Synthesis of nitrogen-doped zinc oxide particles by thermal decomposition of mixture between zinc peroxide aqueous sol and ammonium salts

Naofumi UEKAWA,[†] Yusuke MITANI, Takashi KOJIMA and Kazuyuki KAKEGAWA

Graduate School of Engineering, Chiba University, 1-33, Yayoi-cho, Inage-ku, Chiba-shi 263-8522

The nitrogen-doped ZnO particles were prepared by heating a mixture of an ammonium salt and the aqueous sol of zinc peroxide nanoparticles. In the case that the sol of zinc peroxide nanoparticles were mixed with ammonium nitrate in the sol, nitrogen-doped ZnO particles were obtained by heating the mixture at 573 K for 1 h in the air. The obtained particles showed characteristic Raman peaks that can be assigned to the nitrogen-related local vibrational mode. The strength of the UV-VIS absorption peak, which corresponds to the nitrogen-related impurity state, also increased with increases in the mixed amount of ammonium nitrate (NH_4NO_3). The results of iodometric titration also showed the formation of acceptor states in the obtained nitrogen-doped ZnO particles. The nitrogen-doping successively occurred when the peroxo ions (O_2^{2-}) in the zinc peroxide did not react with the anions in the ammonium salts as an oxidizing agent.

©2009 The Ceramic Society of Japan. All rights reserved.

Key-words : Zinc oxide, Sol, Nitrogen doping, Zinc peroxide

[Received November 10, 2008; Accepted January 15, 2009]

1. Introduction

Many of the characteristics of zinc oxide (ZnO), including its piezoelectricity, photoluminescent (PL) characteristics, and semiconductivity, have been applied to a variety of electrical devices.^{1,2)} In particular, ZnO functions as a wide-gap oxide semiconductor. Doping of Al^{3+} ions and the presence of the oxygen vacancies in the ZnO lattice produce donor levels, producing n-type semiconductivity.³⁾ On the other hand, in recent years, the preparation method for p-type ZnO has been intensively investigated since it can be used for the development of short-wavelength optical devices.^{4,5)} Nitrogen (N) doping by the substitution of nitrogen for oxygen (O) is an effective method for obtaining p-type ZnO.^{6,7)} Theoretical calculations have shown that nitrogen-doping produces a shallow acceptor level approximately 0.1 eV above the valence band in ZnO.⁸⁾ However, there are many difficulties in obtaining p-type ZnO, whose semiconductivity depends with great sensitivity on the doping conditions.⁸⁾ Therefore, the development of simple and effective preparation methods for nitrogen-doped ZnO is a very important issue.

Various preparation methods for nitrogen-doped ZnO material have been reported. The MOCVD methods can be used for preparation of the film samples. Wang et al. have shown the decomposition of diethyl zinc on a substrate at 873 K under an atmosphere of a mixed gas of N_2 and O_2 .⁹⁾ Zhao et al. have employed a spray pyrolysis method to prepare nitrogen-doped ZnO film by decomposition of zinc acetate and ammonium acetate in a N_2 atmosphere.¹⁰⁾ Varghese et al. have obtained nitrogen-doped ZnO nanoparticles using a solvothermal method.¹¹⁾ Li et al. have investigated the semiconductivity of the ZnO particles obtained by decomposition of various precursors such as zinc

peroxide (ZnO_2) and zinc nitrate.⁶⁾

The authors have previously shown that low-temperature heating of zinc peroxide nanoparticles at around 500 K results in ZnO nanoparticles with oxygen vacancies.¹²⁾ Substitution of nitrogen for the oxygen vacancies in the ZnO lattice is considered to be effective in efficiently obtaining nitrogen-doped ZnO. Furthermore, the authors have also developed the solution process to prepare the stable aqueous sol of zinc peroxide nanoparticles, which can form the homogeneous mixture of the nitrogen source for the nitrogen doping and the zinc peroxide nanoparticles. The aqueous sol of the zinc peroxide nanoparticles would then be appropriate as precursors of the nitrogen-doped ZnO. Furthermore, the application of the aqueous solution and sol of the metal peroxides to inorganic reactions is an attractive prospect. Therefore, in this study, the heat treatment of a mixture between zinc peroxide aqueous sol and ammonium salts in air was examined to obtain nitrogen-doped ZnO particles, and application of aqueous sol of the zinc peroxide nanoparticles for nitrogen doping was examined.

