Nano-Floating Gate Memory Devices with Metal-Oxide Nanoparticles in Polyimide Dielectrics

Eun Kyu Kim*, Dong Uk Lee*, Seon Pil Kim*, Tae Hee Lee*, Hyun-Mo Koo, Jin-Wook Shin**, Won-Ju Cho**, and Young-Ho Kim*****

***Abstract*—We fabricated nano-particles of ZnO, In_2O_3 and SnO_2 by using the chemical reaction between metal thin films and polyamic acid. The average size and density of these ZnO, In_2O_3 and SnO_2 nano-particles was approximately 10, 7, and 15 nm, and 2 x 10^{11}, 6 x 10^{11} , 2.4 x 10^{11} cm^{-2}, respectively. Then, we fabricated nano-floating gate memory (NFGM) devices with ZnO and In_2O_3 nano-particles embedded in the devices' polyimide dielectrics and silicon dioxide layers as control and tunnel oxides, respectively. We measured the current-voltage characteristics, endurance properties and retention times of the memory devices using a semiconductor parameter analyzer. In the In_2O_3 NFGM, the threshold voltage shift (ΔV_T) was approximately 5 V at the initial state of programming and erasing operations. However, the memory window rapidly decreased after 1000 s from 5 to 1.5 V. The ΔV_T of the NFGM containing ZnO was approximately 2 V at the initial state, but the memory window decreased after 1000 s from 2 to 0.4 V. These results mean that metal-oxide nano-particles have feasibility to apply NFGM devices.**

***Index Terms*—Nano-floating gate memory, metal-oxide nano-particle, polyimide, nonvolatile**

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I. INTRODUCTION

Nano-floating gate memory (NFGM) is an attractive candidate for use in next-generation nonvolatile memory. It is similar to conventional floating gate memory, but it is has a different structure. An NFGM has nano-particles between tunnel oxide layers and control oxide layers instead of floating gate layers. The NFGM has better electrical characteristics, such as high-speed operation, long retention, and good reliability [1–6]. A method for fabricating metal oxide nano-particles in polyimide (PI) has been developed [4]. The PI can be made into a useful nano-particle matrix and used in electronic and optoelectronic applications because of its good thermal stability and i chemical resistance. We produced Cu_2O, ZnO, Fe_2O_3, In_2O_3 and $Ni_{1-x}Fe_x$ nano-particles in polyimides during the imidization of a polyimide precursor [7–11].

The metal-oxide nano-particles between polyimide layers have high density, high uniformity, and single layer control, meaning that they have for applications in NFGM [12–13].

In this study, we fabricated an NFGM containing metal-oxide nano-particles and analyzed its electrical properties by taking current-voltage (I-V) measurements. We investigated the morphology of the metal-oxide nano-particles embedded in a polyimide matrix using transmission electron microscopy (TEM) .

II. EXPERIMENT

We fabricated nano-floating gate memory that contained metal-oxide nano-particles in a polyimide gate insulator layer on the *p*-type (100) UNIBOND silicon-on-insulator (SOI) wafers with a 100-nm-top Si layer and a 200-nm-buried oxide layer. The phosphorus in-situ doped poly-Si layer, with a thickness of 100 nm, was deposited on the top Si layer of SOI substrates by low-pressure chemical vapor deposition (LPCVD) at 650°C. The Si active region was formed by photolithography and a plasma reactive ion etching (RIE) processes on the phosphorus in-situ doped poly-Si layer. The source and drain regions were defined before performing a polyamic acid (PAA) process because PAA is sensitive to high temperature process. Next, the phosphorus in-situ doped poly-Si layer was partially etched to a depth of 150 nm by an RIE process in order to form the channel region of the NFGM devices. Then, tunnel oxide with a thickness of 4.5 nm was grown by dry oxidation and a metal thin layer with a thickness of 5 nm was deposited on the tunnel oxide using a thermal evaporator. Finally, a coating of 50-nm-thick PAA was spin coated onto the metal thin film. The PAA used was the commercial product biphenyltertracarboxylic dianhydride-phenylen diamin (BPDA-PDA) type (Dupont PI2610D). It is composed of BPDA-PDA in N-methyl-2-pyrrolidone (3 wt.%).

