

Chapter 6 3-D Si Nano-dots/SiO₂ arrays: Fabricated By Pulse

ICP-CVD

6-1. Introduction

Mesoporous silica (MS) naturally has highly surface-areas, contributed from regularly distributed nanopores (2-10 nm) [12], thus being a well three-dimensional (3-D) nanotemplate for accommodating NCs. Although the feasibility of synthesizing semiconducting NCs within MS matrices by CVD [14] and co-operative self-assembly (SA) [28] has been demonstrated, current methods for forming NCs/silica arrays are sensitive to the chemistry of precursors and are time-consuming. In this chapter, we use a Pulse high-density inductively coupled plasma (ICP) process [34] to synthesize densely and uniformly Si (Ge) NCs within MS nanotemplates. A constructed enormous Si (Ge) NCs/silica arrays is an efficient blue-luminescent nanomaterial.

6-2. Pulse ICP-CVD process

6-2.1 Fabrication of MS_{as} films

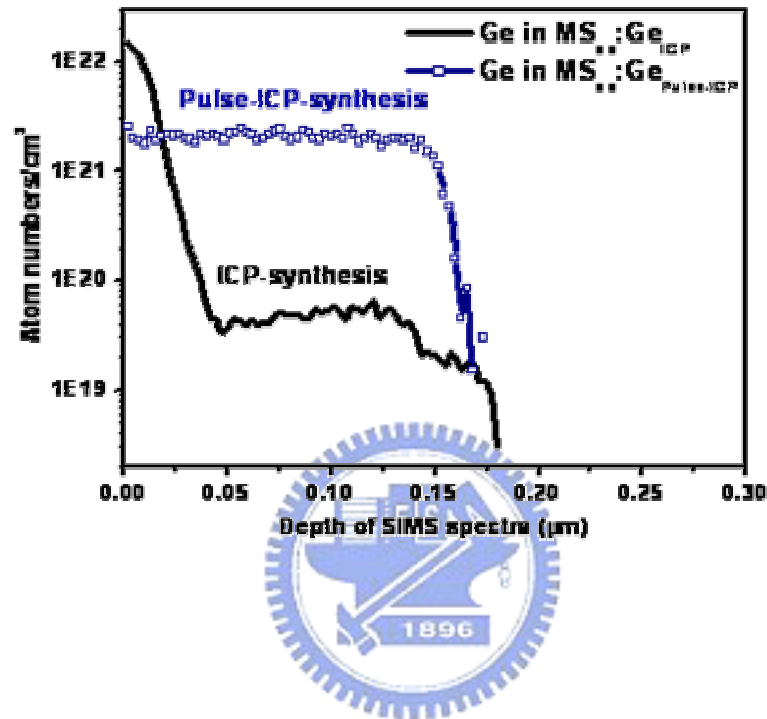
Molecularly templated mesoporous silica (MS_{as}) films are spin-coated on silicon wafers, using sol-gel-prepared precursors that contain the organic template [15] of the triblock copolymer Pluronic P-123 (with a pore-size of ~5 nm). Sequentially, those samples were doped with Pulse-ICP or pure ICP modes using hydrogen diluted SiH₄ (GeH₄) (H₂/SiH₄ ~200), denoted as MS_{as}:Si (Ge)_{Pulse-ICP} and MS_{as}:Si (Ge)_{ICP}. The thickness of two films was ~300 nm and substrate temperatures are both 400°C.

6-2.2 TEM image and Ge-related SIMS spectra

The cross-sectional TEM image and the germanium-related SIMS depth profile for MS_{as}:Ge_{Pulse-ICP}, as shown in Fig. 6-1, verify the existence of 3-D Ge NCs formed by Pulse ICP-CVD in MS_{as} matrices. With reference to the germanium-related SIMS depth profiles for MS_{as}:Ge_{Pulse-ICP}, and MS_{as}:Ge_{ICP} plotted in Fig. 6-1, the mean densities D_{Ge} of the dispersed NCs in those mesostructured films are calculated to be of about $8.0 \times 10^{18}/\text{cm}^3$, and $1.0 \times 10^{18}/\text{cm}^3$, respectively; the results indeed change like

the peak intensities of photoluminescence (PL) from those samples, as shown on Fig. 6-2a. The average sizes of the doped NCs, 2-5 nm, as determined by TEM (only showing the TEM image of $MS_{as}:Ge_{Pulse-ICP}$ on Fig. 6-1), are used to estimate D_{Ge} . Figure 6-2b shows the picture of naked-eye visible blue-PL from $MS_{as}:Si_{Pulse-ICP}$.

