Red luminescence from Si quantum dots embedded in SiO_x films grown with controlled stoichiometry

Zhitao Kang, Brannon Arnold, Christopher Summers, Brent Wagner
Georgia Institute of Technology, Atlanta, GA 30332

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Outline

- **"Quantum phosphor": Thin film Si QDs**
- **Objectives: Developing Si QDs for SSL**
- **Experimental**
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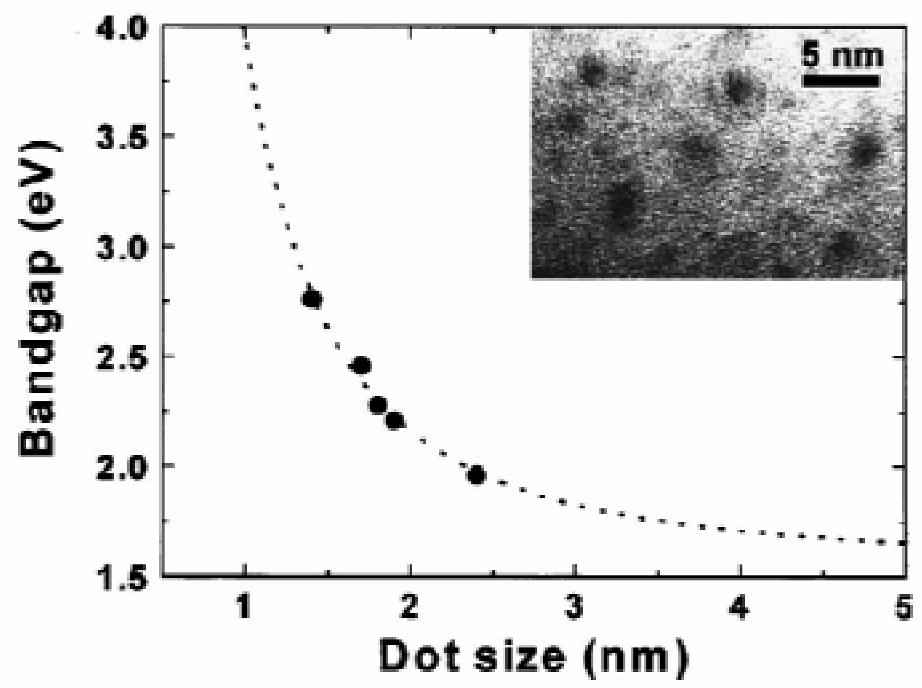
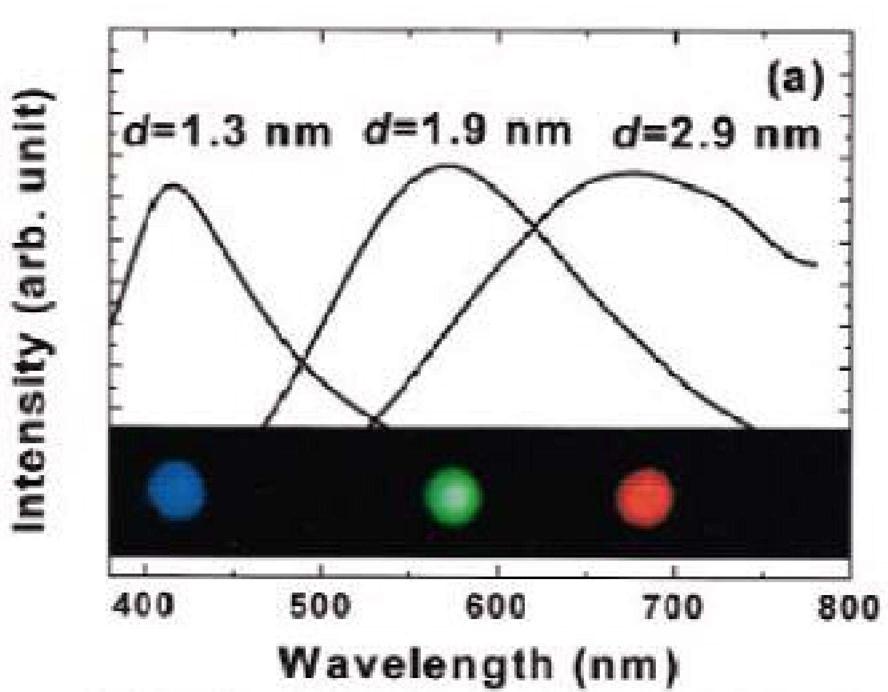
  - Annealing
- **Results and Discussion**
  - Stoichiometry and refractive index
  - Structural analysis
  - Photoluminescence properties
- **Conclusions and Future Work**

