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Er^{3+} related 1.53 μm emission from Er–Si-codoped ZnO multilayer film prepared by rf-sputtering

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ABSTRACT

The near-infrared emission from Er and Si codoped ZnO film, synthesized by cosputtering from separated Er, Si, and ZnO targets, has been investigated. By building the multilayer film structure, controlling the Er concentration, and optimizing the annealing condition, the intensity of Er^{3+} related 1.53 μm photoluminescence (PL), which originates from the transition of Er^{3+}: $^4I_{13/2} \rightarrow {}^4I_{15/2}$, can be modulated. It is shown that the maximum intensities of Er^{3+} related 1.53 μm PL are obtained when the Si:ZnO/Er:Si:ZnO/Si:ZnO sandwiched multilayer film and the alternate Er:ZnO/Si:ZnO multilayer film were annealed at 1000 °C and 950 °C, respectively. The Er^{3+} related 1.54 μm PL intensity of the multilayer film is higher than that of the Er:ZnO monolayer film. This can be attributed to the presence of the silicon nanocrystals that could act as sensitizers of Er^{3+} ions in the multilayer film. The PL of the sandwiched multilayer film and the alternate multilayer film were measured under different temperatures (15–300 K). The sandwiched multilayer film exhibits a nonmonotonic temperature dependence as well as the alternate multilayer film, which differs from that of Er-doped ZnO as previously reported.

1. Introduction

Since Er-related 1.53 μm ($^4I_{13/2}$–$^4I_{15/2}$) emission is within a wavelength range of a minimum loss for silica optical fiber, Er-doped semiconductor has been investigated extensively as one of the promising optoelectronic materials [1–4]. The efficiency of the light generation and its dependence on temperature are important topics. Though the intra-4f transition is forbidden in an isolated Er, a crystal field produced by the solids can make it allowed. The emission spectrum is independent of host materials, but the intensity and efficiency mainly depend on the host materials. It has been reported that oxygen codoping and introduction of wide bandgap materials as host material are effective to enhance the Er-related 1.53 μm emission [5–7]. Furthermore, in order to improve the solid solubility and suppress thermal quench effect, wide bandgap oxide materials are usually selected as host materials.

As a host material zinc oxide (ZnO) with a wide band gap of about 3.37 eV could be considered as a promising candidate for Er doping. Er doped ZnO films have proved to be reliable materials for light-emitting diodes, laser diodes, and optical amplifiers at 1.53 μm in the waveguide structure as well as electrode materials for carrier injection because of their high electrical conductivity.

In order to increase the intensity of Er-related 1.53 μm emission, many relevant experimental works have been carried out. It was proposed that the doping of N or Li into Er-containing ZnO samples was very effective in enhancing the intensity of 1.53 μm emission because they could modify the local structure slightly and resulted in a lower symmetry of the crystal field around Er^{3+} ions [8,9]. It was also founded that indirect excitation with an excitation efficiency was superior to direct excitation of Er^{3+} ions for 1.53 μm emission [10]. In addition, the intensity of the green Er emission in fractal ZnO nanolattice was increased with rising sintering temperature due to the suppression of multiphonon relaxation [11]. Nevertheless, the broadband sensitizer, Si nanocrystal (Si-NC), was rarely studied, which could transfer energy to Er^{3+} ions to enhance the intensity of 1.53 μm emission in ZnO host.

In this work, Si:ZnO/Er:Si:ZnO/Si:ZnO sandwiched multilayer and alternate Er:ZnO/Si:ZnO multilayer films have been synthesized by magnetron sputtering. The Er^{3+} related photoluminescence (PL) of the sandwiched multilayer and alternate multilayer films has been studied. Er^{3+} related PL intensity responses from the sandwiched multilayer and alternate multilayer films, due to ET processes between Si-NCs and Er^{3+} ions, are improved and higher than that of the Er:ZnO film. Moreover, the temperature dependent PL behaviors from the sandwiched multilayer and alternate multilayer films show

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the phenomena that the intensities of 1.54 μm emission are increased with increasing operating temperatures instead of high quenching behavior of Er doped monocrystalline Si.

