EXCIMER-LASER ENHANCED FORMATION OF LUMINESCENT NANOCRYSTAL-Si/SiO_2 SUPERLATTICES

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Outline

- **Si/SiO_2 superlattice for size-controlled, dense nc-Si arrays**
- **Problem of thermal annealing of Si/SiO_2 superlattice**
- **Excimer laser annealing for formation of luminescent nc-Si:**
- **Results**
- **Analysis**
  - **Single-triplet model of nc-Si luminescence**
  - **Comparison of low temperature PL**
- **Conclusion**

Introduction

- **What is nanocrystal Si?**
  - Si crystals in size range in which quantum effects become important

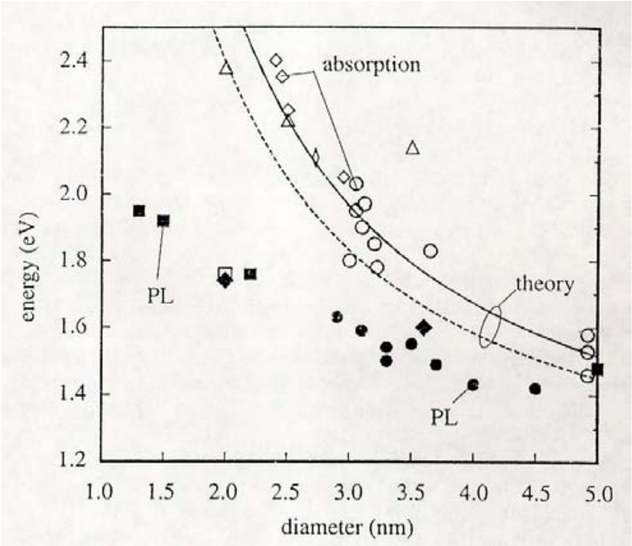
    ➔ Rule of thumb: crystal radius < exciton Bohr radius

Element	Badgap Type	Bulk Bandgap (eV)	Exciton radius (nm)
Si	Indirect	1.12	4.9
Ge	Indirect	0.66	17.7
GaAs	Direct	1.42	14
SiC	Indirect	2.88-3.2	2.7
GaP	Indirect	2.26	1.7

- **Si requires radius of < 5 nm to be “nanocrystal Si”**

Applications of nc-Si

- **Si-based photonics**

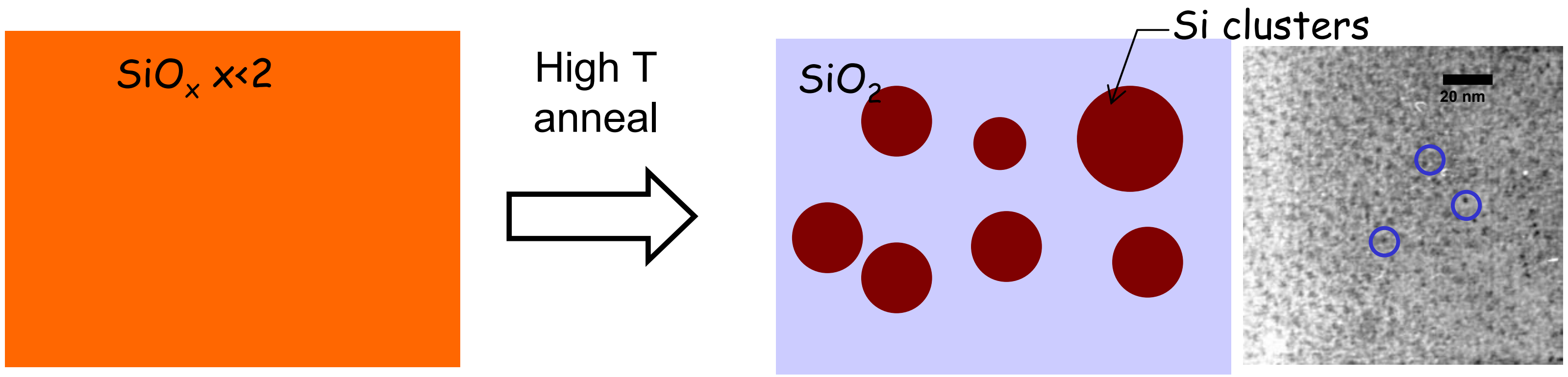


  - Efficient luminescence at room temperature (Canham, APL 1990)

