Sol-gel-derived double-layered nanocrystal memory
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Novel coexisted sol-gel derived poly-Si-oxide-nitride-oxide-silicon type memory

Droplet evaporation-induced ferritin self-assembled monolayer as a template for nanocrystal flash memory
Conventional flash memory devices possess a floating gate structure in which the charge carrier is stored in a poly-silicon film. Because the storage charge leaks readily when the tunneling oxide layer is thinner than 85 nm, floating gate structures face severe scaling issues resulting from defects in the tunneling oxide. A discrete single-layered nanocrystal (NC) memory was proposed recently as a replacement of the single poly-Si film of a floating gate structure. NC memories can preserve the trapped charge efficiently—i.e., they avoid the problems associated with the charge loss of conventional flash memories—while also displaying desirable features such as fast program/erase speeds, low programing potentials, and high endurance.

Many methods have been developed recently for the preparation of a range of NC memories using physical vapor deposition, chemical vapor deposition (CVD), and ion beam synthesis. Wang et al. formed Ge NCs through the cosputtering of Ge, Al2O3, and HfO2. Yeh et al. deposited a nickel layer through electron beam evaporation; prior to forming NiSi2 NCs through annealing at 900 °C, an amorphous Si film was deposited. Liu et al. self-assembled SiGe NCs from a mixture of GeH4 and Si2H6 gases in a room-temperature CVD system. Muller et al. implanted Si ions into an SiO2 layer to form Si NCs.

In addition to these versatile deposition methods for forming NCs, an alternative single-layer NC preparation technique—using a sol-gel spin-coating method—was published recently. During NC formation through spin coating, the sol-gel system of interest was blended in the solution. The most valuable feature of using this sol-gel method is that the precursors and equipment are relatively cheap. We became interested in investigating whether double-layered NCs would perform better than single-layered NC memories.

In this study, we used a sol-gel spin-coating method to fabricate a double-layered NC memory. HfCl4 (99.5%, Aldrich), ZrCl4 (99.5%, Aldrich), and SiCl4 (99.5%, Aldrich) precursors were dissolved in isopropanol (IPA) (Fluka; water content: <0.1%) to prepare a mother solution in which the HfCl4:ZrCl4:SiCl4 molar ratio was 1:1:1. We combined HfCl4, ZrCl4, and SiCl4 to fabricate coexisting hafnium silicate (HfSiOx) and zirconium silicate (ZrSiOx) NC memories.

Figure 1(a) illustrates the fabrication of the sol-gel spin-coating NC memories, beginning with a local oxidation of silicon isolation process on a p-type (100) 150 nm silicon

![Figure 1. (a) Device structure of the double-layered NC memory. (b) TEM image of hafnium silicate and zirconium silicate NCs.](image-url)
substrate. A 4-nm-thick tunneling oxide was grown thermally in a furnace at 925 °C. The charge trapping layer was deposited through spin coating at 3000 rpm for 60 s at ambient temperature using a TEL Clean Track Model-MK8 apparatus (Japan). After spin coating, the wafer was subjected to rapid thermal annealing at 900 °C for 60 s in an O₂ ambient to form the coexisting HfSiₓOᵧ and ZrSiₘOₙ NC memory. A 30-nm-thick blocking oxide was deposited through low-pressure chemical vapor deposition tetraethyloorthosilicate (LPCVD TEOS), followed by deposition of a 200-nm-thick poly-Si gate. After the LPCVD TEOS deposition, the TEOS oxide was densified in a N₂ ambient by annealing at 900 °C for 30 s. Finally, gate patterning, source/drain implanting, and the remaining steps of the complementary metal-oxide semiconductor processes were performed to fabricate the double-layered NC memory.

The high-resolution transmission electron microscopy image in Fig. 1b clearly depicts the transformation of sol-gel film into NCs after annealing at 900 °C for 60 s; we observe two differently colored NCs in this image. We used x-ray photoelectron spectroscopy (XPS) to characterize the nature of the chemical bonding in the NCs. Figure 2 provides a comparison of the XPS results for (a) Hf 4f and (b) Zr 3d bonding in the as-deposited (as-dep) and 900 °C-annealed samples. The Hf 4f peaks for the hafnia film (as-dep) appeared at 17.4 and 19 eV, while the Zr 3d peaks for the zirconia film (as-dep) appeared at 181.9 and 184.3 eV. Interestingly, these peaks for both Hf 4f and Zr 3d shifted toward higher bonding energies after annealing to form the NCs. This observation suggests that the oxygen atoms of Hf–O and Zr–O bonds reacted with their nearby Si atoms, forming hafnium silicate and zirconium silicate. The darker NCs in Fig. 1b are those of high-molecular-weight hafnium silicate; the bright NCs are formed from low-molecular-weight zirconium silicate.

NC memories use channel hot electron injection (CHEI) for charging and band-to-band tunneling-induced hot hole injection (BTBHHI) for discharging. The charge and discharge speeds are closely related to the trapping probability of the NCs. Briefly, the electron carrier in Fig. 3a can be trapped in the HfSiₓOᵧ NCs (e.g., see Ref. 252111-2 Ko, You, and Lei Appl. Phys. Lett. 89, 252111 (2006))
during the charging period. As the hole carrier is injected into the NCs, the trapping capability can influence the discharging speed. In other words, the double-layered NCs in this study may offer a higher trapping probability for the charge carrier than do the single-layered NCs. Figure 3 illustrates the trapping model through which the double-layered NCs improve the hole/electron trapping probability.

Figure 4(a) displays the charging speeds of both a single-layered memory and the double-layered NC memory. We used CHEI to program (charge) the system under conditions of $V_g$ and $V_d$ both being 10 V. Obviously, the double-layered NC memory exhibited a larger value of $V_{th}(t) - V_{th}(t = 10^{-6} \text{ s})$ shift” than did the single-layered NC memory. For example, the values of $V_{th}(t) - V_{th}(t = 10^{-6} \text{ s})$ shift at 1 ms were 0.68 and 1.14 V for the single- and double-layered NC memories, respectively; i.e., the value of $V_{th}(t) - V_{th}(t = 10^{-6} \text{ s})$ shift was improved by 68%, presumably because of the better charge carrier trapping probability of the latter system. We are unaware of any other report describing the performance for double-layered NC memories.

Figure 4(b) displays the discharging speeds of the single- and double-layered NC memories. We used BTBHHI to erase (discharge) the system under conditions where is $V_g$ and $V_d$ were −12 and +10 V, respectively. Again, the double-layered NC memory exhibited a significant value of $V_{th}(t) - V_{th}(t = 10^{-6} \text{ s})$ shift relative to that of the single-layered NC memory; we also attribute this phenomenon to the higher trapping probability of the double-layered NCs.

In summary, we have used a sol-gel spin-coating method to fabricate a double-layered NC memory. From transmission electron microscopy (TEM) and XPS analyses, we confirmed that the NCs consisted of hafnium silicate and zirconium silicate. The double-layered NCs in this study provided a higher trapping probability for charge carriers than did the corresponding single-layered NC devices.

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