“Quantum phosphor”: Thin film Si QDs



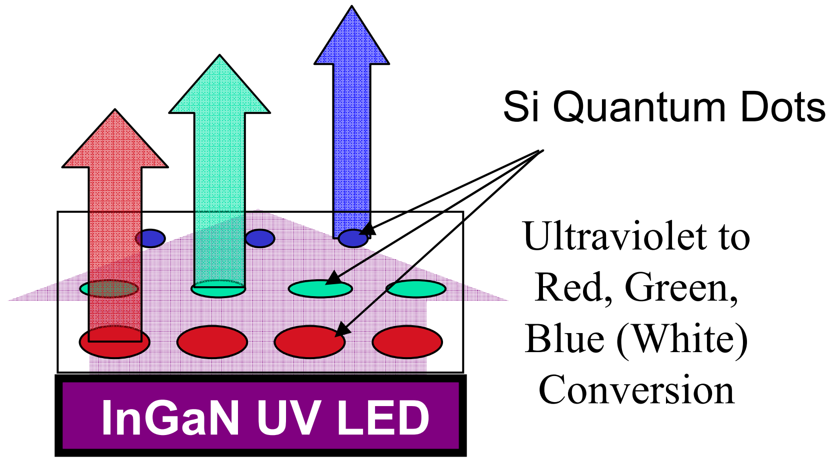


- Bulk Si has a bandgap of ~1.1eV corresponding to a wavelength of ~1100nm
- Bandgap increases with decreasing size due to quantum confinement effect
- Emission throughout the visible can be obtained from thin film Si QDs by controlling their size

Park et al., Appl. Phys Lett., 78, 2575 (2001)

Objectives: Si QDs for Solid State Lighting

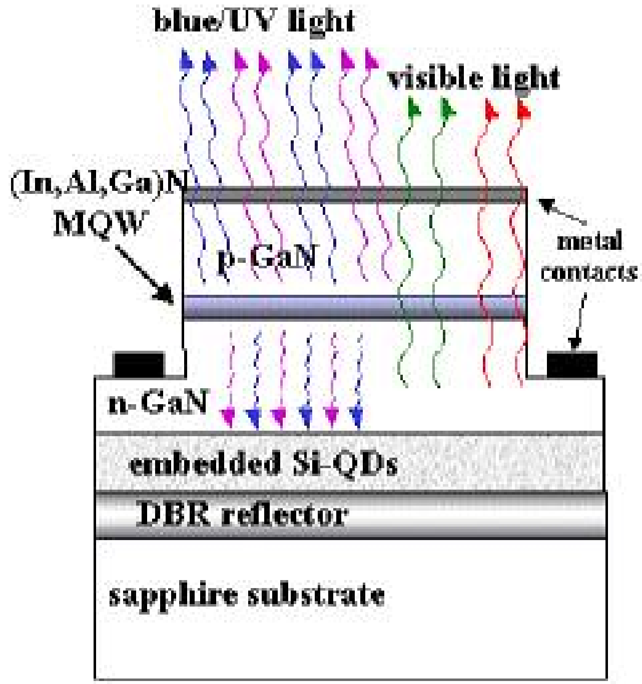
- **Current white LED is fabricated by coating down-converting phosphors onto a III-Nitride LED**
- **Like to replace powder phosphor with Si-like microelectronic technology compatible with LED manufacturing process**
- **Develop thin-film deposition techniques to obtain luminescent Si QDs using controlled stoichiometry materials**
- **Utilize quantum dot/thin film matrix as down conversion photoluminescent emitter to obtain white light with a controlled spectrum**



Low-cost, efficient wavelength converters for LEDs

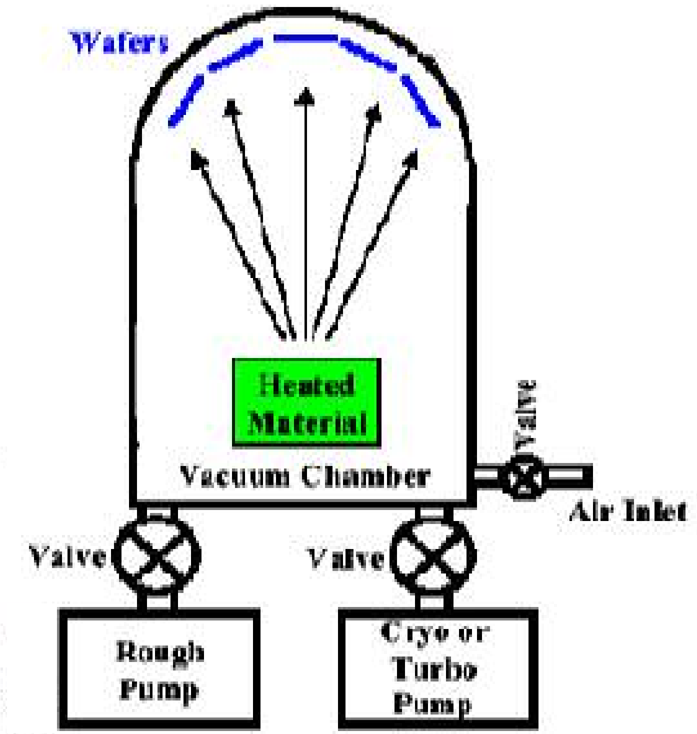
- **Provide a continuous, efficient, less expensive fabrication process to make advanced SSL devices**

Integration of QD Thin Films with LEDs



- QD thin films become part of the substrate upon which LEDs are deposited
- Can be in normal or flip chip configurations
- Can utilize thin film optical structures, such as bragger reflectors, microcavity, antireflection coatings etc., to adjust light output.

