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Study of interfacial reactions and phase stabilization of mixed Sc, Dy, Hf high-*k* oxides by attenuated total reflectance infrared spectroscopy

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ABSTRACT

Grazing angle attenuated total reflectance Fourier transform infrared spectroscopy is applied to study ultrathin film Hf^{4+}, Sc^{3+} and Dy^{3+}oxides, due to its high surface sensitivity. The (multi)metal oxides studied, are of interest as high-*k* dielectrics. Important properties affecting the permittivity, such as the amorphous or crystalline phase and interfacial reactions, are characterized.

Dy_2O_3 is prone to silicate formation on SiO_2/Si substrates, which is expressed in $DyScO_3$ as well, but suppressed in $HfDyO_x$. Sc_2O_3, $HfScO_x$ and HfO_2 were found to be stable in contact with SiO_2/Si. Deposition of HfO_2 in between Dy_2O_3 or $DyScO_3$ and SiO_2, prevents silicate formation, showing a buffer-like behavior for the HfO_2.

Doping of HfO_2 with Dy or Sc prevents monoclinic phase crystallization. Instead, a cubic phase is obtained, which allows a higher permittivity of the films. The phase remains stable after anneal at high temperature.

1. Introduction

Downscaling of CMOS transistors has allowed continuously increasing device speed and improved performance. As a consequence of the miniaturization the gate dielectric, SiO_2, thickness has been decreased strongly. Recently, commercial production has switched to alternative gate dielectric materials with a higher permittivity than SiO_2 ($k = 3.9$), in order to control the leakage current. Due to the higher permittivity, the physical thickness is higher than the effective oxide thickness (EOT), which allows avoiding electron tunneling through the dielectric oxide [1,2].

Hafnium based materials such as amorphous HfO_2 ($k \sim 22$ [3]) and (Hf,Si)O_2 mixed compositions have recently received a great deal of attention. The amorphicity or crystalline phase strongly affects the permittivities which are achieved. The thermodynamically stable crystal structure of HfO_2 at room temperature is monoclinic and is characterized by a $k \sim 16$ [4]. Tetragonal and cubic high temperature phases on the other hand show much higher permittivities ($k \sim 70$ and 29 respectively [4]). These phases have been shown to be stabilized by doping HfO_2 with lanthanides [5–8]. Besides Hf based materials, lanthanide scandates are reported to be promising as high-*k* dielectrics, due to their high permittivity (>20) and crystallization resistance up to high temperatures, which is explained by silicate formation [6,9,10].

Independent of the high-*k* material, MOS device performance is always affected by reactions at the interface with the SiO_x/Si substrate, such as silicate formation or regrowth of interfacial SiO_x. These interfacial layers can be characterized by a lower permittivity and thus lead to undesirable increase of the EOT of the stack. However, often a very thin starting SiO_x is required to obtain layer nucleation e.g. in atomic layer deposition [11–13], and therefore cannot be avoided. The control of its thickness during further processing then remains crucial [1].

The ultralow thickness of the high-*k* layers (<10 nm), necessitates the use of highly sensitive characterization techniques, such as grazing incidence X-ray diffraction (XRD), cross section transmission electron microscopy (TEM), TOF-SIMS (time of flight secondary ion mass spectrometry), or XPS (X-ray photoelectron spectroscopy). FTIR (Fourier transform infrared

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spectroscopy) allows the detection of metal oxide as well as silicate vibrations. Normal transmission measurements are insufficiently sensitive, but the surface sensitivity can be greatly enhanced in attenuated total reflectance (ATR) [14]. The sensitivity enhancement depends on the angle of incidence, the thickness of the air gap and the dielectric constants of the ATR crystal and the film's substrate [15,16].

Here, we apply grazing angle attenuated total reflectance Fourier transform infrared (GATR-FTIR) to several high-*k* films of recent interest, Hf, Dy and Sc oxides, which were deposited by atomic vapour deposition (AVD) or atomic layer deposition (ALD) for high quality film growth with atomic precision. The results contribute to the explanation and understanding of the dielectric properties, demonstrating the potential of GATR-FTIR in high-*k* characterization.

2. Material and methods

All the high-*k* films were grown by AVD (Aixtron Tricent^{TM} reactor) on Si (1 0 0) wafers as described elsewhere [6,9,17,18], with 550 °C susceptor temperature, unless indicated otherwise. Precursors used were tris(6-ethyl-2,2-dimethyl-3,5-decanedionato)dysprosium [Dy(EDMDD)$_3$], tris(6-ethyl-2,2-dimethyl-3,5-decanedionato) scandium [Sc(EDMDD)$_3$], and bis(*tert*-butoxide) bis(methoxymethyl propanoxide) hafnium Hf(O^{t}Bu)$_2$ (mmp)$_2$ combined with molecular O_2. SiO_2 starting oxide was obtained with a thickness of 1.1 nm by chemical oxidation (H_2O/O_3), while thicker SiO_2 was obtained by rapid thermal oxidation. Film thicknesses were determined by X-ray reflectivity. The compositions of the films are determined by X-ray photoelectron spectroscopy ($HfDyO_x$, $HfScO_x$) and Rutherford backscattering spectroscopy ($DyScO_3$). The doped HfO_2 films contain 10% Dy or Sc (90% Hf) and the $DyScO_3$ consists of 50% Dy and 50% Sc unless specified otherwise (percentages ignoring O, e.g. Dy/Dy + Hf). Post deposition anneals were carried out at 1000 °C in N_2 or O_2 for 60 s.

