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Letter to the Editor

Highly efficient broadband near-infrared luminescence in Ni^{2+}-doped glass ceramics films containing cordierite nanocrystals

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ABSTRACT

We report on highly efficient broadband near-infrared photoluminescence (PL) in Ni^{2+}-doped glass ceramics (GCs) films fabricated by annealing Si/Ni^{2+}-doped glass superlattices (SNGS). Over two orders of magnitude enhancement of PL can be achieved in comparison with that from the annealed glass film. The PL lifetime of the annealed SNGS is several milliseconds, which is much longer than those of bulk GCs. The strong PL enhancement results from the formation of high-quality cordierite nanocrystals because the Si layers act as Si source for the crystal growth. This technique can be extended to fabricate other types of high-quality GCs films.

1. Introduction

With the rapid development of optical telecommunication, it is required to improve the transmission capacity of the wavelength division multiplexing (WDM) system. As a result, active ions such as transition metal (Ni and Cr) doped glass and glass ceramics (GCs) showing broadband near-infrared (NIR) photoluminescence (PL) in the range of 1.2–1.6 μm have received great attention [1–8]. In comparison with Cr ions, Ni takes the divalent state in almost all hosts. The detailed structural and optical studies have shown that octahedrally coordinated Ni^{2+} ions incorporated into nanocrystals of transparent GCs are responsible for these useful broadband PL. During the past several years, most researchers focused on the spectroscopic investigation of Ni^{2+}-doped bulk GCs, while little attention has been paid on the fabrication and characterization of GCs films [1–9]. As is well known, planar optical waveguide technologies are the key elements in the modern, high speed optical network. If high-quality Ni^{2+}-doped GCs can be obtained in film form, it holds promise for their wide applications as planar waveguide optical amplifiers and lasers. Therefore, it is an interesting and challenging topic to prepare and characterize high-quality GCs films.

In this work, we report a new approach to prepare Ni^{2+}-doped GCs films that exhibit strong broadband NIR PL. The procedure consists of the formation of Si/Ni^{2+}-doped glass superlattice (SNGS) structures and annealing. We show that the PL intensity of the annealed SNGS (ASNGS) films is more than two orders of magnitude enhanced compared to that of the annealed glass (AG) film prepared by the same procedure. The mechanism of PL enhancement is discussed based on the measurements of high resolution transmission electron microscopy (HRTEM), steady-state and time-resolved PL, and photoluminescence excitation (PLE) spectra.

2. Experimental details

The SNGS films were prepared by sputter-deposition of thin Si and Ni^{2+}-doped glass layers alternatively on fused quartz substrates by using a multi-target sputtering apparatus. The Ni^{2+}-doped glass target (SiO_2: 47.87 mol%, Al_2O_3: 11.28 mol%, MgO: 28.71 mol%, K_2O: 7.89 mol%, TiO_2: 3.98 mol%, NiO: 0.27 mol%) was prepared by a melt-quenching technique. Two kinds of SNGS structures with the thicknesses of the glass/Si layers of 5 nm/3 nm and 5 nm/1 nm were prepared. In both samples, the period

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was 50. As references, single layer Ni^{2+}-doped glass films with almost the same thicknesses were prepared by the same deposition conditions. After deposition, the films were thermally treated in air at 850 °C for 45 min. It is noteworthy that the films would become slightly inhomogeneous when the annealing time is over 45 min. PL measurements were carried out at room temperature with the excitation of a 488 nm line of an Ar^+ laser. The signal was analyzed by a single grating monochromator and detected by a liquid-nitrogen-cooled InGaAs detector. Time-resolved PL measurements were performed by detecting the modulated luminescence signal with a photomultiplier tube (Hamamatsu, R5509-72) and analyzing the signal with a photon-counting multichannel scalar. The excitation source for the time-resolved PL measurements was 405 nm light of a laser diode.

3. Results and discussion

Fig. 1(a) displays the cross-sectional HRTEM (JEOL JEM-2010 microscope) image of an as-deposited SNGS film. A superlattice structure can clearly be seen. After annealing, the structure is almost collapsed and elliptical nanocrystals appear (Fig. 1(b)). The analysis of the corresponding selected area electron diffraction (SAED) pattern in Fig. 1(c) reveals that all the spots can be assigned to cordierite ($Mg_2Al_4Si_5O_{18}$, JCPDS No. 13-0294). The lattice fringe with the inter-planar spacing of 0.82 nm in Fig. 1(d) can be assigned to (0 2 0) planes of the cordierite lattice. In contrast, a different crystal phase is found in the AG film; HRTEM and SAED results reveal that it consists of Ni^{2+}-doped MgO (JCPDS No. 45-0946) nanocrystals (Fig. 2). These results indicate that the Si layers in SNGS act as Si source for the formation of cordierite nanocrystals during annealing.

