Final Report for AOARD Grant FA2386-09-1-4104
“Study on Locally Confined Deposition of Si Nanocrystals in High-Aspect-Ratio Si Nano-Pillar Arrays for Nano-Electronic and Nano-Photonic Applications II”

2010.12.03

Name of Principal Investigators: H.-C. Kuo and G.-R. Lin

- e-mail address : grlin@faculty.nctu.edu.tw; grlin@ntu.edu.tw
- Institution : National Chiao Tung University
- Mailing Address : No. 1 Roosevelt Rd. Sect. 4, Taipei 106, Taiwan
- Phone : +886-2-33669598
- Fax : +886-2-33669598

Period of Performance: 10/30/2009 – 10/29/2010

Abstract:

We investigate the PL characteristics of the equivalent-size controlled Si-QDs by employing the nano-porous AAO membrane as the template for growing Si-rich SiOx nano-rods to achieve the spatially confined synthesis of Si-QD. The ultra-bright PL can be emitted from the SiOx nano-rod in nano-porous AAO membrane. In addition, we preliminarily demonstrate the in-situ high-temperature synthesis of Si nanocrystal based broadband optical waveguide amplifiers with gain coefficient of >100 cm^{-1} and a power gain of >13 dB.

Introduction:

Implementation of Si/Ge nanocrystal based light-emitting diode, optical amplifier, laser diode made on silica and Si nanowire and Al2O3 nanoporous membrane is an intriguing topic, however, which has yet not been completely realized for versatile applications in all-Si-based lighting flexible photonic modules or optical interconnect systems in near future. The main bottleneck is attributed to the inappropriate control on the envorpmental and parametric factors set by the commercial chemical vapor deposition systems. Our previous researches reveal that the analomous gas fluence and flowing rate is mansatory for the synthesis of Si nanocrystals on different nanoporous substrates with a strictly tooling deposition system. In last year, we propose to establish an ultralow-plasma and high-temperature chemical vapor deposition (UPHT-CVD) system which is particularly designed for spatially confined synthesis of size and wavelength controllable Si nanocrystals with optimized quantum efficiency in Si nanowire substrate, SiC or Al2O3 nanoporous membrane.

In this work, we investigate the PL characteristics of the equivalent-size controlled Si-QDs by employing the nano-porous AAO membrane as the template for growing Si-rich SiOx nano-rods to achieve the spatially confined synthesis of Si-QD. The ultra-bright PL can be emitted from the SiOx

Report Documentation Page

Form Approved
OMB No. 0704-0188

1. REPORT DATE **08 DEC 2009**	2. REPORT TYPE **FInal**	3. DATES COVERED **03-06-2009 to 02-12-2010**

4. TITLE AND SUBTITLE **Study on Locally Confined Deposition of Si Nanocrystals in High-Aspect-Ratio Si Nano-Pillar Arrays for Nano-Electronic**	5a. CONTRACT NUMBER **FA23860914104**
	5b. GRANT NUMBER
	5c. PROGRAM ELEMENT NUMBER
6. AUTHOR(S) **Hao-Chung Kuo**	5d. PROJECT NUMBER
	5e. TASK NUMBER
	5f. WORK UNIT NUMBER
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) **National Chiao-Tung University,1001 Ta-Hsieh Rd,Hsinchu 300,Taiwan,TW,300**	8. PERFORMING ORGANIZATION REPORT NUMBER **N/A**
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES) **AOARD, UNIT 45002, APO, AP, 96337-5002**	10. SPONSOR/MONITOR’S ACRONYM(S) **AOARD**
	11. SPONSOR/MONITOR’S REPORT NUMBER(S) **AOARD-094104**

12. DISTRIBUTION/AVAILABILITY STATEMENT

Approved for public release; distribution unlimited

13. SUPPLEMENTARY NOTES

14. ABSTRACT

This is the report of an investigation of the photoluminescence characteristics of equivalent-size controlled silicon quantum dots by employing a nano-porous aluminum oxide membrane as the template for growing silicon-rich nano-rods to achieve the spatially-confined synthesis of silicon quantum dots.

