Evaluation of oxygen vacancies in ZnO single crystals and powders by micro-Raman spectroscopy

Hiroaki FUKUSHIMA, Hiroshi UCHIDA*, Hiroshi FUNAKUBO**, Takashi KATODA*** and Ken NISHIDA†

Department of Communications Engineering, National Defense Academy, Yokosuka, Kanagawa 239-8686, Japan
*Department of Materials and Life Sciences, Sophia University, Chiyoda, Tokyo 102-8554, Japan
**Department of Innovative and Engineered Materials, Tokyo Institute of Technology, Yokohama 226-8502, Japan
***Department of Electronic and Photonic Systems Engineering, Kochi University of Technology, Kami, Kochi 782-8502, Japan

Investigations of defects are important to understand the properties of zinc oxide (ZnO), especially oxygen vacancies, which are intrinsic defects that are easily generated during crystal growth or device processing. In this study, we evaluate the oxygen vacancies in ZnO single crystals and powders using micro-Raman spectroscopy. Reducing ZnO in a hydrogen atmosphere at 400–600°C for 30–240 min changes the amount of oxygen vacancies. Raman spectroscopy reveals a slight shift and a decrease in the $E_2\text{(high)}$ phonon mode, which is related to the oxide ion vibration. The peak position of the $E_2\text{(high)}$ mode shifts toward a lower frequency and the peak intensity decreases as the oxygen vacancies increase. This behavior can be explained by the existence of oxygen vacancies in ZnO. Because the $E_2\text{(high)}$ peak shift and the intensity are scaled in accordance with the amount of oxygen vacancies, these correlations offer a simple and useful probe to evaluate oxygen vacancies in ZnO.

Key-words : Zinc oxide, Raman spectroscopy, Oxygen vacancies, Reduction treatment, $E_2\text{(high)}$ mode, Raman shift

[Received November 11, 2016; Accepted February 7, 2017]
99.998%] and powders (Koch Chemicals Ltd., purity: 99.999%) were obtained from a commercial supplier. To generate various oxygen vacancies, ZnO single crystals and powders were reduced in a hydrogen atmosphere (Ar:H₂ = 96:4) using a rapid thermal annealing (RTA) system. ZnO single crystals were reduced at 600°C for a predetermined period between 30 and 240 min in a hydrogen atmosphere. ZnO powders were reduced at 400°C for a predetermined time between 30 and 90 min since we have previously reported that Zn vacancies are likely generated in ZnO powders reduced at 600°C for 30 min.36

Micro-Raman spectroscopy was performed in the spectral range from 50 to 500 cm⁻¹ using a micro-Raman system (Photon Design NFR-800-NSD) and a wavenumber resolution of about 0.25 cm⁻¹. An Ar⁺/Kr⁺ mixed gas ion laser at 488 and 514.5 nm was used for the excitation. The laser power of the sample surface was approximately 5 mW. The laser spot size on the sample surface was 1–2 μm through an objective lens. The Raman scattering experiments were carried out under a backscattering geometry with a measurement time of 30–100 s at room temperature. The backward scattering light was collected and dispersed by a single spectrometer. Figure 1(a) shows the Raman active phonon mode patterns at Γ-point for wurtzite-type ZnO. Figure 1(b) shows the coordinate system in the experimental configuration and the scattering geometry. The polarization direction of the incident light is parallel to the y-axis [ε₁ = (0 1 0)]. Scattering light is unpolarized. (0001) direction (c-axis) of ZnO is parallel to the z-axis.

Micro-Raman spectroscopy was performed in the spectral range from 50 to 500 cm⁻¹ using a micro-Raman system (Photon Design NFR-800-NSD) and a wavenumber resolution of about 0.25 cm⁻¹. An Ar⁺/Kr⁺ mixed gas ion laser at 488 and 514.5 nm was used for the excitation. The laser power of the sample surface was approximately 5 mW. The laser spot size on the sample surface was 1–2 μm through an objective lens. The Raman scattering experiments were carried out under a backscattering geometry with a measurement time of 30–100 s at room temperature. The backward scattering light was collected and dispersed by a single spectrometer. Figure 1(a) shows the Raman active phonon mode patterns at Γ-point for wurtzite-type ZnO. Figure 1(b) shows the coordinate system in the experimental configuration and the scattering geometry. The polarization direction of the incident light is parallel to the y-axis [ε₁ = (0 1 0)]. Scattering light is unpolarized. (0001) direction (c-axis) of ZnO is parallel to the z-axis.

