Chapter 5 3-D Si Nano-dots/SiO_2 arrays: Fabricated By ICP-CVD

5-1. Introduction

Mesoporous silica (MS) materials have enormous nanopores/silica arrays [12] as luminescent centers [9]. Furthermore, such three-dimensional (**3-D**) nanopores/silica arrays can accommodate dense nanomaterials [14,28]. The feasibility of synthesizing semiconducting and metallic NCs within MS matrices by chemical vapor deposition (**CVD**) [14] and self-assembly [28] has been demonstrated. However, current methods for forming NCs/silica arrays are sensitive to the chemistry of precursors and are time-consuming. High-density plasma (**HDP**)-based synthesis yields reactive species with a high diffusion capability and reduces damage to reacting-interfaces. The process simply controls the grain sizes (crystallinity) of the synthesized materials, as recently shown [29]. The method represents a new means of uniformly and densely doping nanocrystalline materials within an MS matrix. This chapter reports the synthesis of 3-D Si (Ge) NCs in mesoporous silica films using high-density plasma. Those semiconducting NCs/silica arrays exhibit extremely efficient blue-white luminescence.

5-2. ICP-CVD process

5-2.1 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 of the triblock copolymer Pluronic P-123 (**P123**); they are then baked at 110°C for 1 h [15]. The precursor solution was prepared by adding an ethanol solution of P123 to the silica sol-gel, which was made by refluxing a mixture of tetraethylorthosilicate (TEOS), H_2O, HCl, and ethanol at 700C for 90 min. The molar ratios of reactants were 1:0.008-0.03:3.5-5:0.003-0.03:10-34 (TEOS/P123/H_2O/HCl/ethanol). Some MS_{as} films are treated with hexamethyldisilazane (**HMDS**) vapor at 160°C to minimize the number of Si-OH groups on pore-surfaces by a silylating reaction [15]; such films are denoted as **$MS_{as+HMDS}$**. An organic-template in mesostructured films is calcined by furnace annealing (FA) for 1 h in hydrogen environment at 400 ℃, yielding an MS film (with a pore-size of ~5 nm and a pore-wall of ~1.5 nm [15]).

5-2.2 Comparison of different doping methods

For comparison, thermal silicon oxide (SiO_2) was also deposited. Those samples were then doped with Si (Ge) NCs using high-density inductively coupled plasma (**ICP**), plasma -enhanced-CVD (**PECVD**) or implantation. The thickness of all films was ~300 nm. Table **I** summarizes the parameters associated with those NC-synthesis methods.

	MS_{as}:Si_{ICP}	$MS_{as+HMDS}$:Si_{ICP}	MS:Si_{ICP}	MS_{as}:Si_{PECVD}	MS:Si_{IMP}	SiO_2:Si_{IMP} (Ref. 6)
H_2/SiH_4 or GeH_4 (sccm)	50-200/1	50-200/1	50-200/1	50-200/1		
Chamber pressure (mTorr)	~5	~5	~5	~600		
Substrate temperature (^{0}C)	400	400	400	400		
RF power (W)	600	600	600	300		
Implantation dosages (cm^{-2})					10^{13}-10^{17}	$3x10^{16}$-$3x10^{17}$
Implantation energy (KeV)					15-80	160
Normalized peak intensity of PL	600	190	45	85	150	60
Average densities of doped NCs (10^{18}1/cm^3)	1	0.5	0.1	0.18		

Table I : Comparison of NC-synthesis parameters and luminescent performance for mesostructured materials in this study with those of oxide doped with Si by implantation as reported in Ref. 6. The normalized peak intensity of PL for all materials is obtained using the peak intensity of PL for oxide as the normalizing factor.

5-2.3 Analysis of those samples

Fourier transformation infrared spectroscopy (FTIR) was used to monitor the organic template content in the samples. Secondary ion mass spectrometry (**SIMS**) and high-resolution scanning transmission electron microscopy (**STEM**) were employed to identify NCs in mesostructured materials. The room-temperature photoluminescence (**PL**) for all samples was measured using an excitation He-Cd laser (325 nm) at 300 W/cm^2.

5-3. RT PL spectra and other material analysis

5-3.1 PL spectra of those samples

MS materials have intrinsic nanoscaled silica structures, and so are similar to surface-oxidized silicon NCs as irradiative centers [9,15]. The main peak (460 nm) on the PL spectrum of MS (curve a of Fig. 5-1) is attributable to the irradiative defects of neutral oxygen vacancies (**NOV**) [≡Si-Si≡] [15-16].

