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Structural and electrical properties of HfO_2/Dy_2O_3 gate stacks on Ge substrates

E.K. Evangelou [a,*], M.S. Rahman [a], I.I. Androulidakis [a], A. Dimoulas [b], G. Mavrou [b], K.P. Giannakopoulos [b], D.F. Anagnostopoulos [c], R. Valicu [d], G.L. Borchert [d]

[a] Laboratory of Electronics-Telecommunications and Applications, Department of Physics, University of Ioannina, 45110-Ioannina, Greece
[b] Institute of Material Science, NCSR «Demokritos», 15310-Athens, Greece
[c] Department of Materials Science and Engineering, University of Ioannina, 45110-Ioannina, Greece
[d] FRM II of the Technical University of München, D-85747 Garching, Germany

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ABSTRACT

In the present work we report on the structural and electrical properties of metal–oxide–semiconductor (MOS) devices with HfO_2/Dy_2O_3 gate stack dielectrics, deposited by molecular beam deposition on p-type germanium (Ge) substrates. Structural characterization by means of high-resolution Transmission Electron Microscopy (TEM) and X-ray diffraction measurements demonstrate the nanocrystalline nature of the films. Moreover, the interpretation of the X-ray reflectivity measurements reveals the spontaneous growth of an ultrathin germanium oxide interfacial layer which was also confirmed by TEM. Subsequent electrical characterization measurements on $Pt/HfO_2/Dy_2O_3$/p-Ge MOS diodes show that a combination of a thin Dy_2O_3 buffer layer with a thicker HfO_2 on top can give very good results, such as equivalent oxide thickness values as low as 1.9 nm, low density of interfacial defects ($2–5\times10^{12}$ eV^{-1} cm^{-2}) and leakage currents with typical current density values around 15 nA/cm^2 at $V_g = V_{FB} - 1V$.

1. Introduction

The challenge of the semiconductor and integrated circuits industry is to increase the high frequency performance of logic devices keeping at the same time the power consumption low. Bulk hole and electron mobility of Ge are 4.2 and 2.6 times higher than those of Si [1]. In particular, the bulk hole mobility of Ge is the highest of all Group IV and III–V semiconductor materials and this is the main reason why it is currently considered as an excellent alternative to the standard Si-based MOS technology [2–4]. Although high-k dielectrics have beneficial effects on the gate leakage current, they degrade channel mobility slowing down the speed of devices. High mobility substrates such as Germanium can help overcome mobility degradation and further increase performance. In addition, due to lower bandgap, Ge transistors can be operated at lower threshold voltage which could significantly reduce power consumption. Recently, many high-k gate dielectrics (Al_2O_3 [5], ZrO_2 [1,6], HfO_2 [1,7]) on Ge have been thoroughly studied and show promising results in terms of low equivalent oxide thickness (EOT) and enhanced hole mobility. Among these, HfO_2 seems to be one of the most promising candidates for the aggressive scaling of complementary-MOS (CMOS) devices. A key advantage, is that its dielectric permittivity κ is found to be very high, close to the bulk value of 25 [8], which is considerably higher in regard to the values typically obtained when HfO_2 is deposited on Si (κ~15–20).

During the last few years, many attempts have been made to grow ultrathin films of high dielectric constant (high-κ) oxides, such as HfO_2 on Ge (100) substrates. One of the main limitations in integrating germanium, is the formation of a hexagonal GeO_2 interfacial layer (IL) which is thermodynamically unstable and water-soluble, as opposed to SiO_2, hence making it practically unsuitable for device fabrication [1,9,10]. Various approaches [11–13] to limit the interfacial layer growth between HfO_2 and Ge have been shown to have a minor or even no effect, making the interfacial layer seemingly inevitable [14]. As a result, forming a high quality interface between an oxide and a Ge substrate remains a challenge.

