Control of Charged States of Silicon Quantum Dots and Their Application to Floating Gate MOS Memories and Light Emitting Diodes

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1. Research Background

Si-based nanostructure are attracting much attention because of their potential application to charge transfer devices, memories and light emitting devices. Especially, the implementation of silicon-quantum-dots (Si-QDs) as a floating gate in MOSFETs has been intensively studied not only from the viewpoints of their superior retention and endurance characteristics to conventional floating gate structures but also their feasible advantage for multi-valued memory operations [1,2]. To achieve clear multi-valued operations at room temperature and above, discrete charged states in the Si-QDs floating gate with with an areal density comparable to the channel electron density have to be realized and controlled as precise as possible. In our previous work, we have demonstrated spontaneous formation of Si-QDs on thermally-grown SiO_2 with a fairly uniform size distribution and a high areal density ($>10^{11}cm^{-2}$) by controlling the early stage of low-pressure chemical-vapor deposition (LPCVD) from SiH_4 [3], and demonstrated unique multiple-step electron charging in the Si-QDs floating gate even at room temperature [4, 5]. To establish a guideline of device design and fabrication, a clear insight into the charging and discharging characteristics of the Si-QDs is imperative.

In this paper, our resent results on the characterization of electronic charged states of undoped and p-doped Si QDs, multistep electron charging characteristics to the Si QDs floating gate in n-MOSFETs are reviewed with emphasis on discrete charged states in Si-QDs. The preliminary results on the application of multiple-stacked Si-QDs with ultrathin SiO_2 interlayers to light emitting diodes are reported.

2. Results and Discussion

2.2 Temporal Decay Characteristics of Electronic Charged States of Si Quantum Dots [6]

We have evaluated the stability of changed states of high density Si-QDs formed on ultrathin SiO_2. By controlling the early stages of LPCVD using SiH_4, hemispherical Si-QDs with an areal dot density of $8 \times 10^{11}cm^{-2}$ were prepared on ~3nm-thick SiO_2 and the dot surface was covered with ~2nm-thick thermally grown SiO_2 by 900ºC in 2% dry O_2 diluted with N_2. The temporal changes in the surface potential induced by electron charging to and discharging from Si-QDs so prepared were measured by AFM/Kelvin probe force microscopy. In electron charging and discharging at Si-QDs, a Rh-coated AFM tip was electrically-biased in the range of -5 to 5V and scanned on the sample surface in a tapping mode. Using a non-contact AFM/Kelvin probe technique, the surface potential changes on Si-QDs by electron injection and extraction are observable, while no potential change was detected elsewhere. The surface potential of changed Si-QDs decays with time at rates depending on change injection conditions. The observed decay characteristics can be interpreted in terms of discharging of stored electrons in Si-QDs due to electron tunneling through the bottom oxide to the substrate and neutralization of stored holes due to recombination with electrons tunneling from the substrates. In the case of electron extraction by the tip bias as high as +4.8V with respect to p-Si(100), the defect generation in oxide is likely to be responsible for a fairly slow decay as observed.

2.3 Characterization of Electronic Charged States of Individual Si QD [7,8]

Previously, we have demonstrated that, for each of Si dots with core heights in the range from 6 to 12nm on ~4nm-thick SiO_2/p-Si(100), the potential changes caused by single electron injection and emission can be detected by the non-contact AFM/Kelvin probe technique[9]. We have extended our research to characterize electronic charged states of Si dots stored in a few electrons or holes [7]. After electron injection to and extraction from Si dots larger than 20nm in height, a unique surface potential image being torus-shape was observable in each of dots, namely the surface potential change caused by charging is smaller in the Si dot center than that in the periphery. Considering the capacitance between the Si dot and the substrate, it is found from the observed surface potential change that a few electrons or holes are retained in the dot of interest. Thus, the observed torus-shape potential image is attributable to columbic repulsion force among charges in the Si dot. In fact, the torus-shaped surface potential change diminishes with time due to the progressive emission of retained electrons to the Si substrate. We have also studied the influence of phosphorous doping to Si QDs on their electron charging and discharging characteristics [8]. P-doped Si-QDs were prepared by a pulse injection of 1% PH_3 diluted with He during the dot formation on thermally-grown SiO_2 from thermal decomposition of pure SiH_4. The potential change corresponding to the extraction of one electron from each of P-doped Si dots was observed after applying a tip bias as low as +0.2V while for undoped Si dots with almost the same size as P-doped Si dots a similarly amount of the potential change was detectable only when a tip bias is increased to ~1V. The result indicates that, for P-doped Si dots, the electron extraction occurs from the conduction band and results in a positively-charged state with ionized P donor. There is no difference in the threshold voltage for electron injection between undoped and p-doped Si dots.