Sample preparation for grazing angle attenuated total reflectance Fourier transform infrared measurement consists of cleaving square pieces (2 cm × 2 cm to 3 cm × 3 cm) from the wafers. GATR-FTIR spectroscopy was carried out by means of a 65° single reflection Ge-ATR (supplied by Harrick), placed in the sample compartment of an FTIR spectrometer (Bruker, Vertex 70). The compartment and the GATR-cell were flushed with dried air and N_2 respectively. Intimate contact between the sample and the Ge crystal is obtained by applying 56 oz in.$^{-1}$ of pressure. Spectra were referenced against the clean Ge crystal and obtained with a spectral resolution of 4 cm^{-1}, in a spectral range from 4000 to 600 cm^{-1}. For the spectra, the ATR signal = (absorbance × wavenumber)/1000 is shown. Since the penetration depth is inversely proportional to the wavenumber this normalizes the spectra to a constant penetration depth. In between the samples, blank 1.2 nm SiO_x/Si samples were measured, showing no changes in the Ge crystal's state, such as scratches, which would affect the spectra and interfere with the comparison of different samples.

3. Results and discussion

3.1. Monometal oxides

3.1.1. Phase identification of hafnium oxide

The permittivity of the HfO_2 layers studied here was determined to be 16, as published elsewhere [6]. This value can be characteristic either for amorphous or monoclinic HfO_2.

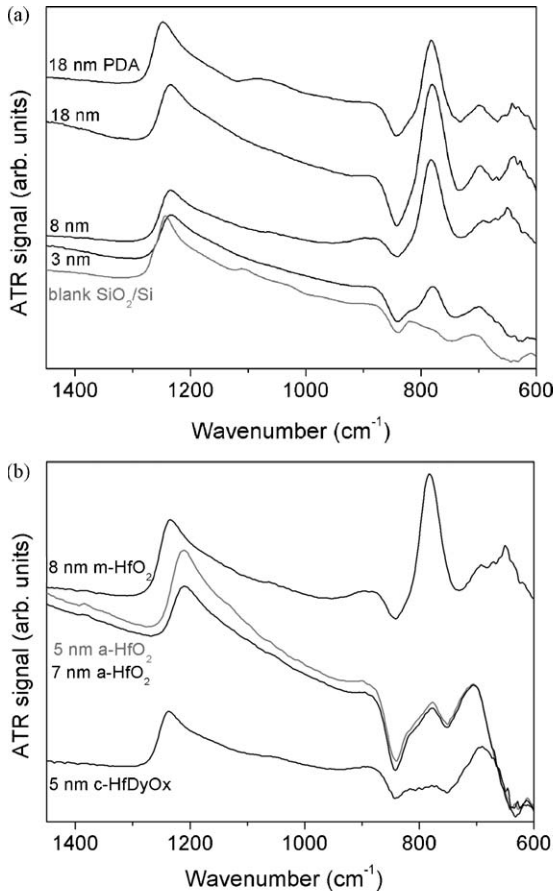

Fig. 1. GATR-FTIR spectra of (a) monoclinic HfO_2 as function of thickness, (b) comparison of different phases of (stabilized) hafnia in films of comparable thickness (a: amorphous, c: cubic, m: monoclinic).

HfO_2 layers with thicknesses of 3, 8 and 18 nm on 1.1 nm SiO_2/Si have been characterized and their spectra are compared to a blank SiO_x/Si substrate (Fig. 1a). Band assignments and interpretations are as follows. At 1240 and 1065 cm^{-1} the longitudinal (LO) and transverse optic (TO) band of SiO_2 are found [15]. At 1100 cm^{-1} Hf–O–Si vibrations would be expected [19], but comparison with the blank substrates shows that any intensity in this area is due to the SiO_2 from the substrate [20]. At 900 cm^{-1} both the blank substrate and the HfO_2 films show slightly increased intensity, which might be ascribed to Si–OH [21]. The band at 780 cm^{-1} can be ascribed to the monoclinic crystal phase of HfO_2, which forms a doublet together with the weaker feature at 690–700 cm^{-1}. Theory predicts this doublet to be situated at 780/694 cm^{-1} and 683/634 cm^{-1} [4], and it has been ascribed experimentally to peaks at 760 cm^{-1} [7] or 752 and 635 cm^{-1}[16,22,23]. Based on the presence of this vibration around 780 cm^{-1} in the spectra of HfO_2 films of all thicknesses studied, it can be concluded that all of these films contain monoclinic HfO_2.

Post deposition anneal in O_2 (PDA, 1000 °C) does not affect the HfO_2 band position and relative intensities. There is no evidence for Hf–O–Si vibrations around 1100 cm^{-1}. It can be concluded that the anneal does not affect the HfO_2 phase present, nor leads to interfacial silicate formation.

Theoretically, it is impossible to observe the bands for the higher-*k* cubic phase of HfO_2, situated at 286 cm^{-1}, in the measurable range of Ge-ATR [4]. Nonetheless, a single band at 695 cm^{-1}, in absence of a feature at 780 cm^{-1}, has been ascribed to cubic HfO_2, because electron diffraction showed the presence of this phase in the samples [7]. The authors however did not demonstrate the absence of a portion amorphous phase, which is also reported to show a single band of similar shape in this wavenumber region of 690 cm^{-1} [3,16,24]. The presence or absence of a shoulder to the high wavenumber side of this band,