# Characterization of Electronic Charged States of P-doped Si Quantum Dots Using AFM/Kelvin Probe

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## Introduction

Carrier confinement and charge storage in nanometer-size Si-based dots have been of increasing interest because discrete charged states resulting from quantum confinement and coulomb blockade effects [1, 2] lead to multivalued operations in floating gate application of such Si quantum dots (Si-QDs) and to well-defined operations of single electron transistors even at room temperature [3]. So far, we have demonstrated that, by controlling the early stages of LPCVD using $SiH_4$, hemispherical single crystalline Si-QDs can be formed on ultrathin $SiO_2$ with a high areal density and a little size distribution [4] and confirmed that, in n-MOSFETs with a Si-QDs floating gate, the threshold voltage is shifted stepwise by multiple-step electron charging to the Si-QDs floating gate at room temperature [5]. The result suggests that the Coulombic interaction among neighboring charged dots play an important role in such multi-valued capability of the Si-QDs floating gate. The evaluation of the number of stored charges in Si dots was also demonstrated separately by using an AFM/Kelvin probe technique, where the surface potential changes due to electron injection to and emission from the Si dots is measured [6]. Single electron (or hole) storage in individual Si dot formed on ultrathin $SiO_2$ has been detected [7] and for Si dots with a Ge core electrons are stored in Si clad and holes in Ge core [8]. All these studies were performed for undoped dots formed on ultrathin $SiO_2$/Si(100).

In this work, we extended our research work to phosphorus doping to Si dots and studied charged states of p-doped Si dots, which are affected strongly by ionized donors if any, before and after electron charging and discharging by the AFM/Kelvin probe technique.

## Experimental

A 4 nm-thick $SiO_2$ layer was first grown at 1000ºC in dry $O_2$ on $n^+$-Si(100) with a resistivity of 0.012 Ωcm. To form surface OH bonds uniformly, the $SiO_2$ surface was exposed to remote Ar plasma and subsequently to remote $H_2$ plasma at 540ºC for 1min in each plasma treatment [9]. After the remote plasma treatments, the formation of Si dots was carried out in the same reaction chamber at 540ºC by LPCVD using pure monosilane under 0.5 Torr. During the Si dot formation, delta doping of phosphorus atoms in Si dots was made by a pulse injection of 1% $PH_3$ diluted with He. Finally, the Si dot surface was oxidized at the same temperature by a remote VHF plasma of 1% $O_2$ diluted with He generated at 0.1Torr [8], which resulted in conformal coverage with a 2.4nm-thick $SiO_2$ layer.

Electron charging to and discharging from p-doped Si dots so-prepared were carried out by scanning the sample surface with an electrically-biased AFM probe tip in a tapping mode at room temperature in clean room air, where a Rh-coated $Si_3N_4$ cantilever with a radius of tip apex of ~100nm was used. Before and after electron charging or discharging, the topographic and corresponding surface potential images were simultaneously taken with a non-contact Kelvin-probe mode (KFM).

## Results and Discussion

For an initial surface before applying any bias, the topographic image shows distinct dots with a height of 2-5nm (Fig. 1 (a)) while the surface potential image is fairly uniform as shown in Fig.1 (b). When the sample surface was scanned by the AFM tip biased at +0.2V with respect to the substrate, the surface potential on most of Si dots is increased by ~30mV (Fig.1(c)) although the topographic image remains almost unchanged. Assuming a simple equivalent circuit for the Kelvin probe method as described in Ref. 7, the measured increase in the surface potential corresponds to the extraction of one electron from the dot. Considering the fact that, for undoped Si dots, such an increase in the surface potential is caused by extraction of a valence electron when the tip bias becomes as high as +1.0V, the result of Fig. 1 (c) implies the electron extraction from the conduction band results in positively-charged dots with ionized donors.

The electron injection to the dots was observable when the tip negatively-biased as much as -2.0V was scanned on the surface (Fig.1 (d)), presumably because the Fermi level of Rh-coated tip is placed at a energy very close to the Si valence band top. From the measured surface potential difference (~90mV in Fig. 1 (d)) between on the Si dot and elsewhere, it is suggested that 2 or 3 electrons are injected and stably retained in each dot. It should be noted that no significant difference in the negative voltage required for electron injection between p-doped and undoped Si dots was observable. We also confirmed that, by scanning the surface of Fig. 1 (d) with the tip biased at +0.5V, an image seen in Fig. 1 (c) was reproduced. The result indicates that a positively-charged state by an ionized donor is stable in the tip bias condition ranging from +0.2 to +0.5V.

