Microstructure of hard and optically transparent HfO₂ films prepared by high-power impulse magnetron sputtering with a pulsed oxygen flow control

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Abstract

Reactive high-power impulse magnetron sputtering was used to deposit HfO₂ films on Si substrates using a voltage pulse duration, t_I , from 100 to 200 μs and an deposition-averaged target power density, $\langle S_d \rangle$, from 7.2 to 54 Wcm^{-2} . The effects of these processing parameters on the microstructure and properties of the films were studied by atomic force microscopy, nano-indentation, X-ray diffraction, electron diffraction and high-resolution transmission electron microscopy. Four HfO₂ films were prepared with (1) $t_I = 100 \mu\text{s}$, $\langle S_d \rangle = 7.2 \text{ Wcm}^{-2}$ (T100S7), (2) $t_I = 200 \mu\text{s}$, $\langle S_d \rangle = 7.3 \text{ Wcm}^{-2}$ (T200S7), (3) $t_I = 200 \mu\text{s}$, $\langle S_d \rangle = 18 \text{ Wcm}^{-2}$ (T200S18) and (4) $t_I = 200 \mu\text{s}$, $\langle S_d \rangle = 54 \text{ Wcm}^{-2}$ (T200S54). All films were found to be composed of an interlayer next to the Si interface followed by a nano-columnar structure layer. The interlayer structure of the films was found to contain a population of lower density nanoscale regions. A reduction in $\langle S_d \rangle$ in films T200S54, T200S18, T200S7 and T100S7 caused an increase in the interlayer thickness and a decrease in the width of the nano-columnar structures from ~46 nm to ~21 nm. This microstructural change was accompanied by a concomitant change of the grain boundary

structure from tight and interlocking in films T200S54 and T200S18, to rough and thicker (~1 nm) boundaries in films T200S7 and T100S7. Films prepared with larger $t_f = 200 \mu\text{s}$ have a monoclinic HfO_2 structure and that with smaller $t_f = 100 \mu\text{s}$ exhibits a mixture of monoclinic and orthorhombic HfO_2 . A high hardness of 17.0-17.6 GPa was shown for films with a monoclinic HfO_2 structure. The films exhibited a refractive index of 2.02-2.11 and an extinction coefficient between 0.1×10^{-3} and 1×10^{-3} (both at a wavelength of 550 nm). High refractive index was achieved for films T200S54 and T200S18 owing to the presence of a dense microstructure with sharp and interlocking grain boundaries.

Keywords: HfO_2 films; Reactive HiPIMS; High-resolution transmission electron microscopy; Electron diffraction; Dense nano-columnar structure

1. Introduction

Hafnium dioxide (HfO_2) has become an important coating material due to its attractive properties. They include high melting point ($\sim 2800^\circ\text{C}$) and excellent thermal stability, high refractive index and low absorption over a broad region (from the near-UV, $\sim 250\text{ nm}$ to the mid-IR, $>12\text{ }\mu\text{m}$), high dielectric constant and high neutron absorption cross section [1]. HfO_2 can find a wide range of applications (semiconductors, optical devices, nuclear industries and coating technologies). For example, HfO_2 -based materials have been explored as thermal barrier coatings for turbine blades operating in harsh and high-temperature environments [2, 3]. HfO_2 films can be used as visible, near-IR and mid-IR antireflection coatings [4-6], UV mirrors with a high damage threshold [7], heat mirrors for energy-efficient windows [8] and chirped mirrors and band pass filters [9]. HfO_2 is also considered to be one of the most promising candidates to replace SiO_2 on Si in gated electronic devices [10].

Reactive dc magnetron sputtering is a suitable technique to deposit HfO_2 films [9, 11-17]. High-power impulse magnetron sputtering (HiPIMS) with a pulsed reactive gas (oxygen) flow control was recently used for high-rate reactive depositions of densified, highly optically transparent, stoichiometric HfO_2 films onto floating substrates [18]. The depositions were performed using a strongly unbalanced magnetron with a directly water-cooled planar Hf target in argon-oxygen gas mixtures. With this method, the HfO_2 films can be fabricated with very high deposition rates (up to 200 nm/min) at an averaged target power density of approximately 30 Wcm^{-2} . The latter is relatively close to a target power density applicable in industrial HiPIMS systems. The HfO_2 films prepared using this technique were hard and exhibited a hardness up to 18 GPa , a refractive index of $2.07\text{-}2.12$ and an extinction coefficient between $\leq 0.1\times 10^{-3}$ and 0.6×10^{-3} at the wavelength of 550 nm . In spite of the oscillating oxygen partial pressure during film depositions, no periodic changes in their compositions were observed [18].