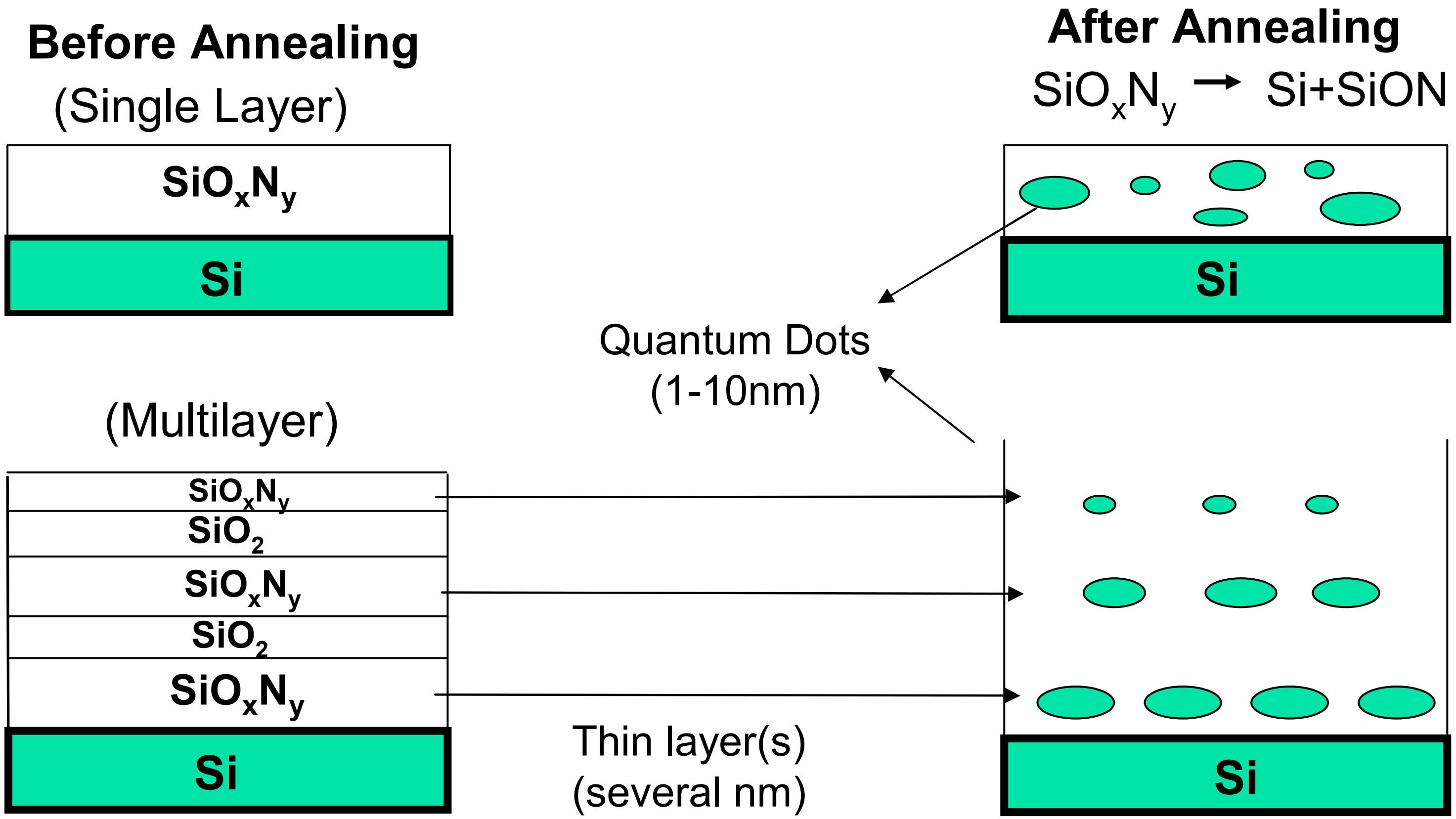
Synthesis of Si QDs films by evaporation



Deposition in commercial Ion Assisted Deposition system

- Thermal or E-beam Evaporation to deposit SiO_xN_y films
- Variables:
  - Source materials: Si, SiO, SiO_2
  - Controlled reactive gas environment (O_2, N_2, H_2)
  - Deposition rate (0.1~2.5nm/s)
  - Thickness (single or multi-layer)
  - Deposition temperature (50 C~300 C)
  - Plasma parameters
- Investigate deposition processes to produce SiO_xN_y layers with controlled stoichiometry, structure and density

Annealing Process to Produce Si QDs



- **Annealing films in inert (N_2) atmosphere converts SiO_xN_y to SiON with excess Si segregating to form Si QDs**
- **QD size controlled by annealing temperature (500-1100°C), SiO_xN_y stoichiometry and layer thickness (1-10nm)**

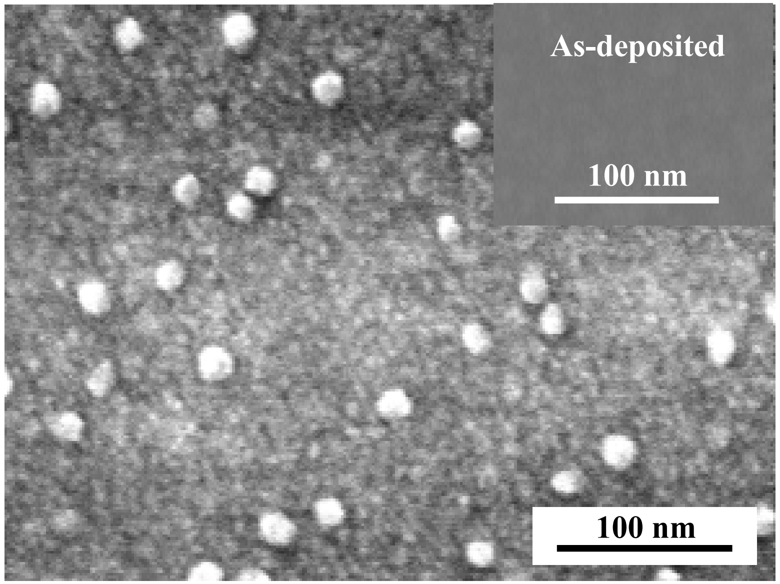
Stoichiometry of as-deposited SiO_x films

