UV 조사에 의한 doped ZnS 나노입자의 annealing 효과

이준우, 조경아, 김현석, 김진형, 박병준, 김상식
고려대학교 전기공학과

Optical annealing of doped ZnS nanoparticles through UV irradiation

Jun Woo Lee, Kyoungah Cho, Hyunsuk Kim, Byung Jun Park, Jinhyoung Kim, and Sangsig Kim
Department of Electrical Engineering, Korea University

Abstract

ZnS nanoparticles were synthesized and doped with Pr^{3+} and Mn^{2+}. Photoluminescence(PL) peaks were observed at 430 nm for pure ZnS, 585 nm for Mn^{2+}-doped ZnS, and at around 430, 460, 480, 495 nm for ZnS nanoparticles doped with Pr^{3+}, respectively. For co-doped sample, both characteristics of doping with each element were exhibited. Optical annealing through UV irradiation was carried out in the two atmospheres; air and vacuum. The increases of the luminescence intensity was more considerable in the air, which is attributed to the photo-induced oxidation. In the case of co-doped sample the change of the emission color was observed by UV annealing.

Key words : ZnS nanoparticles, photoluminescence, UV irradiation, optical annealing

1. introduction

There are considerable studies in the compound semiconductor nanoparticles[1]. In the nano-sized regime of the particle size, below the Bohr radius, the electric and optical properties of the nanoparticles differ from the bulk materials and show high luminescence efficiency. These features have attracted growing interest in a potential application of nanoparticles, especially for electroluminescence(EL)[2]. For this purpose doping process in nanoparticles such as ZnS plays a critical role in the aspect of both high luminescence efficiency and tunable color of EL. Doping an impurity into the host material can modify the dominant recombination path from the surface state (non-radiative recombination) to the localized impurity state(radiative recombination)[1]. In the ZnS nanoparticles there is another interesting phenomenon for the purpose of high luminescence efficiency, that is, a significant increase in the luminescence intensity during exposure to ultraviolet(UV) irradiation[3].

In this paper ZnS nanoparticles were synthesized by wet chemical method and doped with Pr^{3+} and Mn^{2+}; doping with each element and

co-doping with both elements. For all samples photoluminescence(PL) were measured and UV irradiation were carried out.

2. Experiment

For the preparation of pure ZnS nanoparticles, aqueous solutions of 0.1 M $Zn(NO_3)_2H_2O$, 0.1 M Na_2S were produced first by the way that 3.0 g of $Zn(NO_3)_2H_2O$ and 0.8g of Na_2S was added to 100 ml of ultra pure water, respectively. The pH was adjusted to pH 10.3 for 30 ml of Zn^{2+} stock solution by adding 0.1 M aqueous NaOH and then 50 ml of Na_2S was added with stirring. For the synthesis of doped ZnS nanoparticles, 7.5 ml of 0.1M $Pr(NO_3)_36H_2O$ and 3.75 μl of $Mn(NO_3)_2H_2O$ was added respectively to 30 ml of 0.1 M Zinc nitrate aqueous solution which was set to pH 10.3. X-ray diffraction (XRD) patterns of the nanoparticles were obtained with X-ray d ㅏfractometer (Rigaku) with Cu K radiation (λ= 1.542Å). PL were measured at room temperature by 325 nm light from a He-Cd laser. During the UV irradiation at 325 nm excitation wavelength PL were measured as a function of irradiation time in the different atmosphere; air and vacuum at room temperature, respectively.

3. Result and Discussion

From XRD patterns of as-prepared samples we can confirm the synthesis of ZnS nanoparticles with the Zinc Blend structure(JCPDS No. 80-0020); the phase with (1 1 1), (2 2 0), (3 1 1) planes. From the line width the mean crystalline size of the pure ZnS nanoparticles have been estimated to be around 4.5 nm using Debye-Scherrer formula.

