Robust Gate-Injected-Operation of Gold Nanoparticle Nonvolatile Memory with Low-Damage CF₄-Plasma-Treated Blocking Oxide Layer

Yu-Hua Liu¹, Jer-Chyi Wang^{1,2,*}, Tsung-Chin Cheng³, and Chih-I Wu³

¹Department of Electronic Engineering, Chang Gung University, Guishan Dist. 33302, Taoyuan, Taiwan ²Department of Neurosurgery, Chang Gung Memorial Hospital, Guishan Dist. 33305, Taoyuan, Taiwan ³Institute of Photonics and Optoelectronics, National Taiwan University, Taipei 10617, Taiwan Phone: +886-3-2118800 ext.5784 E-mail: jcwang@mail.cgu.edu.tw

Abstract

Carrier injection polarity and data retention characteristics of gold-nanoparticle (Au-NP) nonvolatile memories (NVMs) with low-damage CF₄ plasma treatment on blocking oxide (BO) layer have been investigated. At positive gate bias, holes were injected from the gate into Au-NPs for the memories with CF₄ plasma treatment because of the band engineering of BO layer. The gate-injected holes stored at interface traps between Au-NPs and tunneling oxide layer present extremely low charge loss, promising for future NVM applications.

1. Introduction

Nanocrystal (NC) memory is one of the promising candidates being applied in future NVM due to the potential advantage of the prevention of high leakage current in conventional floating gate flash memory [1]. Among all the materials, Au-NPs have attracted lots of attention because of the high work function, low reactivity, high dot density, and uniform distribution [2]. Moreover, the gate-injected NVMs have been proposed to show better reliability properties compared to the substrate-injected cases [3]. In this work, a new approach to realize the gate injection of Au-NP NVMs was studied by using the CF₄ plasma treatment on BO layer. The holes injected from the gate at positive gate bias can be explained by the band engineering of BO layer and a superior data retention property of Au-NP NVMs is presented.

2. Experimental

The schematic structure of Au-NP NVMs with low-damage CF₄ plasma treatment was shown in Fig. 1(a). After a standard RCA clean, a 3-nm-thick SiO₂ layer was grown in furnace as the tunneling oxide (TO) layer. Next, a 2-nm-thick Au layer was deposited by a thermal evaporator and subsequently subjected to the RTA system to form the Au-NPs. After the Au-NPs had been formed, a 15-nm-thick SiO₂ layer was deposited by a PECVD system as the BO layer. Then, the CF₄ plasma treatment was performed in the PECVD system with a quartz filter embedded to reduce the plasma damage [4]. Finally, a 300-nm-thick Al film was deposited by a thermal evaporator and a gate was lithographically defined and etched. The *C-V* curves were measured by Keithley 4200-SCS and the gate pulse was supplied by Keithley 4225 to operate the devices.

3. Results and discussion

Fig. 1(b) shows the XPS analysis and the data suggests that the fluorine atoms indeed incorporate into the SiO₂ film, further influencing the band structure of BO layer. Fig. 2 presents the programming characteristics of Au-NP NVMs with and without CF₄ plasma treatment on BO layer. The holes injected from the gate at positive gate bias for the sample with CF_4 plasma treatment are observed. In Fig. 3, the energy from the valence band to vacuum level ($E_{\text{vac vb}}$) of SiO₂ film with and without CF₄ plasma treatment was analyzed by the UPS system. The values indicate that the fluorine incorporation can enlarge the band-gap of BO layer. Besides, the electron barrier height ($\Phi_{\rm B}$) between Al gate and BO layer with and without CF4 plasma treatment was extracted in Fig. 4. According to E_{vac_vb} and Φ_B , the energy band diagrams of the Au-NP NVMs without and with CF₄ plasma treatment are demonstrated in Fig. 5(a) and (b) respectively. The change of carrier injection polarity by fluorine incorporation can be referred to two mechanisms. First, a built-in electric field is established by the band-gap modification of BO layer, enhancing the gate injection efficiency. Second, the large $\Phi_{\rm B}$ of CF₄-plasma-treated samples implies the small hole barrier height between Al gate and BO layer, contributing to the increase of programming efficiency of holes injected from the gate. Fig. 6 shows the data retention properties of Au-NP NVMs without and with CF₄ plasma treatment. The sample with CF₄ plasma treatment shows an extremely low charge loss because the holes are stored at interface traps between Au-NPs and TO layer (Fig. 7).

4. Conclusions

In this study, the effects of CF_4 plasma treatment on BO layer of Au-NP NVMs are investigated. The holes injected from the gate at positive gate bias can be referred to the band engineering of BO layer. The superior data retention of CF_4 -plasma-treated Au-NP NVMs is proposed, suitable for the application in future highly-reliable NVM use.

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Fig. 1 (a) Schematic diagram of Au-NP NVMs with CF_4 plasma treatment on BO layer and (b) F 1s XPS spectra of SiO₂ films without and with CF_4 plasma treatment.



Fig. 2 Programming characteristics of Au-NP NVMs without and with CF_4 plasma treatment.



Fig. 3 UPS spectra of SiO_2 film without and with CF_4 plasma treatment. The band diagrams are shown in the inset figure.



Fig. 4 *I-V* characteristics and F-N fitting of Au-NP NVMs without and with CF₄ plasma treatment.



Fig. 5 Energy band diagrams of Au-NP NVMs (a) without and (b) with CF_4 plasma treatment on BO layer under positive gate bias.



Fig. 6 Data retention characteristics of Au-NP NVMs without and with CF_4 plasma treatment on BO layer.



Fig. 7 Energy band diagrams of Au-NP NVMs at retention state (a) without and (b) with CF_4 plasma treatment on BO layer.