Transactions of the Materials Research Society of Japan 25 [1] 249-252 (2000)

Photo-induced Charge Transfer in Oxides and Nitrides Doped with Transition Metal Ions

Kenkichiro Kobayashi, Yasumasa Tomita and Masaya Yano
Department of Materials Science, Faculty of Engineering, Shizuoka University
3-5-1, Jhohoku, Hamamatsu 432-8011 Japan
Fax: 81-53-478-1147, e-mail: kobayasi@mat.eng.shizuoka.ac.jp

The field modulated transmission spectra of a four- layer device of Ga-doped ZnO / Co-doped ZnO / SiO_2 / Ga-doped ZnO are significantly altered by irradiation with light of wavelength < 500 nm. The changes are maintained in the presence of an electric field. The mechanism of photon-induced charge transfer in three-layer device consisting of ITO / AlN / Al is analyzed from spectral dependence of photocurrent.

Key words: photochromism, electric field, Co-doped ZnO, AlN, photocurrent

1. INTRODUCTION

In previous papers [1-3], we proposed field-assisted photochromism for development of an optical storage, and we revealed the mechanism of photon-induced charge transfer in Co- or Cu-doped ZnO films. In a three layer device of electrode / Co-doped ZnO / electrode, memory effect was confirmed in the time dependence of photocurrent at 500 nm. Nevertheless, no changes in transmission spectra were found even after the irradiation of 500 nm. The major reason was ascribed to electron injection from the electrode to the Co-doped ZnO in the dark. The suppression of the electron injection was attempted by employing p-type oxides such as Li-doped NiO and $La_{2-x}Sr_xCuO_4$ which had large work functions. Changes in transmission spectra however were not detected because these p-type oxides were not transparent in the visible region. In the present work, we attempt to suppress the electron injection by two ways; (1) the insertion of insulator SiO_2 film between the Co-doped ZnO and the transparent electrode (Ga-doped ZnO), and (2) the change of a host material from ZnO to AlN having high energy level of the conduction band. Using field modulation transmittance (FMT), we investigate the field-assisted photochromism in a four-layer device consisting of Ga-ZnO / Co-doped ZnO / SiO_2 / Ga-doped ZnO. The charge transfer in a three-layer device of ITO (Indium Tin oxide) / AlN / Al is clarified from current vs voltage characteristics in the dark and under illumination.

2. EXPERIMENTAL

A four-layer device was fabricated by sequential depositions of Ga(2%)-doped ZnO, Co (5%)-doped ZnO, SiO_2, and Ga (2%)-doped ZnO films on a sapphire (0001) substrate by a sputtering technique. In the four-layer device, two Ga(2%)-doped ZnO films were used as bottom and top transparent electrodes. A three-layer device of ITO / AlN / Al was fabricated on a quartz substrate by sputtering and vacuum evaporation techniques. The characterizations of sputtered films were made by X-ray diffraction (XRD) and an atomic force microscope (AFM). FMT was measured by means of a function generator, a high voltage source and a lock-in amplifier. In FMT measurements, square waves (20 V peak to peak at 200 Hz) were superimposed on dc voltage. Spectral dependence of photocurrents in the range of 300 to 780 nm was measured using a pico-ammeter and a monochromatic irradiation apparatus (JASCO CRM-FA) which had a 2 kW Xe lamp.

3. RESULTS AND DISCUSSION

3.1 Field-assisted photochromism of Co-doped ZnO

Preparation conditions of the four-layer device are listed in Table I. As seen in Table I, thick SiO_2 film is grown such that a sufficient insulating property is attained. There are (0002) and (0004) reflections in XRD patterns of Ga- and Co-doped ZnO films grown on sapphire (0001) substrates. Thus, c-axes of these ZnO films are preferentially oriented in perpendicular to the surfaces of the sapphire (0001) substrates. In the four-layer device, no leakage current flows in the range of -400 V to 400 V, where a positive voltage corresponds to the case when the bottom electrode is positively polarized with respect to the top electrode. The SiO_2 film interrupts the electron injection from the Ga-doped ZnO film (the top electrode) to the Co-doped ZnO (the photochromic film). Changes in transmittance at several wavelengths of the four-layer device kept at 30 V were monitored after irradiation with intense light. In Fig. 1, changes in transmittance at 640 and 560 nm are plotted as a function of

Table I. Preparation conditions of four-layer devices.

