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Electrical characteristics of mixed Zr–Si oxide thin films prepared by ion beam induced chemical vapor deposition at room temperature

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ABSTRACT

Mixed Zr–Si oxide thin films have been prepared at room temperature by ion beam decomposition of organometallic volatile precursors. The films were flat and amorphous. They did not present phase segregation of the pure single oxides. A significant amount of impurities (–C–, $–CH_x$, –OH, and other radicals coming from partially decomposed precursors) remained incorporated in the films after the deposition process. This effect is minimized if the Ar content in the O_2/Ar bombarding gas is maximized. Static permittivity and breakdown electrical field of the films were determined by capacitance–voltage and current–voltage electrical measurements. It is found that the static permittivity increases non-linearly from ~4 for pure SiO_2 to ~15 for pure ZrO_2. Most of the dielectric failures in the films were due to extrinsic breakdown failures. The maximum breakdown electrical field decreases from ~10.5 MV/cm for pure SiO_2 to ~45 MV/cm for pure ZrO_2. These characteristics are justified by high impurity content of the thin films. In addition, the analysis of the conduction mechanisms in the formed dielectrics is consistent to Schottky and Poole-Frenkel emission for low and high electric fields applied, respectively.

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1. Introduction

The continuous downscaling of advanced integrated circuits requires the reduction of the gate oxide thickness in metal-oxide-semiconductor (MOS) devices. Today, in conventional SiO_2 based MOS devices, it has been reached the limit in which the leakage current between the gate and the substrate presents a major concern. The substitution of SiO_2 by other dielectrics with higher permittivity and good electrical isolation characteristics will allow the use of higher physical thickness and reduce the leakage current. Among other candidates, ZrO_2 [1] and mixed Zr–Si oxides are currently investigated for this purpose due to their electrical performances [2] and also because they are thermodynamically stable when in contact with silicon [3]. In this context, obtaining flat, compact and amorphous films at room temperature is specially indicated. It is also worth mentioning that ZrO_2 has been proposed to be integrated as high permittivity (high-*k*) gate dielectric into molecular transistors [4].

The use of ion beams to assist the growth of oxide dielectric materials by the decomposition of volatile precursors leads to the formation of amorphous, compact and smooth thin films [5]. However, if the deposition is performed at room temperature, impurities (–C–, $–CH_x$, –OH, and other radicals coming from partially decomposed precursors) could be incorporated into the films. The presence of these impurities may influence the ideal electrical performance of the final devices.

In this paper we report on the electrical characteristics of mixed Zr–Si oxide thin films produced by ion beam induced chemical vapor deposition (IBICVD) at room temperature. This technique has been previously used to produce the single SiO_2 [6,7] and ZrO_2 [8] oxides and other mixed oxide as titanium aluminates [9] or titanium silicates [10]. The permittivity and band gap energies in the mixed oxides have been correlated to their local structure. On the other hand, the dielectric strength of the films as well as the deviations of the typical MOS capacitance–voltage characteristic have been correlated to the presence of impurities linked to the preparation procedure. In addition the conduction mechanisms have been identified.

2. Experimental details

Mixed Zr–Si oxide thin films ($Zr_xSi_{1-x}O_2$ with $0<x<1$) have been prepared at room temperature by ion assisted decomposition of triethoxysilane $(CH_3CH_2O)_3SiH$ (TrEOS) and zirconium tetra-tert-butoxide $Zr[OC(CH_3)_3]_4$ (ZTB) volatile precursors. These precursors are extensively used in the literature to grow pure silicon oxide, zirconium oxide and zirconium silicates due to their high vapour pressure at room temperature [10–13]. They were dosed into the reactor (base pressure $\sim 1\times10^{-4}$ Pa) using leak valves with partial

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pressures in the range between 5×10^{-4} to 2×10^{-3} Pa. A broad ion beam source (HFQ 1303-3), excited by a RF discharge of O_2/Ar mixtures at about 1×10^{-1} Pa total pressure, was used to supply bombarding ions with 400 eV. The partial pressure ratio of the of the bombarding gases $P_{Ar}/(P_{Ar}+P_{O2})$ was set to 0.85. The ion beam current density measured at the sample position was about 5–10 μA/cm^2. In these conditions, the deposition rate was ~1 nm/min. Thin films with thicknesses in the range of 50 to 400 nm were produced. More experimental details regarding the deposition technique can be found elsewhere [5,14].

Thin film composition was obtained by combined ion beam analysis (IBA) techniques using the 3 MV tandem accelerator of National Center for Accelerators (Seville, Spain). Rutherford backscattering spectrometry (RBS) was used for absolute Zr, Si and Ar quantification using $^4He^{2+}$ or $^4He^+$ beams with energies from 1.0 to 3.0 MeV with a surface barrier detector set at 165°. The absolute amount of carbon and oxygen was determined by nuclear reaction analysis using $^{16}O(d,p_1)^{17}O$ and $^{12}C(d,p)^{13}C$, with energies 890 and 980 keV respectively, with a surface barrier detector set at 150° and a 13 μm Mylar filter to avoid that backscattered deuterons reach the detector. For the H quantification we used elastic recoil detection analysis with a 3.0 MeV $^4He^{2+}$ beam, with a surface barrier detector set at 35° and a 13 μm Mylar filter to stop the scattered alpha particles.

