

Atomic Layer Deposition of Zirconium Oxide on Carbon Nanoparticles

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Abstract. In this report we describe preparation of structures containing carbon nanoparticles for potential applications in nonvolatile memories. The carbon nanoparticles were synthesized from 5-methylresorcinol and formaldehyde via base catalysed polycondensation reaction, and were distributed over substrates by dip-coating the substrates into an organic solution. Before deposition of nanoparticles the substrates were covered with 2 nm thick Al₂O₃ layer grown by atomic layer deposition (ALD) from Al(CH₃)₃ and O₃. After deposition of nanoparticles the samples were coated with ZrO₂ films grown from C₅H₅Zr[N(CH₃)₂]₃ and H₂O. Both dielectrics were grown in two-temperature ALD processes starting deposition of Al₂O₃ at 25 °C and ZrO₂ at 200 °C, thereafter completing both processes at a substrate temperature of 300 °C. Deposition of ZrO₂ changed the structure of C-nanoparticles, which still remained in a Si/Al₂O₃/C/ZrO₂ structure as a separate layer. Electrical characterization of nanostructures containing Al₂O₃ as tunnel oxide, C-nanoparticles as charge traps and ZrO₂ as control oxide showed hysteretic flat-band voltage shift of about 1V.

1. Introduction

Nonvolatile semiconductor memory based on storing electric charge in non-contacted floating gates is the dominant memory concept for portable devices [1] that assumes design of memories containing conductive nanodots in (multilayer) gate dielectrics. Applications discussed include the use of ZrO₂ with nanocrystal-embedded non-volatile flash memory devices [2].

In this work we describe the structures with carbon nanoparticles as possible charge traps between ZrO₂ as the control oxide and Al₂O₃ as the tunnel oxide layer grown by atomic layer deposition (ALD). The C-nanoparticles were embedded in Si/Al₂O₃/C/ZrO₂ structures as a separate two-dimensional layer. The idea about the inclusion of the C-nanoparticles into nanostructure was based on the knowledge that carbon is an easily accessible and inexpensive material with high work function



(4.6 eV) as well as on the expectation that C-nanoparticles may act like electron-trapping nanoparticles possessing metallic conductivity.

2. Experimental

The films were deposited in an in-house built atomic layer deposition (ALD) reactor [3] on planar SiO₂/Si and TiN_x substrates. Before deposition of C-nanoparticles all substrates were covered with 2 nm thick Al₂O₃ layer grown from Al(CH₃)₃ (98% Strem Chemicals) and O₃ in two-temperature ALD process starting deposition at 25°C (5 cycles) and completing at 300°C (20 cycles). The C-nanoparticles were covered with ZrO₂ films grown from C₅H₅Zr[N(CH₃)₂]₃ (Air Liquide, Inc.) and H₂O in two temperature ALD process applying first two cycles at 200°C and then 60 cycles at 300°C. Cycle times for C₅H₅Zr[N(CH₃)₂]₃ and H₂O process were 2-2-1-5 s. For Al(CH₃)₃ and O₃ process cycle times of 2-2-2-5 s were applied. The film thicknesses were around 2 nm for Al₂O₃ and 7 nm for ZrO₂. The carbon nanoparticles, deposited by dip-coating in organic solution, were synthesized from 5-methylresorcinol (99.9%, Carboshale Ltd., Estonia) and formaldehyde (37% solution in water, stabilized with 10-15% of methanol, Sigma-Aldrich) via base (Na₂CO₃, 99.8%, Sigma-Aldrich) catalysed synthesis in aqueous media [4] polycondensation reaction. The size of C-nanoparticles measured by small angle X-ray scattering (SAXS) was approximately 50 nm in the solution [5]. After dip-coating and following heating in the reactor up to 300°C the size of C-nanoparticles was 25-30 nm [5]. The film thicknesses were measured using a spectroscopic ellipsometer (SE) GES5-E (SEMILAB, Sopra). The phase composition of the Si/Al₂O₃/C/ZrO₂ structure was evaluated by grazing incidence (GIXRD) X-ray diffraction analysis. The phase composition of C-nanoparticles before and after deposition of ZrO₂ was studied by Raman spectroscopy using a Renishaw inVia micro-Raman spectrometer. The (surface) morphology was investigated by scanning electron microscopy (SEM) using a Dual Beam® equipment Helios NanoLab 600 (FEI Company). The focused ion beam (FIB) of the equipment was used for the preparation of samples for cross-section studies of the Si/Al₂O₃/C/ZrO₂ structures. Electrical characteristics were measured on TiN_x/Al₂O₃/C/ZrO₂/Ti/Al capacitors at room temperature using Hewlett Packard 4282A Precision LCR meter with a frequency range of 100 kHz to 1 MHz, whereby the capacitance-voltage (C-V) scan was made using voltage step of 0.1V and maximum bias voltage of 2 or 3V. The Al/Ti top electrodes of the capacitor structures with an area of 0.204 mm² each were prepared by e-beam evaporation of the metals through a shadow mask.

