Electronic Charged State of Single Si Quantum Dots with and without Ge Core as Detected by AFM/Kelvin Probe Technique

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1. Introduction

Electron charging and discharging properties of nanometer-size Si dots have been evaluated by using an AFM/Kelvin probe technique [1] to get a clear insight into their device applications such as single electron transistors and quantum dot floating gate MOS memories. However, the characterization of the charged states of each of Si dots is still a matter of research because of poor lateral resolution the AFM/Kelvin probe technique. In this work we have extended our research to evaluate the charging states in a single isolated nanometer Si-dot for the sample with a low areal dots density. To enhance the carrier confinement effect, we have also extended our research to prepare the Si dots with a Ge core [2] and investigated the electron charging and discharging mechanism by AFM/Kelvin probe technique as well.

2. Experimental

Hemispherical single-crystalline Si dots were prepared on 4nm-thick SiO_2 thermally-grown on p-Si(100) by controlling the early stages of low-pressure chemical vapor deposition (LPCVD) using SiH_4 [3]. The dot surface was covered with 2nm-thick SiO_2 formed by 900°C oxidation in dry O_2. To prepare Si dots with Ge core, Ge deposition was performed on pregrown hemispherical Si dots/SiO_2 at 400°C using 5% GeH_4 diluted with He and subsequently followed by Si cap deposition under a SiH_4 pressure of 0.02Torr at 540°C, with purging and evacuating the CVD chamber completely between each deposition steps. High-resolution TEM and XPS measurements were carried out to confirm the formation of Si dots with Ge core. Electron and hole injection to each Si dot with or without Ge core was performed by scanning an electrically-biased AFM probe with a tapping mode. The probe biases with respect to the Si(100) substrate were -3V for electron injection and +1 to +3V for electron emission. Before and after electron charging or discharging, the topographic and corresponding surface potential images were simultaneously measured with non-contact Kelvin-probe mode.

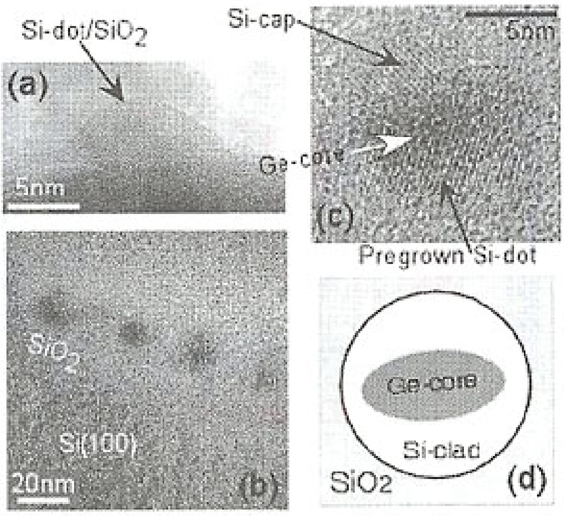


Fig.1. Cross-sectional of HR-TEM images of hemispherical Si dot pregrown on SiO_2 (a) and Si dots with Ge core (b), accompanied with magnified (c) and schematic (d) images of isolated dot.

3. Results and Discussion

Cross-sectional TEM images show spherical nanometer dots made of Si clad and ellipsoidal Ge core, in contrast to hemispherical pure-Si dots pregrown on SiO_2 (Fig. 1). This implies that the strained energy is larger than the bonding energy at Si/SiO_2 interface generated at the Si/Ge interface. Notice that the crystallographic orientation of the Si cap is different from that of pregrown Si dot presumably due to the structural strain at the Si/Ge interface. The orientation of Ge core is not clear because of its poor contrast.