(a)



(b)

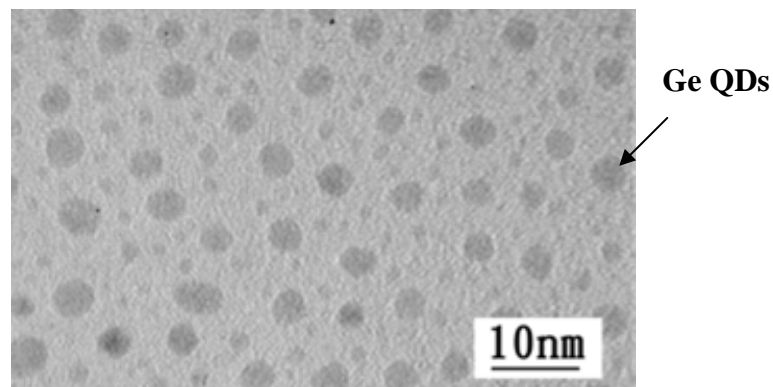
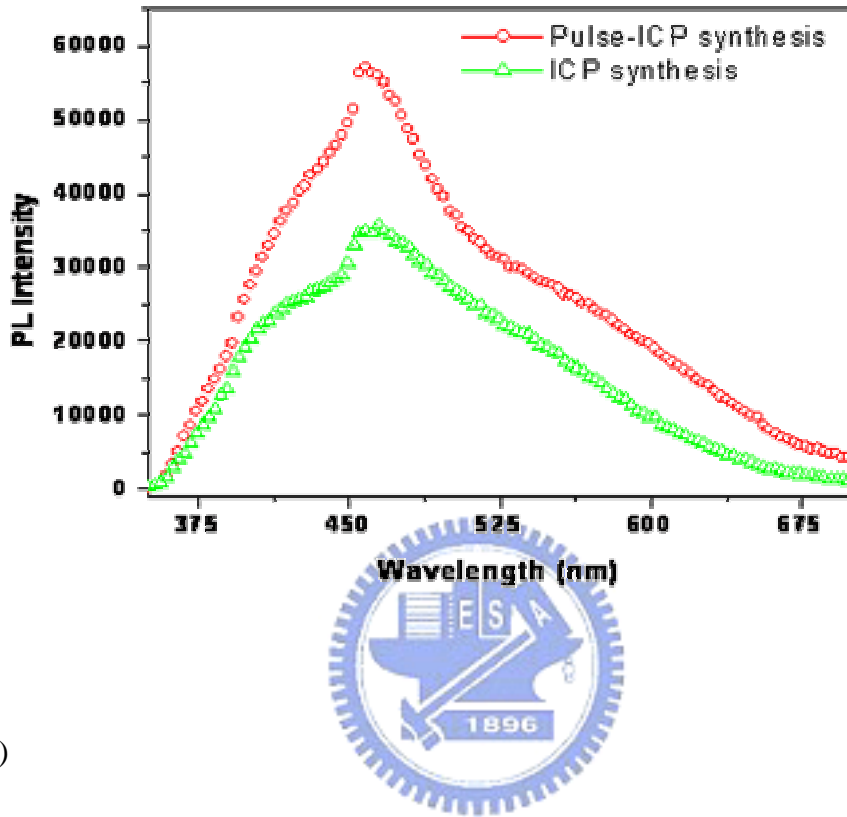


Fig. 6-1: (a) Secondary ion mass spectrometry (SIMS) depth profiles for $MS_{as}:Ge_{Pulse-ICP}$ and $MS_{as}:Ge_{ICP}$ films, and (b) cross-sectional transmission electron microscopy (TEM) image of $MS_{as}:Ge_{Pulse-ICP}$ film for identifying the existence of Ge nanodots and high-density distribution within the mesoporous silica film by Pulse ICP-CVD process.

