Improvement of charge storage characteristics on floating gated nonvolatile memory devices with In$_2$O$_3$ nanoparticles embedded polyimide gate insulator

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Nanofloating gate memory (NFGM) devices using In$_2$O$_3$ nanoparticles as charge storages embedded in polyimide gate insulator were fabricated. Self-assembled In$_2$O$_3$ nanoparticles were formed inside the polyimide matrix as a result of chemical reactions between indium ions and polymer precursors. The average diameter and the particle density were 7 nm and $6 \times 10^{11}$ cm$^{-2}$, respectively. The memory window of fabricated NFGM device due to the charging effect of In$_2$O$_3$ particles was larger than 4.4 V. The charge storage characteristics of NFGM devices with In$_2$O$_3$ nanoparticles embedded in polyimide gate insulator were significantly improved by the postannealing in a 3% diluted hydrogen in N$_2$ ambient. © 2007 American Institute of Physics. [DOI: 10.1063/1.2764558]

As the demands of high density integration and high performance nonvolatile memory for the applications of portable electronic devices are continuously increasing, the nanocrystal memory is proposed as one of the next generation nonvolatile memory devices due to the lower operation voltage and the better scalability.$^{1-4}$ Especially, the metal nanoparticles make the deep quantum wells between control oxide and tunnel oxide due to the difference of work functions.$^{5-7}$ However, there are serious limitations on the fabrication of metal nanoparticle floating gate memory associated with metal diffusion problem or deformation of metal nanoparticles during thermal processes. Recently, the fabrication of Cu$_2$O, ZnO, Fe$_2$O$_3$, or Ni$_{1-x}$Fe$_x$ metal nanoparticles embedded in polyimide layer and the nanofloating gate memory (NFGM) devices with metal oxide nanoparticles embedded in polyimide layer were reported.$^{8-13}$ Since the polyimide layer has good thermal stability and chemical endurance, it can be employed as a matrix of nanoparticles for NFGM. Additionally, the metal-oxide nanoparticles embedded in polyimide layer have attractive characteristics of high density, good uniformity, single layer controllability, and feasibility for NFGM applications. Particularly, the In$_2$O$_3$ nanoparticles embedded in polyimide layers have received much attention due to the nanoelectronic device applications such as the floating gated memories and the quantum-dot tunneling devices.$^{14}$ In this study, the NFGM devices using In$_2$O$_3$ nanoparticles embedded in polyimide gate insulator were fabricated and the charge retention characteristics were measured. In order to improve the electrical characteristics of the NFGM devices, the postannealing process in a 3% diluted hydrogen in N$_2$ ambient was carried out and the effects of postannealing were analyzed.

The NFGM devices consisting of In$_2$O$_3$ nanoparticles and polyimide gate insulator were fabricated on the p-type (100) UNIBOND silicon-on-insulator wafers with a 100 nm top silicon layer and a 200 nm buried oxide layer. The phosphorus in situ doped poly-Si layer of 100 nm thick was deposited on the top Si by low pressure chemical vapor deposition method at 650 °C for source and drain regions. After the formation of active region, the phosphorus doped poly-Si layer was partially removed out to define channel region and then the remained phosphorus doped poly-Si layer at the channel edge serves as source/drain of NFGM devices. Then the growth of tunnel oxide with 4.5 nm thick by dry oxidation and the deposition of indium layer with 5 nm thick by thermal evaporator were followed. The polyamic acid (PAA) layer with a thickness of 50 nm was spin coated on the thin indium layer. The PAA is a commercial biphényltertracarbonyl dihydride-phenylen diam (BPDA-PDA)-type (Dupont PI2610D) and is composed of BPDA-PDA in N-methyl-2-pyrrolidone (3 wt. %). The stacked PAA and indium layers were maintained at room temperature for 24 h in a desiccator to form the indium ions by chemical reactions between PAA layer and indium layer due to indium dissolving process. The curing process was carried out at 400 °C for 1 h after a soft baking of 135 °C for 30 min in the rapid thermal process system in N$_2$ ambient. The In$_2$O$_3$ nanoparticles were formed inside the polyimide matrix as a result of chemical reactions between indium ions and PAA. The Al gate electrode with a thickness of 150 nm was formed by thermal evaporation, photolithography, and aluminum etching processes. The structure of the In$_2$O$_3$ nanoparticles formed inside the polyimide layer was characterized by using FEI Tecnia-300 transmission electron microscope (TEM) system. The electrical characteristics of fabricated In$_2$O$_3$ NFGM such as subthreshold characteristics, output current characteristics, and data retention characteristics were characterized by semiconductor parameter analyzer HP 4156B. Finally, the fabricated NFGM devices were annealed by 3% diluted hydrogen H$_2$/N$_2$ ambient at 400 °C for 30 min in order to improve the charge storage characteristics of NFGM.
Figure 1(a) shows the cross-sectional TEM image of In$_2$O$_3$ nanoparticles embedded in polyimide layer after a curing process of 400 °C for 1 h. The average diameter and the density of In$_2$O$_3$ nanoparticles estimated from the plane-view TEM image were 7 nm and $6 \times 10^{11}$ cm$^{-2}$, respectively. Figure 1(b) shows the molecular structure of BDPA-PDA after a curing process. The In$_2$O$_3$ nanoparticles are formed during curing process by the chemical reaction between indium and PAA, and the dielectric constant of BPDA-PDA polyimide is known as 2.9–3.2.$^{15,16}$