Fourier transform infrared (FTIR) spectra were collected in transmission at normal geometry under dry nitrogen atmosphere in a Nicolet 510 spectrometer with an energy resolution of 0.15 cm^{-1}. Double side polished intrinsic Si(100) wafers (resistivity>5000 Ω cm) were used as substrates for this analysis to avoid absorption in the infrared region. The microstructure of the films was examined by scanning electron microscopy (Hitachi FEGSEM S-5200, 5 kV operating voltage). Surface roughness was evaluated with atomic force microscopy (AFM) with a Nanotec apparatus working in non-contact mode. X-ray reflectivity (XRR) characterization was performed with a Siemens D5000 diffractometer using a standard Cu anode. XRR simulations were performed with a REFSIM code supplied by Siemens.

Surface chemical analysis of the thin films was performed by means of X-ray photoelectron spectroscopy (XPS). Photoelectrons were detected with a PHOIBOS100-5MCD electron spectrometer using an unmonochromatised Al K_α excitation source and 40 eV pass energy. With the same apparatus, reflection electron energy loss spectroscopy (REELS) measurements were performed using 1500 eV electrons. The band gap energy E_g of the samples was obtained after analysis of the REELS spectra using OPTEELS software [15].

The capacitance–voltage (C–V) and current–voltage (I–V) characteristics of the films were evaluated on mixed Zr–Si oxide films deposited on polished *n*-type Si(100) wafers with an electrical resistivity of 1–5 Ω cm. Capacitors were formed with either Al contacts deposited by evaporation or Pt contacts deposited by magnetron sputtering over a mask with 2×10^{-3} cm^2 area holes. The static permittivity of the films was obtained from measurements of capacitance at 100 kHz in the accumulation regime using an ESI2150-LCR apparatus. Breakdown electrical fields were evaluated using the ramp voltage stress method to the capacitors.

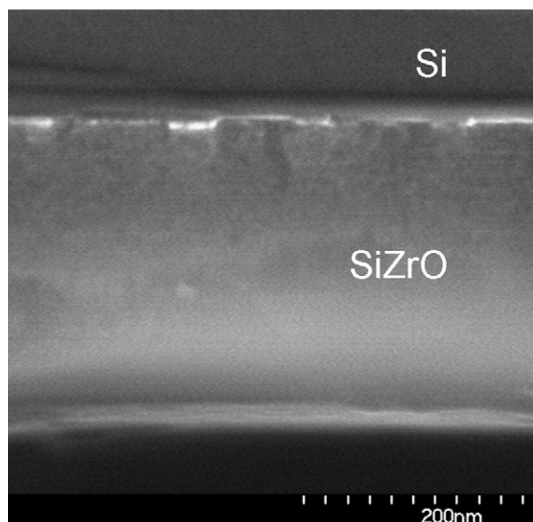

Fig. 1. Cross sectional SEM image of a mixed Zr–Si oxide prepared by IBICVD at room temperature.

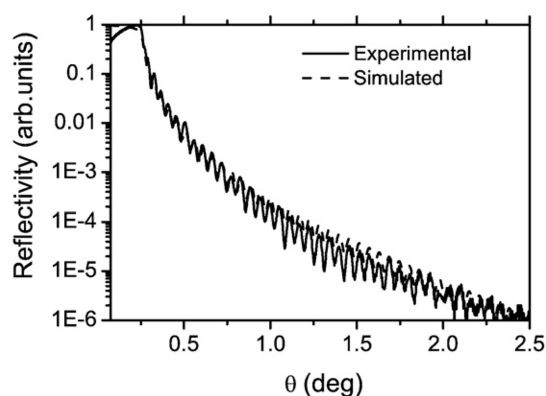

Fig. 2. XRR measurement and fit corresponding to a $Zr_xSi_{1-x}O_2$ ($x=0.55$) thin film.

3. Results

3.1. Microstructure

Fig. 1 shows a cross sectional SEM image of a typical mixed Zr–Si oxide thin film prepared by IBICVD at room temperature. This particular case corresponds to a $Zr_xSi_{1-x}O_2$ film with $x=0.3$ and thickness of 265 nm. The sample appears nearly featureless, without any clear granular or columnar structure. Standard Bragg–Brentano diffraction measurements (not shown) were consistent with a fully amorphous structure in the films.

Fig. 2 shows the XRR signal of a 75 nm thick Zr–Si–O film and the corresponding simulation. It is deduced that the density of this film is 4.1 gr/cm^3 and the interface roughness is about 0.4 nm. This analysis confirms that the substrate–film interface is rather sharp and that the films have low roughness, despite their high thickness. These results are consistent to AFM characterization of the same sample, where the root mean squared roughness obtained in a 5×5 μm image was typically below 0.2 nm.

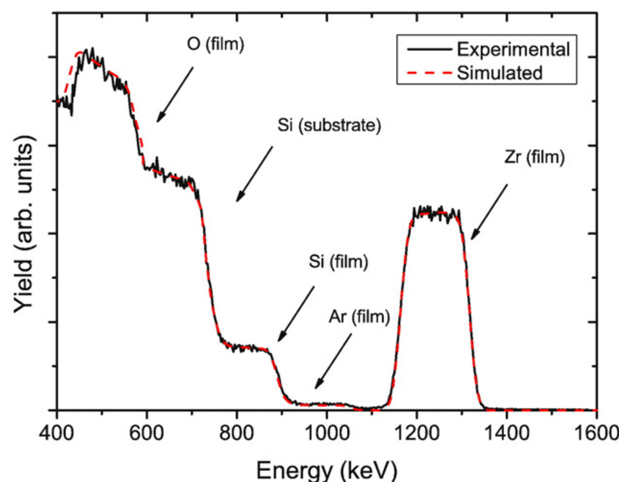

Fig. 3. RBS measurement of a $Zr_xSi_{1-x}O_2$ ($x=0.30$) thin film deposited on a Si wafer and the corresponding SIMNRA simulation.

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