In this work, we have employed high-resolution transmission electron microscopy (HRTEM) and electron diffraction to study the microstructure of four selected representative hard and optically transparent HfO₂ films prepared by high-rate HiPIMS [18]. The motivation for this work was to develop an understanding of the processing-microstructure-property relationship of these films as a function of the deposition parameters, namely deposition-averaged target power density, $\langle S_d \rangle$, and voltage pulse duration, t_l . As an important part of these efforts, we examine (by techniques complementary to those employed in Ref. [18]) whether the feed-back pulsed oxygen flow control (oscillating oxygen partial pressure, and consequently oscillating discharge current and power, on a scale of seconds, see Fig. 1) does or does not lead to a layered structure of the films.

2. Experimental details

2.1. Film preparation

The HfO₂ films were deposited onto Si substrates at a floating potential using a strongly unbalanced magnetron sputter source with a directly water-cooled planar hafnium target (99.9 % Hf purity, diameter of 100 mm and thickness of 6 mm) in a standard stainless-steel vacuum chamber. The target-to-substrate distance was 100 mm. The target surface temperature was kept under 350 °C by using water cooling [19]. The substrate temperature, T_s , reached during depositions without an external heater, was in the range from 80 to 155 °C (see Table 1). The base pressure before deposition was 10^{-3} Pa and a reactive gas (oxygen) was admitted into the vacuum chamber from a source via mass flow controllers and two corundum conduits for deposition. Two O₂ inlets with a diameter of 1 mm were placed symmetrically above the target racetrack at the same distance of 20 mm from the target surface and oriented to the substrate [18]. The total pressure of the argon–oxygen gas mixtures was kept close to 2 Pa with the same argon

partial pressure of 2 Pa for all depositions. The magnetron was driven by a high-power pulsed dc power supply (HMP 2/1, Hüttinger Elektronik). The repetition frequency, f_r , was 500 Hz. The range for t_I was from 100 to 200 μs and that for $\langle S_d \rangle$ was from 7.2 to 54 Wcm^{-2} . Prior to a given deposition, we fix the nominal target power at an essentially constant magnetron voltage during discharge pulses, a preset argon partial pressure, a total oxygen flow rate in both conduits, Φ_{ox} , the O_2 inlet configuration, and a pre-selected critical value (Fig. 1) of the partial pressure of oxygen in the chamber, $p_{\text{ox}}(t)$, which was chosen to be the control process parameter in this case. During the deposition, a process controller used then provides a control feed-back signal to the two O_2 mass flow controllers to adjust the pulsed Φ_{ox} into the vacuum chamber ($\Phi_{\text{ox}} = \text{const}$ or 0) by adjusting the duration of the Φ_{ox} pulses by means of the pre-selected critical value of $p_{\text{ox}}(t)$, which is monitored by the process controller. This feed-back process control is able to maintain a sputter deposition of stoichiometric films in the region between a more and less metallic mode, and to utilize exclusive benefits of the HiPIMS discharges in preparation of films [20]. Fig. 1 shows the basic principle of the pulsed oxygen flow control and discharge characteristics during a controlled reactive sputter deposition of the stoichiometric HfO_2 film at $\langle S_d \rangle = 18 \text{ Wcm}^{-2}$ and $t_I = 200 \mu\text{s}$ (T200S18 film in Table 1). A detailed description of the film deposition parameters is given in Ref. [18]. Four films were prepared in this work (Table 1) for detailed microstructure characterization with (1) $t_I = 100 \mu\text{s}$, $\langle S_d \rangle = 7.2 \text{ Wcm}^{-2}$ (T100S7); (2) $t_I = 200 \mu\text{s}$, $\langle S_d \rangle = 7.3 \text{ Wcm}^{-2}$ (T200S7); (3) $t_I = 200 \mu\text{s}$, $\langle S_d \rangle = 18 \text{ Wcm}^{-2}$ (T200S18) and (4) $t_I = 200 \mu\text{s}$, $\langle S_d \rangle = 54 \text{ Wcm}^{-2}$ (T200S54). All these films exhibited a stoichiometric HfO_2 composition [18].

