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Monolayer FePt nanocrystal self-assembly embedded into atomic-layer-deposited Al_2O_3 films for nonvolatile memory applications

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ABSTRACT

A simple approach is developed to fabricate oxide/FePt nanocrystals/oxide composite films by a combination of chemically-synthesized FePt nanocrystals' self-assembly and atomic layer deposition for zultrahigh-density nonvolatile memory applications. A hexagonally arranged monolayer of well-monodispersed FePt nanocrystals with a grain size of 4.5 nm has been assembled onto atomic-layer-deposited Al_2O_3 oxide by solution-based dip-coating. The lattice constant of this two-dimensional pattern is about 8 nm with the high density of $1.8 \times 10^{12}/cm^2$. A fraction of the Fe is oxidized during annealing at 500 °C for 5 min in O_2 atmosphere, and the core–shell structure is formed with fcc-$Fe_{0.75}Pt$ nanocrystal core and amorphous Fe_2O_3 shell. The metal–oxide–Si capacitors with unannealed and annealed FePt nanocrystals embedded into Al_2O_3 films are electrically measured, and exhibit obvious memory effects with a hysteresis memory window of 4.1 and 8.1 V at the sweeping gate voltage of ±8 V, respectively. The enhanced memory window of samples with annealed FePt nanocrystals can be attributed to the existence of the Fe_2O_3 shell, which introduces additional interface and provides more trap sites for charge trapping storage.

1. Introduction

The floating gate (FG) is the primary technology for constructing flash memories [1]. With downscaling of the device feature size, conventional flash memories are facing a severe challenge as the thinner oxide allows greater tunneling leakage currents, degrading retention characteristics [2]. Because the FG is conductive, all charge will be lost if a leakage path appears in the tunneling oxide. Nanocrystals (NCs) have been proposed to replace the polycrystalline Si layer in the FG nonvolatile memories (NVMs) to achieve small operating voltages and improve reliability [3]. It is expected that dense and discrete NCs in the surrounding dielectric material will have high performance. There are many methods that can be used to form NCs for NVM applications [4]. However, it is very difficult to obtain well distributed NCs. Among various NCs memories, metal NCs memories have drawn much attention due to various advantages [5–14], such as a higher density of states around the Fermi level, stronger coupling with the conduction channel and smaller energy perturbation due to carrier confinement [15,16]. It is worth noting that alloyed FePt NCs have been fabricated by RF sputtering deposition for NVM applications [17,18]. In this method, the FePt alloy chips placed on a silicon oxide target were co-sputtered in RF sputtering equipment. Unfortunately, the FePt NCs had poor separation (~1 nm silicon oxide) in the lateral direction. The FePt alloy may be a promising candidate for NVMs because of its higher work function and good stability [19]. On the other hand, it is well known that atomic layer deposition (ALD) technology, which is based on sequential self-limited and complementary surface chemisorptions reactions, has been developed to deposit inorganic films with easy control of thicknesses down to submonolayer, excellent three-dimensional conformality, large area uniformity and a relatively low temperature process [20–22].

In this work, a new and simple approach that the chemically-synthesized FePt NCs were self-assembly embedded into ALD Al_2O_3 films for NVM applications was reported. The tunneling oxide Al_2O_3 layer was firstly deposited on n-Si (001) substrate by ALD, and then the face-centered cubic (fcc) FePt NCs were assembled onto Al_2O_3 layer by solution-based dip-coating. Next, a thick Al_2O_3 oxide layer was also deposited as a blocking oxide by ALD. A hexagonal FePt NCs assembly monolayer with well-monodispersity and high density of $1.8 \times 10^{12}/cm^2$ has been embedded in ALD Al_2O_3 oxide. Electrical measurement of the memory cells containing FePt NCs reveals a large hysteresis memory window of 8.1 V at the sweeping gate voltage of ±8 V.