2. Experiments

2.1 Preparation of zinc peroxide nanoparticles

The sols containing zinc peroxide nanoparticles were prepared our previously reported method.^{12,13)} To obtain zinc hydroxide ($\text{Zn}(\text{OH})_2$) precipitate, 100 ml of $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ aqueous solution (0.1 mol/l) and 100 ml of NaOH aqueous solution (0.1 mol/l) were mixed. The precipitate was separated from the solution by a centrifuge at 3000 r.p.m. for 5 min. The obtained $\text{Zn}(\text{OH})_2$ was dispersed into distilled water and was again separated by a centrifuge. This procedure was repeated 3 times, and the impurities in the precipitate were removed. The $\text{Zn}(\text{OH})_2$ was then dispersed in 50 ml of H_2O_2 aqueous solution to a concentration of 1 mol/l. The dispersed solution was heated at 348 K for 2 h in a closed glass vessel (200 ml). The resultant solution was a translucent sol of the zinc peroxide nanoparticles.

[†] Corresponding author: N. Uekawa; E-mail: uekawa@faculty.chiba-u.jp

2.2 Preparation of nitrogen-doped ZnO particles

The ammonium nitrate (NH_4NO_3) was dissolved into the zinc peroxide aqueous sol. The molar ratios of $[\text{NH}_4\text{NO}_3]/[\text{Zn}^{2+}]$ ion in the zinc peroxide sol were adjusted to 0, 0.05, 0.1, 0.15, 0.2 and 0.25. The zinc peroxide aqueous sol with NH_4NO_3 was dried at 348 K for 12 h. The obtained powder of the mixture of the zinc peroxide nanoparticles and NH_4NO_3 was heated at temperatures ranging from 473 K to 1073 K for 1 h in air. Furthermore, the same preparation procedure to obtain the nitrogen-doped ZnO was carried out by using other ammonium salts such as ammonium chloride (NH_4Cl), ammonium acetate ($\text{NH}_4(\text{CH}_3\text{COO})$), and ammonium oxalate ($(\text{NH}_4)_2\text{C}_2\text{O}_4$), which were substitute for the NH_4NO_3 .

2.3 Characterization

The structure of the obtained powders was characterized by means of X-ray diffraction (XRD). The XRD patterns of the samples were measured by using Mac Science Co., Ltd. M18X-HF-SRA. Cu was used as the target ($\text{Cu K}\alpha$, 40 kV, 200 mA). An optical system of $\text{SS} = 1^\circ$, $\text{DS} = 1^\circ$, $\text{RS} = 0.15$ mm and a graphite monochromator was used. Raman spectroscopy (JASCO Co., NRS1000) was used to determine the doped nitrogen atoms. The optical absorption spectra of the obtained ZnO powder were recorded (JASCO Co., V-560). The particle shape was observed by field emission-SEM (FE-SEM Hitachi, Ltd., S4700).

Iodometric titrations were employed to determine the number of acceptor states in the obtained nitrogen-doped ZnO particles.⁶⁾ Iodide (I^-) is oxidized by acceptor states as following equation: $3\text{I}^- + 2(\text{acceptor}^+) \rightarrow \text{I}_3^-$. The number of acceptor states can be estimated by the number of the released triiodide (I_3^-) ions, which was titrated with sodium thiosulfide.¹⁴⁾ The number of acceptor states was calculated from the amount of the used trisulfide. The detailed titration process was as follows. 5 ml of 0.5 mol/L KI aqueous solution and 5 ml of 1.0 mol/L HNO_3 were added on 0.2 g of nitrogen-doped ZnO powders, which were completely dissolved. The whole solution was titrated by using solutions of 0.002 mol/L $\text{Na}_2\text{S}_2\text{O}_3$ and starch solution as an indicator. All the distilled water was boiled used were boiled and cooled under N_2 atmosphere. The used flasks were also capped and filled with N_2 gas to prevent oxidation of iodide by air.