Figure 1 shows the PL spectra of the pure and doped ZnS nanoparticles. PL spectra of the ZnS nanoparticles show the maximum at around 430 nm in the blue region upon excitation at 325 nm. This is supposed to be related with the sulfur vacancy which acts as donor site. The orange emission has been observed at around 585 nm from the Mn-doped ZnS nanoparticles. Mn^{2+} possibly substitutes for Zn^{2+} in the ZnS lattice and energy transfer to localized impurity occurs. This orange emission is supposed to originate from the well known $^4T_1 \rightarrow {}^6A_1$ transition in the Mn^{2+}. In the ZnS nanopartricles doped with Pr^{3+} we have observed four main peaks of PL spectra at around 430, 460, 480, 495 nm. Due to the ionic radius (Pr^{3+}:1.01Å, Zn^{2+}:0.74 Å) and the need for the charge compensation of the 3+ charge of the rare-earth ion Pr^{3+} ions may be poorly incorporated into the ZnS lattice and mostly located nearby the surface. Therefore, it is thought that Pr^{3+}ions doped in the ZnS host may consist of a complex electronic structure with other element like oxygen in air. For the co-doped ZnS with Pr^{3+} and Mn $^{2+}$ the white emission has been observed in the range of 400 to 620 nm with five peaks at around 425, 455, 476, 490, and 575 nm. These peaks show the characteristic of both pure ZnS and doped ZnS with each element. Figure 2 and 3 show the varying PL spectra with time for the ZnS:Mn and ZnS:(Pr, Mn) during UV irradiation (325nm excitation wavelength). A significant increase in the luminescence intensity occurs under the exposure to UV irradiation in the ZnS nanoparticles. However, the degree of the enhancement of the PL spectra is different betwe-

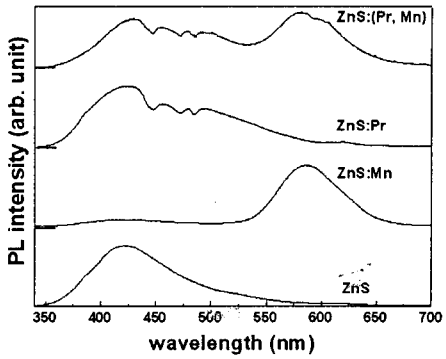

Fig. 1. PL spectra of ; ZnS, ZnS:Mn, ZnS:Pr, ZnS:(Pr,Mn)

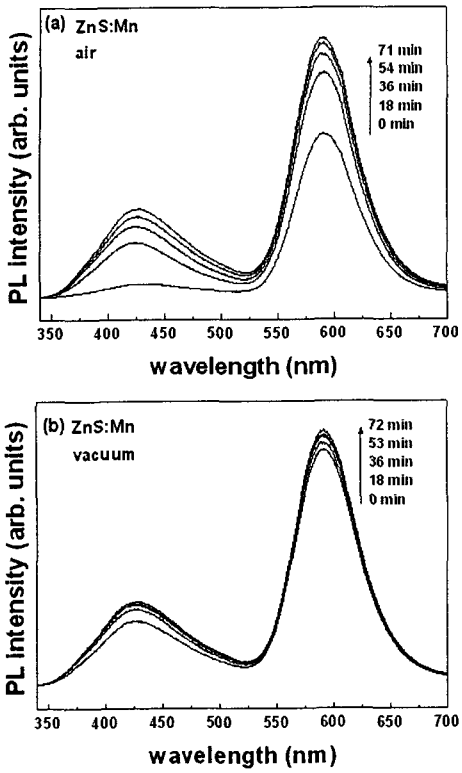

Fig. 2. PL spectra of Mn^{2+}-doped ZnS nanoparticles measured after different irradiation time; (a) in air (b) in vacuum at room temperature

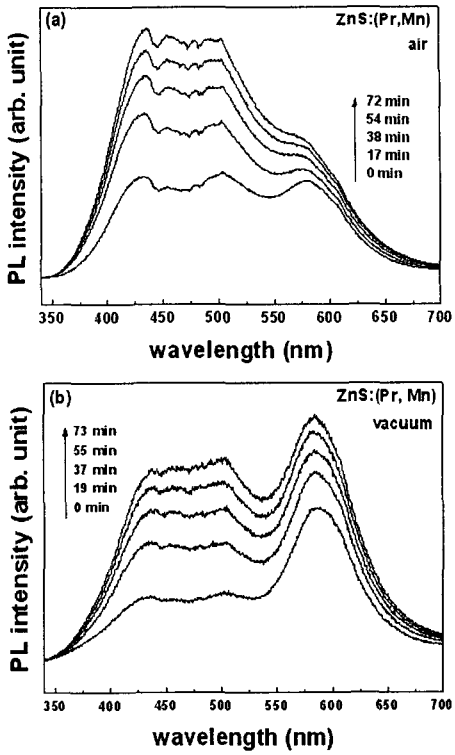

Fig. 3. PL spectra of Mn^{2+} and Pr^{3+} co-doped ZnS nanoparticles measured after different irradiation time; (a) in air and (b) in vacuum at room temperature