The use of rare-earth oxides could be an attractive approach to the passivation problem [15]. It has been shown that combining rare-earth oxides with HfO2 improves EOT and gate leakage, retaining at the same time the good electrical properties of the interface [16]. The growth of an interfacial rare-earth oxide layer which will act as a buffer layer between the Ge surface and the HfO_2 dielectric is also extensively studied from a number of groups with encouraging results [17–19]. A number of these oxides, such as La_2O_3, CeO_2, Gd_2O_3, and Dy_2O_3, can be deposited directly on Ge with improved electrical characteristics [20,21]. Lanthanide oxides have been known to provide various advantages such as good thermal stability, moderate values of the dielectric constant; high conduction offset and low interface trap density [22]. However, their hydroscopic nature could lead to moisture retention and subsequent

* Corresponding author.
E-mail address: eevagel@uoi.gr (E.K. Evangelou).

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reaction with water and, therefore, imposes some challenge in integration issues. At the same time, cerium oxide has been shown recently to improve Ge passivation [23,24] and FETs characteristics [25], but, still, its low bandgap of about 3.3 eV [26] gives rise to leakage current issues.

Finally, regarding Dysprosium oxide, although it has been reported as the least reactive with water and thermodynamically stable with Si [27], preliminary attempts to utilize it in high-κ MOS systems were not successful. However, recent electrical results on HfO_2/Dy_2O_3/n-Ge MOS diodes have demonstrated the potential use of this gate stack in advanced MOS devices [28]. The leakage current density is very low (~15 nA/cm^2) and the capacitance equivalent thickness is calculated [29] to values comparable with the ones observed when HfO_2 was deposited on Ge with ultrathin GeO_xN_y interfacial layer [2]. These structures are a promising candidate in the future high-speed electronics industry. In this work an attempt to investigate the best combination in thickness and potential scaling of HfO_2/Dy_2O_3 gate stack on Ge (100) substrates is presented.

2. Experimental procedure

Dy_2O_3/HfO_2 oxide stacks were prepared by molecular beam deposition (MBD) on p-type Ge (001) with resistivity of ~0.02 Ω cm. Native oxide was desorbed in situ under ultra high vacuum conditions by heating the substrate to 360 °C for 15 min. Subsequently, the substrate was cooled down to 225 °C where the oxide stacks were deposited. The surface was exposed to atomic O beams generated by an RF plasma source with the simultaneous e-beam evaporation of Dy/Hf at a rate of about ~0.15 Å/s. Four different oxide stacks were prepared and their physical properties are given in Table 1.

The film structure was studied by means of X-ray diffraction (XRD) measurements in the Bragg–Brentano geometry. A copper X-ray tube at a high voltage of 40 kV and a current of 40 mA was used on a Bruker AXS D8 diffractometer at FRM-II of the Technical University of München. The thickness of each film was evaluated from high-resolution X-ray reflectivity (XRR) measurements. A 4-bounce Ge (220) Bartels monochromator was used to select the intense monochromatic Cu Kα_1 radiation and to highly collimate the beam. The reflected photon intensity is measured by a NaI scintillation counter with Be window.

The transmission electron microscope (TEM) used was a Philips CM20 with high-resolution and Energy Dispersive X-ray Spectrometry capabilities. The TEM sample preparation consisted of mechanical thinning and Ar ion milling.

Metal–insulator–semiconductor capacitors were finally prepared by shadow mask and e-beam evaporation of 30 nm-thick Pt electrodes to define circular dots, 200 µm in diameter, while the back ohmic contact was made using eutectic InGa alloy. The current–voltage (*I–V*) curves were measured at room temperature with a Keithley 617 Electrometer, where the voltage step used ranged from 20 mV to 50 mV. The capacitance–voltage (*C–V*) and conductance–voltage (*G–V*) measurements were carried out at room temperature with the assistance of an Agilent 4284A LCR meter. All samples were placed in a light-tight, electrically shielded box.

