Charge Storage Mechanism of Si Nanocrystals Embedded SiO₂ Films

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SiO₂/siO₂ₓ/siO₂ₓ₅ sandwich structure was synthesized by reactive magnetron sputtering to achieve various densities of Si nanocrystals and different concentration of Si suboxides. X-ray photoelectron spectroscopy is employed for depth profiling of the chemical structure and charging effect of the sandwich structure. The Si 2p core-levels are found to strongly shift to higher binding energy. The shift can be ascribed to the photoemission-induced charging effect. The opposite trend of the charging effect to the concentration of Si suboxides (Si₂O, SiO and Si₂O₃) indicates that the defects are not responsible for the charge mechanism. The Si nanocrystals concentration dependent charging effect suggests that the nc-Si plays a dominant role for the charge trapping in such films.

Keywords: Si Nanocrystals, Si Suboxides, Charging Effect, X-ray Photoelectron Spectroscopy.

SiO₂ films embedded with Si nanocrystals (nc-Si) have attracted an increasing attention over the past decades due to potential applications in non-volatile flash memory, where fast write/erase speed, long retention time and superior endurance with non-destructive read have been demonstrated.¹,² To date, understanding of the charge trapping and retention mechanism in such nanostructures is still unclear. Several models for long-time charge trapping mechanisms have been proposed, including the quantum size effect of nc-Si and various oxygen-related defects. The observation of quantum confinement energy in nc-Si from high-frequency conductance characteristics³ and the Coulomb blockade charging in the conductance–voltage measurements suggest that the charges are stored in the nc-Si.⁴—⁶ Shi et al.⁷ had compared the electrical behaviors of the MOS diodes annealed in H₂ ambient (low defects condition due to the H₂ passivation) with that of MOS diodes annealed in vacuum (high defects condition). Their investigation demonstrated that the defects play an important role for the charge storage. It is still in debate whether the charges trap mainly in the defects or in the nc-Si.

In this study, X-ray photoelectron spectroscopy (XPS) technique is employed to characterize the chemical structure and binding energy shift of the nc-Si/a-SiO₂ system. It has been reported that the X-ray radiation will leave positive charges in the nc-Si/a-SiO₂ system due to photoemission.⁸—⁹ The charging effect can cause the core-level to shift to a higher binding energy.¹⁰—¹¹ In this paper, SiO₂/siO₂ₓ/siO₂ₓ₅ sandwich structure was synthesized by reactive magnetron sputtering to deliberately achieve various concentrations of nc-Si and Si suboxides (potentially contain high density of oxygen-related defects). XPS depth profiling was carried out on the sandwich structure. By examining the changes of charging effect versus the depth distributions of nc-Si and Si suboxides, the nc-Si was found responsible for the charge trapping mechanism rather than the defects in the oxides.

The SiO₂/siO₂ₓ/siO₂ₓ₅ sandwich structure was synthesized by reactive magnetron sputtering system (E303A, Penta Vacuum) from a 4-inch Si target (99.999% in purity) in a mixed Ar/O₂ atmosphere on P-type (100) Si wafer. The concentration of Si in each SiOₓ (0 < x < 2) sub-layer was controlled by the ratio of the Ar/O₂ flow rate. The base pressure of the deposition chamber was 1.0 × 10⁻⁵ Pa. During deposition, the radio frequency (13.6 MHz) target power was fixed at 150 W. The process pressure and the Ar flow rate were fixed at 0.5 Pa and 80 sccm, respectively. First, the oxygen flow rate was set at 1.5 sccm to deposit the 10 nm relatively low Si concentration bottom layer. Immediately after that, the shutter (between the substrate and the target) was closed and the oxygen flow rate was changed to 0.5 sccm. A waiting time of 10 minutes was respected to achieve the desired stable Ar/O₂ ambient before sputtering the 10 nm high Si concentration
middle layer. Finally, the shutter was closed again and the oxygen flow rate was changed back to 1.5 sccm. The 10 nm low Si concentration top layer was deposited after another waiting time of 10 minutes. A pure a-SiO$_2$ control sample was also deposited by setting the oxygen flow rate at 3.0 sccm. Thermal annealing was carried out in N$_2$ ambient at 1100 °C for 30 minutes. XPS analysis was performed by using a Kratos-Axis spectrometer with monochromatic Al Kα (1486.71 eV) X-ray radiation. The core-level spectra were recorded using pass energy of 40 eV at a normal emission angle. The depth profiling was realized by Ar ion sputtering, which was carried out in situ with the XPS measurement. The formation of nc-Si was confirmed using transition electron microscopy (TEM, JEM2010).

