

Chapter 4 3-D Si Nano-dots/SiO₂ arrays: Fabricated By Ion

Implantation

4-1. Introduction

Mesoporous silica (MS) film is naturally with high surface-areas, contributed from regularly distributed, and uniformly nanopores (2-10 nm) [12], and material characteristics on inner-pore-channel interfaces are chemically, and physically modulated. The MS matrix as host inherently provides three-dimensional quantum-sized environments for doping in them. In this chapter, we demonstrate the high efficiency in luminescence from Si quantum-dots-embedded mesoporous nanoscaled silica matrix by low energy (~15 KeV) silicon ion implanted process to take as the new type photonic emitters. Regularly arranged pores in mesoporous silica materials as photonic emitters and the photoluminescence of blue-white are demonstrated with high cross-section of radiative recombination at Si/SiO₂ interfaces due to their natural structures. Therefore, the silicon ion implant methods significantly improve the Si quantum-dots-embedded-in-nanoscale silica photonic emitter with intensely naked-eye visible photoluminescence.

4-2. Ion implantation process

4-2.1 Spatial dimension of pore nature of MS films

Molecularly templated mesoporous silica (**MS_{as}**) films is firstly synthesized using sol-gel-prepared precursors with different organic templates for the control of pore size (2-5 nm), spin-coated on silicon wafers, followed with baking at 110⁰C for 1h. Organic-template in samples is removed with furnace annealing (FA) in nitrogen at 400⁰C for 1h which resulting in the mesoporous silica (MS) films. X-ray diffraction (XRD) was used to study the pore nature of the MS films. And the pore diameters of MS films were determined by the desorption branch of Kr adsorption-desorption isotherms (shown in Figure 4-1). The thickness of pore wall (spacer~1.4 nm) was estimated by assuming mesoporous channels packed in hexagonal symmetry and the following the equations of thickness of pore wall= pore-to-pore distance (a_0) – pore diameter and $a_0 = 2 \times d_{100} / \sqrt{3}$ where d_{100} is the d-spacing obtained by XRD 0-2 θ

scanning and the average pore size of the MS films after calcinations process was measured by Kr adsorption.

4-2.2 Si implantation with different dosages and energies

The MS films are then doped with Si^+ implantation at dosages of 10^{13} - 10^{16} ions/ cm^2 and energies of 15-80 KeV. The post-doping anneal (PA) with nitrogen at 900°C is performed for 1h, which will help the activation of irradiative defects and the elimination of carrier trapping centers, and also leads to the precipitation of Si nanocrystals (nc-Si) buried in the SiO_2 or SiO_x ($x < 2$) matrix. Room-temperature photoluminescence (PL) for all samples are obtained with excitation of He-Cd laser (325 nm) at 300 W/cm^2 .

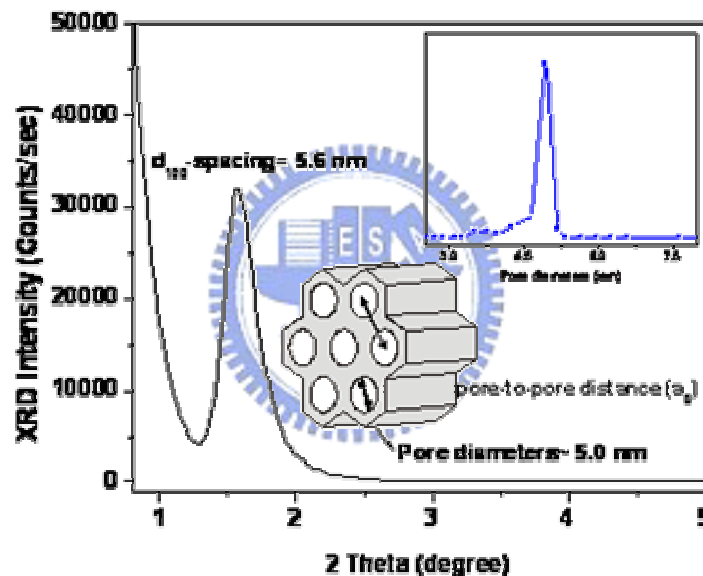


Fig. 4-1: Spatial dimension of pore nature of MS films after calcined process was characterized by X-ray diffraction and desorption branch of Kr adsorption-desorption isotherms.