The brilliant blue-white PL presented in the inset of Fig. 5-1 is for the MS_{as} matrix treated with ICP, using silane-based precursors (**MS_{as}:Si_{ICP}**). The nanoscaled Si_n/SiO_m composites can be regarded as having the rich-Si-modulated-SiO_2 structure, which originates NOV-related PL, so this bright blue-white PL image implies that a large amount of ICP-synthesized silicon NCs are present in MS_{as}:Si_{ICP}.

5-3.2 Examining existence of nanocrystals

For distinguishing dopants from Si, and O contents of mesostructured materials, we synthesized Ge NCs instead of Si NCs within MS_{as} and examined the existence of those NCs using STEM and SIMS.

The d-spacing of 2.35Å ($Ge_{<211>}$) analyzed from the lattices in the marked regions of the cross-sectional STEM image and the germanium-related SIMS depth profile for MS_{as}:Ge_{ICP}, as shown in Figs. 5-2 and 5-3, verify the existence of 3-D Ge NCs formed by ICP in MS_{as}.

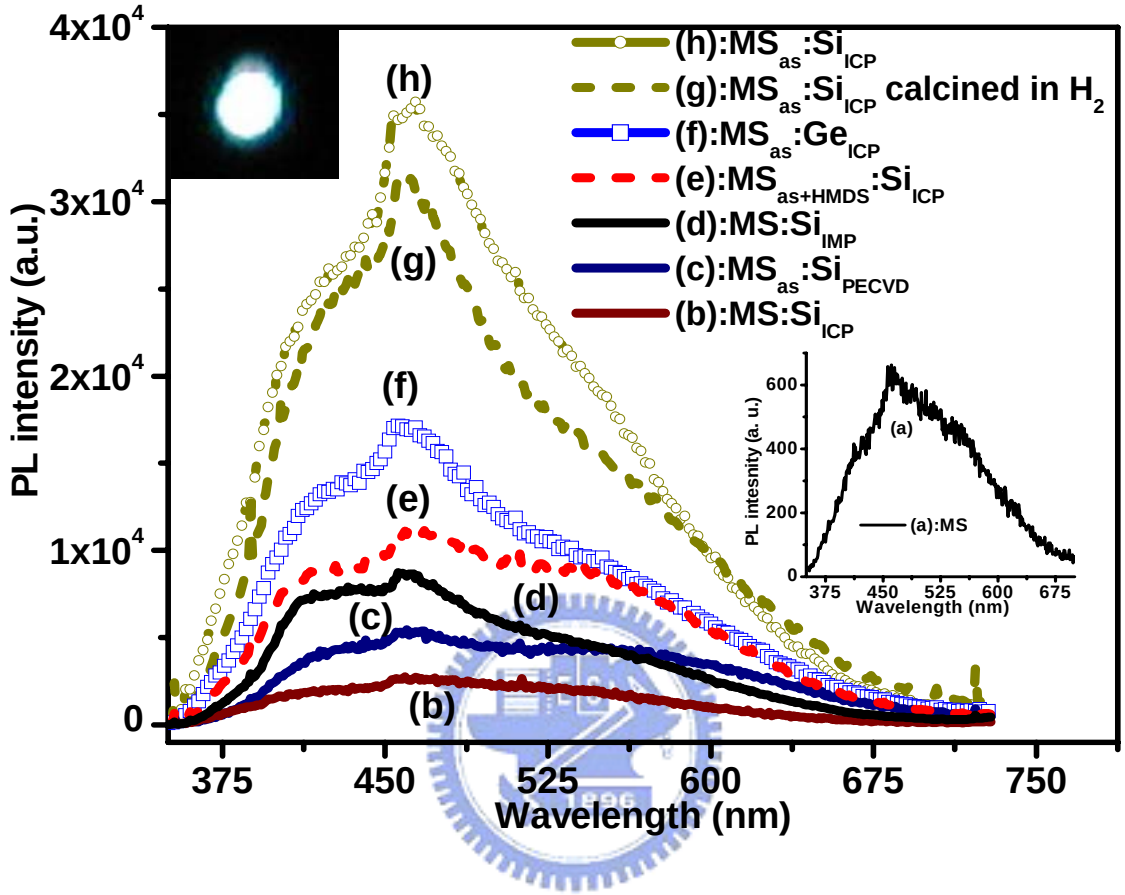

Fig. 5-1: PL spectra of various mesostructured materials (MS, MS_{as}, $MS_{as+HMDS}$) doped with Si or Ge nanodots by high-density ICP. PL curves of MS_{as}:Si_{ICP} untreated with FA (h), and treated with FA in hydrogen (g). PL curves of MS (a), MS:Si_{ICP} (b), $MS_{as+HMDS}$:Si_{ICP} (e), and MS_{as}:Ge_{ICP} (f). PL curve of MS_{as} doped with Si by low-density plasma (PECVD) (c). PL curve of MS doped with Si by implantation (d). Implantation parameters are 15 KeV, and 10^{16} cm^{-2}. Inset is the picture of blue-white PL from MS_{as}:Si_{ICP}.

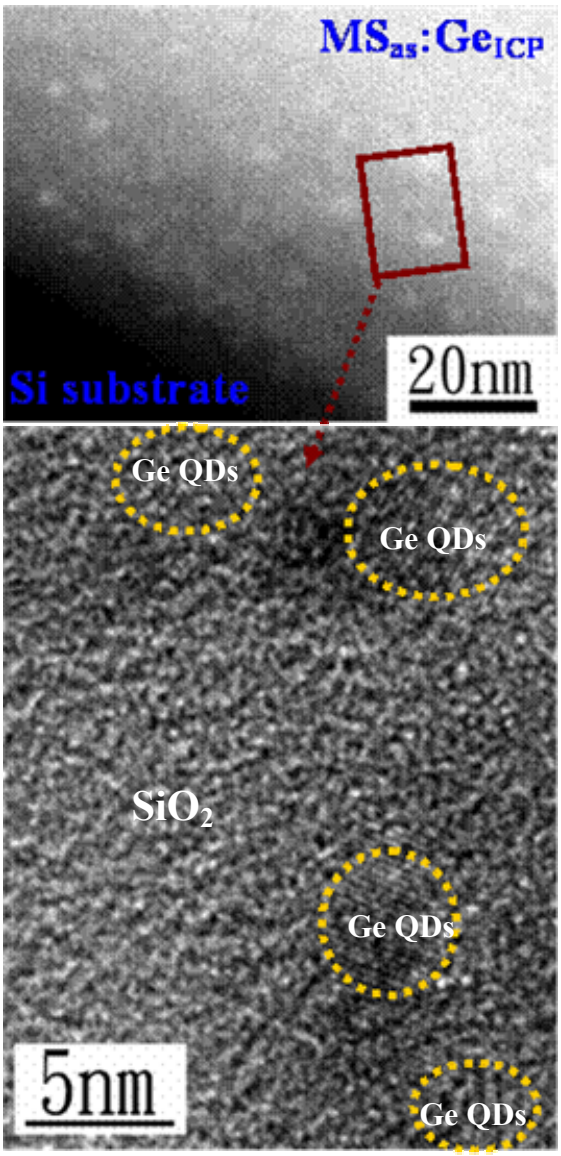

Fig. 5-2: Cross-sectional STEM images of MS_{as}:Ge_{ICP} for identifying the existence of Ge nanodots within them.