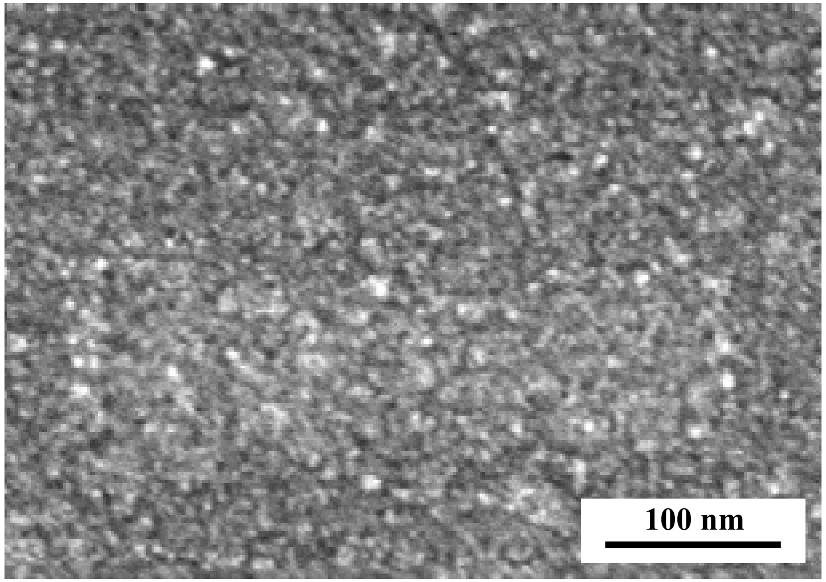
SiO_x thin films prepared by reactive evaporation of SiO in O_2

Sample	O_2 flow (sccm)	SiO Rate (nm/s)	$P_{O_2+H_2O}$ (mbar)	Thickness (nm)	Index	"x" (by EDS)
66	0	2.5	~ 3×10^{-6}	249.3	2.003	~1.0
21	0	0.2	~ 3×10^{-6}	279.7	1.747	1.30
55	5	0.2	2.9×10^{-5}	291.8	1.716	1.45
19	10	0.2	5.5×10^{-5}	319.9	1.648	1.51
59	15	0.2	7.5×10^{-5}	322.1	1.638	1.64
77	20	0.2	1.1×10^{-4}	306.9	1.586	1.80
83	25	0.2	1.4×10^{-4}	337.3	1.513	1.91

- **By controlling the O_2 flow rate and SiO deposition rate, refractive index can be adjusted between 2~1.5, and "x" between 1~2**