## Conclusions

The electron extraction from p-doped Si-dots can be interpreted as the emission of a conduction electron generated from an ionized donor, being different from the emission of valence electrons from undoped Si dots. The phosphorus doping to Si-QDs is a useful way to generate a stable positively-charged state at a low voltage.

## References

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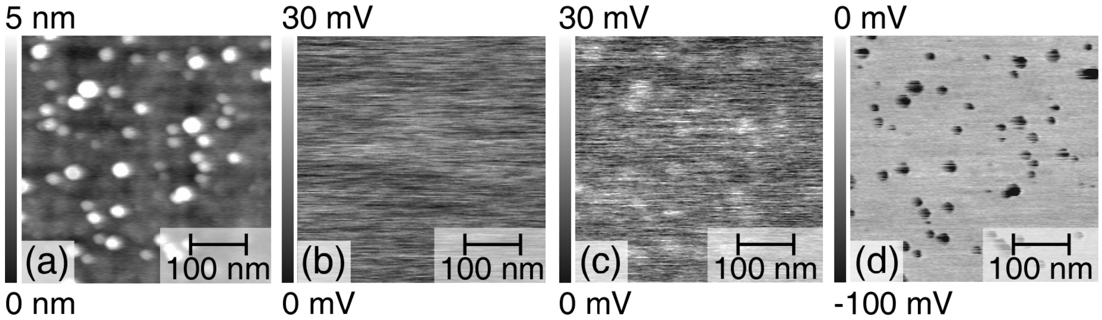

Fig. 1. Topographic image (a) and the corresponding surface potential images of p-doped Si dots measured by a Kelvin probe mode before (b), after electron extraction (c) at a tip biase of +0.2 V and subsequent electron injection (d) at a tip bias of -2.0 V.

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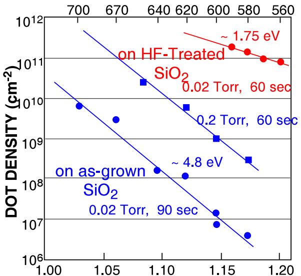
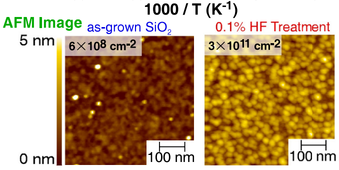
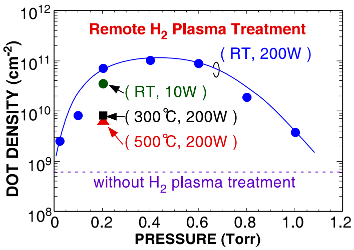
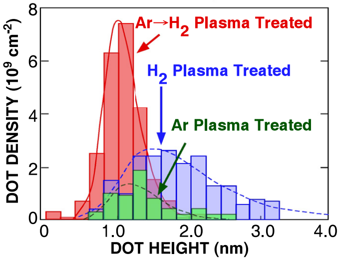
## Background & Motivation





S. Miyazaki et al., Thin Solid Films **369**(2000) 55-59.

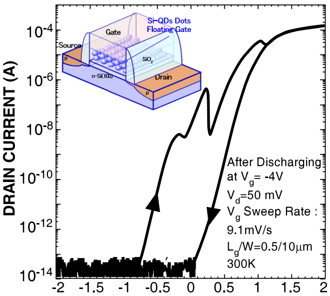




K. Makihara et al., Thin Solid Films **244**(2005) 75-79.

## Previous Work

### Si-QDs Floating Gate MOSFETs



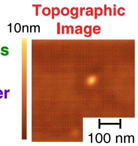
Multivalued memory operations

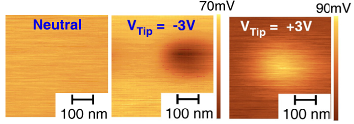
M. Ikeda et al., Jpn. J. Appl. Phys. **42** (2003) 4134-4137

**Charged and Discharged states of undoped Si dot**

**to evaluate charges the number in Si dots**

**AFM/Kelvin Probe Mode**





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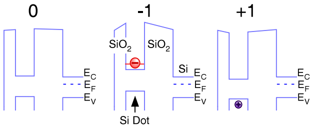


## This Work

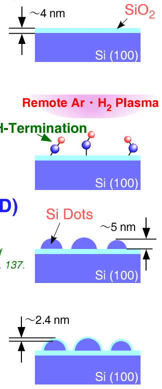
### Phosphorus δ-doping in Si Quantum Dots