Figure 2 shows the schematic of NFGM devices with In$_2$O$_3$ nanoparticles embedded in polyimide gate insulator. The source/drain regions were formed by using the phosphorus doped poly-Si before stacking the tunnel oxide/In$_2$O$_3$ nanoparticles/polyimide layers. The deposition temperature of indium evaporator system was controlled at the temperature under 200 °C to suppress the contamination of indium ion, because the indium ion makes a deep level between Si valance and conduction bands ($E_v+0.16$ eV). The channel length and width of fabricated NFGM are 10 and 20 μm, respectively.

Figure 3 shows the subthreshold characteristics and the output current characteristics of the fabricated NFGM with In$_2$O$_3$ nanoparticles embedded in polyimide gate insulator. The electrical measurements of NFGM were performed at room temperature. The subthreshold slopes were considerably improved from 370 to 158 mV/decade, and the threshold voltage were significantly shifted from −0.5 to 0.75 V after postannealing of 3% diluted hydrogen in N$_2$ ambient at 400 °C for 30 min, as shown in Fig. 3(a). This means that there are numerous positive charges in polyimide gate insulator as well as traps at the interface of tunnel oxide/polyimide, and the postannealing effectively reduces those charges and traps. Furthermore, the output current was improved from 22 to 150 μA/μm at $V_g-V_{th}=2$ V and $V_{ds}=2.5$ V, as shown in Fig. 3(b).
particles, the floating gate cells without In$_2$O$_3$ nanoparticles and the SiO$_2$/In$_2$O$_3$ nanoparticles and the In$_2$O$_3$ nanoparticle/ polyimide. In order to assure that the observed memory effect in fabricated NFGM is due to charging of In$_2$O$_3$ nanoparticles, the floating gate cells without In$_2$O$_3$ nanoparticles were also fabricated. Figure 4(b) shows the threshold voltage shift characteristics of NFGM devices without In$_2$O$_3$ nanoparticles. The change of $\Delta V_{th}$ was almost not observed although the stress voltages were changed from −10 to 10 V. Therefore, it is believed that the charging effects of fabricated NFGM mostly resulted from the In$_2$O$_3$ nanoparticles.

Figure 5 shows the retention characteristics on the In$_2$O$_3$ nanoparticles embedded NFGM and the effect of postannealing in H$_2$ diluted to 3% in N$_2$ ambient. A relatively large initial memory window of 2.6 V was obtained from the NFGM without postannealing for the stress voltage of +10 or −10 V. However, these devices revealed poor retention characteristics because the memory window rapidly decreased to 0.1 V after 10$^3$ s. On the other hand, the memory window and the retention characteristics were considerably improved after postannealing. The initial memory window of NFGM after postannealing was 4.4 V which is larger than that of the NFGM without postannealing. Also, the memory window of 1.4 V was maintained after 10$^3$ s. These improvements are associated with the reduction of interface traps and bulk traps in the stacked insulator layers.\(^{17}\)

In summary, the NFGM devices were fabricated with In$_2$O$_3$ nanoparticles embedded in BPDA-PDA polyimide gate insulator layer. The In$_2$O$_3$ nanoparticles with average diameter of 7 nm and density of about 6×10$^{11}$ cm$^{-2}$ were used as charge storages of NFGM. Also, the thermal oxide of 4.5 nm thick and the polyimide layer of 50 nm thick were stacked as the tunnel oxide and the control insulator, respectively. The postannealing in 3% diluted hydrogen (H$_2$/N$_2$) ambient at 400 °C for 30 min effectively decreased the trap density and improved the electrical characteristics of NFGM. Therefore, it is considered that the NFGM devices with In$_2$O$_3$ nanoparticles embedded in polyimide gate insulator are applicable to the next generation nonvolatile memory devices with high performance and integration density.

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