

Performance Enhancement of Colloidal Synthesis-Coated Au-Nanoparticle Nonvolatile Memory with Low Damage NH₃ Plasma Treatment on SiO₂ Tunneling Layer

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Abstract

A low damage NH₃ plasma treatment on SiO₂ tunneling layer has been proposed to improve the properties of non-volatile memories with colloidal synthesis-coated gold nanoparticles (Au-NPs). The built-in electric field by the introduction of nitrogen atoms within the tunneling oxide can enhance the program and data retention properties. Further, too much nitrogen incorporation will retard the binding of Au-NPs on tunneling oxide, leading to the low NP dot density and small memory window.

1. Introduction

Memory with the semiconductor and metal NPs is one of the promising candidates being applied in future non-volatile memory due to the prevention of high leakage current caused by the thin tunneling layer of the conventional floating gate flash memory [1]. Because of the large work function, the memory with metal NPs is suitable for the storage of electrons in quantum well [2]. Among them, memories with gold NPs (Au-NPs) have attracted lots of attention owing to the human body compatible for biomedical application. To fabricate this memory, colloidal synthesis method was demonstrated for room temperature processing [3]. Nevertheless, the memory characteristics of memories with colloidal synthesis coated Au-NPs were not good enough for high-density storage use [4]. In the work, the NH₃ plasma treatment on SiO₂ tunneling layer was proposed to improve the memory properties. To avoid the plasma damage, a filter was used to shield the UV light, which has been proved by Huang et al. [5]. The program and data retention properties can be effectively enhanced by the built-in electric field within the tunneling oxide.

2. Experimental

Memories with colloidal synthesis coated Au-NPs were treated by low damage NH₃ plasma on SiO₂ tunneling layer. First, n-type Si wafers were cleaned by a standard RCA clean. All wafers were thermally oxidized to grow a 3-nm-thick SiO₂ tunneling layer. Before performing the NH₃ plasma treatment, a filter was set up within the PECVD system, as shown in Fig. 1. Then, the NH₃ plasma treatment of 50 W for 1 to 5 min was performed on the SiO₂ film to introduce the nitrogen atoms. After that, a solution of 3-aminopropyltriethoxysilane (APTES) was dropped on SiO₂ layer, as displayed in Fig. 2. APTES was connected with SiO_x on the surface of SiO₂ and terminated in amino group. The un-reacted APTES were removed by ethanol and DI

water. Subsequently, a solution with Au-NPs (HAuCl₄) was added by drop-wise on the substrate, and amino groups will attract Au-NPs. A 10-nm-thick SiO₂ film was deposited by the PECVD system. Finally, a 300-nm-thick Al film was deposited by a thermal coater to form the gate electrode. The C-V curves were measured by HP4285 LCR meter and the gate pulse was supplied by using an HP8110A.

3. Results and Discussion

Fig. 3 shows the SEM planar images of Au-NPs with NH₃ plasma treatment for 1 to 5 min on SiO₂ tunneling layer. The software, ImageJ, was used for analyzing the dot density and size distribution of Au-NPs, as shown in Fig. 4. The average diameter of Au-NPs was roughly 12 nm for all samples. Nevertheless, due to the NH₃ plasma treatment, dangling bonds on SiO₂ surface were passivated so that functional groups of APTES were rarely connected, resulting in an one order decrease of Au-NP dot density. Fig. 5 presents the C-V curves of the control and 1min samples. The enhancement of programming speed can be ascribed to the formation of trapezoid band diagram of tunneling oxide layer after the NH₃ plasma treatment (Fig. 6). The programming characteristics were displayed in Fig. 7. With the NH₃ plasma treatment for more than 3 min, the programming was significantly degraded, owing to the decrease of Au-NP dot density as revealed in Fig. 4. Fig. 8 shows the retention performance of the memories. With the increase of plasma treatment duration, the charge loss can be improved. Both the low probability of electron lateral migration (Fig. 9) and the trapezoid band diagram of tunneling oxide will contribute to the enhanced retention properties. The activation energy (E_a) was extracted and depicted in inset of Fig. 8. No difference between each sample implies that the filter is effective to reduce the damage.

4. Conclusions

In this paper, the memories with Au-NPs were fabricated by the colloidal synthesis method. The memory properties were enhanced by using the low damage NH₃ plasma treatment on tunneling oxide. This improvement can be ascribed to the formation of trapezoid band diagram of tunneling oxide. However, too much nitrogen will reduce the dot density, contributing to the small memory window.

Acknowledgements

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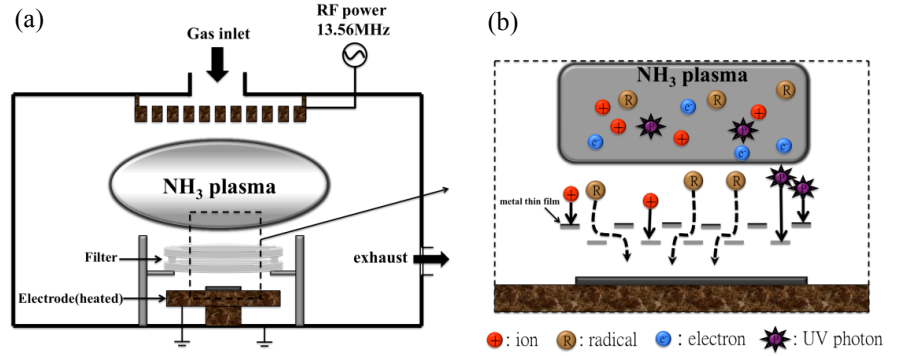


Fig. 1 (a) Low damage NH_3 plasma system with a filter to prevent UV radiation. (b) Zoom in area of plasma, filter and substrate.

