Material Science for Solar Cells:
Structural, Chemical and Optical properties of Amorphous Not Stoichiometric Silicon Oxide Layers Irradiated by CW IR Laser

Rosa Ruggeri, Fortunato Neri and Giovanni Mannino
Outline

- Silicon-based light emitting materials: SRO and Si Quantum Dots
- SiOxNy annealed by IR Laser system
  - Tunable PL from Amorphous layers:
    - Optical characterization
    - Structural characterization
    - Chemical characterization
- Conclusion
Silicon-based light emitting materials

- High temperature furnace annealing of SOR (1100°C, 30min)
- QC model: Direct Band Gap
  - the SMALLER the SiQDs size the LARGER band gap of the material

Silicon-based light emitting materials

Not stoichiometric Silicon oxide

with

high Nitrogen content (10-20 %)

Millisecond Infrared Laser Annealing
( even on not conventional substrates)

Tunable Photoluminescence
from Amorphous NOT Clustered Structures
Laser System

Sample temperature:
✓ Output power
✓ Scanning speed

Annealing time
(few milliseconds):
✓ Laser profile
✓ Scanning speed

GaAs diode
($\lambda = 808$nm)

Rosa Ruggeri,
Joint EPS-SIF International School on Energy
Varenna, 2 August 2012
Experimental

- Sample deposited by PECVD at 280°C between two SiO$_2$ layers or by Sputtering
- Silicon substrate is the absorbing layer
Dependence on Stoichiometry

PE-CVD
✓ Precursor Gas: N₂O and SiH₄
✓ Temperature 280°C

Magnetron co-Sputtering
✓ Target: SiO₂ and Si
✓ Temperature 400°C
Optical Characterization: PL

Spectra recorded at Room Temperature

PE-CVD sample

dependence of the center of the band on the laser power

Up to 135 kW/cm² PL Signal
Above 135 kW/cm² NO PL Signal

Rosa Ruggeri,
Joint EPS-SIF International School on Energy
Varenna, 2 August 2012
Structural Characterization: EF-TEM

- Silicon Plasmon (17 eV) Images

Laser annealed (100 – 135 kW/cm²)

PL Emitting at 950nm

Laser annealed (143 kW/cm²)

From Quantum Confinement Model
950nm PL corresponds to nanocrystals of ~5nm diameter
Silicon quantum dots by IR laser annealing in $\text{SiO}_x\text{N}_y$

Absence of luminescence is due to high concentration of impurities

Dependence on Stoichiometry

PE-CVD
✓ Precursor Gas: N\textsubscript{2}O and SiH\textsubscript{4}
✓ Temperature 280°C

Magnetron co-Sputtering
✓ Target: SiO\textsubscript{2} and Si
✓ Temperature 400°C

Rosa Ruggeri,
Joint EPS-SIF International School on Energy
Varenna, 2 August 2012
Dependence on Stoichiometry

Dependence of the center of the band on the laser power for different stoichiometry

Dependence of EMISSION RANGE ($\Delta \lambda$) on Stoichiometry

The role of N is crucial
Chemical Characterization: XPS

- Spectra acquired in Silicon sp2 region

As deposited  
Laser annealed (950nm)  
Laser annealed (NO PL)

Counts (a. u.)

Binding Energy (eV)

\[ \begin{align*}
\text{Si}^0 & \quad 98 \quad 100 \quad 102 \quad 104 \\
\text{Si}^+ & \quad 98 \quad 100 \quad 102 \quad 104 \\
\text{Si}^{+2} & \quad 98 \quad 100 \quad 102 \quad 104 \\
\text{Si}^{+3} & \quad 98 \quad 100 \quad 102 \quad 104 \\
\text{Si}^{+4} & \quad 98 \quad 100 \quad 102 \quad 104 
\end{align*} \]
Chemical Characterization: XPS

Spectra acquired in Silicon sp2 region

Dependence of EMISSION RANGE

Oxidation State | Binding Energy (eV) | Molecular Configuration
--- | --- | ---
Si | 99.7 | Si
Si | 100.7 | Si
O / Si | 6 | Si
N | 3 | Si
Si | 101.8 | SiO / Si
O | 3 | Si
N | 4 | Si
Si | 102.7 | Si
O | 3 | Si
O | 3 | Si
N | 2 | Si
N | 4 | Si
Si | 103.7 | Si
O | 2

We recognize in Si-O-N bonds the emission center. The red shift is related to Si chemical environment changes. Increasing Laser Power progressively, Si atoms are bound to more electronegative species.

The presence of N makes the oxidation process slower because more complicated molecular configurations are possible. By changing the stoichiometry we can have a wider emission range.

Conclusion

- At low temperature the Si-O-N bonds locally stabilise into N-rich configurations; increasing temperature, they evolve into higher oxidation degree states, i.e. O-rich configurations.

- The variation of the local composition within the amorphous matrix (no clusters visible by TEM) implies a red shift of the emission spectrum.

- When separation phase occurs, metallic Si in the SiDs is not the source of luminescence at room temperature in laser-annealed samples. A post process annealing is necessary to obtain a luminescence signal.

Rosa Ruggeri
Università di Messina
IMM-CNR Catania/rosa.ruggeri@unime.it