Current Applied Physics 15 (2015) 535–540

Contents lists available at ScienceDirect

Current Applied Physics

journal homepage: www.elsevier.com/locate/cap

Charge storage characteristics of nonvolatile memories with chemically-synthesized and vacuum-deposited gold nanoparticles

Jer-Chyi Wang [a, *], Chin-Hsiang Liao [a], Chih-Ting Lin [a], Ruey-Dar Chang [a], Li-Chun Chang [b], Chih-I Wu [c], Jung-Hung Chang [c]

[a] Department of Electronic Engineering, Chang Gung University, Guishan Dist., Taoyuan City 33302, Taiwan
[b] Department of Materials Engineering and Center for Thin Film Technologies and Applications, Ming Chi University of Technology, Taishan Dist., New Taipei City 24301, Taiwan
[c] Graduated Institute of Photonics and Optoelectronics and Department of Electrical Engineering, National Taiwan University, Taipei 10617, Taiwan

ARTICLE INFO

Article history:
Received 23 September 2014
Received in revised form
26 January 2015
Accepted 5 February 2015
Available online 7 February 2015

Keywords:
Chemically-synthesized
Vacuum-deposited
Gold nanoparticle
Potential coupling

ABSTRACT

Carrier injection and charge loss characteristics of nonvolatile memories with chemically-synthesized (CS) and vacuum-deposited (VD) gold nanoparticles (Au-NPs) have been investigated. Compared to CS counterparts, the memories with VD Au-NPs exhibit a higher dot density of 3.77×10^{11} cm^{-2}, leading to a larger memory window. Further, the energy from valence-band edge to vacuum level (E_{VB_vac}) of tunneling oxide for the samples with CS and VD Au-NPs is found to be 9.04 and 9.85 eV respectively. The small E_{VB_vac} value of the memories with CS Au-NPs is resulted from the formation of a thin chemical oxide (SiO_x) on thermally-grown SiO_2 tunneling layer during the chemically synthesized process, contributing to a slow erasing behavior. Besides, the programming of the memories with VD Au-NPs is saturated at high gate bias, which has been well-explained by the electrons induced potential coupling between Au-NPs. Superior data retention property and high temperature dependence of charge loss are observed for the memories with CS Au-NPs, which can be ascribed to the thick tunneling oxide layer by the additional SiO_x film.

1. Introduction

Owing to the high demand of portable electronics, the high-density data storage of nonvolatile memory (NVM) has been extensively developed. The conventional structure of NVM is floating gate (FG), which has reached its physical limitation when the device scales [1]. The unaffordable leakage will contribute to the data retention and endurance issues. Thus, some emerging devices such as the silicon-oxide-nitride-oxide-semiconductor (SONOS) and nanoparticle-type memory have become more and more attractive because of the discrete charge storage concept to prevent the severe leakage [2–6]. It is known that the silicon nanoparticles (Si-NPs) have been used and implemented into mass production level for some embedded memory devices [7]. Moreover, metal nanoparticles with high work-function, like platinum (Pt) and gold (Au) NPs, are promising for the use of nanoparticle-type memory due to the deep potential well, high density of states (DOS) around Fermi level, and small perturbation against the quantum confinement effect [8,9]. The first merit of metal NPs theoretically leads to a long-term retention time because the electrons are confined in a three-dimensional quantum well and hardly escape. Though the metal NPs are not widely used in current complementary metal-oxide-semiconductor (CMOS) process, it is reported that the Au-NPs can be combined with the standard CMOS technology and used for the alternative devices beyond CMOS; for instance, C. Thelander et al. have presented a superior quantum behavior of the single electron transistors (SETs) with Au-NPs [10].

There are lots of methods proposed to form the metal nanoparticles. The way by using the chemically-synthesized (CS) method has been presented for electronic, optoelectronic, biosensing and biomedical applications [11–14]. The CS NPs perform nearly the same nanoparticle size for more uniform bio-related reactions. Another common method of forming metal NPs, called vacuum-deposited (VD), can be achieved by using the film deposition in a vacuum system followed by a suitable rapid thermal annealing process [15]. The VD NPs have been widely studied in semiconductor academia for electronic and optoelectronic use

* Corresponding author.
E-mail address: jcwang@mail.cgu.edu.tw (J.-C. Wang).

http://dx.doi.org/10.1016/j.cap.2015.02.010
1567-1739/

because of the ease of NP formation on wetting layers. Nevertheless, there is no in-depth study related to the charge storage characteristics of metal NPs formed by CS and VD methods for NVM application. In this work, the material, electrical and simulation analyses of the memories with CS and VD Au-NPs have been studied. The energy from valence-band edge to vacuum level of the tunneling oxide layer with CS and VD Au-NPs was obtained by ultraviolet photoelectron spectroscopy (UPS) and the dot size and density of Au-NPs were observed by scanning electron microscopy (SEM) images. A thin chemical oxide layer (SiO_x) formed on thermally-grown SiO_2 layer was observed for the samples with CS Au-NPs by the energy dispersive spectroscopy (EDS) and UPS analyses, contributing to the change of charge storage properties. The carrier injection and charge loss characteristics of the memories with CS and VD Au-NPs were examined and explained by the proposed energy band diagrams.

