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# The charge trapping and memory effect in SiO<sub>2</sub> thin films containing Ge nanocrystals

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## Abstract

In this work, Ge nanocrystals (nc-Ge) embedded in SiO<sub>2</sub> thin films have been synthesized by ion implantation. Both the higher and the lower implantation dose/energy samples exhibit significant memory effect as a result of charge trapping in the nc-Ge. Under a negative gate voltage, either electron trapping or hole trapping dominates, depending on the magnitude of gate voltage and charging time as well as the distribution of nc-Ge. However, under a positive gate voltage, only electron trapping is observed, and the flat-band voltage shift is also affected by the nc-Ge distribution. These results demonstrate that the unconventional memory effect can be modulated by the distribution of nc-Ge.

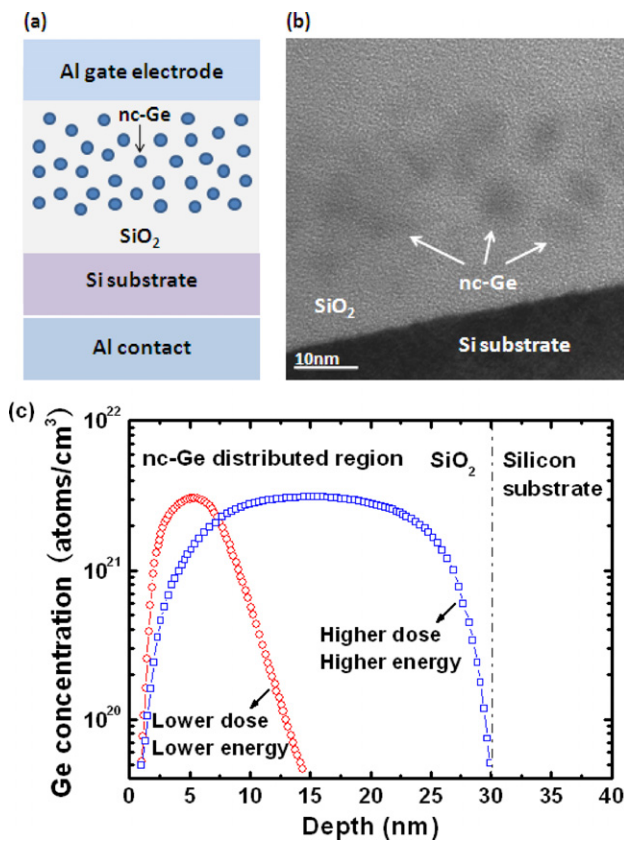
(Some figures in this article are in colour only in the electronic version)

## 1. Introduction

Si nanocrystals (nc-Si) and Ge nanocrystals (nc-Ge) embedded in SiO<sub>2</sub> matrix have been regarded as potential candidates for nonvolatile memory devices [1–6]. In these nanocrystals-based memory devices, the conventional polysilicon floating gate is replaced by isolated nanocrystals embedded in a gate oxide which can enhance the reliability, endurance and the retention time [7–13]. One of the promising techniques being used to synthesize the metal–oxide–semiconductor (MOS) structure is the implantation of ions into SiO<sub>2</sub> thin films followed by a higher temperature annealing. The ion implantation technique is favourable because the density and depth distribution of the implanted ions can be easily controlled. Compared with nc-Si, nc-Ge is considered to have a better performance due to a smaller band gap (~0.66 eV) [4, 5]. In this paper, we have synthesized nc-Ge embedded in SiO<sub>2</sub> thin films with a MOS structure by ion implantation. By controlling the implantation dose and energy (i.e. the distribution of nc-Ge), it is observed that both the higher dose/energy sample and the lower dose/energy sample present unconventional memory effect.