3. Results and discussion

3.1 Zinc oxide formation by heating mixture of the aqueous sol of zinc peroxide nanoparticles and NH_4NO_3

Figure 1 shows the XRD patterns of the particles obtained by heating the mixture of the aqueous sol of zinc peroxide nanoparticles and NH_4NO_3 for 1 h when the molar ratio of $\text{NH}_4\text{NO}_3/\text{Zn}^{2+}$ was 0.1. **Figure 1(a)** shows the XRD pattern of the mixed powder of the zinc peroxide nanoparticles and NH_4NO_3 . The XRD peaks in the **Fig. 1(a)** can be assigned to zinc peroxide, and no XRD peaks corresponding to NH_4NO_3 can be observed. These results suggest that the crystallized particles of NH_4NO_3 which can be detected by the XRD measurement was not formed in the obtained powder during the drying process. When the heating temperature was 473 K, all of the XRD peaks could be assigned to ZnO, as shown in **Fig. 1(b)**. Then, ZnO particles were obtained by heating the mixed powder of the zinc peroxide nanoparticles and NH_4NO_3 to more than 473 K. The half width of the ZnO (1 0 0) plane at 31.8° was decreased when the heating temperature increased from 473 K to 573 K, as shown in **Figs. 1(b)** and **(c)**. On the other hand, the full width at half maximum (FWHM) of the ZnO (1 0 0) plane did not change when the heating tem-

Fig. 1. XRD patterns of the particles obtained by heating the mixture of zinc peroxide nanoparticles and NH_4NO_3 for 1 h. The molar ratio of $\text{NH}_4^+/\text{Zn}^{2+}$ was 0.1. The heating temperatures were: (a) without heating, (b) 473 K, (c) 573 K, (d) 673 K, (e) 773 K and (f) 873 K.

Fig. 2. XRD patterns of the particles obtained by heating the mixture of zinc peroxide nanoparticles and NH_4NO_3 at 573 K for 1 h. The molar ratios of $\text{NH}_4\text{NO}_3/\text{Zn}^{2+}$ were: (a) 0.05, (b) 0.1, (c) 0.15, (d) 0.2 and (e) 0.25.

perature was more than 573 K, as shown in **Figs. 1(c)–(f)**. As such, heating to 573 K appeared to be sufficient to obtain well-crystallized ZnO particles.

In order to investigate the effects of the addition of ammonium salts on the formation behaviour of the ZnO particles, the relation between the molar ratio of $\text{NH}_4\text{NO}_3/\text{Zn}^{2+}$ and the degree of the crystallization of the obtained ZnO particles were examined. **Figures 2(a)–(f)** show the XRD patterns of the particles obtained by heating the mixture of the zinc peroxide nanoparticles and NH_4NO_3 at 573 K for 1 h. The molar ratio of $\text{NH}_4\text{NO}_3/\text{Zn}^{2+}$ was in the range from 0 to 2.5. All of the XRD peaks can be assigned to ZnO. The FWHM of the ZnO (1 0 0) plane in the **Fig. 2(a)** was larger than those of the peaks in the **Figs. 2(b)–(f)**. The FWHM of the ZnO (1 0 0) plane in the **Figs. 2(b)–(f)** did not deepened on the amount of NH_4NO_3 . These results suggested that the crystallite size of the zinc oxide obtained by heating the mixture of the zinc peroxide nanoparticles and NH_4NO_3 was larger than that of the zinc oxide obtained by heating the zinc peroxide nanoparticles. Therefore, the coexistence of the NH_4NO_3 affected the degree of crystallization of the obtained ZnO particles.

3.2 Characterization of the nitrogen-doped ZnO obtained by heating the mixture of the aqueous sol of zinc peroxide nanoparticles and NH_4NO_3