Figure 1 shows the cross-sectional TEM micrograph of the sandwich structure. Nearly spherical-shaped nc-Si in the amorphous matrix of SiO$_2$ are clearly visible in the HRTEM micrograph. There are densely stacked nc-Si in the high Si middle layer and isolated nc-Si in the low Si top and bottom layer. The nc-Si size ranged from 3 to 5 nm resulting in a mean crystal size of 4 nm in diameter.

It has been well known that X-ray irradiation can cause charging on the nc-Si/a-SiO$_2$ system. The photoemission during the XPS measurement will leave positive charges in the SiO$_2$ films embedded with nc-Si, leading to a core-level shift to a higher binding energy. The C 1s core-level shift coincides with that of Si$^{4+}$. Figure 2 show the contaminated C 1s core-level spectra from the surface of the sandwich structure which was embedded with nc-Si and the pure SiO$_2$ control sample, respectively. The charging effect induced by the photoemission can be clearly observed by the C 1s core-level shift. The C 1s core-level of the pure SiO$_2$ control sample has a shift of $\sim$0.6 eV relative to the reference (284.5 eV), while the C 1s peak of the sandwich structure that contains nc-Si shows a shift of $\sim$1.8 eV. The C 1s core-level shift coincides with that of Si$^{4+}$ 2p shown in Figure 3. The Si$^{4+}$ 2p core-levels also shift to higher binding energy by 0.6 eV and 1.8 eV for the pure SiO$_2$ sample and the sandwich structure, respectively. Since Si$^{4+}$ is the host material in the nc-Si/SiO$_2$ system under study, therefore, the Si$^{4+}$ shift is used for monitoring the charging effect in the system during depth profiling. The introduction of the nc-Si into the SiO$_2$ can shift the core-level to higher binding energy by 1.2 eV, which indicates that the charging capability of the nc-Si embedded SiO$_2$ films is greatly enhanced comparing with that of the pure SiO$_2$. However, it is reported that for the nc-Si embedded SiO$_2$ system, the charges can be trapped either inside the nc-Si or the defects in the oxides. As at the same time that the nc-Si is introduced into the SiO$_2$, a large amount of Si suboxides (Si$_2$O, SiO, Si$_2$O$_3$) which potential contain high density of oxygen related-defects were also produced. These defects were reported to be the...
weak oxygen bond (O–O),\textsuperscript{13} the neutral oxygen vacancy (O\(_{\equiv}\text{Si–Si} \equiv \text{O})\textsubscript{3}, where \(\equiv\) represents the bonds to three oxygen atoms).\textsuperscript{13} \(E_g\) center (O\(_{\equiv}\text{Si} \equiv \text{Si} \equiv \text{Si})\textsubscript{4}, where \(\equiv\) represents an unpaired electron and + is an trapped hole)\textsuperscript{14} and the non-bridging oxygen hole center (\(=\text{Si–O}\equiv\)).\textsuperscript{15} By depth profiling of the SiO\(_{3/2}\)/SiO\(_{2}\)/SiO\(_{1.5}\) sandwich structure, we are able to obtain the distribution of the nc-Si and Si suboxides. By monitoring the changes of the charging effects versus the concentration of nc-Si and Si suboxides, one may be able figure out the charge trapping mechanisms of the nc-Si embedded SiO\(_2\) systems.