Charging State and Retention Characteristic of P-doped Si Dots
Using AFM/KFM Probe Technique

## Experimental

### Sample Preparation

Substrate : $n^+$-Si (100) : 0.1～0.12Ω・cm
p-Si (100) : 8～10Ω・cm



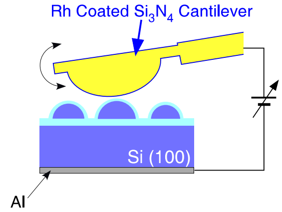
- **RCA Cleaning**
- **Thermal Oxidation**
  - 4 nm-thick $SiO_2$
  - 1000℃, 2% $O_2$
- **Surface Treatment**
  - Remote **Ar** Plasma
  - Remote $H_2$ Plasma
- **Si-Dots Formation (LPCVD)**
  - $SiH_4$: 540,560℃, 0.5Torr

    K. Makihara et. al., Abs. of 12th Int. Conf. of Solid Films and Surf. (Hamamatsu, 2004) p. 137.
- **δ - Doping (1% $PH_3$)**
  - Pulse Injection：1 sec
- **Radical Oxidation**
  - Remote $O_2$ Plasma
  - 540 ℃ 1%$O_2$ in He
- **Al Evaporation**

### Surface Potential Characterization Using KFM

- **Electron Extraction / Injection**

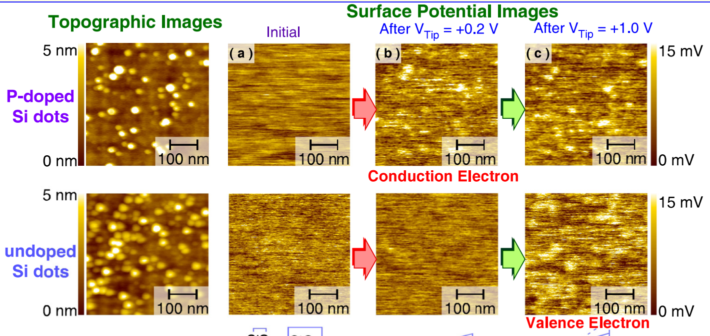
  AFM/Tapping Mode : Contact
  Clean Room in Air

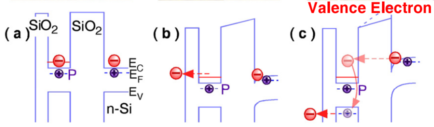


- **Topography & Corresponding Surface Potential Mesurments**

  AFM/Kelvin Probe Mode : Non Contact

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

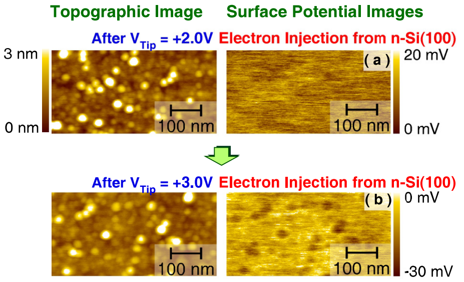


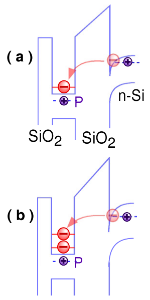


**P-doped Si dots**

**Electron Extraction from the Conduction Band,
Namely Positively-Charged Dots with Ionized P Donors.**

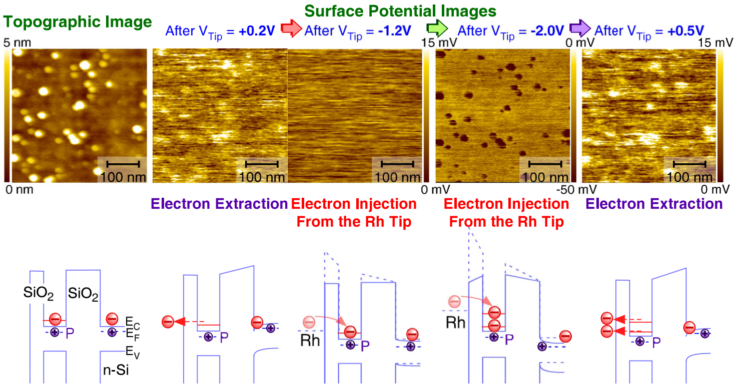
## Electron Extraction and Injection from P-doped Si Dots / $SiO_2$(4nm) / $n^+$-Si(100)





