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Characterization of electronic charged states of P-doped Si quantum dots using AFM/Kelvin probe

Katsunori Makihara *, Jun Xu, Mitsuhisa Ikeda, Hideki Murakami, Seiichiro Higashi, Seiichi Miyazaki

Department of Electrical Engineering, Graduate School of Advanced Sciences of Matter, Hiroshima University, Kagamiyama 1-3-1, Higashi-Hiroshima 739-8530, Japan

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Abstract

Phosphorous doping to Si quantum dots was performed 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, and electron charging to and discharging from P-doped Si dots were studied to characterize their electronic charged states using a Kelvin probe technique in atomic force microscopy (AFM). The potential change corresponding to the extraction of one electron from each of the P-doped Si dots was observed after applying a tip bias as low as +0.2 V while for undoped Si dots, with almost the same size as P-doped Si dots, almost the same amount of the potential change was detectable only when the tip bias was increased to ~1 V. It is likely that, for P-doped Si dots, the electron extraction from the conduction band occurs and results in a positively charged state with ionized P donor.
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Keywords: Si quantum dot; Phosphorous doping; LPCVD; AFM/Kelvin probe

1. 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 plays an important role in such multivalued capability of the Si-QDs floating gate. The evaluation of the number of stored charges in Si dots was also demonstrated by using an AFM/Kelvin probe technique, where the surface potential changes due to electron injection to and emission from the Si dots were 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 of 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.

2. Experimental

The substrates used in this work were n^+-Si(100) and p-Si(100) with resistivities of 0.012 and 0.1 Ω cm, respectively. After conventional wet-chemical cleaning steps, a 4-nm-thick SiO_2 layer was first grown at 1000 °C in dry O_2. To form uniformly surface OH bonds as reactive sites for Si dot formation, the SiO_2 surface was exposed to remote Ar

* Corresponding author. Tel.: +81 82 424 7648; fax: +81 82 422 7038.
E-mail address: semicon@hiroshima-u.ac.jp (K. Makihara).

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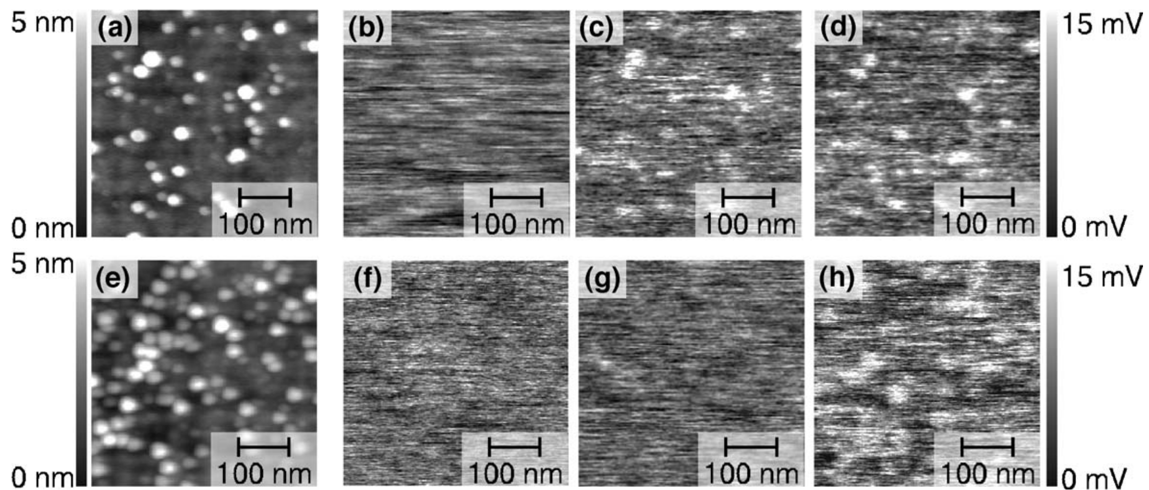

Fig. 1. Topographic images of P-doped (a) and undoped (e) Si dots on ~4-nm-thick SiO_2/n^+-Si(100), and the corresponding surface potential images of P-doped Si (b–d) and undoped dots (f–h) measured by a Kelvin probe mode before (b, f) and after tapping the tip biased at +0.2 V (c, g) and subsequently biased at +1.0 V (d, h).

plasma and subsequently to remote H_2 plasma at 540 °C for 1 min in each plasma treatment [9]. After the remote plasma treatments, the formation of Si dots was carried out in the same reaction chamber at 540 °C 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 0.1 Torr [9], which resulted in conformal coverage with a 2.4 nm-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 ~100 nm 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.