SEM Images of Annealed Films





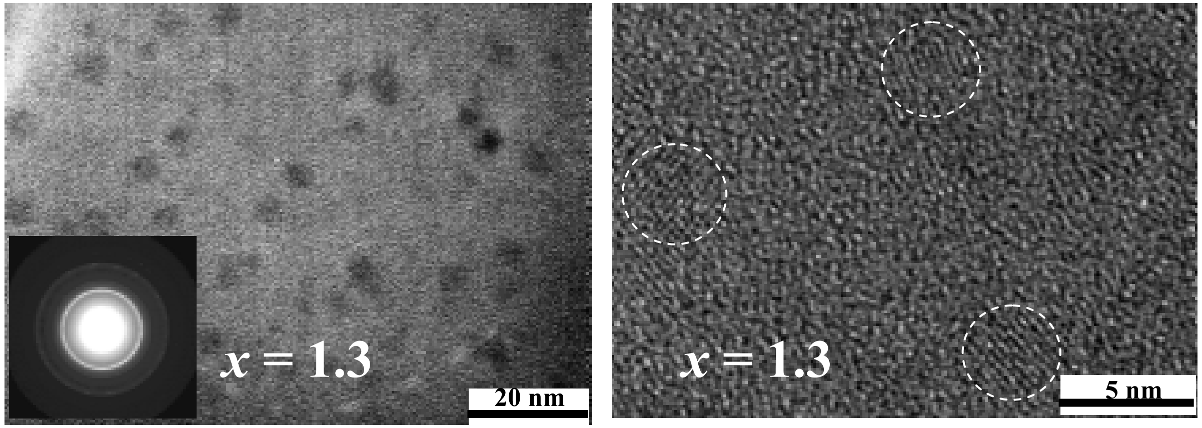
SiO_x film (66) Annealed at 1100°C

Deposition rate: 2.5nm/s
"x"≈1 and n ≈ 2.0
~20nm Si particles observed

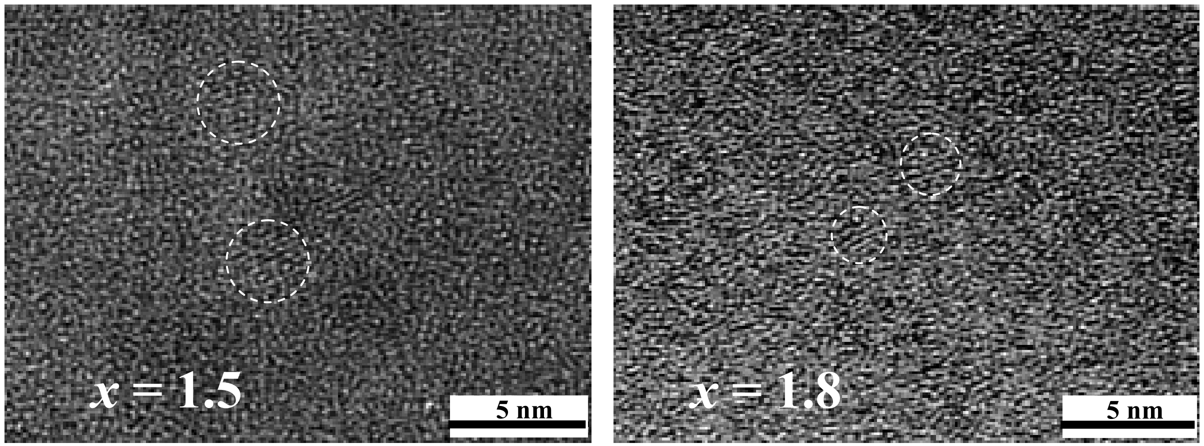
SiO_x film (21) Annealed at 1100°C

Deposition rate: 0.2nm/s
"x"≈1.3 and n ≈ 1.75
<~5nm Si dots observed

HRTEM Images of Annealed Films

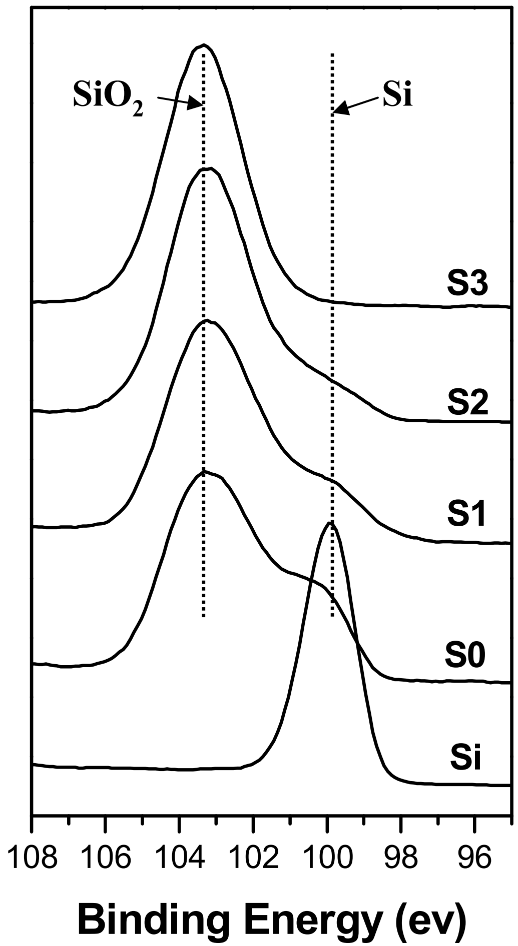


- ~4nm Si crystallized dots were observed from sample with *x* ≈1.3



- Size of Si dots decreases to ~3nm and ~1.5nm with increasing O/Si ratio to 1.5 and 1.8, respectively