- **nm-scale Si electronics**
  - Single electron transistors
  - floating-dot based flash memories (Tiwari, APL 1998)

Forming nc-Si

- **Silicon-rich silicon oxide:**
  - Precipitation of nc-Si from a-SiOx by a high temperature anneal (Shimizu, APL 1993)



- **Advantages:**
  - Robust array of nc-Si with high-quality oxide passivation
  - Full compatibility with the standard Si processes
  - Optical gain demonstrated (Pavesi, Nature 1999)
  - Light emitting diodes with high quantum efficiency at room temperature demonstrated (Franzo, APL 2002)

Disadvantages of using silicon-rich oxide

- **Precipitation dynamics controlled by supersaturation**

Nucleation rate from a homogeneous supersaturated solution =

$$\mathbf{I \propto \exp(-\Delta G_{c.}/kT) \propto \exp(-1/j^2)}$$

Very sensitive to supersaturation!

Growth rate of in case of diffusion-controlled growth =

$$\mathbf{dr/dt \propto D(T)\ (C^s - C^a)/(C^b - C^a)r}$$

For a fixed T, completely determined by supersaturation!

Time-dependent cluster nucleation =

$$\mathbf{\partial Z/\partial t = \partial/\partial n\ (D\ \partial Z/\partial n) + 1/kT\ \partial/\partial n\ (DZ\ \partial G(n)/\partial n)}$$

Zeldovich-Frenkel equation: formally equivalent to diffusion equation,
and thus determined by initial conditions

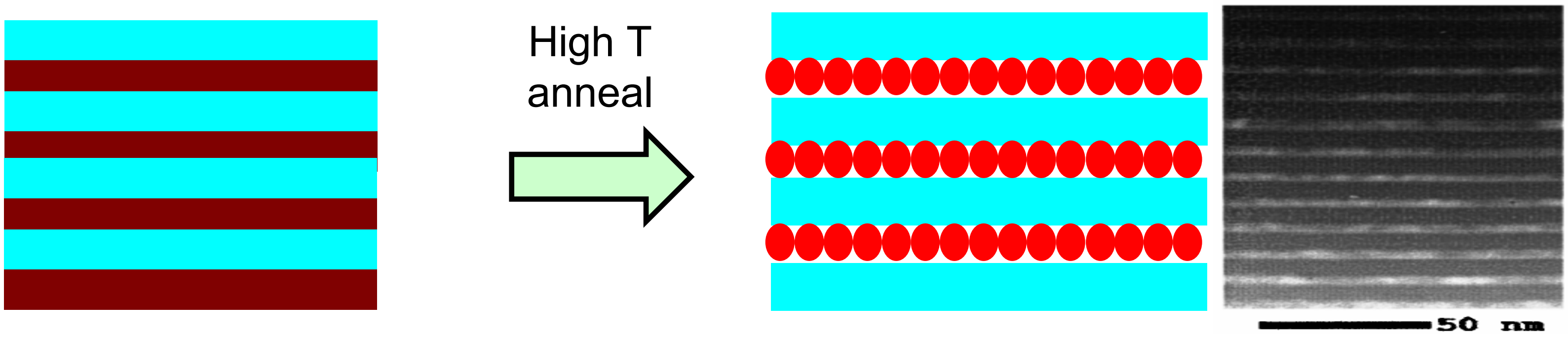
- **Independent, simultaneous control over size and density difficult!**

- **What is usually desired**
  - High density of nanocrystal Si
  - Uniformity of size – to suppress inter-particle energy migration
  - Low thermal budget (low T, short t)

- **Such requirements are difficult to meet with precipitation**
  - High density Si nanocrystals: requires high supersaturation
    ➔ Results in high nucleation rate but also in high growth rate: leads to large Si crystals
  - If we use low supersaturation for small Si nanocrystals
    ➔Results in low nucleation rate and low growth rate: requires very high, long anneals, leads to Ostwald ripening of nucleated Si nanocrystals

