Al₂O₃ nanocrystals embedded in amorphous Lu₂O₃ high-k gate dielectric for floating gate memory application

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Abstract. The integration of nanoparticles has high potential in technological applications and opens up possibilities of the development of new devices. Compared to the conventional floating gate memory, a structure containing nanocrystals embedded in dielectrics shows high potential to produce a memory with high endurance, low operating voltage, fast write-erase speeds and better immunity to soft errors [1]. A significant improvement on data retention [2] can be observed when discrete nanodots are used instead of continuous floating gate as charge storage nodes because local defect related leakage can be reduced efficiently. Furthermore, using a high-k dielectric in place of the conventional SiO₂ based dielectric, nanodots flash memory is able to achieve significantly improved programming efficiency and data retention [3-4]. We have recently successfully developed a method to produce nanodots embedded in high-k gate dielectrics [5-6]. In this paper, we fabricated the memory structure of Al₂O₃ nanocrystals embedded in amorphous Lu₂O₃ high k dielectric using pulsed laser ablation. The mean size and density of the Al₂O₃ nanocrystals are estimated to be about 5 nm and 7x10¹¹ cm⁻², respectively. Good electrical performances in terms of large memory window and good data retention were observed. Our preparation method is simple, fast and economical.

1. INTRODUCTION
Flash memory device incorporating nanocrystals has gained considerable attention as one of the potential candidate for nonvolatile, high density and low memory power memory devices. Conventionally, a nanocrystal floating gate memory is a metal-oxide semiconductor field effect transistor (MOSFET) in which the gate dielectric is replaced by a gate stack, made up of a thin tunneling oxide, a layer of semiconductor of nanocrystals embedded in the dielectric and a thicker oxide. Such memory devices have generated much interest and been widely investigated [1, 7, 8]. Much of the attention is shifted towards semiconductor nanoparticles embedded in silicon dioxide (SiO₂) of a MOS device for the future high speed and low power memory devices in the recent years [1, 9]. The shift from the conventional floating gate (FG) devices to the nanocrystal nonvolatile memories (NCNVM) is due to the limited potential for continued scaling of the FG device structure being the main limitation. From the work of J.D. Blauwe et al, it is known that there is a trade-off between speed and reliability in the typical flash gate to allow sufficient charge transfer rate going back and forth the floating gate with acceptable charge retention [10].
The advantage of having a structure with nanocrystals embedded in the dielectric is that it is likely to produce a memory structure with low operating voltage, high endurance, rapid write-erase speeds and better protected against soft error [1, 7]. The charge exchange between the nanocrystals and the inversion layer has been attributed to the operation of these memory devices. The introduction of high-k dielectric in place of the typical SiO₂ has brought significant improvement to the nanocrystal memory device in terms of its programming efficiency and data retention. [2, 5-7] Up to now, research work on the integration of the nanoparticles into the high-k dielectric materials is still limited.

One of the most promising groups of materials for the next generation of gate oxides are the lanthanide oxides. Lanthanide oxides processes the desired properties that is suited for alternative high-k insulator application which include a large band gap, high relative dielectric constant, and low leakage current [11-14]. In addition, a number of the lanthanide oxides exhibit these desired properties without forming interfacial layer [15]. One of the promising candidate for the next generation of gate oxides is Lu₂O₃ which was reported to have a dielectric constant of around 12 [15, 16], and is anticipated to be thermodynamically stable on Si [17, 18]. As another promising gate dielectric material [19, 20], Al₂O₃ is a robust, high-temperature material expected to withstand Si processing conditions. In this letter, we report a novel method to produce Al₂O₃ nanocrystals in amorphous Lu₂O₃ high-k dielectric matrices by using a variation of the pulsed-laser deposition method with a rotating target. This result opens up possibilities for new advances and applications in memory devices.

2. EXPERIMENTAL

A KrF pulsed laser was used to ablate the target in an ultrahigh vacuum chamber. The wavelength of the excimer laser is 248 nm and the average energy density is of about 1.8 J/cm² with frequency of 5 Hz. The target to be laser ablated was first prepared from a high purity (99.999%) round Lu₂O₃ target (diameter D=25 mm) and a piece of small square single crystal Al₂O₃ target (of about 2 mm in length). The Al₂O₃ target was glued using chemically non-reactive adhesive onto the surface of the Lu₂O₃ target, making a two layer assembly with only physical, but not chemical, contact between them. During the PLD process, the center of the Lu₂O₃-Al₂O₃ target assembly was set to spin slowly about its central axis and the laser beam vaporized the two component materials alternately. The p-type (100) Si substrates were first cleaned using SC1, SC2 solutions, and then dipped in a 1% HF solution to remove the native oxide. The laser deposition was carried out in a high vacuum system with a background pressure of about 6x10⁻⁷ Torr with the substrate at room temperature. During the pulsed laser ablation process, for the tunneling oxide layer deposition, we kept the target stationary while allowing the laser to ablate the Lu₂O₃. Then, to form the nanocrystals embedded inLu₂O₃ matrix, the Al₂O₃-Lu₂O₃ target assembly was set to spin slowly about its central axis and the laser beam vaporized the two component materials alternately. Finally, the laser beam was focused onto Lu₂O₃ for the control oxide layer deposition. After deposition, the thin film was subjected to a post deposition annealing at 400 °C for 60 s in nitrogen ambient. The film structure was examined using high-resolution transmission electron microscope (HRTEM) with JEOL 2010 microscope. Top electrodes of Au with a dimension of 0.5 mm x 0.5 mm were evaporated for electrical measurement. The electrical characteristics of the fabricated metal-insulator-semiconductor (MIS) devices, capacitance-voltage (C-V) and capacitance-time (C-t) were measured using a precision LCR meter (HP 4284A).

