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Blue-green luminescence from Carbon doped Silicon-Rich Silicon Oxide

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Outline

- Introduction: Si photonics
- Experimental details
- C doping effect on visible luminescence of silicon rich silicon oxide
- Tb luminescence from Tb and C co-doped silicon rich silicon oxide
- Implication for Si micro photonics
- Summary and conclusion

Si nano-cluster for base material of micro-photonics

Silicon as photonic materials

- Very faithful technology and process in micro- or nano- scale
- Important related compound for photonics: Si, SiO_2, SiC and Si_3N_4
- 'Silicon' is thus promising candidate for micro-photonics

→And various successful Si photonic devices have been demonstrated (e.g, modulator, MEM optic-switch, and Photonic bandgap)

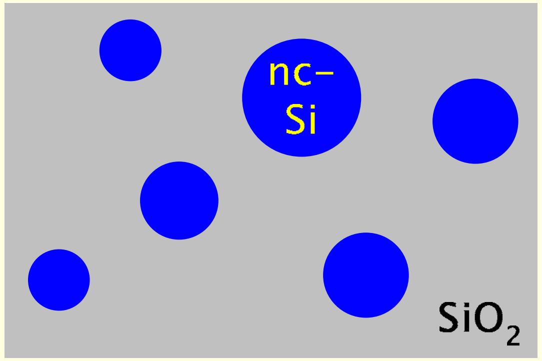
Silicon-rich silicon Oxide (SRSO)

- Nanocluster Si (nc-Si) embedded in SiO_2 matrix
- Quantum confinement effect of nc-Si: increases both oscillator strength and bandgap

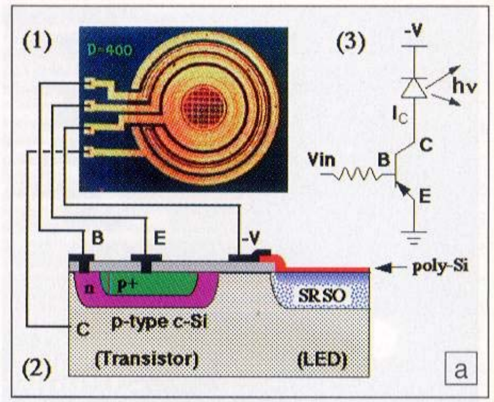
→Efficient visible luminescence at room-temperature

- Easy for formation of dense and robust nc-Si + standard Si process technology

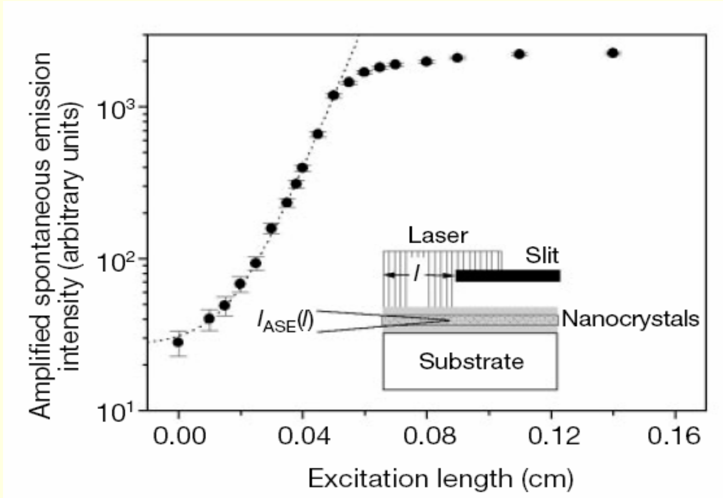
→ Promising candidate for Si microphotonics



State of Art of Si photonics using nc-Si



Nc-Si LED integrated with electric circuit (Hirchman, Nature 1996)



Optical amplification (Pavesi, Nature 2000)

However, several limitations still have to be overcame

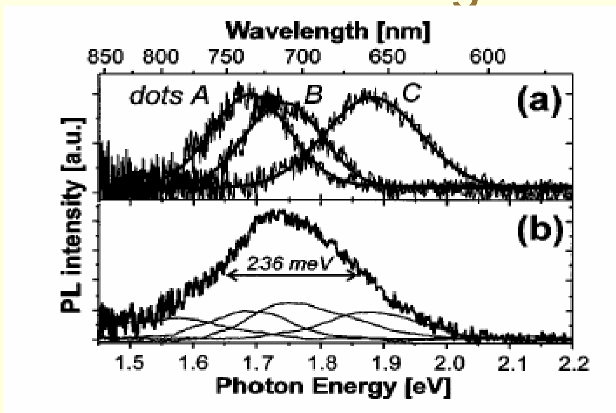
Features of nc-Si:
Limitation for display application

Generally, not visible for eyes

• At most cases weak Red—near infrared luminescence

(Valneta, APL 2002)→

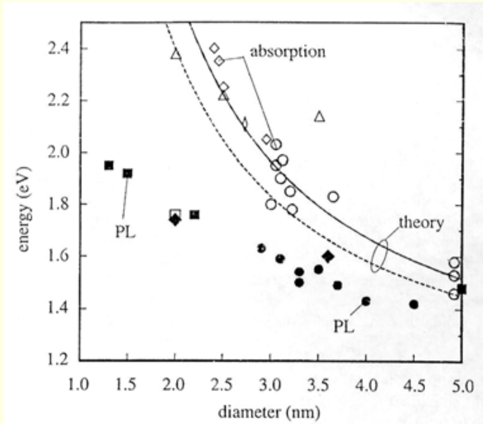
Too broad for even single nc-Si



Low optical transition energy from even 2—3 nm sized nc-Si

• while bangap can exceeds 3 eV, PL peak is limited under 2 eV

(Lanoo, PRB)→



How to induce strong and sharp visible luminescence from SRSO?

