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Hafnium oxide gate dielectrics grown from an alkoxide precursor: structure and defects

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Abstract

We present an infrared spectroscopy and X-ray diffraction study of hafnium oxide gate dielectric films deposited from hafnium tetra–*tert*-butoxide, $Hf(OC(CH_3)_3)_4$. We characterize the crystal phase as a function of thickness and detect the chemical state of impurities in this high-permittivity (high-κ) material. The HfO_2 films are composed of monoclinic crystallites in an amorphous matrix. The crystalline fraction increases with increasing film thickness. Infrared spectroscopy is used to obtain information about impurities, which may help to uncover the nature of electrical defects. We detect and quantify for instance the presence of incorporated hydroxyl groups or water that may be responsible for the deviation from ideal HfO_2 stoichiometry. The concentration of residual C–H bonds is low. However, carbon is incorporated in an oxidized form, possibly as carbonate.

Keywords: Chemical vapor deposition; Infrared spectroscopy; Thin films; Oxides; Metal–oxide–semiconductor structures; Integrated technology

1. Introduction

Silicon oxide and oxynitride, the traditional gate dielectrics in field effect transistors, are rapidly approaching their ultimate thickness. Alternative materials with higher permittivity, so-called high-κ dielectrics, will be needed to continue device scaling [1]. HfO_2 and its silicates and aluminates, deposited by chemical vapor deposition (CVD) or atomic layer deposition (ALD) [2], have emerged as attractive candidates for the first device generations.

Composition, crystal phase, density, and defects have to be controlled in order to optimize the performance of future gate stacks, which requires multiple characterization techniques. Infrared spectroscopy offers outstanding sensitivity to atomic and molecular vibrations with an ability to detect areal densities as low as $10^{12}\,cm^{-2}$, particularly for hydrogen. Composition and crystal structure of dielectrics are accessible through their phonon modes. The phonon spectra may also be important in understanding mobility degradation in FETs; one current theory argues that electron scattering off low frequency phonons in the gate insulator limits charge transport through the channel [3]. In addition, infrared spectroscopy enables in situ characterization of CVD and ALD growth, as we recently demonstrated [4].

Real time infrared observation of HfO_2 growth poses special challenges, however, due to the wide spectral range that has to be monitored. C–H and O–H vibrations are located at $\sim$2700–3800 cm^{-1}. HfO_2 phonon modes, on the other hand, are found at $\sim$100–750 cm^{-1} [5,6], lower than is the case for SiO_2 ($\sim$400–1300 cm^{-1}) and Al_2O_3 ($\sim$350–900 cm^{-1}). In this paper, we report on the level of HfO_2 characterization achievable with readily available infrared detectors and beamsplitters in a commercial spectrometer.

$HfCl_4$ and H_2O are the main precursors currently used in ALD of HfO_2, but Hf amides [7] and Hf alkoxides such as hafnium tetra–*tert*-butoxide [HTB, $Hf(OC(CH_3)_3)_4$] have also been employed. Importantly, alkoxides can be used without an additional O source, although HfO_2 has also been grown with HTB and O_2 [8] and ZrO_2 with zirconium tetra–*tert*-butoxide (ZTB) and O_2 [9,10]. We note that organic precursors might open the way to functionalization of hydrogen-passivated silicon (H/Si), as we recently showed [4]. Herein, we report on HfO_2 growth from HBT [11]. The

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HfO_2 films are close to stoichiometry and very smooth. They exhibit a dielectric constant of ∼24, low leakage current, and reasonable hysteresis [11,12].

2. Experimental

The substrate used in this work was a high-quality SiO_xN_y film on Si (1 0 0) with a thickness of (11.0 ± 1.5) Å as measured by medium energy ion scattering. HfO_2 layers were deposited using the HTB precursor in the 10^{-3} Torr range at 400 °C, without any additional O source [11]. The precursor was held in a small bubbler in a water bath at 25 °C and was introduced into a laboratory-scale ultra-high vacuum/high pressure CVD/ALD reactor (base pressure $\leq 5 \times 10^{-7}$ Torr) through a heated gas line and nozzle.