4-3. Room-temperature PL spectra of $\text{SiO}_2:\text{Si}^+$ and $\text{MS}:\text{Si}^+$

4-3.1 PL spectra of implantation samples

Some peaks (415, 460, and 580 nm) on those PL spectra are respectively attributable to the irradiative defects of two-fold-coordinated silicon lone-pair center related species (SLP) [$:\text{Si}:$] [17], neutral oxygen vacancy (NOV) [$\text{O}_3\equiv\text{Si}-\text{Si}\equiv\text{O}_3$] [16-17], and nonbridging oxygen hole center (NBOHC) [$\text{O}_3\equiv\text{Si}-\text{O}\bullet$] [9]. The PL

spectroscopic properties of the mesoporous silica films are found to be similar to those of surface-oxidized silicon nanocrystals (nc-Si) materials. Referring to photoluminescence (PL) study for Si-implanted SiO₂ matrix (SiO₂:Si⁺), high-temperature-N₂ annealing to form the silicon nanocrystals as irradiative centers is a key step as shown in Fig. 4-2. The Si ion implantation has introduced enormous irradiative defects in the MS and SiO₂ films. The Si and O related-defect species produce on the nc-Si and SiO₂ matrix have been identified as the dominant defects in Si-based doping silica films for the visible light emission [25], while the emission at longer wavelengths are contributed by the nc-Si embedded in the SiO₂ matrix due to the quantum confined effect [26].

4-3.2 Discussion of PL spectra of implantation samples

It is reasonable that the two discrepant mechanisms with different emission ranges may occur in Si-based doping silica material. But, most of the work discussed the nc-Si correlated photoluminescence (PL) characteristics. Recently, the identification of defect category in Si-ion-implant SiO₂ films was intrigued due to the observed stable blue emission at 400-500 nm [7,27]. However, the implanting Si into MS matrix (MS:Si⁺) reveals several interesting phenomena (Fig. 4-2) that the hundred lower Si-dosages in MS (40 KeV, 10¹⁴cm⁻²) without post-furnace-annealing in N₂ environment (PA (N₂)) can emit stronger PL than SiO₂:Si⁺ (40 KeV, 10¹⁶cm⁻²) followed with PA (N₂). The PL spectrum was enhanced obviously for the SiO₂:Si⁺ sample by post-annealing thermal activation, and this phenomenon was not found in the MS:Si⁺ film. However, the excess doping in SiO₂ with post-annealing generates numerous non-nanoscaled precipitations by silicon agglomeration, leading to red-shift in PL [6], or even leaving many non-irradiative centers.

In comparison, the nanoscaled spatial confinement effect within the silica matrix of MS film will directly form Si/nanoscale silica interface (naturally forms nanoscale Si/SiO_x structures within the nanoscale silica matrix of the MS films) without the assistance of post-annealing and allow the usage of high dosages without losing the control of emission-spectra and luminescence efficiency, as evidenced from the PL of MS:Si⁺ (15 KeV, 10¹⁶ cm⁻²). Therefore, low implantation energy is adopted herein for optimizing dopant distribution in MS film with high porosity and for eliminating the damage of MS film at high energy and high dosages implantation.

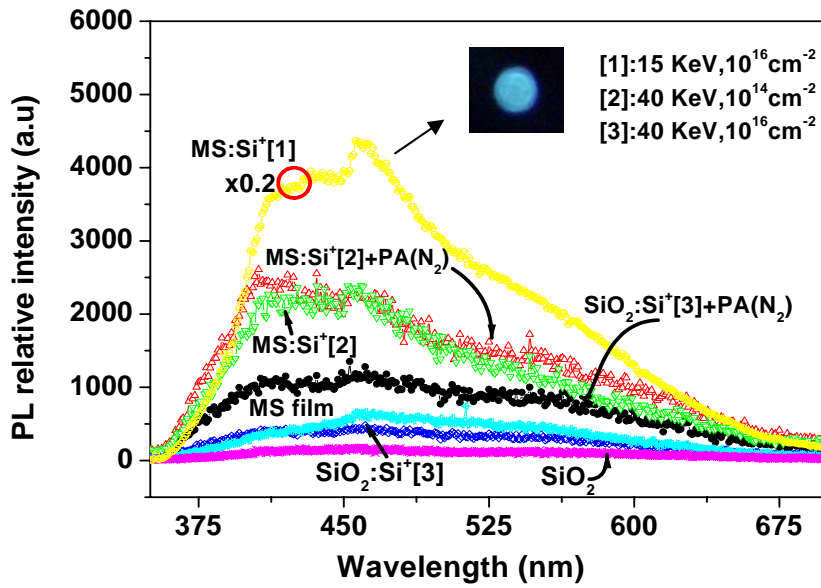


Fig. 4-2: Photoluminescence (PL) spectra of the MS films and SiO₂ film doping by multiple energy and dosages of silicon ion implantation.