	Ga-doped ZnO	Co-doped ZnO	SiO_2
pressure (mTorr)	5	5	7.5
RF power (W)	50	50	65
substrate temp. (°C)	400	200	200
atmosphere ($Ar:O_2$)	1:0	9:1	1:0
deposition period (min)	60	600	540
thickness (nm)	100	1000	1500

wavelength of irradiation light. The transmittance at 640 or 560 nm increases by the irradiation with light in the range of 500 to 380 nm. The increase in the transmittance at 630 nm corresponds to the decrease in d-d absorption of Co^{2+} ions in ZnO. The decrease in the concentration of Co^{2+} ions may be caused by photoionization of Co^{2+} ions because the charge transfer from impurity levels of Co^{2+} ions to the conduction band is induced by the irradiation with light of wavelength < 500 nm [2]. It should be noted that the change in the transmittance is maintained in the presence of an electric field. As seen in Fig. 1, a magnitude of the transmittance change is fairly small, e.g., 0.4 % or less. To detect such small changes with high sensitivity, we develop a technique of field-modulated transmission (FMT). Figure 2 shows the time dependence of FMT at 630 nm. In Fig. 2 (a) weak light of 630 nm for monitoring transmittance is switched on and off while the four-layer device has been kept at 50 V. FMT at 630 nm decreases with time under the irradiation of weak 630 nm light whereas the FMT remains unchanged in the dark. These results suggest that the transmittance at 630 nm is altered by the irradiation with weak light for long time in the presence of an electric field, and that in the dark no change of transmittance due to thermally ionization of electrons (or holes) in traps takes place even in the presence of an electric field. In Fig. 2 (b), both light of 630 nm and a bias voltage are simultaneously switched on and off. FMT is recovered to an initial value when an applied voltage is turned off. The presence of an electric filed is indispensable for the storage of the transmittance change. Figure 3 shows FMT spectra before and after the monitor-light of 630 nm is irradiated for 30 min (an applied voltage of 40 V). The FMT spectra at photon energy > 2 eV are the overlap of fine waves and slightly broad waves. The FMT spectra at photon energy > 2 eV are drastically altered by the irradiation. The fairly broad waves were not found in the four-layer device of ITO / nondoped ZnO / SiO_2 / Ga-doped ZnO[4]. Thus, the fairly broad waves may be assigned to the differential spectrum of d-d

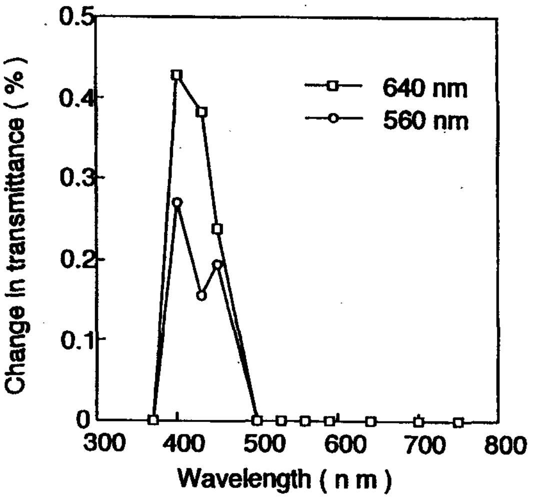

Fig. 1. Changes in transmittance at 640 and 560 nm after light irradiation. The abscissa is wavelength of irradiation light.