3. Results and discussion

Topographic and corresponding surface potential images of the sample with P-doped Si dots formed on ~4 nm-thick SiO_2/n^+-Si(100) are compared with those of an undoped case being similar in dot size as shown in Fig. 1. In both cases, without any bias applied to the sample surfaces, uniform surface potential images were measured as indicated in Fig. 1(b and f). When the AFM tip was biased at +0.2 V with respect to the substrate and scanned on the sample surface, an increase in the surface potential by ~30 mV becomes observable on P-doped Si dots with a dot height of ~5 nm as seen in Fig. 1(g), although surface potential images are more smeared than topographic images because of poor lateral resolution and limited signal-to-noise ratio. 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. Notice that, for the case of undoped Si dots, no change in surface potential image was detectable under the same tip bias condition (Fig. 1(c)), and

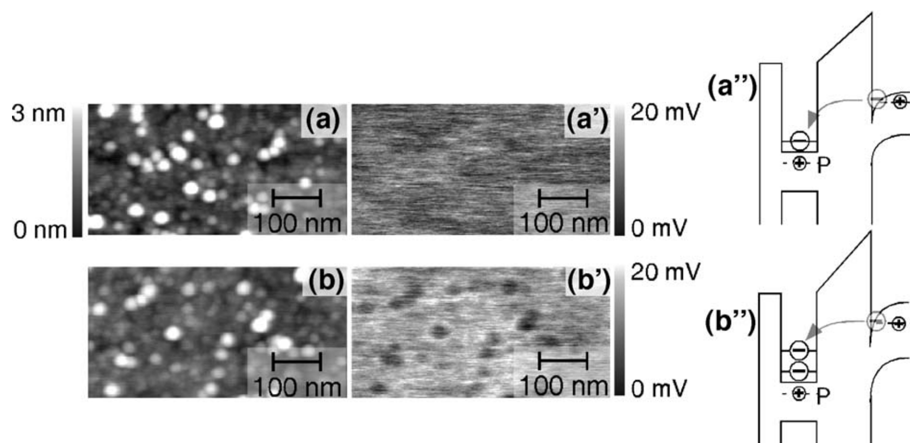

Fig. 2. Topographic images (a and b) and surface potential images (a′ and b′) simultaneously taken after applying positive biases to P-doped Si dots. The AFM tip biases were +2.0 V for (a) and (a′) and +3.0 V for (b) and (b′). The energy band diagrams corresponding to surface potential images were shown in both cases (a″) and (b″) accompanied with schematic illustrations for electron tunneling from the substrate to the dot.

