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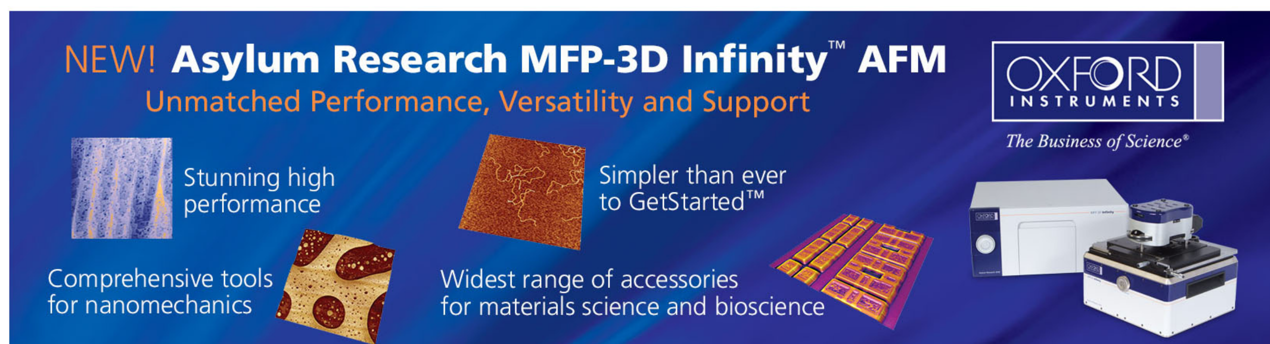

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NiSiGe nanocrystals for nonvolatile memory devices

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In this work, charge-storage characteristics of NiSiGe nanocrystal memory device have been studied. Transmission electron microscope shows that the annealed NiSiGe film has higher nanocrystal size and density distribution. Related material analyses such as x-ray photoelectron spectroscopy, Raman spectroscopy, and energy dispersive spectrometer were used to confirm that the Ge elements provide the additional nucleation centers and enhance the nanocrystals aggregation during thermal process. With the improved nanocrystal formation process, a remarkable improvement of the memory effect is observed by comparing the NiSi and NiSiGe nanocrystals. In addition, the retention characteristics of the nanocrystals memory devices have been discussed. © *2009 American Institute of Physics*. [DOI: 10.1063/1.3080201]

Recently, the conventional floating gate memory faces a challenge of scaling down, such as the thinner tunneling oxide suffer from leakage path generation easily after a long duration operation.[1,2] Therefore, nanocrystal (NC) structure with distributed storage elements was proposed as the next generation structure for nonvolatile memory devices.[3,4] Among the reported material for the application of NC devices, NiSi-based NCs are considered as the possible material for the current manufacturing technology due to its compatibility and low resistivity.[5,6] In addition, previous studies have shown the NC devices need enough energy to help the NCs to aggregate.[7,8] It is disadvantageous to apply the NCs if the NCs need a higher fabricating temperature. Self-assembled method to form NCs indicates that the aggregation of NCs depends on the initial nuclei formation and NC growth rate.[9,10] It had been proposed about the method to enhance the NC aggregation through diffusing the additional elements to form more nucleation centers.[11] Moreover, we believe that the similar idea that the nucleation process improved by the internal elements of the self-assembled layer can also enhance the NC formation.

In this letter, we propose the NC memory structure fabricated by annealing the Ni, Si, and Ge mixed (NiSiGe) film. After a rapid thermal annealing (RTA) process, it is found that the annealed NiSiGe film showed a higher NC size and density distribution than the conventional NiSi NCs obviously. X-ray photoelectron spectroscopy (XPS), Raman spectroscopy, and energy dispersive spectrometer (EDS) were used to confirm that the large size and high density NC is because the internal Ge elements provide additional nucleation centers and enhance the NC formation. In addition, the excellent electrical characteristics of NiSiGe NC memory device have also been demonstrated.

The fabrication of memory structure was started with a dry oxidation at 950 °C to form a 5-nm-thick tunneling oxide on *p*-type (100) Si wafer, which had been removed native oxide and particles by RCA process. Afterward a 6-nm-thick NiSiGe thin film was deposited by cosputtering the $NiSi_2$ and Ge targets simultaneously. Then, a 20-nm-thick capped oxide was deposited to form a trilayer structure by plasma enhanced chemical vapor deposition (PECVD). Subsequently, a RTA at 600 °C was performed for 30 s in N_2 ambient to form NC structure. After the RTA process, a 30-nm-thick blocking oxide (SiO_2) was capped by PECVD system. Finally, Al gate electrode was patterned to form metal-oxide-insulator-oxide-silicon (MOIOS) structure. In addition, the structure with NiSi NCs was formed by the same process for comparison. Transmission electron microscopy (TEM), Raman spectroscopy, XPS, and EDS were used to analyze the NCs formation. Related electrical measurements such as capacitance-voltage (*C-V*), retention measurement were used to study the charge-storage ability of the NCs memory devices.

