Fabrication of Multiply-Stacked Structures Consisting of Si-QDs with Ultrathin SiO_2 and Its Application of Light Emitting Diodes

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Abstract

We have fabricated Si quantum dots (Si-QDs) multiply-stacked in SiO_2 matrix as an active layer for light emission by repeating a process sequence of Si dot formation from thermal decomposition of SiH4 on SiO_2, surface oxidation by remote O_2-plasma and subsequent surface modification by remote Ar- and H_2-plasmas. By injection of electrons from semitransparent Au top electrode and simultaneously holes from the p-Si(100) substrate, light emission in the visible and near-infrared regions was observed at room temperature. The light intensity was linearly increased with forward current but no emission was detected under backward conditions In addition, in phosphorus doping to Si-QDs, a significant enhancement of the emission efficiency and a decrease in the threshold voltage are demonstrated.

Introduction

Nanometer-scale silicon structures have been intensively studied because their unique physical properties associated with carrier confinement effect and Coulomb blockade motivate us to introduce new functionalities to Si-based devices. As for charge transfer and storage devices, resonant tunneling diodes [1], single electron transistors [2] and quantum-dots (QDs) floating gate memories [3-5] have been fabricated and their feasibility has been demonstrated. In addition, visible light emission from Si nanostructures including porous Si [6-7] has stimulated considerable interest and research activity to develop Si-based light emitting devices [8, 9]. Despite many efforts, the improvement of the efficiency in electroluminescence and its stability are still major challenges. Recently, we developed a fabrication method [10] for multiple-stacked Si-QDs embedded into SiO_2 matrix, where Si dot formation by chemical vapor deposition (LPCVD) using pure SiH_4 are combined sequentially with surface oxidation and subsequent surface modification by remote plasmas.

In this work, we focus electrically stimulated light emission from Si-QDs multiple-stacked structures in comparison to their photoluminescence properties.

Experimental

After conventional wet-chemical cleaning steps of p-Si(100) wafers with a resistivity of 8 - 10 Ωcm, the wafer surfaces were oxidized at 1000 ºC in dry O_2 to form 4nm-thick SiO_2. The SiO_2 surface was exposed to remote plasmas of pure Ar and subsequently H_2 at 560 ºC for 1min in each steps, which resulted in the uniform formation of surface OH bonds. Subsequently, Si-QDs were formed from the thermal decomposition of pure SiH_4 under 0.5Torr at 560 ºC [11] and followed by radical oxidation of 1%O_2 diluted with He under 0.1Torr at 560 ºC to cover the dot surface conformally with ~2.4nm thick SiO_2. In remote plasma generation, a 60 MHz power source was used. By repeating such a process sequence consisting of the surface oxidation and modification by remote plasma treatments and the Si dot formation by LPCVD, a Si QDs multiple-stacked structure embedded in the SiO_2 network was formed. For a light emitting diode structure, after N_2 annealed at 1000ºC, semitransparent Au (~40nm in thickness) and Al were formed as front and back electrodes, respectively, by thermal evaporation.

Results and Discussion

Current-voltage (I-V) characteristics of fabricated diodes with Si dots multiple-stacked structures shows clear rectification properties in which electron injection from Au gate and hole injection from p-Si(100) occur at negative gate voltages, namely at the forward bias condition (Fig. 1). When the negative gate voltage exceeds around -10V, a kink in the I-V curves appears and electroluminescence (EL) becomes observable in the range from near-infrared to visible region even at room temperature as shown in Fig. 2. And the EL intensity increases linearly with increasing current. With increasing negative gate bias from -10 to -20V, the EL was enhanced by more than one order of magnitude. No EL was detected at positive gate voltages.

When comparing the EL spectrum with photoluminescence (PL) spectrum taken at room temperature under excited by a 325nm light from a He-Cd laser, there is a significant difference in the wavelength region below 1μm as shown in Fig.3.

This can be attributed to the difference in the recombination mechanism between electrically-injected carriers and photogenerated carriers. Considering that, under 325nm irradiation, electrons and holes can excite at higher energy states than the case of electrical injection, the observed difference can be interpreted in terms of the energy difference in electronic states involving radiative recombination. And we realize that ultra thin SiO_2 layer is suitable for bipolar injection into quantized states in the Si QDs stack, especially for hole injection in the EL. In addition, no fatigue in EL was confirmed for long time operation except for some degradation in EL by heating under DC operation.

