CHEMISTRY OF MATERIALS

VOLUME 15, NUMBER 4 FEBRUARY 25, 2003

Communications

Preparation of p-Type ZnO Films by Doping of Be−N Bonds

Masahiro Sanmyo, Yasumasa Tomita, and Kenkichiro Kobayashi*

Department of Materials Science, Faculty of Engineering, Shizuoka University, 3-5-1, Johoku, Hamamatsu, 432-8561 Japan

Received October 31, 2002
Revised Manuscript Received January 2, 2003

Zinc oxide (ZnO) with a wide band gap of 3.37 eV has attracted considerable attention from the viewpoint of ultraviolet laser diodes. The formation of a p−n junction is required for the fabrication of a laser diode. An n-type ZnO has been obtained by doping Group III elements.[1] Unfortunately, no one succeeded in the growth of p-type ZnO, except for recent reports.[2,3] No hole conductivity was confirmed in ZnO films doped with N atoms of a few percent.[4] These results imply that the bonding states of Zn−N bonds are located apart from the top of the valence band.[5] If tight metal−N bonds are incorporated into ZnO, the bonding states of metal−N bonds are expected to be located close to the top of the valence band. From preliminary band-structure calculations of ZnO containing metal−N bonds, it was found that Be−N bonds in ZnO were shallow acceptor levels. Such modifications of the N-related acceptor levels were proposed by Yamamoto and Yoshida.[6] In the present work, we prepare ZnO films doped with N and Be atoms by RF sputtering of a target of ZnO, on which the surface Be compounds are deposited simultaneously by dc sputtering of a target of Be in a N_2 atmosphere. The characterization of sputtered films is carried out by X-ray diffraction (XRD) and X-ray photoelectron spectroscopic (XPS) measurements. The role of Be−N bonds in the hole conductivity is discussed.

A target of ZnO (99.999%) powders was fixed in a chamber, whereas a target of Be (99.9%) was mobile. A substrate holder was placed above the ZnO target. In the case of the preparation of Be-compound films, the surface of the Be target was directed upward, whereas in the preparation of ZnO films containing Be and N atoms the surface of the Be target was directed downward so that sputtered Be compounds were deposited on the surface of the ZnO target. In the latter case, the direct deposition of Be compounds on a substrate was interrupted by inserting a shutter between the Be target and the substrate. The sputtering of ZnO and Be was independently carried out by rf and dc magnetron techniques. The concentration of Be compounds in ZnO was altered by dc power, which was changed from 0 to 17 W. ZnO films were grown on (0001)-sapphire and glass substrates heated at 200 °C at a pressure of 1×10^{-2} Torr in a N_2 (99.999%) atmosphere. The lattice parameters of ZnO films were determined from XRD measurements. The compositions of ZnO films were determined from XPS measurements. The resistivity was measured by a four-point probe van der Pauw method. Types of carriers were determined by Seebeck-effect measurements, in which a temperature gradient of 70 °C was present between two Au electrodes and the resultant thermoelectromotive force of 0.5 mV or more was detected.

---

(1) Minami, T.; Sato, H.; Nanto, H.; Takata, S. *Jpn. J. Appl. Phys.* **1985**, *24*, L781.
(2) Minegishi, K.; Koiwai, Y.; Kikuchi, Y.; Yano, K.; Kasuga, M.; Shimizu, A. *Jpn. J. Appl. Phys.* **1997**, *36*, L1453.
(3) Joseph, M.; Tabata, H.; Kawai, T. *Jpn. J. Appl. Phys.* **1999**, *38*, L1205.
(4) Nakahara, K.; Takasu, H.; Fons, P.; Yamada, A.; Iwata, K.; Matsubara, K.; Hunger, R.; Niki, S. *J. Cryst. Growth* **2002**, *237−239-(P1)*, 503.
(5) Matsushima, S.; Kobayashi, K. *Electrochemistry* **2000**, *68*, 537.
(6) Yamamoto, T.; Yoshida, H. K. *Jpn. J. Appl. Phys.* **1999**, *38*, L166.

10.1021/cm025747y CCC: $25.00 © 2003 American Chemical Society

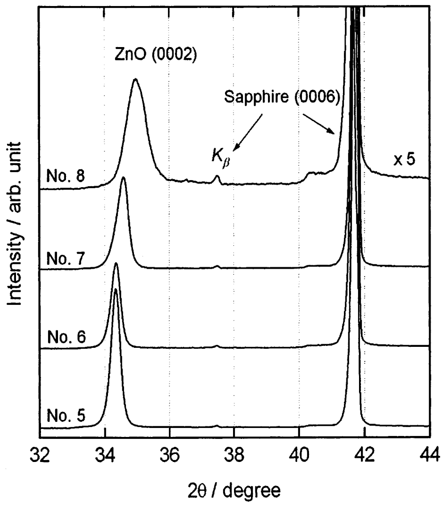

Figure 1. XRD patterns of samples 5, 6, 7, and 8.