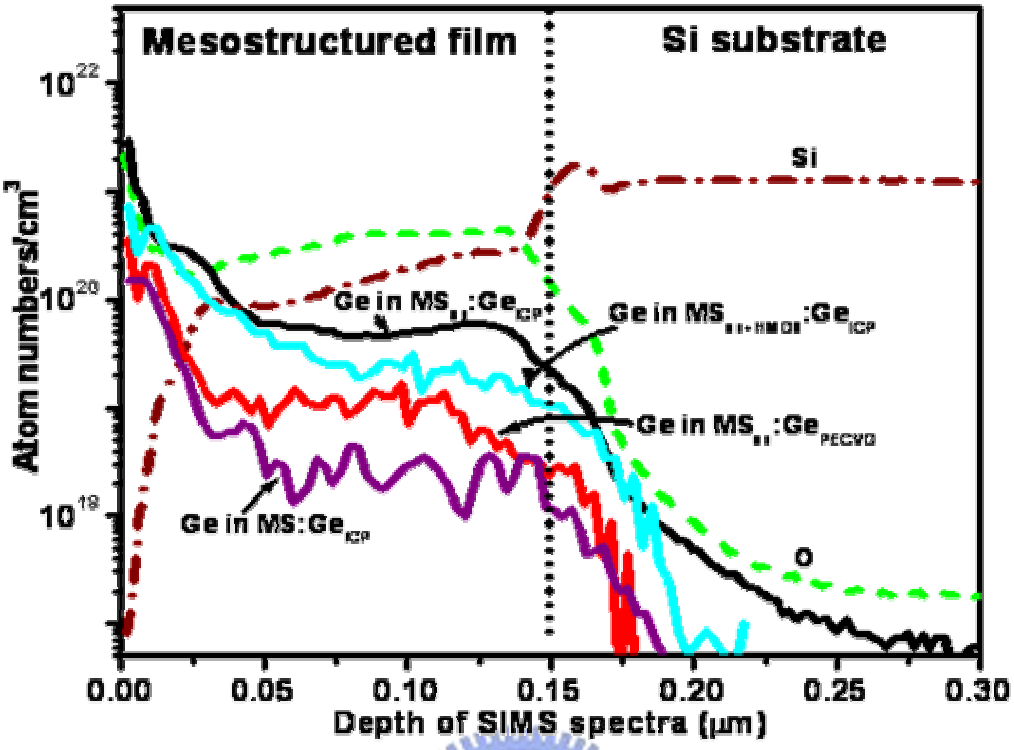

Fig. 5-3: SIMS spectra of MS:Ge_{ICP}, MS_{as}:Ge_{PECVD}, $MS_{as+HMDS}$:Ge_{ICP}, and MS_{as}:Ge_{ICP}.

5-3.3 Hydrogen-elimination reaction

The formation of nanoclusters in nanopores of mesostructured films using ICP, involves numerous reactions. Firstly, ICP-dissolved SiH_n (GeH_n) species in the form of nanoscaled clusters diffuse into nanopores, and are then absorbed and embedded in the organic-template (P123) of MS_{as}. These abundant Si-OH groups on intrachannel surface of MS_{as} are sufficiently active to function as anchoring sites for SiH_n (GeH_n) through hydrogen-elimination reaction (HER) [Si-OH+ SiH_n (GeH_n) → Si-O-SiH_m (GeH_m) + H_2] [14]. The further HER [Si-O-SiH_m (GeH_m) →. Si-O-Si_n $(Ge)_n$ + H_2] [14] converts Si-O-SiH_m (GeH_m) species into Si_n (Ge_n) cluster in nanoporous MS_{as}.

Figure 5-4 schematically depicted this ICP-based Si (Ge) NC-synthesis. Unlike high-density ICP, which yields reactive species with a high diffusion capability, the plasma sources (such as PECVD) without this characteristic, fail to drive the species into the matrix and are responsible for weak PL from PECVD-treated samples (curve c of Fig. 5-1). Notably, an extremely high hydrogen flow with a dilution ratio of

50-200 promotes the formation of dots within the MS_{as} by making the reactive species highly mobile [30], and by controlling the size of nanodots on the nanoscale [29].

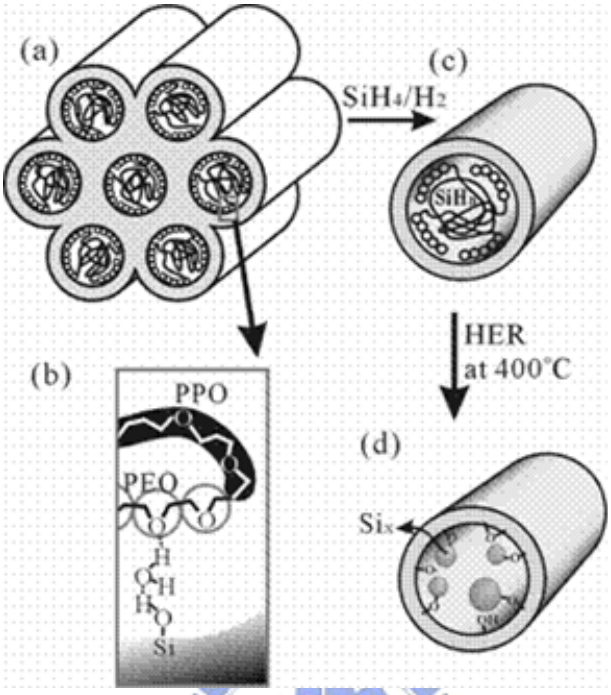

Fig. 5-4: Schematic representation of template containing mesoporous silica, MS_{as} (a), and a magnification showing the interactions between channel surface and P123 polymer (b). Illustrations of SiH_n species embedded in organic templates of a MS_{as} film (c) and silicon clusters, Si_x, formed in the channels (d) through HER reactions after high density ICP treatment, finally followed with FA in hydrogen.