Note should be taken that our Si-rich oxide films were synthesized by reaction of the sputtered Si atoms with oxygen. It was therefore quite possible that the oxidation proceeded with zero, one, two, three, or all four Si–Si bonds being replaced by Si–O bonds. We thus expect five oxidation states Si\(^{n+}\) (\(n = 0, 1, 2, 3\) and 4) corresponding to the five chemical structures including Si, Si\(_2\)O, SiO, Si\(_2\)O\(_3\) and SiO\(_2\), respectively, exist in the magnetron sputtered films. With the possible existence of the five oxidation states in mind, deconvolution of the XPS curves was carried out by decomposing the spectrum into five Gaussian peaks following the reported fitting procedures.\textsuperscript{16} The deconvolution of XPS curve was conducted by decomposing the Si 2p line into Si 2p\(_{1/2}\) and Si 2p\(_{3/2}\) lines with intensity ratio 1:2 and a fixed spin-orbit splitting of 0.6 eV as an atomic property. Only the sum of the Si 2p\(_{1/2}\) and 2p\(_{3/2}\) partner lines is shown for a clear presentation. The full width at half maximum (2\(\Gamma\)) was assumed to be the same for both lines, but allowed to vary from Si\(^0\) to Si\(^{3+}\), and the relative weight \(W\) was allowed to vary without constraint. The deconvolution of the Si 2p spectra at different depths is shown in Figure 4. Figures 4(a)–(d) show the Si 2p core-levels at the depths of 2 nm, 8 nm, 12 nm and 22 nm, respectively. The total Si concentration is calculated to be \(~\leq 40\text{ at.}\%\) in both the low Si top and bottom layer, and increase to \(~\leq 76\text{ at.}\%\) in the high Si middle layer. The Si 2p spectrum shown in Figure 4(b) (at the depth of 8 nm) is speculated to be obtained at the interface between the top layer and the middle layer.

As can be observed from Figure 4, not only the total Si concentration changes with the depth, but the peak areas of the five oxidation states also change, showing that the concentrations of the five oxidation states vary with the depth. The depth distribution of the relative concentration of each oxidation state can be obtained by calculating the ratio of \(I_{\text{Si}^{n+}}/I_{\text{total}}\) (\(n = 0, 1, 2, 3\) and 4) at various depths, where \(I_{\text{Si}^{n+}}\) is the peak area of the oxidation state Si\(^{n+}\) and \(I_{\text{total}}\) is the total area of the Si 2p peaks. The sum of the relative concentrations of Si suboxides (Si\(_2\)O, SiO and SiO\(_2\)) and nc-Si (Si\(^0\)) versus the depth are shown in Figure 5. From the depth distribution of the Si suboxides and the nc-Si, one can observe that different concentrations of nc-Si and Si suboxides along depth have been achieved in our SiO\(_{3/2}\)/SiO\(_{2}\)/SiO\(_{1.5}\) sandwich structure. The majority Si atoms in the low Si top and bottom layer have been oxidized into SiO\(_2\), leaving only small amount of Si suboxides and low density of nc-Si, while there are high concentration of Si suboxides and high density of nc-Si in the high Si middle layer. For example, the concentrations of the nc-Si are \(~\leq 9\text{ at.}\%\) in the low Si top and bottom layer, \(~\leq 51\text{ at.}\%\) in the high Si middle layer,

![Fig. 4. Si 2p core-level spectra obtained at the depth of 2 nm (a), at the depth of 8 nm (b), at the depth of 12 nm (c) and at the depth of 22 nm (d).](image-url)
Fig. 5. Binding energy shifts of Si\(^{4+}\) and Si\(^0\) species relative to the references at various depths. The squares and circles represent the Si\(^{4+}\) shift and Si\(^0\) shift, respectively. The depth profiling of the Si suboxides and nc-Si concentrations is included for comparison, the triangles and stars represent the nc-Si concentration and Si suboxides concentration, respectively.

and the concentrations of the Si suboxides are ~16 at.% in the top and bottom layer, ~36 at.% in the middle layer.