3. Results and discussion

The SEM analysis was used to explore the morphology of Si/Al₂O₃/C substrates covered by C-nanoparticles before (not shown) and after the ALD of ZrO₂ (Figure 1, left panel). The adhesion and coverage of C-nanoparticles was quite uniform all over the substrate. The mean diameter of the particles was ~45-60 nm. In order to evaluate the conformality, cross-section images of the Si/Al₂O₃/C/ZrO₂ structure were taken (Figure 1, right panel). C-nanoparticles were uniformly covered with ZrO₂ films and remained in the structure as a separate layer between Al₂O₃ and ZrO₂.

Figure 2 represents the grazing incidence (GIXRD) X-ray diffraction patterns of Si/Al₂O₃/C/ZrO₂ and Si/Al₂O₃/ZrO₂ nanostructures, i.e. the structures with and without C-nanoparticles, respectively. The ZrO₂ films grown to thicknesses of 7 nm otherwise consisted essentially of tetragonal (or cubic) phase. The film deposited on a sample without the C-nanoparticles between Al₂O₃ and ZrO₂ layers showed preferential (100) orientation while that deposited on C-nanoparticles did not (Figure 2). This difference is not surprising because complex surface shape of the sample with nanoparticles, differently from that of a planar surface of the Si/Al₂O₃/ZrO₂ structure, makes available all possible orientations of the thin film deposited on this kind of surface.

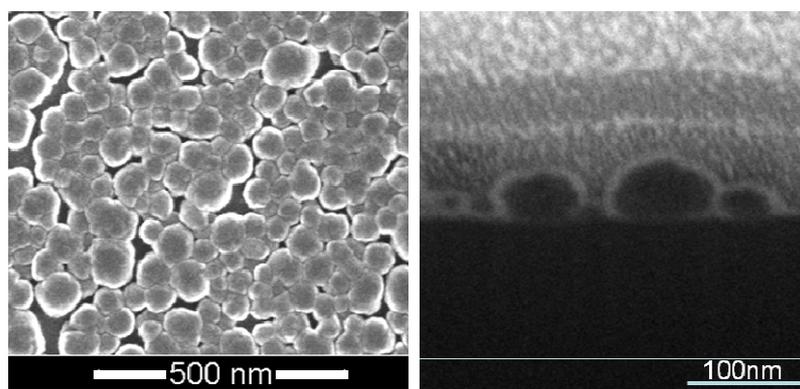


Figure 1. Representative bird-eye view (left panel) and SEM –FIB cross-section image (right panel) of the Si/Al₂O₃/C/ZrO₂ structure. C-nanoparticles were layered on 2 nm thick Al₂O₃ pre-deposited on Si substrate, and then covered with 7 nm thick ZrO₂.

Raman spectra taken from C-nanoparticles before and after deposition of zirconium oxide in Si/Al₂O₃/C/ZrO₂ nanostructures (Figure 3) demonstrated shifts in the peak positions after deposition of ZrO₂. Before deposition of ZrO₂ the characteristic peak apparent at 1590 cm⁻¹ indicated the formation of extremely small crystals of carbon-based materials which may be referred to as a monocrystalline graphite first described by Tunistra and Koenig [6] in 1970. In the Si/Al₂O₃/C/ZrO₂ structure the peak was much weaker and broader, and additional peaks at 1540 and 1640 cm⁻¹ appeared. A reason for these additional peaks is the activation of otherwise forbidden vibration modes by structural disorder [7,8]. Although the structure of C-nanoparticles changed during deposition of ZrO₂ the particles still formed of a separate layer in the structure similarly to that observed in our previous work [5].