(a)



(b)



Fig. 6-2: (a) PL spectra of mesostructured film (MS_{as}) doped with Si nanodots by high-density ICP and Pulse-ICP process. (b) Picture of naked-eye visible blue-white photoluminescence from $MS_{as}:Si_{Pulse-ICP}$.

6-3. Mechanism of Pulse ICP-CVD-based 3-D NCs-synthesis

6-3.1 Mechanism of 3-D NCs-synthesis

The mechanism of Si_n (Ge_n) NCs formed in the nanopores of the MS matrices using a Pulse ICP-CVD process involves numerous reactions. Firstly, the pure- H_2 -ICP-plasma (step-A of Fig. 6-3) removes organic-templates of MS matrices lightly for enabling limited nucleation sites of Si-OH on pure-surfaces. Sequentially, ICP-dissolved SiH_n (GeH_n) species (step-B of Fig. 6-3) in the form of nanoclusters diffuse into the nanopores, and are then absorbed and embedded in the residual organic-template of MS_{as} , eventually reacts with the nucleation sites [14]. Therefore, both self-limiting reaction [34] and hydrogen-elimination reaction (HER) [14] govern the conversion of ICP-dissolved species in mesostructured films into Si_n (Ge_n) NCs. Precise controls for Pulse ICP-CVD makes $\text{MS}_{\text{as}}:\text{Si}$ (Ge)_{Pulse-ICP} as an efficient blue-luminescent nanomaterial.

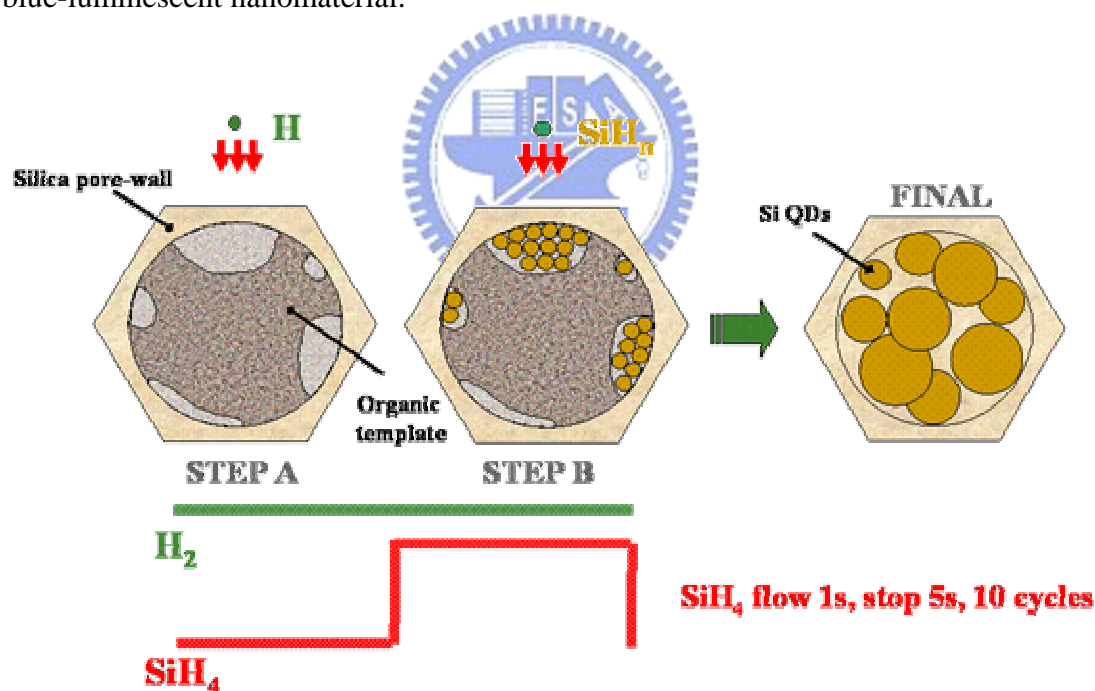


Fig. 6-3: Schematic mechanism of 3D Si nanodots formed by a pulse high-density inductively coupled plasma (ICP) process.

