Available online at www.sciencedirect.com
ScienceDirect
Journal of Crystal Growth 305 (2007) 30–35
JOURNAL OF CRYSTAL GROWTH
www.elsevier.com/locate/jcrysgro

Tin-induced enhancement of photoluminescence and crystal growth in Si-rich silica films

C. Ma, L. Bi, J.Y. Feng*

Department of Materials Science and Engineering, Key Laboratory of Advanced Materials, Tsinghua University, Beijing 100084, PR China

Received 28 January 2007; accepted 28 January 2007
Communicated by M. Schieber
Available online 20 April 2007

Abstract

The effect of local Sn-doping on the photoluminescence (PL) properties of the Si-rich silica (SRSO) thin film was investigated. In order to dope Sn into the SRSO film, we introduced a Sn interlayer in the film. After annealing at temperatures higher than 1000 °C, the PL intensity of the Sn-doped samples was about 2 times higher than that of the undoped ones, while Sn-doped and undoped samples annealed at lower temperatures had almost the same PL intensities. The microstructure and mechanism of the PL improvement of this SiO_x/Sn/SiO_x system were analyzed by Raman scattering spectroscopy, Auger electron spectroscopy, and X-ray diffraction.

PACS: 68.35.Dv; 78.55.−m; 81.15.Cd

Keywords: A1. Crystallization; A1. Direct band gap; A1. Photoluminescence; A1. Sn-doping; B1. Si-rich silica films

1. Introduction

Due to the quasi-direct band structure and good compatibility with common microelectronic fabrication techniques, Si rich silica (SRSO) films are considered to have potential performance in Si-based optoelectronic devices. Ever since the first discovery of strong room temperature light emission from silicon nanostructures in 1990 [1], SRSO films and their properties have triggered great interest of many researchers in the past few decades [2,3]. However, the light emission property of this film is still not good enough to meet the requirements of practical application. One of the major problems is the low photoluminescence (PL) efficiency, which is due to the indirect band gap of Si nanocrystals (NCs). In order to gain a higher PL efficiency, a lot of attempts have been made such as doping rare earth (RE) [4,5], or metal elements [6,7], etc. Although the PL property has been improved by these methods, the PL efficiency is still not high enough for practical use because the indirect-band-gap structure of Si NCs is still unchanged.

Soref and Perry [8] had calculated the energy band of $Si_{1-x}Sn_x$. The result indicated that this binary system should have a direct band gap structure if given a proper x. Hence the major disadvantage of SRSO system of having an indirect band gap would be overcome if Sn atoms could be included into the Si-NC lattice. A direct band gap as well as a high PL efficiency that could meet the requirement of practical use might be obtained in Si-NC rich silica films. As far as we know there have been few reports about the PL property of Sn-doped SRSO system till now. This work tries to introduce Sn atoms into the Si NC lattice of SRSO films by adding a Sn interlayer in the film and annealing. The microstructure and PL properties of this system are also investigated.

2. Experimental details

A 250 nm thick layer of SiO_x, a 10 nm thin interlayer of tin and another 250 nm thick layer of SiO_x were deposited consequently onto the (1 1 1) oriented p-type Si substrate. The SiO_x layers were deposited by reactive RF magnetron

*Corresponding author. Tel.: +86 10 62771575; fax: +86 10 62771160.
E-mail address: fengjy@mail.tsinghua.edu.cn (J.Y. Feng).

0022-0248/$ - see front matter © 2007 Elsevier B.V. All rights reserved.
doi:10.1016/j.jcrysgro.2007.01.049

sputtering, while the tin interlayer was deposited by direct current sputtering. The background vacuum was better than 6×10^{-8} Torr before the deposition process started. A SiO_x layer of 250 nm was firstly deposited onto the substrate by sputtering a Si (99.9999%) target in an Ar and O_2 mixed atmosphere with a pressure of 3.75×10^{-3} Torr. The flow ratio of Ar/O_2 was fixed at 40/1. The x here was 1.5, which was measured by Auger electron spectroscopy (AES) and would be discussed later. Then a 10 nm Sn layer was deposited onto the $SiO_{1.5}$ layer in Ar ambient with a pressure of 7.5×10^{-3} Torr. Finally, a 250 nm $SiO_{1.5}$ layer was deposited on the Sn layer with the same experiment parameters as the first one. Thus the stacking sequence of the deposited films was $SiO_{1.5}$ (250 nm)/Sn (10 nm)/$SiO_{1.5}$ (250 nm)/substrate. The 500 nm thick $SiO_{1.5}$ films without tin interlayers were also prepared for comparison. In addition to samples deposited on Si substrates, samples of all these films deposited on SiO_2 substrates were also prepared for the Raman scattering spectroscopy analysis. The as-deposited samples were annealed in N_2 for 1 h with a pressure of 3.75×10^{-3} Torr at 600, 800, 900, 1000 and 1100 °C, in order to make Sn atoms diffuse into $SiO_{1.5}$ layers and let Si NCs crystallize.

PL spectra and Raman scattering spectra were measured using an XY triple spectrograph equipped with a liquid N_2-cooled CCD camera. The 514.5 nm line Ar^+ laser was employed to excite the luminescence with a spot of about 5 μm in diameter and excitation power of 0.047 mW. All the PL and Raman scattering spectra were taken at room temperature. AES was employed to investigate the depth profile of the elements. The sputtering rate was set as 30 nm/min. The phases and crystal forms were characterized by a D/max-rB X-ray diffractometer.