Be-compound films were deposited on Si(100) substrates heated at 500 °C, together with the sputtering of the ZnO target. A shutter was interposed between the ZnO target and the Si substrate so that no ZnO film was deposited on the Si substrate. Sputtered films (samples 1, 2, 3, and 4) were prepared for 5 h at a dc power of 17 W, together with ZnO sputtering at a rf power of 50, 70, 120, and 150 W, respectively. From XRD measurements, it is confirmed that sample 1 is a mixture of $Be_8O_5N_2$ and Be_3N_2, samples 2 and 3 are $Be_8O_5N_2$, and sample 4 is BeO, respectively. At a higher rf power, the nitridation of Be is hindered by the O_2 gas evolved in the sputtering of ZnO. Accordingly, the sputtering of ZnO at a lower rf power is desirable for doping of N atoms into ZnO.

ZnO films (samples 5, 6, 7, and 8) were deposited on sapphire substrates for 120 min at 50-W rf power and dc power of 0, 0.8, 1.7, and 3.0 W, respectively. These samples (5, 6, 7, and 8) have almost the same thickness of 200−220 nm and the grain size of 50−100 nm. XRD patterns of these samples are shown in Figure 1. In the XRD patterns for the samples 5, 6, 7, and 8, ZnO(0002) peaks appear at 34.33°, 34.34°, 34.57°, and 34.97°. There are no peaks originating from Be compounds such as Be_3N_2, $Be_8O_5N_2$, and BeO. The *c*-axis lengths for the samples 5, 6, 7, and 8 are estimated to be 0.5224, 0.5223, 0.5189, and 0.5132 nm. The *c*-axis length is shortened with dc power of the Be sputtering. The *c*-axis length for the sample 5 is slightly longer than that of single-crystalline ZnO ($c = 0.52066$ nm). As will be discussed later, sample 5 contains a large number of N atoms. However, the slight change of the *c*-axis length is not attributable to N atoms because ZnO films with a *c*-axis of 0.5224 nm were prepared by sputtering in an Ar atmosphere. The slight change of the *c*-axis length may be caused by damages produced by plasma. This means that N atoms doped into ZnO have little influence on the *c*-axis length. Assuming a linear relationship between the *c*-axis length and Be concentration,[7] the Be concentration is estimated to be 0.1, 4.1, and 10.9% for the samples 6, 7, and 8, respectively.

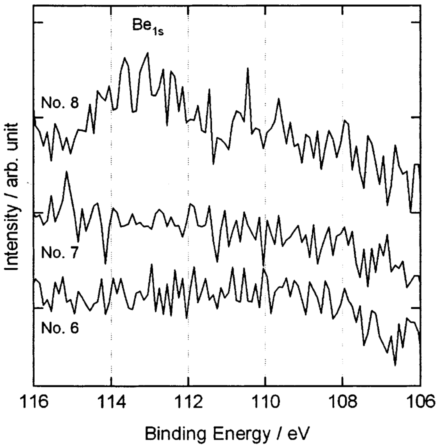

Figure 2. XPS spectra around the Be_{1s} core level of samples 6, 7, and 8.

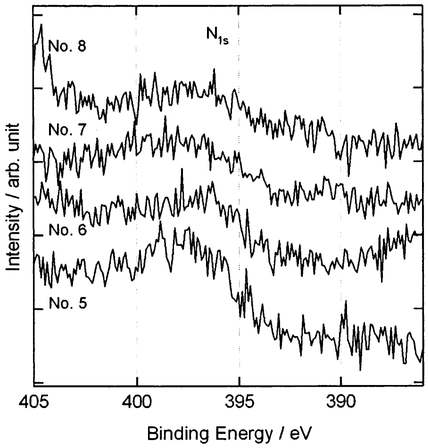

Figure 3. XPS spectra around the N_{1s} core level of samples 5, 6, 7, and 8.

Figure 2 shows XPS around the Be_{1s} core level for samples 6, 7, and 8. For samples 6 and 7, no Be_{1s}-related peaks appear in XPS spectra. The Be_{1s} signal level in samples 6 and 7 is probably below a sensitivity limit of our XPS measurements because the incorporation of Be atoms into ZnO is confirmed from the shift of the *c*-axis length of ZnO. For sample 8, a weak peak is seen around 113.5 eV, which is close to the binding energy of oxides of Be, 113.7 eV, or nitrides, 114.0 eV (the binding energy of Be in metallic states is 111.8 eV).[8] It is considered that Be atoms in the ZnO film are bound to O or N atoms. Spectra in the N_{1s} region for samples 5, 6, 7, and 8 are shown in Figure 3. For the sample 5 (N-doped ZnO), a peak appears around 397.5 eV, which is almost identical to the binding energy of N atoms bound to Zn atoms (Eb = 396.9 eV).[9] For samples 6, 7, and 8 peaks appear in the range of 396−398 eV. The binding energy corresponds to that of nitrides of Be (Eb = 397.4 eV) or nitrides of Zn (Eb = 396.9 eV).

