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Photoluminescence of Tb^{3+}-doped SiN_x films with different Si concentrations

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Abstract

Tb^{3+}-doped SiN_x films (SiN_x:Tb^{3+}) were prepared by plasma-enhanced chemical vapor deposition (PECVD) and ion-implantation. And the effects of the SiN_x substrates with different Si concentrations on the light emission of Tb^{3+} were investigated. Experimental results show that two groups of photoluminescence (PL) peaks of Tb^{3+} ions were observed in different SiN_x:Tb^{3+} films. And the PL intensity increased with annealing temperature. The defect states of N and Si dangling bonds of the SiN_x substrate had little effect on the light emission of Tb^{3+} after the high-temperature annealing. For the annealed Si-rich SiN_x (SRN) film, Si nanoclusters precipitated from the host matrix. The increased oxygen concentration and the optical absorption due to the band tail states and Si nanoclusters of the annealed SRN film decreased the light emission of Tb^{3+} ions.

Keywords: PL; Tb; Ion-implantation; PECVD

1. Introduction

Silicon-based light emitter is one of the key opponents of silicon photonics system. It has stimulated great interests since the discovery of the light emission from porous silicon in 1990 [1]. Many efforts have been devoted to develop highly efficient luminescence from silicon-based light emitters [2]. Rare-earth (RE)-doped silicon light emitter is one of the most favorite candidates [3,4]. It has luminescence with wavelengths from the near infrared up to ultraviolet. Tb-doped silicon dioxide (SiO_2:Tb^{3+}) is intensively investigated. Tb^{3+} ion has high internal quantum efficiency, and its wavelength of the most intensive luminescence is centered at about 545 nm. It has intense light emission even at room-temperature. Therefore, it has attracted great attention [5–8]. However, the large band gap of SiO_2 ($\geq$8 eV) will make efficient carrier injection difficult. So, the electroluminescence (EL) of nearly all RE-doped Si dioxide (SiO_2:RE) systems depend on the impact excitation by hot electrons, which will require high operating voltage. It is not compatible with ultra large scale integrated circuit (ULSI) operation parameters. Furthermore, the host materials of SiO_2 can be degraded by hot electrons, resulting in short device lifetime [9]. An important alternative method could be using silicon nitride as the host material to solve these problems. Silicon nitride is proved to be an effective medium to excite RE ions [10,11]. It has a band gap only about 4–5 eV [12–15]. The injection of electrons will be facilitated and the operating voltage will be decreased. Moreover, silicon nitride is a better substrate than silicon dioxide in getting efficient light emission from Tb^{3+} ion. It is reported that the luminescence of Tb^{3+} ions will be enhanced in silicon nitride films with less oxygen concentration [16]. And integrated photoluminescence (PL) intensity of the Tb-doped silicon nitrides (SiN_x:Tb^{3+}) is stronger than that of SiO_2:Tb^{3+} [17]. It means that SiN_x:Tb^{3+} system may have the advantages of improved quantum efficiency of the light emission from Tb^{3+} ions.

Generally, SiN_x films may have different Si concentrations according to different deposition parameters. And the operating voltage of the SiN_x film to inject electrons efficiently will be further reduced if Si quantum dots, acting as the channel for leakage current, precipitate from the Si-rich SiN_x (SRN) substrate after high-temperature annealing treatment. However, the effects of the SiN_x films with different Si concentrations on the light emission of Tb^{3+} ions need to be investigated.

In this article, plasma-enhanced chemical vapor deposition (PECVD) is used to deposit silicon nitride films with different Si concentrations. And Tb^{3+} ions were introduced into the

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SiN_x films by ion-implantation with the advantages of accurately controlled distribution, concentration of implanted ion and improved reproducibility over co-sputtering [18] and PECVD with rare-earth ions introduced by carrier gas flow [16]. The UV–vis absorption spectra and defects related luminescence of SiN_x films were characterized. The PL properties of SiN_x:Tb^{3+} films were studied. The effects of annealing temperature, Si concentration and the microstructure of the SRN film on the PL properties of SiN_x:Tb^{3+} films were discussed in detail.

2. Experiment

About 200 nm of SiN_x films were deposited by PECVD on 4-in., (1 0 0) oriented, p-type silicon wafer with the resistivity of 5–10 Ω cm. Meanwhile, SiN_x films with the same deposition parameter were also grown on quartz for the measurement of the optical absorption property. The substrates were maintained at 300 °C and the total gas pressure of the reactive chamber was kept constant at about 20 Pa during the deposition. The gas ratios of NH_3:SiH_4 (N_2 diluted) were 3, 6 and 15, samples of which were specified as N3, N6 and N15, respectively. The gas ratios were chosen to deposit the SiN_x films with large difference of Si concentrations. Then all the films were annealed at 1150 °C for 1 h in the flowing N_2. Tb^{3+} ions were implanted into the SiN_x films at 100 keV and the incident angle of 60° with the dose of 3×10^{15} cm^{-2}. Afterwards, post-annealing was performed at 800 °C and 1000 °C for 1 h in the flowing N_2, respectively. The infrared absorption spectra of the films were measured using a Bruker IFS 66v/S Fourier transform infrared (FTIR) spectrometer under vacuum. The UV–vis absorption spectroscopy was performed on a Hitachi U-4100 spectrophotometer. The room-temperature PL signal was detected by a photomultiplier tube (HITACHI F-4500 FL Spectrophotometer) and the SiN_x:Tb^{3+} films were excited by a Xe lamp at the wavelength of 250 nm. The SiN_x films were excited by 325 nm He–Cd laser to measure defects related luminescence and a photo multiplier tube was used to detect signals. The microstructure of SiN_x films was characterized by a transmission electron microscope (TEM) of JEOL 2010.

