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Effects of charge storage dielectric thickness on hybrid gadolinium oxide nanocrystal and charge trapping nonvolatile memory

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ABSTRACT

The characteristics of hybrid gadolinium oxide nanocrystal (Gd₂O₃-NC) and gadolinium oxide charge trapping (Gd₂O₃-CT) memories were investigated with different Gd₂O₃ film thickness. By performing the rapid thermal annealing on Gd₂O₃ films with different thickness, the Gd₂O₃-NCs with the diameter of 6 –9 nm for charge storage, surrounded by the amorphous Gd₂O₃ (α -Gd₂O₃) layer, were formed. The α -Gd₂O₃ layer was considered to be the charge trapping layer, resulting in the large memory window of Gd₂O₃-NC/CT memories with thick Gd₂O₃ film. The charge trapping energy level of the Gd₂O₃-NCs and α -Gd₂O₃ layer was extracted to be 0.16 and 0.45 eV respectively by using the temperature-dependent retention measurement. Further, after a 10⁶ program/erase cycling operation, the memory with thin Gd₂O₃ film suffered from a 30% charge loss because of the traps within the α -Gd₂O₃ layer. The Gd₂O₃ film thickness of 10 nm was optimized to exhibit superior performances of the Gd₂O₃-NC/CT memory, which can be applied into the nonvolatile memory.

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1. Introduction

As the charge storage capacity of the conventional floating gate (FG) nonvolatile memory increases, the feature size of the device needs to be shrunk. The scaling of the floating gate structure approaches high difficulty beyond 32 nm node technology, primarily due to the high charge leakage current resulted from the conductive poly-silicon charge storage layer and the thin tunneling oxide [1-3]. To solve this, one promising candidate is to adopt the discrete charge storage nodes like the nanocrystals (NCs) embedded in the bottom and top dielectrics for the replacement of the poly-silicon layer [4-6]. The lateral charge leakage current can be effectively suppressed by the discontinuous storage nodes, thus enhancing the immunity of the vertical leakage current through the tunneling oxide. It is reported that the NC memories can be fabricated by lots of materials and formation strategies, which have high potential to be applied in the charge storage devices by taking the advantages over the conventional FG nonvolatile memory [7,8]. Recently, the Ge and Si NCs are proposed for the nonvolatile memory use because of the simple fabrication and complementarymetal-oxide-semiconductor (CMOS) compatible process [9-11]. The metal NCs such as Au, Pt, WSi₂, and Ni embedded in the

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dielectric layers can exhibit long data retention owing to the high work function [12-17]. In addition, the metal-oxide NC memory fabricated by HfO₂-NCs embedded in a SiO₂ matrix have been presented to have superior memory characteristics, especially for the large memory window and good data retention and endurance properties [18,19]. It is found that the presence of charge traps within the metal-oxide NCs as well as the surrounding dielectrics can provide the high charge storage capacity, thus the high tolerance for charge loss can be achieved [20].

Previously, the gadolinium oxide nanocrystal (Gd₂O₃-NC) has been reported to be the probable candidate as nonvolatile memories [21,22]. The Gd₂O₃-NCs can be formed by rapid thermal annealing (RTA) of the Gd_2O_3 film at an optimized temperature. The crystallized Gd₂O₃ (c-Gd₂O₃) with low energy band-gap (5.44 eV) surrounded by the amorphous Gd_2O_3 (α -Gd₂O₃) layer with high energy band-gap (6.19 eV) has been found to realize the Gd_2O_3 -NCs [21,23]. The band-gap offset to achieve the electrons stored in Gd₂O₃-NCs is responsible for the charge storage of Gd₂O₃-NC memories, which is different from any other NC memory proposed before [4–19]. Furthermore, the charge trapping energy level of the Gd₂O₃-NCs can be extracted from the data retention characteristics [23]. It is expected that there may be some traps within the surrounding α -Gd₂O₃ layer, and some literature pointed out that the traps within the surrounding dielectric layer will affect the reliability behaviors of the NC memories [24,25]. To solve the problem, the CF₄ plasma treatment on the Gd₂O₃-NC memory has been







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Fig. 1. Schematic structure and HRTEM image of the Gd₂O₃-NC/CT memory with the Gd₂O₃ film thickness of (a) 10 and (b) 20 nm. The tunneling oxide (TO), blocking oxide (BO), Gd₂O₃-NC, and α-Gd₂O₃ layer were indicated in the figures.