2.2. Film characterization

The surface morphology of the HfO_2 films was investigated using atomic force microscopy (AFM) in a Park XE 70 AFM system using a tapping mode. The crystallographic structure of the films was studied by X-ray diffraction (XRD) in a Bruker D8 Advance Diffractometer using Cu

K_α radiation at room temperature. The microstructure of the films was studied by TEM. Cross-section and plan-view TEM specimens were prepared by the procedure of mechanical grinding, polishing, dimpling and Ar-ion milling. Selected-area electron diffraction (SAED) patterns and HRTEM images were recorded in a Hitachi H-9500 electron microscope (300 keV). Nano-indentation measurements were performed in a Hysitron Ubi 1 Nanomechanical Test Instrument to determine film hardness, H , and the effective Young's modulus, $E^*=E/(1-\nu^2)$, where E and ν are the Young's modulus and Poisson's ratio, respectively. A cube corner diamond tip was used for the measurements.

The refractive index, n , and extinction coefficient, k , were determined by variable angle spectroscopic ellipsometry (VASE) using a J.A. WoollamCo. Inc. instrument. The measurements were performed using angles of incidence of 65° , 70° and 75° in reflection and the optical data were fitted using the WVASE software. The optical constants averaged over the film thickness (Table 1) were obtained using an optical model consisting of a c-Si substrate, a homogeneous HfO_2 layer described by the Cauchy dispersion formula with an Urbach absorption tail and a surface roughness layer. In addition, the thin interlayer observed by TEM (see below) was characterized using an alternative optical model in which the interlayer was represented by an additional layer (with the thickness given by TEM) described by the Cauchy dispersion formula, inserted just above the Si substrate. The n_{550} and k_{550} values were obtained at the specific wavelength of 550 nm.

3. Results and discussion

3.1. AFM studies

The surface morphology and roughness of four HfO_2 films were investigated using AFM in the non-contact mode with a scanning size of $1 \times 1 \mu\text{m}^2$. Figs. 2(a), (b) and (c) show 3D AFM images of films T200S54, T200S18 and T200S7, respectively, exhibiting a coarser granular

structure. The structures in the three films have a similar grain size varying from 25 nm to 120 nm in diameter with an average size of ~70 nm. Fig. 2(d) shows 3D AFM image of the film T100S7, exhibiting smaller granular structures compared to the former three films. These granular structures have a size varying from 20 nm to 80 nm with an average size of ~45 nm. All films were smooth and the average mean roughness, R_a , was ~0.66 nm, 1.07 nm, 0.60 nm and 0.85 nm for films T200S54, T200S18, T200S7 and T100S7, respectively.

3.2. XRD studies

We examined the crystal structure of the films using θ -2 θ XRD prior to conducting systematic TEM analysis (Fig. 3). It should be noted that HfO_2 has been reported to have four possible crystal structures: monoclinic (m- HfO_2 , PDF#: 01-075-6426, $a = 5.1187 \text{ \AA}$, $b = 5.1693 \text{ \AA}$, $c = 5.297 \text{ \AA}$, $\beta = 99.18^\circ$, $P2_1/c$) [21], orthorhombic (o- HfO_2 , PDF#: 01-070-2832, $a = 5.0073 \text{ \AA}$, $b = 5.2276 \text{ \AA}$, $c = 5.058 \text{ \AA}$, $Pbcm$) [21], tetragonal (t- HfO_2 , PDF#: 08-0342: $a = 5.14 \text{ \AA}$, $c = 5.25 \text{ \AA}$, $P4_2/nmc$) [21] and cubic (fcc, $a = 5.11 \text{ \AA}$) [22]. Formation of orthorhombic HfO_2 phase has been reported in Ref. [12]. Selected peaks of the monoclinic and orthorhombic HfO_2 phase are marked in Fig. 3.

As can be seen in Fig. 3, the XRD patterns from the T200S54 and T200S18 films exhibit peaks at 2θ positions of 23.62° , 27.76° , 33.74° , 35.34° , 44.66° , 49.94° , 54.76° and 60.92° corresponding to lattice spacing of $3.76 \text{ \AA}$, $3.21 \text{ \AA}$, $2.65 \text{ \AA}$, $2.54 \text{ \AA}$, $2.03 \text{ \AA}$, $1.82 \text{ \AA}$, $1.67 \text{ \AA}$, $1.52 \text{ \AA}$, respectively. Those peaks can be identified as the (011), ($\bar{1}1$), (002), (200), (121), (022)/(220), (122) and (131) of the monoclinic HfO_2 structure. The asymmetry present in the ($\bar{1}1$) of film T200S18 can be attributed to possible existence of a second phase or to texture in this film.