In order to further examine the details of the effect of the coexisting NH_4NO_3 on the decomposition process of the zinc peroxide nanoparticles, the Raman spectra of the obtained particles were obtained. In general, the presence of an oxygen vacancy and the doped nitrogen can be detected by using Raman peaks. **Figure 3** shows the Raman spectra of the obtained ZnO particles by heating the mixture of NH_4NO_3 and the zinc peroxide nanoparticles at 573 K for 1 h when the molar ratio of $\text{NH}_4\text{NO}_3/\text{Zn}^{2+}$ was in the range from 0 to 0.2. Figure 3(a) shows the Raman spectrum of the ZnO particles obtained by heating the zinc peroxide nanoparticles at 573 K for 1 h without NH_4NO_3 . The spectrum in Fig. 3(a) exhibits transitions near 330 cm^{-1} , 383 cm^{-1} , and 437 cm^{-1} shift. The peaks at 330 cm^{-1} and 437 cm^{-1} can be assigned to the lattice vibrational mode 2E_2 (M) and E_2 (high) of ZnO.¹⁵⁾ The peak at 383 cm^{-1} can be assigned to the lattice vibrational mode A_1 (TO) mode of ZnO.¹⁵⁾ In contrast, new Raman peaks appeared at 275 cm^{-1} , 507 cm^{-1} , and 583 cm^{-1} , as shown in Figs. 3(b) and (c), when the mixture of NH_4NO_3 and zinc peroxide nanoparticles was heated at 573 K for 1 h. These peaks correspond to the nitrogen-related local vibration modes.¹⁶⁾ Furthermore, the peak intensity, which corresponded to the nitrogen-related local vibration, increased with increase in the molar ratio of $\text{NH}_4\text{NO}_3/\text{Zn}^{2+}$. According to the Raman spectra, we can conclude that nitrogen-doped ZnO particles were obtained by heating the mixture of the aqueous sol of zinc peroxide nanoparticles and NH_4NO_3 . The homogeneous dispersion of NH_4NO_3 on the surface of the zinc peroxide nanoparticles played an important role for the nitrogen doping.

When the nitrogen doping successfully occurred, acceptor states should be formed. The acceptor states can accept electrons from iodide (I^-) anions. Then, the number of the acceptor states formed by nitrogen doping can be determined by using iodometric titration method.⁶⁾ The number of acceptor states per Zn^{2+} ion were calculated from the results of iodometric titration. According to the results of the titration, the acceptor states were not detected in the ZnO particles obtained by heating the zinc peroxide nanoparticles at 573 K for 1 h. When the nitrogen-doped ZnO particles prepared by heating the mixture of the zinc peroxide nanoparticles and NH_4NO_3 whose molar ratio of $\text{NH}_4\text{NO}_3/\text{Zn}^{2+}$ were 0.05 and 0.1, the number of the acceptor states per a

Fig. 3. Raman spectra of the particles obtained by heating the mixture of zinc peroxide nanoparticles and NH_4NO_3 at 573 K for 1 h. The molar ratios of $\text{NH}_4\text{NO}_3/\text{Zn}^{2+}$ were: (a) 0, (b) 0.1 and (c) 0.2.

Zn^{2+} ion of the obtained nitrogen-doped ZnO was 0.0037 and 0.0068, respectively. Accordingly, the results of the iodometric titration showed the presence of the acceptor states in the ZnO particles obtained by heating the mixture of zinc peroxide and NH_4NO_3 . The formation of acceptor states also indicated that the nitrogen-doping successfully occurred. Furthermore, the number of the acceptor states per Zn^{2+} ion increased with the increase of the molar ratio of $\text{NH}_4\text{NO}_3/\text{Zn}^{2+}$ in the mixture of the zinc peroxide nanoparticles and NH_4NO_3 . The doped amount of nitrogen can be regulated by the molar ratio of $\text{NH}_4\text{NO}_3/\text{Zn}^{2+}$ in the mixture.

In order to further examine the details of the obtained ZnO particles, the UV-VIS absorption spectra were measured, as shown in Figs. 4(a)–(e). The strong absorption around 400 nm corresponds to the electron transition between the band gap of ZnO. The UV-VIS absorption spectra in Figs. 4(b)–(e) have other broad shoulder peaks from 400 nm to 700 nm. The intensity of these broad peaks increased with increases in the molar ratio of

Fig. 4. UV-VIS spectra of the particles obtained by heating the mixture of NH_4NO_3 and zinc peroxide nanoparticles at 573 K for 1 h. The molar ratios of $\text{NH}_4\text{NO}_3/\text{Zn}^{2+}$ were: (a) 0.05, (b) 0.1, (c) 0.15, (d) 0.2 and (e) 0.25.

Fig. 5. UV-VIS absorption spectra of the particles obtained by heating the powders in the air at 573 K for 1 h. The heated powders were: (a) the powder obtained by drying the zinc peroxide sol, (b) the mixed powder of NH_4NO_3 and the zinc peroxide powder obtained by drying the zinc peroxide sol, and (c) the powder obtained by drying the mixture of the zinc peroxide sol and NH_4NO_3 . The molar ratio of $\text{NH}_4\text{NO}_3/\text{Zn}^{2+}$ = 0.2.