1st HINT.

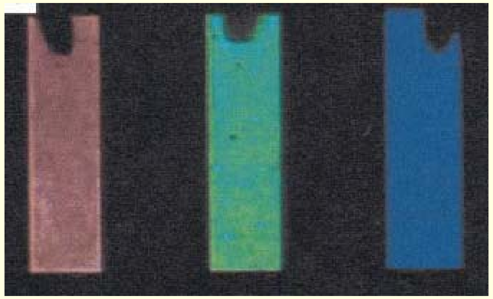
Rare-earth doped wide bandgap material (e.g., GaN)

If bangap is wide enough to excite incorporated RE ions

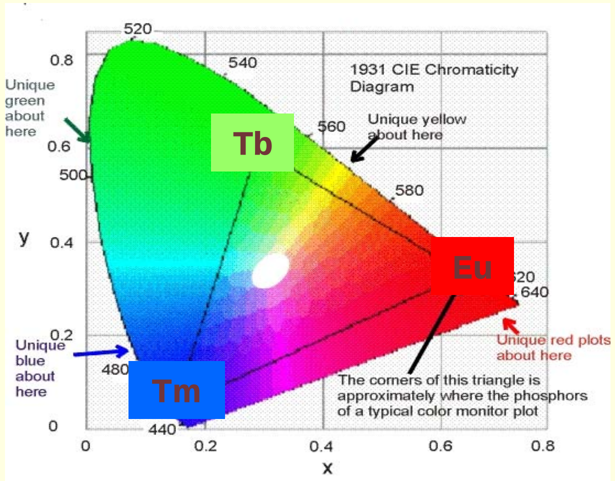
→ Sharp visible 4f transitions of RE ions are feasible

→ Some visible 4f transitions of RE ions: correspond to primary color standard for RGB (Red:Eu or Pr, Green:Er or Tb, Blue:Tm)

Solution 1. Rare earth doping into SRSO



Electroluminescences of RE doped GaN (Steckl *et al.*)



CIE chromacity diagram

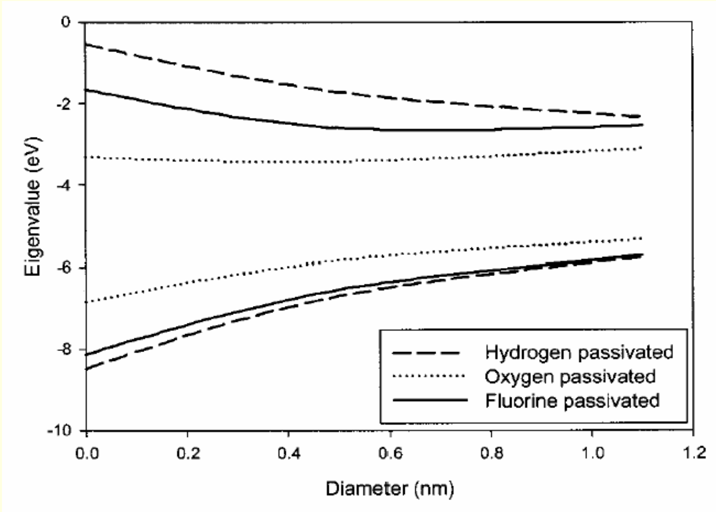
Surface states of nc-Si: determines optical transition

2nd HINT

The effect of passivation on the optical transition of nc-Si

Si=O bonds in SRSO: responsible for strong stokes shift

Species of nc-Si surface passivation → Strongly modify electronic states and optical transition



(Puzder, JCP)

Solution 2. Suitable impurity incorporation into SRSO for the increase of optical transition energy

Blue-white luminescence of SRSO:C and its utilization for visible phosphors

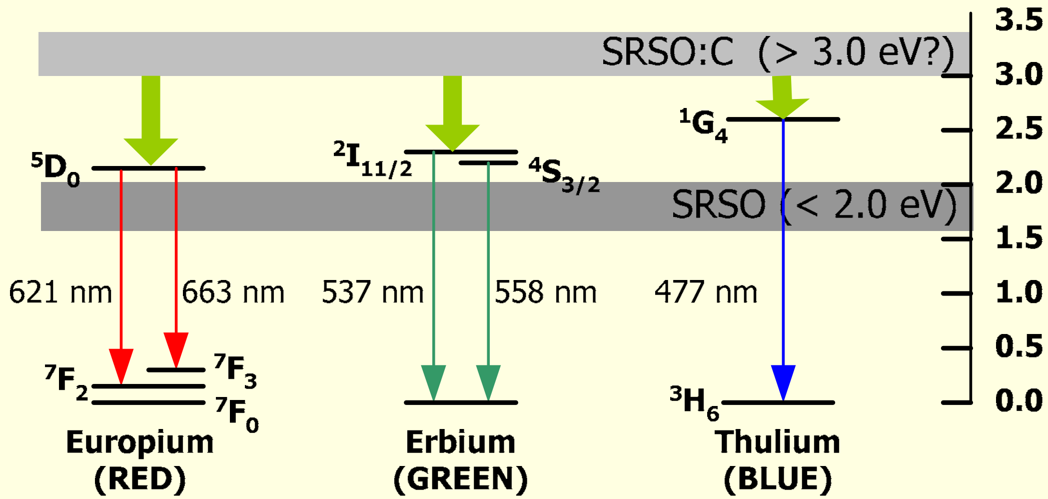
Incorporation of suitable impurities to SRSO film