Besides the concentrations of the five oxidation states, the binding energy of each oxidation state can also be obtained from the peak deconvolution. The core-level shift of Si\(^{4+}\) relative to the Ref. [11] (Si 2p in pure SiO\(_2\)) as a function of the depth is shown in Figure 5. To clarify the charging mechanism in the system, the binding energy shift of nc-Si (Si\(^{4+}\)) relative to reference (bulk Si) is also included in Figure 5. For the binding energy shift of the nc-Si, besides the charging effect, the quantum confinement effect of charges in the nc-Si can also shift its core-level to higher binding energy as discussed later. The binding energy shifts of both Si\(^{4+}\) and nc-Si demonstrate the same trend in Figure 5. The Si\(^{4+}\) and the nc-Si shifts are ~1.9 eV and ~1.3 eV, respectively, in the low Si top layer, but both decrease to almost zero in the high Si middle layer, and then increase again in the low Si bottom layer, returning to almost the same level as in the top layer. However, an increase in the concentrations of the Si suboxides in the middle layer can be observed in Figure 5. One may expect that there should be also an increase in the binding energy shift in the middle layer if the charges are trapped in the Si suboxides. The opposite trend of the binding energy shift with depth distribution of Si suboxides enables us to exclude the defects-related trapping mechanism in our films. Therefore it is speculated that the enhanced charging capability of our films is due to the formation of nc-Si.

But, one also should note that there is also no always consistent between the binding energy shift and the nc-Si concentration. A nc-Si concentration depended binding energy shift has been observed in Figure 5. As can be observed, there is strong charging effect in the low Si top and bottom layers which contain low density of nc-Si.

While both the Si\(^{4+}\) and Si\(^0\) shift decrease with increasing nc-Si concentration, and almost vanished when a densely stacked nc-Si layers are formed in the high Si middle layer. It is suggested that the charging effect is reduced with increasing nc-Si concentration. The effect of the nc-Si distribution on the charging effect can be explained in terms of the charges diffusion as illustrated in Figure 6. Charging diffusion can take place due to the charge transfer from the charged nc-Si to the adjacent uncharged nc-Si by tunneling or other transport mechanisms. In the high Si middle layer densely stacked nc-Si layers may be formed. The charge induced by the photoemission can easily diffuse out to the nc-Si that are not under the X-ray illumination, and thus the charge can be dissipated quickly, leading to a drastic reduction in the charging effect in this region.

Assuming the photoemission-induced charges are trapped in the nc-Si. This charging effect will shift the Si 2p core-levels of all Si species to higher binding energy by the same amount. However, for the nc-Si, charge trapping in the quantum dot will cause a self charging energy (because of quantum confinement effect) which lead to an extra shift of the Si\(^{4+}\) core-level to higher binding energy besides the charging effect. It is well known that the charging of quantum dot with one elementary charge will cause a self charging energy \(E_c = e^2/2C_{dot}\) where \(e\) is the elementary charge of 1.6 × 10\(^{-19}\) coulomb, and \(C_{dot}\) is the self-capacitance of the nc-Si. This self-charging energy will shift the Si\(^{4+}\) core-level to higher binding energy by \(E_c\). The self-charging energy is calculated to be 0.12 eV for a 3 nm nc-Si, and decreases to 0.08 eV for a 5 nm nc-Si.

As the photoemission-induced charging effect and the self-charging energy (because of quantum confinement effect) of the nc-Si both could shift the Si\(^{4+}\) core-level to a higher binding energy independently, the Si\(^{4+}\) shift would be larger than that of Si\(^{4+}\). That is why the nc-Si shift is slightly larger than that of Si\(^{4+}\) in the high Si middle layer. This phenomenon also confirms our assumption that the charge trapping in the nc-Si is dominant in our film. For these
nc-Si distributed in the low Si top and bottom layer, they are separated from each other with a larger spacing due to the low concentration, thus the charge diffusion is much more difficult to take place. Therefore, the charging effect is much more significant in these two regions.