Fig. 6. FE-SEM images of the particles obtained by heating the mixture of zinc peroxide nanoparticles and NH_4NO_3 at 573 K for 1 h. The molar ratios of $\text{NH}_4\text{NO}_3/\text{Zn}^{2+}$ were: (a) 0, (b) 0.1 and (c) 0.2.

$\text{NH}_4\text{NO}_3/\text{Zn}^{2+}$. Accordingly, the broad absorption peaks from 400 nm to 700 nm corresponded to the impurity states formed by nitrogen-doping. The substitution of nitrogen for the oxygen successively occurred and the change in the electronic structure affected the UV-VIS absorption spectra. Therefore, nitrogen-doped ZnO particles can be obtained by a relatively low-temperature heating process at 573 K in air. Furthermore, the simple preparation process of the nitrogen-doped ZnO particles was enabled by using zinc peroxide nanoparticles and ammonium salts as a precursor.

In order to examine the effect of the mixing the zinc peroxide nanoparticles and NH_4NO_3 in the aqueous sol on the nitrogen doping, the UV-VIS adsorption spectrum of the ZnO powders obtained by heating the dried mixture of the zinc peroxide sol and NH_4NO_3 was compared with that of the mixture of NH_4NO_3 powder and the zinc peroxide powder obtained by drying the zinc peroxide sol. In this case, the mixing was carried out by using an agate mortar and a pestle. The UV-VIS absorption spectra were shown in **Figs. 5(a)–(c)**. The drying condition was at 348 K for 12 h and the heating condition was at 573 K for 1 h. The molar ratio of $\text{NH}_4\text{NO}_3/\text{Zn}^{2+}$ was 0.2. The UV-VIS absorption spectrum in Fig. 5(b) has the broad shoulder peaks from 400 nm to 700 nm which corresponded to the nitrogen-doping as compared with the spectrum shown in Fig. 5(a). This result suggests that the nitrogen-doped ZnO was obtained by heating the mixture of NH_4NO_3 powder and the zinc peroxide powder obtained by drying the zinc peroxide sol. Furthermore, the absorption intensity of this broad peak shown in Fig. 5(c) was stronger than that shown in Fig. 5(b). This result suggests that the doped amount of nitrogen in the particles obtained by heating the powder prepared by drying the mixture of the zinc peroxide sol and NH_4NO_3 were larger than that obtained by heating the mixture of NH_4NO_3 powder and the zinc peroxide powder. Therefore, the formation of the homogeneous mixed state in the aqueous sol was important to obtain the nitrogen-doped ZnO particles.

The particle morphology reflects the formation process of the nitrogen-doped ZnO particles. Therefore, the FE-SEM images of the obtained ZnO particles were examined. **Figure 6(a)** shows the FE-SEM image of the ZnO particles obtained by heating the zinc peroxide nanoparticles at 573 K for 1 h. The average particle size of the obtained ZnO particles was 27 nm. In contrast, the average diameters of the nitrogen-doped ZnO particles obtained by the mixture of NH_4NO_3 and the zinc peroxide nanoparticles in **Figs. 6(b) and (c)** were 105 nm and 120 nm, respectively. The average diameters of the obtained ZnO particles from the mixture of the zinc peroxide nanoparticles and NH_4NO_3 were larger than those obtained from the zinc peroxide nanoparticles, though

Fig. 7. Raman spectra of the nitrogen-doped ZnO particles heated in air for 1 h. The nitrogen-doped ZnO particles were prepared by heating the mixture of zinc peroxide nanoparticles and NH_4NO_3 at 573 K for 1 h. The molar ratio of $\text{NH}_4\text{NO}_3/\text{Zn}^{2+}$ was 0.2. The heating temperatures were: (a) 573 K, (b) 773 K, (c) 873 K, (d) 973 K and (e) 1073 K.

the heating temperature was same as that shown in Fig. 6(a). ZnO particles with an average diameter greater than 100 nm can be obtained by heating the zinc peroxide nanoparticles to more than 1073 K, as previously reported in our literature. In general, NH_4NO_3 melts around 443 K.¹⁷⁾ It is therefore considered that the acceleration of the grain growth in the mixture of the zinc peroxide nanoparticles and NH_4NO_3 is related to the rapid diffusion process in the molten salt. The dissolution-precipitation process in the molten salt affects the grain growth and the nitrogen-doping process. Accordingly, the ammonium salt played an important role not only as a nitrogen source but also in the formation of the reaction atmosphere.