Despite the differences among the mobility of reactive species generated by ICP, PECVD and even pure-CVD [14], **HER** still dominates the conversion of ICP-dissolved species in mesostructured films into Si_n (Ge_n) nanoclusters; hence, the efficiency of ICP-based NC-synthesis is expected to increase with the content of organic-templates (for trapping reactive species) and the number of Si-OH anchoring sites (for HER) on the pore-surfaces [14]. Therefore, silylated MS_{as} (denoted as $MS_{as+HMDS}$) and calcined MS_{as} (denoted as MS) films, both of which have few hydroxyl groups and the latter of which has no organic-template, respond relatively inefficiently to the formation of nanodots by ICP, so weak PL is observed from $MS_{as+HMDS}$:Si_{ICP} and MS:Si_{ICP}. (See curves e and b of Fig. 5-1).

5-3.4 Analysis of Ge-related SIMS spectra

With reference to the germanium-related SIMS depth profiles for MS_{as}:Ge_{ICP}, $MS_{as+HMDS}$:Ge_{ICP}, MS_{as}:Ge_{PECVD} and MS:Ge_{ICP} plotted in Fig. 5-3, the mean densities $D_{Ge(Si)}$ of the dispersed semiconducting NCs in those mesostructured films are calculated to be of about $1.0x10^{18}/cm^3$ (or $0.7x10^{12}/cm^2$ per each lattice layer), $0.5x10^{18}/cm^3$, $0.18x10^{18}/cm^3$ and $0.1x10^{18}/cm^3$, respectively; the results indeed change like the peak intensities of PL from those samples, as indicated in Table **I**. The average sizes of the doped semiconducting NCs, 3-5 nm, as determined by STEM (only showing the STEM image of MS_{as}:Ge_{ICP} on Fig. 5-2), are used to estimate $D_{Si(Ge)}$. The data in Figs. 5-1 and 5-3 and Table **I** for various NC-synthesis methods clearly reveal the high effectiveness of high-density plasma in forming 3-D semiconducting NCs.

Moreover, the processing time (20 second) for forming nanoclusters in an MS_{as} film using ICP is far shorter than that using CVD (which is several tens of hours) [14]. This advantage alleviates the thermal pyrolysis of organic-templates during ICP-based NC-synthesis, and so the template-assisted species-trapping effect remains, encouraging the HER reaction (or the formation of Si (Ge) NCs).

5-3.5 Analysis of FTIR spectra

The change in the content of organic-templates is identified by FTIR, as shown on curves a, and b of Fig. 5-5. Applying hydrogen-calcination to MS_{as}:Si_{ICP} films completely removes templates (as verified by the absence of the films' FTIR signal at 2830-3040 cm^{-1} as shown on curve c of Fig. 5-5) and retains the PL strength (curve g in Fig. 5-1).

The best PL quantum efficiency (QE) of mesostructured materials with embedded NCs can exceed 1% (at total PL energy~20 μW), which is near the efficiency reported for near-infrared emission from quantum-confined Si NCs [10,31]. Herein, the QE of PL is defined as the ratio of average emitted photo numbers, n, to excitation photo numbers, m, where the value of n is calculated from total PL energy and PL spectra.