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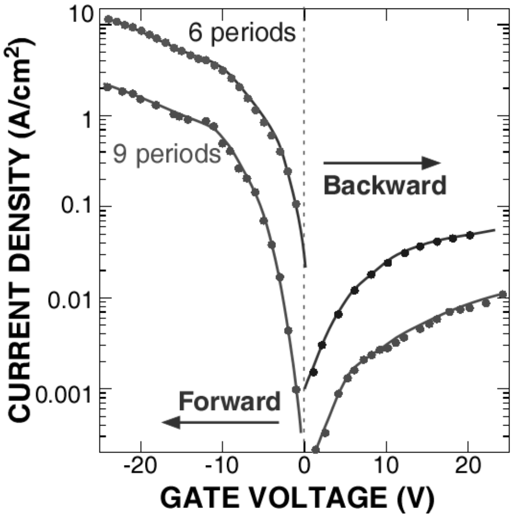

Fig. 1 Current-voltage characteristics for diodes with semitransparent Au electrode on 6- or 9- stacked Si dots/SiO_2 structures on p-Si(100).

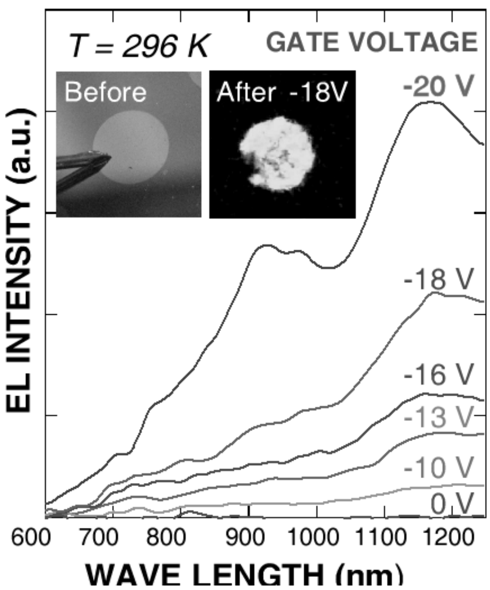

Fig. 2 EL spectra measured at different negative gate voltages. Photographs taken at 0V (a) and at -18V in dark (b) at room temperature are also shown. Inhomogeneity in the EL seen in the photo is attributable mainly to the inhomogeneity in semitransparent Au gate.

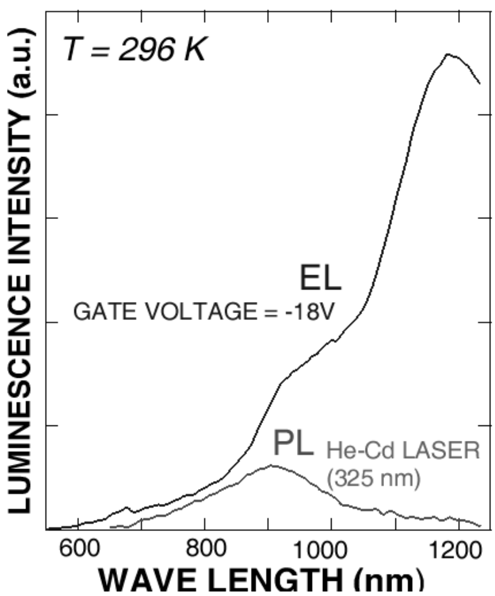

Fig. 3 Comparison between EL and PL spectra. The PL spectrum of 6-stacked Si-QDs/SiO_2 structure was taken under 325 nm excitation at room temperature.

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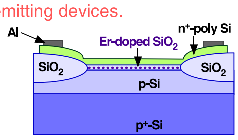
Background & Motivation

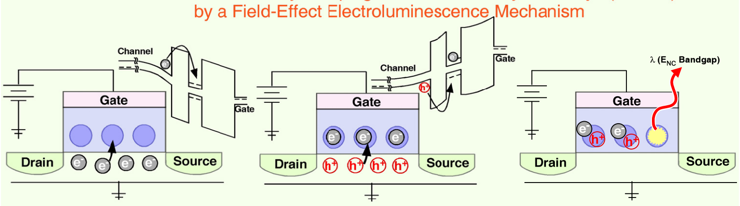
Visible light emission from Si nanostructure has stimulated considerable interest and research activity to develop Si-based light emitting devices.