2.4 Characterization of Multistep Charging to Si-QDs Floating Gate in n-MOSFETs [10,11]

We have fabricated n-MOSFETs with a doubly-stacked

Si-QDs floating gate and confirmed the multi-step electron charging to the Si-QDs floating gate associated with Coulomb blockade effect from distinct bumps in drain current-gate voltage characteristics observed in ramping up the gate voltage after complete discharging at room temperature [4, 12]. We have also found that, in the temporal change in the drain current at a constant gate bias, the electron injection to the Si-QDs floating gate proceeds stepwise through a fairly long metastable state prior to the next charging and is accelerated by temperature and visible light irradiation as well as gate bias [11-13]. It is likely that, during the metastable state, injected electrons are redistributed in the Si-QDs floating gate to trigger further electron injection. To gain a better understanding of the charging characteristics of the Si-QDs floating gate, the temporal change in the drain current after applying positive pulsed gate biases have been measured systematically as functions of pulse voltage height and width [10]. The electron charging with pulsed gate biases below certain height and width can not create a metastable state. As shown in Figs. 1 and 2, the drain current measured at zero gate bias, after the positive gate pulse below 1.25V in Fig. 1 or below 0.95s in Fig. 2, increases temporarily to some current level reflecting the electron emission from the Si-QDs floating gate and in a little while decreases significantly down to the current level for the metastable charged state. Note that an increase in the pulse height only by 10mV from 1.24V or in the pulse width by 50ms from 0.9 can generate a metastable charged state. The results indicate that the pulse height and width are crucial factors to realize the charge distribution for a stable charged state.

2.4 The Application of Multiple-Stacked Si QDs to Light Emitting Diodes [14-16]

The multiple-stacked structures of Si-QDs with ultrathin SiO_2 interlayers have been fabricated by repeating a process sequence of Si dot formation from thermal decomposition of SiH_4 on SiO_2, surface oxidation by remote O_2-plasma and subsequent surface modification by remote Ar- and H_2-plasmas, and applied to as active layers of light emitting diodes (LEDs) with semitransparent Au gate. Under forward bias conditions over a threshold bias as low as -10V for LEDs with 6-periodic dot stack, stable light emission in the visible and near-infrared regions was observed at room temperature as a result of the injection of electrons from semitransparent Au top electrode and simultaneously holes from the p-Si(100) substrate to the dot stack. The light intensity was linearly increased with forward current but no emission was detected under backward conditions. In addition, we have found that phosphorus δ-doping to Si-QDs causes a significant enhancement in the emission efficiency and a decrease in the threshold voltage presumably because of an improvement of hole injection rate.

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4. M. Ikeda, et al., Jpn. J. Appl. Phys. 42 (2003) 4131.
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13. T. Nagai et al., *Ext. Abst. of Int. Conf. on Solid State Devices and Materials* (Tokyo, 2004) pp. 126-127.
14. K. Makihara et al., *Proc. of Asia-Pasific Workshop on Fund. & Appl. of Adv. Semicond. Devices* (Seoul, 2005) pp. 173-176.
15. K. Makihara et al., *Ext. Abst. of 1st Int. Workshop on New Group IV Semicond. Nanoelectro.* (Sendai, 2005) pp. 47-48.
16. K. Makihara et al., *Ext. Abst. of 2005 Int. Meeting for Future Electron Devices, Kansai* (Kyoto, 2005) pp. 93-94.

