PHYSICAL REVIEW B **68**, 045421 (2003)

Enhancement of band-edge photoluminescence of bulk ZnO single crystals coated with alkali halide

Yoshiyuki Harada
Applied Physics, Department of General Education, Osaka Institute of Technology, Ohmiya, Asahi-ku, Osaka 535-8585, Japan

Satoshi Hashimoto
Department of Environmental Sciences, Faculty of Science, Osaka Women's University, Daisen-cho, Sakai City, Osaka 590-0035, Japan

(Received 4 March 2003; published 25 July 2003)

We have studied coating effects of bulk ZnO crystal by means of photoluminescence (PL) measurements. Bulk crystal surface of ZnO is once covered by the melt of alkali halide at high temperature and is coated with thin alkali halide crystal. At low temperature, band-edge PL intensity of the ZnO crystal coated with KCl or KI is about 300 times larger than that of a polished crystal. In the no-coating ZnO crystal treated by the same thermal conditions, the enhancement of the PL intensity is only about 20 times larger. The enhancement of band-edge PL also occurs considerably at room temperature. The experimental results including the PL spectra in the visible light region, suggesting the qualitative improvement of ZnO surface by the coating, are discussed in terms of the incorporation of halogen ions supplied from alkali halide into oxygen vacancies.

DOI: 10.1103/PhysRevB.68.045421 PACS number(s): 78.40.Fy, 78.55.Et

I. INTRODUCTION

Until now, much attention has been paid to semiconducting material, zinc oxide (ZnO), for device applications such as transparent electrodes, solar cell, piezoelectric transducers, sensors, phosphors, and window materials of display because of a wide variety of optoelectric properties. In particular, ZnO is an attractive material for blue and ultraviolet (UV) laser devices because of large band-gap energy (3.3 eV),[1] and large binding energy of exciton (~60 meV).[2] As is well known, ZnO crystals show band-edge and visible photoluminescence (PL) bands which strongly depend on the samples. It seems that the intensity of the band-edge PL strikingly competes with that of the visible PL.[3–5] Thus it is very important to let band-edge PL intensity increase for the application. It is desirable to decrease visible PL intensity related to deep defects. The green band seen in the visible region has been related to oxygen vacancies as reported by Vanheusden *et al.*[6] In order to reduce the density of oxygen vacancies, a lot of efforts have been made, such as annealing under excess oxygen ambient[4,5,7,8] and passivating by hydrogenation during the crystal growth.[3] These methods are quite effective to grow high quality ZnO layers, which are interior parts in multilayered structures and have no open surfaces.

Very recently, we have succeeded preparation of good micron-sized ZnO particles by embedding them in thin alkali halide crystal.[9–11] In the prepared particles, a free exciton (FE) line is clearly observed at low and high temperatures. Furthermore, an intense sharp line, which is attributed to the transition of excitons bound to interface between a ZnO particle and alkali halide medium, appears, although it is hardly observed in ZnO powder material and bulk crystal. The facts have been further examined by microscopic cathodluminescence measurements in a single micron-sized ZnO particle.[12] According to the results, it is confirmed that radiative recombination of the excitons effectively occurs at specific areas in the surface of the single particle.

In order to investigate coating effects of the ZnO surface in detail, PL measurements have been carried out by the use of bulk ZnO single crystal coated with alkali halide crystal. In the present paper, we report remarkable enhancement of the band-edge PL in ZnO crystals. The qualitative improvement of the ZnO surface by the coating of alkali halide is discussed.