To confirm conformal coverage and/or high

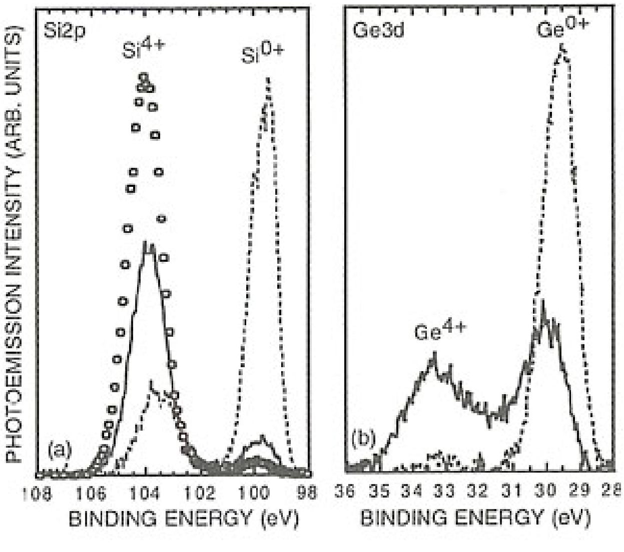


Fig. 2. Si2p (a) and Ge3d core-line (b) spectra of Si-dot formation on SiO_2 (sample(S):open circles), Ge deposition on sample(S) (sample(GS):solid line) and Si deposition on sample(GS) (sample(SGS):dashed line).

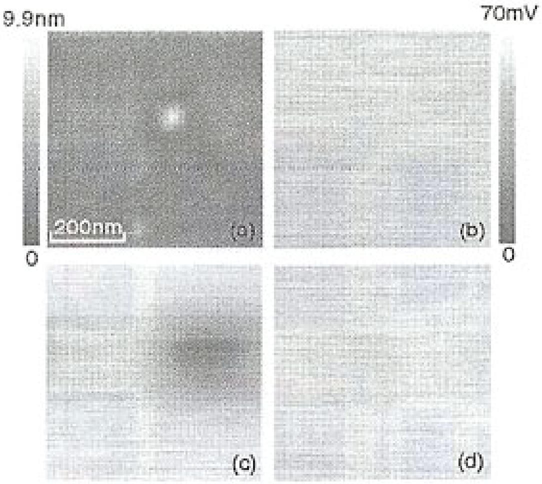


Fig.3. Topographic image (a) and corresponding surface potential images of an isolated Si dot with a core height of ~7.9nm measured by AFM/Kelvin probe mode before (b) and after injected (c) at −3V, and after electron emission at +2V from the charged Si dot in the tapping mode (d).

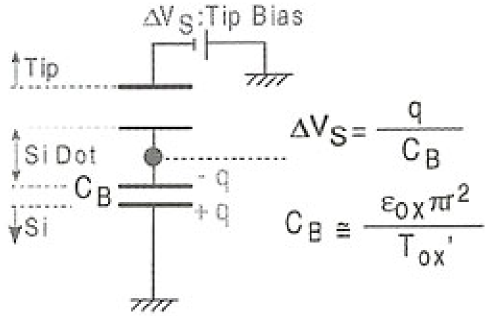


Fig.4. Equivalent circuit of AFM/Kelvin probe measurement, where ΔVs is tip bias, q and C_B are the electronic charge in dot and capacitance between the dot and the substrate, respectively. T_{ox}' is equivalent oxide thickness, ε_{ox} is SiO_2 dielectric constant and r is dot height.

selectivity at each LPCVD, Si2p and Ge3d spectra for each deposition step were taken at photoelectron take-off angle of 15° as presented in Fig. 2. For the sample of Si dots on SiO_2, an intense peak due to Si^{4+} in the underlying SiO_2 layer and the native oxide on the top surface of Si dots is observed at 104eV accompanied with the weak signals that were peaked at 99eV due to Si^{0+} in the Si dots. The $Si2p^{4+}$ signals are significantly weaken with further deposition of Ge and Si. In the same time, the $Si2p^{0+}$ signals increase markedly with Ge deposition, indicating that the Ge coverage of Si dot surface results in the efficient suppression of native oxidation of Si dots during air exposure. Correspondingly, the chemically-shifted Ge3d signals assigned to Ge^{4+} in native oxide of Ge is clearly observable at ~33.5eV for the sample (GS) after Ge deposition. When the Si deposition follows the Ge deposition (SGS), the Ge^{4+} signals almost completely disappear while the Ge signals peaked at 29.5eV become stronger. This indicates that the Ge surface was fully covered with Si.

