Nanocrystallization and interfacial tension of sol-gel derived memory

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Nanocrystallization and interfacial tension of sol-gel derived memory

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The formation of the nanocrystals (NCs) by using the sol-gel spin-coating method at various annealing temperatures had been studied. The film started to form the islands at 600 °C annealing, and finally transferred into NCs at 900 °C. A model was proposed to explain the transformation of thin film. The morphology of sol-gel thin film at 600 °C annealing was varied and had higher interfacial energy. The crystallized process at 900 °C annealing could minimize the energy. The retention for 900 °C annealed sample exhibited less than 30% charge loss after 10^6 s at 125 °C measurement. © *2008 American Institute of Physics*. [DOI: 10.1063/1.2904626]

The conventional floating gate (FG) nonvolatile memory[1,2] (NVM) suffers from a charge loss problem as the feature size of the device continues to shrink.[3] A discrete nanocrystal (NC) memory was then proposed as a replacement of the conventional FG memory.[4] The NC memory is expected efficiently to preserve the trapped charge due to the discrete charge storage node, while also demonstrate excellent features such as fast program/erase speeds, low programing potentials, and high endurance.[5–8] We have proposed a sol-gel spin-coating method[9,10] to fabricate the charge trapping film or NC for the memory, and this approach is relatively cheap, simple, and can be fabricated in a normal atmospheric pressure instead of high-vacuum system.

The crystallization of transferring the charge trapping thin film into the NC phase during thermal annealing is dependent on the sol-gel composition, preparation solvent, and annealing temperature. The formation of coexisting hafnium silicate and zirconium silicate NC memory has been previously published.[10] In general, the NC formation is related to the solid phase segregation induced seeding effect.[11] However, the effect of annealing temperature that controls the formation of NC, degree of crystallization, interfacial energy, and charge retention in the sol-gel derived memory is still unclear.

Prior to various annealing treatments, the sol-gel thin film was deposited by the spin-coating method from the precursors of zirconium tetrachloride, hafnium tetrachloride, and silicon tetrachloride. The above precursor was dissolved in ethanol, and a suitable amount of hydrochloric acid serving as the catalyst for hydrolysis and condensation was added into the solution. The molar ratio for $ZrCl_4$, $HfCl_4$, $SiCl_4$, and ethanol in the sol-gel solution was 1:1:1:1000. After preparation, the solution was stirred for 0.5 h and then spin coated onto the Si substrate by using a Tokyo Electron Limited (TEL) system (Clean Track Model-MK8). After thin film deposition, these samples were subjected to rapid thermal annealing (RTA) treatment at various temperatures for 60 s under an O_2 ambient to form the NCs.

The fabrication of sol-gel spin-coating NC memory was started with local oxidation of Si process on a *p*-type (100) silicon substrate. A 10 nm tunneling oxide film was thermally grown at 925 °C in a furnace. The sol-gel film was then formed through spin coating and RTA process mentioned above. The 20 nm blocking oxide was deposited by plasma enhanced chemical-vapor deposition tetraethylorthosilicate, followed by a 200-nm-thick poly-Si gate was deposited. Finally, gate pattering, source/drain (S/D) implanting, and the rest of the subsequent metal-oxide-semiconductor processes were used to fabricate the NC-NVM devices.

The cross-sectional high resolution transmission electron microscope (TEM) images of the sol-gel derived thin films that annealed at 400, 600, and 900 °C are illustrated in Fig. 1. The sample in Fig. 1(a) after 400 °C RTA exhibits a continuous and smooth film. This observation suggests the annealing at 400 °C has no effect on the film's morphology. As to the sample annealed at 600 °C, Fig. 1(b) reveals the morphology of thin film is discontinuous and uneven. The sol-gel film is gradually transferred into islands (in inset). If the annealing temperature is elevated to 900 °C, the film illustrated in Fig. 1(c) is complete transferred into NCs. The crystal size is estimated to be 6–10 nm. Literature has proposed the spinodal decomposition effect[12] to explain the annealing effect for formation of zirconium silicate. We infer that the darker NCs in Fig. 1(c) are formed from the high-molecular-weight hafnium silicate, and the bright NCs are from the low-molecular-weight zirconium silicate.[10]