➔ Can modify surface states of nc-Si

➔ Can further enhance both optical gap and luminescence efficiency

➔ Can be utilized as wideband gap material for visible phosphors (such as rare earth ions)

➔ Finally, strong sharp visible luminescence may be feasible from nc-Si



➔ NOW, we propose C dope doped SRSO (SRSO:C) as host matrix for sharp and visible 4f transition of incorporated RE ions

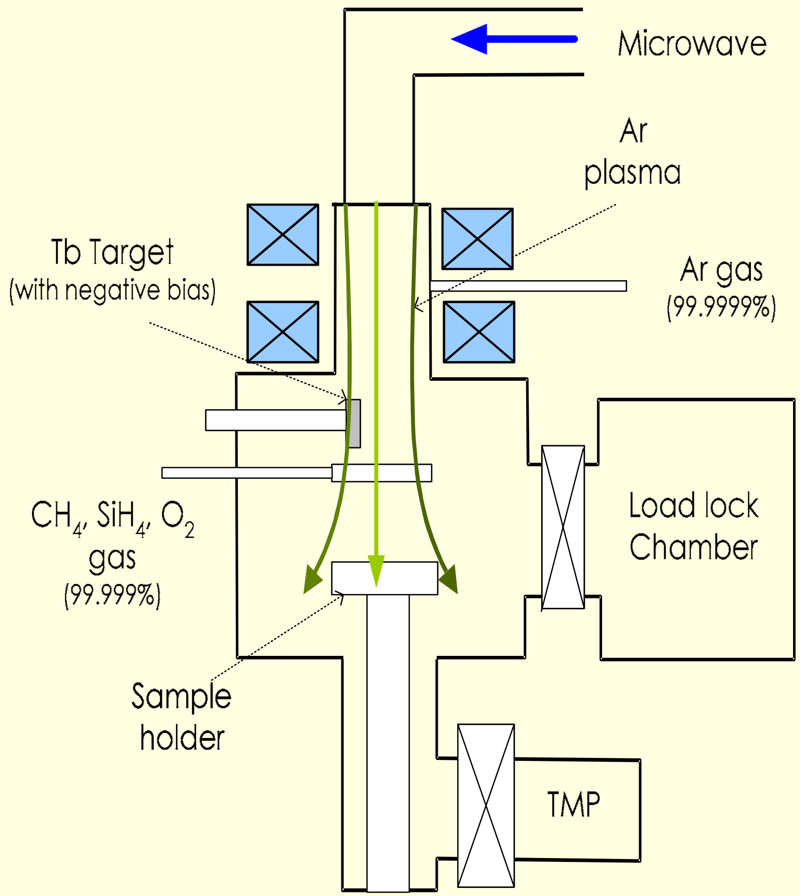
Experimental details

Film fabrication

• **Deposition method:** ECR-PECVD

• **Gases:** SiH_4, O_2 (fixed) & CH_4 (varied)

• **Tb doping:** concurrent sputtering of solid target



Film Characterization

• Rutherford backscattering Spectroscopy

• Wavelength dispersion X-ray spectroscopy

• FTIR & SEM

Experimental details (cont'd)

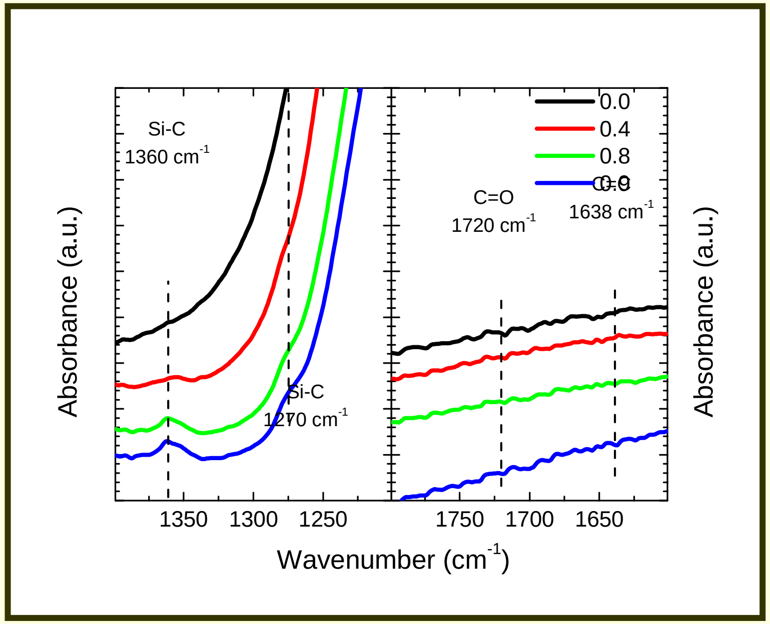
Post treatment

- **Thermal Annealing:** 700—1250 °C for 30 min under Ar environment
- **Hydrogenation:** thermal anneal @700 °C for 1h flowing H_2 forming gas