15. SUBJECT TERMS

Electro-optics, nano photonics, semiconductor

16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT	18. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON
a. REPORT **unclassified**	b. ABSTRACT **unclassified**	c. THIS PAGE **unclassified**	**Same as Report (SAR)**	**5**	

Standard Form 298 (Rev. 8-98)
Prescribed by ANSI Std Z39-18

nano-rod in nano-porous AAO membrane. The synthesizing mechanism for such a spatially confined synthesized of Si-QD buried between 1D SiOx nano-rod and 2D thin-film is elucidated. High-resolution transmission electron microscopy (HRTEM) is performed to determine the spatially confined size distribution of the Si-QDs. Furthermore, to realize the concept of spatially confined synthesis between theory of Si atomic diffusion and crystal nucleation mechanism, the effective diffusion characteristics of Si in sub-stoichiometric SiOx is also to determine. Study on controllable Si-QD size uniformly for improving the standard deviation of Si-QD size dependent spectral linewidth is emphasized. The relationship between Si-QD size and annealing temperature for controlling the emission wavelength, and temperature effect on spatially confined synthesis of Si-QD are proposed to promote the light emission power.

Experiment:

The nano-porous AAO membrane with specified pore diameter of 100±5 nm (Fig.1 (a) and (b)) was used as a template to deposit the 1D Si-rich SiOx nano-rods through plasma-enhanced chemical vapor deposition (PECVD) at RF power, working pressure, working temperature, and N2O/SiH4 flowing ratio of 50 W, 0.5 Torr, 350oC and 5.5, respectively. All of the SiOx-on-AAO samples were deposited within 120 seconds to preserve the sample thickness. To precipitate Si-QD, the 1D Si-rich SiOx nano-rod embedded in nano-porous AAO specimens were annealed in quartz furnace with flowing nitrogen gas at temperature varying from 350 to 800oC. To confirm the results of spatially confined synthesis of Si-QDs, the SiOx film grown on (100)-oriented p-type Si substrate is also prepared for comparison. In particular, the Si-rich SiOx films were also annealed at 1100oC14, for precipitating the Si-QD in the host matrix without spatial confinement. Subsequently, the room-temperature PL of the samples pumped by He-Cd laser at wavelength and average power of 325 nm and 6.3 W/cm2, respectively, was analyzed using a fluorescence spectrophotometer (CVI, DK240) with a single-grating of 0.06 nm resolution and converted into electrical signal by a photomultiplier (Hamamatsu, model R928) with operational voltage of 1.0 volt. In addition, the working distance between the focusing lens and the sample was fine-tuned to maximize the PL intensity. The HRTEM (JEOL, JEM-2010) and TEM X-ray energy-dispersive spectrometer (TEM-XEDS, Link ISIS 300) were employed to characterize the Si-QD size and O/Si composition ratio within 1D SiOx nano-rods and 2D SiOx thin-film. In addition, the Si-QD distributions have also been obtained by processing HRTEM images, and the lattice spacing of Si-QD was confirmed by using the related software (Digital Micrograph 3.3.1 and Origin R7.0 SRO).

Results and Discussion:

First of all, the ultralow-plasma and high-temperature CVD method for spatially confined synthesis of size and wavelength controllable Si nanocrystals in Al2O3 nanoporous membrane has been demonstrated. We have focused on the nanocrystallite Si based colorful MOSLEDs with broadband wavelength tunability made by Si-rich SiOx/SiNx multi-layer with buried Si nanoclusters of precisely controlled size on roughened Si nano-pillars or Al2O3 nanoporous membrane Si substrate. Important roles of the interfacial diffusion effect induced dislocation and phase transitions in Si-rich SiOx/SiNx multilayered thin films system, the surface energy and solute strain energy effects in surface segregation, and strain induced grain boundary migration in SiOx-Al2O3 nanocomposite material, the impact of ripening effect on self-aggregated nano-clusters with reducing surface energy, the charge capacity within the hydrogen passivated Si nanocrystal will be realized to achieve non-stoichiometric and nanocrystal-enriched synthesis for enabling wavelength tunable luminescence. We have demonstrated the spatially confined synthesized of SiOx nano-rod in nano-porous AAO membrane with ultra-bright PL after lower annealing temperature at 500oC. A higher concentration with volume density of 5.51×10^{18} cm^{-3} and tiny size with diameter of only 2.0±0.1 nm of the excessive Si-QD can easier be obtained. HRTEM results indicate that the geometric form varied from 2D to 1D could also effectively reduce a standard deviation of Si-QD size from 25% to 12.5%. By using the diffusion controlled growth mechanism to estimate the diffusion characteristics, we obtain the activation energy of 6.284 kJ/mole and diffusion length of 1.74 nm for SiO1.5 nano-rod in nano-porous AAO membrane to corroborate the spatially confined Si-QD precipitation. These results also indicate that the varied composition ratio of SiOx host matrix will affect the value of activation energy. In contrast, the same SiOx film grown on smooth Si wafer only exhibits a PL intensity of 0.08 count/nm. The PL can further broaden and red-shift to 600 nm for 800^{o}C annealed sample, however, while the PL intensity greatly attenuates due to both the enlargement of Si-QD size and the reduction of the emission photon energy. In addition, raising annealing temperature beyond 800^{o}C, also leads to crack the nano-porous AAO membrane due to an extremely large bending strain. The impact of this work elucidates that the monotonically decreasing dimension of SiOx host matrix can concurrently contribute to the spatially confined precipitation of Si-QD and low temperature phase-separation between Si-QD and SiO2 matrices, thus facilitating super-luminescent PL with enhanced power, blue-shifted wavelength, and narrowing spectral linewidth.

