Role of germanium in the reduced temperature dependence of Ti-based nanocrystals formation for nonvolatile memory applications

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Role of germanium in the reduced temperature dependence of Ti-based nanocrystals formation for nonvolatile memory applications

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We investigated the physical and electrical characteristics of Ti-based nanocrystals (NCs) with composition of germanium fabricated by cosputtering titanium silicide and germanium targets for low temperature applications of nonvolatile memory. The addition of Ge significantly reduces the thermal budget necessary for Ti-based NCs formation to 500 °C in 2 min due to the rise of its morphological instability and agglomeration properties. Compositions characteristics were analyzed by x-ray photon-emission spectroscopy and formations of NCs were observed by transmission electron microscopy. Additionally, capacitance-voltage characteristics, data retention, and endurance properties are characterized to demonstrate its advantages for nonvolatile memory device applications. © 2009 American Institute of Physics. [doi:10.1063/1.3279131]

Nonvolatile memory (NVM) devices with metal nanocrystals (NCs) as floating storage nodes have received much attention due to their higher energy state density, stronger coupling with the device channel, a wide range of available work functions, and strong charge confinement.[1–3] It can be applied for ultralow-power and high-density memories with long retention time, due to strong quantum confinement of charges in the NCs. Among them, titanium (Ti)-based NCs, such as titanium nitride (TiN) and titanium oxide (TiO_2),[4–6] were one of the excellent materials for NVM applications due to its easy fabricated, low cost, good heat stability, and excellent compatibility with complementary metal-oxide-semiconductor process. However, all of the fabrication temperatures to exhibit NVM characteristics in reports were not less than 900 °C. Such a high temperature process does not suit for low temperature applications, for example, fabrications on a glass substrate, and so on. According to the investigations, presence of germanium in Ti silicide affects obviously not only the phase formation temperature but also its morphological stability: A low resistance film of Ti germanosilicide can be formed at a lower temperature than that of Ti silicide was required.[7] In addition, the alloys get a poor morphological stability due to the lowering of agglomeration temperature with germanium (Ge) composition.[8–10] Therefore, addition of Ge to Ti silicide seems to provide a desirable trend to format Ti-based NCs at a relatively low temperature. In this study, we demonstrated a lower temperature fabrication of Ti-based NCs with composition of Ge for NVM applications.

After a RCA clean process of a p-type silicon (100) wafer, a 4 nm thick tunnel oxide was thermally grown by a dry oxidation process. A 10 nm thick Ti-based germanosilicide layer was deposited by cosputtering with $TiSi_2$ and Ge targets in Argon (Ar) ambiance at a pressure of 7.6 mTorr to act as a charge tapping layer. The applied direct current powers on $TiSi_2$ and Ge targets were fixed at 100 and 50 W, respectively. Then, a thinner silicon dioxide layer (10 nm) was deposited by plasma enhanced chemical vapor deposition before any thermal treatments in order to reduce a possible contamination on the trapping layer during exposure to atmosphere. Subsequently, a rapid temperature annealing was carried out at different temperatures of 400, 500, and 600 °C for 2 min to format NCs dots. After the samples were annealed, another 30 nm thick silicon oxide, i.e., a total thickness of 40 nm including the previous oxide, was deposited to act as a blocking oxide. Finally, a 500 nm thick Al gate electrode was deposited and patterned by shadow mask to form a capacitor structure. For comparison, control samples with only a 10 nm thick $TiSi_2$ film as a trapping layer were also fabricated in the same following conditions.

Figure 1 shows cross-sectional transmission electron microscopy (TEM) of the Ti-based germanosilicide samples after annealed at (a) 500 °C and (b) 600 °C. Formation of NCs dots were observed in both of the samples annealed at 500 and 600 °C in Fig. 1. Nevertheless, a continuous Ti-based germanosilicide film was observed to be maintained even after a 400 °C annealing treatment (not showed here). According to the TEM results, therefore, a higher temperature treatment than 400 °C was essential to separate the
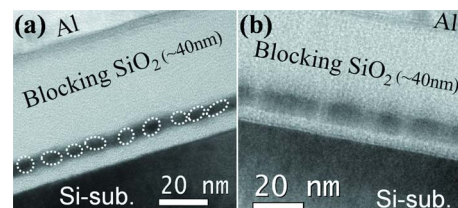

FIG. 1. (Color online) Shows cross-sectional TEM of the Ti-based germanosilicide samples after annealed at (a) 500 °C and (b) 600 °C.

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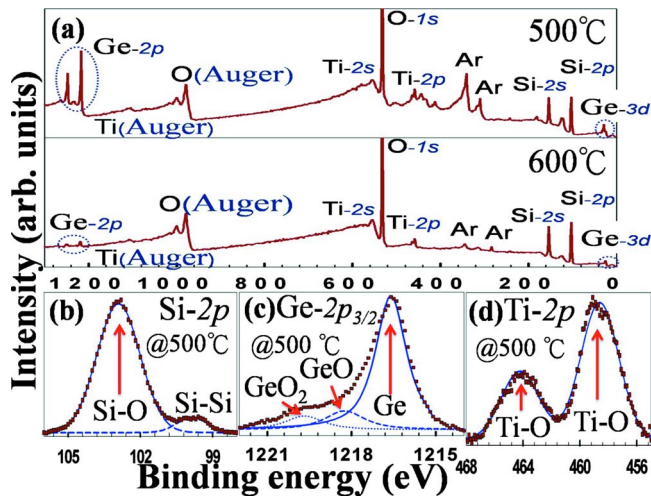
FIG. 2. (Color online) (a) Shows a comparison on overall region XPS spectra between the Ti-based germanosilicide samples annealed at 500 and 600 °C. Figures 2(b)–2(d) show XPS of Si, Ge, and Ti on the samples after annealed at 500 °C, respectively.
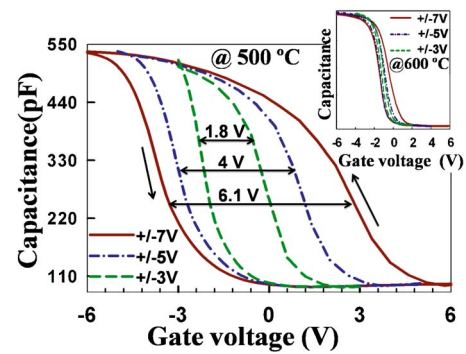