## 2. Experimental details

SiO<sub>2</sub> thin films of 30 nm thickness are thermally grown on p-type (1 0 0)-oriented Si wafers at 950 °C in dry oxygen. Ge ions are then implanted into the SiO<sub>2</sub> thin films with various combinations of energy and dose to form different distributions of Ge ions in SiO<sub>2</sub>. One sample is fabricated with a higher Ge ions dose of  $1 \times 10^{16} \text{ cm}^{-2}$  at a higher implantation energy of 16 keV. The other sample is fabricated with a lower Ge ions dose of  $2 \times 10^{15} \text{ cm}^{-2}$  at a lower implantation energy of 2 keV. The two samples are subjected to 800 °C furnace annealing for 1 h in ambient N<sub>2</sub>. Finally, both the Al gate electrodes and backside contacts with a thickness of 200 nm are deposited using the e-beam evaporator system for the two samples to form the MOS structure. The MOS structure is presented in figure 1(a). The cross-sectional transmission electron microscope (TEM) image confirms the formation of the nc-Ge embedded in SiO<sub>2</sub> matrix as shown in figure 1(b). The implanted Ge depth profiles in the SiO<sub>2</sub> thin films are measured by the secondary ion mass spectroscopy (SIMS). As revealed by the SIMS shown in figure 1(c), for the sample with the higher dose and energy, the implanted Ge distributes throughout the entire ~30 nm oxide region with the peak concentration located at a depth of ~15 nm underneath the

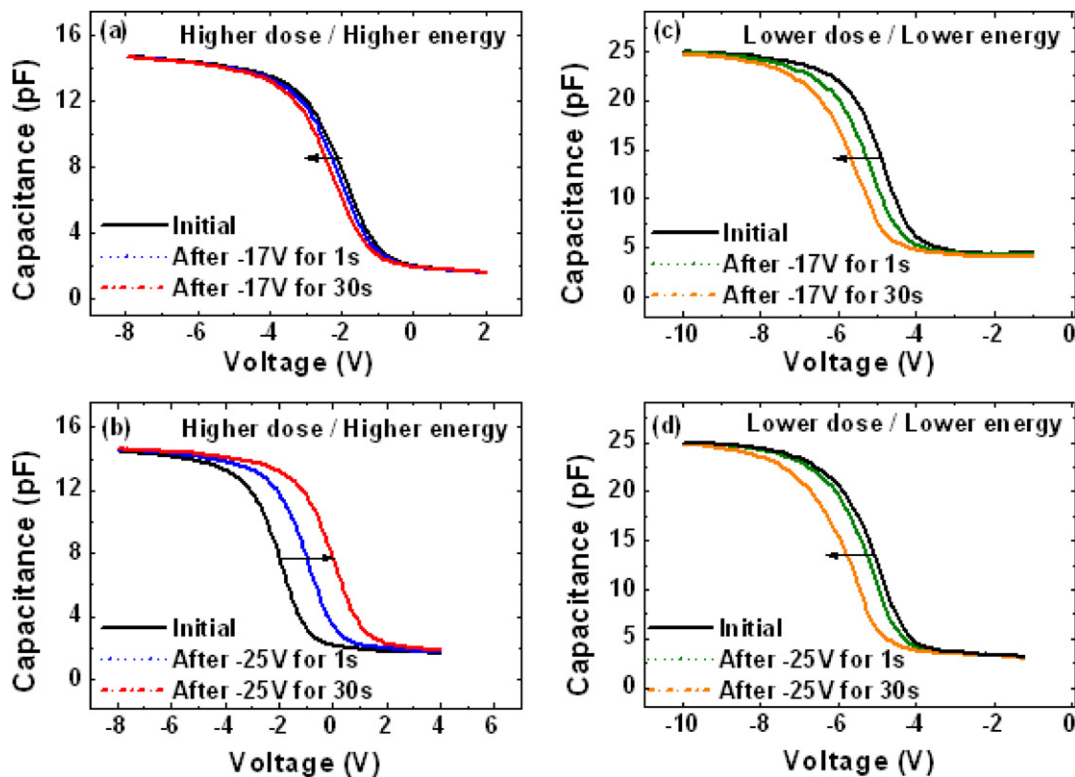


**Figure 1.** (a) Schematic illustration of the MOS structure. (b) Cross-sectional TEM image of nc-Ge embedded in SiO<sub>2</sub>. (c) Distribution of nc-Ge in SiO<sub>2</sub> measured from SIMS for the higher and lower dose/energy sample, respectively.