The nature of the chemical bonding for the transformation of thin film into NC was characterized by using x-ray photoelectron spectroscopy (XPS) analysis. Figure 2 provides a comparison of the XPS results for (a) Si 2*p*, (b) Zr 3*d*, (c) Hf 4*f*, and (d) O 1*s* bonding for samples annealed at different temperatures. Figure 2(a) shows the increasing of binding energy of Si 2*p* from 100.40 eV (400 °C RTA) to 100.95 eV (900 °C RTA) with annealing temperature. This observation relates to the oxidization of the Si atom toward blueshift. Both binding energies of Zr 3*d* and Hf 4*f* shown in Figs. 3(b) and 3(c) exhibit the shifting to the higher energies upon increasing the annealing temperature. This observation suggests that the oxygen atoms of Zr–O and Hf–O bonds reacted with their nearby Si atoms, forming hafnium and zirconium silicate.[13] As to the O 1*s* spectra in Fig. 3(d), each peak can be deconvoluted into two peaks, i.e., the higher and

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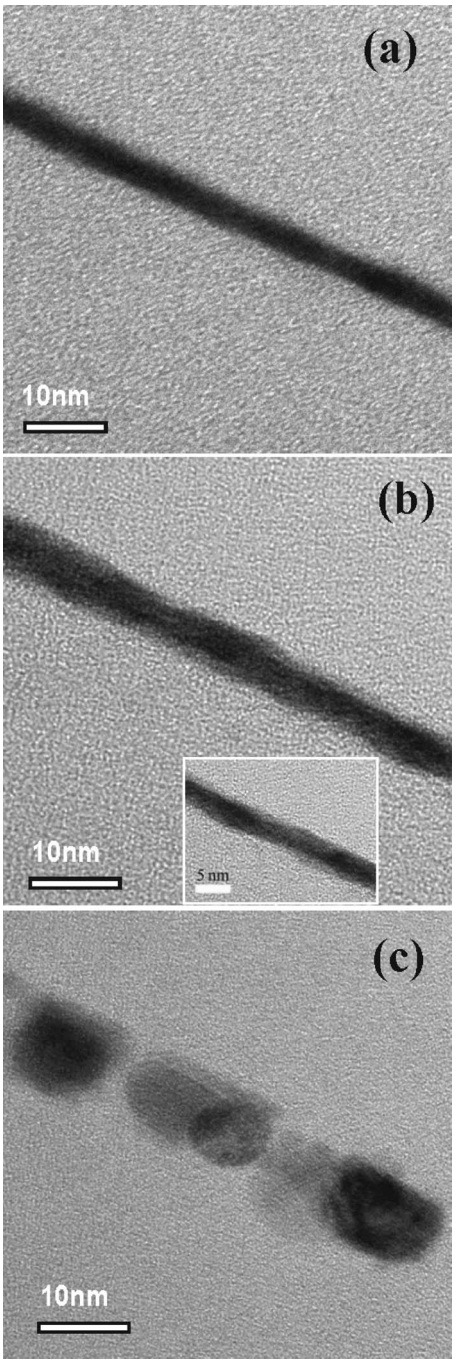

FIG. 1. Cross-sectional TEM micrographs of the thin film transformation after (a) 400 °C, (b) 600 °C, and (c) 900 °C annealing.