Infrared absorption measurements were carried out in a Fourier-transform infrared spectrometer (Nicolet 760) equipped with DTGS and MCT detectors and a Ge-on-KBr beam splitter. Transmission spectra were taken at near- and off-normal (45°) incidence at room temperature, using the SiO_xN_y/Si substrate as reference. The acquisition time was ∼10 min and the resolution 4 cm^{-1}. Normal incidence spectra were smoothed (450–1000 cm^{-1}) or their resolution degraded to 8 cm^{-1} (2500–3800 cm^{-1}). X-ray diffraction (XRD) data were collected on a HiStar area detector (Bruker-AXS) using graphite-monochromatized Cu Kα radiation from an Enraf FR571 rotating anode. The regions for signal integration were $-170 < \theta < -10°$ and $23 < 2\theta < 43.5°$. Film thicknesses were measured by RBS. The areal densities obtained are converted to film thicknesses assuming a HfO_2 density of 9.68 g/cm^3. In general, RBS data analysis confirms that the films are oxygen-rich as grown [11].

3. Results and discussion

3.1. Crystal phase

Infrared spectra displayed in Fig. 1a (450–1000 cm^{-1}) show distinct vibrational features superimposed onto a very broad band rising towards low frequencies. Bands at 505 and 750 cm^{-1} are observed in both normal and oblique geometries and are thus assigned to transverse-optical (TO) phonon modes. The feature at 690 cm^{-1} appears only at oblique incidence, characteristic of a longitudinal-optical (LO) phonon mode [13]. The position of these bands is consistent with monoclinic HfO_2 (not cubic or tetragonal) [5,6]. The broad band originates from an amorphous HfO_2 matrix [6,9]. Importantly, the intensity of the features due to crystalline HfO_2 rises faster with increasing film thickness than the broad band intensity. This shows that the monoclinic fraction increases with increasing film thickness.

These findings are in agreement with the XRD data (Fig. 1b). The XRD features become more sharp and intense with increasing film thickness, and are consistent with monoclinic HfO_2 [14,15]. Using peak and background intensities in Fig. 1b to estimate the degree of film crystallinity, we find that the concentration of monoclinic HfO_2 in the amorphous matrix more than doubles in the thickness range studied (Fig. 1b).

3.2. Defects and impurities determined from infrared spectroscopy

All vibrational features expected for pure HfO_2 are located below ∼800 cm^{-1}. However, we also observe absorption bands at higher frequencies (Fig. 2), suggesting the presence of impurities. For thick films, the absorption intensities scale approximately linearly with thickness, indicating that impurities are incorporated into the films. In the 2800–3000 cm^{-1} region (C–H stretch), the trend is less clear, possibly due to surface contamination from atmospheric hydrocarbons.

3.2.1. Hydroxyl groups and water

We start our discussion with the broad absorption centered at 3400 cm^{-1} (Fig. 2b) [16]. Such a broad band arises from H-bonded OH groups, e.g. in liquid and solid water, with maxima at 3400–3490 and 3220 cm^{-1}, respectively [17,18]. Another characteristic signature of bulk water at 1645–1650 cm^{-1} [17,18] may be hidden in the tail of C-related features (Fig. 2a). O–H stretching frequencies of ∼3400 cm^{-1} have likewise been reported for monolayer-level H_2O adsorption at single-crystal surfaces [19] and for OH groups on or inside HfO_2 [20]. Both H_2O and Hf-bonded OH groups can therefore account for the O–H stretching band observed in our study.

From the intensity of the O–H stretch, we estimate $\sim 5 \times 10^{16}$ O–H bonds cm^{-2} in the 750 Å HfO_2 film, assuming similar absorption cross sections for O–H stretches in H_2O and in Hf–OH [21]. This density is in reasonable agreement with the density of O-containing species lost after a mild (200 °C) anneal in high vacuum ($\sim 6 \times 10^{16}$ cm^{-2} as determined by RBS), indicating that most O–H groups are due to incorporated H_2O, possibly from exposure to atmosphere during sample transfer. However, also some OH groups generated during growth might remain unreacted, due to steric hindrance [10].