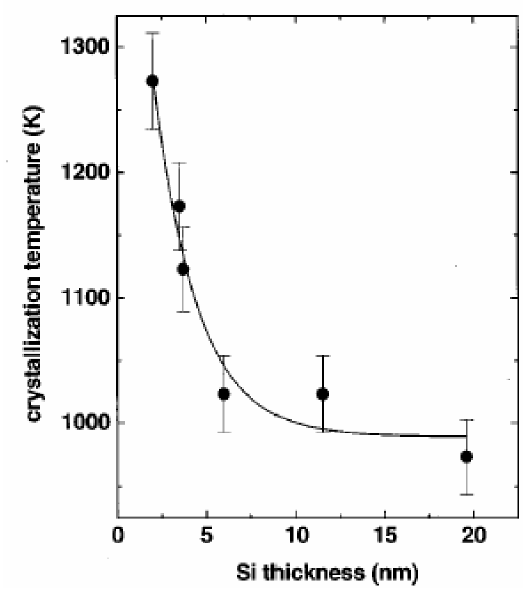
Si/SiO_2 superlattice

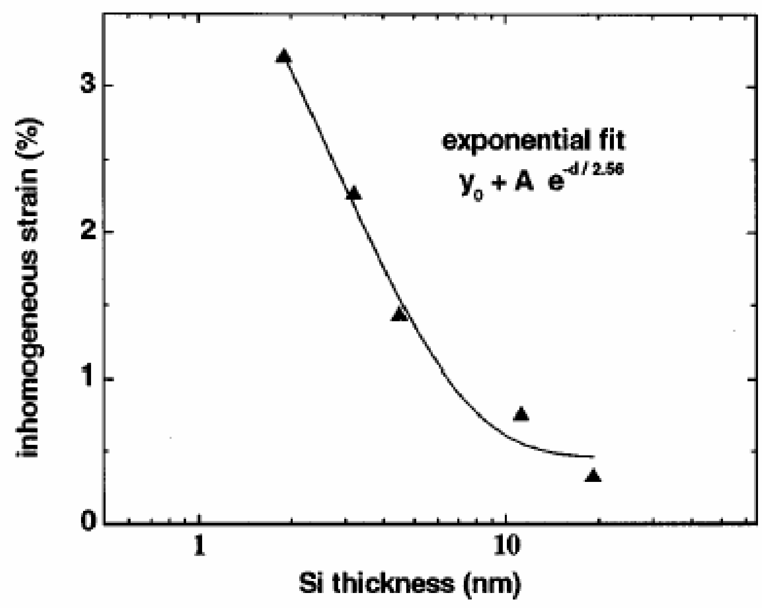
- **nm-thin Si/SiO_2 superlattice**
  - Crystallization of a-Si/SiO_2 superlattice (Tsybeskov, APL)



- **Advantages:**
  - nc-Si size controlled by the original a-Si layer thickness
  - nc-Si density controlled by deposition, not by precipitation
  - nc-Si location controlled in the vertical dimension
  - Full compatibility with the standard Si processes