The amount of oxygen vacancies was estimated using the following procedure. For a single crystal, the weight of the reduced ZnO was measured using an analytical balance. The mass decrement was equivalent to the amount of oxygen vacancies. For a powder, the reduced ZnO was thermally treated in air (re-oxidized) using thermal gravimetric and differential thermal analysis (TG-DTA). A BRUKER WS003 system was used to measure the TG-DAT data. Then the ZnO powders were heated from room temperature to 600°C at a rate of 10°C/min. The mass increment of ZnO was equivalent to the amount of oxygen vacancies.

3. Results and discussion

Figure 2 shows optical photographs of ZnO single crystals [Fig. 2(a)] and powders [Fig. 2(b)] before and after reduction in a hydrogen atmosphere for various times. Prior to the reduction, the ZnO single crystal is transparent and its surface is flat. Afterwards it becomes translucent and its surface is rough. Although the ZnO powder is initially white, it turns slightly black after reduction. The color becomes more intense as the reduction treatment time increases because the absorption of the reduced ZnO increases at shorter wavelengths in the visible light range.

Figure 3(a) shows the Raman spectra of ZnO single crystals before and after the reduction treatment in a hydrogen atmosphere at 600°C for 30–240 min. Prior to the treatment, a typical ZnO Raman spectrum is observed. The intense Raman peaks around 99 and 438 cm⁻¹ correspond to the E₂(low) and E₂(high) modes, while the weak peaks around 330 and 380 cm⁻¹ are the second order and A₁(TO) modes, respectively. The Raman spectra show a typical wurtzite ZnO structure. These spectral features and the observed phonon frequencies of ZnO agree well with those previously reported.32 The reduction treatment does not alter the spectral features. Figure 3(b) shows the E₂(high) mode before and after the reduction treatment. The E₂(high) peaks shift to the lower side as the reduction treatment time increase, while that of the E₂(low) mode is almost the same, confirming that only oxygen vacancies are generated in ZnO. Figures 3(c) and 3(d) shows the Raman shift and the Raman intensity of the E₂(high) mode in ZnO single crystal from Fig. 3(b), respectively. As the reduction treatment time increases, the E₂(high) mode shifts toward a lower frequency and the Raman intensity of E₂(high) decreases.

Figure 4(a) shows the Raman spectra of ZnO powder before and after the reduction treatment in a hydrogen atmosphere at 400°C for 30–90 min. Similar to that for the single crystals, a typical ZnO Raman spectrum is observed. Figure 4(b) shows the Raman spectra of the E₁(high) mode before and after the reduction treatment. Figures 4(c) and 4(d) show the Raman frequency and the Raman intensity of the E₁(high) mode as functions of the reduction treatment time from Fig. 4(b), respectively. Similar to that for a single crystal, the E₂(high) mode shifts toward a lower frequency and the Raman intensity of the E₂(high) decreases as the reduction treatment time increases.

Figure 5 shows the amount of oxygen vacancies in ZnO single crystals [Fig. 5(a)] and powders [Fig. 5(b)] as functions of the reduction treatment time. For both sample types, the amount of oxygen vacancies increases as the reduction treatment temperature increases.

Figure 6 shows the Raman frequency (a) and the intensity (b) of the E₂(high) phonon mode for single crystals and powders of ZnO as functions of the oxygen vacancies ratio. The Raman frequency of the E₂(high) phonon mode decreases linearly as the
oxygen vacancies increase. On the other hand, the Raman intensity of the $E_{2g}$ (high) phonon mode decreases linearly as the oxygen vacancies increase. Because good correlations are observed between the Raman frequency, the intensity of the $E_{2g}$ (high) phonon mode, and the amount of oxygen vacancies in ZnO, the Raman frequency and the intensity of the $E_{2g}$ (high) mode can be used to evaluate the oxygen vacancies in ZnO.

