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Optical characteristics of Ge doped ZnO compound

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Abstract

The compound of ZnO: Ge which can be used as a blue light emission material has been prepared by the solid state reaction method. We have discussed the optical properties of the compound by photoluminescence (PL) measurements. We discovered that Zn_2GeO_4 phase is formed by the heavy doping of Ge atoms, and the solid solubility limit of Ge in ZnO is about 0.7 mol%. From the observed PL spectra of the compound there is a blue shift up to 0.7 mol%, but in concentrations higher than 0.7 mol% a red shift is observed. We can explain the shift of PL peak by Burstein-Moss and the band tail effects.

Keywords: Impurities; Optical properties; Powder-solid state reaction; Spectroscopy; ZnO

1. Introduction

Nowdays the developments of the blue, green, and red emission materials which can be of practical use has been widely studied. In particular, ZnO is one of the most remarkable materials, for it has the large band gap of 3.3 eV as well as the free exciton energy of 60 meV at room temperature.[1] ZnO has the excellent optical, electric, and acoustic properties, therefore its commercial use, such as SAW (surface acoustic wave) filter, gas sensor, window of the solar cell, varister, and transparent electrode, have been realized.[2–4]

Ryu et al. reported the light emission properties of GaN and ZnO in the visible region in order to check the possibility of the application, where the structure of ZnO is similar to that of GaN.[5] Reynolds et al. reported that they used ZnO as a substrate to get the high quality GaN thin film[6] and simultaneously they studied the light emission properties in the visible region from the basis of the similarity of the materials. The research on the blue emission materials has been done and discussed on GaN, ZnO, ZnS, and ZnO alloys.[7–9] ZnS has been studied as a material which can be used for either a blue emission or a red one, but S is easily dissociated. This property causes the material to have the short durability, which plays a role in undermining the light emission property. Therefore the research on the light emission material in which the activator is added to ZnO and ZnO alloy has been widely done in order to develop the material that has the structural stability and the high efficiency.[8–10] In this paper, for the purpose of developing the blue emission material we prepare ZnO: Ge by the solid state reaction method where Ge is added by the unit of mol% to ZnO powder.

2. Experiment

We prepare ZnO: Ge compound by the solid state reaction method in which ZnO (99.99%, Aldrich Chem. Co.) and GeO_2 (99.99%, Aldrich Chem. Co.) powder are used. GeO_2 is measured by the unit of mol% and mixed with ZnO for 10 h. In order to remove its humidity, it is dried at 100 °C in the oven for 6 h. The mixed material is sealed in the quartz tube under the pressure of 10^{-5} torr, and it is sintered at 1100 °C for 6 h. For the accurate measurement of the temperature, we contact the thermocouple to the quartz tube. The structural change of the compound is observed by XRD (Rigaku D/max 2100 H), where Cu $K_{\alpha 1}$ radiation is used ($\lambda = 1.5406$ Å). In order to investigate the optical properties of the compounds we measure PL spectrum by using the monochromator. He-Cd laser (kimmon, IK 3252 R-E) with 325 nm is used in this experiment.

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3. Results and discussion

ZnO has the wurzite structure, and its lattice constants are regarded as $a = 3.2427$ Å and $c = 5.1948$ Å, respectively.[11] Fig. 1 shows the results of XRD measurement according to the addition of Ge atoms. As shown in the figure, above 0.7 mol% there are new XRD peaks compared with those of the pure ZnO specimen. These XRD peaks are formed from Zn_2GeO_4 compound and marked with an arrow. These marked peaks are (113), (410), and (223) from the low angle side. From XRD results we conclude that the solid solubility limit of Ge to ZnO is 0.7 mol%. As well as, the peaks that represent the (100) and (001) of the pure ZnO are shifting to the lower angle region according to the addtion of Ge atoms.