For electron charging experiment of isolated Si dot with a core height of 7.9nm, the surface potential change of ~70mV on the Si dot is observed by electron injection, and vise versa, although no change in the topographic images is detected as shown in Fig.3. Using an equivalent circuit model for Kelvin probe measurements (Fig. 4) the observed potential change is equal to the theoretically-predicted value for charging and discharging of the dot by one electron. In addition, Si dot with a core height as large as 13nm, in which a few electrons can be stored, show the multi-level temporal charge in the surface potential after electron charging, implying that stored electron are emitted stepwise. For an isolated Si dot with Ge core with a total dot height of ~16nm, the surface potential change near the edge of the charged dot is much higher than the center after electron injection, while for hole injection, the maximum potential change appear in the center of the dot as seen in the charge injection to pure Si dots. These results suggest that injected electron(s) and hole(s) are located in the Si clad and the Ge core, respectively, as expected from the energy band diagram for an Si/Ge heterojunction.

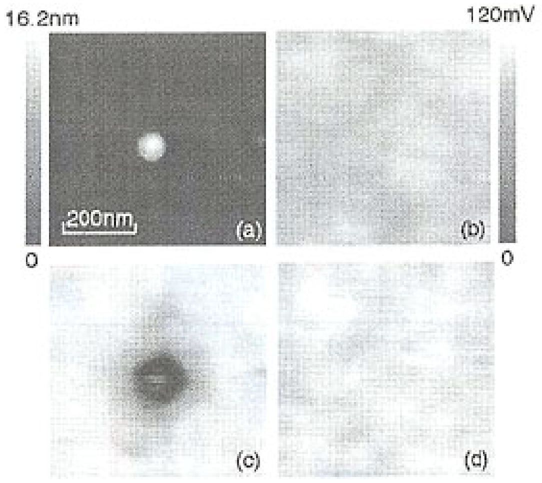


Fig.5. Topographic image (a) and corresponding surface potential images of an isolated Si dot with a Ge core with a total dot height of ~16nm measured by AFM/Kelvin probe mode before (b) and after injected (c) at −3V, and after electron emission at +1V from the charged Si dot in the tapping mode (d).

4. Conclusions

We have detected the charging state of a single Si dots with and without Ge core by the surface potential change by electron charging to neutral dot, discharging of the charged dot and electron extraction from the neutral dots by a AFM/Kelvin probe technique.

References

[1] N. Shimizu, M. Ikeda, E. Yoshida, H. Murakami, S. Miyazaki, M. Hirose, Jpn. J. Appl. Phys. **39** (2000) 2318.

[2] Y. Darma, R. Takaoka, H. Murakami, S. Miyazaki, Nanotechnology 14 (2003) 413.

[3] S. Miyazaki, Y. Hamamoto, E. Yoshida, M. Ikeda, M. Hirose, Thin Solid Films **369** (2000) 55.

Background & Motivation (I)

Nanometer size Si dots involving Qoulomb blockade and/or quantum size effect are attracting much attention because of their potential application to novel functional devices which operate at room temperature, namely :

- Resonant Tunneling Device (M Fukuda et al., APL(1997.)
- QD Floating Gate Memory (A. Kohno et al., JJAP(2001))
- Single Electron Transistor (Y. Takahashi et al., IEEE Trans. Elect. Devices (1996))

Major concerns for multivalued memory devices:

- Well-defined electron charging and discharging characteristics
- long retention time (even at 100°C)
- high-speed writing and erasing operation at low voltages

To enhance carrier confinement

- Si dots with Ge core

To get a clear insight to the electron charging and discharging properties of SiQDs floating gate

Previous works

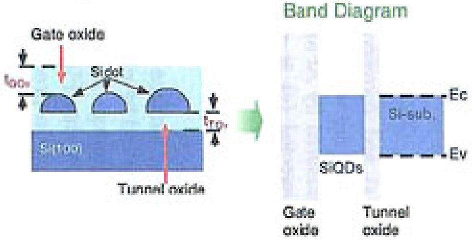
- AFM/Kelvin probe investigation of charging state of Si quantum dots

Focus on this works

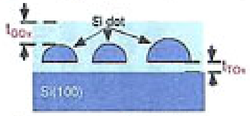
- Charging state characterization of single Si quantum dots with and without Ge core by AFM/Kelvin probe.

