Charging mechanism in a SiO$_2$ matrix embedded with Si nanocrystals

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One of the applications of a Si nanocrystals (nc-Si) embedded in a SiO$_2$ matrix is in the area of nonvolatile memory devices based on the charge storage in the material system. However, whether the charge trapping mainly occurs at the nc-Si/SiO$_2$ interface or in the nc-Si is still unclear. In this work, by x-ray photoemission spectroscopy analysis of the Si $2p$ peaks, the concentrations of both the nc-Si and the Si suboxides that exist at the nc-Si/SiO$_2$ interface are determined as a function of thermal annealing, and the charging effect is also measured by monitoring the shift of the surface C 1$s$ peak. It is observed that the annealing-caused reduction of the total concentration of the interfacial suboxides is much faster than that of both the C 1$s$ shift and the nc-Si concentration. In addition, the trend of the C 1$s$ shift coincides with that of the nc-Si concentration. The results suggest that the Si nanocrystal, rather than the nc-Si/SiO$_2$ interface, plays the dominant role in the charging effect. © 2006 American Institute of Physics. [DOI: 10.1063/1.2374929]

Si nanocrystals (nc-Si) embedded in SiO$_2$ films have potential applications in nonvolatile memory devices. For the nonvolatile memory application, the nc-Si is normally confined in a narrow layer in the gate dielectric near the substrate. Charging/discharging the nc-Si leads to the flat-band voltage shifts, yielding two distinguishable memory states. There have been many studies on the nc-Si nonvolatile memory devices. However, there are few experimental studies so far on the charging mechanism of the nc-Si/SiO$_2$ system. It is still in doubt whether the charging mainly occurs at the nc-Si/SiO$_2$ interface or inside the nc-Si. In this work, an x-ray photoelectron spectroscopy (XPS) experiment is carried out on the system of nc-Si embedded in SiO$_2$ thin films synthesized by Si ion implantation followed by thermal annealing. The C 1$s$ core level on the sample surface due to contamination is used to monitor the charging effect, while the Si $2p$ peaks are analyzed to obtain the information of the concentrations of the nc-Si (Si$^0$) and the Si suboxides (Si$^{1+}$, Si$^{2+}$, and Si$^{3+}$) that exist at the nc-Si/SiO$_2$ interface. By examining the changes of the charging effect and the concentrations of the nc-Si and the Si suboxides with thermal annealing, one may be able to answer the question whether the nc-Si or the nc-Si/SiO$_2$ interface plays a dominant role in the charging effect.

SiO$_2$ thin films of 30 nm in thickness were grown on $p$-type Si wafers with (100) orientation by thermal oxidation in dry oxygen at 950 °C. Then Si ions were implanted into the SiO$_2$ films with the dose of $8 \times 10^{16}$ cm$^{-2}$ at 1 keV. Thermal annealing was carried out in N$_2$ ambient. For the experiment of annealing temperature, the temperature was varied from 700 to 1100 °C but the annealing time was fixed at 20 min; for the experiment of annealing time, the time was varied from 0 to 100 min, while the annealing temperature was kept at 1000 °C. The XPS experiment was performed by using a Kratos Axis spectrometer with monochromatic Al $K\alpha$ (1486.71 eV) x-ray radiation. Si $2p$ spectra were taken to study the changes in the concentrations of five Si oxidation states. C 1$s$ spectra due to the surface carbon contamination were also rerecorded to monitor the x-ray-induced charging effect in the samples.

It has been known that x-ray irradiation can cause charging in both SiO$_2$/Si system and nc-Si/SiO$_2$ system. For the system of nc-Si embedded in a SiO$_2$ matrix, photoemission may leave positive charges in the nc-Si and SiO$_2$ as well as at the nc-Si/SiO$_2$ interface, leading to a core level shift to a higher binding energy. The C 1$s$ core level shift shown in Fig. 1 is an indicator of the charging effect. The C 1$s$ core level on pure SiO$_2$ surface has a shift of $\sim 0.8$ eV relative to the C 1$s$ reference, while it shows shifts of $\sim 2.1$ and $\sim 1.6$ eV for the as-implanted sample and the sample annealed at 1100 °C for 20 min, respectively. This indicates that the charging effect is greatly enhanced by the introduction of the nc-Si into the SiO$_2$ matrix. The reduction of the charging effect of the annealed sample is mainly attributed to the reduction of the nc-Si concentration due to the surface oxidation, as discussed later.

Figures 2(a) and 2(b) show the XPS Si $2p$ core level peaks for the as-implanted and the sample annealed at 1100 °C for 20 min, respectively. Five oxidation states Si$^{n+}$ ($n=0$–4) could exist in the Si-implanted SiO$_2$ films. Here Si$^0$ and Si$^{2+}$ correspond to the nc-Si and SiO$_2$, respectively, while Si$^{n+}$ ($n=1$–3) correspond to the Si suboxides.