The effect of heating the nitrogen-doped ZnO particles in air was also examined. **Figure 7** shows the Raman spectra of the nitrogen-doped ZnO particles heated in air for 1 h. The nitrogen-doped ZnO particles that were heated in air were prepared by heating the mixture of the zinc peroxide nanoparticles and NH_4NO_3 ($\text{NH}_4\text{NO}_3/\text{Zn}^{2+} = 0.2$ molar ratio) at 573 K for 1 h. The Raman peak at 437 cm^{-1} in Fig. 7(a) can be assigned to the lattice vibrational mode of ZnO. The Raman peaks at 275 cm^{-1} and 583 cm^{-1} in Fig. 7(a) can be assigned to the nitrogen-related local vibration modes. When the nitrogen-doped ZnO particles were heated at 773 K for 1 h in the air, the peak intensity of the nitrogen-related vibration modes at 275 cm^{-1} and 583 cm^{-1} decreased relatively slightly as compared with the lattice vibrational mode of ZnO at 437 cm^{-1} . Furthermore, when the heating

Fig. 8. UV-VIS absorption spectra of the nitrogen-doped ZnO particles heated in the air for 1 h. The heated nitrogen-doped ZnO particles were prepared by heating the mixture of zinc peroxide nanoparticles and NH_4NO_3 at 573 K for 1 h. The molar ratio of $\text{NH}_4\text{NO}_3/\text{Zn}^{2+}$ was 0.2. The heating temperatures were: (a) 573 K, (b) 773 K, (c) 873 K, (d) 973 K and (e) 1073 K.

temperature increased from 773 K to 973 K, the intensity of the peaks corresponding to the nitrogen-related local vibration modes greatly decreased as compared with the ZnO lattice vibrational mode, as shown in Figs. 7(b)–(d). This result indicated that the heating of the nitrogen-doped ZnO particles in air caused a substitution of the nitrogen atoms in the nitrogen-doped ZnO particles to oxygen atoms. Furthermore, as shown in Fig. 7(e), the whole Raman peaks in the spectra of the nitrogen-doped ZnO particles heated at 1073 K for 1 h can be assigned to the ZnO lattice vibrational mode. Accordingly, the heating of the nitrogen-doped ZnO at 1073 K caused a substitution of oxygen atoms for the whole nitrogen atoms in the nitrogen-doped ZnO particles.

In order to clarify the effects of heating in air, the UV-VIS spectra were also examined. **Figures 8(a)–(e)** show the UV-VIS absorption spectra of the nitrogen-doped ZnO particles heated for 1 h. These spectra show a strong absorption around 400 nm corresponding to the electron transition between the band gap of ZnO and other broad shoulder peaks from 400 nm to 700 nm corresponding to the impurity states formed by the nitrogen-doping. This result in the UV-VIS spectrum agrees with the Raman spectrum shown in Fig. 7(a). Furthermore, the strength of the absorption, which corresponds to the impurity state of the nitrogen-doping from 400 nm to 700 nm, gradually decreased when the heating temperature increased in a range from 573 K to 973 K, as shown in Figs. 8(a)–(d). Finally, when the nitrogen-doped ZnO was heated at 1073 K for 1 h, no absorption corresponding to the impurity states appeared in the spectrum shown in Fig. 8(e). Accordingly, this result indicates that the substitution of oxygen for nitrogen successfully occurred by heating in air at 1073 K for 1 h and that pure ZnO particles were obtained. As shown in Fig. 7(e), the Raman spectrum of the nitrogen-doped ZnO particles heated at 1073 K for 1 h also supports the above result.

3.3 Effect of the ammonium salts mixed with the zinc peroxide nanoparticles on the nitrogen-doping

In order to examine the effects of anions in the ammonium salts mixed with the zinc peroxide nanoparticles on the nitrogen-

Fig. 9. UV-VIS absorption spectra of the particles obtained by heating the mixture of zinc peroxide nanoparticles and ammonium salts at 573 K for 1 h. The molar ratio of ammonium salts/ Zn^{2+} was 0.2. The used ammonium salts were: (a) NH_4NO_3 , (b) $(\text{NH}_4)_2\text{C}_2\text{O}_4$, (c) NH_4Cl , and (d) $\text{NH}_4(\text{CH}_3\text{COO})$.