- **Problems of Si/SiO_2 superlattice**





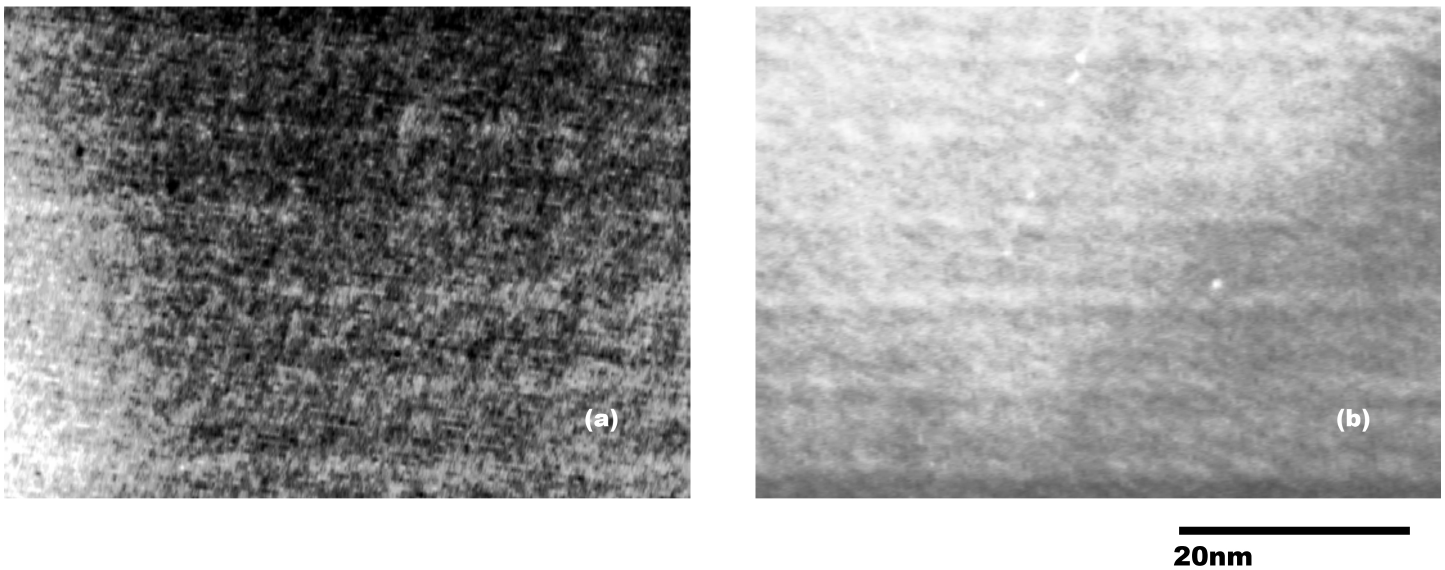
- Strong inhomogeneous strain due to crystallization of a-Si in a-SiO_2 matrix (Zacharias, PRB2000)
- Drastically increases the crystallization temperature (Zacharias, APL 1999)
- 2 nm or below: nearly impossible to crystallize while maintaining the layer integrity

- **Proposal: Excimer laser annealing of a-Si/SiO_2 superlattices**
  - Excimer laser annealing – sufficient to melt bulk a-Si layers
  - Used to produce high-quality polysilicon thin films for TFT applications
  - Low thermal budget process – substrate temperature kept low
  - Maybe excimer laser anneal can produce ultra-thin crystalline Si layers?

Experiment

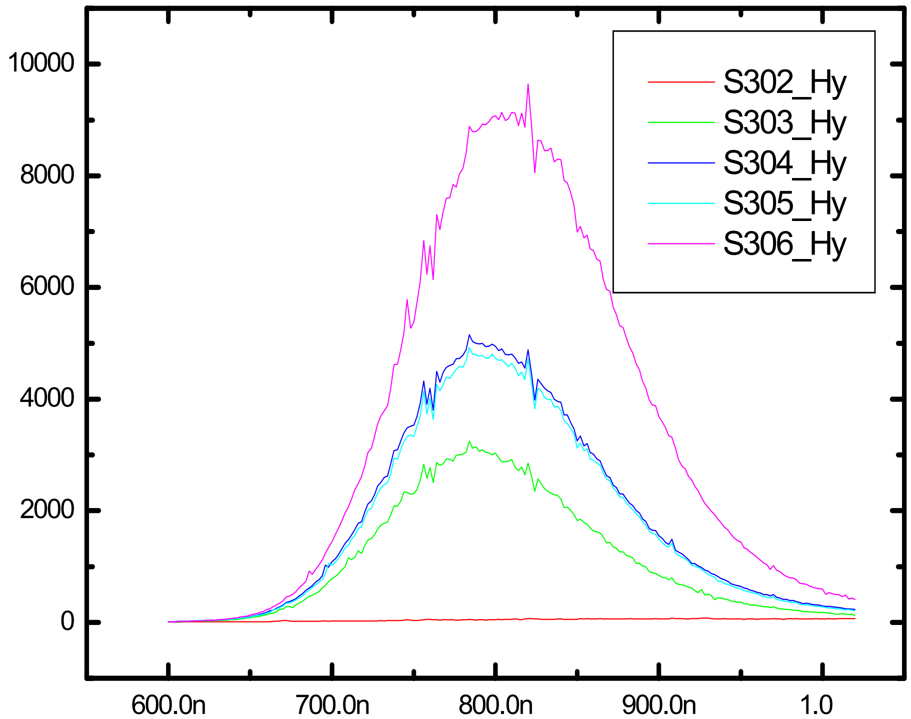
- **Experimental conditions**
  - **Film deposition: ECR-PECVD of SiH_4 and O_2**
    - Film structure: Si layer → 2 nm in all cases (20 layers)
      SiO_2 layer → 5nm thin (21 layers)
  - **For excimer laser anneal:**
    - 30 nsec XeCl excimer laser (308 nm, 3 pulses at RT)
    - Laser power: variable
  - **Anneal**
    - Anneal temp: 1000 , 1100 , 1200 °C
    - Anneal time: 30 min , 1h
  - **Hydrogenation**
    - 1 hr anneal in flowing forming gas environment for 1 hr
  - **Photoluminescence**
    - 488 nm line of an Ar laser, 200 mW
    - GaAs:Cs PMT, employing lock-in technique