Figure 1 shows the plane-view and cross-sectional TEM images of the NiSi [Figs. 1(a) and 1(c)] and NiSiGe [Figs.

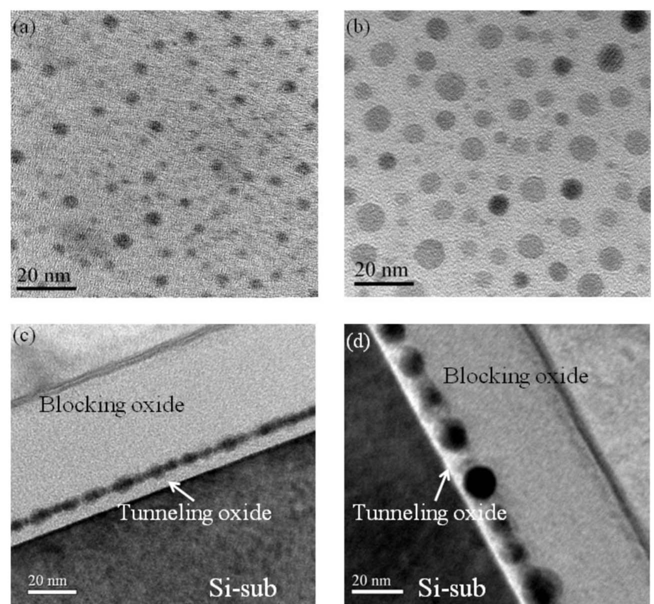

FIG. 1. The plane-view and cross-section TEM micrographs of the annealed NiSi [(a) and (c)] and NiSiGe [(b) and (d)] film.

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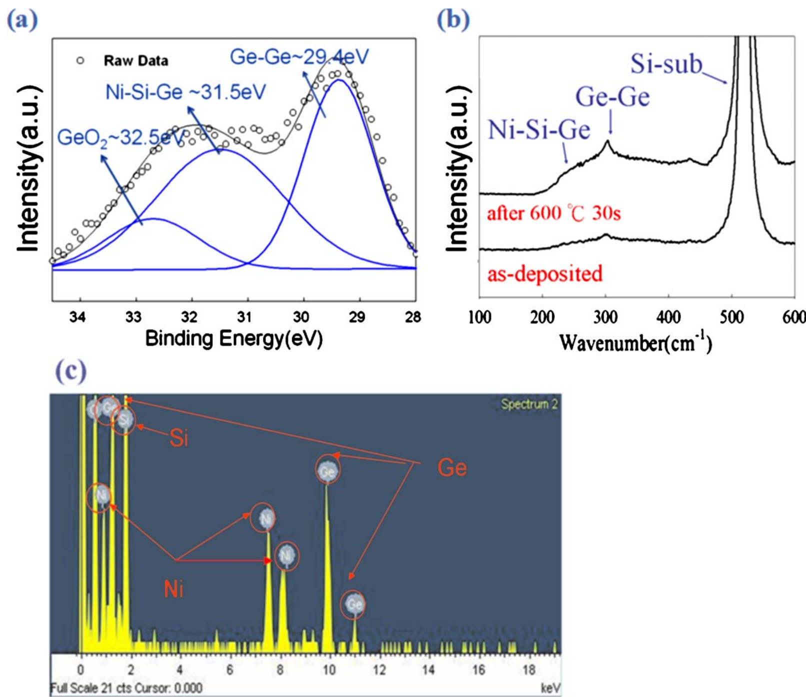

FIG. 2. (Color online) (a) The Ge 3*d* XPS spectra, (b) Raman spectroscopy, and (c) EDS of the NiSiGe film after the thermal annealing.

1(b) and 1(d)] layer after thermal annealing process. After the 700 °C RTA process, it is found that the NiSi NCs aggregated at the tunneling oxide obviously. The size and density of the NCs (>2 nm) calculated from the plane-view TEM is about 2–3 nm and 3.02×10^{11} cm^{-3}, respectively. In addition, the aggregation of the NiSiGe NCs also can be found in annealed NiSiGe film (600 °C). It is confirmed the NiSiGe NCs, which is about 8–10 nm and 4.95×10^{11} cm^{-3}, reveal a better NC growth process than the NiSi NCs. We think that the internal Ge of NiSiGe film play an important role for the NC improvement because the internal Ge elements can provide additional nucleation centers and lower the NC formation temperature. An early nuclei formation brings the enhancement of the NCs size and density.