3. Results

3.1. Photoluminescence

Fig. 1 shows the PL spectra of $SiO_{1.5}/Sn/SiO_{1.5}$ and $SiO_{1.5}$ films after annealing in N_2 for 1 h at 600, 800, 900, 1000 and 1100 °C, respectively. The peak shapes of the $SiO_{1.5}/Sn/SiO_{1.5}$ samples are almost the same as those of the $SiO_{1.5}$ samples. Both of the Sn-doped and undoped samples annealed at temperatures below 900 °C show asymmetric PL peaks, which could be fitted into two Gaussian peaks. The peak positions of the $SiO_{1.5}/Sn/SiO_{1.5}$ films and those of the $SiO_{1.5}$ films are also the same at all the annealing temperatures. This result indicates that the PL mechanism of the $SiO_{1.5}/Sn/SiO_{1.5}$ films and that of the $SiO_{1.5}$ films are the same: the double peaks of samples annealed at temperatures lower than 900 °C originate from NBOHC (non-bridging oxygen hole center) defects and the Si═O related state at the boundary between the amorphous Si (a-Si) nanoclusters and SiO_2 matrix [10]. The PL peaks of samples annealed at temperatures higher than 1000 °C originate mainly from Si NCs, which would dominate the PL in SRSO films annealed at these temperatures [11]. Hence, Sn doping does not provide any new light-emitting center in our samples.

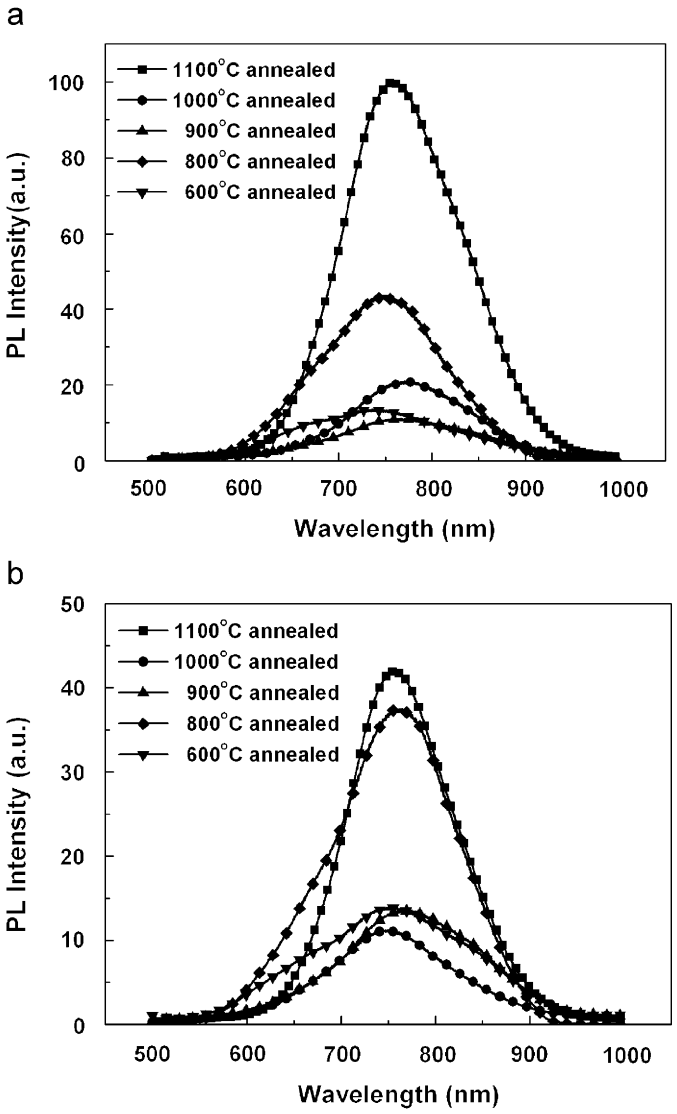

Fig. 1. PL spectra of (a) $SiO_{1.5}/Sn/SiO_{1.5}$ films and (b) $SiO_{1.5}$ films annealed at 600, 800, 900, 1000, 1100 °C, respectively.

While the PL peak positions of $SiO_{1.5}/Sn/SiO_{1.5}$ and $SiO_{1.5}$ films are almost the same at all the annealing temperatures, the PL intensities show interesting differences. Fig. 2 is the comparison of the PL intensities of $SiO_{1.5}/Sn/SiO_{1.5}$ and $SiO_{1.5}$ samples annealed at different temperatures. It is noteworthy that the PL intensities of $SiO_{1.5}/Sn/SiO_{1.5}$ are about 2 times higher than that of $SiO_{1.5}$ at annealing temperatures higher than 1000 °C, which are the annealing temperatures that Si NCs dominate the luminescence [11]. This phenomenon indicates that Sn-doping indeed improves the PL intensity of Si NCs in SRSO films. However, the PL intensities of the two groups of samples are almost the same at other annealing temperatures. The variations of the PL intensity with the annealing temperature also show no differences: The PL