Background & Motivation (II)

SiQDs for electron storage nodes



For high speed operation



- Decrease in SiO_2 thickness
  - Improve writing/erasing time
  - Degradation in charge storage

To enhance retention time

- Increase in SiO_2 thickness
- SiQDs stacked structure
  - Demerit: Low speed operation

Si Dots with Ge Core

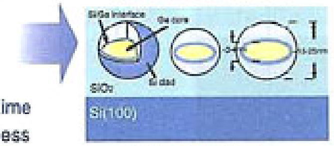
Si Dots with Ge core for electron storage nodes

Expectation:

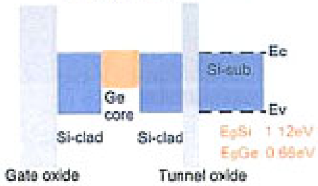
- enhance retention time
- good in writing/erasing time

Ge core cladded with Si

- Good Si/SiO2 interface instead of poor Ge/SiO2 interface



Band Diagram



Experimental

Formation of Si Dots

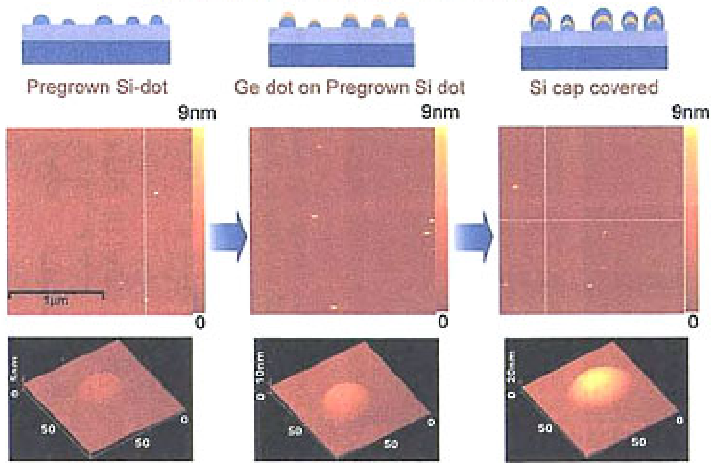
- Precleaned HF-last:
  NH₄OH:H₂O₂:H₂O=0.15:3:7; 80°C,10min, 4.5% HF 2min
- Oxidation:
  2% Dry O_2 dilute in N_2 1000°C, 10min
- Si dots Formation by LPCVD
  100% SiH_4, 585°C, 50 mTorr, 1min
- Surface Oxidation:
  2% Dry O_2 dilute in N_2 900°C, 1min
- Evaporation:
  Al electrode

Formation of Si Dot with Ge Core

- Precleaned HF-last
- Oxidation
- Dot Formation by LPCVD
  - Si-Dot
    100% SiH_4, 560°C, 0.1 Torr, 1min
  - Ge-Core
    5% GeH_4, 400°C, 0.2Torr, 3min
  - Si-Cap
    100% SiH_4, 540°C, 0.02Torr, 30sec
- Evaporation
  Al electrode

AFM Images of Selective Ge-Dot Growth on Pregrown Si Dot & Selective Si-Cap Growth on Ge/Si Dot