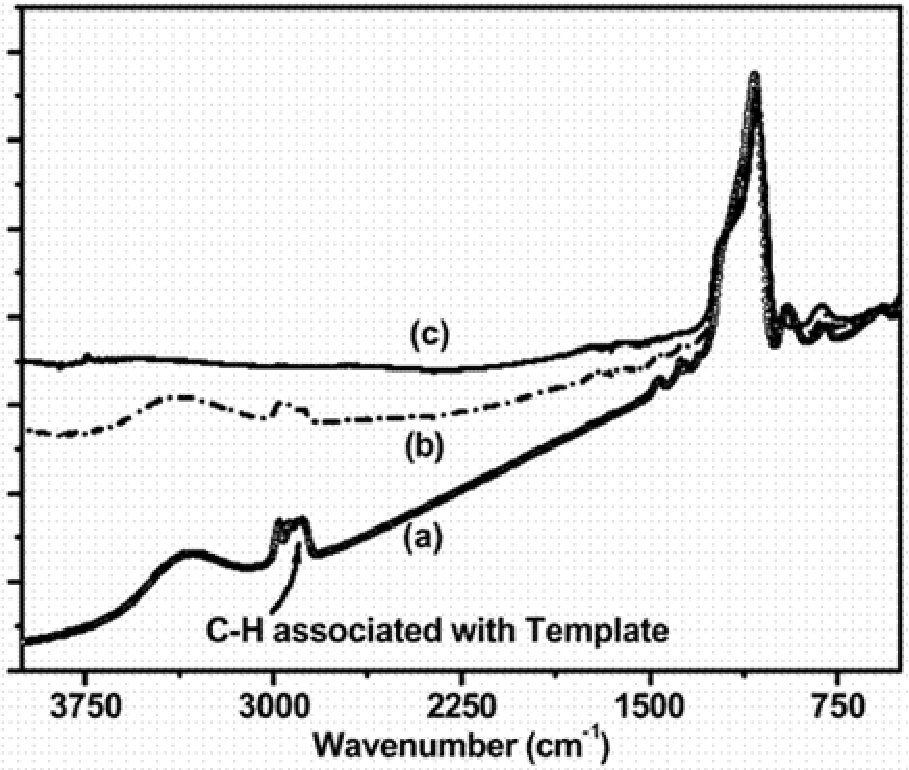

Fig. 5-5: FTIR spectra of MS_{as} (a), MS_{as}:Si_{ICP} before (b) and after (c) treated with hydrogen-annealing.

5-3.6 Discussion of PL spectra

Comparing the PL characteristics of mesostructured films doped with Si using ICP, to those doped using implantation (**MS:Si_{IMP}**), is instructive. Optimal implantation parameters for MS:Si_{IMP} as a luminescent material are determined to be a dosage of 10^{16} cm^{-2} and an energy of 15 KeV when concerning those factors of density of irradiative centers increased by the implantation dosage, damage to nanopores/silica arrays caused by the high implantation dosage and energy and the porosity-related implantation-depth effect. The originations of blue-PL from Si-implanted MS are tentatively attributed to implantation-induced Si-related, and O-related defects [15] and dopants-embedded pore-wall composites (the rich-Si-modulated-SiO_2 structure). The blue-PL peak intensity for MS_{as}:Si_{ICP} is four times stronger than that for supreme **MS:Si_{IMP}**, as revealed by curves h and d of Fig. 5-1. It is almost one order of magnitude higher than that for oxide doped with an extremely high Si dosage of 10^{17} cm^{-2} (**SiO_2:Si_{IMP}**), as reported by P. Mutti et al. [6].

Analyzing Ge-related SIMS for MS_{as}:Ge_{ICP} obtains the average concentration for ICP-synthesized Ge in MS_{as} of about $2.0x10^{20}$ atoms/cm^3, which value exceeds the ~10^{20} atoms/cm^3 for materials implanted with a dosage of 10^{17} cm^{-2}, so the efficiency of PL from MS_{as}:Si $(Ge)_{ICP}$ exceeds that from MS:Si_{IMP} or even from SiO_2:Si_{IMP}.

Many studies [24,31-32] have reported that the peak photo energy of quantum-confinement (QC)-related PL from Si NCs depends on the crystallite size. The wavelength of QC-related PL emitted from ICP-synthesized Si (Ge) NCs with 3-5 nm in diameter was thus predicted to range from 640 to 800 nm. However, the range of wavelengths of the PL spectra for MS_{as}:Ge $(Si)_{ICP}$ was found to locate at the blue-white band (375-675 nm) and coincide with those for MS or even MS:Si_{IMP} (curves a, d, f and h in Fig. 5-1). Moreover, Baron et al. reported that CVD-synthesized NCs are well bonded with the underneath oxide layer [33]. Therefore, the surface-states of high-quality NC-oxide interfaces formed by ICPCVD are suggested to be the dominant photoemission centers [10,31].

5-4. Conclusion

Three-dimensional Si (Ge) nanocrystals (NCs) were dispersed within the nanopores of mesoporous silica films by high-density plasma (HDP), low-density plasma or implantation. Surface states of the resulting Si (Ge) NCs/silica arrays initiate blue-white photoluminescence (PL). HDP makes reactive species highly mobile and enables deposited NCs bonded with pore-wall well, therefore, efficiently constructing photoemission arrays. The mean density of HDP-synthesized semiconducting NCs is as high as $1x10^{18}$/cm^3. Accordingly, blue-PL of arrays obtained with HDP, which is 4-7 times stronger than those obtained with other methods, exhibits quantum-efficiency of 1%, near the reported value for green-to-red light emission from quantum-confined Si NCs.