).
19. K. B. Oldham and J. C. Myland, *Fundamentals of Electrochemical Science*, Academic Press, New York (1994).
20. S. Hotchandani, I. Bedja, R. W. Fessenden, and P. V. Kamat, *Langmuir*, **10**, 17 (1994).
21. J. Zhang, S. A. Wessel, and K. Colbow, *Thin Solid Films*, **185**, 265 (1990).