II. EXPERIMENT

Two kinds of bulk ZnO single crystals (A and B) grown by the hydrothermal method were used. The polished and chemically etched crystals, which were made by (A) Scientific Production Company Goodwill, Russia, and (B) Atomergic Chemetals Co., NY, were commercially supplied from Furuuchi Chem. Co., Ltd. The samples ($12\times 8\times 0.5\ \mathrm{mm}^3$) having the crystal face of (0001) were washed by organic solvents. Each sample was divided into four parts. Two of them were coated with thin alkali halide crystals, KCl and KI, which are used to check the halogen ion dependence. The method of the coating is briefly shown in Figs. 1(a)–(c): (a) The ZnO crystal is put on a quartz plate ($8\times 8\times 1\ \mathrm{mm}^3$). (b) A small amount of alkali halide powder (~20 mg) is placed on a step of quartz plate. (c) In N_2 gas atmosphere, the powder is melted by an electric furnace above the melting temperature of the alkali halide (~800 °C). The melting temperature of ZnO (1975 °C) and quartz (~1300 °C) is much higher than that of alkali halides. The melt is infiltrated into the gap between two plates through the capillarity. The surface of ZnO is covered by the melt, after infiltrating the melt into the whole area of the gap. The melt is solidified by natural cooling. It is noted that the ZnO crystal and the quartz plate are glued together by the thin alkali halide crystal. Present thin crystal of alkali halide is not opaque but perfectly transparent. In Fig. 1(d), resulting sample crystal of ZnO and light beams for optical measurements are shown schematically. Another one was annealed under the same thermal and ambient gas conditions. This sample is named an

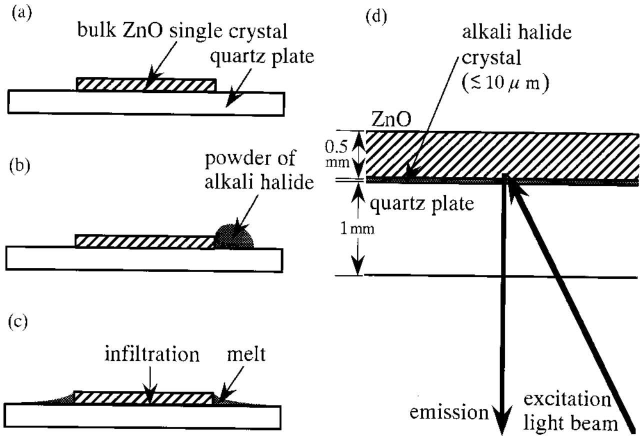

FIG. 1. Schematic illustrations of coating method and a sample of coated ZnO crystal. (a) Bulk ZnO single crystal is put on a quartz plate. (b) A small amount of alkali halide powder is placed on a step of quartz plate. (c) Above the melting temperature, the melt infiltrates into the gap of two plates, and it is solidified. (d) A relation between a coated ZnO crystal with thin alkali halide crystal and light beams of excitation and emission.

annealed crystal. The rest one used for a reference is called a polished crystal.

For PL measurements, a He-Cd laser with the wavelength of 325 nm and with the maximum power of 50 mW was used as an excitation light source. Emitted light from a sample surface was dispersed by a monochromator (SPEX 750M) with a 1200/mm grating. The light signal was detected by a photon-counting system with a photomultiplier. All spectra were measured with a spectral resolution of less than 0.05 nm. Temperature of the sample was controlled between 9 and 300 K using a conventional cryostat cooled by a closed-cycle cryogenic refrigerator.

III. RESULTS AND DISCUSSION

Figure 2 shows logarithmic display of PL spectra in a blue-UV region at 9 K for four ZnO (A) samples: (a) a coated crystal with KCl, (b) a coated crystal with KI, (c) an annealed crystal, and (d) a polished crystal. The PL intensities of these spectra are able to relatively compare with each other because the measurements have been carried out under the same conditions. In the polished crystal without coating and annealing treatments, the PL intensity is very weak. Two PL peaks at 3.361 and 3.373 eV are due to transitions of bound exciton (BE) and FE, respectively. The PL intensity for the annealed crystal is stronger than that of the polished crystal. The annealing treatment probably causes to increase luminescent centers associated with the band-edge PL. Similar optical enhancement of band-edge PL has been observed in ZnO phosphor powders annealed at about 900 °C.[6] Furthermore, as seen in Figs. 2(a) and (b), drastic enhancement of the PL intensity in the coated ZnO crystals with KCl or KI occurs in the whole energy region indicated. The PL spectra for the both coated ZnO crystals are almost the same with each other, except for slight differences in peak positions and PL intensities. Thus enhancement of the band-edge PL hardly depends on the kind of halogens.