Photoluminescence Measurement

- **Pump Source:** 325 nm of HeCd laser
- **Detectors:** InGaAs(Cs) photomultiplier tube or Charge coupled device
- **Luminescence decay traces:** recorded with digitizing oscilloscope using mechanical chopper

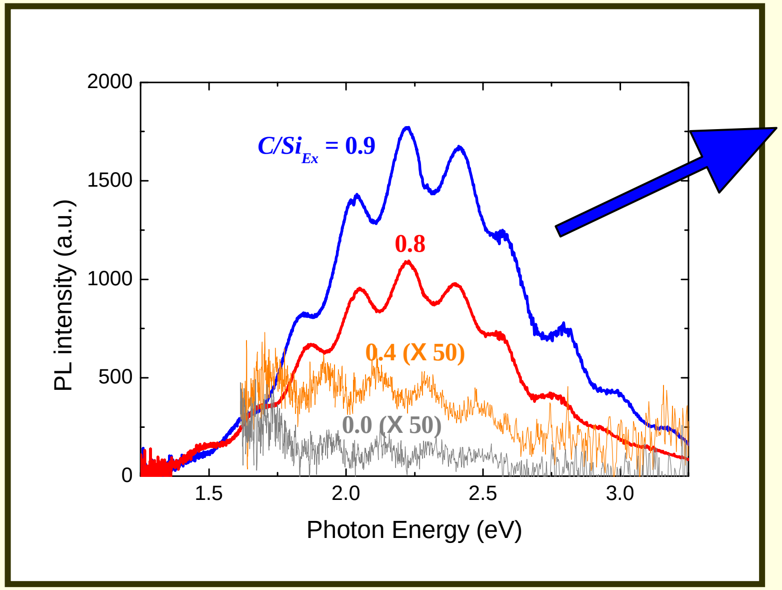
Infrared absorption: FTIR

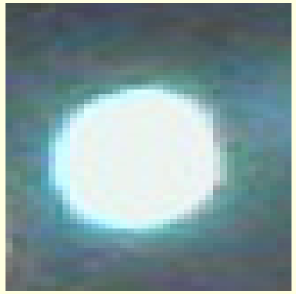


- Films were annealed for 5min @ 950 °C under Ar environment
- Confirmed Si-C bonds (1360 and 1270 cm^{-1})
- NO C=O (1720 cm^{-1}) and C=C (1638 cm^{-1}) bonds
- Incorporated C ions are bonded only with Si
- Excluded the possibility of the presence of silicon oxycarbide phase

Strong visible luminescence : effect of carbon

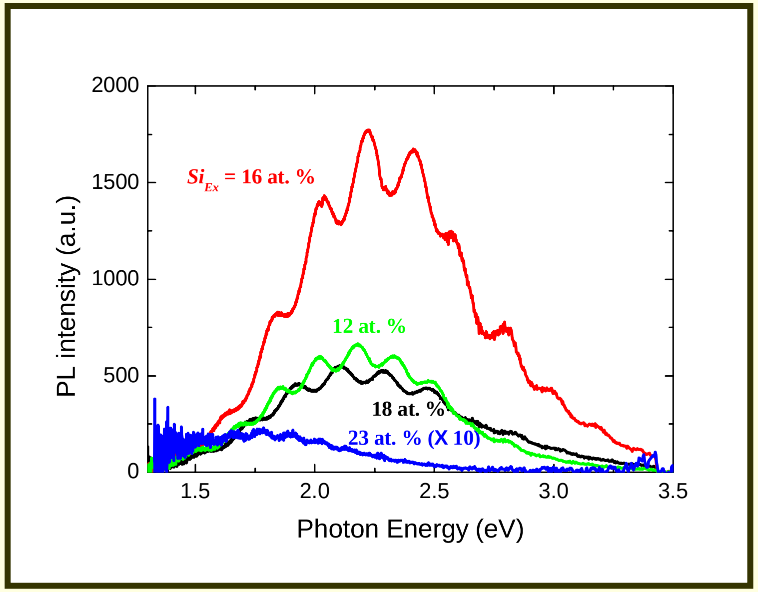
Camera image →

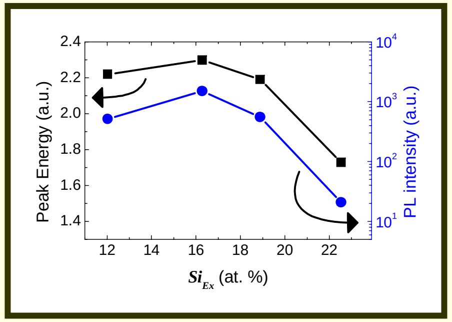




- Films were annealed for 5min @ 950 °C under Ar environment
- Sigmoid oscillation in PL spectra: due to internal reflection
- Very little PL without C, and ~ 500 folds increase of PL by C doping
- Intense blue-white luminescence, visible to naked eyes, under ambient condition