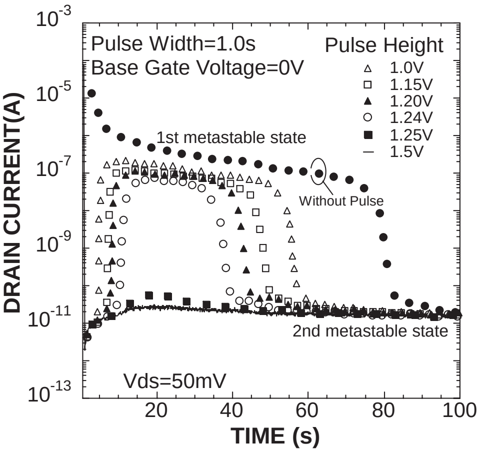

Fig. 1 Temporal changes in the drain current measured at $V_g = 0V$ and $V_d = 50mV$ after applying pulsed gate biases with different pulse heights. The pulse width was fixted at 1.0s. Before the measurement, the Si-QDs floating gate of an n-MOSFETs was completely discharged at $V_g = -4V$.

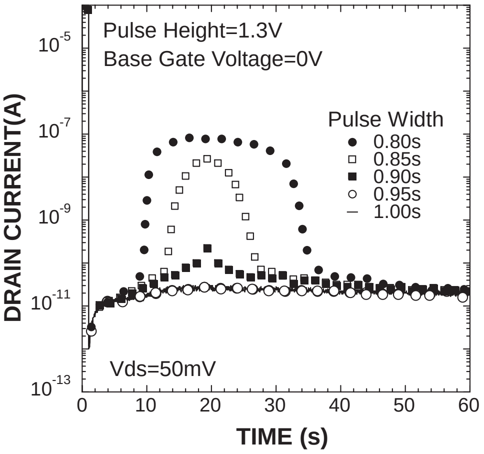

Fig. 2 Temporal changes in the drain current measured at $V_g = 0V$ and $V_d = 50mV$ after applying pulsed gate biases with different pulse widths. The pulse height was fixted at 1.3V.

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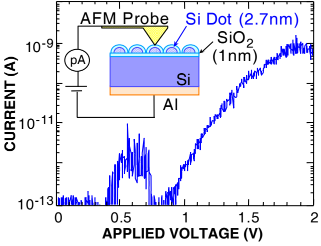
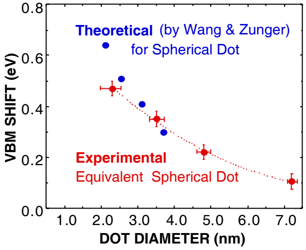
Silicon Quantum Dots for New Functionality

Resonant tunneling through a single Si-QD at 300K



M. Fukuda et al. APL (1997)

High energy shifts in valence band maximum



S.A.Ding et al. APL (1998)

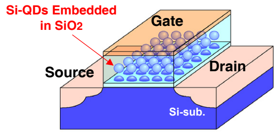
- Quantum Size Effect
- Coulomb Blockade

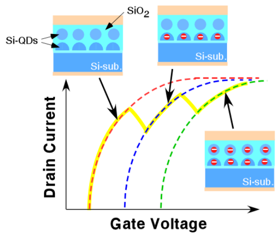
⇨ Novel Functional Devices

- **QDs Floating Gate Memory** — A. Kohno et al. JJAP (2001), S. Tiwari et al. APL (1996)
- **Single Electron Transistor** — Y. Takahashi et al. IEDM (1994, 1998)

Si-QDs Floating-Gate MOS Memories
— Multivalued & Low-Voltage Operations at Room Temp. —

Floating Gate Application of Si Quantum Dots





☆ Control of Discrete Charged States in Si-QDs

⇩

Electrical Interaction & Coupling among Electronic States in Neighboring QDs

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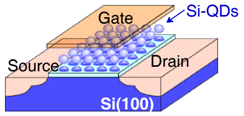
Key Issues on Si-QDs Formation for Floating Gate Application

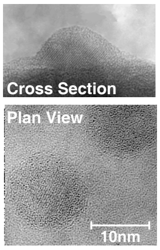
- The areal dot density comparable to the electron concentration in channel (higher than ~10^{11}cm^{-2})