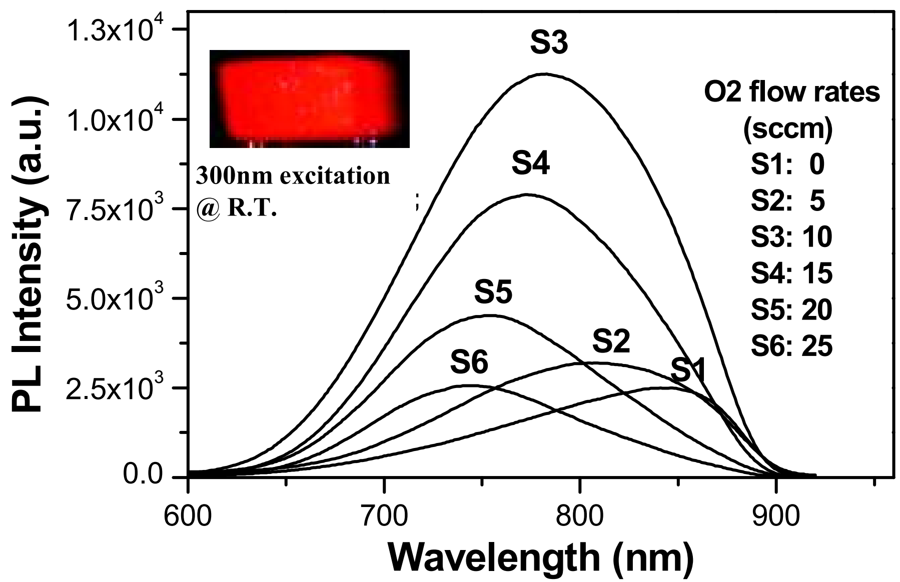
Surface composition and structure

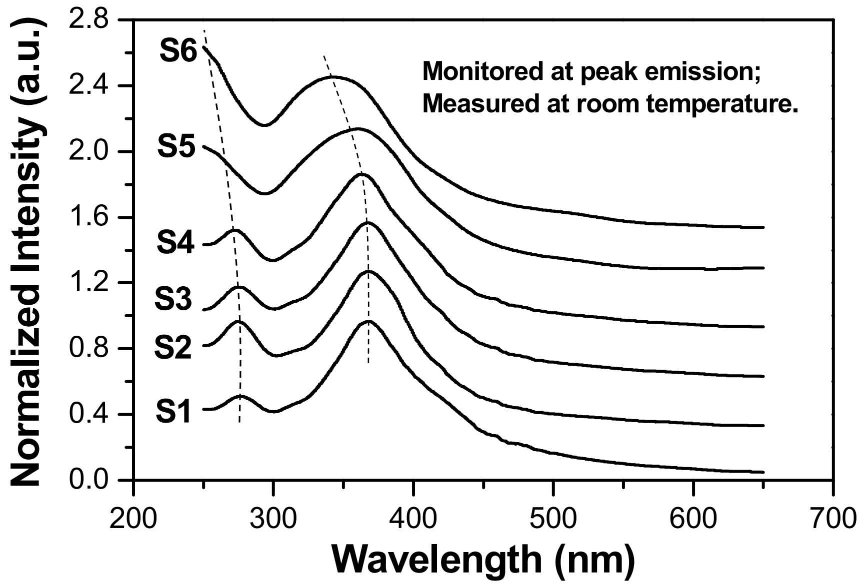


XPS spectra of the SiO_x films after annealed at 1100°C for 1h

- 99.7eV peak due to crystalline silicon
- Peak at 103.4 eV detected from the film samples due to SiO_2 phase;
  - Low energy shoulder attributed to elemental Si, indicating the existence of Si QDs in films.
- With increasing oxygen content in the films, the intensity of the Si shoulder decreases.

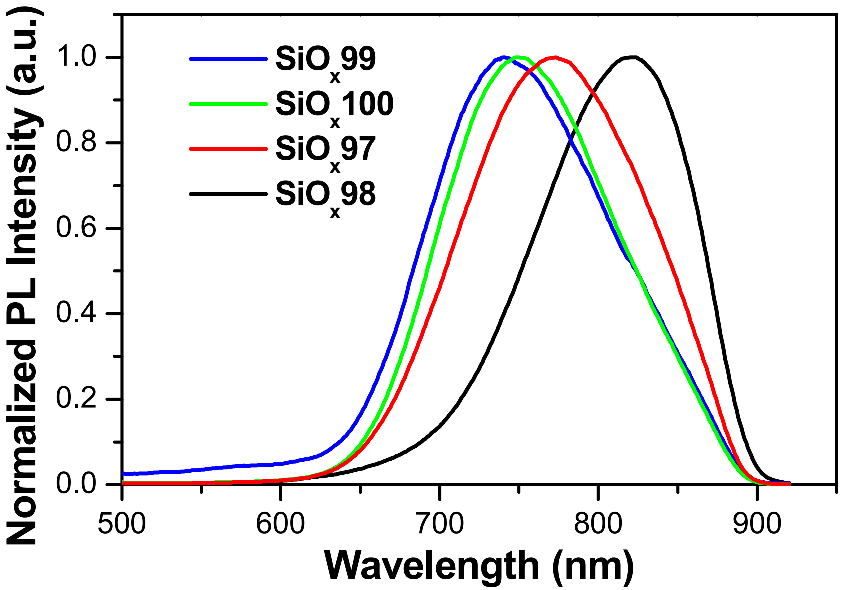
PL and PLE vs O_2 flow rate (Red)



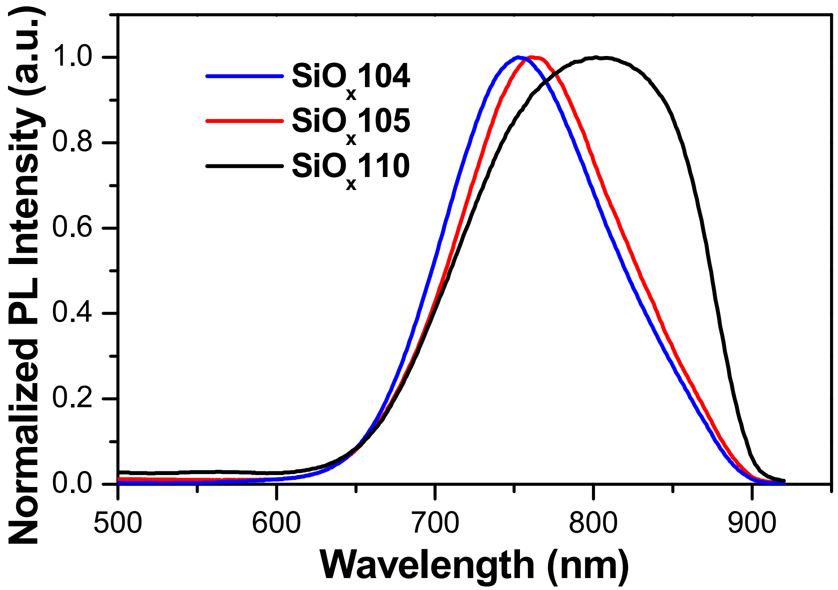


- **Visible red luminescence from SiO_x films annealed at 1100°C for 1h (300nm excitation at room temperature)**
  - Intense red PL observed from all the samples with n = 1.75 ~1.50
  - Blue shift with increasing O_2 flow rate due to smaller Si QDs
  - Intensity peaked at O_2 flow rate of 10 sccm
- **Two PLE peaks centered at 280nm and 370nm, respectively**