- Er-doping SiO_2
  M. E. Castagna et al., Physica E **16** (2003) 547
- Er-doping Si
  H. Ennen et al., Appl. Phys. Lett. **43** (1983) 943
- Porous Si
  S. S. Iyer et al., Mater. Res. Soc. Symp. Proc. **256** (1992)
- **Si Quantum Dots**
  K. Shiba et al., Jpn. J. Appl. Phys. **36** (1997) 1279



can be prepared by controlling the early states of LPCVD

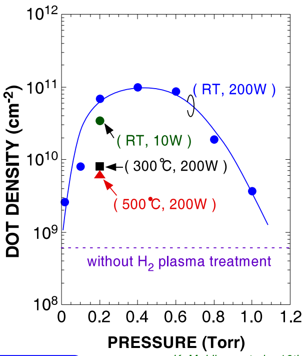
☆ A Scheme for Electrically Pumping Dense Si Nanocrystal Arrays (Si-QDs) by a Field-Effect Electroluminescence Mechanism

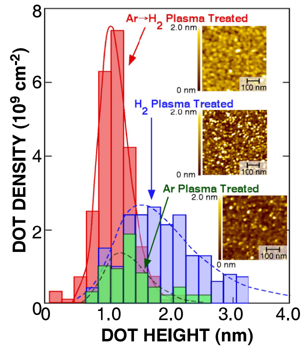


R. J. WALTERS, G. I. BOURIANOFF AND H. A. ATWATER, **Nature Materials** 4, 143-146 (01 Feb 2005)

Previous Work

Si dot formation by SiH_4-LPCVD and dot surface modification by remote plasma treatment





K. Makihara et al., 12th Int. Conf. on Solid Films and Surface (Hamamatsu, 2004). p137

This Work

Si Dots Multiple-Stacked Structures through All-Dry Process steps

Si-Based Light Emission Devices

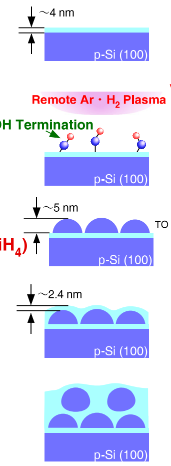
Experimental

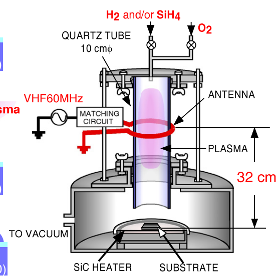
Substrate : p-Si(100)

- **Thermal Oxidation**
  ~ 4.2 nm-thick SiO_2
  1000 ℃, 2% O_2 in N_2
- **Surface Modification**
  Remote Ar Plasma
  - 100 W, 0.1 Torr, 1 min,

  Remote H_2 Plasma
  - 200 W, 0.2 Torr, 1 min,
- **Si-Dots Formation**
  LPCVD (560 ℃ , 0.5 Torr, SiH_4)
  - δ - Doping (1% PH_3)
  - Pulse Injection : 1 sec
- **Remote Plasma Oxidation**
  Remote O_2 Plasma
  ~ 2nm-thick SiO_2
  - 560 ℃ 1%O_2 in He
  - 50 W, 0.1 Torr, 10 min,
- **Post Annealing (N_2)**
  1000 ℃, 30 min

6, 9, 10 cycles



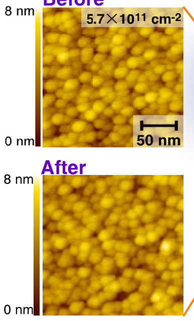


- **Metal Electrodes**
  Thermal Evaporation
  Front : Au
  Back : Al
- **Electroluminescence**
  I-V

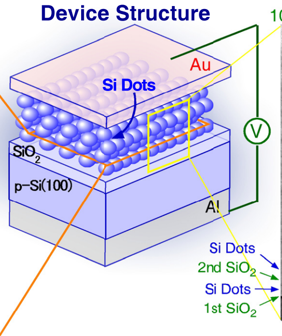
AFM Images Taken Before & After Remote O_2 Plasma Oxidation and Cross-Sectional TEM Images of Fabricated Stacked Structure