Dot Density as low as: ~2 X 10^8 cm^{-2}

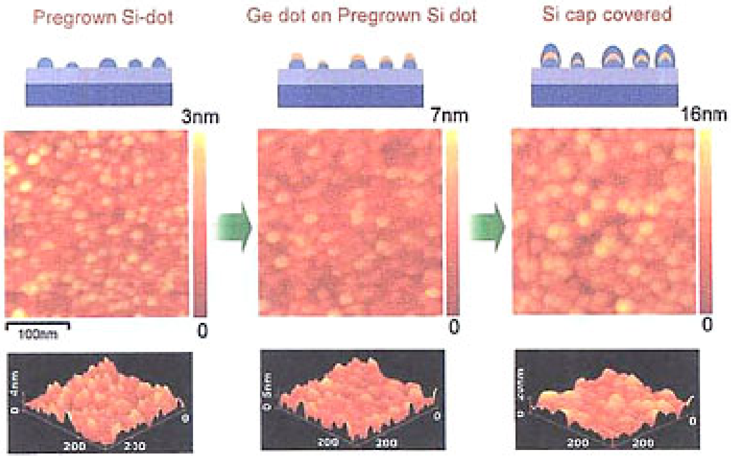


Pregrown Si-dot

Ge dot on Pregrown Si dot

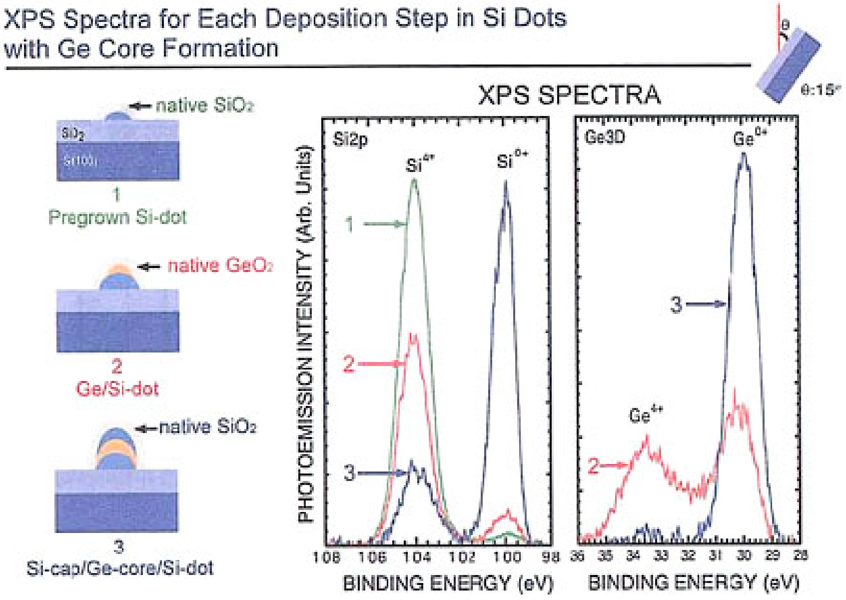
Si cap covered

Dot Density as high as:~1.5 X 10^{11}cm^{-2}

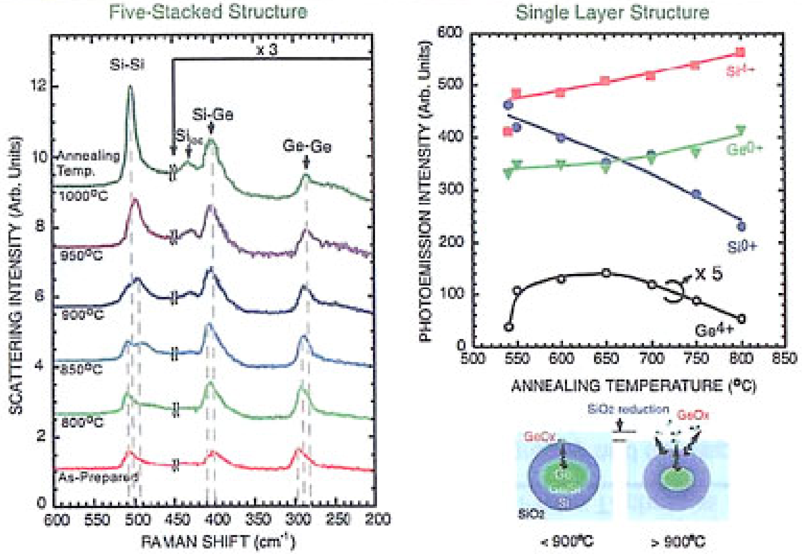


The dot density remains unchanged with Ge deposition and Si cap formation, while the dot height increases with progressive Ge and Si deposition.