4-3.3 The best condition of implantation samples

The PL intensities at 460nm peak for SiO₂:Si⁺ and MS: Si⁺ samples vary with multiple-recipe Si ion-implantation processes at different dosages and energies, as shown in Fig. 4-3. The dominant PL peak from MS films implanted with high dosages coincides with neutral oxygen vacancy (NOV) related PL irradiative centers due to the fact that those external Si-nanoclusters crossed with the nanoscale silica matrix to form a rich-Si-modulated-SiO_x environment. For SiO₂, PL peak intensity at 460 nm increases with implanted dosages shown in Fig. 4-3 (a) and is almost invariable with implanted energy shown in Fig. 4-3 (b). But for MS films, PL peak intensity at 460 nm increases with implanted dosages at low implanted energy (~15 KeV) and reduces with implanted dosages at high implanted energy (>40 KeV) shown in Fig. 4-3 (a). Lower implantation energy (~15 KeV) is adopted herein for optimizing dopant distribution in MS film and for eliminating the damage of MS film at high energy and high dosages implantation. Therefore, the best condition for PL peak intensity at 460nm is implantation energy at 15 KeV and implantation dosage at 10¹⁶ cm⁻².

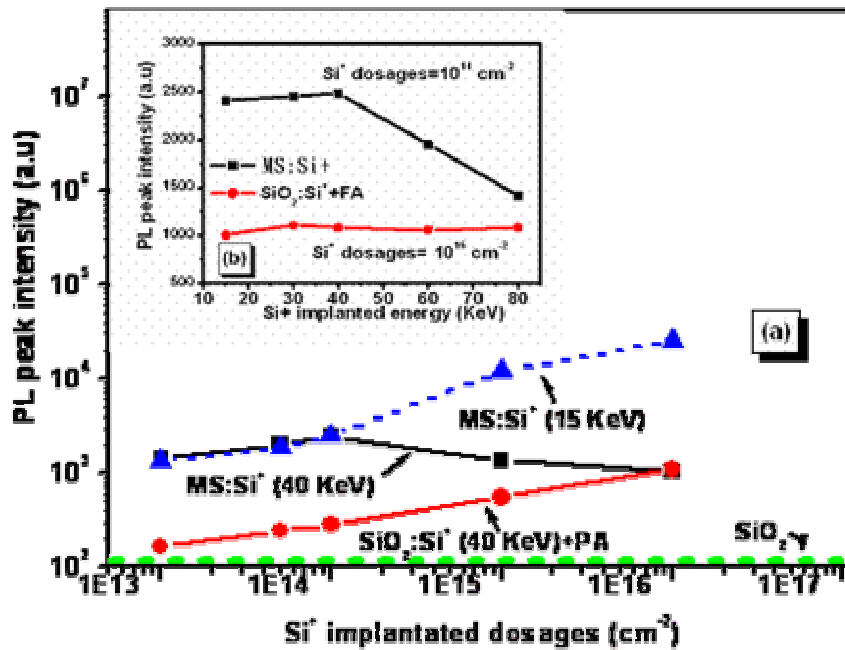


Fig. 4-3: The PL intensity at 460nm peak for SiO₂:Si⁺ and MS:Si⁺ samples variation with multiple-recipe Si ion-implantation processes at different dosages and energies.

4-4. Conclusion

We demonstrated the high surface area nature of mesoporous silica film and low energy (~15 KeV) silicon ion implanted methods show naked-eye visible photoluminescence. At the same implanted dosage (10¹⁶ cm⁻²), PL peak intensity at 460nm in MS:Si⁺ is tenfold higher than that in SiO₂:Si⁺+PA. For high-dosage-implanted MS matrix, low implantation energy is adopted for eliminating the damage.