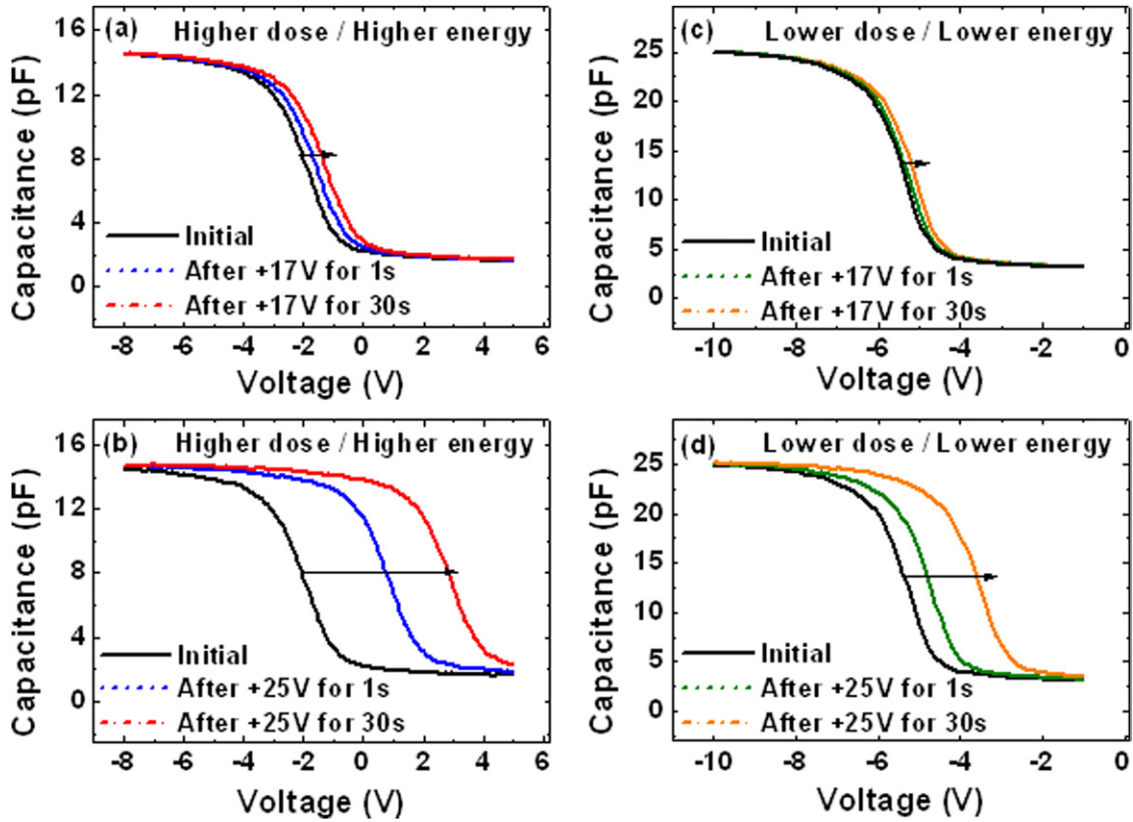
oxide surface. However, for the sample with the lower dose and energy, the implanted Ge distributes from the oxide surface to a depth of  $\sim 15$  nm, and the Ge concentration reaches its maximum at a depth of  $\sim 5$  nm. In particular, the Ge peak concentration is the same ( $\sim 3 \times 10^{21}$  atoms  $\text{cm}^{-3}$ ) for the two samples. The experiment of charge trapping in the nc-Ge embedded in SiO<sub>2</sub> thin films is carried out by applying a voltage to the gate electrode with a Keithley 4200 semiconductor characterization system, while capacitance–voltage ( $C$ – $V$ ) measurement is performed in a dark environment at room temperature with a HP4284A LCR meter at the frequency of 1 MHz.

### 3. Results and discussion

To study the charging behaviours of nc-Ge for the two samples,  $C$ – $V$  measurement is investigated systematically. For the higher dose/energy sample, the application of  $-17$  V for 1 and 30 s leads to a slight negative flatband voltage shift ( $\Delta V_{\text{FB}}$ ) of  $-0.15$  and  $-0.32$  V, as shown in figure 2(a). Interestingly, the application of  $-25$  V for 1 and 30 s induces a dramatic positive  $\Delta V_{\text{FB}}$  of  $+1.05$  and  $+2$  V as shown in figure 2(b). On the contrary, for the lower dose/energy sample, the application of  $-17$  V for 1 and 30 s causes a larger negative  $\Delta V_{\text{FB}}$  of  $-0.38$  and  $-0.77$  V as shown in figure 2(c), and the application of  $-25$  V for 1 and 30 s also induces a negative  $\Delta V_{\text{FB}}$  of  $-0.2$  and  $-0.73$  V as shown in figure 2(d). The negative  $\Delta V_{\text{FB}}$  indicates positive charge trapping in the nc-Ge embedded in SiO<sub>2</sub> thin films. In contrast, the positive  $\Delta V_{\text{FB}}$  suggests negative charge trapping in the nc-Ge. Namely, the negative gate voltage results