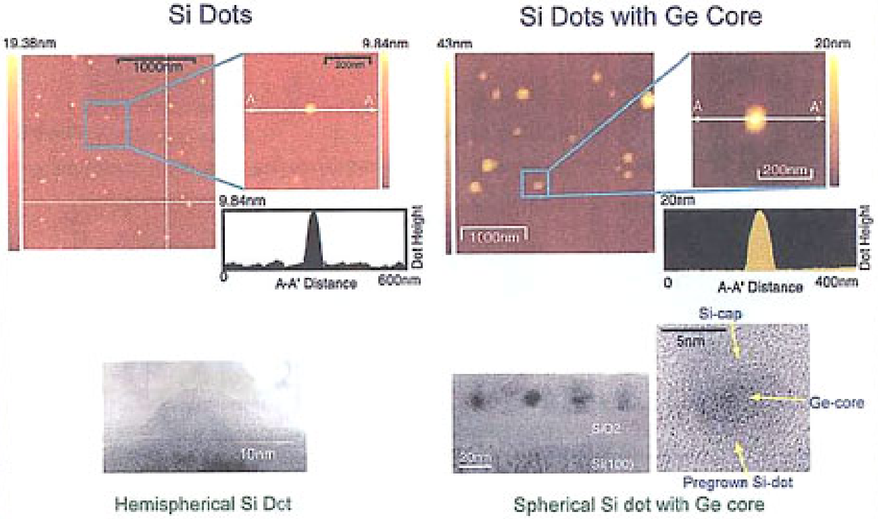
XPS Spectra for Each Deposition Step in Si Dots with Ge Core Formation



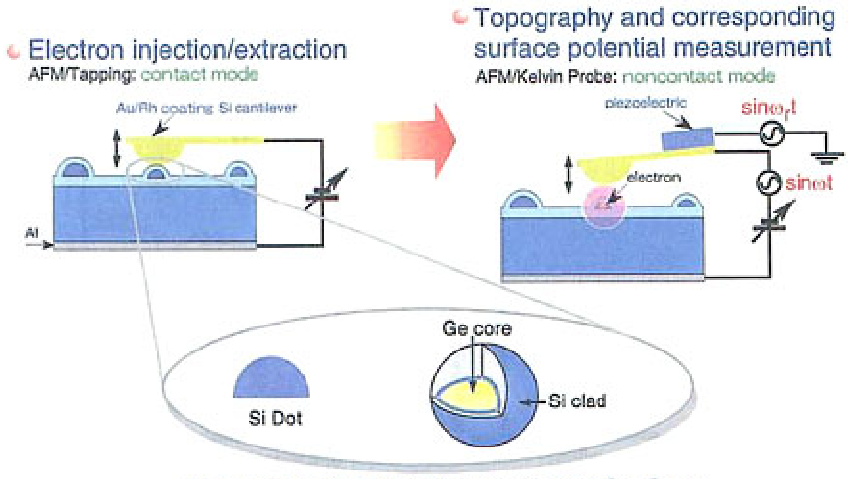
Raman and XPS Spectra of Si Dot with Ge Core before and after Annealing



AFM and Cross-Section TEM Images of Si Dots with and without Ge Core on Ultrathin SiO2



Schematic Experiment of Electron and Hole Injection Followed by Surface Potential Measurement by AFM/Kelvin Probe Technique

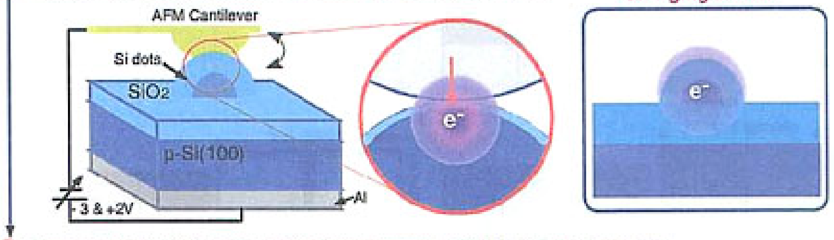


For Isolated Si Dot with and without Ge Core

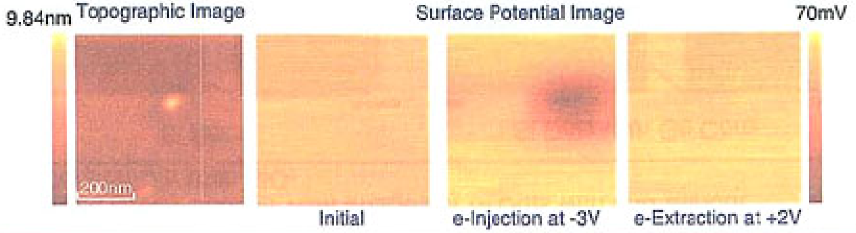
Electron Injection & Extraction in Si Dot Followed by Surface Potential Measurement by AFM/Kelvin Probe Technique