The XRD patterns of the T200S7 and T100S7 films exhibit broad peaks at 2θ positions of 24.08° , 27.9° , 31.03° , 33.9° , 49.7° and 54.76° corresponding to lattice spacing of $3.69 \text{ \AA}$, $3.19 \text{ \AA}$,

2.88 Å, 2.64 Å, 1.83 Å and 1.67 Å, respectively. Those peaks are also consistent with the (011), ($\bar{1}$ 11), (111), (002), (022) and (122) of the m-HfO₂ structure [21]. However, the latter peaks are broad and the presence of another phase can't be excluded.

3.3. HRTEM investigation

The detail microstructure of the films was studied using cross-section and plan-view TEM. The cross-section TEM images of all four films show a very uniform and smooth film surface and a sharp interface with the Si substrate. The T200S54, T200S18, T200S7 and T100S7 film thickness obtained from the cross-section TEM measurements was about 1000 nm, 1100 nm, 1000 nm and 960 nm, respectively.

3.3.1. Films T200S54 and T200S18

Films T200S54 and T200S18 exhibited a grain structure separated by thin boundaries as shown by the plan-view TEM images in Figs. 4(a) and (b). The grain boundaries possess a uniform thickness. The HfO₂ grains in T200S54 film have an average size of ~46 nm, larger than those in T200S18 (~38 nm). Figs. 4 (c) and (d) are SAED patterns taken from film T200S54 and T200S18, respectively. The diffraction rings 1, 2, 3, 4, 5, 6, 7 and 8 in Fig. 4(c) have a lattice spacing of 5.02 Å, 3.71 Å, 3.15 Å, 2.83 Å, 2.59 Å, 2.33 Å, 2.18 Å and 2.03 Å which can be determined to be the (100), (011), ($\bar{1}$ 11), (111), (200), (012), ($\bar{1}$ 21) and (121) or (112) of the m-HfO₂ (PDF#: 01-075-6426) [23], respectively. The diffraction rings 1, 2, 3, 4, 5 and 6 in Fig. 4(d) have the same lattice spacing as those in Fig. 4(c) indicating that the T200S18 film has also a m-HfO₂ structure. The intensity of the diffractions in Fig. 4(c) doesn't exhibit clear inhomogeneity over the rings indicating that there is no texture in film T200S54. However, the diffraction rings 3 and 5 in Fig. 4(d) exhibit clear and strong inhomogeneity in intensity. Roughly, half of the symmetric quarter of the rings 3 and 5 in Fig. 4(d) show diffractions attesting to the presence of texture in the T200S18 film.

Fig. 5(a) is a typical cross-section TEM image of the T200S54 film taken from an area away from the Si substrate presenting columnar structures with a column width of ~46 nm. Fig. 5(b) is a SAED pattern taken from the latter HfO₂ columnar structures. Similar to Fig. 4(c), no strong inhomogeneous distribution of diffraction intensity along the rings was observed further confirming the absence of texture in this film. Observations revealed the presence of a HfO₂ interlayer just above the interface with the Si substrate before the formation of the columnar structure, Fig. 5(c). The interlayer has a continuous homogenous structure and a hilly interface with respect to the columnar structure with a thickness of ~10 nm.

Figs. 5(d) and (f) are typical cross-section TEM images of film T200S18 taken from an area away and close to the Si substrate, respectively. The T200S18 film possesses also a columnar structure, similar to T200S54. The interlayer in the T200S18 film is, however, much thicker than that in T200S54 with a thickness of ~55 nm. Fig. 5(e) is a SAED pattern taken from the HfO₂ columnar structures in the T200S18 film showing strong inhomogeneous distribution of diffraction intensity along the rings further indicating formation of texture in the HfO₂ columnar structures.

Figs. 6(a) and (b) are HRTEM images taken from the film area that contains columnar structures in plan-view TEM foils of T200S54 and T200S18 film, respectively. The grains in both images are directly and tightly attached to each other with uniform thin and atomically sharp boundaries. Nanoscale lower density regions with a size of 2-3 nm were more frequently observed in Fig. 6(b) than in Fig. 6(a) indicating that the T200S18 film may possess larger volume fraction of lower density regions.

