Key Engineering Materials Vols. 421-422 (2010) pp 123-126
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doi:10.4028/www.scientific.net/KEM.421-422.123

Preparation of N-doped ZnO Films by MOCVD

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Keywords: P-type ZnO, MOCVD, N-doping, PN-diodes

ABSTRACT

Crystalline ZnO films were grown on Y-stabilized ZrO_2 substrates heated at 300 - 600 °C in NH_3 atmosphere. It is clarified from Fourier transform infrared measurements that N-doped ZnO films grown at 350 and 400 °C contain N-C and Zn-H bonds. In the devices of n-type ZnO/N-doped ZnO/Au, a good rectification characteristic is attained for an N-doped ZnO film deposited at 300°C, whereas a linear current vs. voltage characteristic is seen for a film deposited at 500 °C.

INTRODUCTION

Zinc Oxide with a wide band gap of 3.37 eV has attracted considerable attention from viewpoint of an ultraviolet light emitting diode (LED). The formation of a p-n junction is required for the fabrication of ZnO-based ultraviolet LED. P-type ZnO films doped with N atoms have been prepared by sputtering and pulsed laser deposition techniques. A sputtering technique has an advantage that N atoms are easily doped into ZnO films but has a disadvantage that a large amount defects are produced by plasma [1]. Pulsed laser deposition is inapplicable to mass production of LEDs [2]. In contrast, metal-organic chemical vapor deposition (MOCVD) is a powerful technique for the mass production of LEDs, but p-type ZnO films were not easily prepared by MOCVD because of the incorporation of impurities originating from precursors. In this work, we attempt to prepare p-type ZnO films by MOCVD in which the NH_3-catalytic decomposition of zinc clusters, $Zn_4O(CH_3COO)_6$, is adopted. The chemical species arising from the zinc clusters are analyzed from Fourier transform infrared (FTIR) spectra of N-doped ZnO films. The carrier types of N-doped ZnO films are determined from current vs. voltage characteristics of devices of n-type ZnO/N-doped ZnO/Au.

EXPERIMENTAL

Zinc acetate dehydrate was preheated at 100 °C for 30 min, and subsequently was heated at 170 °C to form volatile zinc clusters, $Zn_4O(CH_3COO)_6$. Vapor of the zinc clusters was transported to a chamber by Ar-carrier gas. N-doped ZnO films were deposited on Y-stabilized ZrO_2 (YSZ) heated at temperatures of 300 to 600 °C at 260 Pa in atmospheres of Ar + NH_3. Devices of n-type ZnO/N-doped ZnO/Au were fabricated by the sequential deposition of films: an n-type ZnO films were deposited on YSZ substrates heated at 650 °C in an Ar atmosphere, followed by the deposition

of the N-doped ZnO films, and finally Au electrodes were deposited on the N-doped ZnO films by vacuum evaporation. The n-type ZnO film showed a low resistivity of 2×10^{-3} Ωcm, and thus was used as a transparent electrode. The crystallinity of ZnO films were characterized by X-ray diffraction (XRD) measurements. The concentration of N atoms in films was evaluated from X-ray photoelectron spectroscopy (XPS). FTIR measurements were performed to assign impurities in N-doped ZnO films.

RESULTS AND DISCUSSION

The deposition of films proceeded at a substrate temperature of 400 °C or more in an Ar atmosphere, and at > 150 °C in NH_3 atmosphere. The addition of NH_3 into an ambient gas enhances a film-growth rate. In an Ar atmosphere, the Zn-clusters are decomposed at a higher temperature [3]; $Zn_4O(CH_3COO)_6 \rightarrow 4ZnO + 3CH_3COCH_3 + 3CO_2$, while incomplete decomposition occurs at a low temperature; $Zn_4O(CH_3COO)_6 \rightarrow 3Zn(CH_3COO)_2 + ZnO$. In NH_3 atmosphere, the clusters are decomposed into ZnO, CH_3COOH and CH_3CONH_2 [4]. In part, Zn-N bonds are formed in the decomposition processes, as in the case of the formation of ZnS films from the clusters and H_2S [5].