Electron injection & electron extraction (AFM/Tapping mode)

Charging Model



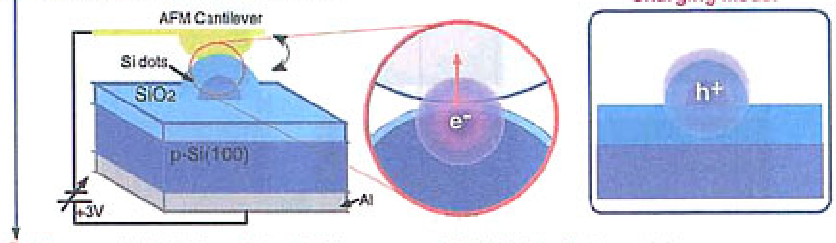
Topographic & Surface Potential Measurement (AFM/Kelvin Probe mode)



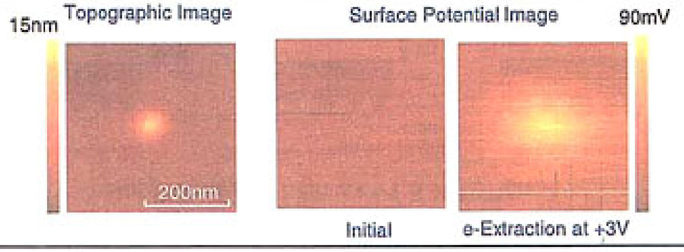
Hole Injection in Si Dot Followed by Surface Potential Measurement by AFM/Kelvin Probe Technique

Hole Injection (AFM/Tapping mode)

Charging Model

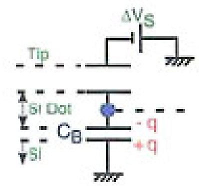


Topographic & Surface Potential Measurement (AFM/Kelvin Probe mode)



Equivalent Circuit of Electron Injection Characteristics in Si Dot and Estimated Electron number

An Equivalent Circuit Under KFM

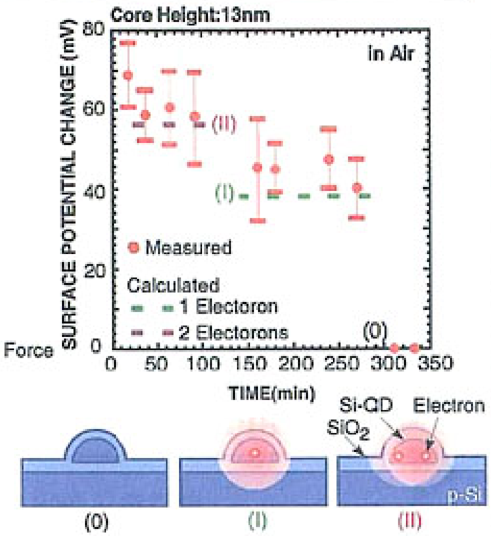


$\Delta V_S = \frac{q}{C_B}$ $C_B = \frac{\varepsilon_{ox}\pi r^2}{T_{ox}'}$

$r = r_{dot} + \Delta r$, Δr: Spread of Electric Lines of Force

$T_{ox}' = T_{ox} + \frac{\varepsilon_{ox}}{\varepsilon_{Si}}\frac{r_{dot}}{2}$ ε:Dielectric Const.