Fig. 7(a) is a cross-section HRTEM image of the T200S54 HfO₂ film showing two columnar structures (C₁ and C₂) and a boundary in between. It was observed that each column has a single crystal structure regardless of the formation of lower density nanoscale regions within each grain.

The interface between the HfO₂ interlayer and Si substrate in T200S54 is shown by the HRTEM image in Fig. 7(b). The HfO₂ interlayer is composed of a nanocrystalline structure with a size of several nm and is well attached to the Si substrate. Fig. 7(c) is a magnified cross-section TEM image of T200S18 film showing the HfO₂ interlayer, columnar structure layer and their interface. Contrary to the columnar structure area (C₀), a high population of lower density nanoscale regions were observed in the interlayer region (I). However, the interlayer region (I) is a highly crystalline structure despite the high population of the lower density regions, Fig. 7(d). The crystal size in region (I) in T200S18 is in the 10s of nm, much larger than that in T200S54, Fig. 7(b). It is interesting to note that an abrupt drop in the frequency of these nanoscale regions occurs across the boundary from region I to C₀, Fig. 7(d).

Film T200S54 deposited with $t_I = 200 \text{ } \mu\text{s}$ and $\langle S_d \rangle = 54 \text{ Wcm}^{-2}$ consists of a continuous interlayer with a thickness of $\sim 10 \text{ nm}$ and columnar structures with a width of $\sim 46 \text{ nm}$. The nano-columnar structures were interlocked directly without formation of amorphous boundaries. Film T200S54 has a m-HfO₂ structure without any texture. Such a film microstructure possesses a $H = 17.6 \text{ GPa}$, $E^* = 176.8 \text{ GPa}$, low $k_{550} = 1.0 \times 10^{-3}$ and high $n_{550} = 2.11$ (Table 1).

Film T200S18 was produced by reducing $\langle S_d \rangle$ from 54 Wcm^{-2} to 18 Wcm^{-2} while keeping the same $t_I = 200 \text{ } \mu\text{s}$. This film possesses the same m-HfO₂ structure but a different film microstructure exhibiting: (i) a significant increase in the interlayer thickness from 10 nm to $\sim 55 \text{ nm}$ (average value); (ii) slight reduction of the nano-columnar structure width from ~ 46 to $\sim 38 \text{ nm}$; and (iii) texture with the $(\bar{1}11)$ either parallel or perpendicular to the film surface, Figs. 3 and 5(e). The nano-columnar structures in film T200S18 were also interlocking directly without formation of amorphous boundaries. The T200S18 film has almost the same hardness and modulus as T200S54 but a lower $k_{550} = 0.3 \times 10^{-3}$ and $n_{550} = 2.07$ value (Table 1). Thus, reducing $\langle S_d \rangle$ at $t_I = 200 \text{ } \mu\text{s}$, refines the microstructure and develops texture.

3.3.2. Films T200S7 and T100S7

The microstructure of these films is presented by the plan-view TEM images shown in Figs. 8 (a) and (b). The grains in these films are separated by distinct boundaries instead of atomically thin boundaries. After examining a large number of grains, the average size for film T200S7 and T100S7 was ~24 nm and ~21 nm, respectively. More details of the grain structure is shown by the HRTEM images in Fig. 9. Well defined and low density boundaries with a thickness of ~1 nm are evident in the grain structure. SAED pattern analysis from the T200S7 film, revealed the same m-HfO₂ structure as in the films T200S54 and T200S18. Fig. 8(c) is a SAED pattern taken from a plan-view TEM foil of the T100S7 film. Some differences can be observed in this pattern compared to those shown in Figs. 4(c) and (d). The lattice spacing of the diffraction rings 1, 2, 3, 5, 6, 7 and 8 measured from Fig. 8(c) is 5.10 Å, 3.64 Å, 3.15 Å, 2.56 Å, 2.22 Å, 2.04 Å and 1.82 Å, respectively. The most intense diffraction ring 4 is actually composed of two sub-rings with a d-spacing of 2.96 Å (inner ring, 4a) and 2.83 Å (outer ring, 4b). The diffractions rings in Fig. 8(c) cannot be indexed by a single phase. Comprehensive studies of SAED patterns show that the T100S7 film possesses both monoclinic and orthorhombic HfO₂ phases. Fig. 8(d) depicts a comparison of the SAED patterns taken from the T200S7 (left) and T100S7 (right) film. A list of the d-spacing measured from the SAED patterns of the four films and the relevant data of the m-HfO₂ (PDF#: 01-075-6426) and o-HfO₂ (PDF#: 01-070-2832) is given in Table 2. All diffraction rings for the T200S7 film (left of Fig. 8(d)) can be indexed by m-HfO₂. Diffraction rings 1, 2, 3, 4b, 5, 7, 8 for the T100S7 film (right of Fig. 8(d)) can be indexed by m-HfO₂, while diffraction rings 1, 2, 4a, 5, 6, 7, 8 can be indexed by o-HfO₂. In other words, diffraction rings 1, 2, 5, 7, 8 are common for both m-HfO₂ and o-HfO₂, while rings 3 and 4b uniquely belong to m-HfO₂ phase, and rings 4a and 6 belong to o-HfO₂. The indices of the diffraction rings are listed in