- **Fabricated samples**



(a) Thermal anneal (b)Thermal anneal + excimer

Results



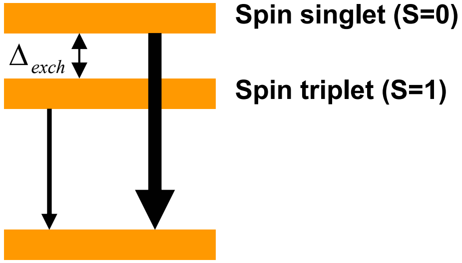
<1> Raw sample	<2> At 500°C for 1 hour in Furnace & exposed 3 shots of at $504 mJ/cm^2$	<3> At 1100°C for 1 hour only
<4> At 1100°C for 1 hour & exposed 3 shots of $256 mJ/cm^2$	<5> At 1100°C for 1 hour & exposed to 3 shots of at $372 mJ/cm^2$	<6> At 1100°C for 1 hour & exposed to 3 shots at $504 mJ/cm^2$

- Excimer laser anneal increases the PL intensity nearly 3-fold over thermal anneal alone
- Slight redshift of the PL peak
- No PL when excimer laser annealed only

➔ Are we really looking at nc-Si luminescence?

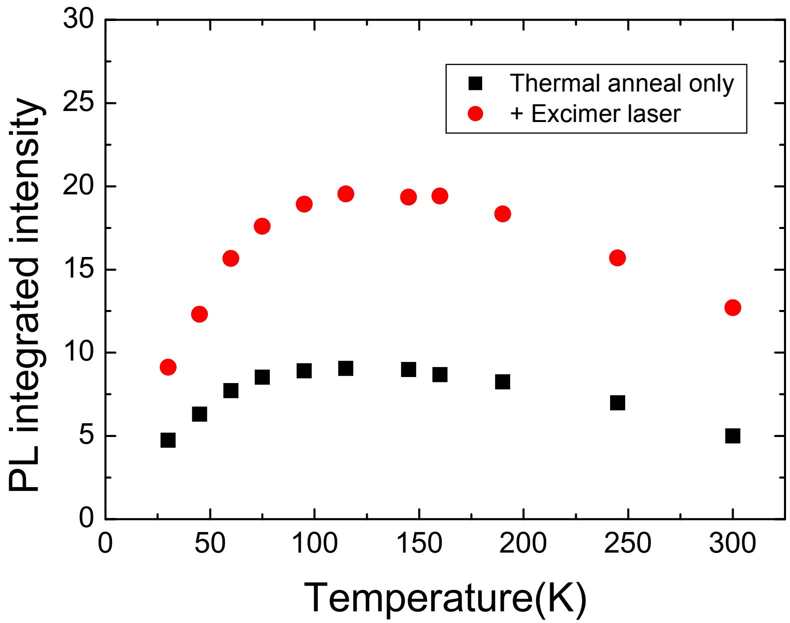
Analysis of luminescence:

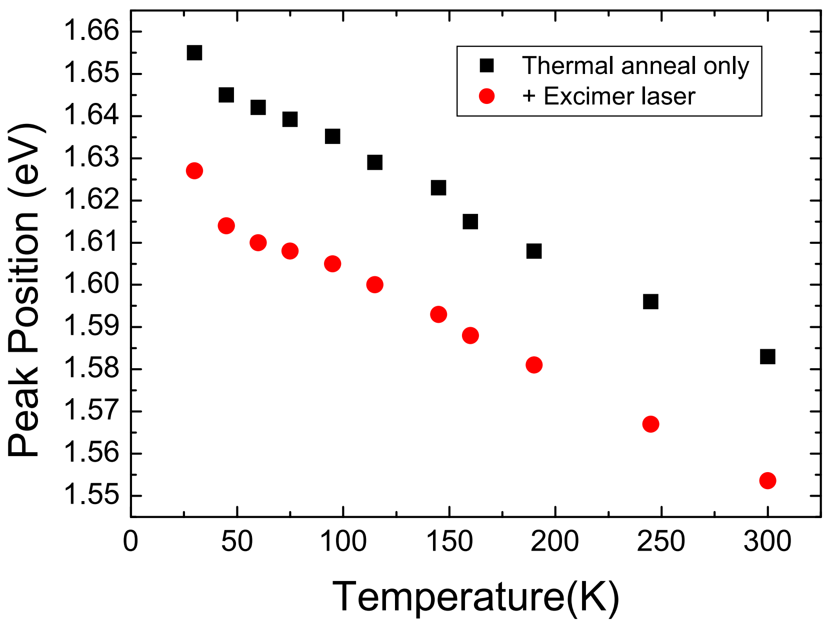
- **Single-triplet model of nc-Si luminescence**
  - nc-Si luminescence due to excitons localized on the nc-Si surface
  - Exchange splitting of “dark” triplet and “bright” singlet
  - Used to explain temperature dependence of PL intensity and lifetime (Reboredo, PRB 2000, Brongersma APL 2000)



$$R_R = \frac{3R_T + R_S \exp(-\Delta_{exah} / kT)}{3 + \exp(-\Delta_{exch} / kT)}$$