The PAA and the metal film were maintained at room temperature for 24 hours in desiccators and then metal ions were formed by the chemical reaction between the PAA and the thin metal film during the indium dissolving process. The curing of samples was carried out at 400°C for 1 hour after soft baking at 135°C for 30 minutes in a rapid thermal process (RTP) system in an N_2 atmosphere. The metal-oxide nano-particles were formed inside the polyimide matrix during the curing process by the chemical reaction between metal ions and PAA. Aluminum with a thickness of 150 nm was deposited by thermal evaporation and the gate electrode was formed using photolithography and aluminum etching.

Fig. 1 shows a cross-sectional schematic diagram of an NFGM fabricated with metal-oxide nano-particles. The structure of the metal-oxide nano-particles formed in the polyimide layer was determined using an FEI Technia 300 TEM system. The subthreshold characteristics, output current characteristics, and data retention characteristics of the NFGM containing metal-oxide nano-particles and a polyimide gate insulator were determined using a HP 4155B semiconductor parameter analyzer.

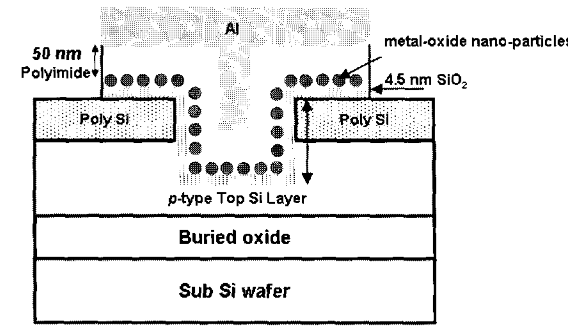

Fig. 1. Cross-sectional schematic diagram of NFGM containing metal-oxide nano-particles.

III. Results and Discussions

Fig. 2 shows TEM images of metal-oxide nano-particle embedded in a polyimide insulator. In Fig. 2(a), the ZnO nano-particles have an irregular shape with a diameter and density of 10 nm and $2\text{x}10^{11}$ cm^{-2}, respectively. The In_2O_3 nano-particles in the polyimide layer are spherical, with an average diameter of 7 nm and a nano-particle density of approximately 5.8×10^{11} cm^{-2}. Figs. 2 (c) and (d) show TEM images of plane and cross-section views of SnO_2 nano-particles. These SnO_2 nano-particles are irregular spheres, with average diameters of approximately 15 nm. The density of the SnO_2 nano-particles is estimated from the plane-view TEM image to be approximately $2.4\text{x}10^{11}$ cm^{-2}.

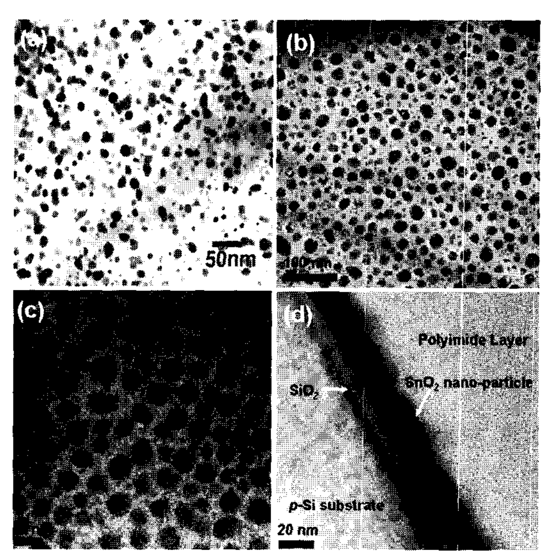

Fig. 2. TEM images of metal-oxide nano-particles. Plane-view of TEM images with (a) ZnO, (b) In_2O_3 and (c) SnO_2. (d) Cross-sectional image of TEM of SnO_2 nano-particles between SiO_2 and polyimide layers.