Table 2. The above analysis clarifies the nature of the broad XRD peaks observed for this film, Fig. 3.

Figs. 10(a) and (b) are cross-section TEM images showing the presence of a columnar structure in these films away from the Si substrate similar to the previous two films. Figs. 10(c) and (d) are SAED patterns taken from film T200S7 and T100S7, respectively, presenting strong inhomogeneous intensity distribution along the diffraction rings indicative of texture formation. The line profiles along the vertical direction passing through the center of the SAED (i.e. film growth direction) in Figs. 10(c) and (d) show diffractions similar to the XRD patterns of the T200S7 and T100S7 film, respectively. For example, the diffraction rings *a*, *b*, *c* and *d* in Fig. 10(c) correspond to (110), ($\bar{1}$ 11), (111) and (002) of m-HfO₂. Diffraction rings *b* and *d* show much stronger intensity than *a* and *c* at the intersection with the vertical dash line, in a good agreement with the XRD of the T200S7 film. Similarly, the intersection of ring *c* with the vertical line in Fig. 10(d) depicts higher intensity than that of *a* and *d*, but lower than that of *b*, in a good agreement with the XRD of the T100S7 film. Figs. 10(e) and (f) show the interlayer structure between the Si substrate and the columnar structure in film T200S7 and T100S7, respectively. Both interlayers show a continuous homogenous structure and a hilly interface with respect to the columnar structure. Both interlayers possess a similar thickness with an average value of ~60 nm.

Fig. 11(a) is a cross-section HRTEM image of the T200S7 film presenting columnar structures and well defined boundaries. The lattices within or around the two regions marked by “*” are either highly distorted or disordered. The spots marked by “x” correspond to point defects that were likely produced by dislocations. Fig. 11(b) is a cross-section HRTEM image of the T200S7 film showing atomic structure near the interface (white dot line) between the HfO₂ interlayer and columnar structure layer. Similar to the previous films, a high population of lower

density nanoscale regions were observed in the interlayer, while their number was drastically reduced in the columnar region. Fig. 11(c) is a HRTEM image of the interlayer/columnar structure boundary marked as *M-N* in Fig. 10(e). The interface appears brighter while the lattice fringes in the columnar structure extended to the interlayer region without interruption after crossing the interface. Such contrast difference between the interface and surrounding structures is due to the mass variation of the sample indicating the lower density present at the interface. Fig. 11(d) is a HRTEM image of the interface between the HfO₂ interlayer and Si substrate in T100S7 film. Similar to the previous films, the HfO₂ interlayer is composed of a distribution of lower density nanoscale regions with a size of several nm up to 10 nm.

It is noted that a further reduction of $\langle S_d \rangle$ from 54 (T200S54) and 18 Wcm⁻² (T200S18) to 7.3 Wcm⁻² at the same $t_I = 200 \mu\text{s}$ still produces a m-HfO₂ structure in T200S7 film and a similar film microstructure to that in T200S18 film. The trend observed previously continues with (i) the average interlayer thickness increasing to ~60 nm, (ii) the microstructure refinement exhibiting a columnar width of ~24 nm, (iii) a m-HfO₂ preferred orientation with the ($\bar{1}$ 11) and (002) parallel to the film surface, Figs. 3 and 10(c), and (iv) lower $n_{550} = 2.02$ and slightly lower $k_{550} = 0.2 \times 10^{-3}$. However, the boundaries between the nano-columnar structures in T200S7 were relatively thick with an average size of ~1 nm. Additionally, the boundaries contained several lower density regions, Figs. 8 (a) and 9(a). The T200S7 film has nearly the same H and E^* as film T200S18, Table 1.