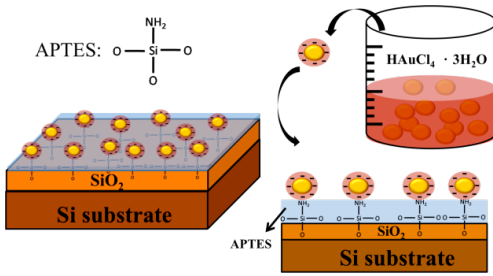


Fig. 2 Schematic diagram of Au-NPs formation by using the APTES for nanoparticle binding.

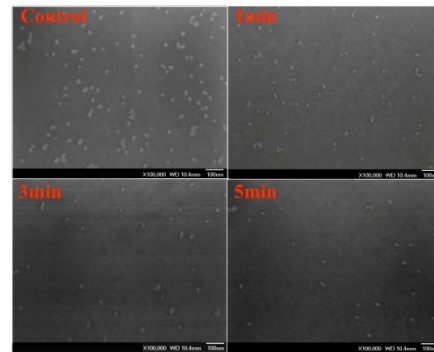


Fig. 3 Planar SEM images of Au-NPs with four NH_3 plasma treatment time on SiO_2 tunneling layer.

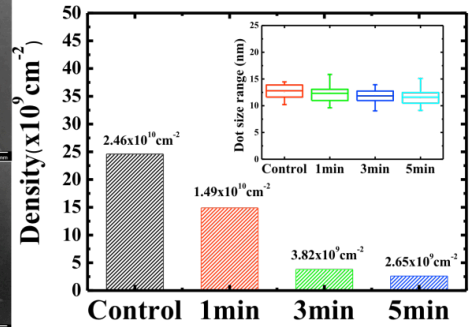


Fig. 4 Au-NP dot density with different plasma treatment time on SiO_2 tunneling layer. The distribution of dot diameter was shown in inset figure.

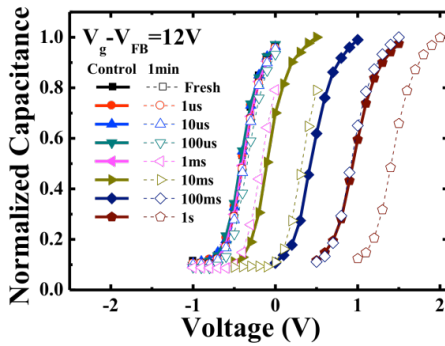


Fig. 5 C - V plot of programming speed for the memories without and with NH_3 plasma treated for 1 min. The samples were programmed at $V_g - V_{FB} = 12\text{V}$.

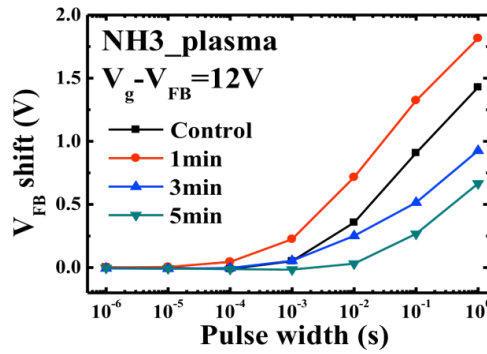


Fig. 6 Programming speed of the memories with different NH_3 plasma treatment time. The samples were programmed at $V_g - V_{FB} = 12\text{V}$. Optimized memory window was obtained at NH_3 plasma treatment for 1 min.

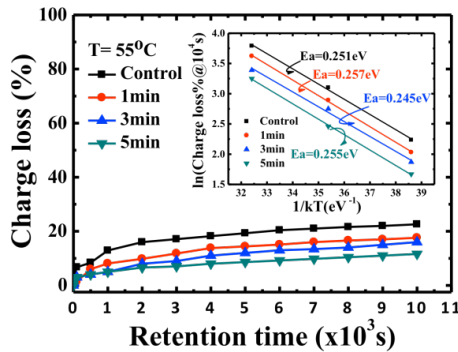


Fig. 8 Retention characteristics of the memories with Au-NPs treated by different NH_3 plasma treatment time at 55°C . The inset shows the activation energy of the memories.

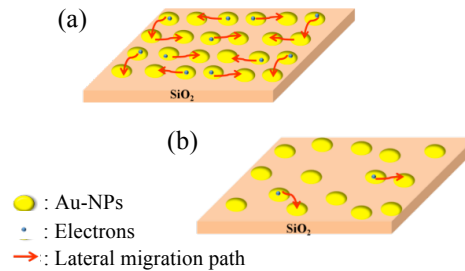


Fig. 9 Schematic diagram of lateral electron migration with (a) high and (b) low dot density of Au-NPs. The low dot density can improve the retention properties.

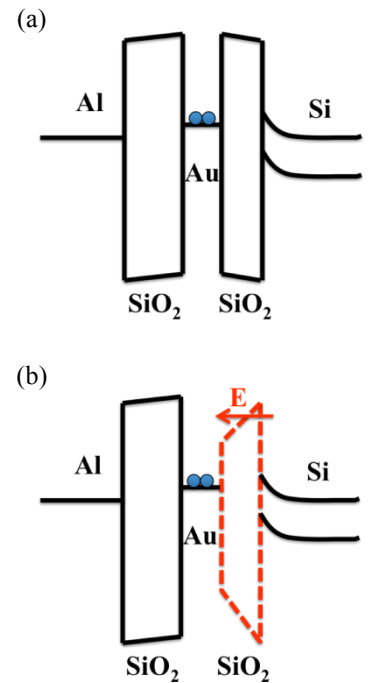


Fig. 7 Band diagram of the memories (a) without and (b) NH_3 plasma treatment. The trapezoid band diagram of tunneling oxide can be obtained to improve the program and retention properties.