**Figure 2.** (a)–(d) Shifts in  $C$ – $V$  characteristics after an application of  $-17$  V for 1 s and 30 s and  $-25$  V for 1 s and 30 s for the higher and lower dose/energy sample, respectively.



**Figure 3.** (a)–(d) Shifts in  $C$ – $V$  characteristics after an application of +17 V for 1 s and 30 s and +25 V for 1 s and 30 s for the higher and lower dose/energy sample, respectively.

in both positive and negative charge trapping simultaneously, which are the two competing processes determined by the magnitude of the negative gate voltage, charging time and the distribution of nc-Ge. The detailed physical mechanism will be further discussed.

Figure 3 shows the  $C$ – $V$  shifts driven by the positive gate voltage for the two samples. It is worth noting that all positive gate voltages lead only to positive  $\Delta V_{FB}$ . For the higher dose/energy sample, the application of +17 V for 1 and 30 s produces a positive  $\Delta V_{FB}$  of +0.32 and +0.66 V as shown in figure 3(a). In particular, the application of +25 V for 1 and 30 s induces a remarkable positive  $\Delta V_{FB}$  of +2.8 and +4.85 V as shown in figure 3(b). However, for the lower dose/energy sample, the application of +17 V for 1 and 30 s causes a smaller positive  $\Delta V_{FB}$  of +0.06 and +0.22 V as shown in figure 3(c), and the application of +25 V for 1 and 30 s leads to a positive  $\Delta V_{FB}$  of +0.58 and +1.8 V as shown in figure 3(d). The positive  $\Delta V_{FB}$  indicates that only negative charges are trapped in the nc-Ge embedded in  $\text{SiO}_2$  thin films. Obviously, the charge trapping depends on the voltage polarity and the magnitude of the gate voltage from figures 2 and 3. The capability of charge storage in the nc-Ge and the effect on  $\Delta V_{FB}$  exhibit the memory effect. It will be shown later that charge trapping (not only the amount of charge but also the charge polarity) is also determined by the charging time and the distribution of nc-Ge.

Actually, the positive charge trapping in the nc-Ge is due to the hole injection from the Si substrate, and the negative charge trapping in the nc-Ge is due to the electron injection from either the metal gate or the Si substrate depending on the voltage

polarity. Under a negative gate voltage, both electron injection from the metal gate and hole injection from the Si substrate occur simultaneously. Either the electron trapping or hole trapping dominates, depending on the distribution of nc-Ge. This argument is directly supported by our experimental results, as discussed later. On the other hand, under a positive gate voltage, only electrons will be injected into the nc-Ge from the Si substrate.

The scenario of negative gate voltage and positive gate voltage discussed above is clearly demonstrated by figures 4(a) and (b) which show  $\Delta V_{FB}$  as a function of gate voltage for different charging times for the two samples. It is clearly seen that with the magnitude of negative gate voltage  $\Delta V_{FB}$  is initially negative and then changes into more positive for the higher dose/energy sample, whereas  $\Delta V_{FB}$  is always negative for the lower dose/energy sample. Such results reflect the difference in nc-Ge distribution between the two samples. For the higher dose/energy sample, the more positive  $\Delta V_{FB}$  represents that the electron injection from the metal gate dominates. However, for the lower dose/energy sample, only negative  $\Delta V_{FB}$  is observed, indicating that the hole injection from the Si substrate is the dominant process.