6-3.2 XPS spectra of Ge NCs/Silica arrays

XPS spectra (3d levels) of $MS_{as}:Ge_{Pulse-ICP}$ is shown in Fig. 6-4. For this 3d level, the spectrum is split in two contributions related to the Ge-Ge and Ge-O bonds. The evidence of the presence of suboxidized GeO_x structure, juxtaposed with Ge still remaining in the Ge NCs, confirms surface-states of high-quality Pulse ICP-CVD NCs/oxide interfaces (Ge=O) as dominant photoemission centers.

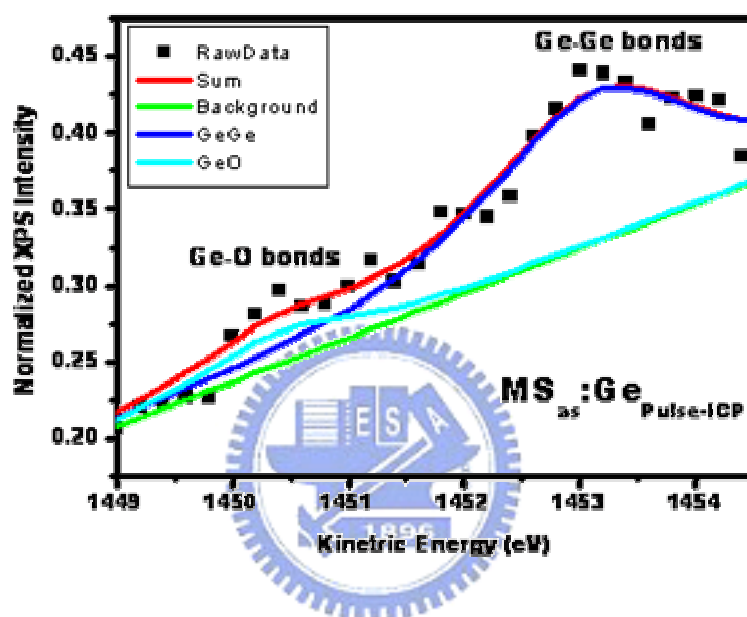


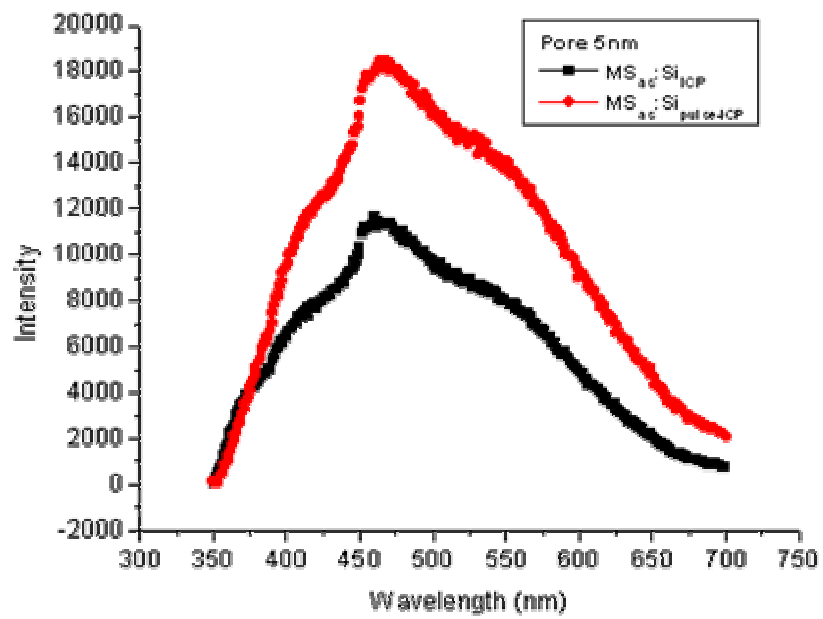
Fig. 6-4: X-ray photoelectron spectroscopy (XPS) of the Ge NCs/Silica arrays formed by Pulse ICP-CVD process.

