Journal of Luminescence 131 (2011) 786–789

Contents lists available at ScienceDirect

Journal of Luminescence

journal homepage: www.elsevier.com/locate/jlumin

Analysis of the effect of annealing on the photoluminescence spectra of Cu^+ ion implanted ZnS nanoparticles

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ARTICLE INFO

Article history:
Received 30 November 2008
Received in revised form
30 November 2010
Accepted 3 December 2010
Available online 13 December 2010

Keywords:
Ion implantation
ZnS nanoparticles
Photoluminescence
Annealing

ABSTRACT

In the present study, we report the photoluminescence (PL) study of nanoparticles of ZnS implanted with Cu^+ ions at the doses of 5×10^{14}, 1×10^{15} and 5×10^{15} ions/cm^2 and annealed at 200 and 300 °C. The photoluminescence spectra of the samples implanted at lower doses of 5×10^{14} and 1×10^{15} ions/cm^2 and annealed at 200 and 300 °C showed peaks at around 406, 418 and 485 nm. The PL emission peak at 485 nm was attributed to the transition of electrons from conduction band of ZnS to the impurity level formed by the implanted Cu^+ ions. In the PL spectrum of the sample implanted at the highest dose of 5×10^{15} ions/cm^2, in addition to the emission peaks observed in the PL spectra of the samples implanted at lower doses, a peak at around 525 nm, the intensity of which decreased with increase in the annealing temperature, was observed. The emission peak at 525 nm was attributed to the transitions between sulfur and zinc vacancy levels. The full width at half maximum (FWHM) of the emission peak at 406 nm was observed to decrease with increase in annealing temperature, indicating lattice reconstruction. The observation of copper ion impurity related peak at 485 nm in the PL spectra of samples of the present study indicated that the doping of copper ions into the ZnS lattice is achievable by implanting Cu^+ ions followed by annealing.

1. Introduction

Research on nanosized semiconductors stimulated great interest in the recent past due to their unique properties and potential applications in diverse areas such as photocatalysis, solar cells, display panels, etc. [1–4]. These materials show unusual luminescence properties induced by quantum size effect. Efforts have been made in realizing luminescence tunable materials simply by changing the particle size and size distribution, and great progress has been achieved in this direction [4–9]. ZnS is a direct, wide band gap material, which emits in the UV region. If ZnS can be made to fluoresce in the visible region by doping it with suitable dopants, it can be used as an efficient phosphor. A considerable amount of work has been focused on doping ZnS nanoparticles in which the dopants can act as recombination centers for the excited electron–hole pairs and thus result in strong and characteristic luminescence. The first report on doping of nanocrystals was on ZnS:Mn system [10]. This was followed by a number of reports on doped ZnS nanoparticles [11–17]. By taking advantage of developments in preparation methods, both transition metal ions and rare earth ions have been doped into ZnS nanoparticles. Examples include ZnS:Mn [10–12], ZnS:Ag [18], ZnS:Ni [19], ZnS:Co [20], ZnS:Sm [21], ZnS:Eu [22], ZnS:Tb [23] and ZnS:Cu [14–17], the last one being the focus of the present study. Nanosized ZnS:Cu finds extensive applications in electroluminescent devices [4] and this material is identified as a good cathode ray tube (CRT) phosphor [14]. Reports on detailed study of the luminescent properties of ZnS:Cu nanocrystals prepared by chemical methods are available in the literature [14–17,24]. Sang et al. [24] reported the microstructural and luminescent properties of the ZnS:Cu nanocrystals incorporated into PVA film matrix. Temperature dependence of the luminescence of nanocrystalline ZnS:Cu and the life time of luminescence has been investigated in detail by Bol et al. [14]. A detailed study of the effect of synthesis temperature on particle size and shape and the photoluminescence characteristics of ZnS:Cu nanocrystals was done by Lee et al. [4].

