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ELECTRICAL PROPERTIES OF ELECTROCHROMIC INDIUM NITRIDE THIN FILMS PREPARED BY RF ION PLATING

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Abstract

Electrical properties of electrochromic (EC) InN thin films prepared by rf ion plating were studied. There was a correlation between the electrical properties and the electrochromism in the InN films, particularly, carrier concentration changes were responsible for the electrical resistivity changes of the films due to the electrochromism. These carrier concentration changes were caused by chemisorbed hydroxyl groups and protons. From these results, it was proved that the carrier concentration changes of the InN films was responsible for the electrochromism in the visible and near-infrared region.

Key words : InN, electrochromism, electrical properties, ion plating, IR spectra

1. INTRODUCTION

Electrochromic (EC) materials reversibly change their optical properties when a voltage is applied across them. Accordingly, they can be applied to optical switching devices for automobile or architectural windows. Among many kinds of EC materials, indium nitride (InN) is particularly interesting since it is one of the few nitrides which show electrochromism. In addition, its EC properties and mechanism are less-studied.

The EC behavior of the InN films in the visible and near-infrared regions differs from that

in the infrared region. In the previous paper¹⁾, we reported that the electrochromism of InN films was caused by chemisorbed hydroxyl groups and protons. However, optical modulation due to the electrochromism have not been investigated. In the infrared region, optical absorption of n-type semiconductors is mainly governed by free electrons in a conduction band²⁾. Since the InN is a n-type semiconductor, the electrochromism in the infrared region is considered to depend on its electrical properties. Therefore, in order to make the EC mechanism clear, it is important to investigate the relationship between the electrical properties and the

electrochromism.

In this paper, we report on the electrical properties of the EC InN films. The electrical properties are discussed in terms of EC properties and reacting ions observed by IR transmission spectra and X-ray photoelectron spectra.

2. Experimental

InN thin films were prepared by rf ion-plating. A schematic diagram of the ion plating apparatus is shown in Fig. 1. The apparatus had a bell-jar type vacuum chamber of 340mm in diameter and 600mm in height. After evacuation by rotary and oil diffusion pumps, the chamber was filled with N_2 gas up to 0.65 Pa. Then, glow discharge plasma was generated and indium metal of 7N purity was evaporated in the nitrogen plasma. InN thin films were deposited onto glass substrates ($76\text{mm} \times 26\text{mm} \times 1\text{mm}$) and silicon wafers ($10\text{mm} \times 20\text{mm} \times 0.2\text{mm}$). The substrate temperature was kept at 150°C during deposi-

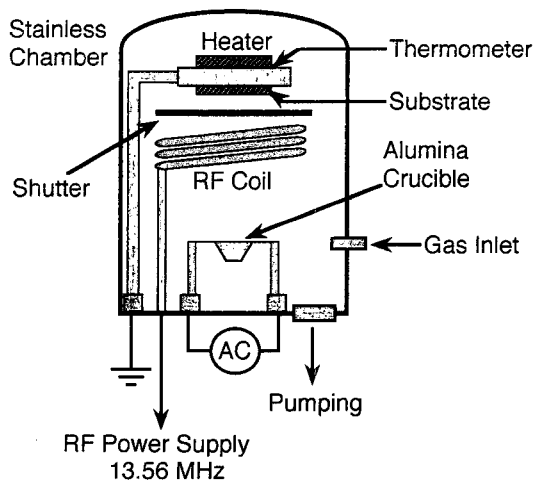


Fig. 1 Schematic diagram of rf ion-plating apparatus.

tion.

EC coloration of the films was carried out in a cell filled with $0.5\text{M Na}_2\text{SO}_4$ aqueous solution. A platinum plate, a saturated calomel electrode (SCE) and a glass substrate coated with an InN thin film were placed in the cell and used as counter, reference and working electrodes, respectively. A potential was applied to the InN film and remained for 1 min. After this EC coloration, each sample was rinsed with pure water in order to remove electrolyte, and then dried. Optical transmission spectra of the films were measured with a double-beam optical spectrometer. Electrical properties of the films were measured by the van der Pauw method. X-ray photoelectron spectra and infrared transmission spectra were also measured.