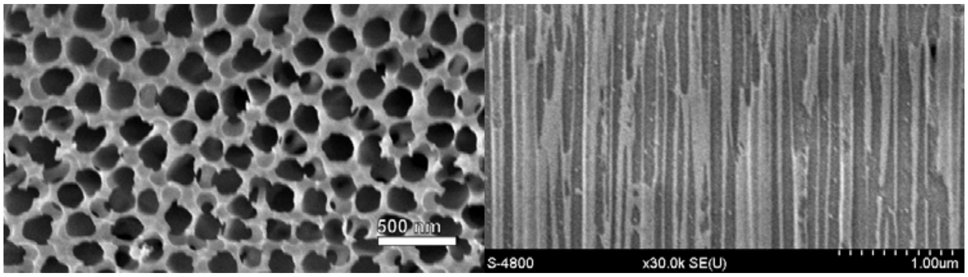

Fig. 1 The plane-view and cross-sectional FESEM micrograph of 1D Si-rich SiOx nano-rod buried nano-porous AAO membrane, respectively.

Such Si nanocrystals synthesized in Si nanopillars or Al2O3 nanoporous membrane for white-light emitters with optimized quantum efficiency is characterized. Previously, the maximum electroluminescent power and external quantum efficiency up to 10 μW and 1% are proposed.

However, this relies on the optimization on the critical reactant-gas recipe and detuning fluence ratios of diluted Silane, nitrious oxide and ammonia during for the UPHT-CVD synthesis of Hydrogen passivated Si nanocrystal within these nanoporous membranes at extremely low plasma power. Besides, the study on phase transitions in multilayered thin films system, interfacial segregation phenomenon, ripening effect and tunable composition ratio with controllable Si nanocrystal size for improving the size dependent quantum efficiency and charge capacity must take into consideration. Moreover, the reduction on escaping rate of electrons from Si nanocrystals needs to be achieved for overcoming the by-passing effect of carriers and to promote the light emission efficiency. The spatially confined synthesis of Si quantum dots (Si-QDs) embedded in low-temperature (500^{o}C) annealed Si-rich SiOx nano-rod deposited in nano-porous anodic aluminum oxide (AAO) membrane using PECVD with ultra-bright photoluminescence spectra are characterized. In comparison with the same SiOx film grown on planar Si substrate, a blue-shifted PL by $\Delta\lambda$= 96 nm is clearly observed from such 1D Si-rich SiOx nano-rods in nano-porous AAO membrane. In particular, a narrower PL spectral linewidth (FWHM) shrinks from 210 to 140 nm with the PL intensity enhancing up to two orders of magnitude, corresponding to the reduction on both the average Si-QD size and its standard deviation from 2.6±0.2 to 2.0±0.1 nm and from 25% to 12.5%, respectively. The diffusion controlled growth mechanism is also employs to determine the activation energy of 6.284 kJ/mole and diffusion length of 1.74 nm for $SiO_{1.5}$ nano-rod in nano-porous AAO membrane to corroborate the spatially confined Si-QD precipitation. HRTEM results verify that the variation on the geometric form of the host matrix from 2D to 1D could effectively constrain the SiOx nano-rod diameter for unifying the buried Si-QD size at even lower annealing temperature. Raising the annealing temperature beyond 800^{o}C not only red-shifts the PL wavelength, but also leads to a monotonic reduction on PL intensity and cracks the nano-porous AAO membrane due to an extremely large bending strain.

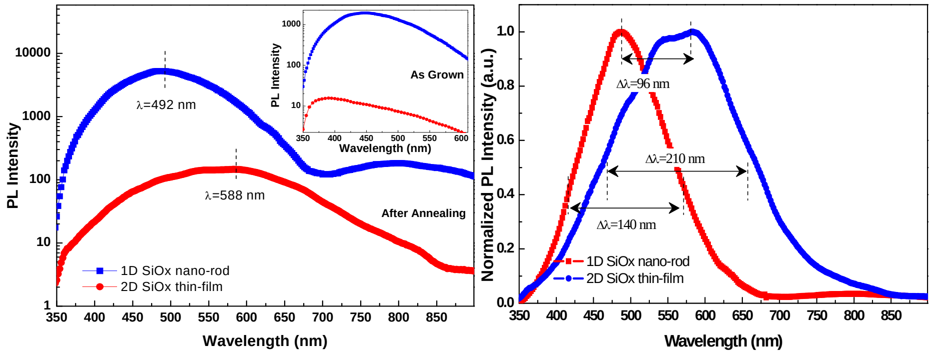

Fig. 2 (a) PL spectra and (b) normalized PL intensity of Si-QD embedded in 2D SiOx thin-film and 1D SiOx nano-rod at optimized annealing condition.