$$R_{tot} = R_R + R_{NR}$$

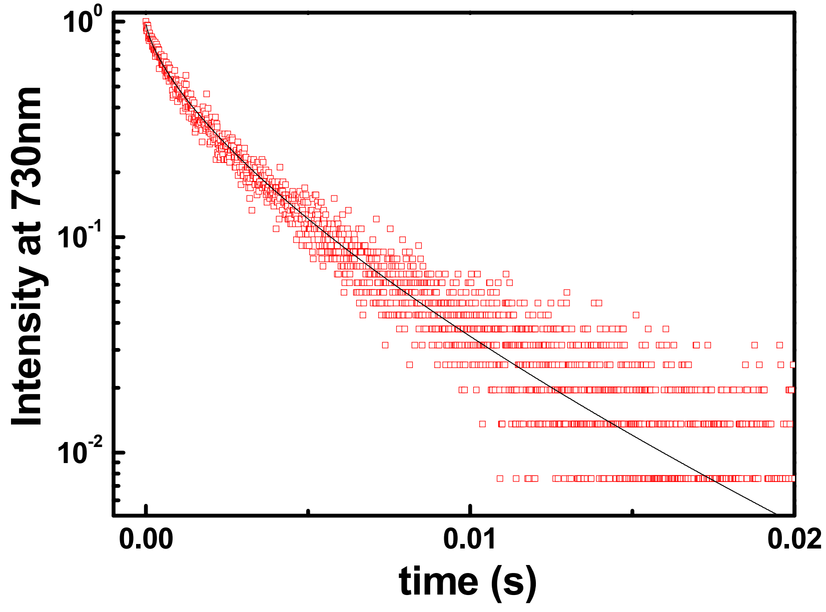


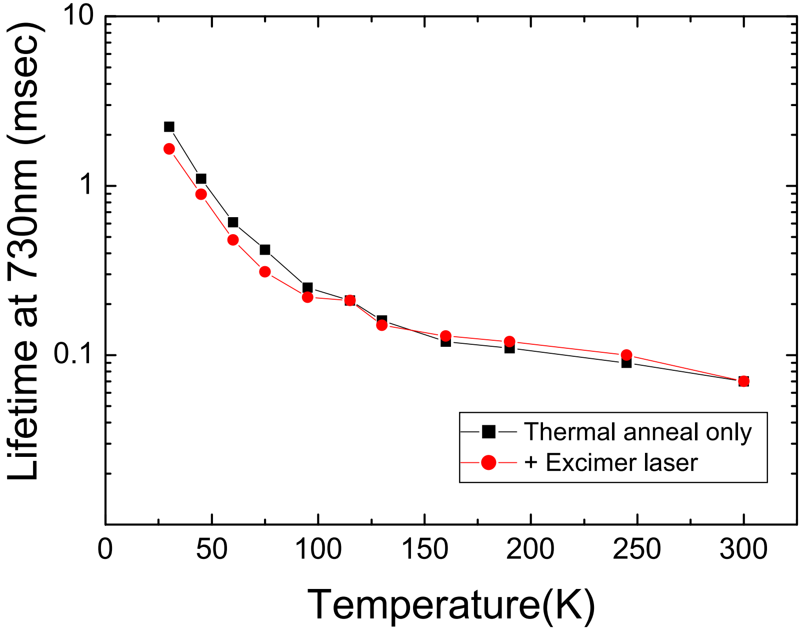


- PL intensity: first increases with temperature, then decreases
- Monotonic redshift of peak position with temperature

➔Consistent with nc-Si luminescence

- Excimer laser anneal has little effect on temperature dependence of PL intensity

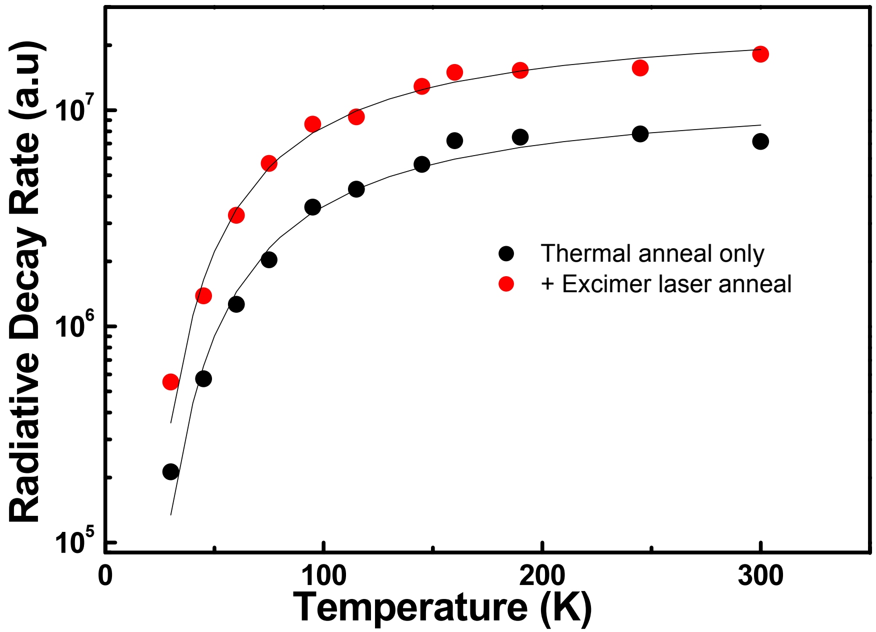




- PL decay well-described by a stretched exponential function ($I \propto \exp[-(t/\tau)^\beta]$)
- Monotonic decay of lifetime with temperature from > 2msec to < 100 usec

➔ Consistent with nc-Si luminescence

- Excimer laser anneal has no effect on the luminescence lifetime



- $I_{PL} \propto \frac{R_R}{R_{tot}} N_{exc} \Rightarrow I_{PL} R_{tot} \propto R_R$ at constant pump power

- Radiative decay rate well described by the singlet-triplet model of nc-Si luminescence
- Exchange splitting: 12 meV for both films

➔ In good agreement with previously reported values for nc-Si

- Excimer laser anneal has no effect on the exchange splitting

Discussion

- **Photoluminescence properties:**
  - Peak shape, energy, lifetimes, and temperature dependence consistent with nc-Si luminescence
  - Exchange split in good agreement with previously reported values