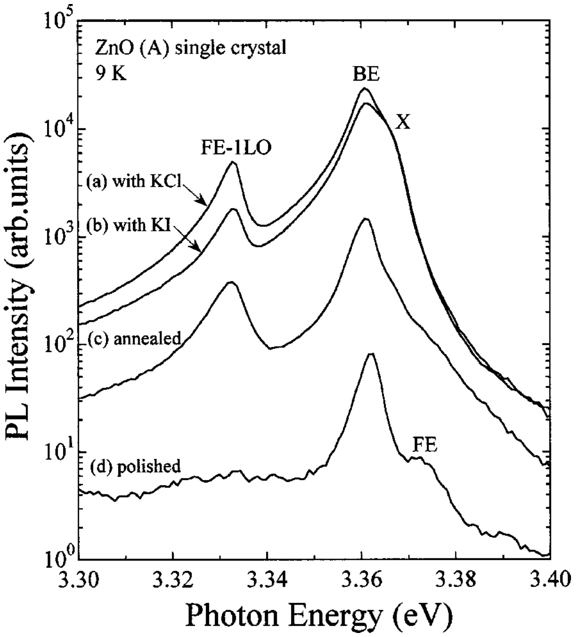

FIG. 2. Logarithmic display of PL spectra in a blue-UV region measured at 9 K is shown for four ZnO (A) samples; (a) a coated crystal with KCl, (b) a coated crystal with KI, (c) an annealed crystal, and (d) a polished crystal.

An intense PL peak labeled X appears at the same energy of 3.366 eV as that of the embedded ZnO particles in alkali halides,[10] and is most likely due to a transition of excitons bound to ZnO surface reported by Savikihin *et al.*[13] A FE emission associated with one longitudinal-optical (LO) phonon appears at 3.31 eV in a similar manner to that of the annealed crystal. The peak height of band-edge PL which includes the BE, X, and FE emissions is about 300 times larger than that of the polished crystal.

We show temperature dependence of PL spectra for the ZnO (A) crystal coated with KCl in Fig. 3. The BE and X lines decrease rapidly with increasing temperature, while intensities of the FE and the FE-1LO lines remain even at 300 K. The behavior of the FE is caused by having the large binding energy.[2] These characteristic features are consistent with the previous results observed in ZnO particles embedded in alkali halide.[9]

At room temperature, PL measurement was carried out for the same four samples. Figure 4 shows PL spectra in a blue-UV region at room temperature for the ZnO (A) samples: (a) a coated crystal with KCl, (b) a coated crystal with KI, (c) an annealed crystal, and (d) a polished crystal. The broad PL bands corresponding to transitions of the FE and its phonon replicas appear at around 3.3 eV. The trend is the same as the case at low temperature in Fig. 2. The fact reveals that luminescent efficiency of the band-edge PL increases by the coating of alkali halide.

It is essential for evaluation of crystalline quality to consider visible PL in contrast with band-edge PL in semiconductors. The visible PL is seriously depending on the related defects. PL spectra in visible region at 9 K for ZnO (A) samples are shown in Fig. 5: (a) a coated crystal with KCl,

