ELSEVIER

Journal of Alloys and Compounds 408–412 (2006) 1234–1237

Journal of ALLOYS AND COMPOUNDS

www.elsevier.com/locate/jallcom

Photoacoustic spectra on Pr doped ZnO powders

Y. Inoue*, M. Okamoto, T. Kawahara[1], J. Morimoto

Department of Materials Science and Engineering, National Defense Academy, 1-10-20 Hashirimizu, Yokosuka, Kanagawa 239-8686, Japan

Received 30 July 2004; received in revised form 20 November 2004; accepted 15 December 2004
Available online 14 July 2005

Abstract

Photoacoustic (PA) spectroscopy is a powerful tool for examining optical properties as non-radiative recombination in powdered samples that are difficult to measure by the conventional reflection or transmission spectroscopy because of the light scattering. We applied the PA spectroscopy to evaluate the non-radiative transition of the Pr^{3+} in ZnO powders with various Pr concentrations and sintering temperatures. The PA spectra seems to depend on the inner state of the Pr^{3+} in ZnO matrix, where the Pr can easily segregate to the ZnO grain boundaries and form intergranular phase based Pr_2O_3.

Keywords: Semiconductors; Grain boundaries; Impurities in semiconductor; Electronic states; Light absorption and reflection

1. Introduction

ZnO is a promising material used in the various application fields. The Pr doped ZnO base varistors have been widely used for circuit protection due to electric surge absorbing, and their nonlinear current–voltage characteristics are attributed to the double Schottky barriers at grain boundaries in ceramic semiconductors. So many researchers have investigated to clarify this varistor characteristic and the formation mechanism and so forth [1–3]. On the other hand, the rare earth doped materials have been widely studied as the optical materials, and Eu doped ZnO phosphor is one of such materials, which shows yellow to red luminescence from trivalent rare earth doped in ZnO [4–7]. Furthermore, luminescence from Pr^{3+} ions in the oxides and fluorides have been much reported [7–10]. Thus the rare earth doped materials seem to be interesting in both the electric and optical devices, particularly Pr^{3+} doped ZnO shows unique property because of its varistor characteristic, where the Pr_2O_3 could to be located in the boundaries of ZnO grains.

Photoacoustic (PA) spectroscopy with microphones can detect acoustic waves generated in the samples excited by the incident light [11]. The PA technique can sensitively and directly evaluate non-radiative recombination process related to the defects through the heat contrary to photoluminescence (PL) that can detect radiative recombination process [12–14]. It is important to evaluate the characteristics and properties of material in process without slice or contact. In this article, we applied the PA technique to the Pr doped ZnO powders, to study Pr concentration and sintering temperature dependence in the PA spectrum on Pr^{3+} ions in ZnO matrix. The non-radiative recombination in Pr^{3+} levels depend on inner states of Pr^{3+} ions in ZnO matrix.

2. Experimental procedures

The starting materials were ZnO powders (99.99% purity: Japan Pure Chemical) and Pr_2O_3 powders (99.9% purity: Japan Pure Chemical). 0.25, 0.5, 1.5 and 2.5 mol% Pr_2O_3 were mixed to ZnO powders, where we call these powders as 0.5, 1, 3 and 5 mol% Pr doped samples to express the Pr concentration. The starting powders were mixed in an agate mortar for 1 h, and encapsulated in a quartz glass tube in a vacuum. Then mixed powders were sintered at 600, 800

---

* Corresponding author. Tel.: +81 46 841 3810x3664;
fax: +81 46 844 5910.
E-mail address: g42029@nda.ac.jp (Y. Inoue).

[1] Present address: The Institute of Scientific and Industrial Research, Osaka University, 8-1 Mihogaoka, Ibaraki, Osaka 567-0047, Japan.

0925-8388/$ – see front matter © 2005 Elsevier B.V. All rights reserved.
doi:10.1016/j.jallcom.2004.12.182

and 1000 °C for 24 h with the heating and cooling speed of 5 °C/min. Wakiya et al. reported that the ZnO–Pr_2O_3 binary system showed simple eutectic type of phase diagram with the eutectic temperature of 1382 ± 5 °C [2]. The crystal structure of the resulting samples were checked by X-ray diffraction (XRD) using Cu Kα line with 40 kV and 100 mA (M21X, Mac science).

