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Mechanisms of light emission from terbium ions (Tb^{3+}) embedded in a Si rich silicon oxide matrix

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ABSTRACT

Mechanisms of light emission in Tb doped Si rich SiO_x matrix prepared by magnetron sputtering are studied by photoluminescence spectroscopy (PL). Characteristic PL peaks of Tb^{3+} ions and Si nanocrystals are simultaneously observed with an inverse relationship between their intensity. With a prolonged heat treatment at high temperatures, light emission from Tb^{3+} ions enhances at the expense of total quenching of the PL signal from the nanocrystals. It is suggested from the annealing studies as a function of process conditions and structural characterization that the light emission from Tb ions is mediated by trap states formed in the band gap of the oxide matrix by $Tb_xSi_yO_z$ complexes or excess Si states.

1. Introduction

There is a strong interest to combine electronic and optoelectronic functionalities of Si on the same chip platform for the future information technology. However, the limitations (indirect photon transitions, short non-radiative recombination lifetime, etc.) of Si, especially for the efficient light emitting device applications, require new physical and engineering approaches for Si based photonics and its integration to mature Si integrated circuit (IC) technology. After the intense luminescence observation from porous Si by Canham [1], the route has mainly been changed to exploiting the light emission from Si nanocrystals for this integration. The nanocrystalline Si in silicon dioxide (SiO_2) matrix has proven to be the most attractive approach due to its stability and reproducibility. It has been shown that the wavelength of the light emission can be controlled between 700 nm and 1000 nm by engineering the size of Si nanocrystals embedded in SiO_2. Up to now, some important device applications and physical phenomena have been demonstrated that open the road towards the robust Si photonics totally compatible with Si process technology [2–5].

However, light emission from Si nanocrystals is very broad and generally stays in the near infra red region. To overcome this limitation for the device applications in the visible range, the most appealing solution seems to be rare earth (RE) doping of SiO_2 system with or without excess Si. Intense research have been conducted on doping of Si nanocrystal systems, generally Si rich oxide with different RE elements, and their characteristic sharp emission lines in the infrared and visible part of the optical spectrum have been demonstrated [6–8]. In this approach Si nanocrystal or some clusters with RE atoms in the SiO_2 matrix were used as the sensitizer (energy donor) for the RE ions (energy acceptor). The excitation energy was first absorbed by the synthesizer and then transferred either directly or indirectly over any possible states to RE ions which originate geminate thermalization through its atomic states.

Among the rare earth doping systems, Er has attracted great attention due its emission wavelength at 1553 nm which is very useful for telecommunication applications. Moreover, it was shown that Er emission at this wavelength can be enhanced with Si nanocrystals which act as an efficient synthesizer. In this case, the conduction band edge of Si nanocrystals is at a higher energy facilitating an efficient energy transfer to nearby Er^{3+} ions. The synthesizer role of Si nanocrystals and their energy transfer mechanisms to the Er^{3+} ions are well understood [9].

Having sharp emission lines at blue and green colors, Terbium (Tb^{3+}) is an attractive energy acceptor for Si systems for practical applications like visible lightening, lab-on-chip biological diagnostics and silicon based optoelectronics [10–13]. Although Tb^{3+} ions have been successfully used as an excitation acceptor on Si systems, the energy absorption and transfer mechanisms to Tb atoms is still under debate and optimum layer parameters have not been evolved yet.

Tb atoms are incorporated into a SiO_x matrix with either excess Si or excess O and prepared by deposition techniques such as ion implantation [11], sputtering [13], and PECVD [14]. The light emission from the $^5D-^7F_j$ ($j = 6, 5, 4, 3$) transitions are typically

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observed in both Si rich and O rich systems. Having an efficient light emission from different SiO_x based matrices; the involvement of Si nanocrystals does not seem to be a necessity for the optical emission from Tb^{3+} ions. On the other hand, the light emission from Si nanocrystals is usually not seen simultaneously with Tb^{3+} related emissions. This was interpreted as the proof of fertilizing effect of Si nanocrystals [15]. We discuss below this critical question with some new experimental data obtained from Si rich SiO_x systems and show that the PL quenching from Si nanocrystal might be related to the structural deformation of Si nanocrystals with the formation of a new composite structure with Tb, Si and O.

It is known that the light emission from RE elements takes place through either intra 4f transitions or transitions between 5d and 4f energy levels. Emission efficiencies of these levels are very sensitive to the chemical environment of the ions within the matrix [15]. The electronic alignment of these orbitals with the surrounding matrix seem to be highly sensitive to chemical configuration of the Tb^{3+} ions as well as the composition of the matrix. It was proposed that the number of oxygen atoms involved in the Tb clusters formed in the matrix is important for the efficient light emission [15,16]. However, the details of the chemical environment of Tb ions in the matrix and its effect to the light absorption and energy transfer mechanisms for light emission is still not known.

In this study, the light emission from Tb^{3+} ions deposited into a SiO_x matrix with excess Si and the effect of process conditions have been investigated by the photoluminescence (PL) spectroscopy. We have observed that the Tb related light emission is sensitive to the annealing conditions as reported by others [15]. To understand the possible fertilizing effect of the Si nanocrystal and the effect of process condition on the Tb^{3+} luminescence, we have studied the evolution of Si rich SiO_2 matrix with Tb ions in a series of heat treatment processes. We have observed simultaneous light emission from Tb ions and Si nanocrystals under certain conditions. Prolonged annealing at high temperatures enhances the Tb related emission while suppressing the light emission from the nanocrystals. We discuss this and other observations on Tb^{3+} emissions with possible chemical configuration of Tb clusters formed in the oxide layer with excess Si.

