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Influence of Mg ion concentration in ZrO_2 gate dielectric layered silicon based MOS capacitors for memory applications: Thorough understanding of conduction processes

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ABSTRACT

Various high-κ metal-oxide-semiconductor (MOS) capacitors with different concentrations of Mg doped ZrO_2 ($Mg:ZrO_2$) gate dielectric on p-type silicon (100) substrates were fabricated by using electron beam evaporation. A uniform and crack free dielectric layers of $Mg:ZrO_2$ having RMS surface roughness in the range from 0.25 to 0.83 nm were achieved. The dielectric layers were structurally and electrically studied. Structural analysis from GIXRD and Williamson-Hall plots revealed that Mg incorporation into ZrO_2 lattice has stabilized the tetragonal phase and the residual strain in the tetragonal stabilized $Mg:ZrO_2$ layers had increased with increasing Mg concentration. Elemental composition studies of different layers in the MOS capacitors using Rutherford backscattering spectrometry (RBS) revealed the presence of very thin, unintentional and non-stoichiometric SiO_x interfacial layer between dielectric and semiconductor interfaces. Thickness of the $Mg:ZrO_2$ dielectric layers in the MOS capacitors measured by using RBS and cross-sectional field-emission scanning electron microscopy was in the range from 44.7 to 96.6 nm. A high dielectric constant of 29.8 with the equivalent oxide thickness of 6.5 nm was achieved in the 5 mol% $Mg:ZrO_2$ dielectric layer. The hysteresis in the C-V characteristics of the MOS capacitors has been explained in detail based on the interactions of Mg ions with oxygen vacancies in the dielectric layer. Various conduction mechanisms have been elucidated to explain the leakage currents in the MOS capacitors. The decrease in Schottky and Poole-Frenkel barrier heights at the lower voltages (0 to − 3V) was found responsible for the increase in the leakage current as the Mg ion concentration was increased. Space charge limited conduction mechanism has been found to be dominant in larger applied voltage region (− 3V to − 10V). The Fowler-Nordheim tunneling and trap-assisted tunneling were dominant at the higher negative voltage regions greater than − 10V.

1. Introduction

As the metal oxide semiconductor technology is progressing day by day, there is a high demand for compact and low power consuming microelectronic devices. Scaling down the MOS devices can improve the speed and performance of the device with high packing density and reduced power consumption. A quantum tunneling limit has been reached by the conventionally used SiO_2 gate dielectric material where large leakage currents became a serious issue. Replacing SiO_2 layer with high-κ materials by achieving the desired equivalent oxide thickness with relatively higher physical thickness is a key solution to this problem. Various studies on high-κ materials such as HfO_2, ZrO_2, Al_2O_3, Ta_2O_5, TiO_2, $HfSiO_4$ and $ZrSiO_4$ have been done to replace SiO_2 dielectric layer and to reduce the leakage currents [1–8]. Presently HfO_2 is a leading commercial material as a gate dielectric in silicon CMOS industry [9,10] due to its excellent thermal stability with silicon, high dielectric constant value (~25), high heat of formation, wide band gap and reasonable band gap offsets with silicon. Similarly, ZrO_2 is also a promising material as like HfO_2 since both of them have similar physical properties as Zr and Hf falls in the same group of periodic table and have almost same ionic radii due to lanthanide contraction in Hf ion. Moreover, ZrO_2 can be cheaply available as compared to HfO_2; therefore it became a material of our interest to investigate as a gate dielectric in MOS devices for memory storage applications. The ZrO_2 is a high melting point ceramic material having a dielectric constant of about 22. In addition to microelectronic applications, it also has a wide range of applications such as biomaterials in prosthodontics [11] and orthopedics [12]; solid electrolyte materials [13]; thermal barrier

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coatings [14]; and high reflectivity mirrors [15], beam splitters [16] and edge filters [17] in optical devices.

