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The formation of Yb silicates and its luminescence in Yb heavily doped silicon oxides after high temperature annealing

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ABSTRACT

We report on the formation of ytterbium (Yb) silicates and its photoluminescence (PL) properties for heavily Yb doped Si oxide films after various annealings. X-ray diffraction patterns and transmission electron microscopy indicate that different Yb silicates have formed in the oxides upon 1100 and 1200 °C annealing. The Yb PL intensities after the high temperature annealings are much stronger than those after lower temperatures, which indicates that the Yb silicates have higher emission efficiency than the Yb configurations found for lower temperature annealing. The PL intensities of the films can be altered considerably by secondary oxidizing or annealing in forming gas (N_2 + 7% H_2) ambience.

1. Introduction

The Yb^{3+} ion has the simplest (4f) energy level scheme among the rare earth (RE) active ions, consisting of a single excited state ($^2F_{5/2}$) at about 1.26 eV above the ground state ($^2F_{7/2}$). This leads to several advantages for some applications and Yb^{3+} emission has been studied extensively for applications such as near infrared light source and laser pumping. The excitation mechanism for Yb^{3+} in different environments is thus important. For example the formation of Si (or Ge) nanostructures in material systems containing Yb^{3+} has been reported to enhance the Yb photoluminescence (PL) by an energy transfer from the nanostructures to Yb^{3+} [1–5]. The Yb^{3+} ions can also be excited by defects in silica when co-doped with Al, P, F or Ge in silica fibers [6–10]. Defects commonly considered as efficient in transferring excitation energy to RE ions include oxygen deficient centers (ODCs) and non-bridging oxygen hole centers (NBOHC) [11,12]. Moreover, the Yb emission can be used as pumping source to excite erbium (Er) emission in (Yb, Er) co-doped systems [13–15], since Yb ~980 nm emission is coincident with the excitation energy of Er^{3+} to the second excited state. Recently, "quantum cutting" of solar spectrum photons by using RE^{n+}–Yb^{3+} couples (where RE^{n+} could be europium (Eu), terbium (Tb), cerium (Ce), or praseodymium (Pr) ions, etc.) [16–20] have also attracted great interest. In that process high energy solar photons are absorbed by the RE^{n+} and then down-converted into two or more lower energy Yb^{3+} photons, which are suitable for band-to-band transition in single crystal Si. The process can improve the photovoltaic conversion efficiency of Si-based solar cells. In the literature much attention has been on the energy transfer efficiency from oxide defects, Si nanostructures or RE^{n+} ions to Yb^{3+} ions. There have been fewer research reports on the structural evolution and the formation of Yb silicates in silica upon high temperature annealing which have relatively high luminescence efficiency. In this work, we have deposited Yb heavily doped Si oxide films and studied the relation between the film structure and its PL property, especially in the case of high temperature annealing, to investigate the formation and emission properties of Yb silicates. This research could contribute to the above mentioned Yb applications.

2. Experimental details

The Yb-doped silicon oxide films were deposited on Si substrate by magnetron sputtering two composite targets separately or jointly. One composite target was SiO_2 + Yb_2O_3 made by attaching pure quartz plates on the surface of an Yb_2O_3 target (with purity of 99.99%), and the other was Si + SiO_2 made by placing small Si pieces on a SiO_2 target (with purity of 99.99%). The sputtering conditions were identical during the film depositions. The base vacuum

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pressure was around 4.4×10^{-4} Pa and the working gas (argon) pressure was 1.2 Pa. The sputtering power applied on the targets was always 120 W. The Si substrates were rotated during deposition to obtain lateral uniformity. Thus, an Yb doped Si oxide film (labeled as sample K) was fabricated by sputtering only the SiO_2 + Yb_2O_3 target, and an Yb doped Si-rich oxide film (labeled as sample L) was grown by sputtering the SiO_2 + Yb_2O_3 and Si + SiO_2 targets jointly. The film thickness of sample K is ~760 nm and the concentrations of Si, O, and Yb in the oxide are 27.0, 57.5 and 15.5 at%, respectively, characterized by using Rutherford backscattering spectroscopy (RBS), while sample L has a film thickness of ~1500 nm, and the contents of Si, O, and Yb are 29.3, 55.0 and 15.7 at%. Note that the Yb concentrations of the two sample types are much higher than those typically reported in the literature for Yb doping. After deposition, all the Si wafers with films were cleaved into small sample pieces and heat treated at various temperature and gas ambience which will be indicated in the text.

The PL spectra were recorded by using a Lab RAM HR Microscopic Fluorescence Image System, where the visible to near-infrared PL was excited by using the 325 nm line of a He–Cd laser and detected by a spectrometer employing a charge-coupled device (CCD) array, while the excitation spectra were recorded with a FLS 980 fluorescence spectrophotometer equipped with a liquid nitrogen cooled PMT detector (R5509). The crystallinity of the films was investigated by X-ray Diffraction (XRD) (Rigaku D/MAX-2500). Transmission Electron Microscopy (TEM) including high resolution TEM (HRTEM) was used to investigate the distribution of crystalline material, and TEM equipped with energy dispersive X-ray spectroscopy (EDS) was used to investigate the distribution of elements and identify the formation of Yb silicates in the oxides. X-ray photoelectron spectroscopy (XPS) analysis was performed by using a Thermo Fisher Scientific USA ESCALAB 250 system with monochromatic Al Kα X-ray radiation (150 W). All the measurements were performed at room temperature.