☆ Uniformity in Size & Spatial Distribution



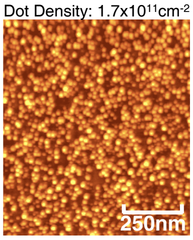
Spontaneous Formation of nc-Si on SiO$_2$ by LPCVD

HR-TEM Images



on as-grown SiO$_2$
600℃, 0.2Torr, 36s

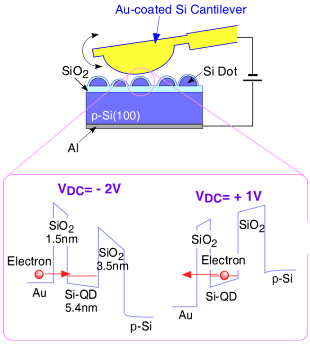
AFM Image
Dot Density: 1.7x10^{11}cm^{-2}



on HF-treated SiO$_2$
560℃, 0.2Torr, 90s

S.Miyazaki et al. TSF (2000)

Surface Potential Changes due to Electron Charging & Discharging of Si-QDs as Detected by a AFM/Kelvin Probe Method

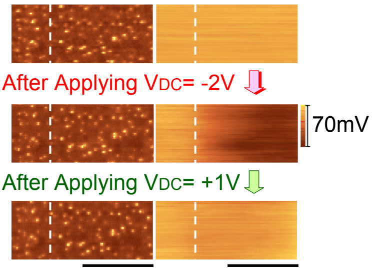


Topographic Image

Potential Image

After Applying V_{DC}= -2V ⇩

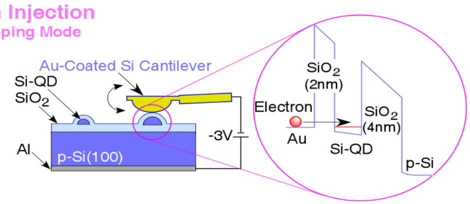
After Applying V_{DC}= +1V ⇩



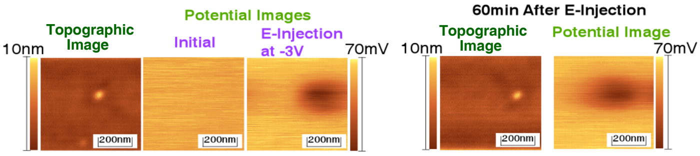
N. Shimizu et al, JJAP 39 (2000)2318

Electron Injection to Single Si-QD

- Electron Injection
  in AFM/Tapping Mode

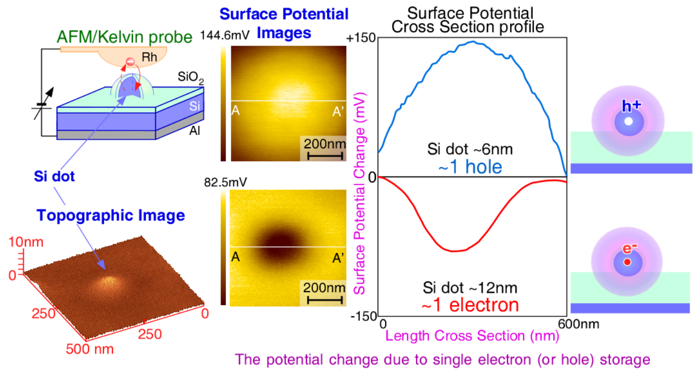


- Topographic & Potential Images
  in AFM/Kelvin Probe Mode



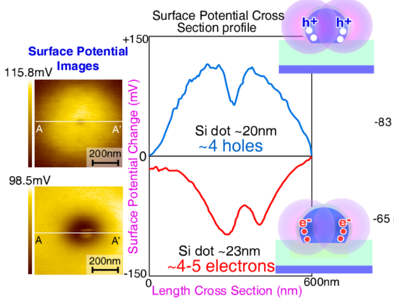
Evaluation of Charged & Discharged States of Single Si Dot

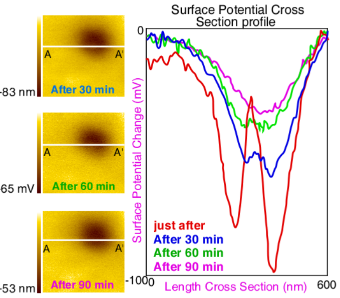
The surface potential changes with electron charging and discharging of an individual Si dots were measured by an AFM/Kelvin probe technique.