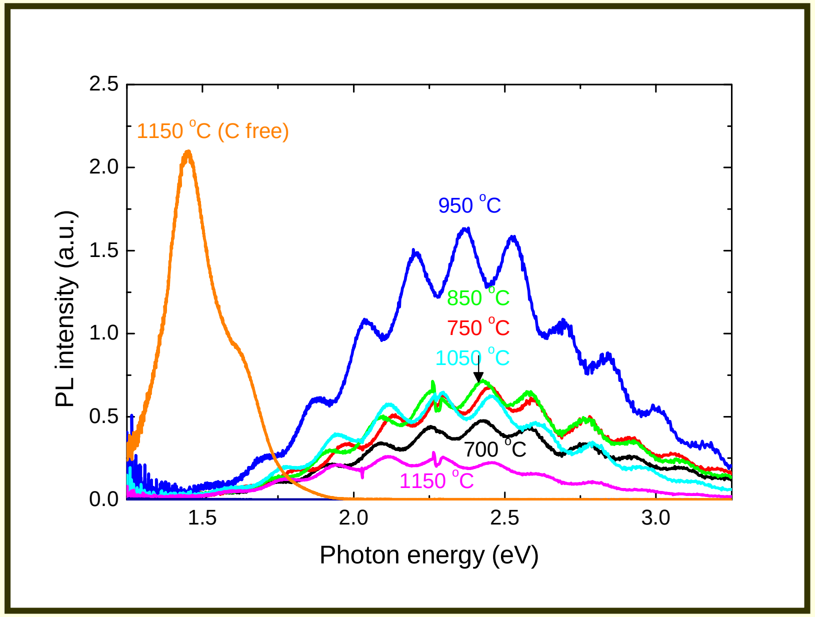
The effect of excess Si content on visible luminescence of SRSO:C

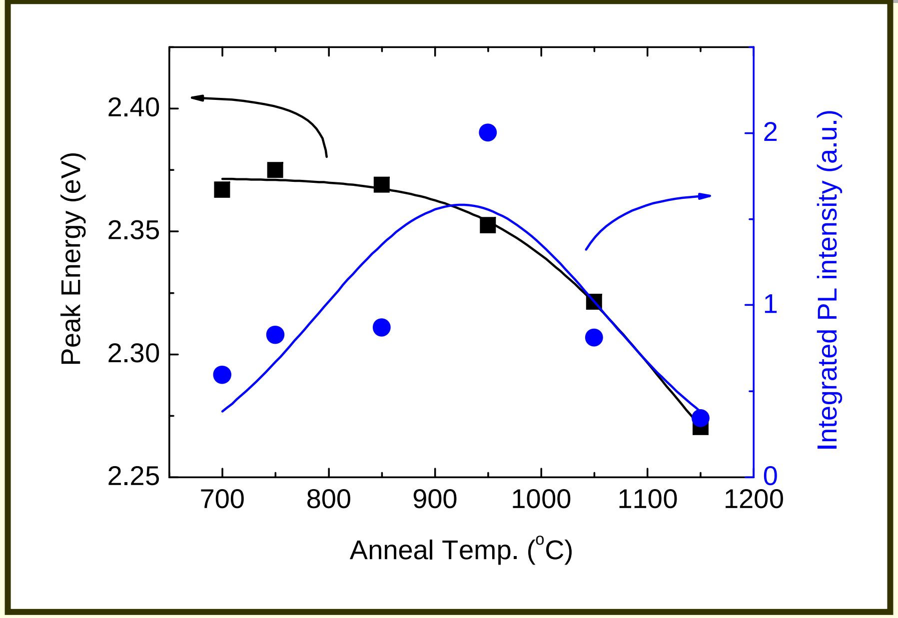




- The C to excess Si ratio is almost constant (near unity)
- The increase of C and excess Si
  - ➔ Strong red shift from 2.3 to 1.7 eV
  - ➔ Reduction of PL intensity by 100 times
- Red Shift of PL peak : consistent with C free SRSO

The effect of anneal temperature on visible luminescence of SRSO:C





- Si content: 39 at. % with C to excess Si ratio of ~ 0.9
- All films were annealed and hydrogenated
- PL intensity of SRSO:C is larger than that of SRSO by factor of 3 (between optimum films)
- The increase of C and excess Si
  - ➔ Strong red shift from 2.46 to 2.25 eV
- Red shift of PL peak by increase of anneal temperature: consistent with C free SRSO

The origin of visible luminescence of $SRSO:C$

The origin of luminescence

- Exact origin is not clear
- C is essential for blue-white luminescence
- Overall trend can be consistently explained with those of nc-Si

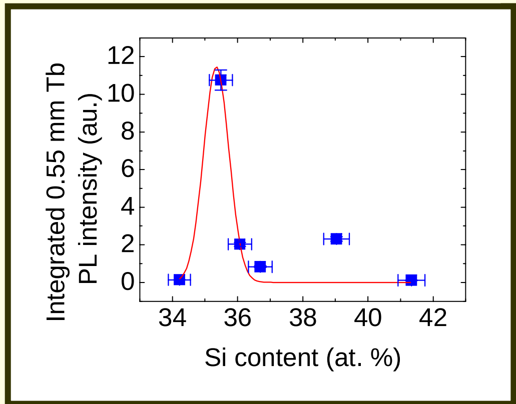
➔SiO_2 like matrix embedded with nc-Si which incorporate a high concentration of C