Fig. 2 shows the shift of the obtained lattice constants in our experiment. As shown in the figure, the lattice constant increases up to the solid solubility limit, but when the contents of Ge are over the solid solubility limit, they decrease. In general, when Ge it is doped to ZnO, Ge is replaced into the vacancy of Zn ion or remains as an interstitial ion. The ion radius of Ge is 0.53 Å, which is smaller than that of Zn ion, 0.74 Å, therefore the inter-atomic distance Ge-O will become shorter than the bonding length of Zn-O. As a result, the lattice constant will decrease. On the contrary, when Ge is placed as an interstitial ion, the atoms are rearranged and placed on the equilium state due to the coulomb interaction between Zn^{2+} and O^{2-} ions, so the lattice constants will increase. From the above results, it is confirmed that under the solid solubility limit Ge atoms exist as the interstitial ones, and over the solid solubility limit Ge atoms contributes to the formation of Zn_2GeO_4, which means that they do not exist as the interstitial atoms any longer.

Fig. 3 shows PL spectra of the compound measured at room temperature in which Ge is doped with 0.1 mol%. As shown in the figure, when we separate the measured spectrum, the peaks of 3.1 and 3. 25 eV are revealed.

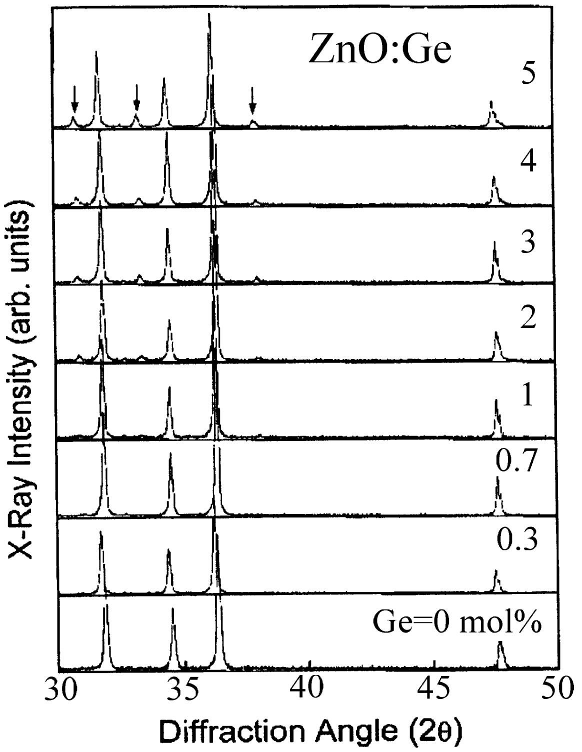

Fig. 1. XRD pattern of Ge doped ZnO compound.

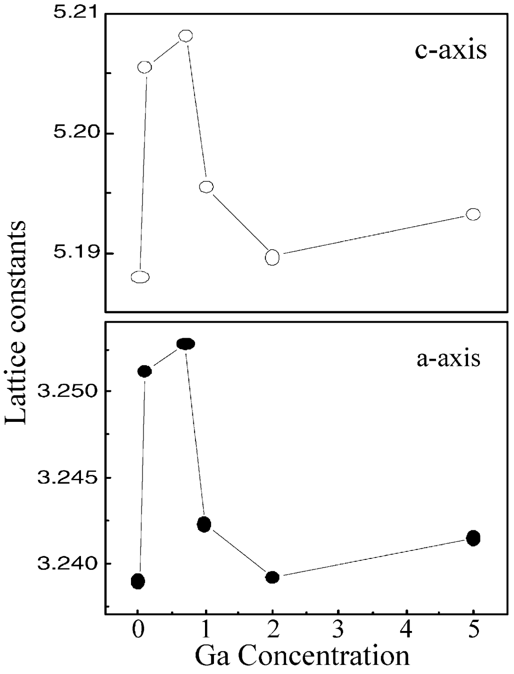

Fig. 2. The change of the lattice constants in Ge doped ZnO compound.