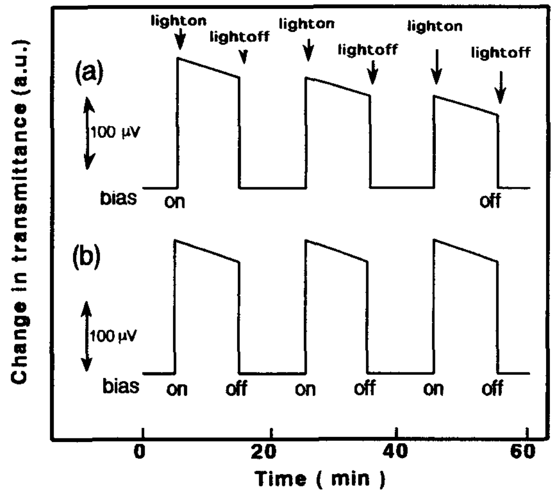

Fig. 2. Time dependence of FMT at 630 nm. (a): light is switched on and off, (b) light and bias voltage are simultaneously switched on and off.

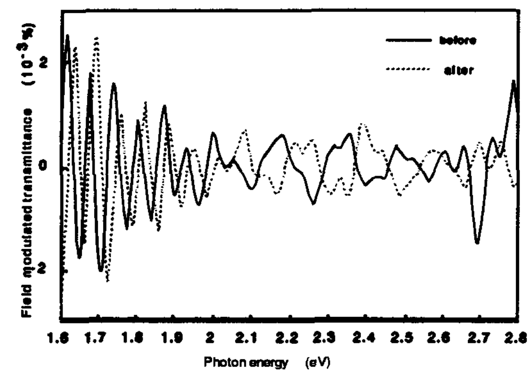

Fig. 3. FMT spectra before and after irradiation with light of 630 nm for 30 min.

absorption of Co^{2+} ions. The FMT spectra at photon energy < 2 eV are constructed from only fine waves with an interval of 0.06 eV, and peaks in the fine waves are shifted toward higher photon energy after the irradiation with weak light of 630 nm. The fine waves were also observed in a four-layer device of Ga-doped ZnO / nondoped ZnO / SiO_2 / Ga-doped[4]. In the four-layer device involving nondoped ZnO, the peaks of the fine waves were shifted toward higher energy with increasing an applied voltage, but the peak shift was not caused by the light irradiation. It was clarified from field-dependence of the peak shift that the appearance of the fine waves was induced by the Kerr effect in a refractive index of ZnO. Accordingly, the peak shift after the light irradiation suggests that an electric field in the Co-doped ZnO film increases although an applied dc voltage is kept to be constant. This means that the space charge is newly formed in the Co-doped ZnO film after the light irradiation. Figure 4 shows FMT spectra around 1.77 eV of the four-layer device kept at 60 V after the irradiation of intense light of 750, 650, 500 and 400 nm for 10 s. The irradiation with light of 500 nm or less effectively shifts the peak toward a higher value although slight shift is observed after the irradiation with light of 750 or 650 nm. This means that the space charge of Co^{3+} ions is effectively formed by the irradiation of light at 500 nm or less. The results are consistent with the interpretation that the photoionization of Co^{2+} ions occurs at 500 nm or less. The reverse shift in the peaks in the fine waves is not attained by any irradiation of light although the peak shift is extinguished by switching off a bias voltage. The results are explained as follows: the photoreduction of Co^{3+} ions to Co^{2+} ions takes place by the optical hole transfer from Co^{3+} impurity levels to the valence band and successive hole transport to the top Ga-doped ZnO electrode. In the four-layer device, the hole transport is interrupted by the SiO_2 film.