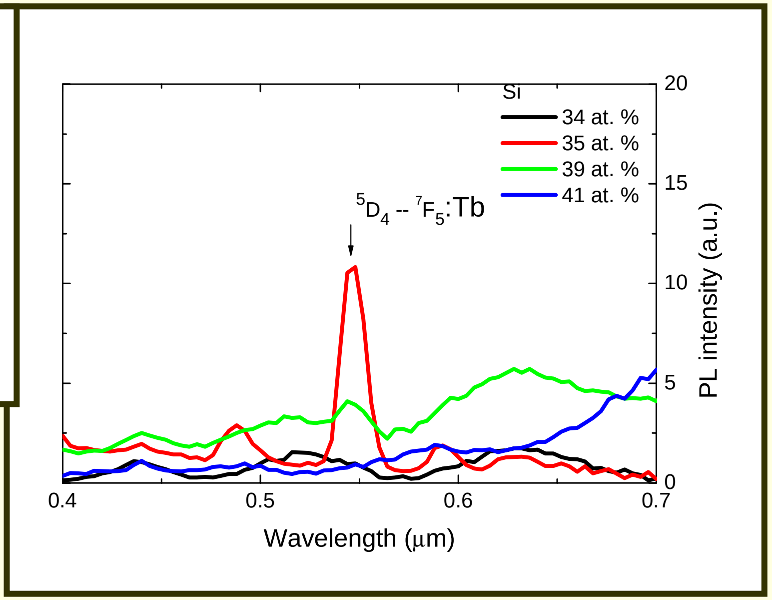
➔Luminescence due to excitons being confined in C-doped nc-Si

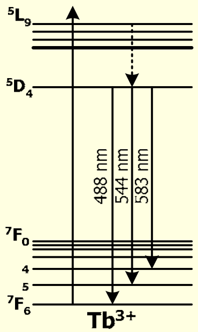
Now check the feasibility of visible RE luminescence!!!

Firstly tried with Tb for green (λ~550 nm)

Tb^{3+} luminescence in SRSO: effect of Si content



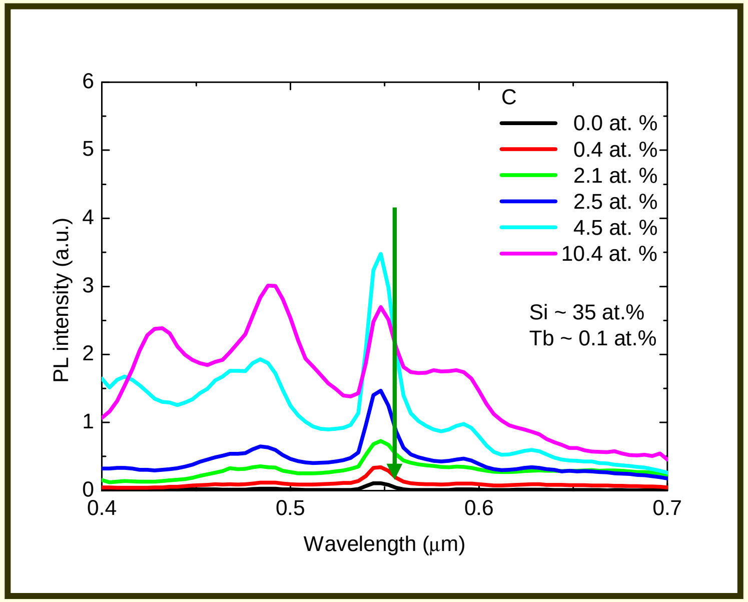


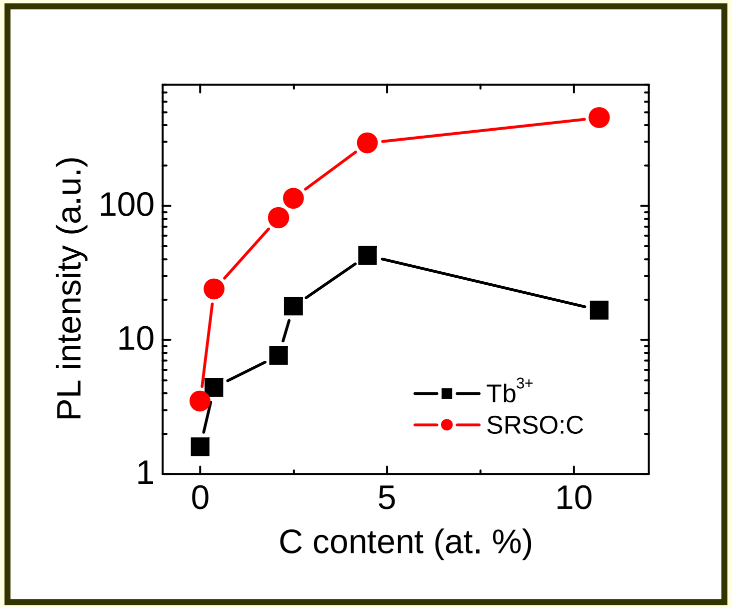


←Energy diagram of 4f transition of Tb^{3+} ions

- Weak background luminescence: maybe due to oxide defects
- Clear 543 nm PL due to $^5D_4 \rightarrow {}^7F_5$ 4f transition of Tb^{3+} within a narrow range of Si content (35– 37 at. %)