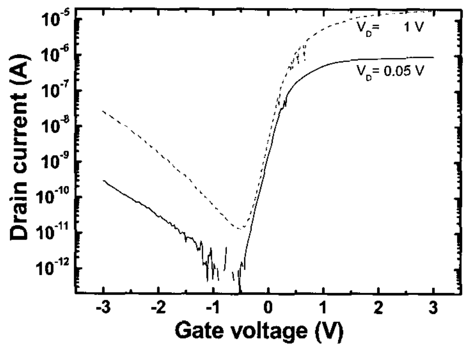

Fig. 3. I_d-V_g characteristics of NFGM without metal-oxide nano-particles.

Fig. 3 shows the subthreshold characteristics of an NFGM that does not contain metal-oxide nano-particles. The channel length and width are 10 and 20 μm, respectively. The subthreshold swing is approximately 158 mV/dec at a threshold voltage of 0.3 V [14]. Therefore, BPDA-PDA polyimide can be used as a gate insulator.

Fig. 4 (a) and (b) show the subthreshold characteristics of an NFGM containing metal-oxide nano-particles. We measured the characteristics of this NFGM at room temperature. The subthreshold swings estimated from I_d-V_g curves of figs. 4 (a) and (b) were about 390 mV/dec and 314 mV/dec, respectively. The degradation of subthreshold swings observed in figs. 4 (a) and (b) is probably due to the polyimide control gate insulator having a low dielectric constant. Additionally, the interface trap states at tunneling oxide/polyimide interfaces generate additional capacitance, which in turn degrades the subthreshold swing.

Fig. 5 shows the retention characteristics of the NFGM containing In_2O_3 and ZnO nano-particles. The stress voltages for programming and erasing the NFGM containing In_2O_3 nano-particles were at +10 and -15 V, respectively (See Fig. 5 (a)). The threshold voltage shift (ΔV_T) was about 5 V at the initial state of programming and erasing operations. However, the memory window rapidly decreased after 1000 s from 5 to 1.5 V. Furthermore, the retention characteristics of the NFGM containing ZnO nano-particles show the stress voltages of programming and erasing were fixed at +10 and -10 V, respectively (See Fig. 5 (b)). The ΔV_T was about 2 V

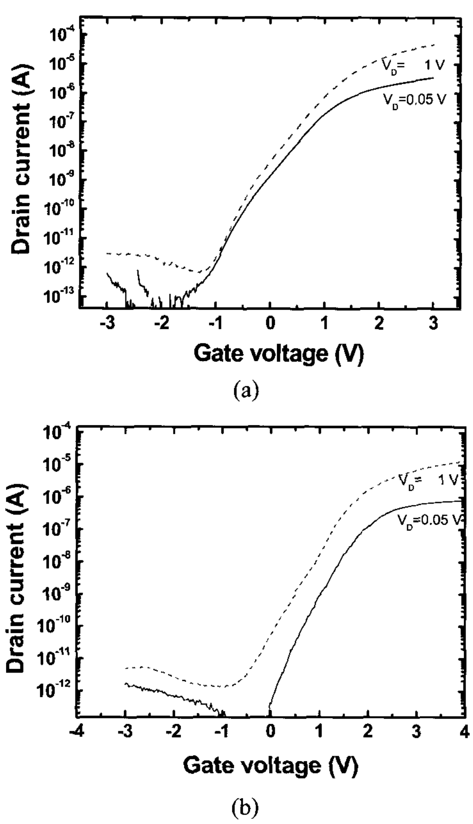

Fig. 4. I_d-V_g characteristics of NFGM containing (a) In_2O_3 and (b) ZnO nano-particles.