ZrO_2 has mainly three different thermodynamically stable polymorphs [18]; generally it exists as in monoclinic phase at lower temperatures (< 1200 °C) and transforms into higher symmetrical tetragonal phase in the temperature range between 1200 and 2370 °C and further finally transforms into highest symmetrical structure as cubic phase at higher temperatures (> 2370 °C) [19]. A much higher crystalline stability of zirconia at lower temperatures can be achieved by doping cations (such as Y^{3+}, Ca^{2+}, Mg^{2+} and Ce^{3+}) of larger ionic size and lower charge state than zirconium ion. Sayan et al. [20] showed that tetragonal phase stabilization of ZrO_2 has increased its dielectric constant and as well as band gap of the material which has in turn improved channel mobility and reduced the gate leakage currents of a silicon based MOSFET. Sasaki et al. [21] have achieved an equivalent oxide thickness of less than 1.5 nm by using 8 mol% yttria stabilized zirconia as a gate dielectric material. Achieving equivalent oxide thickness in sub-nanometers with less leakage current is the present challenge in high-κ materials. A smallest leakage current of about 10^{-10} A/cm^2 has been reported by Jeong et al. [22] using amorphous yttria stabilized zirconia as gate dielectric layer.

Recent studies showed that the thin films of MgO of band gap 7.8 eV are thermodynamically stable directly with the silicon substrate. Vangelista et al. [23] have studied their electrical properties of the MOS capacitors with MgO as a gate dielectric material which showed a dielectric constant of 11 and a leakage current density of 2×10^{-4} A/cm^2. Additionally, the mechanical and optical properties of MgO-ZrO_2 composite thin films deposited in different partial pressures of oxygen have been studied by Jena et al. [17] where the refractive index of the films are found to be increased with increasing partial pressure of oxygen up to 1×10^{-4} mbar and decreased when further increasing the partial pressure. Hence Mg^{2+} ions in ZrO_2 gate dielectric could improve the electrical properties of silicon MOS capacitors by increasing the dielectric constant of gate material and reduce the gate leakage currents. Therefore, incorporating Mg^{2+} cations into ZrO_2 gate dielectric layer and their effect based on dopant concentration on the dielectric constant and leakage currents in the silicon based MOS capacitors have been investigated in this present work.

2. Experimental

Thin films of Mg doped ZrO_2 (Mg: ZrO_2) on a (1 × 1 cm^2) p-type Si (100) substrates with a resistivity of 8–10 Ω cm were deposited by using electron beam evaporation technique (Model: 12A4D, Make: Hind High Vacuum Pvt. Ltd., India). Silicon wafers were cleaned with a three step standard RCA procedure [24–27] where they were first dipped into a solution of NH_4OH, H_2O_2 and H_2O prepared in the volume ratio of 1:1:5 respectively (SC-1) for 10 min, then into the HF solution prepared with 1:30 vol ratio of hydrofluoric acid and H_2O respectively for 30 s, and finally into a solution of HCl, H_2O_2 and H_2O in the volume ratio of 1:1:5 respectively (SC-2) for 10 min. The wafers were immediately cleaned in flowing water for 5 min after each step. Followed by cleaning, the silicon wafers were dried with argon gas flow and used as substrate for the thin film deposition. The target pellet used in the thin film deposition were prepared from the 600 °C annealed powders of 0, 3, 5, 8 and 10 mol% Mg: ZrO_2 synthesized by co-precipitation method [28]. Zirconiumoxychloride ($ZrOCl_2 \cdot 8H_2O$) and magnesium nitrate ($Mg(NO_3)_2 \cdot 6H_2O$) were used as initial precursors and NH_4OH solution as precipitating agent in the co-precipitation reaction. These powders were pressed under uniaxial pressure of 5 t to get a dense pellet that was used as target for e-beam evaporation. While depositing thin films, a base pressure of 10^{-5} mbar and working pressure of 8×10^{-5} mbar were maintained and the thickness of the films was monitored in-situ by quartz digital thickness monitor. The substrate to target distance was kept at 25 cm. The current in the electron beam gun was varied between 120 and 150 mA at a constant voltage of 5.2 kV. Since this work deals with the structural properties of polycrystalline Mg doped ZrO_2 thin films and the crystallization temperature of these films were found below 500 °C as revealed by Differential Scanning Calorimetry (see Fig. S1 in supplementary information), all the as-deposited thin films were post annealed at 500 °C. Finally the thin films were made into (Ag/Mg: ZrO_2/Si/Ag) MOS structure by depositing thermally evaporated Ag on top of the film and bottom of the substrate for electrical contacts.