4. Conclusions

For both ZnO single crystals and powders, the Raman spectrum of the $E_{2g}$ (high) mode, which is related to oxygen ion vibrations, shifts towards a lower frequency and decreases as the oxygen vacancy concentration increases. Thus, the Raman frequency shift and intensity decrease of the $E_{2g}$ (high) mode are associated with the amount of oxygen vacancies in ZnO, the Raman frequency and the intensity of the $E_{2g}$ (high) phonon mode can be used to evaluate the oxygen vacancies in ZnO.

Fig. 3. (a) Raman spectra of ZnO single crystals thermally treated at 600°C in a hydrogen atmosphere for various times. (b) Enlarged view of the $E_{2g}$ (high) mode spectra. (c) Raman frequency of the $E_{2g}$ (high) mode for single crystals as a function of the reduction treatment time. (d) Raman intensity of the $E_{2g}$ (high) mode for single crystals as a function of the reduction treatment time.

Fig. 4. (a) Raman spectra of ZnO powders thermally treated at 400°C for various reduction times in a hydrogen atmosphere. (b) Enlarged view of the $E_{2g}$ (high) mode spectra. (c) Raman frequency of the $E_{2g}$ (high) mode for powders as a function of the reduction treatment time. (d) Raman intensity of the $E_{2g}$ (high) mode for powders as a function of the reduction treatment time.

Fig. 5. Amount of oxygen vacancies in (a) single crystals and (b) powders of ZnO as functions of the reduction treatment temperature.
and accurate method to evaluate oxygen vacancies in ZnO. Hence, Raman spectroscopy is a powerful tool to investigate oxygen vacancies with a relatively high spatial resolution.

