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Physica E 26 (2005) 24–27
PHYSICA E
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Photoluminescence properties of impurity-doped ZnS nanocrystals fabricated by sequential ion implantation

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Abstract

We have studied photoluminescence (PL) spectrum and dynamics of Cu- and Al-doped ZnS (ZnS:Cu,Al) nanocrystals fabricated by sequential implantation of Zn^+, S^+, Cu^+, and Al^+ ions into Al_2O_3 matrices. These samples exhibit intense green PL under UV light excitation. The space- and time-resolved PL measurements show that the broad green PL is due to the donor–acceptor (DA) pair luminescence of single ZnS:Cu,Al nanocrystals.

PACS: 78.67.Bf; 81.07.Bc; 78.55.Et; 61.72.Vv

Keywords: Nanocrystal; Ion implantation; ZnS; Photoluminescence

1. Introduction

Recently, there have been many studies on the fabrication and optical properties of semiconductor nanocrystals, because they will become new functional materials for future optoelectronic devices [1]. In particular, the semiconductor nanocrystals doped with luminescence centers exhibit efficient luminescence even at room temperature. Many different techniques have been developed for the fabrication of high-quality semiconductor nanocrystals [2–5]. We have successfully demonstrated that ion implantation followed by thermal annealing is one of the most useful methods for the fabrication of compound nanocrystals showing efficient luminescence [6–9]. In addition, impurity-doped semiconductor nanocrystals can be simply fabricated by sequential ion implantation of the elements, forming compound semiconductors and impurities [5]. In this work, we have fabricated ZnS nanocrystals doped with Cu and Al (ZnS:Cu,Al) by ion implantation and

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1386-9477/$ - see front matter
doi:10.1016/j.physe.2004.08.016

studied their photoluminescence (PL) properties using space- and time-resolved spectroscopy. ZnS:Cu,Al bulk crystals are applied to phosphors for cathode-ray tube display, because they exhibit an intense green luminescence. The study of optical properties of ZnS:Cu,Al nanocrystals is important for the development of nanocrystal phosphors with efficient luminescence efficiencies and the understanding of the impurity-related optical transitions in semiconductor nanocrystals.

2. Experimental

The ZnS:Cu,Al nanocrystals embedded in *c*-axis-oriented single crystal α-Al_2O_3 were used as the samples in this work. Cu- and Al-doped ZnS nanocrystal samples were fabricated by ion implantation of Zn^+ ($1.0 \times 10^{17}\,cm^{-2}$ at 420 keV), S^+ ($1.0 \times 10^{17}\,cm^{-2}$ at 225 keV), Cu^+ ($1.0 \times 10^{16}\,cm^{-2}$ at 400 keV) and Al^+ ($1.0 \times 10^{16}\,cm^{-2}$ at 170 keV) into the Al_2O_3 substrate, and then the samples were annealed at 1000 °C for 60 min in flowing 96% Ar + 4% H_2 atmosphere. X-ray diffraction examination indicated that the ZnS nanocrystals are prepared as a mixture of hexagonal and cubic ZnS crystals [9].

Time-resolved PL spectra were measured by using 325-nm and 300-fs laser pulses from an optical parametric amplifier and a streak camera. A scanning near-field optical microscope (SNOM) system (JASCO, NFS-330) was used for the PL spectrum measurement from single ZnS:Cu,Al nanocrystals. The SNOM-PL measurements were performed using an illumination and collection mode, under 325 nm He–Cd laser light excitation. The spectral sensitivity of the measuring systems (streak camera and SNOM systems) was calibrated using a tungsten standard lamp.

3. Results and discussion

Fig. 1 shows macro-PL, PL excitation (PLE), and absorption (ABS) spectra of ZnS:Cu,Al nanocrystals measured by conventional optics at 14 K. In the PLE and ABS spectra, the band-to-band transition of ZnS nanocrystals is observed above ~3.8 eV. The PLE spectrum shows the broad peak around 4.0 eV. From the difference between the peak energy of the PLE spectrum and the exciton energy of a ZnS bulk crystal, the average size of ZnS nanocrystals is estimated to be ~10 nm. The hump is observed around 3.4 eV in the ABS and PLE spectra. In ZnS:Cu,Al bulk crystals also, a similar hump is observed and is assigned to the transition of an electron from the Cu acceptor to the conduction band [10].

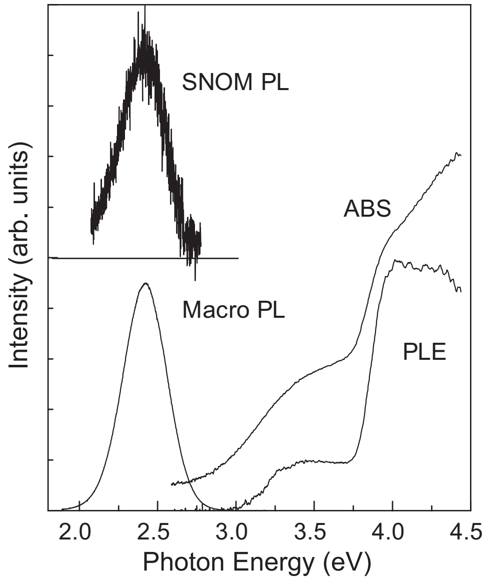

Fig. 1. Macro-PL, PLE, and ABS spectra of ZnS:Cu,Al nanocrystals at 14 K and the SNOM-PL spectrum of ZnS:Cu,Al nanocrystals at 20 K.

This sample shows a broad PL band around 2.4 eV under 325 nm light excitation. The PL spectrum is similar to the donor–acceptor (DA) pair luminescence of ZnS:Cu,Al bulk crystals [11,12]. In the SNOM experiment several bright spots are observed on the sample surface. The peak energy and spectral width of the SNOM PL do not depend on the monitored position. A typical SNOM-PL spectrum at 20 K is shown in Fig. 1. In the SNOM-PL spectrum, the broad PL band appears around 2.4 eV. Furthermore, we can point out that the SNOM-PL spectrum is very similar to the macro-PL spectrum. These results are completely different from the PL properties of shallow impurities in CdS nanocrystals fabricated