Film T100S7 prepared with a similar $\langle S_d \rangle = 7.2 \text{ Wcm}^{-2}$ but reduced $t_I = 100 \mu\text{s}$ possesses a monoclinic as well as orthorhombic HfO₂ structure. This film has an average interlayer thickness of ~60 nm. The nano-columnar structures have an average width of ~21 nm with thick boundaries similar to those in the T200S7 film and an average thickness of ~1 nm. The boundaries also contain lower density regions, Fig. 9(b). The m-HfO₂ crystals show a preferred

orientation with the $(\bar{1}11)$ parallel to the film surface, Figs. 3 and 10(d), where the orientation of the o-HfO₂ crystalline is random. The T100S7 film has nearly the same k_{550} and n_{550} as the T200S7 film but exhibits a reduction in $H = 13.4$ GPa and $E^* = 162.0$ GPa, Table 1. The aforementioned results suggest that a long t_l promotes formation of m-HfO₂ while shorter t_l promotes formation of o-HfO₂. This structural change from m-HfO₂ to o-HfO₂ is associated with the observed reduction in H and E^* in the films. Such effects are in agreement with previous observations [23, 24].

3.4. Effect of deposition parameters on the HfO₂ film microstructure and properties

The observed microstructures in the four HfO₂ films prepared by varying t_l from 100 μs to 200 μs and $\langle S_d \rangle$ from 7.2 Wcm^{-2} to 54 Wcm^{-2} provide a valuable insight into understanding the relationship between the deposition parameters, microstructure and film properties. All four HfO₂ films have nearly the same thickness of ~ 1 μm and are composed of an interlayer right above the Si substrate followed by a nano-columnar structure layer. A distribution of lower density nanoscale regions were observed in all four films and their number was significantly higher in the interlayer than in the columnar structure.

The HfO₂ crystal structure and its grain orientation within the film, the size of the nano-columnar structure and the thickness of the interlayer were found to be strongly affected by the deposition parameters t_l and $\langle S_d \rangle$. The effects of the variation of deposition parameters t_l and $\langle S_d \rangle$ on the nano-columnar structure size are depicted in Fig. 12(a). As noted earlier, $\langle S_d \rangle$ seems to play a predominant role. In particular, decreasing $\langle S_d \rangle$ while t_l remains constant (films T200S54, T200S18, T200S7), reduces the lateral size of the nano-columnar structures in the films, Fig. 12(a). Even though higher $\langle S_d \rangle$ is not expected to lead to significantly higher energy delivered into the growing films per deposited particle (see the close relationship between $\langle S_d \rangle$ and a_D in Table 1), it has two important effects. First, it leads to higher growth temperature

(increasing during the deposition) up to 155, 130 and 80-90 °C for $\langle S_d \rangle = 54, 18$ and 7 Wcm^{-2} , respectively. The consequently higher mobility of film atoms can naturally increase the column width (46, 38 and 21-24 nm for $\langle S_d \rangle = 54, 18$ and 7 Wcm^{-2} , respectively). Second, it leads to higher energy of some of the particles bombarding the growing films (stronger high-energy tail [20]). The energetic bombardment may, for example, destroy (amorphize) some of the crystals soon after their nucleation (see e. g. [25]), opening a larger space for the growth of the remaining ones. In parallel, shorter t_1 leads to a "less effective" utilization of the same $\langle S_d \rangle$ (e.g. the higher degree of ionization leads to a higher fraction of sputtered Hf atoms attracted back to the target [18], see also lower a_D in Table 1). The consequently lower energy delivered into growing films and lower growth temperature (up to 90 °C for T200S7 and up to 80 °C for T100S7) leads to a further slight but measurable reduction of column size (24 nm in T200S7 and 21 nm in T100S7). The combined effect is presented in Fig. 12(b) which shows an almost linear relationship between $(t_1 \langle S_d \rangle)^{1/2}$ and column width. In parallel to the aforementioned qualitative phenomena, the exponent is quantitatively consistent with the horizontal distance traveled (area affected) by arriving particles (particularly those from the $\langle S_d \rangle$ -dependent high-energy tail) during the pulse: the dependence on $t_1^{1/2}$ is the well-known relationship valid for a random walk, and the dependence on $\langle S_d \rangle^{1/2}$ yields a linear dependence on what can be a measure of the particle velocity. The easier growth of wide columns at better kinetic conditions is also consistent with the fact that their growth starts sooner (not only in time units but also in terms of deposited monolayers), note the thinnest interlayer (10 nm) in the sample prepared with the highest $\langle S_d \rangle = 54 \text{ Wcm}^{-2}$.