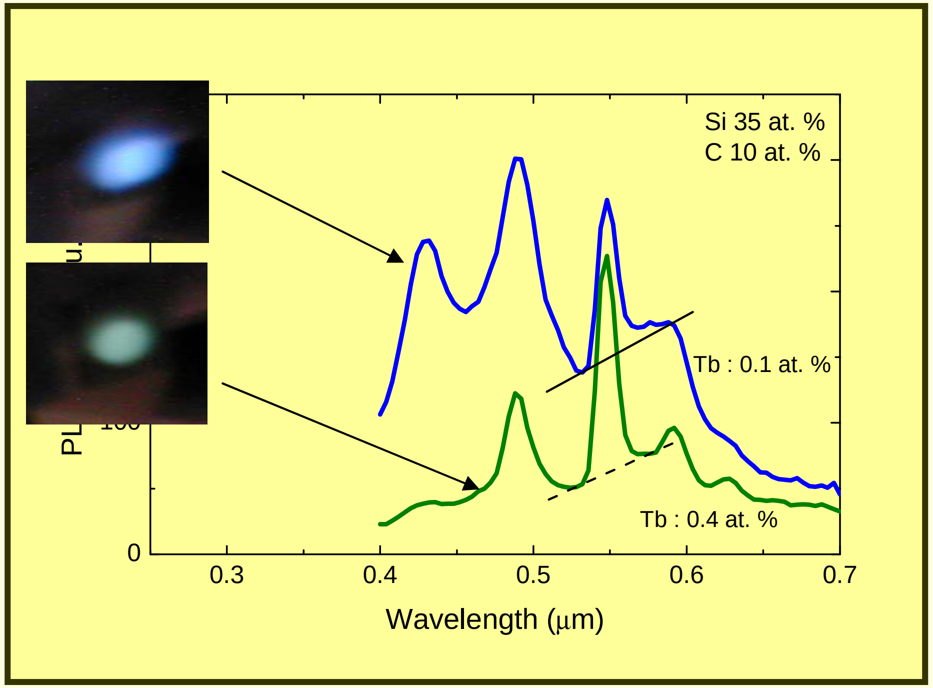
Enhanced Tb^{3+} luminescence in SRSO by C co-doping





- Broad background luminescence (400-700 nm) due to oxide SRSO:C
- As C content increases both SRSOC and Tb^{3+} luminescence increase
- Tb^{3+} PL is enhanced more than 30 times by C co-doping!!!

Effect of Tb concentration on Tb and C-doped nc-Si luminescence

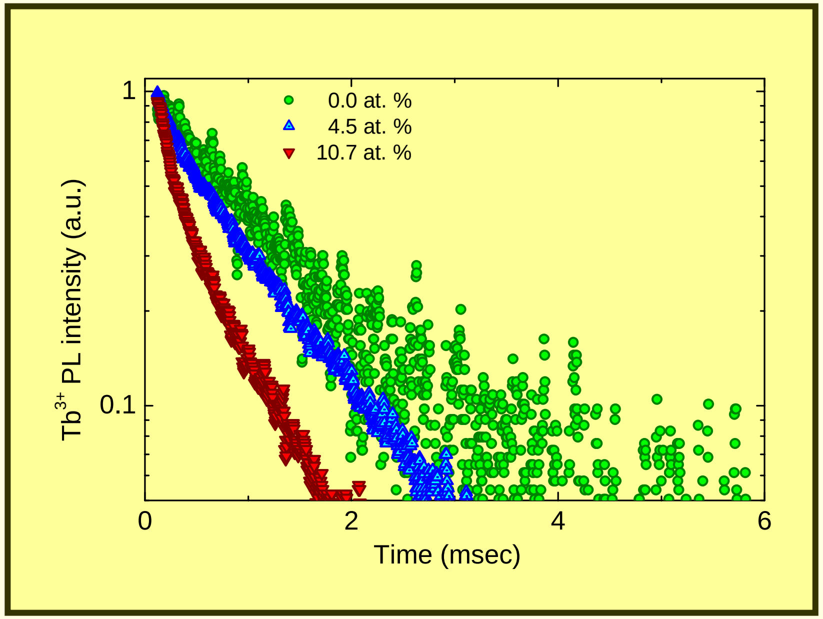


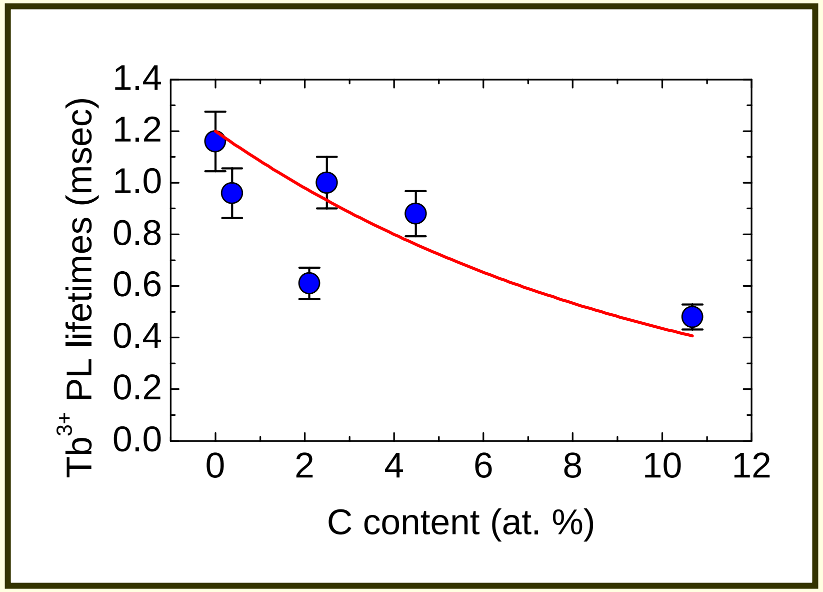
- For low Tb content, bluish white and greenish white for high Tb content
- As Tb content increases