3. Results and discussion

The distribution of the implanted Tb^{3+} ions inside the SiN_x films is calculated according to Monte Carlo simulations of TRIM 98 [19]. The implantation yielded a Gaussian depth distribution of Tb^{3+} ions, with a peak concentration of 1.3×10^{21} cm^{-3} at the depth of about 16 nm. Since the maximum depth range amounts to 27 nm, all the implanted ions were stopped within the films. Assuming the densities of all the SiN_x films are the same as the density of the amorphous Si_3N_4, i.e. 3.1 g cm^{-3}, the maximum atomic concentration of Tb ions is about 1.4 at.%. It should be noted that the calculation only provides the distribution of Tb^{3+} ions in as implanted SiN_x:Tb^{3+} films. After annealing process, its distribution is changed due to the diffusion of the Tb^{3+}, which is depends on annealing temperature and diffusion ability, etc.

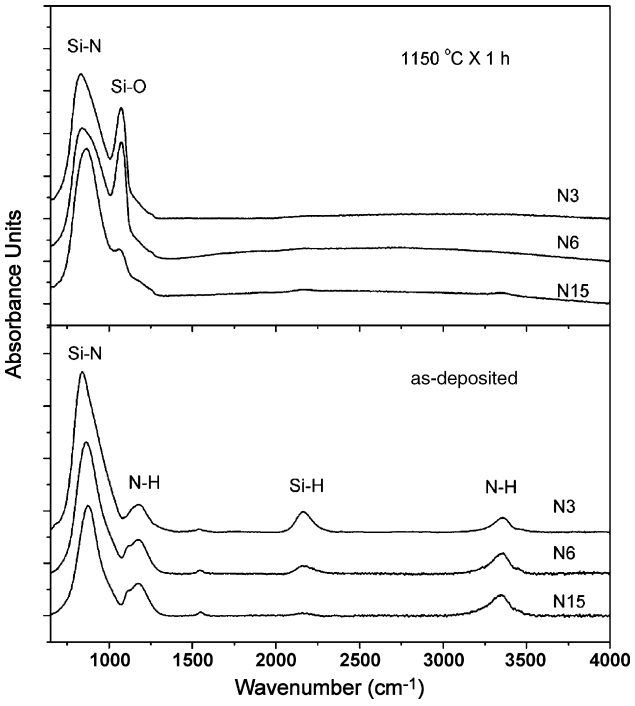

Fig. 1. FTIR spectra of the as-deposited and annealed (1150 °C for 1 h) N3, N6 and N15 SiN_x films.

The FTIR results of the as-deposited and annealed N3, N6 and N15 films are shown in Fig. 1. The signals from the Si substrates were subtracted from the spectra, and the base line was corrected. For the as-deposited SiN_x films, it can be seen that a lot of H related bonds including the bending mode of N–H bond at 1170 cm^{-1}, the stretching mode of N–H bond at 3350 cm^{-1} and the Si–H bond at 2200 cm^{-1} [20,21] are inside the films. The peak of the Si–N bond is at about 860 cm^{-1}. We also found that the peak intensities of Si–H and N–H bonds are different for those samples. And the peak of the Si–N bond is at 841, 864 and 874 cm^{-1} for N3, N6 and N15, respectively, which is caused by the difference of Si concentrations in these SiN_x films. Generally, the silicon concentrations of the SiN_x film decrease with the increasing of the gas ratio of NH_3:SiH_4. In addition, according to the results of XPS (see Ref. [22]), the ratio of Si:N in N15 film is almost 0.75, i.e. the film is nearly stoichiometric. While the ratio of Si:N in N3 film is about 1.4. Therefore, the N3 film is Si-rich and the Si concentration is much higher than that of the N15 film. Therefore, it can be concluded that the peak of Si–N bond increases reversely with the Si concentrations of the SiN_x films. The peak intensity of Si–N bond increases with the Si concentrations and the intensity of N–H increases reversely.

For the annealed SiN_x films, it can be seen that the absorption of the H related bonds disappears due to the escape of the H from the SiN_x films. It also results in the densification of the SiN_x films. Moreover, the absorption peak due to Si–O bond is observed at 1071 cm^{-1} [20,21], which means that there are oxygen related bonds inside the films. It is caused by the slight oxidation under high-temperature annealing. It is also found that the ratio of the peak intensities of Si–O to Si–N bond and the intensity of Si–O bond increase from N15 to N3 film. It means