doping, the UV-VIS absorption spectra of the particles obtained by heating a mixture of zinc peroxide nanoparticles and ammonium salts at 573 K for 1 h were measured. When the mixtures with ammonium nitrate (NH_4NO_3) or ammonium oxalate ($(\text{NH}_4)_2\text{C}_2\text{O}_4$) were heated, the UV-VIS absorption spectra of the obtained particles had a broad shoulder peak from 400 nm to 700 nm corresponding to the nitrogen-doping, as shown in **Figs. 9(a) and (b)**. Accordingly, the results indicate that the nitrogen-doping successfully occurred in the above cases. In particular, the nitrogen-doped ZnO was obtained when the mixture of ammonium oxalate and zinc peroxide nanoparticles was used even though the nitrogen was only included in ammonium ion of ammonium oxalate. This result indicated that the nitrogen atoms in the nitrogen-doped ZnO were supplied from the ammonium ions in the ammonium salts.

In contrast, when the mixture with ammonium chloride (NH_4Cl) and ammonium acetate ($\text{NH}_4(\text{CH}_3\text{COO})$) was heated, the UV-VIS absorption spectra of the obtained particles did not have any shoulder peak from 400 nm to 700 nm and the only strong absorption appeared around 400 nm, which corresponds to the electron transition between the band gap, as shown in Figs. 9(c) and (d). These results on the UV-VIS spectra indicate that the particles obtained by heating the mixture of the zinc peroxide nanoparticles and ammonium chloride or ammonium acetate were ZnO particles without nitrogen-doping. Accordingly, the nitrogen-doping of the obtained ZnO particles depended on the ammonium salt heated with the zinc peroxide. In a previous paper, the authors showed that the thermal decomposition of zinc peroxide forms zinc oxide with oxygen vacancies.¹⁸⁾ The decomposition of the zinc peroxide is a disproportionate reaction: $\text{O}_2^{2-} \rightarrow \text{O}^{2-} + 1/2\text{O}_2$. As previously shown, this reaction can be divided into a reduction reaction and an oxidation reaction: $\text{O}_2^{2-} \rightarrow \text{O}_2 + 2\text{e}^-$ and $\text{O}_2^{2-} + 2\text{e}^- \rightarrow 2\text{O}^{2-}$.¹²⁾ When the O_2^{2-} ions in the oxide lattice decompose, oxygen vacancies are formed by the reduction reaction of $\text{O}_2^{2-} \rightarrow \text{O}_2 + 2\text{e}^-$ since the O_2^{2-} ions in the lattice are lost to form O_2 molecules in the gas phase. As shown in Figs. 9(c) and (d), in the case that ammonium chloride or ammonium acetate are mixed with the zinc peroxide nanoparticles, the particles obtained by heating the mixture at 573 K for 1 h are ZnO particles without nitrogen-doping. This result indicates that the O_2^{2-} ions react with the acetate ions and chloride

ions in the ammonium salts as oxidizing agents. Then, the reaction of O_2^{2-} ions as a reduction agent ($\text{O}_2^{2-} \rightarrow \text{O}_2 + 2\text{e}^-$) cannot occur, and oxygen vacancies in the ZnO lattice therefore do not form. However, the formation of oxygen vacancies is required for nitrogen-doping. Therefore, when the ammonium acetate and ammonium chloride were used, nitrogen-doping did not occur, as shown in Figs. 9(c) and (d). In contrast, in the case that ammonium oxalate and ammonium nitrate were mixed with the zinc peroxide nanoparticles, the particles obtained by heating the mixture at 573 K for 1 h were nitrogen-doped ZnO particles, as shown in the Figs. 9(a) and (b). The oxalate ions and nitrate ions did not react with the O_2^{2-} ions in the zinc peroxide so that the dominant process of the decomposition of the O_2^{2-} ions became a reduction reaction ($\text{O}_2^{2-} \rightarrow \text{O}_2 + 2\text{e}^-$).¹⁹⁾ Therefore, the oxygen vacancies formed by the decomposition of the O_2^{2-} ions played an important role in nitrogen-doping.