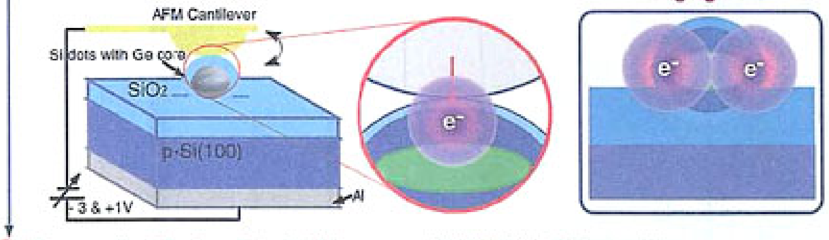
ΔV_S:Change in Surface Potential



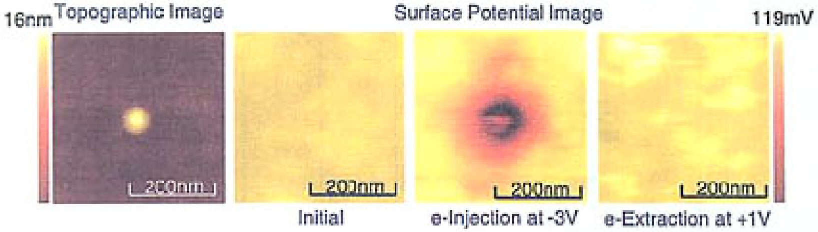
Electron Injection & Extraction in Si Dot with Ge Core Followed by Surface Potential Measurement by AFM/Kelvin Probe Technique

Electron injection & electron extraction (AFM/Tapping mode)

Charging Model



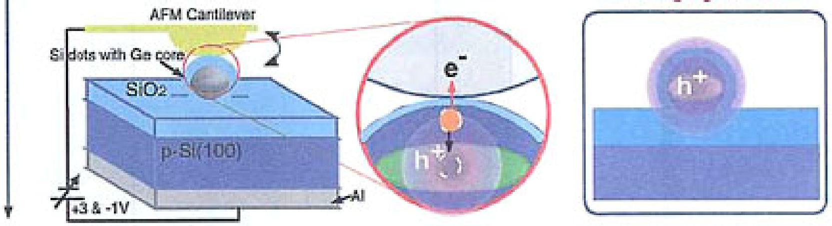
Topographic & Surface Potential Measurement (AFM/Kelvin Probe mode)



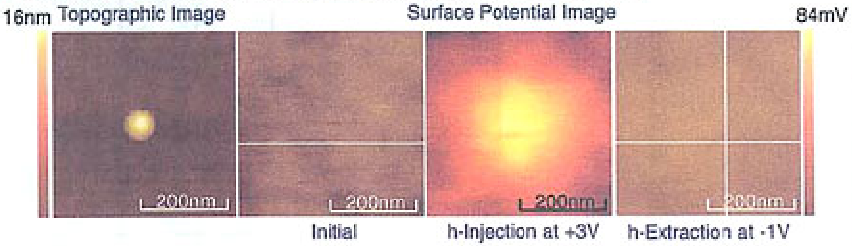
Hole Injection & Hole Extraction in Si Dot with Ge Core Followed by Surface Potential Measurement by AFM/Kelvin Probe Technique

Hole Injection & Hole Extraction (AFM/Tapping mode)

Charging Model



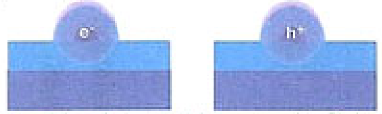
Topographic & Surface Potential Measurement (AFM/Kelvin Probe mode)



Summary

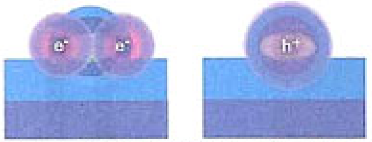
We have detected the charging state of a single Si dots with and without Ge core by the surface potential change by electron charging to neutral dot, discharging of the charged dots and electron extraction from the neutral dot by a AFM/Kelvin probe technique.

For pure single Si dot



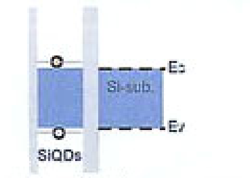
- Hole(s) and electron(s) are stored in Si dot
- Two electrons retained in Si dot and emit one by one with time.

For single Si dot with Ge core

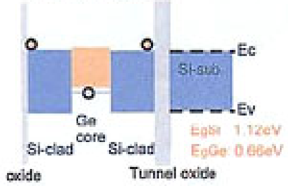


- Electron(s) are located in the Si clad and hole(s) are stored in Ge core

Band Diagram



Band Diagram



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