AFM Image

1st Si dots formation on 4nm-thick SiO_2

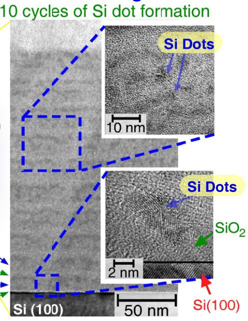


Device Structure



TEM Images

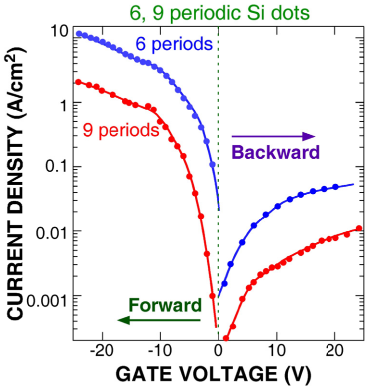
10 cycles of Si dot formation



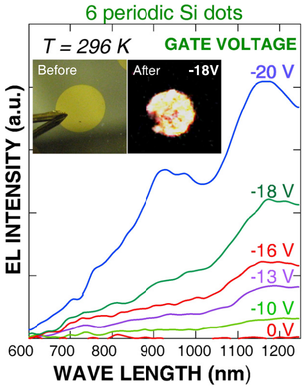
- The surface morphology remains almost unchanged by remote O_2 plasm oxidation.
- Si dots with an average size of ~ 4 nm are stacked with ~2 nm thick SiO_2 interlayers.

Current - Voltage Characteristics & Electroluminescence of Si Dots Multiple-Stacked Structure

6, 9 periodic Si dots

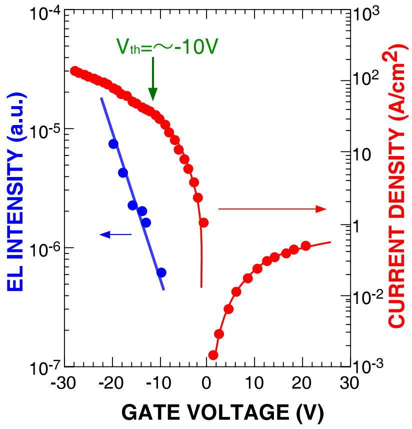


6 periodic Si dots



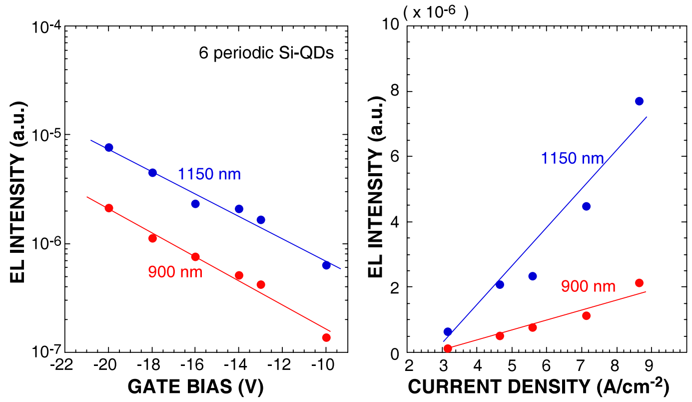
- I-V characteristics show clear rectification properties.
- EL becomes observable in the range from near-infrared to visible region.

Gate Bias Dependence of EL Intensity and Current-Voltage Characteristics for 6 stacked Si Dots/SiO_2 Structures



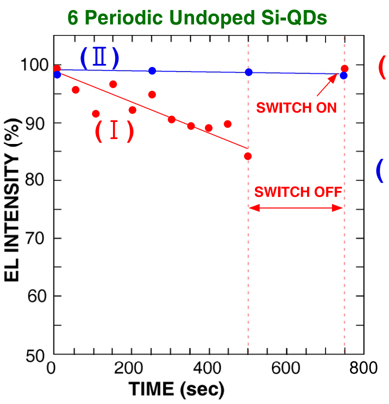
- The EL intensity increases exponentially with forward gate bias.
- The EL was achieved only in the negative gate voltage side while no EL signals can be detected at positive gate voltages.

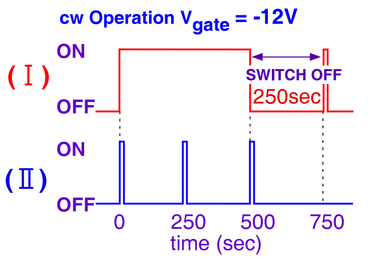
EL Intensity as a Function of Gate Bias & Current Density



- The observed linear correlation between the EL intensity and injected current density implies that the emission comes from the electron-hole recombination in Si dots and/or the localized states in SiO_2 layer near the Si-dot/SiO_2 interfaces rather than the hot electron mechanism.

