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Transmission electron microscopy studies of HfO_2 thin films grown by chloride-based atomic layer deposition

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Abstract

Detailed transmission electron microscopy characterization of HfO_2 films deposited on Si(1 0 0) using atomic layer deposition has been carried out. The influence of deposition temperature has been investigated. At 226 °C, a predominantly quasi-amorphous film containing large grains of cubic HfO_2 (a_0 = 5.08 Å) was formed. Grain morphology enabled the nucleation sites to be determined. Hot stage microscopy showed that both the cubic phase and the quasi-amorphous phase were very resistant to thermal modification up to 500 °C. These observations suggest that nucleation sites for the growth of the crystalline cubic phase form at the growing surface of the film, rather homogeneously within the film. The films grown at higher temperatures (300–750 °C) are crystalline and monoclinic. The principal effects of deposition temperature were on: grain size, which coarsens at the highest temperature; roughness with increases at the higher temperatures due to the prismatic faceting, and texture, with texturing being strongest at intermediate temperatures. Detailed interfacial characterization shows that interfacial layers of SiO_2 form at low and high temperatures. However, at intermediate temperatures, interfaces devoid of SiO_2 were formed.
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1. Introduction

HfO_2 has a number of interesting properties, which see it being investigated for a range of applications. The drive to reduce complimentary metal oxide semiconductor (CMOS) dimensions requires replacement of the gate dielectric materials for SiO_2 [1]. A number of candidate materials are under active consideration, and considerable interest in HfO_2 has been shown. It has been applied as gate insulator on field effect transistors [2], and as a dielectric in capacitors [3] and as a tunnel dielectric in nanocrystal nonvolatile memory devices [4]. HfO_2 also has a high refractive index and finds application in optical coatings for laser mirrors due to its high damage threshold [5], and shows potential as a scintillator material, where high density and luminescence yield [6] are needed for efficient absorption and detection of highly-energetic particles and radiation.

The physical properties of HfO_2 can be tailored by controlling the deposition conditions, particularly deposition temperature, film thickness and composition. Low temperature deposition results in amorphous films [7], as does alloying or laminating films with other oxides such as Al_2O_3 [8]. These are beneficial for MOSFET and DRAM applications in order to minimise leakage current, which are associated with grain boundaries [7,8]. Fortunately, ultrathin films needed for these applications tend to be amorphous compared with thicker films grown at similar temperatures [11,14,15]. Also amorphous materials may be desirable for optical coatings in order to produce homogeneous material and flat interfaces, since surface roughness arises from crystalline growth [9–11]. Crystalline HfO_2 on the other hand shows much stronger photoluminescence than amorphous materials and so is desirable for scintillators in order to obtain higher emission efficiency [6].

Atomic layer deposition (ALD) is an attractive technology for the deposition of HfO_2 films, since it offers convenient and accurate thickness control at the (sub)monolayer level. The

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Table 1
Summary of film deposition conditions and parameters

Temperature (°C)	Cycles	Thickness (nm)	Structure	Grain size (nm)	EDS Cl (at.%)[a]	Interfacial SiO_2 (nm)
226	700	97 ± 5	a/c	60 ± 15	<5	1.9 ± 0.4
300	800	91 ± 3	c	38 ± 10	<0.5	0.0
350	1000	100 ± 5	c	42 ± 14	0	0.0
400	1000	93 ± 2	c	31 ± 9	0	0.8 ± 0.2
450	1100	97 ± 6	c	38 ± 11	0	1.1 ± 0.2
750	1100	98 ± 5	c	53 ± 16	0	3.4 ± 0.3

Notes a: amorphous; c: crystalline; a/c: mixed amorphous/crystalline.
[a] EDS values are estimates based on Cl peak intensities relative to Hf.

surface limiting nature of the reactions leads to highly conformal films, permitting deposition even within high aspect ratio structures [12]. A number of studies involving ALD of HfO_2 have been carried out. The main precursors used have been $HfCl_4$ and H_2O [6,11,13–23]. However, HfI_4 and H_2O or O_2 have also been used [11,24,25], along with a number of organometallic [26] and inorganic precursors [27].