en in the air and in the vacuum. In the air, PL intensity increases more rapidly and considerably than that in the vacuum. This tendency is observed for all samples of the pure and doped ZnS nanoparticles. Several mechanism have been suggested; photo-induced polymerization and photo-induced oxidation[3]. Among them photo-induced oxidation is supposed to be the most plausible thing for our samples which were prepared without any passivating material. Under UV irradiation, oxygen is adsorbed onto the suface of the ZnS nanoparticles. The product of the photo-induced oxidation such as $ZnSO_4$ acts as a good passivating layer on the surface of nanoparticles and reduce the number of dangling bond, which serves as surface trap for the non-radiative recombination. Therefore, the surface passivation effect by means of photo induced oxidation under UV irradiation can block the non-radiative recombination path and induce more radiative recombination of charge carriers[3]. For the doped ZnS nanoparticles, other mechanisms can be suggested by taking into account the effect of the distribution of Mn^{2+} ions in the ZnS crystal lattice on luminescence and temperature dependence of the distribution of Mn^{2+}. Most of the dopants are thought to be located nearby the surface than interior of ZnS nanoparticles. The inhomogeneous distribution of Mn^{2+} leads to the formation of Mn^{2+} pairs by isotropic exchange interaction between Mn^{2+} ions. This increases the non-radiative recombination since its probability is proportional to the inverse of the distance between the ions. When temperature increases, Mn^{2+} ions can gradually diffuse into the ZnS crystal lattice and this process makes the distribution of ions more ho-

mogeneous[4, 5]. The same effect occurs during UV irradiation. This reduces non-radiative recombination owing to Mn^{2+} pairing, so the luminescence intensity can be enhanced.

Other effect of UV irradiation can be presented in the consideration of the change of the structure around impurity such as bonding angle during irradiation. When ZnS nanoparticles are exposed under UV light, the restoration of the twisted bonding angle occurs. This effect can improve the luminescence efficiency of nanoparticles and help impurities emit their own original emission. During UV irradiation the color of the emission changes from orange to white mixed with orange because the degree of the enhancement of luminescence peaks related to the ZnS doped with Pr^{3+} is larger than that of peaks related to the ZnS doped with Mn^{2+}. This can be explained by the relative difference of the contribution of the better surface passivation which occurs through photo-induced oxidation. The localization of charge carrier on Mn^{2+}ions competes with the traping of the charge carrier at surface state. However, once localization (which is faster process than traping in surface state) occurs, the effect of the surface passivation is less important in the case of Mn^{2+} ion[3]. So the effect of UV irradiation is larger in the case of pure ZnS and Pr^{3+}-doped ZnS nanoparticles, which are thought to be related to the oxygen of the surface than in the case of Mn^{2+}

4. Conclusion

ZnS nanoparticles were synthesized and doped with Mn^{2+} and Pr^{3+} by a wet chemical method. For each sample optical properties were investigated through PL. For all samples the enhancement of PL intensity was observed under UV irradiation. Photo-induced oxidation is regarded as a main mechanism and other mechanism such as diffusion of impurities into the lattice and restoration of bonding angle occurred at the same time. During UV irradiation on the ZnS:(Pr, Mn), the degree of the enhancement of peaks is different. Therefore we observed the change of emission color to the white.

Reference

[1] R. N. Bhargava, D. Gallagher, X. Hong, and A. Nurmikko, "Optical properties of Manganese-Doped nanocrystals of ZnS", Phys. Rev. Lett., Vol. 72, p. 416, 1994.

[2] Y. Hovii, M. Kitagawa, H. Taneoka, and H. Kusano et al., " Electroluminescence properties of PVCz electroluminescent devices doped with nano-crystalline particles", Mater. Sci. Eng., Vol. B85, p. 92, 2001.

[3] A. A. Bol, and A. Meijeri, "Luminescence Quantum Efficiency of nanocrystalline ZnS:Mn^{2+}. 2. Enhancement by UV irradi ation", J. Phys. Chem. B, Vol. 105, p. 10203, 2001.

[4] B. Xia, I. W. Lenggoro, and K. Okuya, "Synthesis and Photoluminescence of Spherical ZnS:Mn^{2+} Particles", Chem. Mater., Vol. 14, p. 4969, 2002.

[5] I. Yu, and M. Sen, "Effect of Mn^{2+} dis tribution in Cu-modified ZnS on the con centration quenching of electro luminescence brightness", Appl. Phys. Lett., Vol. 66, p. 424, 1995.