Decay Characteristics of Electronic Charged States of Si Quantum Dots as Evaluated by an AFM/Kelvin Probe Technique

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1. Introduction
Discrete charged states of Si quantum dots (Si-QDs) originating from quantization and charging effects have motivated us to apply Si-QDs to charge storage nodes for floating gate MOS memories [1, 2] and to charge transfer nodes for single electron devices [3]. So far, we have reported the self-assembling formation of Si-QDs from chemical vapor deposition (LPCVD) of pure SiH4 [4] and demonstrated well-defined multiple-step charging characteristics of the Si-QDs floating gate even at room temperature [5]. We have also shown that, using an AFM/Kelvin probe (KFM) technique, the amount of charges stored in each Si-based QD with different dot sizes can be evaluated from the surface potential change with electron injection to and extraction from the Si-QDs [6]. As for the floating gate application of Si-QDs, the charge retention characteristics of the Si-QDs formed with a practically high areal density is one of major issue.

In this work, the temporal decay of the surface potential of Si-QDs on tunnel SiO2 has been systematically studied by the AFM/KFM technique.

2. Experimental
A ~3nm-thick SiO2 layer was grown on p-Si (100) with a resistivity of 8–12Ωcm at 1000°C in a 2% dry O2 diluted with N2, and dipped into a 0.1% HF solution to prepare the surface terminated with OH bonds acting as reactive sites during SiH4-LPCVD. By controlling the early stages of the LPCVD, hemispherical single-crystalline Si dots were self-assembled at 580°C on the ultrathin SiO2 layer at a pressure of 0.8Torr. The areal density and average dot height evaluated by AFM were 4.0 × 10¹¹cm⁻² and ~2.6nm, respectively. After the Si dot formation, the dot surfaces were covered with ~2nm-thick thermally grown SiO2 by 900°C in dry O2. The process sequence consisting of the Si dot formation and the surface oxidation were repeated twice. For electron injection to and electron extraction from the dots, a Rh-coated AFM cantilever made of Si3N4 was biased in the range from -4V to +4.8V with respect the Si(100) substrate and operated in a tapping mode, where the tip apex was ~100nm in radius. After charging and discharging of Si-QDs, the topographic and surface potential images were simultaneously taken with a non-contact KFM mode.

3. Results and Discussion
No change in topographic images with electron injection and extraction was confirmed. In this experiment, because of poor special resolution in the surface potential images for such a high areal dot density, the change in the average surface potential among the dots was only evaluated. As shown in the Fig. 1, when the surface is scanned with the AFM tip biased at -4V with respect to the substrate in the tapping mode, a distinct decrease in the surface potential of corresponding area, which is associated with electron injection to the dot, is observed but, in the unbiased area, no change in the surface potential is detectable. Subsequently by scanning with the tip biased at +4V in the central part of electron pre-injected region, the surface potential raises by almost double the change caused in electron injection, which makes the reverse contrast in the surface potential image. The result indicates that electrons

Fig. 1. (a) Topographic image and corresponding surface potential images measured by the Kelvin probe mode (b) before, (c) after electron injection at a tip bias -4V (d), after electron extraction from the electron pre-injected area at a tip bias +4V.
are extracted from the dots and holes are retained in the dots although electron tunneling into the dots through the 3nm-thick bottom oxide from the inversion region of the substrate may partly compensate for such discharging. We have also confirmed that such surface potential changes do not occur on a single SiO$_2$ layer without Si dots under the same conditions. For the case with a dot density as low as ~10$^8$cm$^{-2}$, the surface potential change in each of dots can be measured as reported in Ref. 6.