3. Results and discussion

Fig. 1 shows the PL spectra of sample K annealed in flowing N_2 for 30 min at the temperatures as is indicated. There are three evident emission bands present on each spectrum with peak positions at around 425, 525, and 977 nm, respectively. The intensities of the 425 and 525 nm bands vary little with the anneal temperature increasing from 600 to 1000 °C, but decrease slightly upon 1100 and 1200 °C annealing, while the 977 nm band has increased after 1200 °C annealing and the shape of the band is quite different from what it is after the other temperatures anneals, which indicates the Yb ions exist in a different crystal field. These spectra also comprise small emission peaks at around 380, 616 and 755 nm independent of the anneal temperatures. For the origin of these bands, it is clear that the 977 nm peak is from the $^2F_{5/2}$–$^2F_{7/2}$ transition in Yb^{3+}.Yb^{3+} obviously has no direct transitions resulting in emission of visible photons given its simple energy level diagram, so for the other peaks we may search among Yb^{2+} and defects considering both the spectral positions and the annealing characteristics reported for similar systems. Defects (ODCs or NBOHCs) of the oxides could have such annealing characteristics as those of Fig. 1. The 425 nm band (as well as the 380 nm shoulder) is possibly from some ODCs which are normally responsible for the short-wavelength emissions in RE doped oxides. The 616 nm and 756 nm bands are likely both from NBOHCs, while the latter could be from a long-wavelength NBOHC formed due to interaction between an NBOHC and an impurity in glassy matrix [8]. The origin of the 525 nm band is in debate. It could be from some Si-ODC [10], but the band also matches the emission from Yb^{2+}. This will be discussed further in later paragraphs.

Fig. 2 presents the PL spectra of sample L after identical thermal treatments presented in Fig. 1 for sample K. Note that sample L has a higher Si concentration but nearly identical Yb concentration to those concentrations for sample K. It can be seen that after 600 °C annealing, three emission band- (or peak-) structures appear in the spectrum with positions located at 425, 517 and 977 nm, respectively, which is similar to those of sample K, but the emission intensities are relatively weak. The wavy structures seen superimposed on the spectrum are possibly interference fringes of the emitted light from the film. For increasing anneal temperature up to 1000 °C it is seen that the PL intensity from the film increases gradually, and the short-wavelength emissions become dominant. However, after 1100 and 1200 °C annealing, the PL intensities are enhanced significantly, the 517 nm band becomes the major emission of the film, and the Yb PL also have increased much.

Comparing Figs. 1 and 2, the variations of the PL spectra with anneal temperature are different for the two samples. Since the two samples have nearly identical Yb concentration in the oxides, then the differences could be related to the difference of Si content in the two films. Generally defects in silica and in Si-rich oxides are different [21], heavy Yb doping could further distort the Si oxide network and generate various defects in Si oxides [7,8,10,22]. The 525 nm band of sample K and the 517 nm band of sample L, could originate from some Si-ODC under lower temperature annealing (<1100 °C). After the high temperature annealing (1100 °C or beyond), the Yb PL of both samples K and L was significantly enhanced, which could be due to a common structural change in the two sample films. For example, structures containing Yb^{2+} sites could have formed and be responsible for the 525 nm and 517 nm

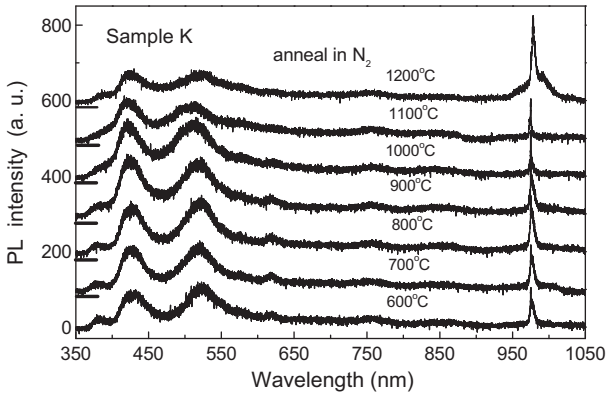

Fig. 1. The PL spectra of sample K annealed in N_2 for 30 min at the temperatures indicated.

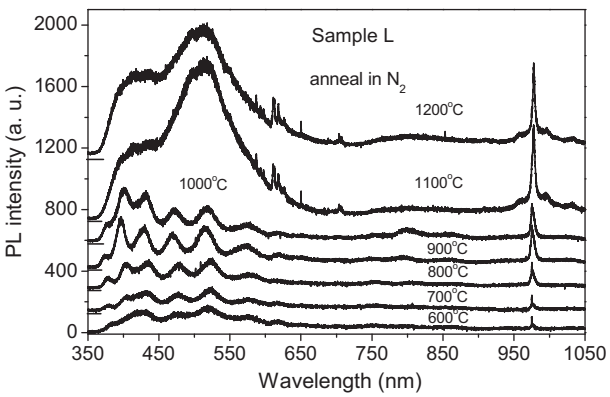

Fig. 2. The PL spectra of sample L annealed in N_2 for 30 min at the temperatures.