3. Results and discussion

3.1. Structural characterization

3.1.1. X-ray diffraction measurements

Fig. 1 illustrates the X-ray diffraction patterns of the as-deposited films. A diffraction is observed for all samples at 31.71°, which corresponds to the “forbidden” (200) diffraction of Cu Kα from Ge, due to multiple diffraction. The full width at half maximum (FWHM) of the Ge (200) line is equal to 0.1°, determining the angular resolution of the diffractometer at 30°.

Broad and faint peaks are observed for scattering angles between 28° and 30°, which are attributed to Bragg diffraction from crystal planes of the thin films. This reveals the existence of nanocrystallites, while the peak position of the diffraction lines allows the determination of the phase of crystallization. Fitting the diffraction peaks by a single Gaussian, the peak positions are determined with an uncertainty of ±0.1°, while the FWHMs are found one order of magnitude broader than the Ge (200) width, suggesting crystal size effects and/or strain. No diffraction peak is observed in the case of sample #3, mainly because of the extremely thin oxide layers present.

Sample #1 shows a broad diffraction peak at 30.0° (Fig. 1) with FWHM of 2.2°, which is attributed to the dysprosia crystallization. The crystal structure of bulk Dy_2O_3 is cubic with a lattice parameter of $a = 10.665$ Å, according to the JCPDS No. 22-0612 [30]. The most intense peak corresponds to the diffraction of X-rays from the (222) plane and for the Cu Kα radiation the scattering angle is expected at 29.0°. The scattering angle shift by 1°, between the experimental and the predicted peak position, signifies strain effects. Recently measured grazing incidence diffraction patterns of Dy_2O_3 thin films (50–120 Å) on Si (100) confirm the crystallization in the cubic system, while similar scattering angle shifts are attributed to short range order and are correlated with deviation from the stoichiometric Dy_2O_3 [31].

Sample #4 shows a diffraction peak at 28.6° (Fig. 1) with a FWHM of 1.3°, which is attributed to the HfO_2 crystallization, as the Dy_2O_3 layer is too thin to provide a measurable diffraction line. The broadening w_{size} of the diffraction line due to the average crystallite

Table 1
Structural properties such as thickness, roughness, electron density of thin films assembling the gate stacks, as extracted from X-ray reflectivity measurements and electrical characteristics such as effective dielectric constant (κ) values, flatband voltage shift (V_{FB}), hysteresis and interface state density (D_{it}) of the gate stacks studied are given in the table.

Sample	Layer	Thickness (Å)	Roughness (Å)	Electron density (e/Å^{-3})	Mass density (g/cm^3)	κ (effective)	V_{FB} (V)	Hysteresis (V)	D_{it} ($\times 10^{12}$ eV^{-1} cm^{-2})
#1	Dy_2O_3	84	10	2.1	9.3	19	−0.05	0.52	2.5
	GeO_2	20	4	1.1	4.0				
	Ge	Substrate	2	Fixed	5.3				
#2	HfO_2	44	7	2.5	10.7	17	−0.56	0.30	3.9
	Dy_2O_3	49	8	1.8	8.3				
	GeO_2	21	6	1.1	4.1				
	Ge	Substrate	2	Fixed	5.3				
#3	HfO_2	45	6	2.5	10.8	16	−0.17	0.44	5.5
	Dy_2O_3	22	6	1.8	8.3				
	GeO_2	8	6	1.0	3.8				
	Ge	Substrate	2	Fixed	5.3				
#4	HfO_2	71	7	2.4	10.1	18	0.02	0.44	5.0
	Dy_2O_3	19	4	1.8	8.1				
	GeO_2	11	5	1.1	3.9				
	Ge	Substrate	5	Fixed	5.3				

The mass density is evaluated from the electron density, under the assumption that the stoichiometry of the layers is preserved (see text). The electron density of Ge substrate is considered as fixed and equal to 1.4 e/Å^{-3}.