2. Experimental procedure

Magnetron co-sputtering technique was used to produce 100 nm film having Si rich SiO_2 with elemental Tb using DC power of 150 W for Tb target and RF power of 350 W for SiO_2 target on *p*-Si wafer. Tb atoms were incorporated into the film by placing Tb pieces (with an approximate diameter of 0.5 cm) on the Si target which was sputtered with DC power of 150 W. For the sputtering process, electronic grade (6.0) Argon gas was used at 4×10^{-3} Torr pressure and 20 sccm flow during the deposition. Samples were then annealed between 700 and 1000 °C under nitrogen (N_2) and vacuum ambient for different durations. The elemental composition of the films was obtained by energy dispersive spectroscopy (EDS), from which we determined the composition of the as-deposited film as 43% Si, 48% O and 9% Tb. The PL measurements were performed at room temperature by using 325 nm He–Cd laser with an output power of 50 mW.

3. Results

3.1. Effect of a matrix on light emission

Fig. 1 shows the PL results of the Tb doped sample with excess Si after the annealing at different temperatures. We identify two emission bands having peak positions at about 541 nm and 760 nm. The peak at 760 nm is generally attributed to the Si nanocrystals formed

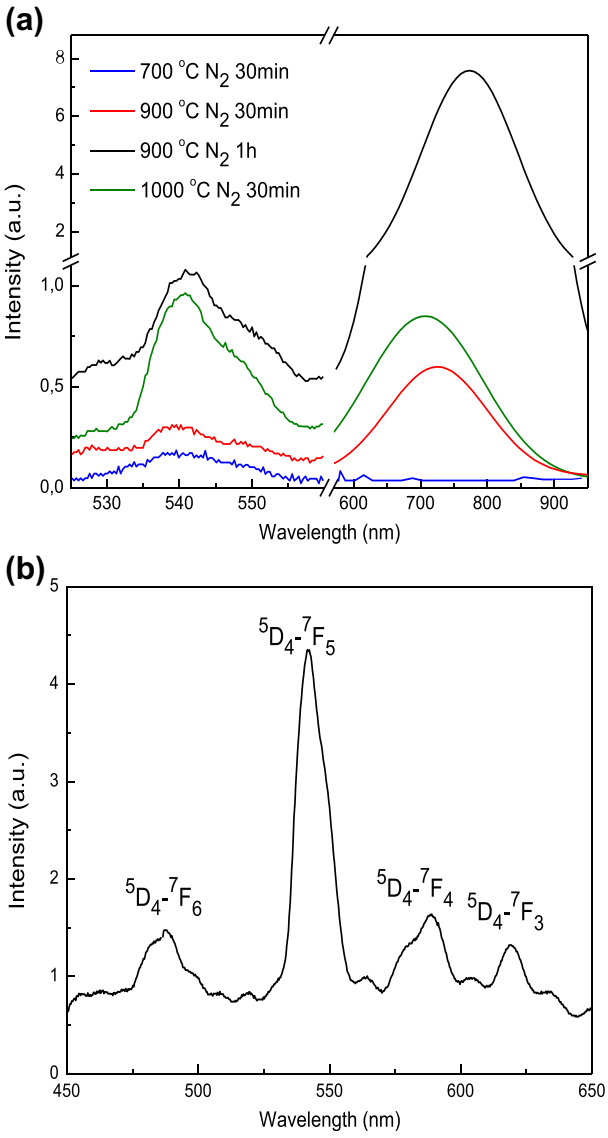

Fig. 1. (a) Room temperature PL spectrum of the Tb doped sample with excess Si. The evolution of the peaks from Si nanocrystals and Tb ions are seen. (b) PL spectrum of the same sample after annealing at 1000 °C for 1 h. The PL peak of Si nanocrystals disappeared in this case.

in the SiO_2 matrix [2]. Although the origin of the light emission from the Si nanocrystals is still under debate the most general consensus is that this peak is generated by the excitonic transitions within the nanocrystals. From our earlier studies, we know that the Si nanocrystal peak shifts to higher wavelength with increasing nanocrystal size as a result of quantum size effect in the low dimensional structures [17]. This is perhaps the most convincing evidence for the excitonic emission in these structures. As reported by us and others, the Si nanocrystal peak usually emerges after an annealing process at temperatures above 900 °C. With further annealing at the same temperature, the intensity of the peak increases with a shift to the longer wavelengths as a result of increase in the amount of the nanocrystals and their average size [18]. However, contrary to this general tendency of pure Si nanocrystal system, we observe a blue shift and intensity drop in the PL spectrum after the annealing at 1000 °C for 30 min. Furthermore, the PL peak from the Si nanocrystals quenches completely after a prolonged annealing at the same temperature as shown in Fig. 1b. In a recent article reporting the quenching of light emission from Si nanocrystals with the Tb ions, the quenching effect was interpreted as an evidence of efficient