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LaAlO₃ Nanocrystals Embedded in Amorphous Lu₂O₃ High-k Gate Dielectric for Floating Gate Memory Application

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A novel method to fabricate the memory structure of LaAlO₃ nanocrystals embedded in amorphous Lu₂O₃ high-k dielectric by the pulsed laser deposition method using a rotating target was successfully developed. The average mean size and aerial density of the LaAlO₃ nanocrystals are estimated to be about 6 nm and 1.1 × 10¹² cm⁻², respectively. Superior performances in terms of a large memory window, long data retention, and robust endurance were observed.

**Results and Discussion**

Figure 1a shows the planar TEM image of the synthesized LaAlO₃ nanocrystals, with its corresponding electron diffraction pattern on the top left corner. The average diameters of the LaAlO₃ nanocrystals are approximately 6 nm, and the area density of the nanocrystals is estimated to be about 1.1 × 10¹² cm⁻². Figure 1b shows a cross-sectional HRTEM image of the Lu₂O₃ thin film on the Si substrate. The LaAlO₃ nanocrystals embedded in Lu₂O₃ can be clearly seen between the tunnel oxide and the control oxide, and the shape of the LaAlO₃ nanocrystals is almost spherical. In this sample with LaAlO₃ nanocrystals, Lu₂O₃ was used as the control and tunneling oxide layer in the trilayer memory structure of Lu₂O₃/LaAlO₃/Lu₂O₃. The total physical thickness, the thicknesses of the control and the tunneling oxide layer are about 15, 4, and 5 nm, respectively. It can also be confirmed that the Lu₂O₃ thin films still remained amorphous after PDA at 400°C, and there is no observable interfacial layer between Si substrate and Lu₂O₃ film. By controlling the exposed area ratio of Lu₂O₃/LaAlO₃ under the laser ablation along with the target rotation speed, the size and densities of nanocrystals, the distribution of these nanocrystals can also be controlled.

**Experimental**

Samples were prepared using the PLD method. Briefly, a KrF-pulsed laser beam of 248 nm wavelength and the energy density is 1.5 J/cm² with frequency of 5 Hz was used to ablate the target in an ultrahigh vacuum chamber. The targets to be laser ablated consisting of one piece of high-purity (99.999%) Lu₂O₃ round target (diameter D = 25 mm) and a piece of small, square, single-crystal LaAlO₃ target (of about 3 mm in length) were first prepared. The LaAlO₃ target was glued onto the surface of the Lu₂O₃ target making a two-material assembly with only physical, but not chemical, contact between them. During the PLD 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 in the Lu₂O₃ matrix, the LaAlO₃/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. The ablated materials were deposited on p-type Si(100) wafer substrates which were first cleaned using SC1, SC2 mixtures, and then dipped in a 1% HF solution to remove the native oxide. The deposition and growth of the films on the substrate were carried out in a high vacuum system with a background pressure of about 5 × 10⁻⁷ Torr, with the target rotating at about 30 rounds/min and the substrate at room temperature. The distance between the target and substrate was 11 cm. After deposition, the thin film was subjected to a postdeposition annealing (PDA) at 400°C for 60 s in a nitrogen ambient. The film structure was examined using high-resolution transmission electron microscope (HRTEM) with a JEOL 2010 microscope. Top electrodes of Au with a dimension of 0.5 × 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). The OR-X 420 programmable function generator was connected to the HP 4284A through a switch and the C-V measurements were performed after the stress of the periodic pulses to identify the relationship of threshold voltage shift (memory window) vs pulse cycles.
Figure 2 shows the typical high frequency (1 MHz) capacitance-voltage hysteresis of sample with LaAlO$_3$ nanocrystals embedded in amorphous Lu$_2$O$_3$ dielectric and reference sample without LaAlO$_3$ nanocrystals.

In contrast, the controlled sample without LaAlO$_3$ nanocrystals shows no obvious flatband voltage shift, suggesting that the large memory effect observed in the sample with LaAlO$_3$ nanocrystals is caused by the charges stored in the LaAlO$_3$ 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. Since the processes for fabricating the two samples are the same, except for the LaAlO$_3$ nanocrystals, the hysteresis effect produced by the essential trap charges and interfacial states should be the same for the two samples, and can, therefore, be ruled out. The injected charges stored in nanocrystals and/or at the interface of the nanocrystals$^{17}$ is a more plausible explanation for the large hysteresis of the sample with LaAlO$_3$ nanocrystals.

The memory data retention characteristics at room temperature and 125°C for this nanocrystal floating gate memory capacitor were also studied as shown in Fig. 3. The memory capacitor is first charged for 10 s at a bias voltage of 10 V. Then, the decayed capacitance measurement was carried out under a −3 V bias voltage. It can be seen that after 700 s of stress, the decayed capacitance for the memory capacitor is only about 4% at room temperature and 17% at 125°C, suggesting a good charge retention characteristics. In Figure 3.

Figure 3. Normalized capacitance decay characteristics at room temperature (solid line) and 125°C (dash line) for LaAlO$_3$ nanocrystals embedded in amorphous Lu$_2$O$_3$ dielectric memory device.

Figure 1. (a) Planar TEM image of LaAlO$_3$ nanocrystals embedded in amorphous Lu$_2$O$_3$ dielectric matrix. Inset: we show the electron diffraction pattern for LaAlO$_3$ nanocrystals. (b) Cross-sectional TEM image of LaAlO$_3$ nanocrystals embedded in amorphous Lu$_2$O$_3$ dielectric matrix.
our experiments, the LaAlO$_3$ nanocrystals have a dimension of ~6 nm, therefore, the coulomb’s blockade effect and the quantum confinement effect might be significant for the write/erase process. According to the work of Kim et al., the storage charges in the localized nanocrystals exhibit a long-term retention property. As shown in our figures, isolation of LaAlO$_3$ nanocrystals has been embedded at the middle of the dielectric matrix and results in a good memory storage effect.

Figure 4 shows the endurance characteristics obtained after cycling the structure between 6 V (write-electron injection to the nanocrystals) and ~7 V (erase-electron ejection from the nanocrystals). The cycling was interrupted at specific times and CV measurements were recorded. Even though 10$^7$ pulse cycles were performed, it retains a large memory window without catastrophic decline as the previous reports on nanocrystal memory devices.

Many methods have been explored by various groups in order to fabricate the nanocrystals embedded in the high-k matrix. This work has managed to fabricate high density of nanocrystals embedded in high-k matrix using in situ pulsed laser deposition followed by postdeposition annealing. In comparison, our method is much more simplified and straightforward, attaining a compatible memory window. Moreover, we offer the flexibility for controlling the size and densities of the nanocrystals by controlling the exposed area ratio of Lu$_2$O$_3$:LaAlO$_3$ under laser ablation and the target rotation speed. Further investigations are in progress in this aspect.

Conclusions

In summary, we have successfully developed a method to fabricate the memory structure of LaAlO$_3$ nanocrystals embedded in amorphous Lu$_2$O$_3$ high-k dielectric using pulsed laser deposition. The mean size and aerial density of the LaAlO$_3$ nanocrystals are estimated to be about 6 nm and 1.1 $\times$ 10$^{12}$ cm$^{-2}$, respectively. Good performances in terms of a large memory window, long data retention, and robust endurance were observed.

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