From figures 4(a) and (b), we can also observe that  $\Delta V_{FB}$  is always positive under the positive gate voltage for the two samples. Furthermore,  $\Delta V_{FB}$  increases with the magnitude of positive gate voltage, which verifies that more injected electrons from the Si substrate are trapped in the nc-Ge. Additionally, the value of positive  $\Delta V_{FB}$  for the higher dose/energy sample is larger than that for the lower dose/energy

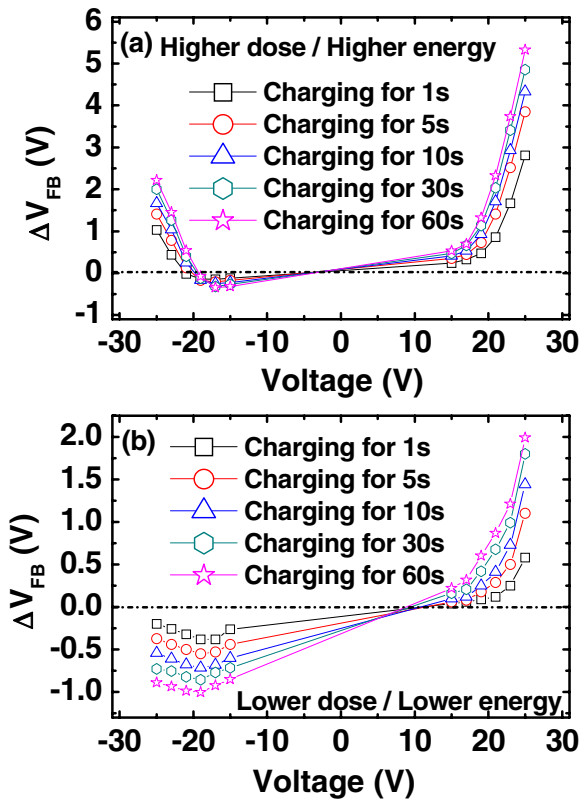


Figure 4. Flat-band voltage shift  $\Delta V_{FB}$  as a function of gate voltage for different charging times (a) for the higher dose/energy sample and (b) for the lower dose/energy sample.

sample. For instance, after charging +25 V for 60 s,  $\Delta V_{FB}$  reaches a tremendous +5.3 V for the higher dose/energy sample but  $\Delta V_{FB}$  is only +2 V for the lower dose/energy sample. This indicates that the amount and density of injected electrons for the higher dose/energy sample are more than those for the lower dose/energy sample.

By the above discussions, we can find that both the higher and lower dose/energy samples exhibit a peculiar memory effect. It should be mentioned that it is very important for the distribution of nc-Ge to determine the unusual memory effect. Under the negative gate voltage, the electron (hole) trapping in the nc-Ge closer to the Si substrate (i.e. farther away from the gate electrode) is easier (more difficult) to occur when the energy band of the nc-Ge concerned is lower relative to the Fermi level of the metal gate. The higher dose/energy sample has numerous nc-Ge distributed nearer the Si substrate while nc-Ge in the lower dose/energy sample is distributed closer to the gate electrode. This is the reason why electron trapping is more significant in the higher dose/energy sample while hole trapping is more significant in the lower dose/energy sample. On the other hand, under the positive gate voltage, there is only electron trapping in the nc-Ge. However,  $C-V$  measurement is more sensitive to the electron trapping near the  $\text{SiO}_2/\text{Si}$  interface. At the same time, the electron injection from the Si substrate to the nc-Ge nearer the interface is also easier. Due to the distribution of Ge concentration throughout the entire  $\text{SiO}_2$  region for the higher dose/energy sample, the value of positive  $\Delta V_{FB}$  for the higher dose/energy sample is larger than that for the lower dose/energy sample.