proposed to passivate the defects and modify the energy band diagram of the Gd₂O₃ film, efficiently improving the memory characteristics [25]. Nevertheless, the charge trapping characteristics of the α -Gd₂O₃ layer within the Gd₂O₃-NC memory has not yet been understood. In this paper, the thickness of the Gd₂O₃ film was varied to investigate the effect of charge storage dielectric thickness on hybrid Gd₂O₃ nanocrystal (Gd₂O₃-NC) and Gd₂O₃ charge trapping (Gd₂O₃-CT) memory. It can be found that with the increase of Gd₂O₃ film, the large memory window was obtained for the Gd₂O₃-NC/CT memory due to the thick α -Gd₂O₃ layer for charge trapping. Further, the charge trapping energy level of the α -Gd₂O₃ layer was found to be higher than that of Gd₂O₃-NCs, which will influence the memory with thick Gd₂O₃ layer after 10⁶ program/erase (P/E) operation cycles.

2. Experimental

The Gd₂O₃-NC/CT memory devices were fabricated on 4 inch n-type (100) silicon wafers. After the standard RCA clean, a 3-nmthick silicon dioxide film was thermally grown at 850 °C in an N₂ and O₂ mixed ambience using a horizontal furnace as the tunneling oxide. Then, the gadolinium oxide (Gd₂O₃) film was deposited on the tunneling oxide by RF sputtering with a pure gadolinium (99.9% pure) target in oxygen (O₂) and argon (Ar) mixture ambience at room temperature. The proportion of oxygen and argon ambient flow rate was 1:7, and the pressure of the chamber was 20 mtorr for amorphous Gd₂O₃ formation. The thickness of the Gd₂O₃ film was assigned to be 6, 10, 15, and 20 nm for the investigation of the charge storage dielectric thickness effect. After the charge storage dielectric films had been formed, the samples were subjected to the rapid thermal annealing (RTA) system at 900 °C for 30 s in N₂ ambient to form the Gd₂O₃-NCs surrounded by the α -Gd₂O₃ layer. Next, in order to form the blocking oxide, 8-nm-thick of SiO₂, using mixed SiH₄ and N₂O gases, was deposited using plasma enhanced chemical vapor deposition (PECVD) at 300 °C. The gas flow ratio of the SiH₄ and N₂O gases was set to be 5:200 in order to lower the deposition rate for better SiO₂ quality. After that, a 300-nm-thick aluminum (Al) film was deposited by thermal evaporator with a pure Al ingot (99.9999% pure), and a gate was defined lithographically and etched. The NC dot size of the Gd₂O₃-NC/CT memories and the film thickness of surrounding α -Gd₂O₃ layer were examined by the high resolution transmission electron microscopy (HRTEM). For the electrical analysis, the high frequency (1 MHz) capacitance–voltage (C-V) curves were measured by HP4285 precision LCR meter and the program and erase characteristics were measured by HP8110 pulse generator to supply the gate pulse.

3. Results and discussion

3.1. Material analysis and basic memory characteristics

Fig. 1(a) and (b) shows the schematic structure and the corresponding HRTEM image of the Gd₂O₃-NC/CT memories with the Gd₂O₃ film thickness of 10 and 20 nm, respectively. The crystallized Gd₂O₃-NC surrounded by the amorphous Gd₂O₃ (α -Gd₂O₃) layer can be observed in these images. The diameter of the Gd₂O₃-NCs was found to be approximately 6–9 nm regardless of the thickness of Gd₂O₃ film, which was identical to our previous study [19]. In addition, the Gd₂O₃-NCs were located at the top of the Gd₂O₃ film, which was due to the top lamp RTP system (JETFIRST 100 from AnnealSys). The heat was provided from the top of the process wafer and the Gd₂O₃-NCs were formed by the re-crystallization of the nuclei sites at the top side. Thus, large proportion of the thick Gd₂O₃ film was amorphous phase (α -Gd₂O₃) and located at the bottom of the dielectric film, as revealed in Fig. 1(b).

Fig. 2 demonstrates the capacitance–voltage (C-V) hysteresis memory window of the Gd₂O₃-NC/CT memories with different



Fig. 2. High frequency C-V characteristics of the Gd₂O₃-NC/CT memories with different Gd₂O₃ film thickness. The curves were measured by sweeping the gate voltage from -13 to 13 V and then swept back. The maximum capacitance and relative permittivity of the Gd₂O₃ film were shown in the inset figure.

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