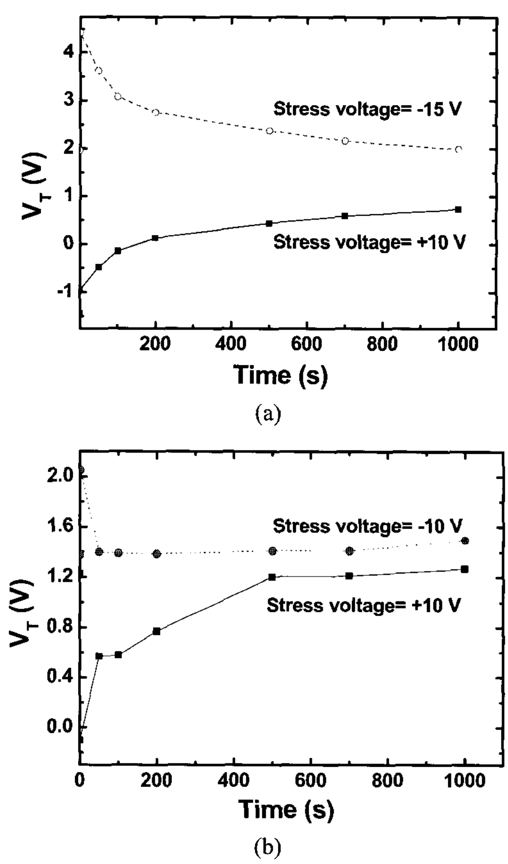

Fig. 5. Retention characteristics of NFGM containing (a) In_2O_3 and (b) ZnO nano-particles.

at the initial state, but the memory window was decreased after 1000 s from 2 to 0.4 V. Because the electrical properties of the polyimide control gate insulator and tunnel oxide were not optimized with metal-oxide nano-particles during the fabricating process of the NFGM, the leakage paths remained in the insulators. This caused the loss of stored charges from the In_2O_3 and ZnO nano-particles to the control gate or silicon substrate. Nevertheless, the electrical characteristics of the NFGM containing In_2O_3 and ZnO nano-particles embedded in polyimide layer mean that metal-oxide nanoparticles may still have applications in NFGM devices.

IV. CONCLUSIONS

We fabricated NFGM devices with In_2O_3 and ZnO nano-particles embedded in polyimide dielectrics. After curing at 400°C for 1 hour, the ZnO, In_2O_3 and SnO_2 nano-particles were spherical with an average diameter of 10, 7, and 15 nm, respectively. The particle densities were 2×10^{11}, 5.8×10^{11}, and 2.4×10^{11} cm^{-2}, respectively. The I-V characteristics mean that the NFGM devices with In_2O_3 and ZnO nano-particles embedded in polyimide have feasibility of applications in non-volatile memory applications.

To enhance the memory characteristics of such NFGM devices, the electrical properties of the polyimide control gate insulators and tunnel oxides need to be optimized.

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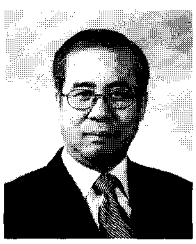

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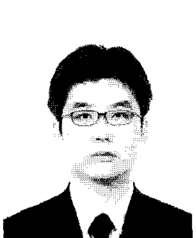

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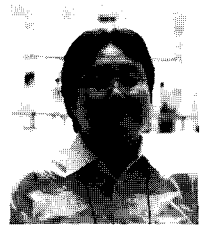

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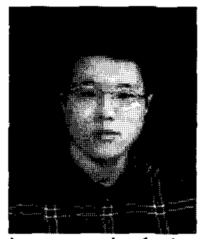

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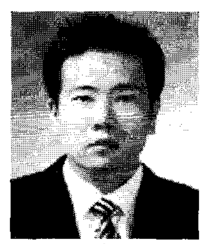

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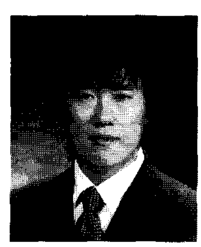

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