PA spectra were measured by using a gas-microphone system. A 500 W Xe lamp coupled with a monochromator was used for the light source. The incident light was mechanically chopped at 20 Hz. The wavelength of the excitation light beam was scanned from 350 to 650 nm with a 1 nm step. The PA signal intensity was normalized by the PA signals from carbon black to eliminate the effects of the spectral response of the optical apparatus. All measurements were carried out at room temperature.

Before the PA measurement, the calcined samples were ground in an agate mortar to homogenize the powder size. All XRD patterns except for 0.5 mol% Pr doped samples showed weak peaks of Pr_2O_3 with the ZnO main peaks, but the lattice constants of ZnO did not change both in a-axis and c-axis ($a = 3.251$ Å and $c = 5.207$ Å). 0.5 mol% doped samples sintered at all temperature in this experiments did not show the Pr_2O_3 peaks.

3. Results and discussion

PA spectra on ZnO and Pr_2O_3 powders are shown in Fig. 1, which are starting materials without sintering. For ZnO (◯), the PA signal intensity decreases abruptly above 380 nm because of the absorption at near band edge of ZnO, following the flat PA signal above 440 nm. For Pr_2O_3 (△), three peaks A1, A2 and B can be observed, which are caused by the non-radiative recombination in Pr^{3+} ions.

Here, these peaks appear to be broad in contrast to sharp peaks which are peculiar to trivalent rare earth ion as shown in the other optical spectra such as PL. The reason for this discrepancy is the difference of detectable relaxation process from the excited state after the absorbed energy. In principle, PA spectra exhibits the non-radiative quantum efficiencies through heat generation throughout the spectral region of interest [11,12]. In view of the light absorption, PA peaks are similar to the excitation peaks of PL as a way of thinking. Hence, we can consider that the existence of upper level related with transition process is designated as the position at the wavelength which indicates the largest intensity within each broad peak for acceptable resolution [13,14].

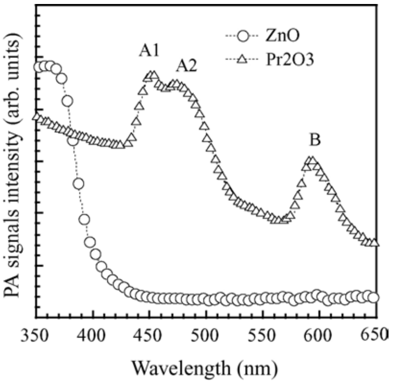

Fig. 1. PA spectra on ZnO and Pr_2O_3 powders. Circles and triangles designate for ZnO and Pr_2O_3, respectively.

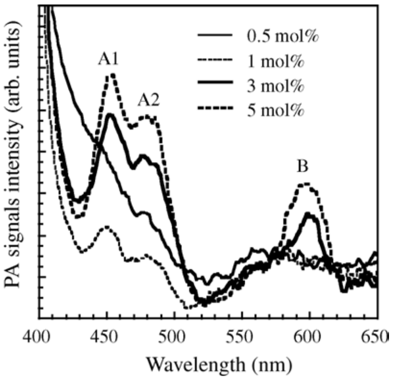

Fig. 2. PA spectra on 0.5, 1, 3, 5 mol% Pr doped ZnO sintered at 800 °C. Thin solid line, thin dotted line, thick solid line and thick dotted line express 0.5, 1, 3 and 5 mol% Pr doped ZnO, respectively.

The peak around 452 nm labeled as A1 relates to the transition from $^3P_2$ to the ground state as the light absorption between these levels, where Pr should absorb incident light around 452 nm [8–10,15]. Similarly, the peak labeled as A2 is the triplicate peaks related with $^1I_6$, $^3P_1$ and $^3P_0$ state, and the peak around 593 nm should be assigned to the transition between $^1D_2$ level and base, which we call as peak B.

Fig. 2 shows the PA spectra for Pr doped ZnO with the concentration of 0.5, 1, 3 and 5 mol% Pr, and which are sintered at 800 °C. A1, A2 and B designated in Fig. 2 correspond to those in Fig. 1. Peak A2 can be observed for all samples, but peak A1 is observed only more than 1 mol% Pr doped samples. On 0.5 mol% Pr doped samples, peak A1 is not seen because of the layer tail of the PA signal at the shorter wavelength region.

This indicates that many levels related with non-radiative recombinations in this region are introduced in 0.5 mol% Pr doped samples [13]. These levels seem to be assigned to native defects levels such as Zn vacancies enhanced by Pr doping [3].