3.2.2. Carbon-containing species

Focusing now on the medium frequency region (Fig. 2a), we observe a dominant feature at 1583 cm^{-1} and a broad band extending down to 1250 cm^{-1}. Individual bands at 1375 and 1455 cm^{-1} are discernible for thick films. We note the absence of any signal at 1190 cm^{-1}, where condensed HBT absorbs strongly [22]. Our spectra show therefore that butoxy groups are completely decomposed during growth.

Infrared absorption in the 1300–1700 cm^{-1} range has previously been observed for CVD of ZrO_2 using ZTB and O_2

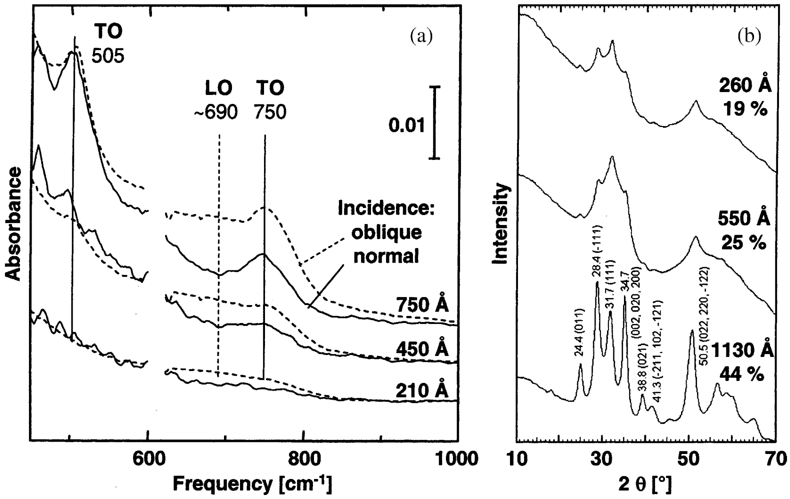

Fig. 1. (a) Transmission infrared spectra from HfO_2 films of the indicated thickness acquired with a DTGS detector in the phonon region, for normal and oblique (45°) incidence. A signal at ~610 cm^{-1} is due to bulk Si phonon modes and has been removed for clarity. The symbols TO and LO mark transverse- and longitudinal-optical phonon modes of monoclinic HfO_2. (b) XRD data for HfO_2 films of the indicated thickness. Peak positions and assignments are given in the figure. A relative concentration of monoclinic HfO_2 in the amorphous matrix is quoted next to each spectrum.

[9], but was not discussed, except for a tentative assignment of a 1370 cm^{-1} mode to monoclinic ZrO_2, which seems unlikely [23]. For electron beam evaporated HfO_2, spectral features around ~1600 cm^{-1} were attributed to H_2O incorporated in oxide pores [24]. Similarly, bands at 1575 and 1630 cm^{-1} for Hf silicates prepared in solution were assigned to Hf–OH and H_2O, respectively [6].

However, the presence of water or OH alone cannot account for all the absorption bands observed in our study. We suggest that C-containing species are responsible for the observation of other spectral features in Fig. 2a. This is supported by X-ray photoelectron spectra (not shown), which indicate that a small concentration of oxidized carbonaceous species are present. We therefore consider possible C species and their vibrational signatures.

First, we turn our attention to stretching frequencies of O–C–O units, e.g. of carbonates (CO_3) or of carboxylates (COO–R) such as formate (COO–H) or acetate (COO–CH_3). Such moieties are likely responsible for some of the observed infrared signals. Monodentate carbonate (having one point of attachment), for example, exhibits symmetric and asymmetric O–C–O stretches at 1300–1370 and 1470–1530 cm^{-1}, respectively [25], and may therefore be present in our films. Bidentate carbonate (having two points of attachment) on HfO_2 gives rise to bands at 1300–1315 and 1570–1575 cm^{-1} [20,26], inconsistent with our observations. For formate on a HfO_2 surface, frequencies of ~1360 and 1575 cm^{-1} have been reported [26]. A study of $HfO(CH_3COO)_2$-containing gels assigned features at 1410–1450 and 1560 cm^{-1} to bidentate acetate, while a