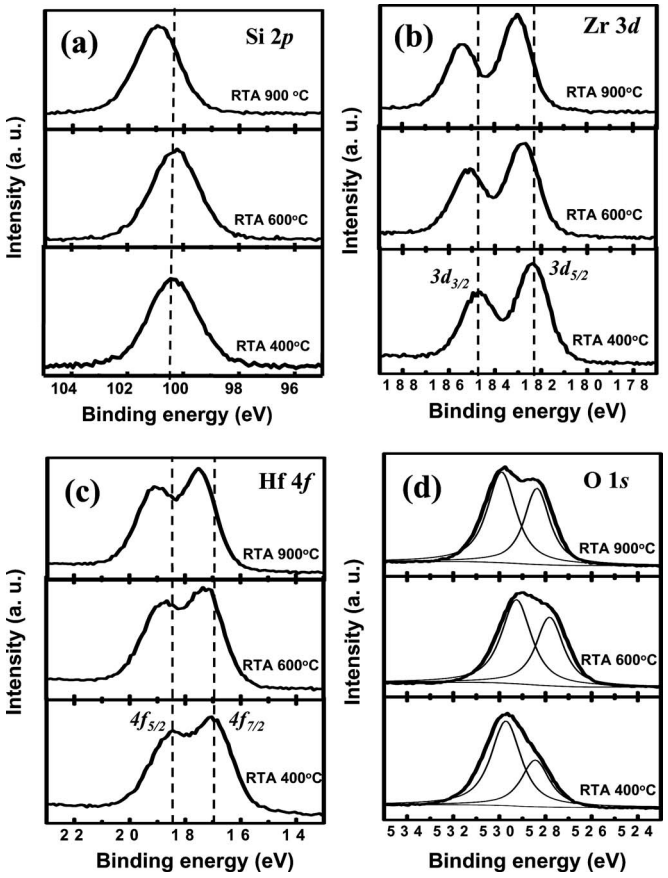

FIG. 2. (a) Si 2*p*, (b) Zr 3*d*, (c) Hf 4*f*, and (d) O 1*s* XPS spectra of the sol-gel thin films after different annealing temperatures.

lower energy peaks, which are respectively attributed to the SiO_2 and metal-rich silicate.[14] If the annealing temperature is increased, the intensity ratio of lower energy peak to higher energy peak is increased. This result indicates the hafnium and zirconium silicates were toward the bonding of metal-rich silicate. This finding is also consistent with the observation of Hf 4*f* and Zr 3*d* spectra.

Figure 3(a) shows the interfacial tension (interfacial energy per unit area) of the hafnium and zirconium silicates as a function of annealing temperature.[15] As Fig. 3(a) depicted, the interfacial energy abruptly increases from 400 to 600 °C RTA, and then slightly decreases from 600 to 1050 °C. As Fig. 1(a) mentioned, the surface at 400 °C RTA is still smooth and possesses the lowest energy. The surface morphology of 600 °C RTA sample is rough in Fig. 1(b), implying that the surface is unstable and in higher energy state. At 900 °C RTA, the interfacial energy is decreased in comparison with 600 °C RTA due to the formation of NC. We proposed a model in Fig. 3(b) to describe the observed transformation phenomenon on the sol-gel film. The sol-gel film is continuous and smooth as deposited and retains the same morphology at 400 °C annealing. It becomes unstable at 600 °C annealing, and phase change is then observed in order to reduce the surface energy. Upon 900 °C annealing, the sol-gel film reaches a stable state due to the formation of NCs.

The sol-gel derived NC was used as the charge trapping purpose in the NVM device. Figures 4(a) and 4(b) illustrate the retention characteristics for the devices annealed at 600 and 900 °C, respectively. For both samples at 25 °C measurement, the retention times can be extrapolated up to 10^6 s for only ~5% charge loss, while ~10% charge loss at 85 °C measurement. As the measuring temperature increased to 125 °C, a significant charge storage at 10^4 sec is observed for the 600 °C annealed sample, while the 900 °C annealed sample still retain its good characteristic for <20% charge loss. This result explains the importance of NC formation for the NVM. The NC discretely disperses in the charge trapping layer, which alleviates the charge loss problem when defects exist in the thin tunneling oxide. The inset of Fig. 4(b) shows the I_d-V_g characteristic for the 900 °C annealed sample. We use channel hot electron injection to program and band to band tunneling induced hot hole injection to erase. The V_{th} shift after programing can be up to 9 V, which is much better than our previous reports.[9,10]