Thin films were structurally characterized by grazing incidence x-ray diffraction (GIXRD) by using a Rigaku Smart Lab X-ray diffractometer. The grazing incidence angle was kept at 0.5° and 2θ scan was performed from 20° to 80° with a step size of 0.01° and a scanning time of 0.15 s/step. With the same X-ray diffractometer facility, X-ray reflectivity (XRR) studies were performed with the thin films. An incident parallel beam of X-rays of 0.05 mm width was used with the help of Soller slit and 2θ/ω scan was performed in an angular range of 0.2–10° with a step size of 0.01°. The experimental data obtained from XRR was fitted using Globalfit software [29] in order to study the internal physical properties of thin film layers such as density, layer thickness and roughness. Rutherford Backscattering Spectrometry (RBS) measurements were done using a beam of $^4He^+$ particles (α-particles) with 2 MeV energy which was made incident on the thin films in RBS where 1.7 MeV tandetron accelerator (High Voltage Engineering Europa) was used to accelerate the α-particles. The elemental compositions of the thin films layers along with layer thickness and density were studied by fitting the experimental RBS data by using SIMNRA software [30]. The cross-sectional thicknesses of the thin films were studied by imaging using an ultra high resolution scanning electron microscope (ZEISS Gemini Ultra 55). Atomic force microscopy (Bruker Dimension Icon AFM) in a tapping mode was done to know the topography and surface roughness of the thin films. The MOS capacitors were electrically characterized where the capacitance-voltage characteristics were obtained using Agilent E14980A LCR meter with an AC signal of 1 kHz frequency and 1 V; and the gate voltage was swept from + 2 to − 2 V and vice-versa. The current-voltage characteristics of the MOS capacitors were obtained by using Kiethley 238 current source meter where the leakage currents were measured by applying gate voltage in the range from 0 to - 15V.

3. Results and discussion

3.1. Structural analysis

The Mg:ZrO_2 thin films were structurally characterized using GIXRD as shown in the Fig. 1 where the diffraction patterns confirmed the polycrystalline nature of the thin films. The thin films of ZrO_2 containing 0 mol% Mg had a mixed phase of both monoclinic and tetragonal crystal structures. The obtained diffraction peak positions are matched with the ICDD data corresponding to the monoclinic (card no.: 01-083-0944) and tetragonal (card no.: 01-079-1765) phases. Each diffraction peak in the Fig. 1 corresponding to a crystallographic plane is marked with its corresponding miller index. As it can be noticed from the XRD patterns shown in Fig. 1, the thin films of Mg:ZrO_2 with 3, 5, 8 and 10 mol% Mg have a single phase of tetragonal crystal structure. Thermal analysis by using Differential Scanning Calorimetry (see Fig. S1 in supplementary information) showed that the crystallization temperatures of Mg doped zirconia nano-particles with various Mg concentrations were found below 500 °C. It can be confirmed from DSC and XRD that incorporation of Mg ions into the ZrO_2 matrix has stabilized the tetragonal phase of zirconia thin films when post annealed at 500 °C. Jing et al. [31] had depicted the crystallization temperature of Sc stabilized zirconia at 455 °C. The crystallization temperatures in ZrO_2 depend on the amount of dopant ions and ionic radius of the dopant [32].

The crystallite sizes and micro-strains in the crystal lattice were found by using Williamson-Hall (W-H) plot shown in Fig. 2. The linear fit in the plot follows Eq. (1), and accordingly, using the slopes and y-