SiO_x films Prepared from other sources



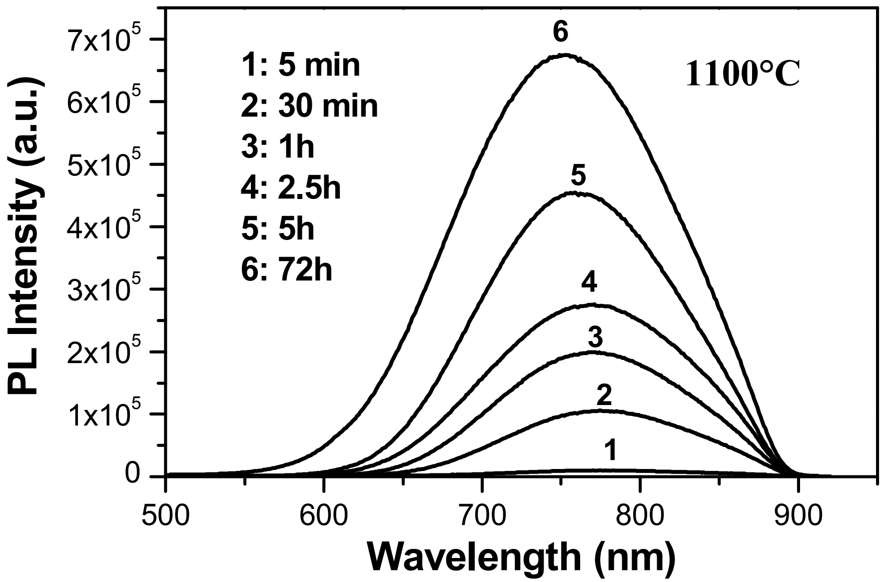
Reactive evaporation: Si + O_2



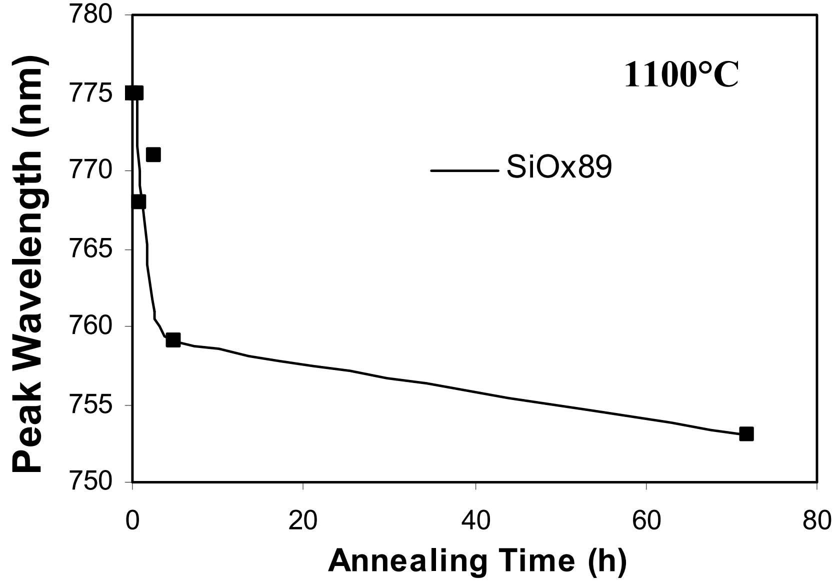
Co-evaporation: SiO + SiO_2

- **Similar red PL was also observed from SiO_x films prepared from Si, SiO/SiO_2 sources.**
- **Blue shift was also observed by controlling the O/Si ratio.**