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2. Experimental details

2.1. Preparation of FePt NCs

Monodispersed FePt NCs with a grain size of 4.5 nm were prepared by the chemical solution method [23–25]. $Pt(acac)_2$ and $Fe(CO)_5$ were used as the starting reagents. The detailed synthesis process has been described in Ref. [23]. The FePt NCs are stabilized with the surfactants of oleic acid (OA) and oleylamine (OAm). OAm binds to Pt through the amino group and OA binds to Fe through the carboxylic acid group [26]. Finally, the FePt NCs were dispersed in octane and stored in a glass bottle under nitrogen gas.

2.2. Preparation of Al_2O_3/FePt NCs/Al_2O_3/n–Si(001) stack structure

n-Type Si (001) wafers with a resistivity of 1–10 Ω cm were the starting substrates. A 4 nm-thick Al_2O_3 layer was deposited at 200 °C on HF-treated n-Si (001) substrates ($1.0 \times 1.0\ cm^2$) as the tunneling oxide by ALD using sources of $Al(CH_3)_3$ and H_2O. Then, self-assembled FePt NCs monolayer was obtained by dip-coating onto Al_2O_3 surface using 2 mg/mL FePt colloid dispersion (FePt NCs dispersed in octane) with small amounts of OA and OAm. Samples of self-assembled FePt NCs on Al_2O_3 coated TEM grids were also prepared for plan-view TEM observation. The resulting FePt NCs layer was dried, then annealed at 500 °C for 5 min under O_2 atmosphere by rapid thermal annealing. Finally, a 20 nm-thick ALD Al_2O_3 layer was fabricated as control oxide layer to obtain Al_2O_3/FePt NCs/Al_2O_3/n-Si(001) stack structure. Pt gate electrodes with spot area of $1.54 \times 10^{-4}\ cm^2$ were deposited on the surface of the stack layers by sputtering using a shadow mask. Silver glue was then spread on the back side of the Si substrates to act as the bottom electrodes.

2.3. Characterization

Surface morphology of the annealed FePt NCs-assembled layer was characterized by atomic force microscope (AFM, asylum research cypher scanning probe microscope). The phase of the annealed FePt NCs was characterized by means of X-ray diffraction (XRD, D/max 2000, Rigaku) using Cu Kα radiation ($\lambda = 1.5418$ Å) operated at 40 kV and 40 mA. The morphology, distribution, crystal structure of the FePt NCs layer (on Al_2O_3 coated TEM grids) were observed using a transmission electron microscope (TEM, Tecnai G^2 F20 S-Twin, FEI) operating at 200 kV. The cross-sectional TEM sample of the Al_2O_3/FePt NCs/Al_2O_3/n-Si(001) NCs-assembled thin stack layers was also examined. The chemical components were analysed via X-ray photoelectron spectroscopy (XPS, Thermo Fisher K-alpha) with a monochromatic Al Kα source ($h\nu = 1486.6$ eV) for excitation of photoelectrons. Charge effects were calibrated by setting the C 1s photoemission at 284.6 eV. Capacitance–voltage (C–V) measurements were performed using a Keithley 4200 semiconductor characterization system at room temperature after the fabrication of MOS capacitor.

3. Results and discussion

Fig. 1 shows the AFM topography image of the dip-coated FePt NCs on ALD Al_2O_3 film after annealing at 500 °C for 5 min in O_2 atmosphere. The FePt NCs are observed with uniform and dense distribution with the range of 0–6 nm in the vertical dimension, indicating a monolayer of FePt NCs. The XRD profiles of as-synthesized and annealed FePt NCs are illustrated in Fig. 2. They exhibit nearly same XRD patterns with two broad peaks at 39.8° and 46.3°, corresponding to the fcc-FePt (111) and (200) reflections, respectively. This implies that the fcc crystalline phase keeps unchanged after annealing of FePt NCs in O_2 atmosphere. Especially, as-synthesized and annealed FePt NCs show similar full width at half maximum (FWHM) of the XRD peaks, meaning that no obvious coalescence or sintering between FePt NCs occurs during annealing at 500 °C in O_2 atmosphere.