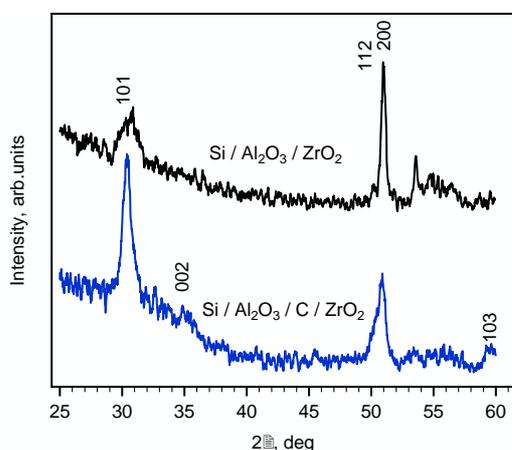


Figure 2. GIXRD patterns of zirconium oxides in Si/Al₂O₃/C/ZrO₂ and Si/Al₂O₃/ZrO₂ nanostructures. Miller indices of tetragonal phase are shown at the positions of corresponding reflections.

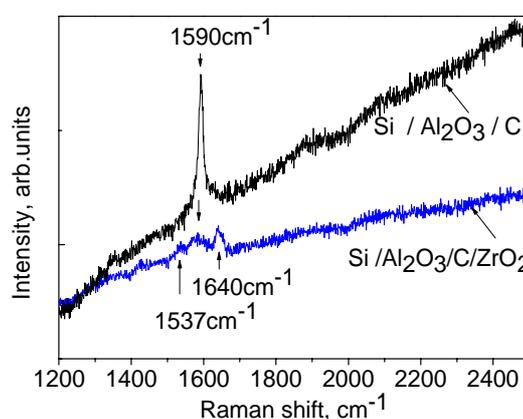


Figure 3. Raman spectra obtained from C-nanoparticles in Si/Al₂O₃/C and Si/Al₂O₃/C/ZrO₂ nanostructures. Only the region implying characteristic wavenumbers of carbon are shown.

Figure 4 shows the C–V curves of the TiN/Al₂O₃/C/ZrO₂ capacitors with the measurement frequency as the parameter. Capacitance density at 500 kHz of the structure at accumulation was 1.72 nF/mm² and hysteresis at 500 kHz was approximately 1V (Figure 4. inset). For comparison, capacitor structures with a single ZrO₂ film grown from C₅H₅Zr[N(CH₃)₂]₃ and O₃ did not show that wide

hysteresis at the same frequencies [8]. The flat-band shift in nanostructures with C-nanoparticles between tunnel and control oxides refers to certain memory effect.

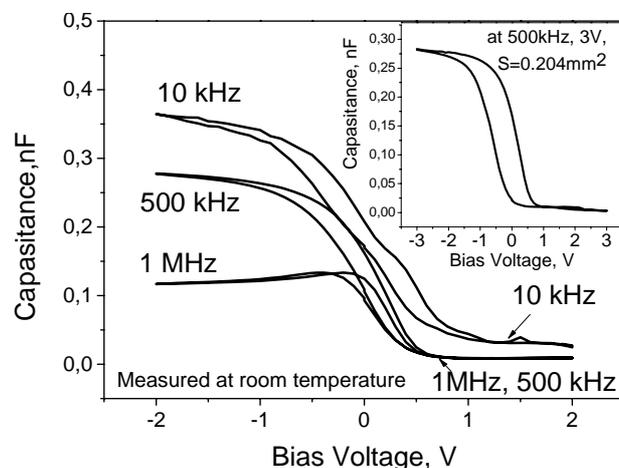


Figure 4. Capacitance-voltage characteristics of the $\text{TiN}_x/\text{Al}_2\text{O}_3/\text{C}/\text{ZrO}_2$ capacitors, the measurement frequencies are indicated by labels. Flat-band shift measured at 500 kHz are depicted by inset.

4. Summary

$\text{Si}/\text{Al}_2\text{O}_3/\text{C}/\text{ZrO}_2$ nanostructures consisting of Al_2O_3 adhesion layer, C-nanoparticles and ZrO_2 top layer were prepared. Upon deposition of ZrO_2 from $\text{C}_5\text{H}_5\text{Zr}[\text{N}(\text{CH}_3)_2]_3$ and H_2O at 300°C , the structure of C-nanoparticles was changed, but the carbon particles remained in a $\text{Si}/\text{Al}_2\text{O}_3/\text{C}/\text{ZrO}_2$ structure as a separate layer. C-nanoparticles were covered by ZrO_2 with good conformity and uniformity. The preferred growth phase of the ZrO_2 film was tetragonal (or cubic) in $\text{Si}/\text{Al}_2\text{O}_3/\text{C}/\text{ZrO}_2$ nanostructures. Electrical characterization of $\text{TiN}_x/\text{Al}_2\text{O}_3/\text{C}/\text{ZrO}_2$ nanostructures was conducted, revealing flat-band voltage shift, i.e. hysteresis in C-V curves reaching 1V.

Acknowledgments

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