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The sum of the Si 2p intensity ratio is set to 1 by decomposing the spectrum into the Si 2p core level peaks. A curve fitting to the Si 2p core level peaks is carried out by decomposing the spectrum into the Si 2p partner lines for the five oxidation states. The spin-orbit splitting is fixed at 0.6 eV, and the Si 2p 1/2 and 3/2 intensity ratio is set to 3/2 for all of the five oxidation states. Only the sum of the Si 2p 1/2 and 3/2 partner lines is shown in Fig. 2 for a clear presentation. As can be observed in Fig. 2, the peak areas of the five oxidation states change with annealing, showing that the concentrations of the five oxidation states vary with the annealing. The relative concentration of each oxidation state can be obtained by calculating the ratio of \(I_{Si^{n+}}/I_{total}(n=0\text{--}4)\), where \(I_{Si^{n+}}\) is the peak area of the oxidation state Si\(^{n+}\) and \(I_{total}\) is the total area (\(=\Sigma I_{Si^{n+}}\)) of the Si 2p peaks. It can be observed from Fig. 2 that after the annealing at 1100 °C for 20 min, the SiO\(_2\) (Si\(^{4+}\)) concentration increases, while the concentrations of both the Si suboxides (Si\(^{1+}\), Si\(^{2+}\), and Si\(^{3+}\)) at the interface and the nc-Si (Si\(^{0}\)) decrease. The reduction of the suboxides is due to the thermal decomposition of the suboxides. The thermal decomposition during the annealing is to form stoichiometric SiO\(_2\) and Si nanocrystals. In other words, the thermal decompositions lead to the growth of both SiO\(_2\) and the nc-Si. However, although the annealing was carried out in nitrogen gas with purity better than 99.99%, there is some residual oxygen presented in the furnace, and some of the nc-Si is oxidized during the annealing. Therefore, the Si\(^{0}\) concentration decreases, while the Si\(^{4+}\) concentration increases after the annealing.

Figures 3(a)–3(c) show the C 1s shift, the total concentration (\(2I_{Si}/I_{total}\)) of the interfacial suboxides, and the nc-Si concentration as a function of the annealing temperature, respectively. The annealing time is fixed at 20 min. The C 1s shift decreases with annealing temperature, showing that the charging effect is reduced by annealing. However, it should be noted that the reduction of the charging effect is not drastic. For example, the C 1s shift decreases from ~2.1 eV of the as-implanted sample to ~1.6 eV of the sample annealed at 1100 °C for 20 min. The shift of 1.6 eV is still much larger than that (0.8 eV) of the pure SiO\(_2\) sample, indicating that the system of nc-Si embedded in SiO\(_2\) maintains a good charge storage capability. The total concentration of the interfacial suboxides and the nc-Si concentration both decrease with annealing temperature, as shown in Figs. 3(b) and 3(c), respectively. The decrease of the total concentration of the interfacial suboxides is attributed to the thermal decomposition of the suboxides, and the decrease of the nc-Si concentration is due to the oxidation of the nanocrystal by the residual oxygen during the annealing, as pointed out earlier. From a comparison among the annealing-temperature effects on the C 1s shift [Fig. 3(a)], the total concentration of the interfacial suboxides [Fig. 3(b)], and the nc-Si concentration [Fig. 3(c)], one may conclude that the nc-Si plays a more important role in the charging effect than the nc-Si/SiO\(_2\) interface. For example, with a reference to the as-implanted sample, the annealing at 700 °C causes relative reductions (in percentage) of ~10% in the C 1s shift, ~25% in the nc-Si concentration, and ~55% in the total concentration of the interfacial suboxides. The reduction of the total concentration of the interfacial suboxides is much faster than that of both the C 1s shift and the nc-Si concentration, suggesting that the interface would not play a dominant role in the charging effect.

The conclusion that the nc-Si plays a more important role in the charging effect than the nc-Si/SiO\(_2\) interface is further supported by the experiment of annealing time, as shown in Fig. 4. The experiment was carried out at a fixed temperature of 1000 °C. As shown in Fig. 4(a), the total concentration of the interfacial suboxides decreases with increasing the annealing time.
concentration of the interfacial suboxides is drastically reduced from $\sim60\%$ for the as-implanted sample to $\sim10\%$ after the annealing for 20 min and remains unchanged for prolonged annealing. However, as shown in Fig. 4(b), the C 1$s$ shift is gently reduced from $\sim2.1$ eV for the as-implanted sample to $\sim1.6$ eV after the annealing for 20 min and remains at $\sim1.8$ eV for prolonged annealing. Most importantly, the trend of the C 1$s$ shift with annealing time coincides with that of the nc-Si concentration with annealing time, as shown in Fig. 4(b). This strongly suggests that the nc-Si plays a key role in the charging effect.

In summary, the experiments of annealing effects on the C 1$s$ shift, the total concentration of the interfacial suboxides, and the nc-Si concentration have been carried out. It is observed that the annealing-caused reduction of the total concentration of the interfacial suboxides is much faster than that of both the C 1$s$ shift and the nc-Si concentration. In addition, the trend of the C 1$s$ shift with annealing time coincides with that of the nc-Si concentration with annealing time. The results suggest that the nc-Si rather than the nc-Si/SiO$_2$ interface plays the dominant role in the charging effect in the system of nc-Si embedded in SiO$_2$.

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