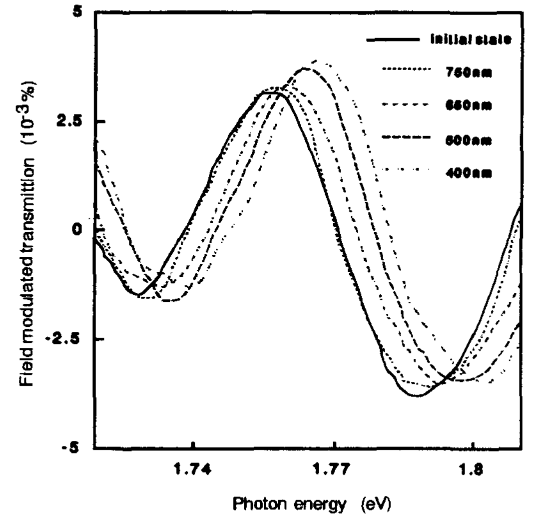

Fig. 4. FMT spectra around 1.77 eV of four-layer device kept at 60 V after irradiation with intense light of 750, 650, 500 and 400 nm for 10 s.

Table II. Preparation conditions of three-layer devices.

	ITO	AlN
pressure (mTorr)	10	10
RF power (W)	30	150
substrate temp. (°C)	250	200-450
atmosphere ($Ar:N_2$)	1:0	2: 3
deposition period (min)	40	300
thickness (nm)	100	1000

3. 2 Photon-induced charge transfer in nonodoped AlN film

Preparation conditions, together with the thickness of each film, are listed in Table II. XRD patterns of AlN films are shown in Fig. 5. At a low substrate temperature of 250 °C or less, there exist weak AlN(10 $\bar{1}$0) reflections besides AlN (0002) reflections. In contrast, there are only AlN (0002) reflections for the AlN films deposited at 300 °C or more. The c-axes of these films are preferentially oriented in perpendicular to the substrate surface. In an AFM topograph of AlN film deposited at 200 °C, no particles are seen but the surface roughness is fairly large, e.g., 75 nm. In AFM topographs of the surfaces of films deposited at 250 °C or more, particles are seen on the surfaces and the particle size increases with an increase in a substrate temperature, e.g., 50 nm at 250 °C and 95 nm at 400 °C. For the fabrication of a three-layer device, AlN film is deposited on ITO film grown on a quartz substrate. The orientation and the surface topograph of the AlN film deposited on the ITO film are the same as those of

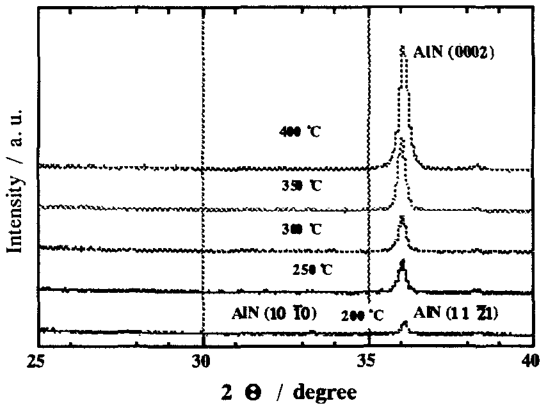

Fig. 5. XRD patterns of AlN films prepared on quartz substrates at temperatures of 400, 350, 300, 250 and 200 °C.

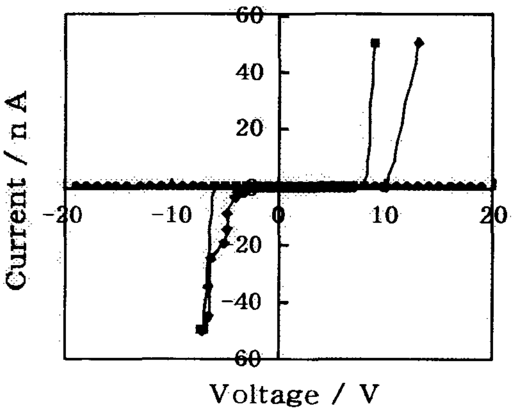

Fig. 6. Current vs voltage characteristics of three-layer device. Full diamonds: the first voltage sweep; full squares: the second voltage sweep; full circles: the third voltage sweep.