However, even after much research, controlled doping of nanoparticles is still a challenging problem. Ion implantation, in spite of having the undesirable effects on luminescent properties of the material due to ion beam induced lattice defects and/or low dopant activation efficiency, is being practiced for a long time for introducing dopants into a semiconductor. This technique can also be used for creating high resistance regions for interdevice isolation. There are a number of reports on ion implanted ZnO thin films [25–27,33]. The effects of O^+ ion implantation on the structural,

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doi:10.1016/j.jlumin.2010.12.004

optical and electrical properties of spray pyrolyzed ZnO thin films were reported by Vijayakumar et al. [25]. The influence of the implantation of transition metal and rare earth ions and subsequent thermal annealing in air on the structural and luminescent properties of ZnO samples was investigated by Monteiro et al. [26]. Detailed studies of Cu^+ ion implantation on insulators and semiconductors have been reported [25–33]. Townsend et al. [28] and Wu et al. [29] reported in detail the cathodoluminescence and ion beam luminescence from copper nanoparticles produced by ion implantation of Cu^+ ions into bulk silica and also from copper incorporated within alumina in pulsed laser deposition. Ishizumi et al. [32] have reported the photoluminescence spectrum of copper and aluminum codoped ZnS (ZnS:Cu,Al) nanocrystals fabricated by sequential implantation of Zn^+, S^+, Cu^+, and Al^+ ions into Al_2O_3 matrices. Sakaguchi et al. [33] used ion implantation technique to dope ZnO thin films with copper ions. However to the best of our knowledge, no work has been reported on doping nanostructured ZnS using ion implantation technique.

In our previous work [34] we studied the photoluminescence and Raman spectra of as-prepared and Cu^+ ion implanted samples of nanoparticles of ZnS and observed that Cu^+ ions were not effectively doped into the unannealed Cu^+ ion implanted samples. In the present work, we report the study of photoluminescence of Cu^+ ion implanted nanostructured ZnS samples, which were annealed at 200 and 300 °C.

2. Experimental

Nanoparticle samples of ZnS used in the present study were synthesized by a procedure reported earlier [34]. Pellets of nanoparticles of ZnS were implanted with a mass analyzed beam of 400 keV Cu^+ ions at doses of 5×10^{14}, 1×10^{15} and 5×10^{15} ions/cm^2 at room temperature using 1.7 MV Tandetron accelerator. The beam current density was kept at 120 nA/cm^2. A vacuum of 4×10^{-7} Torr was maintained inside the sample chamber. Post-implantation annealing of the samples was carried out in a conventional tube furnace at 200 and 300 °C for 2 h under a continuous flow of argon gas. High-resolution transmission electron microscopy (HRTEM) of the unimplanted sample was carried out using JEOL 2010F electron microscope at an acceleration voltage of 200 kV. Room temperature photoluminescence (PL) was recorded using T64000 Jovin-Yvon spectrometer with a CCD detector and 1800 g/mm grating. A He–Cd laser of wavelength 325 nm was used as the excitation source.

3. Results and discussion

Figs. 1–4 show the photoluminescence (PL) spectra of nanostructured ZnS samples implanted with Cu^+ ions and post-implantation annealed at 200 and 300 °C. The spectra show three peaks at around 406, 418 and 485 nm for Cu^+ ion implanted samples at the doses of 5×10^{14} and 1×10^{15} ions/cm^2 (Figs. 1 and 2). In the PL spectra (Figs. 3 and 4) of the sample implanted with Cu^+ ion at the highest dose of 5×10^{15} ions/cm^2, no peak was observed at around 485 nm but instead a peak appeared at around 525 nm. The peak observed at around 525 nm in the PL spectra (Figs. 3 and 4) exhibited an asymmetrical broadening toward the lower wavelength side and a hence a Gaussian fit was applied to the spectra and the peak was deconvoluted. In a previous work [34], the present authors reported the photoluminescence spectra of unimplanted and unannealed Cu^+ ion implanted nanostructured ZnS pellets. Photoluminescence emission peaks were observed at around 412 and 518 nm in as-prepared samples and in the samples implanted with Cu^+ ions at higher doses of 1×10^{15} and 5×10^{15} ions/cm^2. Photoluminescence spectra of samples implanted at a lower dose of

