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Interfacial modulation and electrical properties improvement of solution-processed ZrO_2 gate dielectrics upon Gd incorporation

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In this work, the band gap, interfacial properties and electrical properties of Gd doped ZrO_2 high-k gate dielectric films deposited by solution method have been systematically investigated. Results have shown that Gd doping can increase band gap energy from 5.65 to 5.92 eV and effectively restrain the formation of low-k SiO_x interfacial layer between dielectric and Si substrate. Moreover, the conduction band offset is increased from 2.57 to 3.06 eV by Gd doping, which effectively reduces the leakage current density to 1.8×10^{-6} A/cm^2.

1. Introduction

With the rapid development of ultra large scale integrate circuit (ULSIC), high k gate dielectrics are supposed to be replacements for conventional SiO_2 which is experiencing great challenges when the device downscales to ever-smaller dimensions, evidenced by severely poor reliability and high leakage current [1,2]. Materials such as ZrO_2, HfO_2, TiO_2, Al_2O_3, rare earth oxides are promising materials and have attracted considerable attention as gate dielectrics [3–10]. Except those high dielectric constant metal oxides, polymeric nanocomposites associated with high dielectric permittivity have also been promising materials applied in high-speed integrated circuits [11–13]. Among these materials, Zr-based oxide, a leading candidate for replacing SiO_2, has high dielectric constant (k~25), large band gap of ~5.8 eV and high thermal stability in contact with Si [14–16], which has stimulated further research to modify ZrO_2 and optimize its electrical properties for possible application in more advance CMOS technology. Recently, more attention has been attracted to modification of high-k materials by rare earth (RE) oxides, which can control the amount of oxygen vacancies, improve the interface quality and crystalline temperature, increase dielectric constant and modify electric structure. The result of Gd incorporation that helps increase band gap, conduction band offset and conduction band minimum, and reduce oxygen vacancies simultaneously has been reported by Xiong [17]. By far, the effects of RE modified ZrO_2, especially solution-processed Gd-doped ZrO_2 high k films which have been found to have fewer oxygen vacancies, greater band gap and better electrical properties compared with pure ZrO_2 are seldom reported.

Nowadays, solution-processed high-k gate dielectrics applied in thin-film-transistors is gradually attracting more attention. Compared with various deposition methods, solution processing is becoming a popular deposition method because of its simplicity, low cost, low processing temperature, easy controllability of chemical stoichiometry, and mass productivity [18].

In current work, Gd has been selected as a dopant for ZrO_2 via a solution-based route to improve the quality of interface between gate dielectric and Si substrate and modulate the electrical

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properties of gate dielectrics. The effects of Gd doping on the band gap, band offset, interfacial structure and electrical properties of ZrO_2 were comprehensively studied.

2. Experimental details

For Gd-doped ZrO_2(Gd:ZrO_2)solution, Zirconium oxychloride octahydrate ($ZrOCl_2 \cdot 8H_2O$) and Gadolinium nitrate hexahydrate ($Gd_2(NO_3)_3.6H_2O$) were chosen for the preparation of the precursor solution. $ZrOCl_2 \bullet 8H_2O$ and $Gd_2(NO_3)_3.6H_2O$ were dissolved in 2-methoxyethanol ($C_3H_8O_2$) and the concentration of precursor solution was controlled to be 0.1 M. The precursor solutions with different compositions (the mole ratio of Gd/(Zr + Gd) is 0%, 5%, 10% and 15%) were add with 6.67 M H_2O_2 and then stirred vigorously for 720 min using magnetic stirrer under room temperature. To get a clear transparent sol-solution, the solutions were filtered through a 0.22 μm syringe filter before spin coating.

2.1. Film characterization

Gd doped ZrO_2 films were deposited on *n*-type Si and glass substrates by spin-coating. Before deposition, *n*-type Si(100) and glass substrates with a resistivity of 2–5 Ω cm were pr-cleaned by a modified RCA (Radio Corporation of American) to remove any organic compounds and other impurity element. Then, silicon wafers were dipped in 1% buffered HF solution to remove any native oxide. Finally, the Si and glass substrates were dried by N_2 gun and cleaned by Ar plasma to get a hydrophilic surface. The thin films were deposited by spin-coating at 5000 rpm for 25 s. The sol-gel equipment is Spin Master 100 which is manufactured by SHANGHAI CHEMAT ADVANCED CERAMICS TTECHNOLOGY CO, LTD. After deposition, there was a soft bake to evaporate the organic solvent. The spin-coated Gd:ZrO_2 films were soft baked at 240 °C for 5 min and then cooled to room temperature. At the end, all the samples were annealed in vacuum ambient at 400 °C for 120 s. These film thicknesses were confirmed by spectroscopic ellipsometry (SE, SC630, SANCO Co, Shanghai). The film composition and interface information of Gd:$ZrO_2$with Si substrate were invested by X-ray photoelectron spectroscopy (XPS, ESCALAB 250Xi Thermo Scientific) equipped with Al Kα radiation source (1487.6 eV) and all the collected data were corrected with the binding energy of C 1s peak (284.8 eV). Another group of Gd:ZrO_2 films deposited on quartz wafers were used to explore the optical properties. The deposition process was repeated 6 times. The absorption was measured using an Ultraviolet–visible spectroscopy (UV–vis, Shimadzu, UV-2550).