4. Conclusion

Nitrogen-doped ZnO particles were prepared by heating a mixture of ammonium salts and the aqueous sol of zinc peroxide nanoparticles. In the case that the aqueous sol of zinc peroxide nanoparticles were mixed with ammonium nitrate, the nitrogen-doped ZnO was obtained by heating the mixture at 573 K for 1 h. The obtained particles showed characteristic Raman peaks that can be assigned to the nitrogen-related local vibrational mode. The strength of the UV-VIS absorption peak, which can be assigned to the nitrogen-related impurity state, also increased with increases in the mixed amount of ammonium nitrate. The homogenous mixture of the zinc peroxide nanoparticles and ammonium salts in the aqueous sol and the homogeneous dispersion of ammonium salts on the surface of the zinc peroxide played an important role for the nitrogen doping. According to the FE-SEM images of the nitrogen-doped ZnO particles, even if the heating temperature of the mixture was 573 K, relatively large particles were observed. This result indicates that a rapid grain growth process took place in the molten salt of the ammonium nitrate. In addition, the effects of anions in the ammonium salts on the nitrogen-doping were investigated. In the case that the O_2^{2-} ions in the zinc peroxide nanoparticles reacted with the anions to form oxygen vacancies, nitrogen-doping successfully occurred. Accordingly, the role of O_2^{2-} ions as a reducing agent is important for nitrogen-doping.

Acknowledgement This research was supported by the Science Research Grant from the Ministry of Education, Culture, Sports, Science and Technology, Japanese Government.

References

- 1) G. Thomas, *Nature*, **389**, 907 (1997).
- 2) H. Ohta, K. Kawamura, M. Orita, N. Sarukura, M. Hirano and H. Hosono, *J. Appl. Phys.*, **89**, 5720–5725 (2001).
- 3) H. F. Chen, H. J. Ko, S. K. Hong and T. Yao, *Appl. Phys. Lett.*, **76**, 559–561 (2000).
- 4) S. M. Lukas and L. M. Judith, *Mater. Today*, **10**, 40–48 (2007).
- 5) M. H. Huang, S. Mao, H. Feick, H. Q. Yan, Y. Y. Yu, H. Kind, R. Russo and P. D. Yang, *Science*, **292**, 1897–1899 (2001).
- 6) J. Li, R. Kykyneshi, J. Tate and A. W. Sleight, *Solid State Sci.*, **9**, 613–618 (2007).
- 7) D. C. Look, D. C. Reynolds, C. W. Litton, R. L. Jones, D. B. Eason and G. Cantwell, *Appl. Phys. Lett.*, **81**, 1830–1832 (2002).
- 8) S. B. Zhang, S. Huai and A. Zunger, *J. Appl. Phys.*, **83**, 3192–3196 (1998).
- 9) W. Wang, S. Yang, J. Wang, M. Li, X. Jiang, G. Du, X. Liu and R. P. H. Chang, *J. Cryst. Growth*, **226**, 123–129 (2001).
- 10) J. Lu, Z. Ye, L. Wang, J. Huang and B. Zhao, *Mater. Sci. Semi. Processing*, **5**, 491–496 (2003).
- 11) N. Varghese, L. S. Panchakarla, M. Hanapi, A. Govindaraj and C. N. R. Rao, *Mater. Res. Bull.*, **42**, 2117–2124 (2007).
- 12) N. Uekawa, N. Mochizuki, J. Kajiwara and K. Kakegawa, *Phys. Chem. Chem. Phys.*, **5**, 929–934 (2003).
- 13) N. Uekawa, J. Kajiwara, N. Mochizuki, K. Kakegawa and Y. Sasaki, *Chem. Lett.*, **2001**, 606–607 (2001).
- 14) D. C. Harris, M. E. Hills and T. A. Hewston, *J. Chem. Educ.*, **64**, 847–850 (1987).
- 15) A. Kaschner, U. Haboeck, M. Strassburg, G. Kaczmarczyk, A. Zeuner, H. R. Alves, D. M. Hofman and B. K. Meyer, *Appl. Phys. Lett.*, **80**, 1909–1911 (2002).
- 16) L. L. Kerr, X. Li, M. Canepa and A. J. Sommer, *Thin Solid Films*, **515**, 5282–5286 (2007).
- 17) C. N. R. Rao and K. J. Rao, *Prog. in Solid State Chem.*, **4**, 131–185 (1967).
- 18) T. X. Wang and T. J. Lou, *Mater. Lett.*, **62**, 2329–2331 (2008).
- 19) N. Uekawa, T. Kudo, Y. J. Wu and K. Kakegawa, *J. Ceram. Soc. Japan, Suppl.*, **112**, S37–S40 (2004).