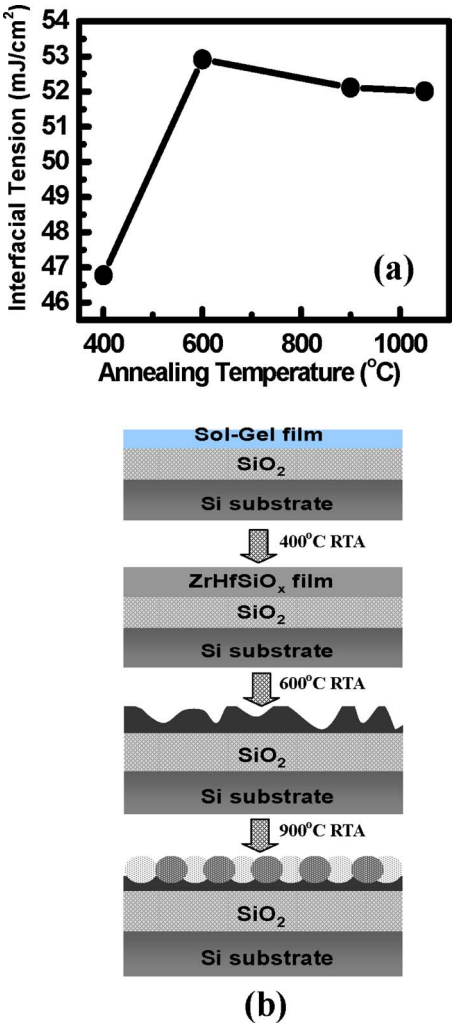

FIG. 3. (Color online) (a) Interfacial tension of the sol-gel thin film as a function of annealing temperature. (b) Transformation processes of the sol-gel thin film into NC after different annealing temperatures.

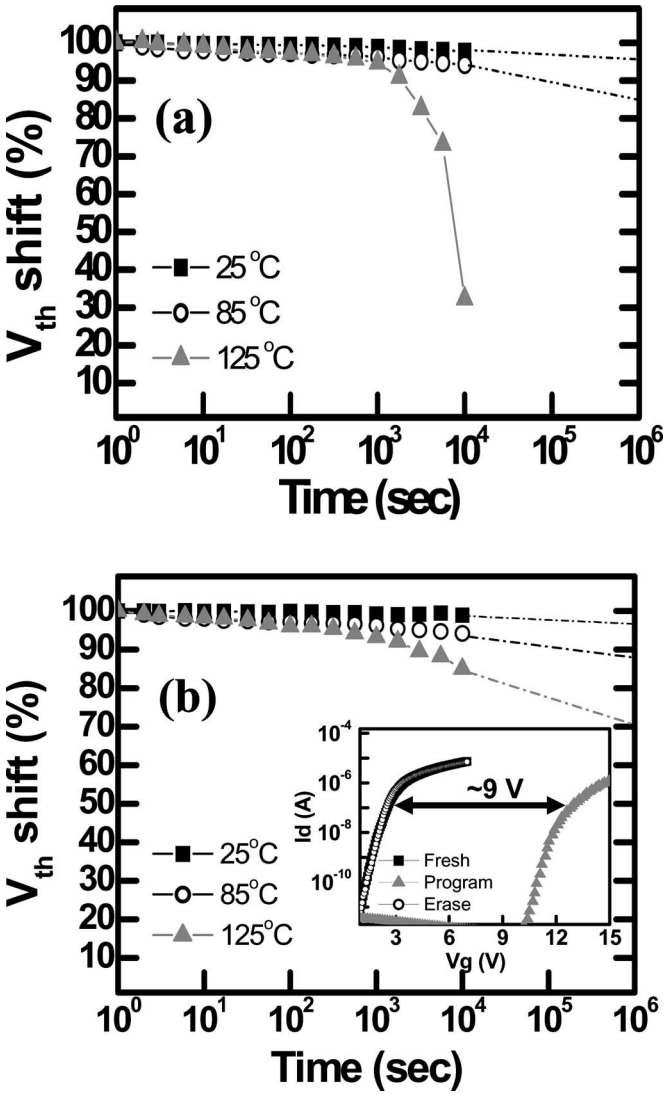

FIG. 4. Retention characteristics of the NC memories annealed at (a) 600 °C and (b) 900 °C at measurement temperatures of 25, 85, and 125 °C. Inset of (b): the I_d-V_g curves of the NC memory in the programed/erased state.

In conclusion, we have discussed the NCs formation of the sol-gel spin-coating thin film at different annealing temperatures. The XPS characterization indicated the annealing treatment under oxygen ambient can activate the formation of metal silicates (i.e., hafnium silicate and zirconium silicate). Together with the TEM images and interfacial energies, we propose a model to explain the transformation of thin film into NCs. The 400 °C treatment has no effect on the thin film, while 600 and 900 °C anneals affect the film's morphology. The film after morphology change has higher interfacial energy and crystallization can minimize the energy. The sol-gel derived NCs successfully played the role of charge trapping purpose in the memory. The 900 °C annealed sample demonstrates the satisfactory retention characteristic than the 600 °C annealed sample due to the NC formation. The large V_{th} shift of the 900 °C annealed sample is potential for future multibit application.

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