6-4. RT PL spectra with different pore size and thickness

6-4.1 PL spectra with different pore size

For comparison, we use cetyltrimethylammonium bromide (CTAB) template (with a pore-size of ~2 nm) instead of triblock copolymer Pluronic P-123 (P123) template (MS_{as} film thickness was the same ~300 nm). Fig. 6-5 shows room-temperature photoluminescence spectra with difference pore. Pulse ICP-CVD process enhances PL total intensity more conspicuously in CTAB template than in P123 template. It presumes that hydrogen diluted SiH_4 (GeH_4) of pure ICP process flow into pore with difficulty for small pore (2 nm). Reversely Pulse ICP process is self-limiting reaction, so vapor flow into pore easily.

(a)



(b)

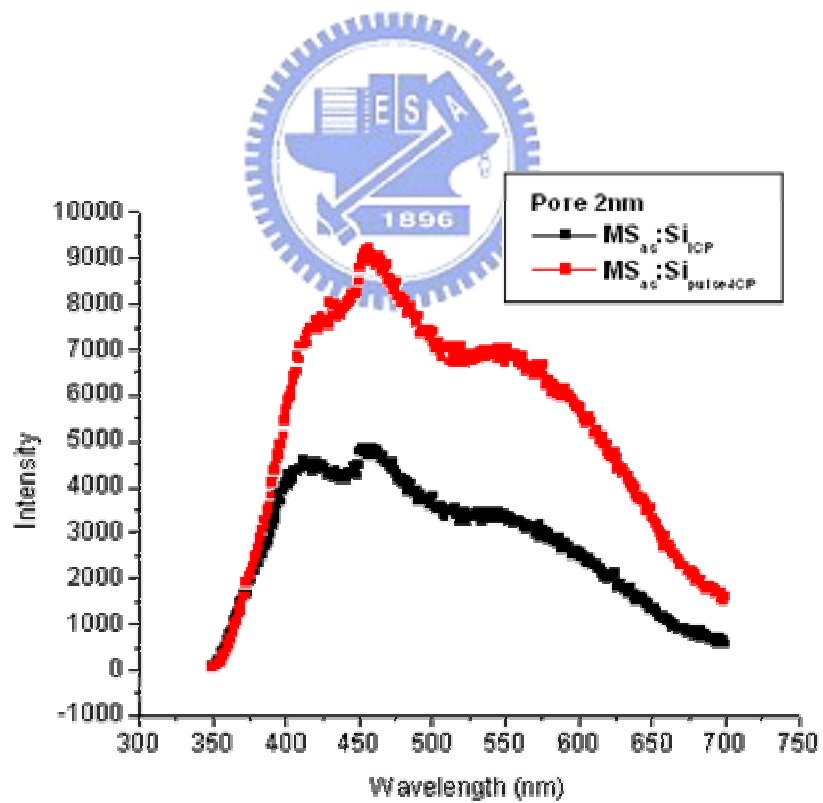


Fig. 6-5: (a) Room-temperature photoluminescence spectra with pore-size 5 nm (b) Room-temperature photoluminescence spectra with pore-size 2 nm.

6-4.2 PL spectra with different thickness

We change molecularly templated mesoporous silica (MS_{as}) film thickness (~ 90 nm) and spin-coated on silicon wafer (pore-size was the same ~ 5 nm). Fig. 6-6 shows room-temperature photoluminescence spectra with difference thickness.