In order to confirm the attribution of the Ge elements during the NC formation process, the related material analyses was used. In the result of Ge 3*d* XPS analysis, a binding energy is found at ~31.5 eV, reported by the previous literature indicated as nickel germane silicide (Ni–Si–Ge) binding[12] Additionally, the appearance of peak at 29.4 eV means the precipitation of the Ge. Figure 2(b) is the Raman spectra of the annealed NiSiGe samples. It can be seen that for the annealed NiSiGe film, there is a broad peak at about 220 cm^{-1}, corresponding to the Ni–Si–Ge phase. Whereas a Ge–Ge peak peaks at about 300 cm^{-1} was found at 600 °C thermal annealed samples.[13] Also, the EDS analysis was used to analyze the compositions of the NCs. The electron beam was focused at the NCs region about 10 nm during the EDS analysis. We found that the NCs composed with Ni, Si, and Ge elements. Through the results of the material analyses, it is believed that the main composition of the NCs is not pure $NiSi_2$ because the Ge can be the initial nucleation centers to form the NCs. According the reported literature, the Ge elements tend to precipitate during the thermal annealing.[14] Compared with the NiSi mixed film, the NiSiGe layer offers more additional nucleation centers for the NC formation. Therefore, the NiSiGe film can provide a more complete nucleation process and induce a higher size and density distribution even at lower fabricating temperature.

Figure 3 shows the *C-V* hysteresis after bidirectional sweeps, which implies electron charging and discharging effect of the MOIOS structure. In Fig. 3(a), the conventional NiSi NC memory device shows flatband voltage (V_{FB}) shift of 4.5 V under ±10 V gate voltage operation. In contrast to the NiSi NCs, the NiSiGe NC memory device exhibits 9 V flatband voltage shift in Fig. 3(b). The larger window of NiSiGe NCs due to the improved NCs formation is advantage to be defined as "1" or "0" for the logic-circuit design.

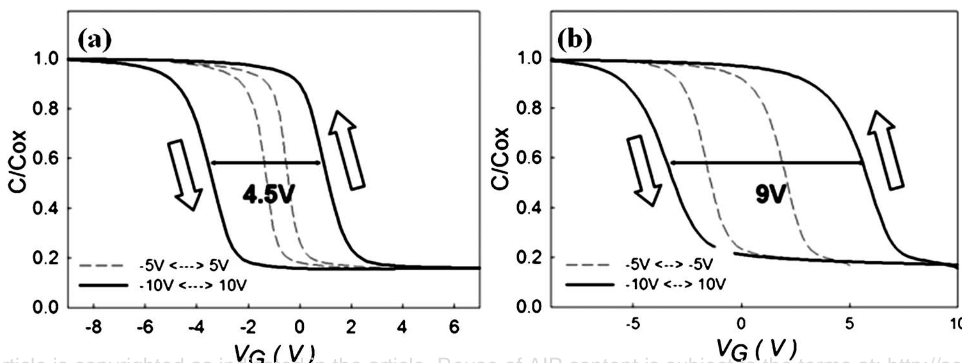

FIG. 3. High-frequency (1 MHz) *C-V* characteristics of the MOIOS structures: (a) with NiSi NCs and (b) NiSiGe NCs as the trapping layer of the memory device.

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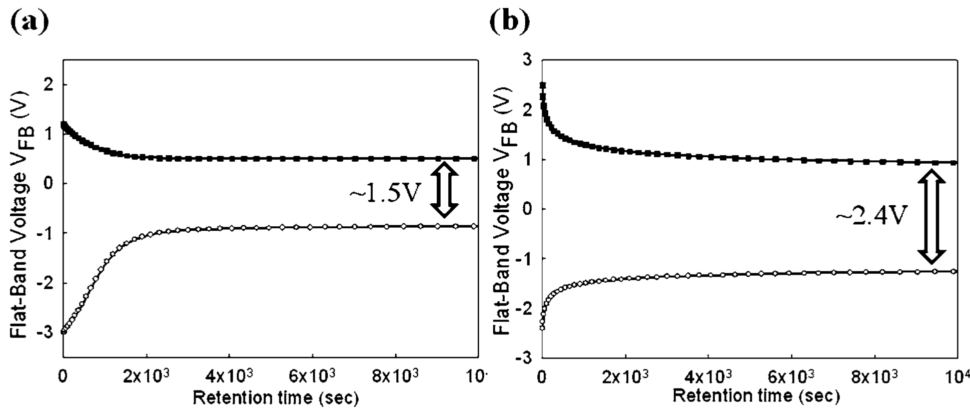

FIG. 4. Retention characteristic of the (a) NiSi and (b) NiSiGe NCs memory device.

Figure 4 shows the retention characteristic of (a) NiSi NC and (b) NiSiGe NC devices. It is found that the NiSiGe NC device reveals better charge-storage ability than the NiSi NCs after 10^4 s. The better retention characteristic is because the NiSiGe NCs have lower quantum confinement effect due to the larger NC size distribution.[15] Also, it is confirmed the Ge elements of the NiSiGe film did not damage the tunneling oxide quality.[16]

In conclusion, we demonstrate the NiSiGe NCs memory device formed by annealing the NiSiGe film. It is confirmed the Ge element of NiSiGe film can offer more nucleation centers and enhance the NiSiGe NCs formation by the related material analyses. Evan at lower annealing temperature, the NiSiGe film obtains larger NC size and higher density distribution. Furthermore, the NiSiGe NC memory device shows superior charge-storage ability to the conventional NiSi NCs due to the improved NC formation process. The good retention characteristic of NiSiGe NCs device is also advantageous to apply into the current memory fabricating process.

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