FIG. 3. (Color online) And its inset show a comparison of high frequency capacitance-voltage characteristics on the Ti-based germanosilicide samples annealed at 500 and 600 °C, respectively.

10 nm thick blanket Ti-based germanosilicide layer into NCs structures. The size of NCs also expanded to ~9 nm with a higher thermal treatment of 600 °C.

Figure 2(a) shows x-ray photon-emission spectroscopy (XPS) spectra of overall region on the Ti-based germanosilicide samples annealed at 500 and 600 °C, detected with Ar ion milling of the 10 nm thick blocking oxide. The elemental Ti, Si, Ge peaks appeared in the sample annealed at 500 °C. However, after undergoing a 600 °C heat-treatment, the Si and Ti peaks still can be detected and nearly intact with the exception of Ge peaks, indicating thermal desorption of Ge atoms occurred severely. From the point of view of quantitative XPS analysis, the atomic concentration ratio of Ge $2p$/Ti $2p$ was also reduced obviously from 3.62 in the 500 °C-treated condition to 0.41 in the 600 °C-treated condition though the intensity of Ti $2p$ was somewhat reduced, associated with incomplete or excess milling of the blocking oxide. Decrease of Ge may be mainly caused from the production of Germanium monoxide (GeO) by oxidation of Ge during the annealing process because the GeO phase is too thermodynamically unstable to sublime at the annealing condition.[11,12] This phenomenon can also be inferred somewhat from observing the decrease of contrast between NCs and SiO$_2$ in the TEM results of Fig. 1. Peak signals referred to Si–Si and Si–O bonds[13,14] in Si $2p$ spectrum as well as Ge–Ge bond in Ge $2p_{3/2}$ spectrum were observed in the sample annealed at 500 °C and shown in Figs. 2(b) and 2(c), respectively. The appearance of Si–Si/Ge–Ge bonds could be related to formation of Si–Ge (Ref. 15) and contributed from the Si–Ge precipitates.[16] In Ti $2p$ spectrum of Fig. 2(d), Ti–O peak signals referred to TiO$_2$ (Ref. 17) were detected in the sample annealed at 500 °C. It is probably due to that the trace O$_2$ in RTA ambiance or the absorbed O$_2$ on the wafer surface during wafer transportation (air exposure) induced the formation of TiO$_2$, a thermodynamically stable phase, during annealing process.[18,19] According to the XPS results, therefore, compositions of the NCs formatted after the 500 °C annealing treatment were confirmed as titania-germanosilicide.

Figure 3 and its inset show a comparison of high frequency capacitance-voltage characteristics on the Ti-based germanosilicide samples annealed at 500 and 600 °C, respectively. The sample annealed at 500 °C exhibited a large flat band voltage shift of ~1.8, 4, and ~6.1 V under sweeping gate voltages of 3/−3, 5/−5, and 7/−7 V, respectively. Additionally, the observed counterclockwise hysteresis loops indicated that charge carriers were injected from the silicon substrate through the tunnel oxide. However, the sample annealed at 600 °C exhibited no obvious flat band voltage shifts with gate bias voltages as shown in the inset of Fig. 3. By contrast, its control sample without Ge composition in charge trapping layer also showed no flat band voltage shifts after annealed at 500 or 600 °C (not showed here). Moreover, Ge NCs reported in past researches for NVMs applications[20–22] were almost fabricated above this temperature. Therefore, we suggest that the exhibition of large memory effect was strongly associated with the addition of Ge in Ti-based NCs, but not Ge or TiO$_2$ NCs only.

Figure 4 shows retention and endurance characteristics of the titania-germanosilicide NCs memory capacitor annealed at 500 °C. After the device was operated in the program/erase of +5 V/−5 V condition, the memory window retained ~0.93 V after 10^7 sec as well as ~3.5 V after 10^5 times programmed /erased cycles.

In conclusion, the memory effects of the titania-germanosilicide NCs fabricated by cosputtering titanium silicide and germanium targets were fabricated and demonstrated at relatively low temperature of 500 °C due to the presence of Ge atoms. The thermal desorption of Ge atoms was also observed to degrade the characteristic of threshold voltage shift severely while further increasing the annealing temperature to 600 °C.
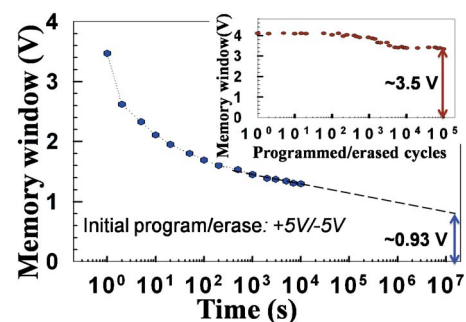

FIG. 4. (Color online) Shows retention and endurance characteristics of the titania-germanosilicide NCs memory capacitor annealed at 500 °C.

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