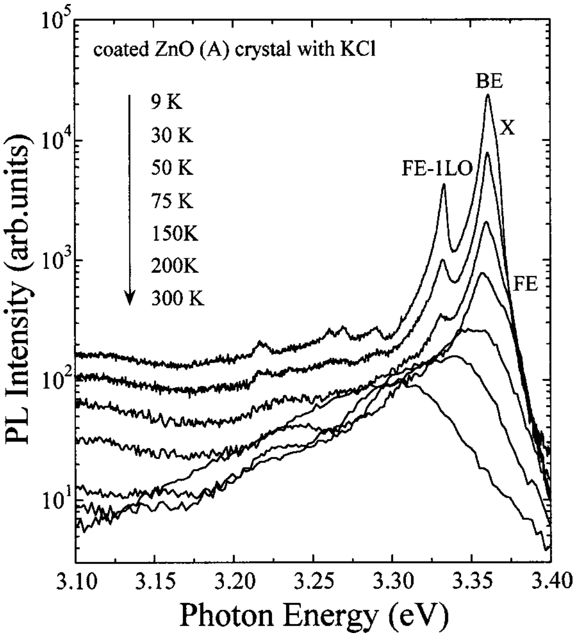

FIG. 3. Temperature dependence of PL spectra for the coated ZnO (A) crystal with KCl. Temperatures are corresponding to the order indicated.

(b) an annealed crystal, and (c) a polished crystal. Here, a spectrum of coated crystal with KI is excluded because it is almost the same as the spectrum of coated crystal with KCl. The visible PL intensity centered at around 2.35 eV for the annealed crystal is the strongest among three samples. The PL peak corresponds to the well-known green band emission.[6] The strong green band having oscillatory structure reveals that oxygen vacancies increase by the annealing. This structure is due to LO phonons as reported by Reynolds *et al.*[14] In the coated crystal, the PL intensity decreases to a level of the polished crystal, while the peak position shifts to the lower energy at 2.1 eV. This band corresponds to the so-called yellow band emission, which has been explained by arising from transition of single negatively charged interstitial oxygen ions.[5] The spectral change in the coated crystal demonstrates that alkali halide decreases the total number of the oxygen vacancies, but increases that of the interstitial oxygen ions.

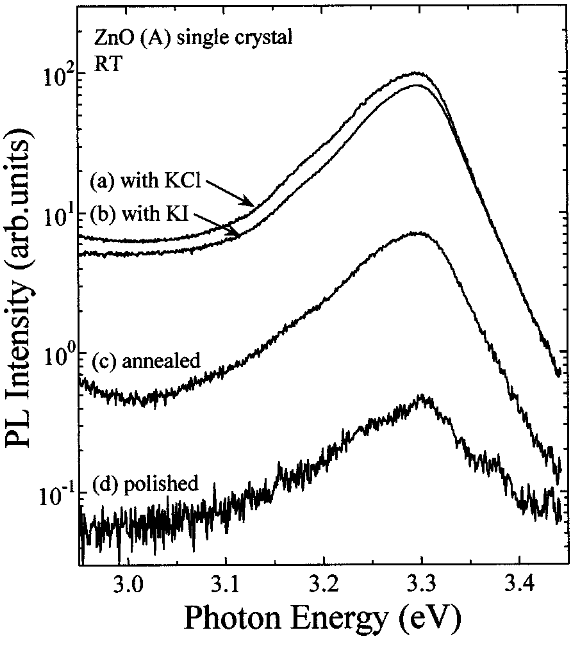

FIG. 4. PL spectra in a blue-UV region at room temperature for ZnO (A) samples: (a) a coated crystal with KCl, (b) a coated crystal with KI, (c) an annealed crystal, and (d) a polished crystal.

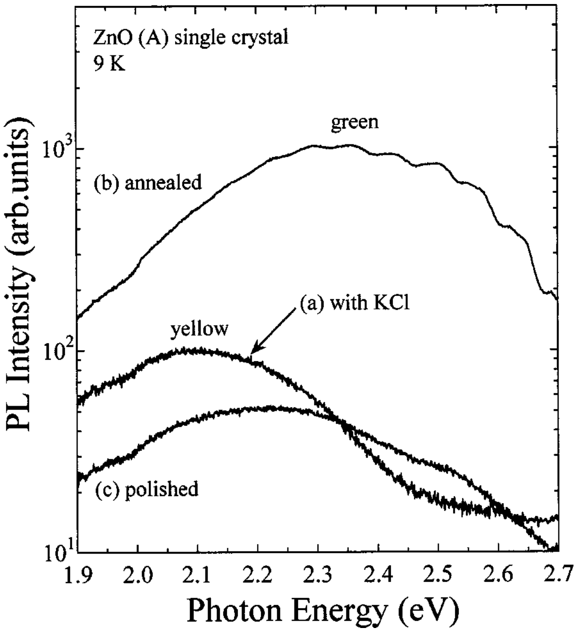

FIG. 5. PL spectra in a visible region at 9 K for ZnO (A) samples; (a) a coated crystal with KCl, (b) an annealed crystal, and (c) a polished crystal.