2. Experimental details

The substrates used were p-type (100)-oriented Si single crystals with the resistivity of 3–5 Ω cm. The Si:ZnO/Er:Si:ZnO/Si:ZnO sandwiched multilayer and alternate Er:ZnO/Si:ZnO multilayer films were deposited on thermally oxidized Si substrates by radio frequency magnetron sputtering from separated Er, Si and ZnO targets. The sandwiched multilayer film consisted of one layer of 60 nm Er–Si-doped ZnO (Er:Si:ZnO) sandwiched with two layers of 10 nm Si-doped ZnO (Si:ZnO). The alternate multilayer film consisted of 20 alternate layers of 6 nm Er-doped ZnO (Er:ZnO) and 2 nm Si-doped ZnO (Si:ZnO). As comparison, the Er:ZnO monolayer film with 60 nm thickness was also prepared. The thickness of each layer is varied by deposition time as measured by a thickness monitor (Maxtek TM-100), respectively. This kind of sandwiched and alternate multilayer structures could lead to an improvement of the emission efficiency of rare earth (RE) ions by decreasing the probability of nonradiative processes which could be affected by the local density of optical state [12–14]. The background vacuum was better than 6×10^{-4} Pa before the deposition. During the deposition, the substrate temperature was kept at 150 °C. The sputtering pressure of Ar gas was controlled around 3 Pa and the flux was about 70–80 SCCM. Finally, to activate both Er^{3+} ions, as-deposited samples were annealed for 30 min at different temperatures in the range of 700–1100 °C under N_2 ambient.

The schematic diagram of Er–Si-codoped ZnO sandwiched multilayer and alternate multilayer films is shown in Fig. 1. The RE doping concentrations of the Er containing ZnO films are investigated by using Rutherford backscattering. The energy of He^+ ion beam in RBS was 2 MeV. The backscattered ions were detected by an Au/Si surface barrier detector placed at a scattering angle of 165°. Phase structures were investigated by a D/MAX-IIIC X-ray diffractometer (XRD) using Cu K_α radiation ($\lambda = 0.154$ nm). Raman spectra were measured using a Raman microscope (Jobin Yvon LabRam HR800) with a 514 nm Ar^+ laser. PL spectra were measured through a single grating monochromator using a long-wavelength enhanced InGaAs detector (response range 1300–1700 nm). Five excitation lines (457 nm, 476 nm, 488 nm, 496 nm, and 514 nm) from Ar^+ laser were chosen as pumping sources. The excitation power was 100 mW. All spectra were corrected for the monochromator and detector spectral responses. PL measurements were carried out at temperatures of 15–300 K by using a closed-cycle helium cryostat.

3. Results and discussion

Firstly, the compositions and structures of the Er–Si-codoped ZnO films are determined by RBS, XRD and Raman. Fig. 2 shows the typical RBS spectrum of the Er–Si-codoped ZnO sandwiched multilayer film on thermally oxidized Si substrate. The arrows in the figure indicate RBS energies corresponding to Er, Zn, Si and O located at the sample surface. The plateau of the RBS signal around 0.8 MeV is attributed to the signal of Si from oxidized Si substrate. All signals from different elements and layers were separated from the RBS spectrum by using SIMNRA60 program [15]. This is estimated roughly that the average Si content in Er:Si:ZnO layer is ~10 at.% and the average Er content is about 2 at.%.