2.2. Metal insulator semiconductor (MIS) device fabrication

To investigate the electrical properties, MIS capacitors composed of Al/Gd:ZrO_2/Si/Al structures were fabricated. The Al top electrode was deposited above Gd:ZrO_2 film as a metal gate electron via shadow mask with diameter of the circular aluminum of 200 μm by direct current sputtering. On the back side of the sample, Al film was also deposited as a back electron. Electrical characteristics are extracted by capacitance-voltage (*C-V*) and current-voltage (*I-V*) measurements. A semiconductor device analyzer (Agilent B1500A) combined with Cascade Probe Station was used for *C-V* and *I-V* measurement at room temperature. Short circuit and open circuit calibration were performed before real measurements. Sinusoid signal with high frequency of 1 MHz was superimposed upon a direct current (DC) voltage which was applied between top and bottom electrodes. And the DC voltage was swept from negative to positive or back and forth to perform single and double sweeps. Additionally, the leakage current properties were measured by Agilent B1500A. All the electrical tests were performed in a dark box.

3. Results and discussions

3.1. Interfacial properties analysis

The binding energy profile and chemical composition of Gd:ZrO_2 samples were investigated by XPS. The binding energy has been calibrated by centering the C1s at 284.8 eV. As shown in Fig. 1, survey spectra showed signals related to Zr, Gd, O, Si, and C components. The chemical composition of each Gd:ZrO_2 thin film investigated by XPS was proportional to the Gd and Zr content, which indicates the Gd is successfully incorporated into the ZrO_2 film.

The O 1s core level XPS spectra are demonstrated in Fig. 2. Using

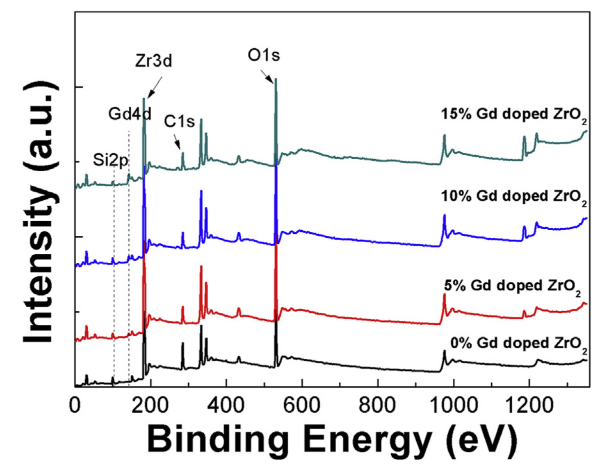

Fig. 1. Wide survey XPS spectra of the Gd doped ZrO_2 film on Si substrate.

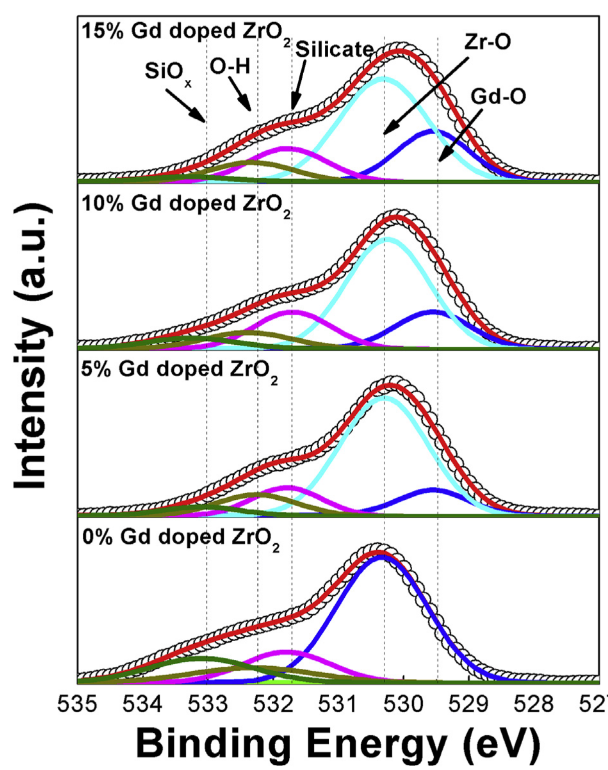

Fig. 2. O 1s XPS spectra of Gd:ZrO_2/Si stack.