Present results suggest that coating with alkali halide effectively improves optical properties in ZnO crystal. In other words, it enhances the band-edge PL intensity and decreases the green band intensity. When a lot of oxygen vacancies in ZnO crystal are included, the green band emission appears in addition to the band-edge PL. Annealing treatment in N_2 gas atmosphere at high temperature increases the amount of oxygen vacancies, resulting in the green band emission. Conversely, coating on ZnO crystal with alkali halide reduces the amount of oxygen vacancies. As a result, the green band emission decreases.

In order to examine reproducibility of the coating effects in ZnO, similar samples are prepared in another bulk ZnO crystal obtained from a different source. Figure 6 shows PL spectra for three ZnO (B) samples: (a) a coated crystal with KCl, (b) an annealed crystal, and (c) a polished crystal. The band-edge PL intensity for the coated crystal with KCl is about 100 times larger than that of the polished crystal. In the polished sample, a weak band-edge PL is only observed in almost the same intensity as the visible PL. Therefore enhancement of band-edge PL is confirmed for the bulk ZnO (B) samples.

We have already reported that optical properties are considerably affected by halogens in ZnO particles embedded in

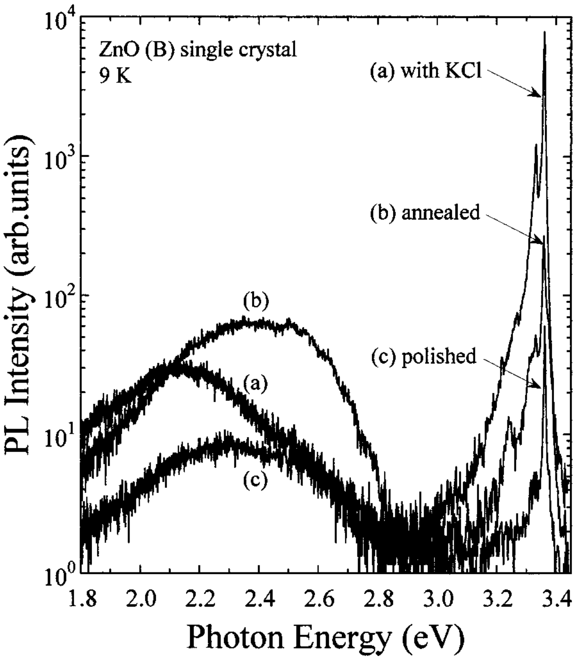

FIG. 6. PL spectra measured at 9 K are shown for three ZnO (B) samples: (a) a coated crystal with KCl, (b) an annealed crystal, and (c) a polished crystal.

alkali halide.[11] The results provide that halogen ions penetrate into ZnO surface and cause crucial changes in the band-edge PL spectrum. It is well known that a halogen atom substitutes for an oxygen site and acts as a role of donor in ZnO.[14] Since a lot of oxygen vacancies present in the surface of a ZnO crystal, halogen-donors are increased by incorporation of halogen ions into oxygen vacancies. The increase of the donors causes to increase excitons bound to the surface of ZnO crystal. As a result, the X line related to the surface enhances efficiently. On the other hand, the oxygen vacancies decrease by supplementing with the incorporation of the halogen ions. Optical enhancement of the band-edge PL is occurred in contrast with the visible PL, suggesting qualitative improvement of the ZnO surface.

