



Development of all-solution-processed nanocrystal memory



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ABSTRACT

We developed an all-solution-processed nanocrystal memory containing high density ($\sim 1 \times 10^{12}$ particles·cm⁻²) Au-SiO₂ core-shell nanoparticles (NPs) within a uniform HfO₂ matrix. High-quality HfO₂ high-κ oxide composed of ultra-thin (<10 nm) tunnel and control oxide layers were prepared on a silicon substrate by the spin-on sol-gel process. The Au-SiO₂ core-shell nanocomposite was also constructed by solution process using 3-aminopropyltrimethoxysilane (APTMS) as a functional mediator. This APTMS provides dual functions: (1) to serve as a binder for catching colloidal Au NPs onto the HfO₂ substrate, and (2) to form a protective layer to cover up the Au NP core. The APTMS shell layer was well controlled through the self-assembly monolayer (SAM) layer-by-layer process with a self-limiting feature. It thermally decomposed into sub-nano thick SiO₂ shell by post-deposition annealing, playing a key role in surmounting the deficiency of HfO₂ for the use of both the tunnel oxide and the control oxide in the nanocrystal memory. This approach efficiently improved the application of a crystalline HfO₂ nano-film for electronic device. By elaborately integrating the solution processes of the HfO₂ oxide layer and the Au-SiO₂ core-shell NPs, a high-performance nanocrystal memory was obtained. This study demonstrated the potential of chemical solution process for nanofabrication application.

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1. Introduction

Silicon nanocrystals (NCs) were first introduced as a replacement for the conventional floating gate by Tiwari et al. for scaling of the nonvolatile memory structure [1]. To improve the performance, metal NCs were proposed due to their high density of states, strong coupling with the conduction channel, wide range of available work functions, and small energy perturbation due to carrier confinement [2–7]. Among the metal NCs formation techniques, the colloidal synthesis method has been shown to be effective for size/shape control of metal materials [8–11]. Several efforts have been made to investigate the device performance of metal NC memories embedded with colloidal Au, Pt, Ni, Co or W nanoparticles (NPs) for charge storage [12–16]. Otherwise, high-κ dielectrics, such as HfO₂, were also introduced to facilitate the equivalent oxide thickness (EOT) scaling, the interpoly leakage current reduction, and the field-sensitive tunneling of memory

device [17,18]. However, the ability of HfO₂ to suppress charge leakage would be low due to its relatively low barrier height, abundant oxygen vacancy and crystalline structure, leading to poor retention properties [19,20]. If the high-barrier oxide in the amorphous structure was used instead of HfO₂, a good charge retaining could be obtained, but the tunneling efficiency will be substantially decreased as the overall barrier profile is too high to induce a tunneling at a moderate voltage. Lo et al. has reported the charge storage characteristics of metal-oxide-semiconductor (MOS) structure containing Au NCs on a tunnel oxide composed of triply stacked SiO₂, HfO₂, and Al₂O₃ layers [19]. This MOS structure exhibited high charge injection and detrapping efficiency for program and erase operations with long-term charge retention. This high performance is attributed to the bandgap engineering of tunnel oxide with a multistacked concave barrier, from which the effective thickness of the tunneling barrier can be greatly reduced under a moderate bias, while a thick and high barrier is retained for charge retention.

In this paper, we developed an all-solution-processed nanocrystal memory containing Au-SiO₂ core-shell NPs within a crystalline HfO₂ matrix using a mass-productive spin-coating method.

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The important advantages of chemical solution process are high purity, good uniformity, lower processing temperature, precise composition control of multicomponent compounds, simple and cheap process equipment. However, it is difficult for chemical solution processed film with nano thickness to achieve superior property. In this study, the HfO₂ composed of ~5.4 nm tunnel oxide and ~9.5 nm control oxide behaved good electric property, while it was prepared by the cost-effective sol-gel method in comparison with the vacuum deposition technique [21]. The HfO₂ was fabricated by careful control of the sol-gel synthesis, the deposition processes, and the thermal conditions to achieve the high quality. The colloidal Au NPs were prepared by the reduction method and SAM on APTMS modified HfO₂ tunnel oxide. The grafting characteristic of APTMS on HfO₂ surface is critical for assembling high-density NPs with good uniformity. To construct the core-shell NPs, the APTMS was further assembled to cover up the NPs to form an APTMS shell. Both the quality of the APTMS layer on HfO₂ or Au NPs surface improved with the APTMS assembly cycles. Then, the APTMS layer thermal decomposed into amorphous SiO₂ shell by annealing to form an Au-SiO₂ core-shell nanocomposite. Core-shell NC memory devices have attracted interest because the shells have the ability to resist the thermal process and to fine-tune their properties [22–25]. The shell layer has been prepared by a variety of methods, such as thermal treatment of core NPs with exposure to O₂ ambient [22,23], chemical vapor deposition (e.g. atomic layer deposition) [24,25], and solution synthesized core-shell colloidal NPs [26–28]. O₂ annealing of NPs to form oxide shell is a simple method but highly limited by the core material. It is challenging for film deposition techniques to envelop the NPs in oxide with nanoscale thickness, high coverage, and nanoscale uniformity. Moreover, the chemical solution syntheses of colloidal core-shell NPs are usually complicated and contain anionic surfactants. In this present study, the sub-nanometer thick SiO₂ shell was developed using only APTMS molecule due to its self-limiting feature during SAM process. This APTMS mediated SiO₂ shell not only constructed a concave barrier structure along the vertical stack direction, but also built high barrier for suppressing charge migration between NPs. By integrating the solution processes of the HfO₂ oxide layer and the Au-SiO₂ core-shell nanocomposite with well controlled deposition and thermal conditions, a high performance nanocrystal memory containing Au-SiO₂ core-shell NPs within the HfO₂ matrix was obtained. The high-level retention characteristic of the device was discussed in terms of the distribution and stability of NPs, interface property and microstructure of NPs/HfO₂ matrix, and the bandgap barrier structure. Such a solution process developed by this study is valuable not only for memory but also for optical device application. It provides a simple method to construct an HfO₂/SiO₂/Au NPs nanocomposite, which is of interest for optical material [29–31].

