The effect of annealing on the photoluminescence of Si/SiO$_x$

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Abstract: The photoluminescence (PL) of annealed porous SiO$_2$ film embedded by Si nanocrystals (Si-NCs) has been found emitting blue-light at room temperature deposited by plasma-enhanced chemical vapor deposition (PECVD) at near-atmosphere pressure. The SiO$_2$ films obtained by PECVD had rare Si-NCs embedded in them. The blue-light emission peak located at 418 nm of porous SiO$_2$ films was faint because their surface was passivated by hydrogen. In order to improve the PL intensity, the deposited films were annealed in primary gas at 500°C for 3 hours. Compared to unannealed films, the PL peak of annealed films shift from 418 nm to 397 nm, and the intensity strengthened obviously. The transmission electron microscopy (TEM) and Fourier transform infrared spectroscopy (FTIR) revealed that Si-NCs emerged after annealing while Si-H bonds decreased. Si-NCs were thought as the origin PL of 397 nm. The decrease of Si-H irradiative centers improved the PL intensity.

Key Words: Photoluminescence, Si nanocrystals (Si-NCs), annealing

1. Introduction

The discovery of efficient room-temperature photoluminescence (PL) from Si nanostructures such as porous Si [1] and Si ultrafine particles [2] has stimulated a worldwide research. Si nanocrystals (Si-NCs) embedded in SiO$_x$ (Si/SiO$_x$) are considered as one of the most promising Si-based light-emitting materials because of their appreciable and stable light emission, as well as their robust structure. In recent years, plasma-enhanced chemical vapor deposition (PECVD) is often used to prepare SiO$_x$ films. Compared with the conventional CVD method, the deposition temperature of PECVD is lower, and the optical and electrical properties of the films are accommodated easily by changing the process parameters [3,4]. Si/SiO$_x$ is usually prepared by thermal annealing of amorphous silicon suboxides (a-SiO$_x$, 0<x<2) deposited by various methods [5–10], since a-SiO$_x$ is thermodynamically unstable.
and a chemical disproportionation reaction takes place upon high temperature annealing, leading to the formation of Si/SiO$_x$[6,11].

In this paper, the blue emission characteristics of as-prepared and annealed Si/SiO$_x$ were investigated. It was found that the blue emission intensity was dependent on the Si-NCs after annealing. After coating with annealing, the intensity increased.

2. Experiment

In the experiments, the plasma discharge zone was formed and concentrated between two paralleled comb electrodes supplied with 20kHz, 7500V high voltage. The substrate was put 2 cm away from the plasma zone along the downstream direction of the carrier gases. Silane (SiH$_4$) was used as the precursor gas and carried into the system by a mixture of argon and hydrogen (Ar:H$_2$=95:5). The flow rate of SiH$_4$ and the carrier gas was fixed at 20 sccm and at 2L/min respectively through mass flow controllers. The operation pressure was kept at 200 Torr. The deposition time was 5 minutes for all the samples. Because of higher pressure, the deposited SiO$_x$ film obverses porous. After deposition, the SiO$_x$ film was annealed in primary gas at 500$^0$C for 3 hours.

PL experiment was performed by HITACHI F-4500 Fluorescence Spectrophotometer with an excitation wavelength of 320 nm. The crystallinity of deposited nanomaterials was characterized with Hitachi H — 800 transmission electron microscopy (TEM). The deposited films were scraped from substrate and mixed with KBr powder and characterized by NEXUS — 670 Fourier transform infrared spectra (FTIR) for their chemical structure.

3. Results and discussions

Fig.1 depicted the PL spectra of the as-prepared and the annealed Si/SiO$_x$ films. The PL spectrum of as-prepared Si/SiO$_x$ film exhibited the broad peak from 400nm to 470nm, whose center located at 418nm. After annealing at 500$^0$C for 3 hours, the intensity of the sample was stronger than that of the as-prepared one. Furthermore, the PL center blue shifted to 397nm, which was reported in paper [12].

The FTIR spectrum of the as-prepared and the annealed Si/SiO$_x$ films was shown in Fig.2. The peaks at around 1083 cm$^{-1}$, 820 cm$^{-1}$ and 460 cm$^{-1}$ were from Si-O-Si stretching modes [13]. The oxygen might originate from the survived water in pores of the porous SiOx

![Fig.1. PL spectra of as-prepared and annealed Si/SiO$_x$.](image-url)
films or the survived oxygen in reactant gas. The absorption peak at 621 cm\(^{-1}\) originated from the Si-Si bonds vibration on the surface and near surface region of SiO\(_x\) film [14]. 875 cm\(^{-1}\) was related to the Si-H vibration because hydrogen was absorbed on the surface of the porous SiO\(_x\)[15]. It could be seen that the intensity of the Si-O-Si modes increased after annealing, indicating that the porous SiO\(_x\) was more oxidized during annealing. Moreover, the intensity of Si-H decreased after annealing, meaning that hydrogen on the surface was desorbed during annealing.

TEM analysis was performed to confirm the formation of Si-NCs in the SiO\(_x\) after annealing. Fig.3 (a) revealed that no crystal was observed before annealing, SiO\(_x\) was amorphous. Such tiny Si-NCs exhibited diameters of only 1.6-2.0 nm after annealing Si/SiO\(_x\).

Before annealing, 418 nm PL originated from the oxygen bonds within the film before annealing-induced regrowth [16]. Amorphous SiO\(_x\) possessed huge number of Si-H dangling bonds, which can also act as radiative centers. After annealing, the amorphous SiO\(_x\) crystallized into crystalline silicon. Blue shift to 397 nm of PL came from Si crystalline quantum dots. It was well known that the unstable Si-H dangling bonds were progressively replaced with more stable Si-O-Si bonds during annealing, so in FTIR spectrum of as prepared and annealing porous Si/SiO\(_x\), the peak related to Si-H mode almost disappeared after annealing. Meanwhile, Si-H bonds as radiative centers on the surface were passivated. That is why the TEM images of (a) as-prepared and (b) annealed Si/SiO\(_x\).

![Fig.2. FTIR spectra of as-prepared and annealed Si/SiO\(_x\)]()
PL intensity increased after annealing [17].

4. Conclusion

The blue emission from porous SiO$_x$ as-prepared and annealed was reported. The intensity of PL increased and blue shift at the same time during annealing. Si-NCs emerging after annealing were thought as the origin PL at 397nm. The decrease of Si-H irradiative centers improved the PL intensity.

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