The potential change due to single electron (or hole) storage is detected for Si dots as small as ~10nm in dot height.

Evaluation of Charged & Discharged States of Single Si Dot





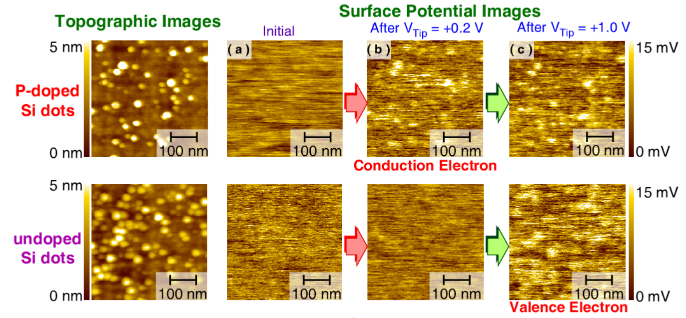
After electron injection to and emission from Si dots as large as ~20nm in dot height, unique surface potential images are observable.

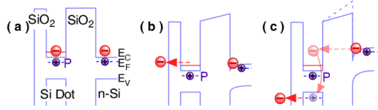
⇨ The potential change in the center of the dot is much smaller than that in the peripheral region.

A torus-shaped potential image is smeared out with time and almost completely disappeared in 90 min after the electron injection.

☆Coulombic repulsion among retained carriers in the dot of interest.

Electron Extraction from P-doped & Undoped Si Dots / SiO_2(4nm) / n^+-Si(100)

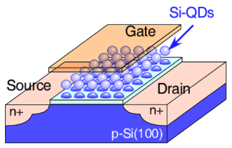


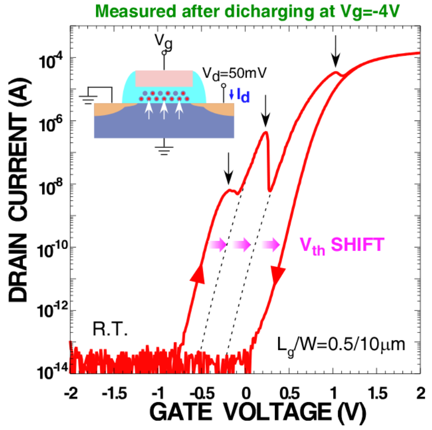


☆ **P-doped Si dots**

Electron Extraction From The Conduction Band, Namely Positively-Charged Dots With Ionized P Donors.

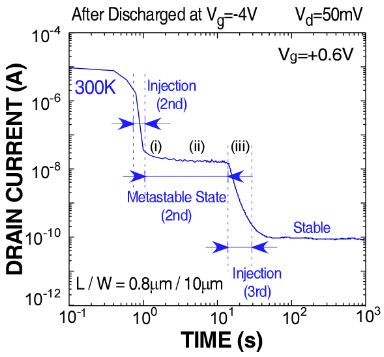
I_d-V_g Characteristics of a Si-QDs Floating Gate nMOSFET

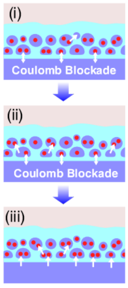




Three current bumps in Id-Vg characteristics indicate the multiple-step electron charging of the Si-QDs floating gate caused by the Coulomb blockade effect.

I_d-t Characteristics at a constant gate voltage



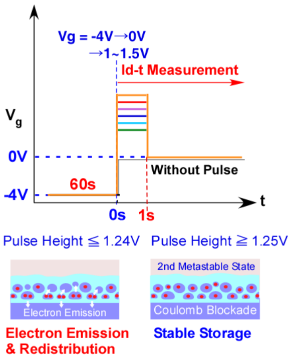


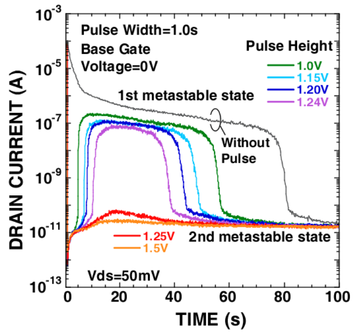
Redistribution of injected electrons

Next electron injection

- A metastable charged state appears prior to a stable charged state and is attributed to the redistribution of injected electrons in the Si-QDs floating gate.