After charge injection, the image contrast in surface potential image fades away with time and no lateral spreading of stored charges is observable. In Fig. 2, the temporal decays in the surface potential after electron injection and extraction at different bias conditions are summarized. For the cases after electron injection at negative biases of -2.0V and larger, the surface potential change decays with almost the same rate being limited by electron tunneling through the bottom oxide to the substrates. Notice that, at negative biases at -1.5V and smaller, although electron injection from the tip to the dots is unlikely considering the energy band diagram between the sample and the tip, the surface potential change attributed to negative charging is observable and shows a fairly fast decay. This result can be interpreted as follows: at such small negative biases, hole injection from the substrate to the dot is possible, which induces electron trapping at the oxide surface. Since the amount of surface potential change due to charging is increase with the charged position measured from the substrate, the total potential change becomes positive. In that case, the recombination of electrons trapped at the oxide surface and holes retained in the dots through the ultrathin top oxide might be responsible for the fast decay. For positive tip biases below +4V, electron extraction was not observable because of electron tunneling from the substrate. For the case after electron extraction at +4.8V, the decay curve shows two components the origins of which are not identified yet. The initial fast decay component and the second slow component might be attributable to hole tunneling from the dots and the hole emission from the traps generated in the SiO$_2$ layer under such high bias conditions.

In conclusion, the temporal decay of charged states of high density Si-QDs can be characterized by not only discharging process through the bottom tunnel oxide but also the neutralization due to carrier recombination.

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This Work

The temporal decay of the surface potential of electronic charged Si-QDs on tunnel SiO$_2$ has been studied by the AFM/KFM technique.

Experimental

Sample Preparation
- Substrate: n$^+$-Si (100) : 0.12~0.19 Ω·cm
- RCA Cleaning
- Thermal Oxidation
  - 3 nm-thick SiO$_2$
  - 1000°C, 2% O$_2$
- Surface Treatment
  - 0.1% HF
- Si-Dots Formation (LPCVD)
  - a SiH$_4$: 580°C, 0.8 Torr, 60sec
- Thermal Oxidation
  - 2 nm-thick SiO$_2$
  - 900°C, 2% O$_2$
- Al Evaporation

Surface Potential Characterization Using KFM

Electron Extraction / Injection
- AFM/Tapping Mode: Contact
- Clean Room in Air
- Si-Dots Formation
- HF-treated
- as-grown

AFM/Kelvin Probe Mode: Non Contact

Temporal Change in Surface Potential Image Taken After Electron Injection to Si Dots on 3nm-thick SiO$_2$ / p-Si(100)

When the surface is scanned with the AFM tip biased at -4V, a distinct decrease in the surface potential of corresponding area, which is associated with electron injection to the dot, is observed.

Electrons are extracted from the dots and holes are retained in the dots although electron tunneling through the bottom oxide from the inversion region of the substrate may partly compensate for such discharging.

The injected electrons in dot are tunneling through the bottom oxide to the substrate.
In-plane spreading of stored electrons is unlikely.
Temporal Decays in the Surface Potential of Si Dots on 3nm-thick SiO₂ / p-Si(100) after complete neutralization of pre-charged states caused at different tip biases and temporal decay characteristics at a tip bias as low as -0.5V were made.

Temporal Decays in the Surface Potential of Si Dots on 3nm-thick SiO₂ / n-Si(100) after electron injection and extraction at different bias conditions are summarized.

Evaluation of Damage Induced by Charge Injection of High Voltage

The charging to the sample on p-Si(100) at a tip bias as low as -0.5V was made after complete neutralization of pre-charged states caused at different tip biases and temporal decay characteristics were measured to evaluate the damage at high bias condition.

Temporal Decay after Electron Injection to the Pre-Biased Area

No change in the decays is observable for the cases after negatively charged at -0.5V and -4.0V, while for the case after positively charged at -4.8V negatively charged state generated at -0.5V is markedly prolonged.
The prolonged decay implies that defects in the top oxide generated by applying at a tip bias of -4.8V and electrons are injected in Si-QDs through the defects even at the tip bias as small as -0.5V where the Fermi level of the Rh tip can not reach to the energy position corresponding to the bottom of Si conduction band.

The decay can be characterized by the electron tunneling through the bottom tunnel oxide not only for discharging of store electrons but also neutralization of positively-charged states in which stored holes are recombined with electrons tunneling from the substrate.

Negatively-charged states generated for the sample on p-Si(100) at a tip bias insufficient for electron injection to the Si-QDs can be interpreted in terms of electron attachment on the top oxide induced by hole injection from the p-Si(100) substrate and their decay is likely to be controlled by tunneling of attached electrons to the dots.

An extremely slow decay measured for positively-charged states generated on p-Si(100) at a tip bias -4.8V might be attributable to the generation of positive traps in the oxide.

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