As discussed above, for Si\(^0\), besides the charging effect, the quantum size effect of nc-Si will increase the Si\(^0\) shift, one may also expected a higher binding energy shift of Si\(^0\) than that of Si\(^{4+}\) in the low Si top and bottom layer. However, quite contrarily, a smaller binding energy shift of Si\(^{4}\) than that of Si\(^{4+}\) is always observed in these two regions as shown in Figure 5. This can be interpreted by the differential charging (electrostatic charging) effect between the nc-Si and the oxide matrix.\(^6,11\) Differential charging always occur when the sample is partially (semi)conducting and partially insulating under X-ray radiation. This differential charging usually lead to the variation in Si\(^{4+}\)–Si\(^0\) shift with different Si concentration.\(^6,9,11\)

Note that the kinetic energy of the photoelectrons under X-ray radiation can be simply written as:

\[
E_K = h\nu - E_B - \phi_S - q\phi
\]

where \(h\nu\) is the X-ray energy, \(E_B\) is the binding energy, \(\phi_S\) is the work function of the electron spectrometer, \(q\) is the electronic charge, and \(\phi\) is the surface potential. Since the experiments were performed using the same spectrometer, this effect of the spectrometer work function (\(\phi_S\)) on the Si\(^{4+}\)–Si\(^0\) shift should be negligible. Therefore, it can only be differences in the material surface potential that can contribute to Si\(^{4+}\)–Si\(^0\) shift. When characterizing nc-Si/SiO\(_2\) system, one usually assumes that the surface potential is the same for Si\(^0\) and Si\(^{4+}\). However, the differential charging lead to the surface potential differences between Si\(^0\) and Si\(^{4}\), thus the Si\(^{4+}\)–Si\(^0\) shift in the nc-Si/SiO\(_2\) system not only determined by the their chemical shift, but also their surface potential differences.

The positive charges lead to the reduction in Si\(^{4+}\) surface potential, while the increase in Si\(^{4+}\) surface potential, equivalent to a reduction in Si\(^0\) binding energy and an increase in Si\(^{4+}\) binding energy. The Si\(^{4+}\)–Si\(^0\) shift may vary from 3.5–5.0 eV, depending on the nc-Si concentration in the films.\(^8,9,11\) The Si\(^{4+}\)–Si\(^0\) shift decrease with increase nc-Si concentration, and will be the same as that of bulk reference samples when densely stacked nc-Si are formed. The changes of Si\(^{4+}\)–Si\(^0\) shift with nc-Si concentration can be employed to employ why there is no always consistency between the binding energy shift of Si\(^0\) and Si\(^{4+}\) along the depth. Figure 7 shows the Si\(^{4+}\)–Si\(^0\) chemical shift versus depth of the sandwich structure, and the depth distribution of nc-Si also included for comparison. The Si\(^{4+}\)–Si\(^0\) shift is \(-\sim -4.4\) eV in the low Si top and bottom layer which contain low density of nc-Si. However, densely stacked nc-Si are formed in the high Si middle layer, and the Si\(^{4+}\)–Si\(^0\) shift is almost the same as the bulk references. The charging effect cause almost the same core-level shift of both Si\(^0\) and Si\(^{4+}\), while the quantum size effect of nc-Si lead to the core-level shift slightly larger than that of Si\(^{4+}\).

In conclusion, various concentrations of Si suboxides and Si nanocrystals (nc-Si) have been realized by sputtering deposition of SiO\(_1\)/SiO\(_2\)/SiO\(_3\) sandwich structure. The X-ray radiation shifts the Si 2p core levels to higher binding energy due to the photoemission-induced charging effect. The opposite trend of the binding energy shift to the depth distribution of Si suboxides concentrations suggests that the oxygen-related defects are not responsible for charge trapping in the nc-Si/SiO\(_2\) system. The nc-Si concentration dependent charging effect and the quantum charging effect were observed, which demonstrates that the nc-Si plays a dominant role in the charge trapping mechanism in the nc-Si/a-SiO\(_2\) system. The decreasing in binding energy shift with the increasing nc-Si concentration is due to the charging diffusion.

References and Notes


Received: 26 August 2009. Accepted: 23 September 2009.