2. Experimental details

Memory devices with Au-NPs were fabricated on n-type (100) Si wafers by two different NP forming processes. After a standard Radio Corporation of America (RCA) cleaning procedure, a 3-nm-thick SiO_2 film was thermally grown in horizontal furnace at 850 °C in nitrogen and oxygen mixed ambience (99.999% purity) as the tunneling oxide (TO) layer. For the formation of VD Au-NPs, a 2-nm-thick gold film was deposited by a thermal coater at 10^{-6} Torr with a pure gold bullet (99.99% purity). The rapid thermal annealing was then performed in nitrogen ambient at 700 °C for 30 s to form the Au-NPs, as illustrated in the schematic diagram of Fig. 1(a). On the other hand, for the formation of CS Au-NPs in Fig. 1(b), the 3-aminopropyltriethoxysilane (APTES) was first drop-wisely added on SiO_2 film. After a 10-min waiting, all samples were rinsed in ethanol and de-ionized (DI) water to remove the un-reacted APTES. A $HAuCl_4$ solution with the Au nanoparticles for the size of 10 nm was then dropped on APTES and functionalized to from the Au-NPs on SiO_2 film [11]. After the Au-NPs had been formed, a 10-nm-thick SiO_2 film was deposited by the plasma-enhanced-chemical-vapor-deposition (PECVD) system in SiH_4 and N_2O ambient (99.999% purity) of the flow rate of 5 and 200 sccm respectively at 300 °C as the blocking oxide (BO) layer. The chamber of PECVD system was first pumped down to 3×10^{-5} Torr before fabrication and kept at 0.6 Torr with the radio frequency (RF) power of 100 W during the film deposition. Finally, a 300-nm-thick Al film was deposited by a thermal coater at 10^{-6} Torr with a pure Al bullet (99.9% purity). The gate electrode was defined by a photolithography technology and etched by a wet process to obtain an electrode diameter of 180 μm. The schematic structure of the memory devices with CS and VD Au-NPs was displayed in Fig. 1(c). The capacitance–voltage (C–V) curves were measured by using an HP4285 precision LCR meter, and the programming and erasing (P/E) characteristics were carried out by using an HP8110A pulse generator to supply the gate pulse. The Au-NP dot size and density were examined by using the SEM images. Besides, the UPS and EDS analyses were performed to obtain the energy band diagrams of the memories with CS and VD Au-NPs. The Sentaurus TCAD (Synopsys, Inc., 2012.12 Release) was also used to simulate the P/E characteristics of the memories.

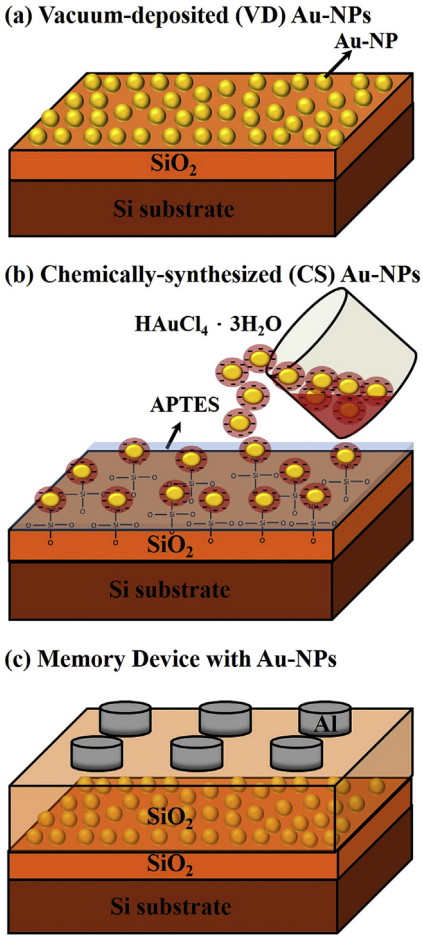

Fig. 1. Schematic structures of (a) vacuum-deposited (VD) and (b) chemically-synthesized (CS) process of Au-NPs, and (c) the final memory device with Au-NPs.

3. Results and discussion

3.1. Material analysis of gold nanoparticles

Fig. 2(a) and (b) demonstrate the SEM images of Au-NPs formed by VD and CS method respectively. Both of these two methods present significant and uniform Au-NPs formation. The analytical

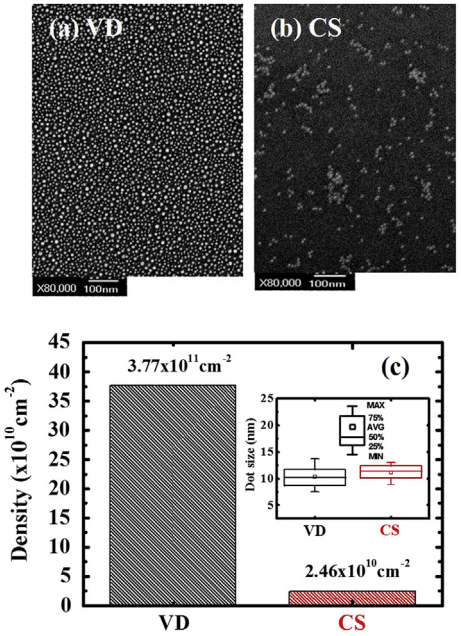

Fig. 2. SEM images of (a) VD and (b) CS Au-NPs, and the statistical distribution of (c) dot density and dot size of CS and VD Au-NPs. The data was analyzed by ImageJ.