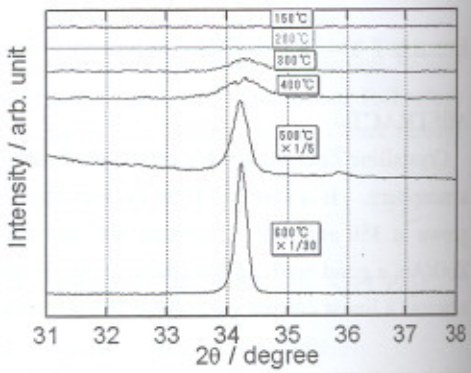

Fig. 1. XRD patterns of films deposited on YSZ heated at temperatures of 150 to 600 °C in 60% NH_3 atmosphere.

Fig. 1 shows XRD patterns of films deposited on YSZ (111) substrates in 60% NH_3 atmosphere. Although the films were deposited at 150 °C or more, the ZnO (0002) diffraction peaks are seen for the films deposited at 300 °C or more. As a substrate temperature increases, an intensity of the ZnO (0002) peak becomes strong but its 2Θ-value is almost unchanged. It is noteworthy that ZnO films are grown on YSZ substrates in an NH_3 atmosphere that is preferable for N-doping into the ZnO lattice.

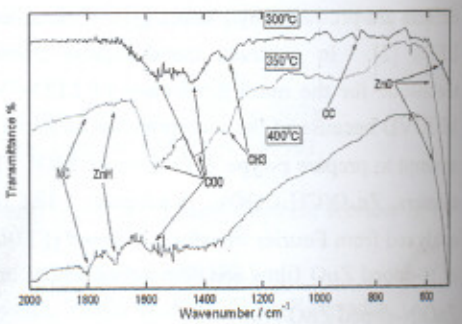

Fig. 2. FTIR spectra of films deposited on KBr substrates heated at 300, 350 and 400 °C in 60% NH_3 atmosphere.

The color of films is dependent on a substrate temperature; yellow at 200 – 300 °C, black at 400 °C, and transparent at 500 °C or more. The color of the films is originated from impurities. In order to clarify species, we measured FTIR spectra of films deposited on KBr substrates. Fig. 2 shows FTIR spectra of the films deposited at 300, 350 and 400 °C in 60% NH_3 atmosphere. For the ZnO film deposited at 300 °C, the

absorption due to ZnO lattice vibrations is seen at 600 cm^{-1} or less. The stretching and bending modes of COO bonds remain at 1564 and 1433 cm^{-1}, which is coincident with those in $Zn(CH_3COO)_2$ rather than zinc clusters, $Zn_4O(CH_3COO)_6$. This means that the decomposition of the zinc clusters is still incomplete at 300 °C in 60% NH_3 atmosphere. In FTIR spectrum of the film prepared at 350 °C, weak absorptions of ZnH and CN are seen besides strong COO and CH_3 absorption. At a substrate temperature of 350 °C, the decomposition of the Zn-clusters is still incomplete whereas organic compounds such as CH_3COCH_3 CH_3COOH and CH_3CONH_2 decompose in part into fragments of H and C-N. At a substrate temperature of 400 °C, the absorption of CH_3 disappears and alternatively the absorptions of Zn-H and N-C bonds clearly emerge, indicating that the Zn-clusters are completely decomposed and a large amount of the fragments of H and C-N acting as donors are incorporated into the film. Impurities related to CN bonds are responsible for the optical properties of the black films grown at 350 – 400 °C.

The carrier types of the N-doped ZnO films could not be determined from Hall-effect measurements because of their high resistivity > 3×10^4 Ωcm. Alternatively, their carrier types are evaluated from current vs. voltage characteristics of the devices constructed from n-type ZnO/N-doped ZnO/Au. Fig. 3 shows a current vs. voltage characteristic of the device of n-ZnO/ N-doped ZnO /Au, where the N-doped ZnO film was grown at 300 °C. The good rectification characteristic is seen in Fig. 3. The rectification characteristic is not due to the interface of the N-doped ZnO and Au, because an ohmic contact is attained for an interface of the N-doped ZnO and Au, as seen in inset. Thus, the N-doped ZnO film grown at 300 °C behaves as p-type. The resistance estimated from dI/dV at a large forward bias is about 10^4 Ω. Fig. 4 shows a current vs. voltage characteristic of the device of n-ZnO/ N-doped ZnO /Au, where the N-doped ZnO film was grown at 350 °C. Notice features in Fig. 4 are that the rectification characteristic is seen but the resistance estimated from dI/dV increases up to 6×10^5 Ω. Similarly, the rectification characteristic is seen for the device consisting of the N-doped ZnO film grown at 400 °C. The resistance of the N-doped ZnO film increases up to 1×10^7 Ω. Fig. 5