Detailed characterization of HfO_2 films has been carried out, with a view to understanding the electrical and optical properties and to establish synthesis–structure–function correlations. In-depth microstructural work has also been done, albeit for films grown over a limited range of deposition temperatures. Much of this work has centred on the issue of the HfO_2/Si interface, and the formation of interfacial layers of oxide/silicate [4,20–25]. Less attention has been paid to the microstructural evolution within HfO_2 films [7,8,16,17]. In this study we have sought to address this issue, by carrying out a systematic, detailed TEM study of the influence of deposition temperature on the nature of HfO_2 films. These films have been grown using the most widely used chemistry ($HfCl_4$/H_2O) over a wide range of temperatures (226–750 °C). As a function of deposition temperature we have investigated the development of structure, the evolution of crystallite size, the development of surface roughness, crystallographic orientation, phase composition as well as the growth and composition of interfacial layers

2. Experimental

The films were grown on Si(1 0 0) substrates in a low-pressure (250 Pa) flow-type reactor described in an earlier paper [15]. Before loading the substrates into the reactor they were etched in HF and then rinsed in deionized water. To deposit the films the substrates were alternately exposed to $HfCl_4$ and H_2O vapours used as metal and oxygen precursors, respectively. $HfCl_4$ was evaporated at 140 °C while the H_2O vapour was generated at room temperature. The partial pressure of H_2O was estimated to be 6 Pa in the reaction zone during the H_2O pulse. The precursors were carried to the reaction vessel in the flow of pure nitrogen and the duration of each precursor pulse was 2 s. Nitrogen was also used as the purging gas that removed the surplus precursors and the gaseous reaction products from the reactor after each exposure period. The duration of purge periods was also 2 s. Hence, a complete ALD cycle that included a $HfCl_4$ pulse, purge period, H_2O pulse and another purge period required 8 s. To ensure sufficient purging of the reaction zone and avoid overlapping of the precursor pulses, the carrier gas flow rate was set at 50 μmol/s. The corresponding linear flow rate of the carrier gas was 2.6 m/s in the reaction zone at the growth temperature (T_G) of 300 °C. The films were grown at temperatures ranging from 226 to 750 °C. The number of ALD cycles applied to grow the films was varied from 700 to 1100 (Table 1) in order to compensate for the effect of temperature on the deposition rate and grow films with similar thickness (100 nm approximately).

Specimens for transmission electron microscopy (TEM) were made in plan view and cross-sectional orientations, using the methods described elsewhere [10]. These were examined using a JEOL 2010F TEM operated at 200 keV. This instrument was fitted with an Emispec scanning TEM system interfaced to an Oxford Instruments energy dispersive X-ray detector system. This permitted qualitative analysis. A Gatan imaging filter (GIF) was also fitted, which permitted energy filtered TEM and electron energy loss spectroscopy (EELS).

3. Results

3.1. Low temperature deposition (226 °C)

Fig. 1a–c shows cross-sectional TEM images of the film. Immediately apparent was the presence of large, discrete crystalline grains within an otherwise amorphous film. Regions of film which were amorphous throughout the thickness were exceptionally flat and uniform. Where the large conical grains broached the surface of the film, surface roughness was introduced, they being typically domed. The mean film thickness, was 97 ± 5 nm. The dark band (≈10 nm thick) in the HfO_2 film, near the interface with the Si substrate, was due to thickness variation in the TEM specimen (confirmed with thickness mapping—not shown). Some of the large conical grains appeared to have their nucleation origin near the interface between the film and the substrate. However, many nucleated part-way through the film (arrowed in Fig. 1a). High resolution TEM (HRTEM) imaging of the outer surface of the film (Fig. 1b) (where one of the domed crystallites broached the surface in Fig. 1a), revealed the crystalline regions. The large crystallite (B) showed strong lattice fringes close to perpendicular to its outer surface. This was surrounded by amorphous HfO_2 (A). Also present were a number of smaller crystallites

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