2.1 Results and Discussion

Fig. 2 shows optical transmittance changes of the InN film due to the electrochromism in the wavelength range between 300 and 3000 nm. In

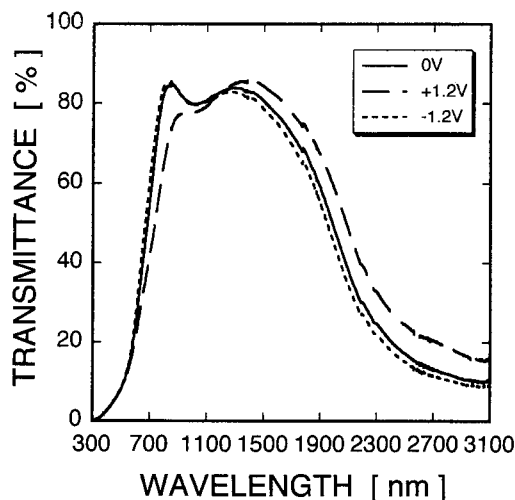


Fig. 2 Ex situ optical transmission spectra of the InN films in the range between 300 and 3000 nm.

the range from 300 to 1100 nm, the transmittance of the film polarized at -1.2 V vs. SCE is the highest in the three spectra, whereas, it is the lowest in the range from 1100 to 3000 nm. Contrary to the above result, the transmittance of the film polarized at $+1.2$ V vs. SCE shows opposite behavior. Although the transmission spectra of the films polarized at 0 and -1.2 V vs. SCE cross at the point around 800 nm, the transmittance difference between them is small. From these results, the EC mechanism in the infrared region is considered to be different from that in the visible and near-infrared regions.

Fig. 3 shown in Fig. 4. With increasing the electrode potential, the carrier concentration decreases from 2×10^{20} to $7.7 \times 10^{19} \text{ cm}^{-3}$, whereas, the Hall mobility remains almost constant. Therefore, this carrier concentration change is concluded to be the origin of the resistivity change due to the electrochromism. It is well known that simple Drude model can be applied to analyzing the free carrier absorption of sem-

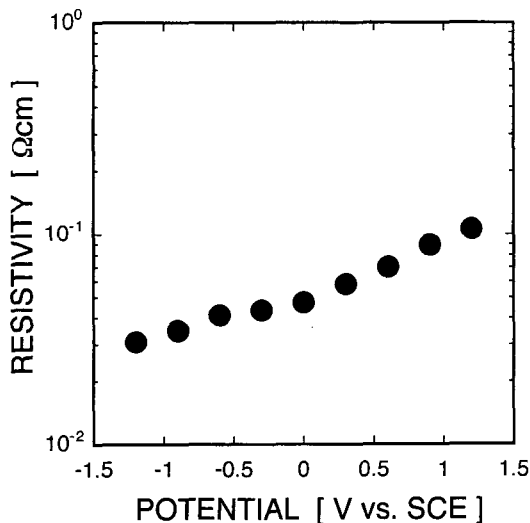


Fig. 3 Electrical resistivity of the polarized InN films.

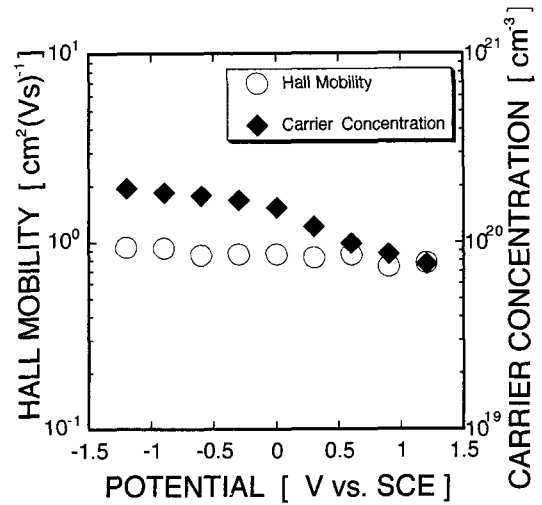


Fig. 4 Hall mobility and carrier concentration of the polarized InN films.

iconductors²⁾. Absorption coefficient (α) (obtained from the Drude model is represented as

$$\alpha_f = Ne^2 \lambda^2 / \pi mc^3 m \tau \quad (1)$$

where N is the carrier concentration, e is the electronic charge, λ is the wavelength of the light, n is the refractive index, m is the effective mass and τ is the relaxation time.

Taking into account of this equation, the transmittance difference in the infrared region shown in Fig. 2 is ascribed to the change in the magnitude of free carrier absorption of the InN film due to the different carrier concentrations.

Fig. 5 shows O 1s spectra of the InN films polarized at -1.2 , 0 and $+1.2$ V vs. SCE. The each spectrum can be deconvoluted into contributions due to oxide, hydroxide, and water. The most intense peak positioned at 531.4 eV is assigned to hydroxyl groups⁴⁾. The others are determined to be 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.

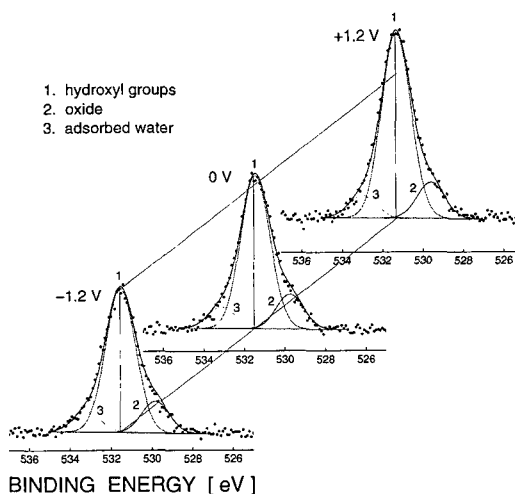


Fig. 5 XPS O 1s spectra of the InN films polarized at +1.2, 0 and -1.2 V vs. SCE.