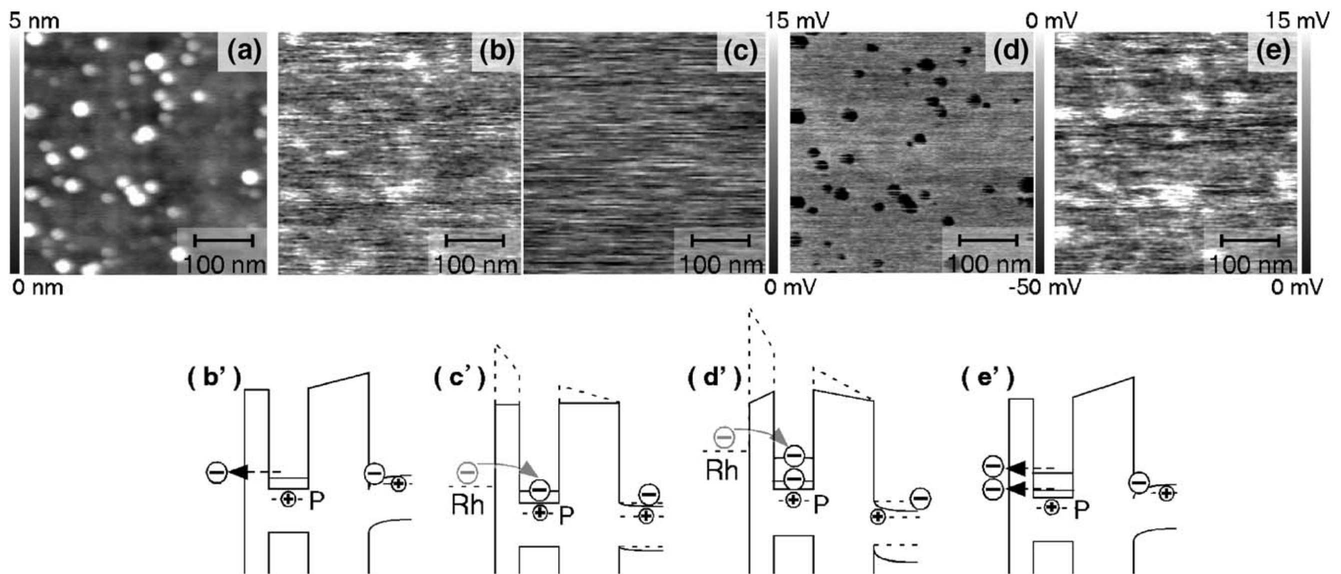

Fig. 3. Topographic image (a), surface potential images of P-doped Si dots after applying different tip biases of +0.2 V (b), −1.2 V (c), −2.0 V (d) and +0.5 V (e). The energy band diagram for each case was also shown in (b′)–(e′).

only by an increase in the tip biased to about +1.0 V, a surface potential change by almost the same amount was measured (Fig. 1(h)) as a result of the extraction of a valence electron. Thus, the result of Fig. 1(c) for P-doped Si dots can be interpreted in terms of the electron extraction from the conduction band, namely, positively charged dots with ionized P donors. It is also interesting to note that for P-doped Si dots, positive charging is not promoted by an increase in the positive tip bias from +0.2 to +1.0 V. This result suggests that electron tunneling through SiO_2 from n^+-Si(100) to the Si dots compensates for the electron extraction from the valence band. In fact, with increasing tip bias from +1.0 V to +2.0 V, the positive charging on P-doped Si dots disappears completely (Fig. 2(a′)), and with tip bias to +3.0 V, a negatively charged state is realized (Fig. 2(b′)), although the topographic image remains almost unchanged. The results of Fig. 2 show that the electron tunneling from n^+-Si(100) substrate to the dots becomes significant under positive tip biases higher than +2.0 V as schematically illustrated in Fig. 2(a″ and b″).

Electron injection from the Rh tip negatively biased to P-doped Si dots was also examined. The positively charged state of P-doped Si dots (Fig. 3(b)) was neutralized by tapping the tip biased at −1.2 V as shown in Fig. 3(c). 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. Further increase in negative tip bias to −2.0 V results in a negatively charged state in the dots as represented in Fig. 3(d) due to the promotion of electron injection from the negatively biased tip to the dot (Fig. 3(d′)). From the measured surface potential difference (~90 mV in Fig. 3(d)) between 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. 3(d) with the tip biased at +0.5 V, an image seen in Fig. 3(e) 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 +1.0 V. A similar result was also obtained for the sample prepared on p-

Table 1
The tip biases required for a positively charged state due to electron extraction from and for a negatively charged state due to electron injection to undoped and P-doped Si dots were summarized for the samples prepared on n^+-Si(100) and p-Si(100)