Contrary to these peak, peak B can clearly be observed only for heavily doped samples more than 3 mol%. This Pr concentration dependence is almost the same for the other temperature sintered samples of 600 and 1000 °C.

Next, we show the sintering temperature dependence of the PA spectra in Fig. 3, where 5 mol% Pr doped samples are plotted. Though each spectral shape seems to be the same, small variation of peak A1 and appearances of peak B at almost fixed wavelength are observed except for peak A2. The peak A2 for the sample sintered at 1000 °C appears to split to the two peaks of A3 (about 480 nm) and A4 (about

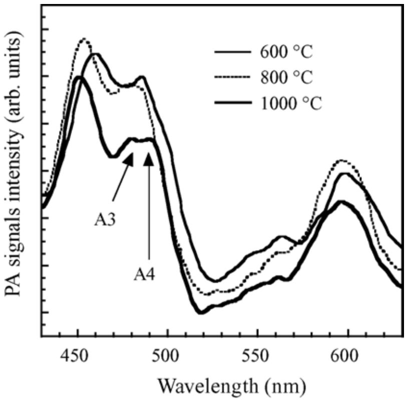

Fig. 3. PA spectra on 5 mol% Pr doped ZnO sintered at 600, 800 and 1000 °C. Thin solid line, thin dotted line and thick solid line are for 600, 800 and 1000 °C, respectively.

489 nm), that seem to be related to $^1I_6$, $^3P_1$ and $^3P_0$ levels [8–10,15], and the A2 for the 600 and 800 °C seems not split to the contrary. Then the comparison of the peak A2 is difficult because of the degeneration.

The Pr concentration dependences of the peak in PA spectra are shown in Fig. 4(a) and (b), where the peak A1 and peak B in samples doped Pr above 1 mol% are plotted, respectively. The peak A1 has large dependence in lightly doped samples and weak dependence in the doped samples above 3 mol%. The Pr concentration dependence is larger in the samples sintered at 600 °C. For peak B only observed in the samples doped above 3 mol%, the Pr concentration dependence is also large in the low temperature sintered samples. These peak variations of Pr concentration dependence and sintering temperature dependence seem to be caused by the difference of inner states of Pr^{3+} ions in ZnO matrix. The Pr_2O_3 can easily segregate at the grain boundaries of ZnO and form intergranular phase [1–3,16]. In other case, some Pr might be doped in ZnO grains with non-equilibrium because of the low sintering temperature. The former is mainly dominant in the samples sintered at high temperature and the latter could have large PA peak variation against the original Pr_2O_3 peaks.

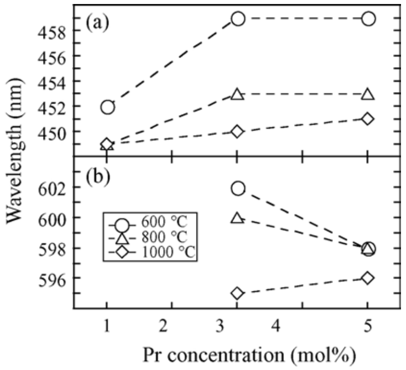

Fig. 4. Pr concentration dependences and sintering temperature dependences of the PA peaks wavelength: (a) and (b) are plotted for peak A1 and peak B, respectively.

In Fig. 4(a), peak A1 on the samples sintered at 600 °C has larger Pr concentration dependence. That sintered at 1000 °C does not show such a large variation and the peak wavelength is almost the same with that of Pr_2O_3 powders shown in Fig. 1. The peak variation is mainly observed in the samples doped less the 3 mol%.

Here, the lanthanide 4f energy-levels are closely connected with the crystal structure of the host lattice and on the optical spectra of the lanthanide ion in host crystal, and Tröster et al. reported the crystal-field parameters for Pr^{3+} taking into account effects of *J* mixing and expanded free-ion Hamiltonian [17]. Moreover, Pr was known to have negligibly low solubility in ZnO [1,3], and was expected to occupy Zn sites in the vicinity of the grain boundaries such as Er in ZnO [3,18].

Thus we can guess that the peak A variation is mainly originated from the Pr doped in ZnO grains with non-equilibrium due to the changing of the crystal-field strength within host ZnO, and the Pr in heavily doped samples above 3 mol% cannot be in the ZnO grains of high temperature sintered samples.