The compositions of samples 5, 6, 7, and 8 estimated from XPS measurements are listed in Table 1. Accuracy of the compositions is about 0.1%. The concentration of Be atoms is about 18% for sample 8. This value is not so deviated from the concentration evaluated from the shift of the *c*-axis length (11%). The Be concentrations for samples 6 and 7 were not determined because of the low sensitivity of the XPS measurements. The high N

---

(7) Sanmyo, M.; Kobayashi, K.; Tomita, Y. *Chem. Lett.* **2002**, *9*, 944.

(8) Soto, G.; Díaz, J. A.; Machorro, R.; Reyes-Serrato, A.; de la Cruz, W. *Mater. Lett.* **2002**, *52*, 29.

(9) Lancaster, G. M.; Rabalais, J. W. *J. Phys. Chem.* **1979**, *83*, 209.

Table 1. Compositions and Electrical Properties of Samples 5, 6, 7, and 8

samples	Zn (%)	O (%)	Be (%)	N (%)	resistivity (Ωcm)	carrier type
5	37.3	56.5	0	6.2	54.0	n
6	42.5	52.3	0 (0.1[a])	5.2	181	n
7	42.5	54.1	0 (4.1[a])	3.4	1.80×10^3	n
8	24.3	56.7	17.8 (10.9[a])	1.2	362	p

[a] Values in the parentheses are estimated from the shift of *c*-axis length.

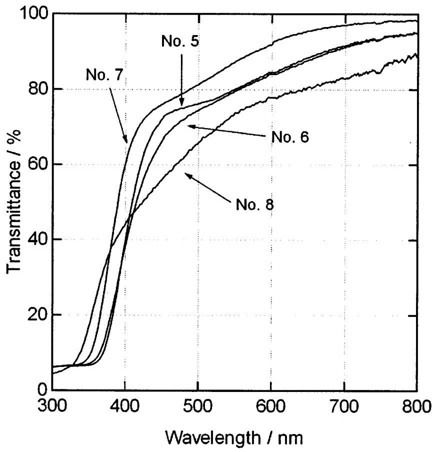

Figure 4. Transmission spectra of samples 5, 6, 7, and 8.

concentration of 6.2% for sample 5 is ascribed to the nitridation of the ZnO powder target because the color of the ZnO powder target was changed from white to black after sputtering in a N_2 atmosphere for a long period of time. For samples 6, 7, and 8, the concentration of N atoms decreases with an increase of dc power of the Be sputtering (cf. Table 1). The presence of Be atoms deposited on the ZnO target prevents the nitridation of ZnO. In fact, the color of the ZnO powder target was not so black after the preparation of sample 8. Figure 4 shows transmission spectra for samples 5, 6, 7, and 8. As the Be concentration increases, these transmission spectra near 350 nm corresponding to the band-gap excitation are shifted toward a shorter wavelength. From plots of $(\alpha\hbar\omega)^2$ vs photo energy ($\hbar\omega$), where α is the absorption coefficient,[10] the optical band-gap energy is estimated to be 3.14, 3.16, 3.30, and 3.38 eV for samples 5, 6, 7, and 8, with an error of about 0.05%. The increase of the band gap energy with the Be concentration suggests the doping of Be atoms into ZnO films. Another feature in the transmission spectra is that absorption is weak at wavelengths >450 nm for samples 5, 6, and 7, whereas somewhat strong absorption is observed in the range of 380−550 nm for sample 8. It seems that localized states in the band gap for sample 8 are different from those for samples 5, 6, and 7.

The resistivity and carrier types of ZnO films are also listed in Table 1. The estimated values of the resistivity include an error of about 0.1%. For the ZnO films with the high resistivity, we could not obtain reliable data of the carrier density and the mobility from Hall-effect measurements. Alternatively, types of carriers were determined from Seebeck-effect measurements in which reliable data on carrier types were obtained for films with the resistivity $<10^4$ Ωcm. As seen in Table 1, sample 5 contains the high concentration of N atoms (ca. 6%) and is an n-type semiconductor with the resistivity of 54 Ωcm. Thus, the electric property of sample 5 is mainly characterized by oxygen vacancies acting as donors, despite coexistence of N atoms and oxygen vacancies. The formation of a large number of oxygen vacancies results from the colored ZnO target, which has been sputtered for a long period of time in a N_2 atmosphere because semi-insulator ZnO films ($\rho > 10^6$ Ωcm) were prepared by sputtering of a new ZnO target in a N_2 atmosphere.[7] With the increase of the Be concentration, the resistivity of samples 6 and 7 (n-type) is enhanced and the hole conductivity is found in sample 8. These results suggest that the presence of Be atoms takes part in the appearance of the hole conductivity. Of course, Be atoms bound to O atoms in ZnO have no influence on the generation of holes. Thus, it is concluded that Be−N bonds play the role of acceptors, as predicted theoretically. The high resistivity of the p-type ZnO film (sample 8) is attributable to either deep acceptor levels of Be−N bonds or the coexistence of oxygen vacancies. For clarifying effects of oxygen vacancies on the resistivity, annealing of the p-type ZnO film in an O_2 atmosphere is in progress.

CM025747Y

---

(10) Mott, N. F.; Davis, E. A. *Electronic processes in noncrystalline materials*; Clarendon Press: Oxford, 1979; p 273.