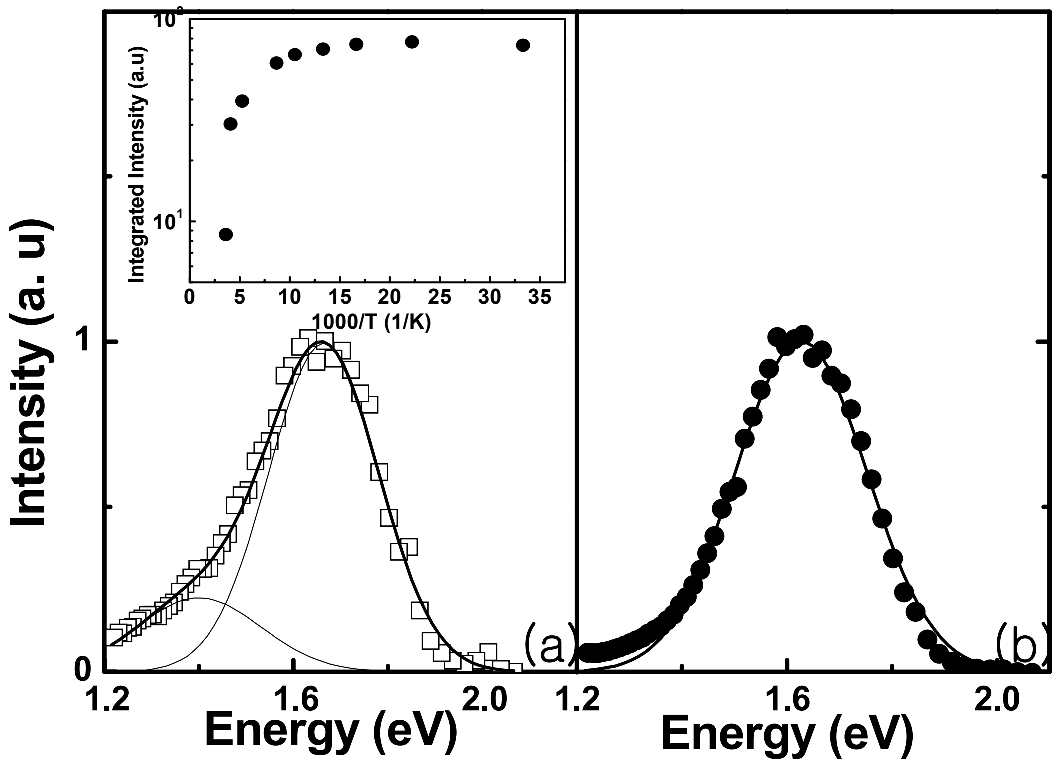
  ➔ **Thermal anneal + excimer laser anneal can greatly enhance nc-Si PL**

- **Excimer laser anneal:**
  - 504 mJ cm^{-2} energy density is sufficient to initiate melting of bulk a-Si layers
  - Total a-Si thickness: 40 nm < expected melt depth: 80 nm
  - Layered structure may inhibit propagation of melt front → but 40 nm is about the absorption depth of the excimer laser beam
  - Melting + recrystallization? → NO. Excimer laser anneal has little effect on nc-Si size, PL intensity and lifetime, and on exchange splitting

  ➔ **nm-thin layers are resistant to excimer laser crystallization as well**
  ➔ **Excimer laser anneal does not enhance formation of nc-Si**

- **What does excimer laser anneal do?**

- **Low-temperature PL spectra**



Thermal anneal

Thermal anneal+ELA

- Thermal anneal only: appearance of 1.4 eV PL peak similar to that of a-Si
- Excimer laser anneal: PL peak remains Gaussian down to 25 K

- **Excimer laser anneal removes defects / amorphous regions:**
  - Similar to what's known from excimer laser anneal of thermally crystallized poly-Si TFT
  - "Activates" nc-Si for luminescence – reverse of what's been reported on ion beam irradiation of nc-Si (Pacifici, PRB 2002)

- **Could we achieve this with thermal annealing? :**
  - No – 1200℃ anneal resulted in spalling of the entire film
  - Prolonged anneal at high temperatures can result in strong redshift of the PL peak.
  - Anneals at high temperatures undesirable from the process point of view

  ➔ **Thermal anneal + excimer laser anneal offers an attractive, low-thermal budget approach on optaining highly luminescent nc-Si arrays**

Conclusion

- **Excimer laser anneal alone does not enhance formation of nc-Si in nm-thin Si layers**
- **Thermal anneal + excimer laser anneal increases the nc-Si luminescence 3-fold**
- **The primary role of excimer laser anneal is removal of defects and amorphous regions to activate more nc-Si without significantly affecting their morphology**

Acknowledgment

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