	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

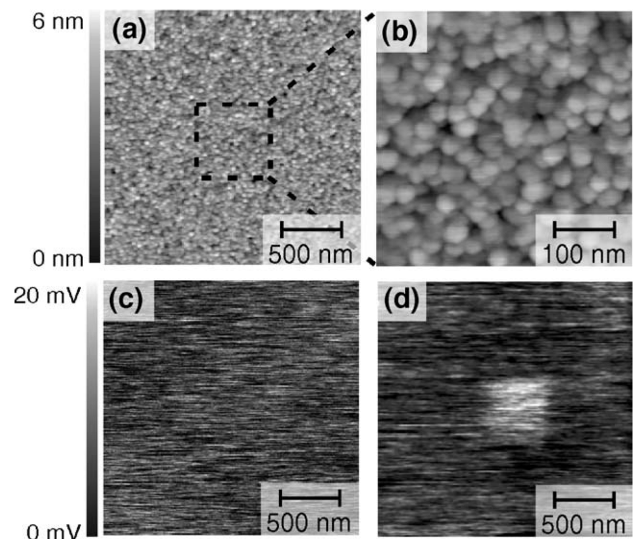

Fig. 4. Topographic image of P-doped Si dot with an areal density of 3×10^{11} cm^{-2} (a), magnified topographic image (b) in the center part of (a) with applied bias at +0.2 V (b), and corresponding surface potential images before (c) and after (d) electron extraction.

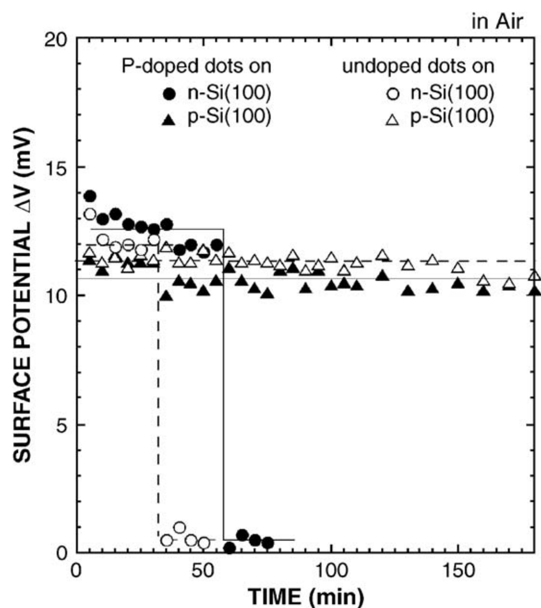

Fig. 5. Retention characteristics of undoped and P-doped Si dots evaluated from the change in the surface potential as seen in Fig. 4. Black and white symbols show the results obtained for P-doped and undoped Si dots, respectively. The circles and triangles denote the dots formed on n^+-Si(100) and p-Si(100), respectively.

Si(100). As summarized in Table 1, there is no difference in the tip bias required for either the extraction of a conduction electron from the P-doped Si dot or the extraction of a valence electron from the undoped Si dot between the samples on n^+-Si(100) and p-Si(100). In addition, the tip bias required for electron injection from the negatively biased tip to Si dots is almost identical in all the cases.

The retention characteristics of positively charged states of P-doped and undoped Si dots with an areal dot density of 2×10^{11} cm^{-2} and an average dot height of 6 nm were also evaluated at room temperature in clean room air as shown in Fig. 4. As indicated in Fig. 1, the positively charged states of P-doped and undoped Si dots were generated at tip biases of +0.2 and +1.0 V, respectively. As shown in Fig. 5, the positively charged states on p-Si(100) were retained over 180 min for both cases on P-doped and undoped Si dots, but in contrast, positively charged states of P-doped and undoped Si dots formed on n^+-Si(100) disappeared after 60 min and 40 min, respectively. Since almost the same results were obtained when the same experiments were made again in 200 min after the first charge injection (Fig. 5), an influence of surface-adsorbed ions generated from water molecules and/or some other surface contaminants on the charge retention characteristics can be ruled out in discussion about the difference in the retention time between the samples shown in Fig. 5. The reduced retention for positively charged states of Si dot on n^+-Si(100) comparison with the case on p-Si(100) indicates that the electron tunneling from the Si(100) substrate is responsible for the neutralization of positively charged states. The observed difference in the retention time between the P-doped and undoped Si dots on n^+-Si(100) can be explained as the difference between localized positive donor(s) or extended hole(s) in the dot.

4. 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.

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