At Last, we preliminarily demonstrate the in-situ high-temperature synthesis of Si nanocrystal based broadband optical waveguide amplifiers. We parametrically detune the UPHT-CVD for fabricating versatile planar or strip-loaded waveguide based featured photonic devices, such as ring resonators and filters, array-waveguide gratings sensors, single-mode planar waveguide amplifier and lasers using Si-rich oxide/nitride multi-layers with buried Si nanocrystals. In particular, the non-stoichiometric Si-rich SiO$_x$ has been synthesized as a host matrix for the Si nanocrystals. The Auger-recombination- and carrier-absorption-free Si nanocrystal waveguide with optical gain ranged from blue to near infrared regions offered by size-tunable Si nanocrystals will be characterized. Broadband amplified spontaneous emission with high net modal gain coefficient of >100 cm-1 and corresponding power gain of >13 dB of the Si nanocrystal waveguide will be demonstrated. We have characterized the blue-yellow-red multi-color strip-loaded SiOx:Si-QD waveguide amplifiers grown by PECVD at changing N2O/SiH4 fluence ratio and RF plasma power conditions. The PL spectra for blue-, yellow-, and red-ASE samples exhibits peak wavelengths at 375, 621, and 801 nm, and the corresponding linewidth are 105, 195, 150 nm, respectively. The blue-ASE sample exhibits the highest Si-QD density up to 3.0×1018 cm-3 with smallest size of 1.7 nm, and its oxygen-related defect (NOV) luminescence is activated more significant than other samples. The maximum gain and loss coefficients for blue-, yellow-, and red-ASE strip-loaded SiOx:Si-QD waveguide of 157 cm^{-1}/19.5 cm^{-1}, 62 cm^{-1}/14 cm^{-1}, and 85.6 cm^{-1}/16 cm^{-1} are obtained, in which the high-gain blue-PL sample exhibits shorter saturation length of 0.25 mm with highest loss coefficient due to scattering loss by Si-QDs of highest density. The product of Si-QDs emission cross section and Si-QDs radiative lifetime for blue-, yellow-, and red-ASE waveguides are 2.34×10^{-21}, 1.78×10^{-21}, and 1.28×10^{-21} cm^2-s.

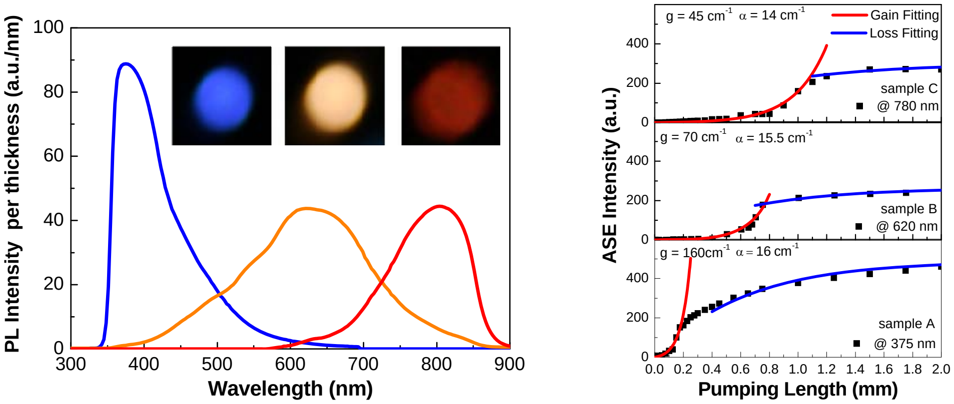

Fig. 3 Left: The spectrum of PL intensity per thickness for three samples. Inset: the PL pattern for three samples. Right: The ASE intensity versus different pumping lengths for three samples.

List of Publications:

1. C.-H. Chang at al., Acta Materialia, 58(4) 1270-1275, 2010.
2. G.-R. Lin et al., Journal of Nanoscience and Nanotechnology, 10(3) 1663-1667, 2010.
3. Y.-C. Lien at al., IEEE Journal of Quantum Electronics, 46(1) 121-127, 2010.