Fig. 3(a) shows the steady-state PL spectra of the AG and ASNGS (Si thickness: 1 nm) films. The ASNGS film shows strong and broad NIR emission in the range of 1120–1620 nm with the peak wavelength of 1355 nm. The AG film also shows broad PL in similar wavelength range, although the peak wavelength is about 50 nm shifted to longer wavelength side. The NIR PL from above two structures can be ascribed to the emission of $^3T_2(^3F) \rightarrow {}^3A_2(^3F)$ of Ni^{2+} in the octahedral sites of cordierite and MgO nanocrystals [5].

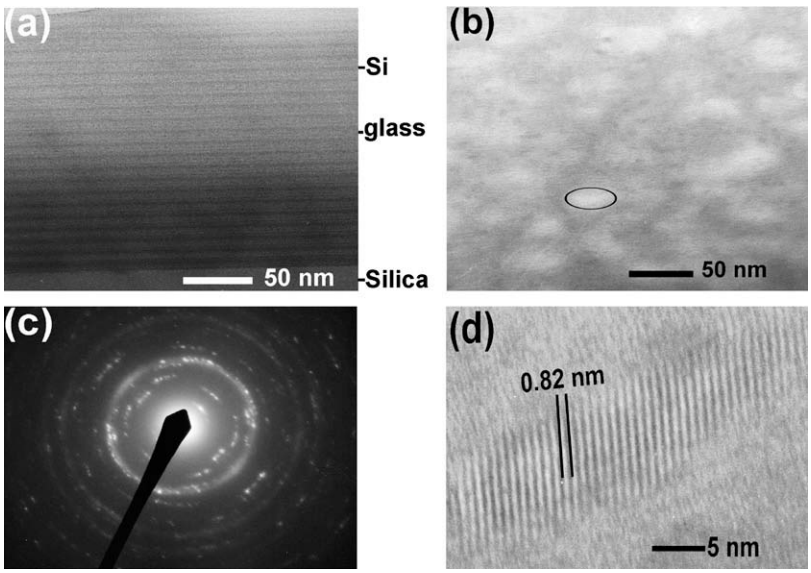

Fig. 1. (a) A typical HRTEM image of as-prepared superlattices (Si layers thickness: 3 nm). (b) HRTEM image of the corresponding annealed sample. The region denoted by black ellipse shows the existence of cordierite nanocrystals. (c) SAED image. (d) HRTEM image of an individual nanocrystal.

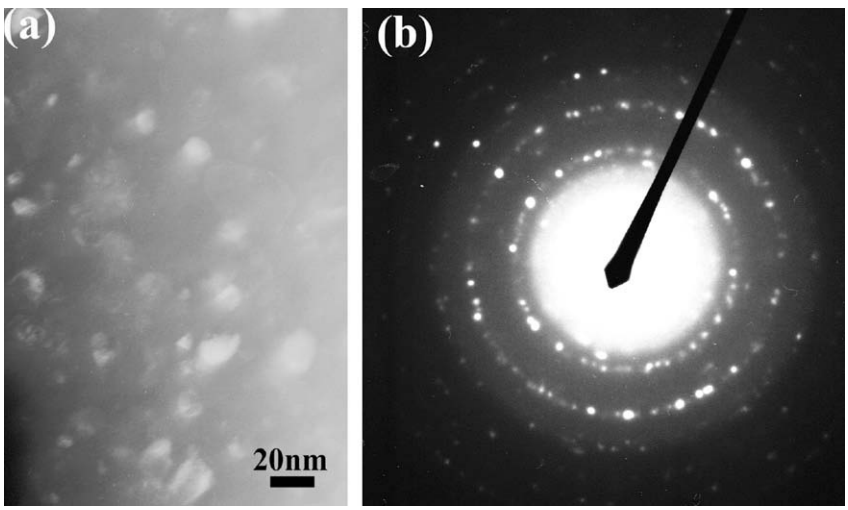

Fig. 2. (a) HRTEM image of the AG film. (b) SAED image.