PHOTOACOUSTIC AND PHOTOLUMINESCENCE SPECTRA OF MANGANESE-DOPED NANOCRYSTLS OF ZnS WITH AND WITHOUT MODIFICATION BY CARBOXYLIC ACIDS

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Manganese-doped ZnS nanocrystals (ZnS:Mn) have been studied from the view point of quantum confinement effects and large luminescent efficiency. The Mn^{2+} ion d-electron states act as efficient luminescent centers while interacting strongly with the s-p electronic states of the host nanocrystal. Recently, it has been reported that the photoluminescence (PL) intensity due to the Mn^{2+} d-d transition is enhanced when ZnS:Mn nanocrystals are modified by carboxylic acids, such as methacrylic and acrylic acids.[1,2] One of the possibility of the PL enhancement with the modification by carboxyl acids is that the carboxyl groups directly coordinate Mn^{2+} ions for the modified nanocrystals. The study of optical absorption is most important to understand the behavior of semiconductor nanocrystals. There have been few investigations on the optical absorption of ZnS:Mn nanocrystals because of the strong scattering in the powdered structure. However, these scattering effects can be minimized by employing a photoacoustic (PA) method which detects acoustic energy owing to heat production by nonradiative processes. In the present paper, we report the optical absorption characteristics by PA spectroscopy for ZnS:Mn nanocrystals with and without the modification by methacrylic and acrylic acids to investigate the electronic states together with the PL measurements.

Nanocrystalline Mn-doped ZnS was prepared from a mixture of zinc acetate and manganese acetate with sodium sulfide and that made in methacrylic and acrylic acids. Nanocrystalline Mn-doped ZnS without carboxylic acids was also prepared and used for comparison. The resulting powders were well separated and washed with methanol several times and were dried.[2] PA measurements were carried out by the normal gas-microphone method. Measurements of the spectra were carried out at room temperature in the wavelength range of 320 to 800 nm with the modulation frequency of 33 Hz.

Figure 1 shows the PA difference spectra (ZnS:Mn – ZnS) with and without the modification by methacrylic and acrylic acids. The PA signal intensity shows a peak around a photon energy of 3.2 eV due to Mn^{2+} ions absorption. The peak intensities with modification are larger than that without modification, indicating the increase of nonradiative relaxation processes by the modification. Figure 2 shows the PL difference spectra (ZnS:Mn – ZnS) with and without the modification. The PL signal intensity shows a peak around a photon energy of 2.1 eV due to Mn^{2+} ions ($^4T_1 \rightarrow {}^6A_1$). The peak intensities with the modification are smaller than that without the modification, also indicating the increase of nonradiative relaxation processes by the modification. The results were different from those of references 1 and 2.

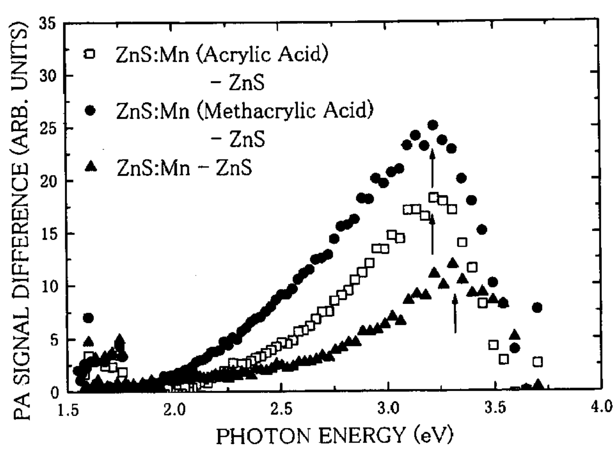

Fig. 1 PA difference spectra of ZnS:Mn system.

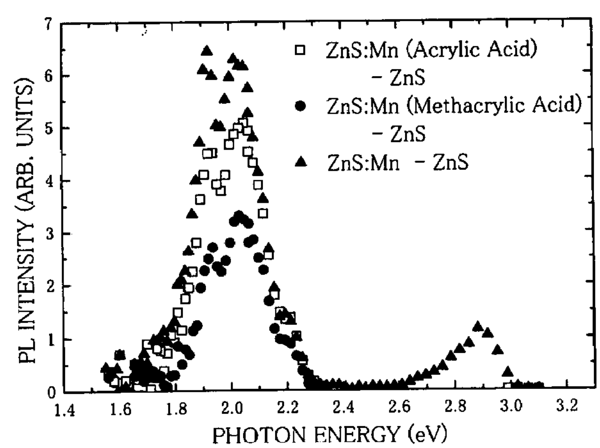

Fig. 2 PL differnce spectra of ZnS:Mn system.

1) T. Igarashi et al., Phys. Rev. B 56, 6444 (1997)., 2) I. Yu, T. Isobe, and M. Senna, J. Phys. Chem. Solids 57, 373 (1996).