In Fig. 4(b), peak B can only be seen in the samples doped with more than 3 mol%, where the excess Pr_2O_3 by precipitation and segregation might mainly be in boundaries of ZnO grains [1–3,16]. In this case, the peak wavelength seems to convergence to the value of Pr_2O_3 powder. Hence the intergranular phase is similar to the precipitated Pr_2O_3 grains and Pr^{3+} in grain boundaries cannot be largely affected by crystal-field contrary to Pr^{3+} in ZnO grains.

The Pr in ZnO can introduce the Schottky barriers to produce the levels occupied by excess electron in grain boundary [1,3,13], where those levels might be assigned as recombination center [6]. If the recombination process might occur efficiently there, the direct charge or energy transfer might occur between levels of Pr^{3+} ions and levels introduced in ZnO and enhance luminescence from levels in Pr^{3+} ions.

Using PA spectroscopy, we can designate the internal levels of Pr^{3+} ion in ZnO, where Pr is mixed in ZnO grain or grain boundary, considering the Pr concentration dependence and sintering temperature dependence. PA technique can be used without contact to monitor the material processing. PA spectroscopy is useful for the further optimization of the Pr doped ZnO especially as optical devices.

4. Summary

The absorption of Pr^{3+} ions in 0.5, 1, 3 and 5 mol % Pr doped ZnO powders with sintered at 600, 800 and 1000 °C were studied using the PA spectroscopy. There are peaks of A1, A2 and B in Pr_2O_3, and the multiple peaks can be observed in Pr doped ZnO matrix. Peak A1 has large Pr concentration dependence in lightly doped samples and peak B can be observed only in heavily doped samples. Thus peak A1 is related to the Pr^{3+} doped in ZnO grains with non-equilibrium and peak B is caused from the Pr^{3+} in grain boundaries. PA technique is useful for the study of inner states of Pr in ZnO matrix.

References

[1] K. Mukae, I. Nagasawa, Adv. Ceram. 1 (1981) 331.
[2] N. Wakiya, S.-Y. Chun, C.H. Lee, O. Sakurai, K. Shinozaki, N. Mizutani, J. Electroceram. 4 (1999) S1–S15.
[3] Y. Sato, F. Oba, M. Yodogawa, T. Yamamoto, Y. Ikuhara, J. Appl. Phys. 95 (2004) 1258–1264.
[4] D. Kouyate, J.C.R. Haret, J. Kossanyi, J. Lumin. 55 (1993) 209–216.
[5] Y. Hayashi, H. Narahara, T. Uchida, T. Noguchi, S. Ibuki, Jpn. J. Appl. Phys. 34 (1995) 1878.
[6] S. Bachir, K. Azuma, J. Kossanyi, P. Valat, J.C.R. Haret, J. Lumin. 75 (1997) 35.
[7] S. Bhushan, A.N. Pandey, B.R. Kaza, J. Lumin. 20 (1979) 29.
[8] M. Arai, N. Matsuda, M. Tamatani, J. Alloys Compd. 192 (1993) 45.
[9] G. Mariotto, F. Tietz, E. Zanghellini, M. Ferrati, J. Lumin. 60/61 (1994) 216.
[10] E. Pinel, P. Boutinaud, R. Mahiou, J. Alloys Compd. 374 (2004) 165.
[11] A. Rosencwaig, A. Gersho, J. Appl. Phys. 47 (1976) 64.
[12] A. Mandelis, E.K.M. Siu, Phys. Rev. B 34 (1986) 7209.
[13] T. Kawahara, Y. Ohbuchi, A. Kimura, Y. Okamoto, J. Morimoto, J. Jpn. Soc. Powder Metall. 49 (2002) 355.
[14] Y. Inoue, Y. Miyauchi, A. Kimura, T. Kawahara, Y. Okamoto, J. Morimoto, Jpn. J. Appl. Phys. 43 (2004) 2936.
[15] M. Gaft, R. Reisfeld, G. Panczer, E. Uspensky, B. Varrel, G. Boulon, Opt. Mater. 13 (1999) 71.
[16] I.G. Solorzano, J.B.V. Sande, K.K. Baek, H.L. Tuller, Mater. Res. Soc. 295 (1993) 189.
[17] Th. Tröster, T. Gregorian, W.B. Holzapfel, Phys. Rev. B 48 (1993) 2960.
[18] U. Wahl, E. Rita, J.G. Correia, E. Alves, J.P. Araújo, The ISOLDE, Appl. Phys. Lett. 82 (2003) 1173.