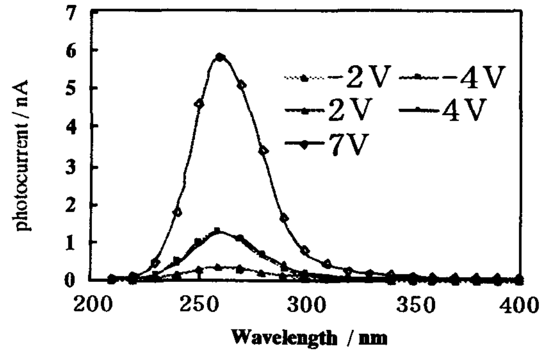

Fig. 7. Spectral dependence of photocurrent of a three-layer device at a bias voltage of 7, 4, 2, -2 and -4 V.

the AlN film deposited on a quartz substrate although crystallinity is slightly degraded. Figure 6 shows typical current vs voltage (I-V) characteristics of the three-layer device in which AlN film is deposited at 300 °C. Similar I-V characteristics are obtained for the device in which AlN films are deposited at 350, 400, 450 and 500 °C. No current flows in the range of -4 to 11 V for the first voltage sweep and in the range of -6 to 8 V for the second voltage sweep. In the third voltage sweep, no current flows in the range of -20 to 20 V. Leakage current observed at the first and the second voltage sweeps is caused by the electrical contact between the top and the bottom electrodes via Al channel formed in grain boundaries of AlN film. The Al channel is broken by the flow of large current at the first and the second voltage sweeps[5]. The I-V characteristics indicate that no electrons or holes are injected from the electrode into the AlN film in the dark. Figure 7 shows spectral dependence of photocurrent in the three-layer device. The photocurrent flows continuously under light irradiation. A magnitude of the photocurrent increases with increasing an applied voltage but is independent of the polarity of an applied voltage. The photocurrent emerges at wavelength < 360 nm and has a maximum at 260 nm. Transmission spectra of AlN films decrease monotonously at wavelength < 360 nm. The photocurrent and the transmittance in the range of 360 to 200 nm are not due to the band-gap excitation because the band gap of AlN is 6.2 eV[6]. The peak in the photocurrent spectra implies that occupied deep levels are lying at 4.6 eV below the bottom of the conduction band, or that empty deep levels are located at 4.6 eV above the top of the valence band. The continuos photocurrent may result from the following two step process: (1) electrons at the occupied deep levels are excited into the conduction band, and subsequently electrons in the valence band are transferred into the vacant deep levels, (2) electrons in the valence band is first transferred to the empty deep levels and then electrons trapped in the deep levels are excited into the conduction band. According to the mechanism of photo-induced charge transfer, the irradiation of light at a wavelength > 360 nm is expected to induce changes in the transmittance. Measurements of transmittance before and after light irradiation are in progress.

4. REFERENCES

1. K. Kobayashi, S. Matsushima and G. Okada, *Chem. Lett.*, 515-518 (1992).
2. K. Kobayashi, Tatsuo Maeda, S. Matsushima and G. Okada, *Jpn. J. Appl. Phys.*, **31**, L1079-1082 (1992).
3. K. Kobayashi, H. Udaka, S. Matsushima and G. Okada, *Jpn. J. Appl. Phys.*, **32**, 3854-3859 (1993).
4. K. Kobayashi, K. Kumegawa, S. Matsushima and G. Okada, *Dennki Kagaku*, **63**, 527 -528, 1995.
5. H. Hasagawa, *Ohyobuturi*, **59**, 653-660, 1990.
6. M. Miyauchi, Y. Ishikawa and N. Shibata, *Jpn. J. Appl. Phys.* **31**, L1714-1717 (1992).

(Received December 16,1999 ; Accepted January 31,2000)