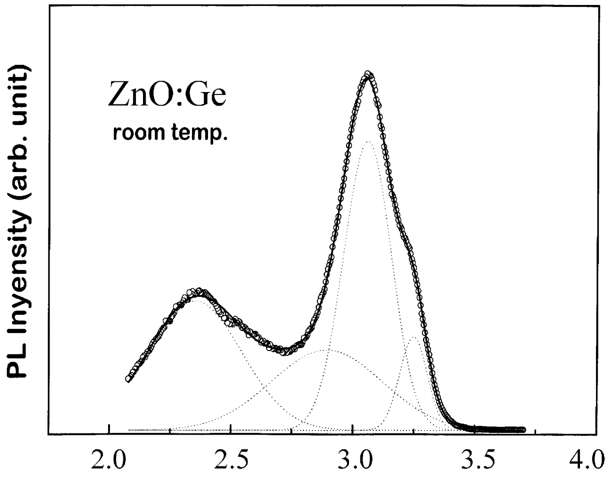

Fig. 3. PL spectrum of Ge doped ZnO compound at room temperature.

The emission of 3.1 and 3.25 eV are the transitions between the oxygen vacancy and the valence band. The emission of 2.4 eV is caused by the transition between the oxygen vacancy and that of Zn. On the contrary, the peak of 2.8 eV is regarded as the transition between the valence band and the donor level which is formed by the replacement of Ge atoms in the Zn vacancies. Until now various kinds of explanations on the defects of ZnO have been done. Fig. 4 is the energy band diagram for the defects of ZnO which were already reported. According to the report, the energy level caused by the interstitial ions of Zn is −50 meV. In the case of oxygen vacancy, the energy levels are located at −40 and −190 meV from the conduction band edge. In the case of Zn vacancy it is placed at −2.5 eV from the conduction band edge.

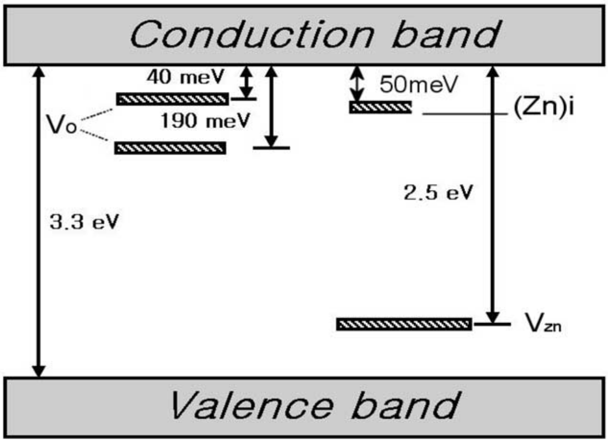

Fig. 4. The energy level diagram found by defects in ZnO compound.

Fig. 5 shows the shift of PL spectra according to the addition of Ge atoms. As shown in the figure, as Ge addition is increased, the intensity of 2.4 eV and 3.1 eV in the spectrum is changed. This phenomenon is considered due to the fact that when the Zn vacancy is replaced by Ge atom, the transition probability between the oxygen vacancy and the Zn vacancy decreases relatively.

Fig. 6 represents the shift of PL peak observed in Fig. 5, where the change of PL peaks of 3.1, and 3.25 eV are shown. In the figure, up to 0.7 mol%, the solid solubility limit of Ge atom, all observed peaks represent a blue shift. These phenomena can be explained by Burstein–Moss shift which is the band filling effect.[12] The other is the reduction of the energy band gap caused by the band tail. When the density of the donor is excessively high, this causes the band tail under the conduction band. This phenomenon can explain the red