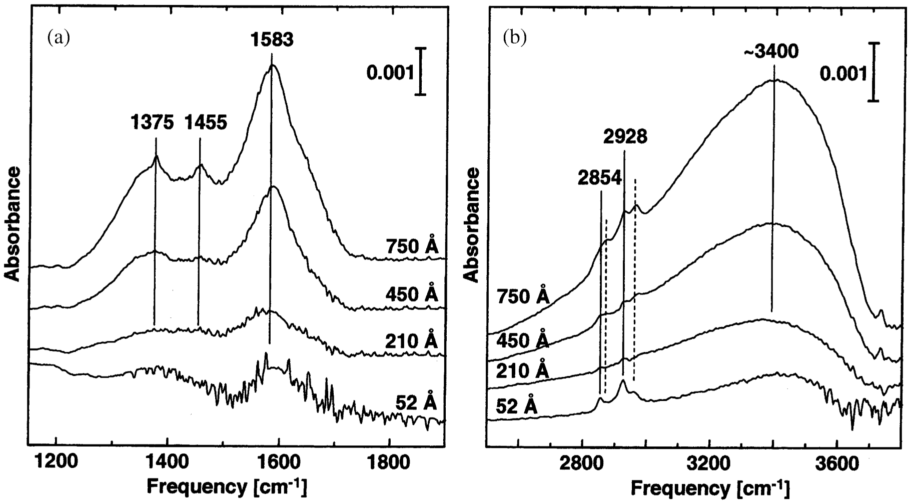

Fig. 2. Transmission infrared spectra from HfO_2 films acquired with an MCT detector (a) in the mid-frequency regime and (b) in the region of C–H and O–H stretch vibrations, recorded at oblique (45°) incidence.

larger splitting was attributed to monodentate acetate [27]. For longer alkylcarboxylates on Al_2O_3, modes are located at 1470 and 1600 cm^{-1} [28].

Finally, the C=C stretch of O–C=C units, at ∼1590 cm^{-1} [29], should also be considered. Interference from C–H bending modes [29] is unlikely since the C–H stretch absorption is weak (see below).

This overview shows that carbonates and carboxylates, as well as O–C=C moieties, may account for the features observed for our HfO_2 films. Incorporation of C from the HTB may result in the liberation of hydrogen. If H atoms remain in the high-κ film, they may be responsible for fixed charge [30]. Hf–H dative bonding could indeed give rise to features we observe at ∼1600 cm^{-1} [31]. However, calculations indicate that H in HfO_2 interacts with O ions rather than with Hf [30].

Additional information can be obtained from the C–H stretch region (2800–3000 cm^{-1}, Fig. 2b). We observe dominant features at 2854 and 2928 cm^{-1}, typical for CH_2 groups, and smaller signals at 2871 and 2961 cm^{-1}, indicative of CH_3 groups [29]. The signal at 2928 cm^{-1} might involve contributions from formate [32], while acetate seems less abundant [33]. The low CH_3 concentration observed confirms that most *t*-butoxy species have decomposed. In particular, we do not detect a strong characteristic absorption feature at 2973 cm^{-1} [34]. Two factors may be responsible for the CH_2 groups observed, either a side reaction during HfO_2 growth, involving dehydration of CH_3 groups, or surface contamination from the atmosphere. Surface contamination was indeed invoked in a study of ZrO_2 growth from ZBT and O_2 [10], where similar C–H stretching bands were observed.

4. Conclusion

Utilizing infrared spectroscopy, we have characterized crystal phonons and chemical defects of HfO_2 gate dielectrics deposited from a HTB precursor. In conjunction with XRD, we have established that the films are composed of monoclinic crystallites in an amorphous matrix. The crystalline fraction increases with film thickness. Such thickness dependence of phase composition may cause corresponding changes in dielectric response, band gap, and band alignment [5,35]. The increase in crystalline fraction may be due to preferential attachment of Hf and O in regular crystal sites once monoclinic nuclei have been formed.

We have detected incorporated hydroxyl or atmospheric water which causes a deviation from HfO_2 stoichiometry, as found by RBS. Complete butoxy group decomposition has been established. However, small amounts of residual carbon are present in oxidized form. These results will have to be correlated to electrical data, combined with quantum chemical calculations. In this way, it can be established which, if any, of the defects observed are electrically active. Experimental correlation will be possible through tuning of defect type and density, e.g. by thermal treatment of the as-deposited films.

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