References

1) R. Zamirin, A. Kaushal, A. Rebelo and J. M. F. Ferreira, Ceram. Int., 40, 1635–1639 (2014).
2) C. G. Van de Walle, Phys. Rev. Lett., 85, 1012–1015 (2000).
3) A. J. Flewitt, J. K. Luo, Y. Q. Fu, L. G. Gancedo, X. Y. Du, J. R. Lu, X. B. Zhao, E. Iborra, M. Ramos and W. I. Milne, J. Non-Newton. Fluid Mech., 222, 209–216 (2015).
4) F. Kohan, G. Ceder, D. Morgan and C. G. Van de Walle, Phys. Rev. B, 81, 15019–15027 (2000).
5) Y. Kim and S. Kang, Acta Mater., 59, 3024–3031 (2011).
6) Z. Wang, F. Wang, L. Wang, Y. Jia and Q. Sun, J. Appl. Phys., 114, 063508 (2013).
7) J. Ye, S. Gu, S. Zhu, T. Chen, W. Liu, F. Qin, L. Hu, R. Zhang, Y. Shi and Y. Zheng, J. Vac. Sci. Technol., A, 21, 979–982 (2003).
8) J. B. Wang, H. M. Zhong, Z. F. Li and W. Lu, Appl. Phys. Lett., 88, 101913 (2006).
9) E. V. Lavrov, J. Weber and F. Bornert, Phys. Rev. B, 66, 165205 (2002).
10) L. S. Vlasenko and G. D. Watkins, Phys. Rev. B, 71, 125210 (2005).
11) A. A. Kahlout, Thin Solid Films, 520, 1814–1820 (2012).
12) M. D. McClusky and S. J. Jokela, J. Appl. Phys., 106, 071101 (2009).
13) A. Janotti and C. G. Van de Walle, J. Appl. Phys., 87, 122102 (2005).
14) F. Oba, M. Choi, A. Togo and I. Tanaka, Sci. Technol. Adv. Mater., 12, 034302 (2011).
15) S. B. Zhang, S. H. Wei and A. Zunger, Phys. Rev. B, 63, 075205 (2001).
16) L. A. Kappers, O. R. Gilliam, S. M. Evans, L. E. Halliburton and N. C. Giles, Nucl. Instrum. Methods Phys. Res. B: Beam Interact. Mater. At., 286, 2953–2957 (2008).
17) U. Ozgur, Ya. I. Alivov, C. Liu, A. Teke, M. A. Ressler, S. Dogan, V. Avrutin, S. J. Cho and H. Morkoc, J. Appl. Phys., 98, 041301 (2005).
18) A. Ghosh and R. N. P. Choudhary, J. Appl. Phys., 105, 124906 (2009).
19) F. Leiter, H. Alves, D. Pfisterer, N. G. Romanov, D. M. Hofmann and B. K. Meyer, J. Phys. B, 340–342, 201–204 (2003).
20) N. Ashkenov, B. N. Mbenkum, C. Bundesmann, V. Riede, M. Lorenz, D. Spemann, E. M. Kaidashev, A. Kasie, M. Schubert and M. Grundmann, J. Appl. Phys., 93, 126–133 (2003).
21) Z. Q. Chen, A. Kawasuso, Y. Xu, H. Naramoto, X. L. Yuan, T. Sekiguchi, R. Suzuki and T. Ohdaira, Phys. Rev. B, 71, 115213 (2005).
22) P. Wu, Q. Li, X. Zou, W. Cheng, D. Zhang, C. Zhao, L. Chi and T. Xiao, J. Phys.: Conf. Ser., 188, 012054 (2009).
23) K. Vanheusden, C. H. Seager, W. L. Warren, D. R. Tallant and J. A. Voigt, Appl. Phys. Lett., 68, 403–405 (1996).
24) K. Vanheusden, W. L. Warren, C. H. Seager, D. R. Tallant and J. A. Voigt, J. Appl. Phys., 79, 7983–7990 (1996).
25) I. Tanaka, F. Oba, K. Tatsumi, M. Kunisu, M. Nakano and H. Adachi, Mater. Trans., 43, 1426–1429 (2002).
26) L. S. Vlasenko and G. D. Watkins, Phys. Rev. B, 72, 035203 (2005).
27) K. Nishida, M. Osada, J. Sakai, N. Ito, T. Katoda, R. Ikariyama, H. Funakubo, H. Moriwake and T. Yamamoto, J. Ceram. Soc. Japan, 121, 598–601 (2013).
28) K. Nishida, M. Osada, H. Moriwake, J. Sakai, N. Ito, M. Nishide, H. Oka, M. Matsuoka, R. Ikariyama, H. Funakubo, T. Katoda and T. Yamamoto, J. Ceram. Soc. Japan, 121, 859–862 (2013).
29) K. Nishida, M. Osada, H. Takeuchi, Y. Ishimoto, J. Sakai, N. Ito, R. Ikariyama, T. Kamo, T. Fujisawa, H. Funakubo, T. Katoda and T. Yamamoto, Jpn. J. Appl. Phys., 47, 7510–7513 (2008).
30) K. Nishida, H. Kishi, M. Osada, H. Funakubo, M. Nishide, H. Takeuchi, T. Katoda and T. Yamamoto, Jpn. J. Appl. Phys., 48, 09KE11 (2009).
31) K. Nishida, H. Funakubo, H. Takeuchi, T. Katoda and T. Yamamoto, Jpn. J. Appl. Phys., 46, 7005–7007 (2007).
32) R. Cuscó, E. A. Lladó, J. Ibáñez, L. Artús, J. Jiménez, B. Wang and M. J. Callahan, Phys. Rev. B, 75, 165202 (2007).
33) T. C. Damen, S. P. S. Porto and B. Tell, Phys. Rev., 142, 570–574 (1966).
34) A. Arguello, D. L. Rousseau and S. P. S. Porto, Phys. Rev., 181, 1351–1363 (1969).
35) K. A. Alim, V. A. Fonoberov and A. A. Balandin, Appl. Phys. Lett., 86, 053103 (2005).
36) H. Fukushima, T. Kozu, H. Shima, H. Funakubo, H. Uchida, T. Katoda and K. Nishida, Applications of Ferroelectric, International Symposium on Integrated Functionalities and Piezoelectric Force Microscopy Workshop (ISAF/ISIF/PFM), 2015 Joint IEEE International Symposium, 28–31 (2015).
37) J. M. Calleja and M. Cardona, Phys. Rev. B, 16, 3753–3761 (1977).