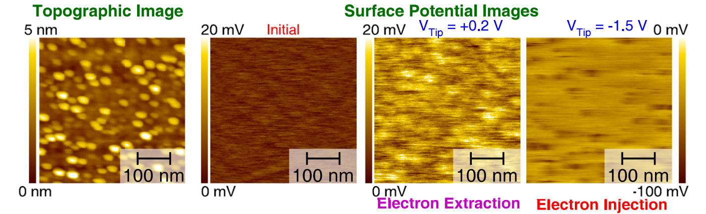
**Electron tunneling from $n^+$-Si(100) substrate to the dots
becomes significant under positive tip biases higher than +2.0V.**

## Electron Injection from Rh Tip to P-doped Si Dots / $SiO_2$(4nm) / $n^+$-Si(100)



The bias condition required for electron injection is consistent with the fact that the Fermi level of Rh lies at an energy position close to the Si valence band top without any external bias.

## Electron Extraction and Injection from $SiO_2$ / P-doped Si Dots / $SiO_2$ / p-Si(100)

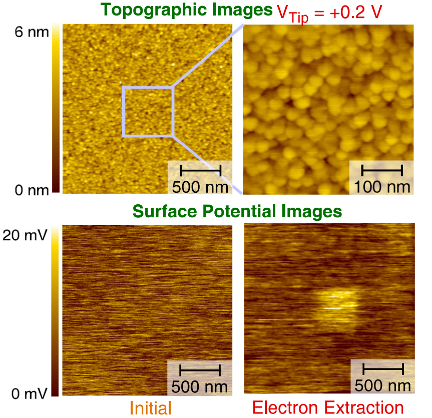


### Tip Biases Required for Electron Extraction and Injection

| | $n^+$-Si(100) | | p-Si(100) | |
|---|---|---|---|---|
| | undoped | P-doped | undoped | P-doped |
| Electron Extraction | + 1.0 V | + 0.2 V | + 1.0 V | + 0.2 V |
| Electron Injection | - 2.0 V | - 2.0 V | - 2.0 V | - 1.5 V |

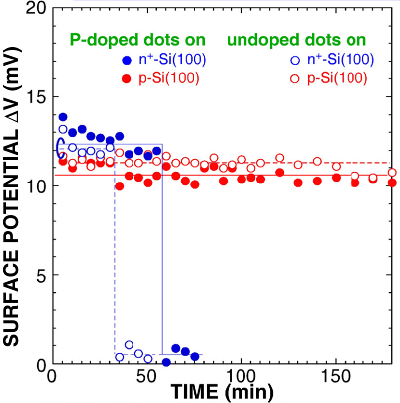
There is no difference in the tip biases required both for the extraction of a conduction electron from the P-doped Si dot and the extraction of a valence electron from the undoped Si dot between the samples on $n^+$-Si(100) and p-Si(100).

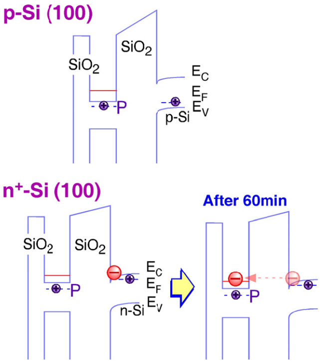
## Electron Extraction from P-doped Si Dots (Dot density : $2 \times 10^{11} cm^{-2}$) on 4nm-thick $SiO_2$ / $n^+$-Si(100)



Positively charged states of P-doped and undoped Si dots were generated at tip biases of +0.2V and +1.0V, respectively. ⇨ **Temporal Change in Surface Potential Images.**

## Retention Characteristics of P-doped & undoped Si Dots





- **p-Si(100)** The positively charged states were retained over 180min for both cases on P-doped and undoped Si dots.
- **$n^+$-Si(100)** The positively-charged states of P-doped and undoped Si dots disappeared after 60min and 40min,respectively.

## Conclusions

**Phosphorus δ-doping to Si Dots**

**Topographic and corresponding surface potential images were simultaneously taken with a non-contact KFM**

Before and after electron charging or discharging

- The electron extraction from P-doped Si dots can be interpreted as the emission of a conduction electron generated from an **ionized donor**, being different from the emission of valence electrons from undoped Si dots.
- The phosphorus doping to Si dots is a useful way to generate a stable positively-charged state at **a low voltage** (**$V_{Tip}$ = 0.2V**).

## Acknowledgments

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