Effect of Annealing Time on PL



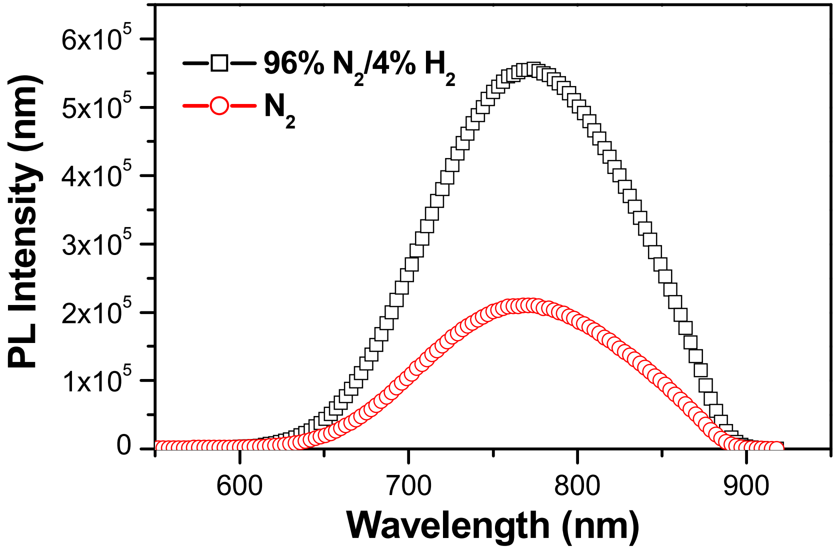
PL spectra vs annealing time

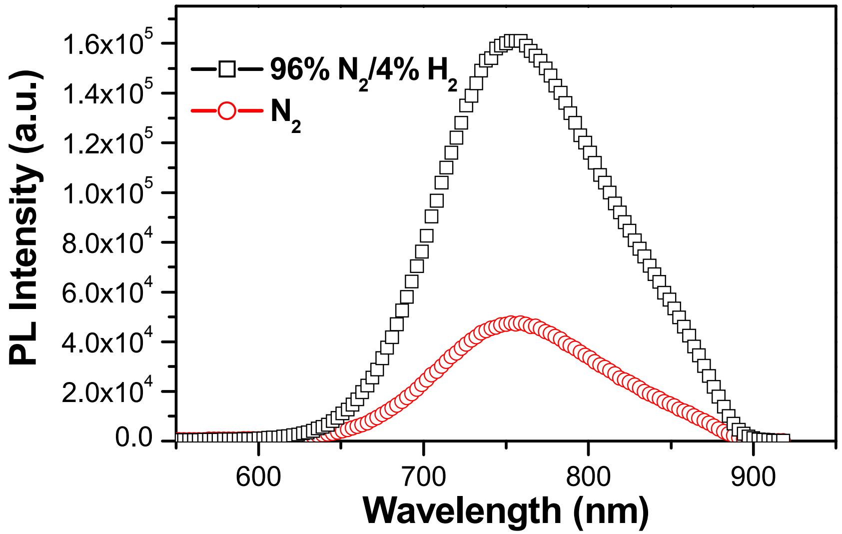


Peak wavelength vs annealing time

- The PL intensity increases continuously with annealing time;
- The peak emission shifts to shorter wavelength indicating decreasing size of Si QDs.

Effect of Annealing Atmosphere on PL



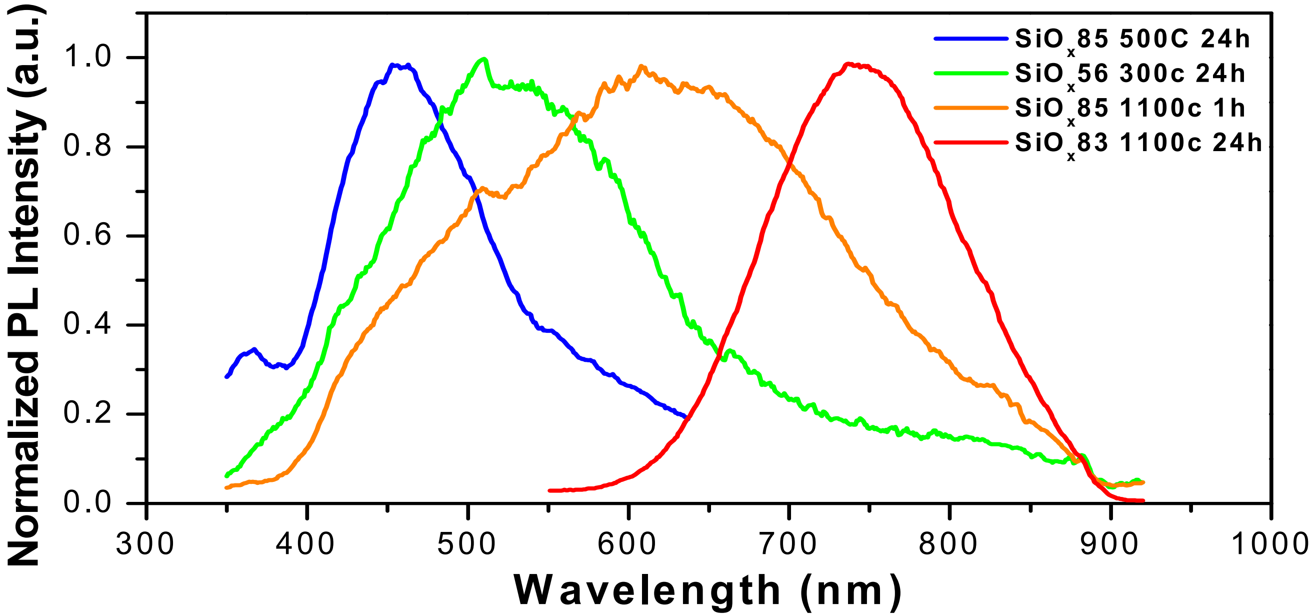


SiO_x89: Evaporation of SiO in O_2;
Rate: 0.2nm/s; O_2 flow: 10 sccm;
1100°c annealing for 1h

SiO_x104: Co-evaporation of SiO and SiO_2;
Rate: 0.05/0.15 nm/s;
1100°c annealing for 1h.

- **The PL intensity improved 2~3 times by annealing in H_2 atmosphere due to better passivation of Si QDs.**

Various Visible Color from SiO_x



- Various visible color, blue, green and orange can be obtained from SiO_x films by controlling the Si/O ratio, annealing temperature and annealing time
- Red emission is most efficient with an external QE estimated to be 1~4%

Conclusions and Future Work

- **Conclusions**
  - **Nanocrystalline Si dots were formed in SiO_x films with controlled stoichiometry**
  - **Strong red PL was obtained from thin film Si QDs**
  - **With an intense PLE band around 370nm which is near the UV LED emission range, these thin film Si QDs show potential for solid state lighting**

- **Future Work**
  - **Synthesize highly efficient green and blue emitting films with amorphous Si QDs**
  - **Develop integrated multilayer Si QD thin films with controlled emission colors and out-coupling techniques to obtain efficient white LEDs.**

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