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
Silicon as photonic materials
- Very faithful technology and process in micro- or nano- scale
- Important related compound for photonics: Si, SiO₂, SiC and Si₃N₄
- ‘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 SiO₂ 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 microphotonic
Examples of nc-Si photonics

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 bandgap 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

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

(Puzder, JCP)
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:** SiH₄, O₂ (fixed) & CH₄ (varied)
• **Tb doping:** concurrent sputtering of solid target

Film Characterization
• Rutherford backscattering Spectroscopy
• Wavelength dispersion X-ray spectroscopy
• FTIR & SEM
Post treatment
- **Thermal Annealing:** 700—1250 °C for 30 min under Ar environment
- **Hydrogenation:** thermal anneal @700 °C for 1h flowing H₂ 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 5 min @ 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

- 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 luminescence

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

⇒ SiO₂ 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**

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

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