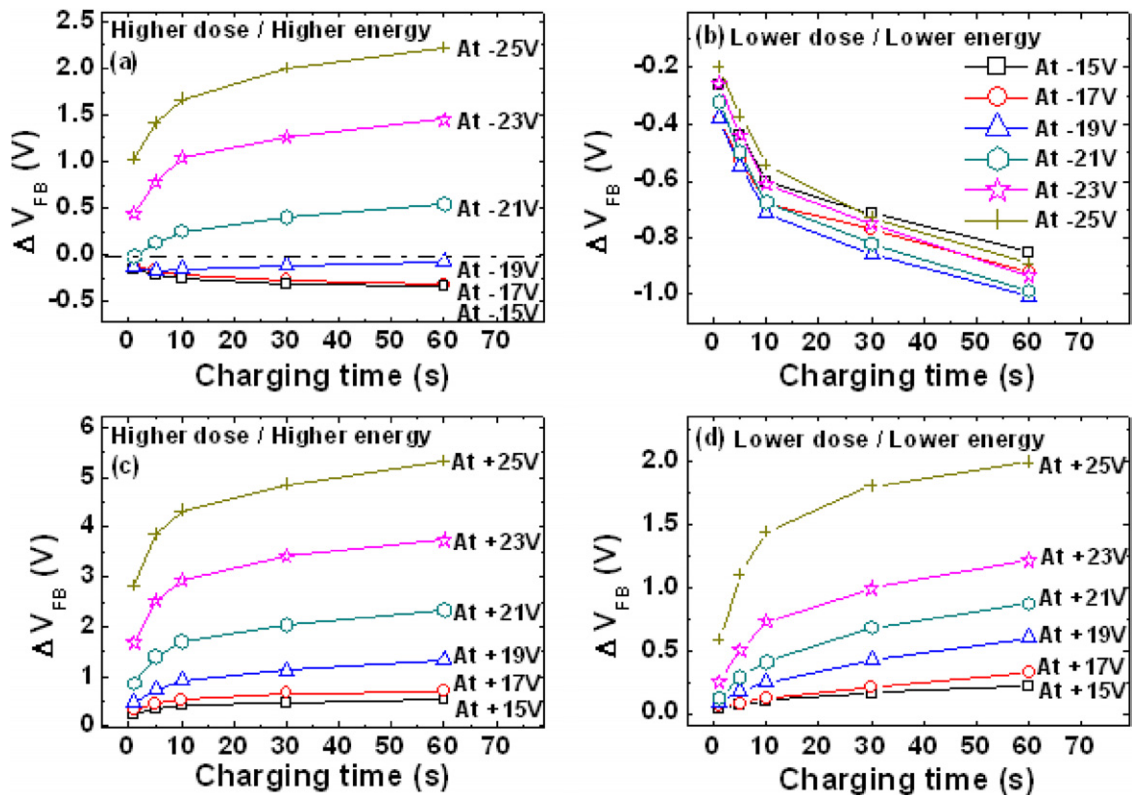


Figure 5. (a)–(d)  $\Delta V_{FB}$  as a function of charging time for different gate voltages for the higher and lower dose/energy sample, respectively.

Figures 5(a)-(d) show  $\Delta V_{\text{FB}}$  as a function of charging time for different gate voltages for the two samples. When the negative gate voltage is applied, for the higher dose/energy sample,  $\Delta V_{\text{FB}}$  is positive when the magnitude of the negative gate voltage is higher than  $-21$  V and increases with charging time rapidly as shown in figure 5(a). For the lower dose/energy sample,  $\Delta V_{\text{FB}}$  is negative in the entire negative gate voltage range and its magnitude also increases with charging time as shown in figure 5(b). Distinctly, the competition between the electron trapping and the hole trapping is affected by the charging time and the distribution of nc-Ge. Nevertheless, when the positive gate voltage is applied,  $\Delta V_{\text{FB}}$  is always positive for the two samples as shown in figures 5(c) and (d), showing only electron injection from the Si substrate. Moreover, the increased amplitude of  $\Delta V_{\text{FB}}$  with charging time for the higher dose/energy sample is larger than that for the lower dose/energy sample. These results show that the memory effect can be modulated by the distribution of nc-Ge.

#### 4. Conclusions

In summary, we have observed a large memory effect in  $\text{SiO}_2$  thin films embedded with nc-Ge synthesized by ion implantation. Either electron trapping or hole trapping in the nc-Ge is feasible, depending on the voltage polarity, the magnitude of gate voltage, charging time and the distribution of nc-Ge. Under a negative gate voltage, electron trapping is more significant in the higher dose/energy sample while hole trapping is more significant in the lower dose/energy sample. Nevertheless, under a positive gate voltage, only electron trapping occurs, and the value of  $\Delta V_{\text{FB}}$  for the higher dose/energy sample is larger than that for the lower dose/energy sample. All experimental results validate that the distribution of nc-Ge can modulate the unconventional memory effect.

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