➔ Suppression of SRSO:C PL

➔ Increase of Tb^{3+} PL

Tb^{3+} luminescence lifetimes of Tb-doped SRSO:C



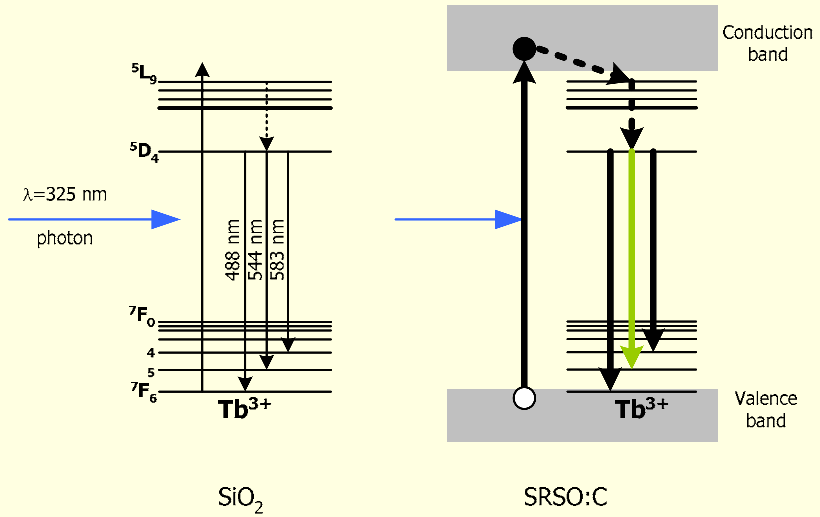


- SRSO:C host luminescence decay is faster than system response (~10 usec) and is excluded
- As C content increases, Tb^{3+} PL lifetimes are decreased from 1.2 to 0.5 msec

➔ Comparable values with those (~ msec) from Tb-doped SiO_2

➔ Luminescent Tb ions are in SiO_2 matrix

Exciton mediated excitation of RE in SRSO:C host



Evidence of energy transfer from SRSO:C to Tb^{3+} ions

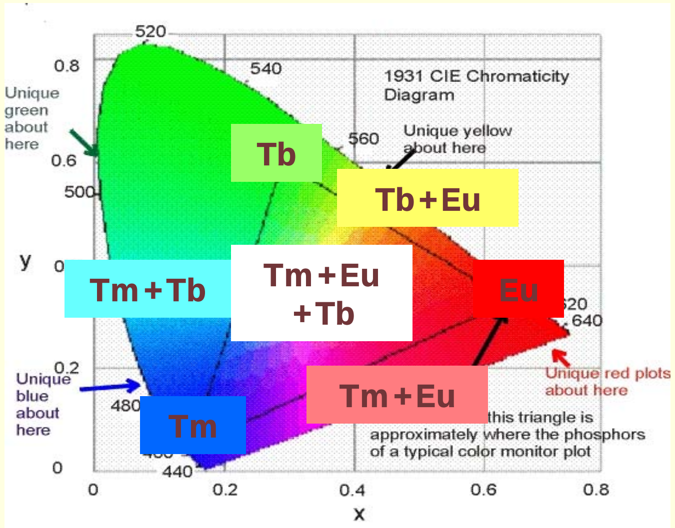
- 325 nm cannot be directly absorbed by Tb^{3+} ions
- Suppression of PL from host matrix by increase of Tb concentration
- Very weak Tb^{3+} PL from Tb-doped silica and narrow range of Si content which can excite Tb^{3+} ions

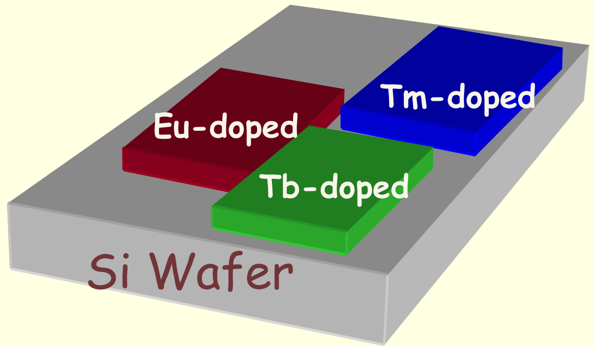
Role of C co-doping on Tb^{3+} luminescence in Tb-doped SRSO:C

- Increase of the number of high-energy excitons that can excite Tb^{3+}

➔ Enhances exciton-mediated excitation rate of Tb^{3+}

Implication: Full color display based on RE-doped SRSO:C





Feasibility of full color by selection/co-incorporation of RE ions

Integrated RGB display pixel on Si wafer using Si compatible technology

Summary And Conclusion

- **Co-doping of C significantly increases blue-white luminescence**

→The recombination of excitons in C rich nc-Si is likely to be origin of visible luminescence

- **Strong sharp green luminescence can be observed from SRSO by co-doping of C and Tb**

→ Efficient energy transfer from high energy excitons to Tb ions leads to efficient Tb^{3+} luminescence in SRSO:C

- **The feasibility of Si based full color display using RE-doped SRSO:C films**