We find that alkali halide contributes to the qualitative improvement of the surface in bulk ZnO. Here, the halogen plays an important role for the improvement independing on the kind of halogen ions. In the case of hydrogenation treatment, hydrogen efficiently passivates the green band emission and enhances the band-edge luminescence of ZnO.[3] The fact is very similar to our results. Since it is difficult to grow high quality ZnO crystal, our method probably becomes very useful for enhancement of the band-edge PL in the viewpoint of optical application. Furthermore, higher doping of halogen donors occurs by the coating with alkali halides in a thin region at ZnO surface. Since alkali halide on ZnO surface can be perfectly washed away by water, the *n*-type surface is obtained easily. By joining the *n*-type ZnO with *p*-type ZnO or other materials, it will be possible to prepare *p-n* junction, laser diode, and other electrical devices. In addition, the interface between a ZnO layer and thin alkali halide crystal could be applied to the fabrication of a new-type metal-insulator-semiconductor structure, though there are serious problems of a large lattice mismatch and physically weak strength of alkali halides. For further investigation, it will be necessary to apply the method for various ZnO crystals such as sputtering thin films and epitaxial layers grown by molecular beam epitaxy method.

IV. CONCLUSIONS

The coating treatment of alkali halide for ZnO crystal enhances the band-edge PL intensity and decreases the green band intensity markedly. The experimental results suggest that surface of ZnO crystal is improved by alkali halide effectively. The improvement is probably due to incorporation of halogen ions supplied from alkali halide into oxygen vacancies on the ZnO surface.

ACKNOWLEDGMENTS

The authors would like to thank Dr. H. Kondo and Dr. T. Hirai for their stimulating suggestion and useful discussion. This work was partially supported by a Grant-in-Aid for Scientific Research from the Ministry of Education, Science, Sports, and Culture, and also supported by the Sumitomo Foundation and the Sasakawa Scientific Research Grant from The Japan Science Society.

---

[1] V. Srikant and D. R. Clarke, J. Appl. Phys. **83**, 5447 (1998).

[2] D. G. Thomas, J. Phys. Chem. Solids **15**, 86 (1960).

[3] T. Sekiguchi, N. Ohashi, and Y. Terada, Jpn. J. Appl. Phys., Part 2 **36**, L289 (1997).

[4] S. H. Bae, S. Y. Lee, H. Y. Kim, and S. Im, Opt. Mater. (Amsterdam, Neth.) **17**, 327 (2001).

[5] X. L. Wu, G. G. Siu, C. L. Fu, and H. C. Ong, Appl. Phys. Lett. **78**, 2285 (2001).

[6] K. Vanheusden, W. L. Warren, C. H. Seager, D. R. Tallant, J. A. Voigt, and B. E. Gnade, J. Appl. Phys. **79**, 7983 (1996).

[7] B. J. Jin, S. Im, and S. Y. Lee, Thin Solid Films **366**, 107 (2000).

[8] J. Chen and T. Fujita, Jpn. J. Appl. Phys., Part 1 **42**, 602 (2003).

[9] Y. Harada, H. Kondo, N. Ichimura, and S. Hashimoto, Jpn. J. Appl. Phys., Part 2 **38**, L1318 (1999).

[10] Y. Harada, H. Kondo, and S. Hashimoto, *Proceedings of the 25th International Conference on Physics of Semiconductors, Osaka 2000*, edited by N. Miura and T. Ando (Springer, Berlin, 2001), p. 1573.

[11] Y. Harada, H. Kondo, N. Ichimura, and S. Hashimoto, J. Lumin. **87–89**, 405 (2000).

[12] T. Ota, S. Sasa, Y. Harada, and S. Hashimoto, Phys. Status Solidi B **229**, 815 (2002).

[13] S. F. Savikhin, A. M. Freiberg, and V. V. Travnikov, JETP Lett. **50**, 122 (1989).

[14] D. C. Reynolds, D. C. Look, B. Jogai, J. E. Van Nostrand, R. Jones, and J. Jenny, Solid State Commun. **106**, 701 (1998).