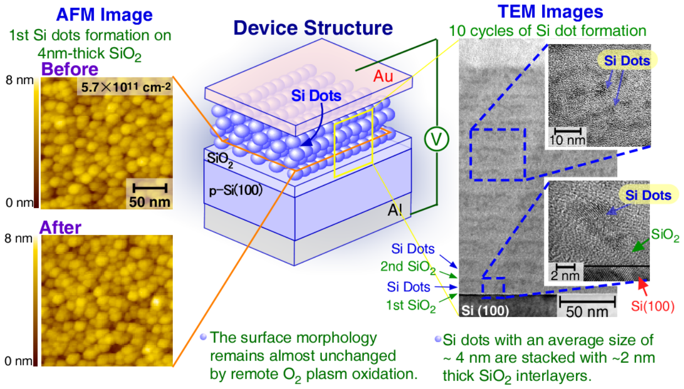
I_d-t Characteristics after Applying Pulsed Gate Biases at Different Pulse Heights





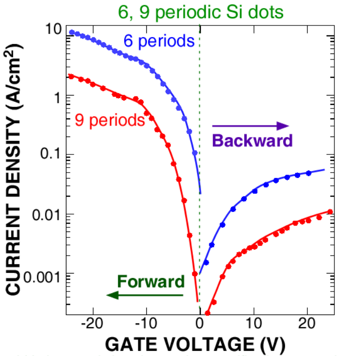
- When the pulse height is increased only by 10mV from 1.24V to 1.25V, an increase in the drain current due to electron emission with time becomes hardly observable.

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

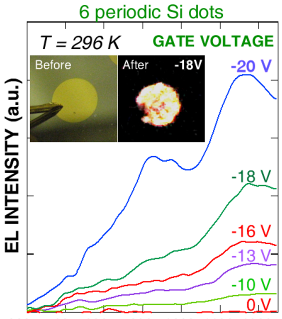


- The surface morphology remains almost unchanged by remote O_2 plasm oxidation.
- Si dots with an average size of ~ 4 nm are stacked with ~2 nm thick SiO_2 interlayers.

Current - Gate Bias Characteristics & Electroluminescence of Si Dots Multiple-Stacked Structure

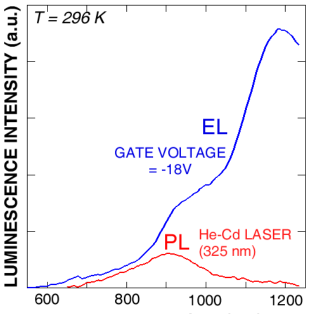


- I-V characteristics shows clear rectification properties in which electron injection from Au gate and hole injection from p-Si(100) occur at negative gate voltages.



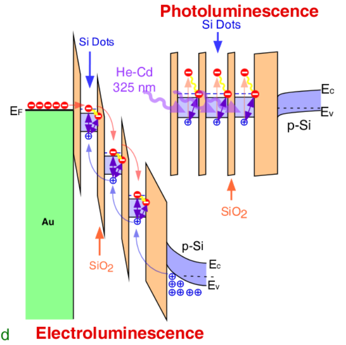
- EL in the range from near-infrared to visible region is observable.
- No EL can be detected in the positive bias region.

EL & PL Spectra of 6 Stacked Si Dots / SiO_2



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

Recombination Mechanism of PL & EL



- 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

Summary

- Confirmation of **single electron or hole storage** in individual Si-QDs by an AFM/Kelvin probe technique.
- Verification of **Coulomb repulsion** among charges stored in a Si-QD.
- Reduction of **the voltage requisite for electron extraction** from Si-QDs by **phosphorus doping**.
- Observation of **multiple step electron injection to the Si-QDs floating gate** and **metastable charged states**.
- Implication of **re-distribution of charges** in the Si QDs floating gate during the metastable states.
- **Light emission from multi-stacked Si-QDs structures** in the visible-near infrared region by electron and hole injection.