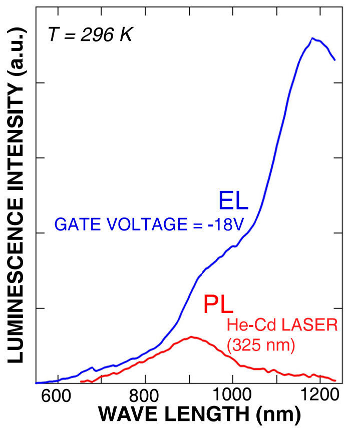
Time Dependent EL Intensity Undoped Si-QDs LED





- No fatigue in EL was detected for long time operation except for gradual decay at a condition without intentional cooling as a result of heating due to current flow.
- Even after such decay, EL is completely recovered by cooling down to room temperature.

Electroluminescence & Photoluminescence Spectra of 6 Stacked Si-QDs / SiO_2

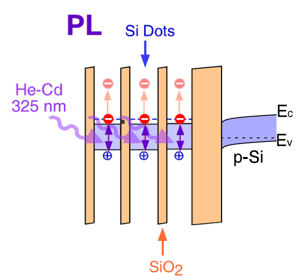


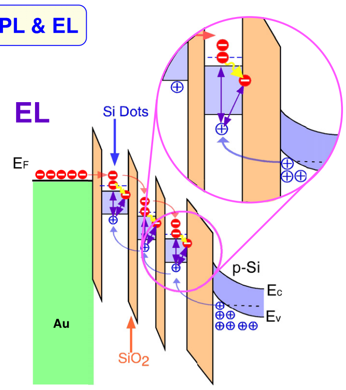
EL : 900 & 1150 nm

PL : 900 nm (1.34 eV)
He-Cd Laser (325 nm)
70 mW / cm^{-2}

- There is a significant difference between EL and PL spectra.
- The observed difference can be interpreted in terms of the energy difference in electronic states involving radiative recombination.

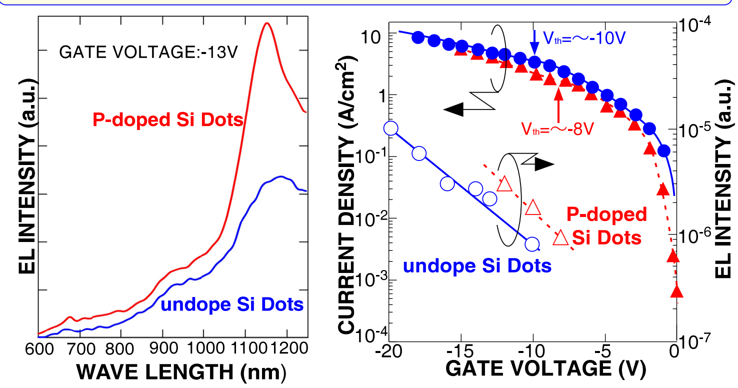
Recombination Mechanism of PL & EL





- Energy relaxation of photo excited electrons and holes to quantized states.
- Energy relaxation to deep localized states becomes significant in the electrical carrier injection.

EL & I-V Characteristics for Undoped & Phosphorus Doped Si-QDs LEDs



- P-doping into Si-QDs plays a role in the improvement of the EL efficiency presumably because the hole injection to Si-QD is a major limiting factor for light emission, being different from the undoped Si-QDs case where both electron and hole into a Si-QD have to be injected well.

Conclusions

Light emitting diodes were fabricated based on Si-QDs Multiple-stacked structures

- Under forward bias conditions over a threshold bias as low as -10V for LEDs with 6-periodic dot stack, a broad and stable electroluminescence was observed in the range of **500 - 1300 nm**.
- EL in the visible-infrared region was measured at **room temperature.**
- The origin of EL can be attributed to the **electron-hole recombination in Si QDs** and the localized states in Si / SiO_2 interface.
- By **P δ-doping to Si dots**, EL was enhanced by a factor of 1.3 for LEDs with 6-periodic dot stack presumably because of an improvement of hole injection rate.

Acknowledgements

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