Fig. 3 shows the XRD patterns of the Er–Si-codoped ZnO alternate multilayer and sandwiched films annealed at different temperatures. For as-grown samples, except for the distinct crystallographic planes identified as Si (400) from Si substrate (JCPDS No. 89-5012) [16], one broad peak structure at about $2\theta = 34.5°$ is detected, indicating that these samples contain the existence of the amorphous ZnO. After annealing, the diffraction peaks from ZnO in the Er–Si-codoped ZnO alternate multilayer and sandwiched annealed film samples are well indexed as the hexagonal wurtzite ZnO phase (JCPDS No. 89-1397) (Fig. 3a and b) [16].This indicates that amorphous ZnO phases have been crystallized into ZnO crystals. For the Er–Si-codoped ZnO alternate multilayer films, with increasing annealing temperature, the preferred orientation of the as-deposited film was changed from (002) to (100) and (004). For the Er–Si-codoped ZnO sandwiched annealed film samples annealed at 1000 °C, there is preferential orientation on (002) plane besides (004) plane. Moreover, other weak diffraction peaks at 28.4° are also detected, corresponding to the (111) of Si phase from Er:Si:ZnO and Si:ZnO layers. This suggests that the Si atoms in Er:Si:ZnO and Si:ZnO layers cluster and crystallize gradually into crystal grains during the thermal annealing process.

To check the existence of Si nanocrystals (Si-NCs), the Raman spectra were measured. Fig. 4 shows the Raman spectra of the Er–Si-codoped ZnO alternate multilayer annealed at 950 °C and sandwiched films annealed at 1000 °C. The Er–Si-codoped ZnO alternate multilayer and sandwiched annealed film samples exhibit a sharp band centered at 517 cm^{-1} appears, corresponding to the TO mode of Si-NCs. It indicates that Si-NCs in Er:Si:ZnO and Si:ZnO layers have been formed via phase separation of Si and ZnO. It is noted that the hexagonal wurtzite structure of ZnO belongs to the space group C^4_{6V} (P63mc) with two formula units per one primitive cell, where all of the atoms occupy the sites of symmetry C_{3V} [17,18]. The Raman active zone-center optical phonons predicted by the group theory are the existence of the following optic modes: $A_1 + 2B_1 + E_1 + 2E_2$ at the Γ point of the Brillouin zone; B_1 (low) and B_1 (high) modes are normally silent; A_1, E_1, and E_2 modes are Raman-active; and A_1 and E_1 also are infrared-active. Thus, A_1 and E_1 are split into longitudinal (LO) and

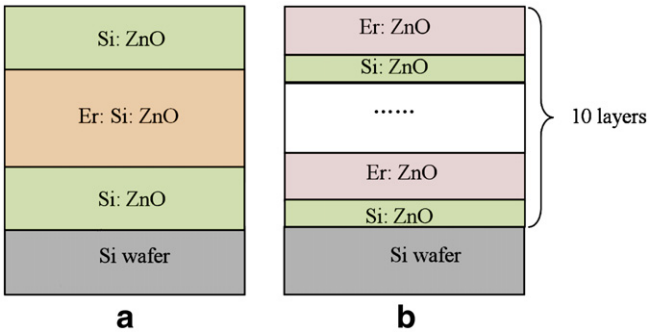

Fig. 1. Schematic diagram of the structures of a) Si:ZnO/Er:ZnO/Si:ZnO sandwiched multilayer film and b) alternate Er:ZnO/Si:ZnO multilayer film.

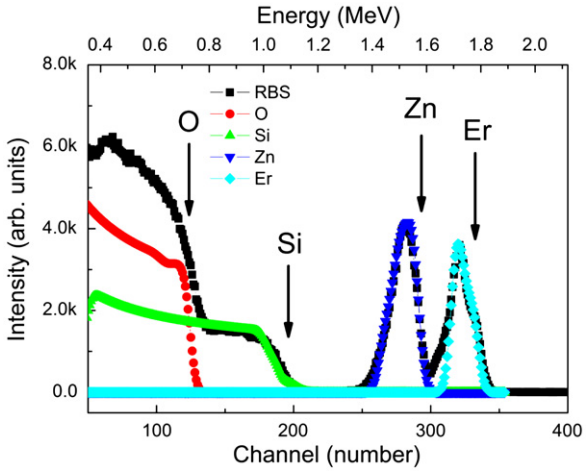

Fig. 2. Typical RBS spectrum of the Er–Si-codoped ZnO sandwiched multilayer film on thermally oxidized Si substrate.