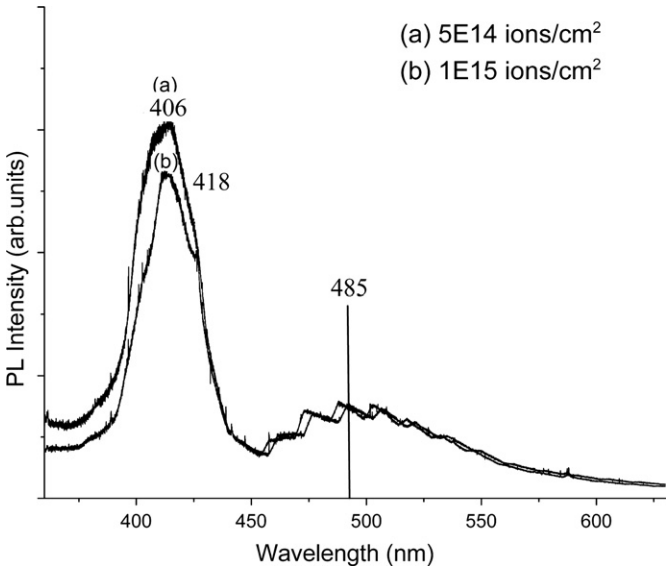

Fig. 1. Photoluminescence spectra of the Cu^+ ion implanted samples annealed at 200 °C.

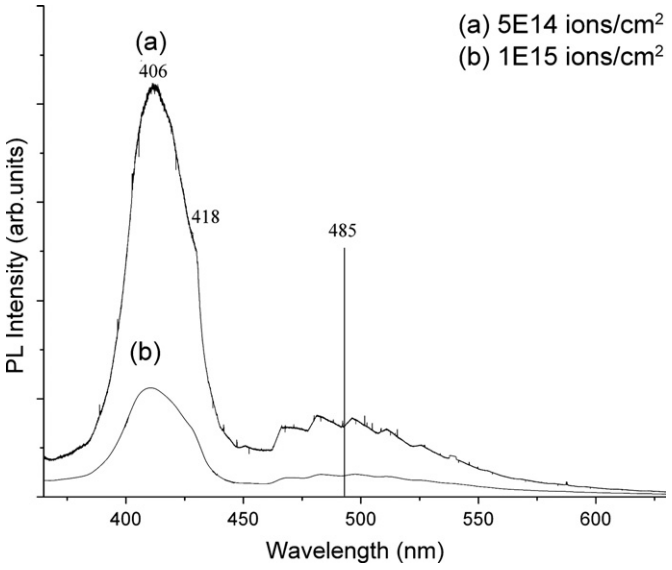

Fig. 2. Photoluminescence spectra of the Cu^+ ion implanted samples annealed at 300 °C.

5×10^{14} ions/cm^2 showed a peak at around 490 nm instead of the peak at 518 nm (Figure 5 of Ref. [34]). The peak at 412 nm was attributed to sulfur vacancies and the peak at around 520–535 nm to transitions of electrons from sulfur vacancy states to zinc vacancy states. However the trap levels within the forbidden gap of chalcogenides due to sulfur vacancies may be of two types, internal sulfur vacancy and surface sulfur vacancy [8]. The surface S^{2-} vacancy state should be located closer to the conduction band than the internal S^{2-} vacancy state because electronic levels of surface S^{2-} vacancies should have smaller binding energies due to the surface effect. Thus the peak observed at around 406 nm in the PL spectra of pellets of ZnS nanoparticles implanted with Cu^+ ions in the present study (annealed samples) can be attributed to surface sulfur vacancies, i.e. to the recombination of electrons at the surface sulfur vacancy with holes at the valance band, and the peak observed at around 418 nm can be attributed to internal sulfur vacancies. Due to ion implantation, the sulfur atoms at the surface