Plan-view and cross-sectional TEM was explored to characterize the morphology, distribution and crystal structure of FePt NCs on Al_2O_3 surface and the cross-sectional structure of memory cell. Fig. 3(a) presents an overview of uniformly distributed FePt NCs on Al_2O_3 surface without annealing. Hexagonally arranged monolayer lattice patterns can be easily identified with lattice constant of ~8 nm. And, the monodispersed FePt NCs are homogeneous with an average diameter of ~4.5 nm. The FePt NCs have a high density of $1.8 \times 10^{12}/cm^2$, in consistent with the observation by AFM. The high-resolution TEM (HRTEM) image in Fig. 3(b) clearly reveals the core–shell structure of the FePt NCs after annealing at 500 °C for 5 min in O_2 atmosphere. An average diameter of ~4.3 nm was obtained by measuring more than 100 different Fe_xPt NC cores from a HRTEM image. And, the measured thickness of the shells is about 1.3 nm. In comparison with the as-prepared FePt NCs, the NCs may lose some Fe element in the cores during annealing. Considering the FePt NCs' quasi-spherical shapes, it can be inferred that about 75% Fe element remains in the cores after annealing, and that the subscript X corresponding to the Fe concentration in the Fe_xPt cores is supposed to be 0.75. Fig. 3(c) shows a representative HRTEM image of one annealed Fe_xPt NC core. The only (200) lattice plane can be recognized, with lattice spacing of 1.95 Å, larger than that of bulk FePt and in good accordance with the above XRD results. The corresponding polycrystalline

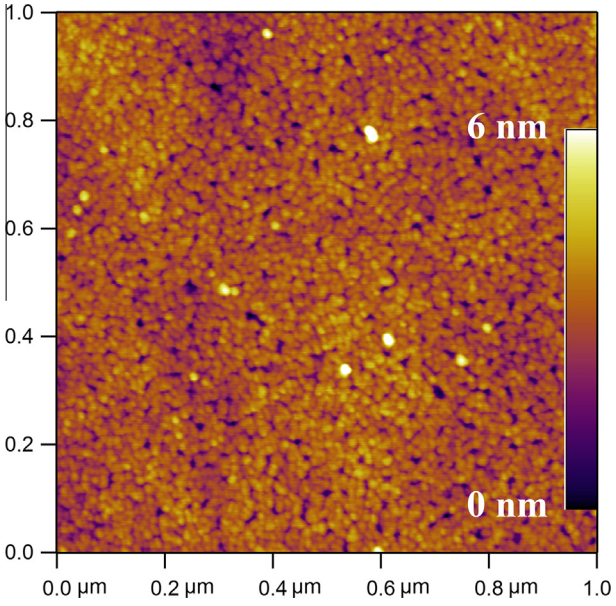

Fig. 1. AFM image of monolayer FePt NCs on ALD Al_2O_3 films after annealing at 500 °C for 5 min in O_2 atmosphere. The area is $1 \times 1\ \mu m^2$.

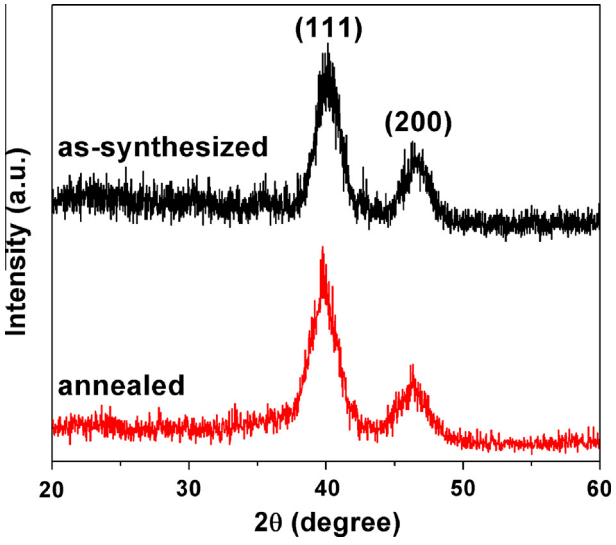

Fig. 2. XRD patterns of as-synthesized and annealed FePt NCs at 500 °C for 5 min in O_2 atmosphere.