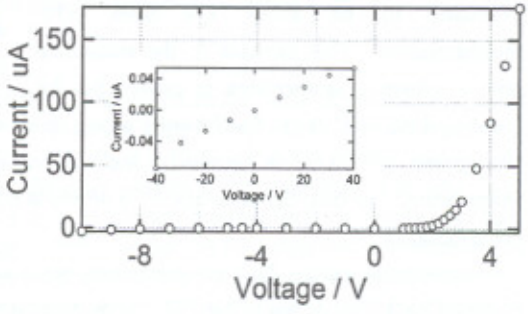

Fig.3. A current vs. voltage characteristic of a device of n-type ZnO / N-doped ZnO (300 °C) /Au. Inset is current vs. voltage curve for Au / N-doped ZnO / Au contacts.

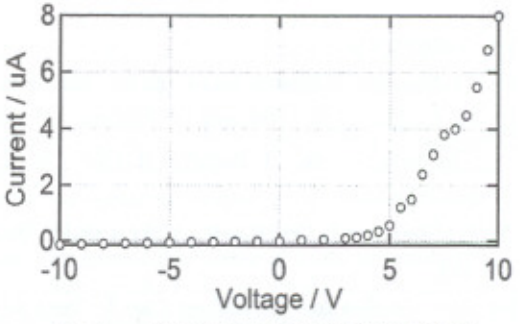

Fig. 4. A current vs. voltage characteristic of a device of n-type ZnO / N-doped ZnO (350 °C) /Au.

shows a current vs. voltage characteristic of the device of n-ZnO/ N-doped ZnO /Au, where the N-doped ZnO film was grown at 500 °C. The linear current vs. voltage characteristic suggests that the N-doped ZnO film grown at 500 °C is an n-type.

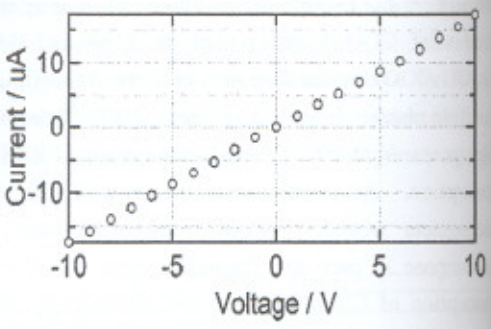

Fig. 5. A current vs. voltage characteristic of a device of n-type ZnO / N-doped ZnO (500 °C) /Au.

The p-type ZnO films are grown at substrate temperatures of 300 to 400 °C. The film grown at 300 °C is yellow due to doped N atoms, and the N-concentration was evaluated to be about 1% from XPS measurements. The increase in the resistance with a substrate temperature is caused by the incorporation of C-N or Zn-H bonds acting as donors. No hole-conductivity of the transparent film grown at 500 °C is caused by the removal of N atoms from the ZnO lattice at a higher temperature. In fact, the presence of N atoms is not detected in the transparent ZnO film by XPS measurements.

Electroluminescence (EL) measurements were carried out using the device consisting of the N-doped ZnO film grown at 300 °C. Unfortunately, no emissions are detected at a forward bias of 10 V or more. The reason for no EL emission is attributable to luminescence properties of the N-doped ZnO film that shows no emission in photoluminescence spectra at room temperature. In the device, the depletion region is mainly formed within the p-type ZnO film, and thus nonradiative recombination of electron-hole pairs occurs in the p-type ZnO film.

REFERENCES

[1] M. Sanmyo, Y. Tomita, and K. Kobayashi, Thin Solid Films, 472 (2005) 189.

[2] A. Tsukazaki, A. Ohtomo, T. Onuma, M. Ohtani, T. Makino, M. Sumiya, K. Ohtani, S.F. Chichibu, S. Fuke, Y. Segawa, H. Ohno, H. Koinuma and M. Kawasaki, Nature Materials, 4, (2005) 42.

[3] L.Hiltunen, M. Leskela, M. Makela and L. Niinisto, Acta Chemica Scandinavia, A41 (1987) 548.

[4] R.M. Gordon and H.B. Silver, Can. J. Chem, 61 (1983) 1218.

[5] M. Tammenmaa, T. Koskinen, L.Hiltunen, M. Leskela and L. Niinisto, Thin Solid Films, 124 (1985) 125.

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