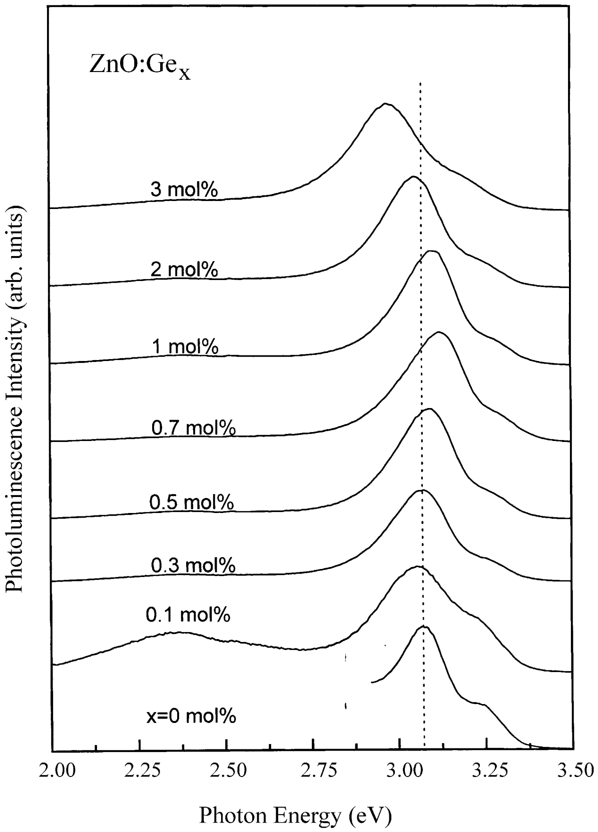

Fig. 5. The change of PL spectrum according to the addition of Ge atoms.

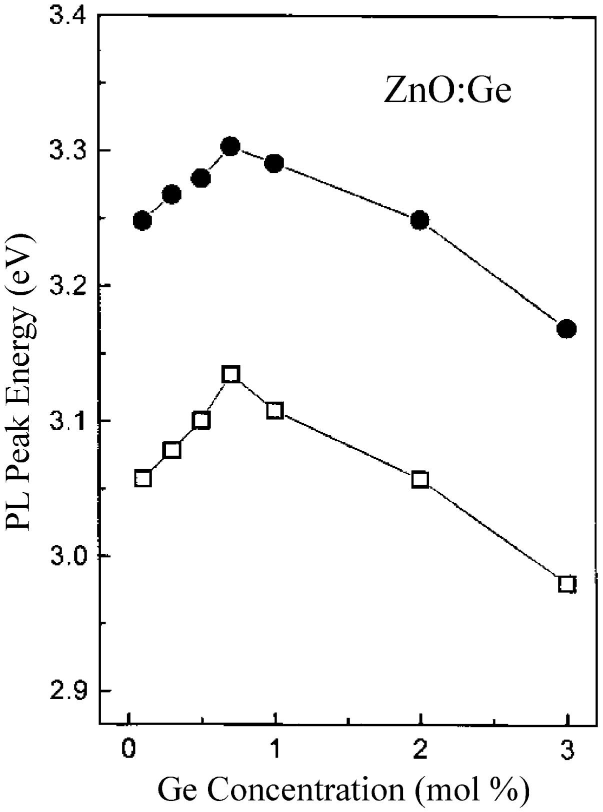

Fig. 6. The shift of PL peak observed in Fig. 5.

shift of PL peak over the solid solubility limit (0.7 mole%).

4. Conclusions

In this study we prepare the compound of ZnO: Ge by the solid state reaction method and investigate its optical properties. From the XRD measurement of the compounds the solid solubility limit of Ge to ZnO is confirmed as 0.7 mole%. In PL measurement we confirm that the emission power of 2.4 eV which is the transition between the oxygen vacancy and the zinc vacancy, decreases according to the increase of Ge dopping. On the contrary, the emission power at 3.1 eV increases relatively. This phenomenon can be understood that when Zn vacancy is replaced by Ge atom, the probability of the recombination between the vacancy of the oxygen and that of the zinc decreases. As a result, the shift of PL spectrum according to the addition of Ge atoms can be explained by the Burstein–Moss and band tail effects.

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