2. Experimental section

2.1. Sample preparation

HF-dipped P-type (100) silicon wafer (Wafer Works Corp., Taiwan) was employed as the starting substrate. Hafnium chloride (HfCl₄, 99.9%, Aldrich, USA) was used as the precursor for the synthesis of HfO₂. A sol solution was first prepared by dissolving HfCl₄ in ethanol (water content < 0.01%). The coating solutions were then obtained by adding appropriate amounts of D.I. water (the molar ratio of HfCl₄:ethanol:D.I. water is 1:1500:15) with vigorous stirring for 2 h. Then, drops of the HfO₂ precursor were spin-coated onto the substrates at 3000 rpm for 30 s. The as-prepared samples were slowly heated on a hot plate from 50 to 450 °C in air to evaporate the solvent. The oxide quality is very

sensitive to this thermal condition. The HfO₂ oxide layers with designed thickness were achieved through repeating cycles. The deposition process of HfO₂ tunnel layers was repeated by 3 cycles. For HfO₂ densification, post-deposition furnace annealing was performed under O₂ at 900 °C for 60 s. A few drops of anhydrous ethanol (water content < 0.2%) solution of 1 mM APTMS (99%, Acros) were then added drop-wise onto the substrates, held for 10 min, and spun out by a spin coater. The substrates were heated at 100 °C for 20 min, following by washing the unreacted APTMS with ethanol and D.I. water. The head-groups of the hydrolyzed APTMS, Si(OH)₃, were chemisorbed on the oxide surface by reacting with OH groups, leading the amino group of APTMS to arrange upward [32]. The deposition of APTMS was conducted by 1–4 repeating cycles (1C–4C). Subsequently, an Au NPs solution was added drop-wise on the substrates, held for 10 min and spun out by a spin coater; finally, the substrates were rinsed with D.I. water and dried under N₂ flow. Au NPs were synthesized by NaBH₄ reduction of HAuCl₄·3H₂O in an ice bath condition [33]. 20 ml volume of ice-cold aqueous solution containing 1 mM HAuCl₄ (49.9%, Alfa Aesar) and 38.8 mM trisodium citrate (ACS grade, J.T.Baker) was prepared in a beaker. To this solution, 0.6 mL of 0.1 mM NaBH₄ (98.0%, Aldrich) solution was quickly added under vigorous stirring. The color of the solution changed from pale yellow to wine-red once the preparation was completed. As illustrated in Fig. S1, the transmission electron microphotograph shows that the Au NPs exhibited spherical shape with the particle size in the range of 3–5 nm. The Au NPs kept stable in solution by surface negative charges due to the absorbed citrate ions. When Au NPs solution was dropped onto the substrate, Au NPs absorbed to the positively charged aminated surfaces by electrostatic interactions [34]. After deposition of Au NPs, the sample was further covered by APTMS for 1–4 cycles. The synthesis process and deposition procedure of this APTMS were identical to those assembled on a substrate. Subsequently, it was covered by spin coating of HfO₂ control oxide layer (five repeating cycles) to construct a Si/HfO₂/APTMS/Au NPs/APTMS/HfO₂ memory structure. The synthesis process and heating procedure (50–450 °C) of HfO₂ control oxide was identical to those of tunnel oxide, but it was not conducted by a 900 °C high temperature annealing for preventing diffusion/reaction of Au atoms. Finally, the memory capacitor was further annealed at 500 °C in an O₂ atmosphere for 10 min to further improve oxide qualities.

2.2. Sample characterization

To analyze the physical characteristics of the Au NPs, the films, and the memory structure, we used UV–Vis spectrophotometer (UV–Vis, Perkin Elmer Lambda 35 UV, Waltham, Massachusetts, U.S.A), particle size analyzer (90PLUS, Brookhaven Instruments Corporation, Buckhead, Atlanta, U.S.A), field-emission scanning electron microscope (FESEM, S4800-II, Hitachi, Tokyo, Japan), X-ray photoelectron spectrometer (XPS, ULVAC-PHI PHI 5000 VersaProbe, ULVAC-PHI, Hagisono, Chigasaki, Kanagawa, Japan), atomic force microscope (AFM, Dimension Icon, Bruker, Billerica, Massachusetts, USA), field-emission transmission electron microscope (FETEM, JEM-2100F, JEOL, Tokyo, Japan), ellipsometer (J. A. Woolam/M44, Lincoln, USA), and X-ray diffractometer (XRD, Bruker D8, Bruker, Hardtstraße, Karlsruhe, Germany). For electrical analyses, the samples were followed by the deposition of 300 nm-thick Al to form both the gate electrode and the back contact. The top Al electrodes were thermally evaporated on the surface of HfO₂ films through a metal mask with holes of 0.2 mm in diameter. The area of the top electrode was determined by OM. The capacitance-voltage (C–V) measurements were conducted using an HP 4294A (Agilent, Santa Clara, California, U.S.A) capacitance meter at room temperature to investigate the electrical properties of the memory structure.

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