3. RESULTS AND DISCUSSION

Figure 1 (a) shows the planar TEM image of the synthesized Al₂O₃ nanocrystals, with its corresponding electron diffraction pattern on the top left corner. The average diameters of the Al₂O₃ nanocrystals are approximately 5 nm and the area density of the nanocrystals is estimated to be about 7x10¹¹ cm². Figure 1 (b) shows a cross-sectional HRTEM image of the Lu₂O₃ thin
film on the Si substrate. The Al₂O₃ nanocrystals embedded in Lu₂O₃ can be clearly seen between tunnel oxide and control oxide, and the shape of the Al₂O₃ nanocrystals is almost spherical. In this sample with Al₂O₃ nanocrystals, Lu₂O₃ is used as the control and tunneling oxide layer in the trilayer memory structure of Lu₂O₃/Al₂O₃/Lu₂O₃. The total physical thickness, the thicknesses of control and tunneling oxide layer are about 25 nm, 8 nm and 4 nm, respectively. It can also be confirmed that the Lu₂O₃ thin films still remain amorphous after PDA at 400 °C and there is no observable interfacial layer between Si substrate and Lu₂O₃ film.

Figure 1. (a) Planar TEM image of Al₂O₃ nanocrystals embedded in amorphous Lu₂O₃ dielectric matrix. On the top left corner, we show the electron diffraction pattern for Al₂O₃ nanocrystals. (b) Cross-sectional TEM image of Al₂O₃ nanocrystals embedded in amorphous Lu₂O₃ dielectric matrix.

Figure 2 (a) shows the typical high frequency (1 MHz) capacitance voltage (HFCV) measurements of two MIS capacitors with and without Al₂O₃ nanocrystals after the bidirectional bias sweeps between 6 V and (-6) V. Figure 2 (b) demonstrates the band diagrams of the operation of the distributed charge storage with Al₂O₃ nanocrystals. The write and erase operation with different gate polarities of the memory device are exhibited. It can be seen that under a low operating voltage, 6 V, a significant threshold voltage shift (~1.2 V) is observed from C-V hysteresis of the sample with Al₂O₃ nanocrystals. In contrast, the controlled sample without Al₂O₃ nanocrystals shows no obvious flat band voltage shift, suggesting that the large memory effect observed in the sample with Al₂O₃ nanocrystals is caused by the charges stored in the Al₂O₃ nanocrystals. Generally, the hysteresis may be introduced by the mixed effects of injected charges stored in the nanocrystals, essential trap charges existing in the oxide or interface states [21]. Since we have used the same processes to produce the two samples with the exception of the presence of Al₂O₃ nanocrystals, the hysteresis effect produced by the essential trap charges and interfacial states should be the same for the two samples. Therefore, it can be concluded that the large hysteresis observed in the sample with Al₂O₃ nanocrystals is caused by the injected charges stored in the nanocrystals and/or at the interface of the nanocrystals [22].

To evaluate the retention time of storage charges in the Al₂O₃ nanocrystal floating gate memory capacitors, the storage charge lifetime must be known. C-t measurement result as shown in Fig. 3 shows the capacitance decrease as a function of discharging time. After injecting electrons at 10 V for 10 s, gate voltage was changed to the flat-band voltage of -3 V and the duration of retention time is expected to be large enough to withstand the loss of charge stored in the memory nodes. It is clearly shown that no significant initial time decay can be observed.
According to the work of Kim et al, the stored charges in the localized nanocrystals exhibit good retention property [23]. In our experiments, Al₂O₃ nanocrystals are well localized at the middle of the dielectric (Lu₂O₃) matrix, hence, the only possibility of charge loss is the tunneling out via the tunneling barrier. Therefore, the stored charges in the localized nanocrystals exhibit good retention properties.

Figure 2. (a) High-frequency (1MHz) capacitance-voltage hysteresis of sample with Al₂O₃ nanocrystals embedded in amorphous Lu₂O₃ dielectric and reference sample without Al₂O₃ nanocrystals. (b) The band diagrams of the operation of the distributed charge storage of Al₂O₃ nanocrystals, where (1) Lu₂O₃ (control oxide); (2) Al₂O₃ nanocrystals embedded in Lu₂O₃; (3) Lu₂O₃ (tunneling oxide)

Figure 3. Normalized capacitance decay characteristics for Al₂O₃ nanocrystals embedded in amorphous Lu₂O₃ dielectric memory device.
4. CONCLUSION
In conclusion, we have successfully developed a novel method to fabricate $\text{Al}_2\text{O}_3$ nanocrystals embedded in $\text{Lu}_2\text{O}_3$ memory device by pulsed laser ablation with a rotating target. Electrical properties have been characterized by means of high-frequency C-V and C-t measurements on the MIS capacitor. This capacitor can be operated under smaller operation voltages, and exhibit large memory window and good retention time.

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