SCE. On the other hand, its peak intensity decreases in the film polarized at -1.2 V vs. SCE, although the peak intensity at 533.0 and 529.8 eV is almost constant. Thus, from the O 1s spectra, it was found that hydroxides were excessively formed in the film polarized at +1.2 V vs. SCE.

Surface bonding state of the InN films is studied by IR transmission spectra. The IR spectra are shown in Fig. 6. Transmittance of the film polarized at +1.2V vs. SCE is higher than the film polarized at 0 and -1.2 V vs. SCE. This is derived from the free carrier absorption as discussed above. In addition, a broad absorption band appears at 3700–3200 cm^{-1} in the spectrum of the film polarized at +1.2V vs. SCE. Although the origin of this absorption band is not clearly identified, similar absorption band is observed in EC nickel oxide films. In the nickel oxide films, there are a sharp absorption band at 3650 cm^{-1} and a broad absorption band at 3400 cm^{-1} which are ascribed to the stretching

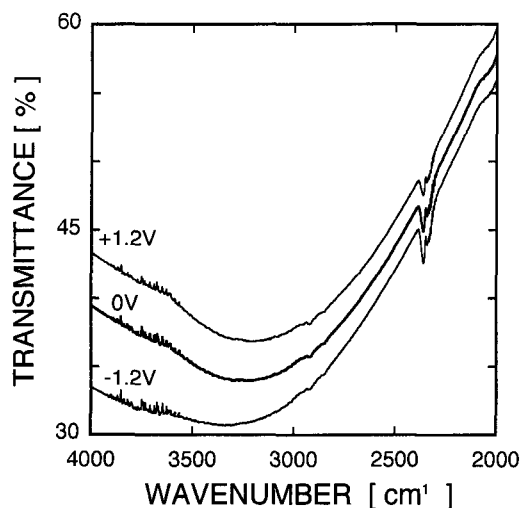


Fig. 6 Ex situ IR transmission spectra of the InN films polarized at +1.2, 0 and -1.2 V vs. SCE

vibration of free OH and bound H_2O , respectively^{5, 6}. Besides them, a peak assigned to the hydrogen bonding in NiOOH is observed at 3450 cm^{-1} ⁷. On the other hand, as shown in Fig. 5 we found that hydroxyl groups were excessively formed in the film polarized anodically, while the peak intensity of the adsorbed water and the oxide remained almost constant. Hence, the broad absorption band is concluded to indicate an increase of hydroxide. However, the detail formula of the hydroxide is not able to be determined from these results. From the results described above, the carrier concentration change due to the electrochromism can be explained as follows. When the film is polarized at +1.2 V vs. SCE in the solution, supplied holes make positive electric charges in the film. In order to compensate these charges, hydroxide ions in the solution react at the interface between the film and the solution. Since the compensating electrons localize at the oxygen atoms of hydroxyl groups, they do not contribute to the electronic

conductivity. Consequently, the carrier concentration of the film polarized at +1.2 V vs. SCE decreases. On the contrary, when the film is polarized at -1.2 V vs. SCE, supplied electrons release the reacting hydroxide ions and make negative charges in the film. To compensate these negative charges, protons react with the film. Since these reacting protons are excited by low thermal energy, they act as donors at room temperature⁹. Accordingly, the carrier concentration of the film polarized at -1.2 V vs. SCE increases.

In our previous paper¹⁾, it was discussed that the chemisorbed hydroxyl groups and protons was responsible for the electrochromism of InN films. In this paper, it is shown that the carrier concentration of the InN films changes due to the electrochromism. Therefore, the carrier concentration changes are concluded to be responsible for transmittance change due to the electrochromism of InN thin films in the infrared region.

4. Conclusions

Electrical properties of the EC InN thin films prepared by rf ion plating were investigated. The carrier concentration of the film polarized at +1.2 V vs. SCE was lower than that of the film polarized at -1.2 V vs. SCE. which is responsible for the electrochromism in the infrared region. From IR transmission spectra and X-ray photoelectron spectra, chemisorbed hydro-

xyl groups were found to increase in the film polarized at +1.2 V vs. SCE. From these results, it was proved that chemisorbed hydroxyl groups reduced the carrier concentration of the InN films. Thus, the electrochromism in the visible and near-infrared regions is due to the optical absorption of chemisorbed hydroxyl groups, on the other hand, the electrochromism in the infrared region is because of the carrier concentration changes.

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