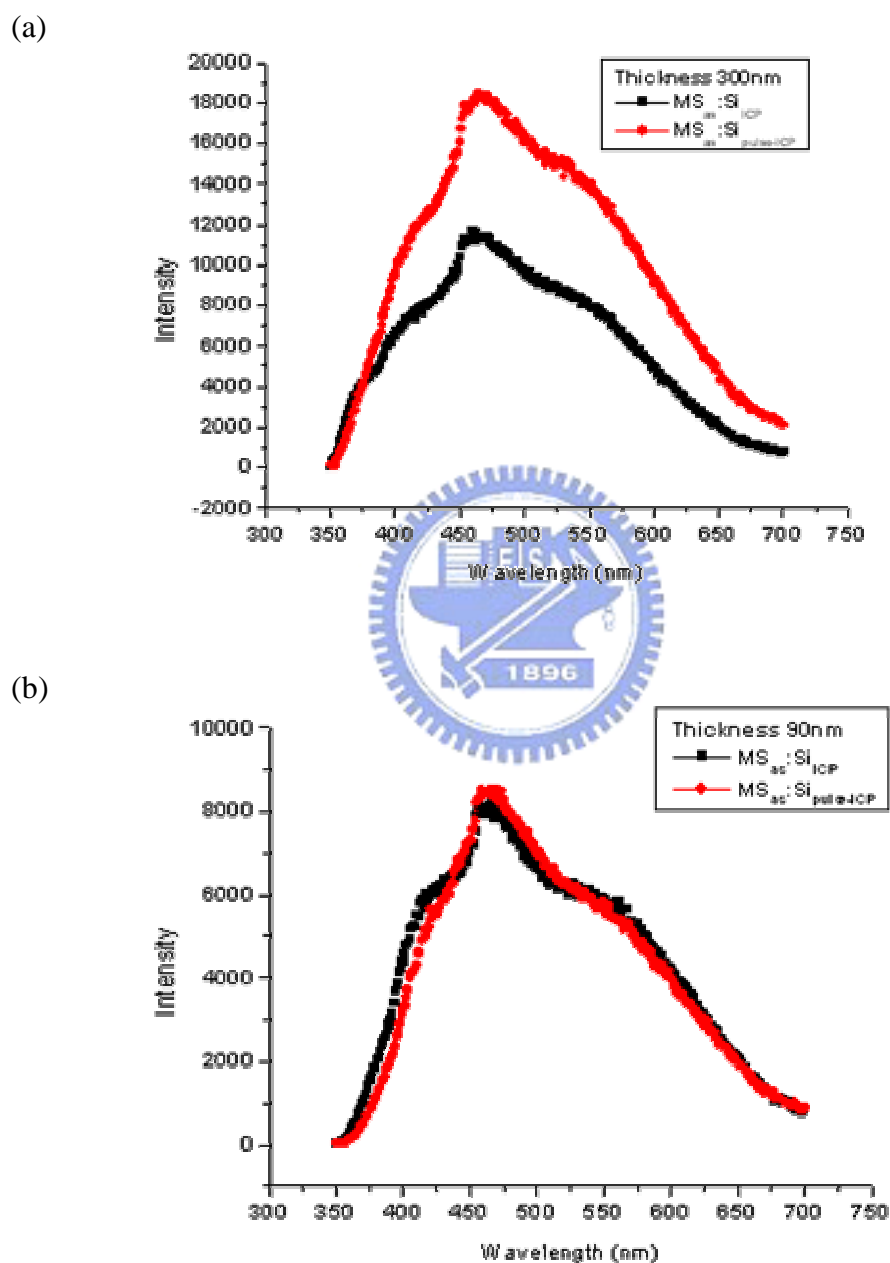


Fig. 6-6: (a) Room-temperature photoluminescence spectra with thickness 300 nm (b) Room-temperature photoluminescence spectra with thickness 90 nm.

Pulse ICP-CVD process is almost no effect in thin film. This phenomenon presumes two possibilities. One is that nanodots are saturated in MS_{as} film whether for pure ICP process or for Pulse ICP process. The other is that the parameter of Pulse ICP process is not suitable. Because there are lower templates in thin film, pure-H₂-ICP-plasma maybe removes organic-templates of MS matrices fast for this parameter. Therefore, new parameters of Pulse ICP process maybe obtain to enhance PL intensity for thin film.

6-5. Conclusion

We establish the feasibility of applying integrated-circuit (IC) compatible skills to construct efficiently blue-white Si light sources. The core-concept is the formation of 3-D semiconducting NCs in the MS matrices by a Pulse ICPCVD-based NC-synthesis method. Those densely dispersed Si (Ge) NCs have good interfaces with nanopores/silica arrays, thus forming Si (Ge) NCs/silica arrays as blue-light emission centers.