Fig. 13 presents the variation of n_{550} vs the lateral size of the nano-columnar structure and interlayer thickness. A general trend is shown where the decrease of the lateral columnar size is accompanied by a somewhat lower n_{550} . This property relates to the film density and the

observed trend is attributed to the increase of the volume fraction of low-density boundaries as the columnar size decreases. Films T200S7 and T100S7 exhibited thick, low density boundaries. On the contrary, films T200S54 and T200S18 exhibited higher density with atomically tight and interlocking boundaries resulting in high n_{550} values (2.11 and 2.07). Refractive indices reported for HfO_2 previously are either similar ($n_{550} \leq 2.09$ [26], $n_{1000} = 2.05$ [16], $n_{550} \leq 2.02$ and 2.1 [14]) or even significantly lower ($n_{550} \leq 1.94$ [6, 27], $n_{550} = 1.90$ [8], $n_{550} \leq 1.89$ [28]). In parallel to the thickness-averaged refractive indices presented above, the aforementioned higher concentration of low-density regions in the interlayers can be quantified by lower refractive indices of the interlayers (second of the two optical models presented in Sec. 2.2). The difference between the thickness-averaged n_{550} and the interlayer n_{550} is $2.02 - 1.94 = 0.08$ for the film T100S7, $2.02 - 1.96 = 0.06$ for the film T200S7, $2.07 - 2.02 = 0.05$ for the film T200S18, and not measurable (see also the low interlayer thickness) for the film T200S54.

The TEM figures show that (except the lower density of the interlayers) all presented films are vertically homogeneous. Note that in parallel to the TEM, this statement is also supported by the low $k_{550} \leq 10^{-3}$. Compositional inhomogeneities would lead to a mixture of stoichiometric HfO_2 with a low k_{550} and substoichiometric HfO_{2-x} with an enhanced k_{550} , and, consequently, the averaged extinction coefficient would be enhanced as well.

The high n_{550} up to 2.11 is important from two points of view: (i) in itself, for some of the applications mentioned in Sec. 1 (leading to a high optical contrast with the air or low- n materials such as SiO_2) and (ii) as a fingerprint of film densification (which in turn affects other functional properties such as the dielectric constant). Note that in parallel to the high refractive index, the densification of the films T200S54 and T200S18 (except the interlayers) is confirmed also by their mechanical properties. $E^* = 176.5 - 176.8$ GPa is consistent with e.g. 164.8 GPa (that of the films reported in Ref. [29] which has m- HfO_2 structure), 163-165 GPa (as-deposited films

in Ref. [30]) or 177-197 GPa (films annealed up to 700-900°C in Ref. [30]). In parallel, $H = 17.5-17.6$ GPa is even higher than 14.8 GPa (m-HfO₂ film in Ref. [29]), 8.3-9.7 GPa (as-deposited films in Ref. [30]) or 12.9-14.4 GPa (annealed films in Ref. [30]).

In addition, let us recall that all films showed very low values of $k_{550} \leq 1 \times 10^{-3}$ (property related to the film stoichiometry). Table 1 shows that the optical quality of the films is higher as $\langle S_d \rangle$ decreases from 54 Wcm⁻² to lower levels. It is interesting to note that the values of $k_{550} \leq 1 \times 10^{-3}$ obtained in this work for HfO₂ films are lower than those obtained ($k_{550} \leq 6 \times 10^{-3}$) for isostructural ZrO₂ prepared by the same technique [19]. The same trend has also been reported for k_{350} in Ref. [16].

4. Conclusions

Reactive high-power impulse magnetron sputtering with a pulsed reactive gas (oxygen) flow control was used to deposit HfO₂ films on Si substrates. The effect of the voltage pulse duration, t_l , and deposition-averaged target power density, $\langle S_d \rangle$, on their microstructure was studied by high-resolution transmission electron microscopy. Four HfO₂ films were prepared with (1) T100S7: $t_l = 100$ μs, $\langle S_d \rangle = 7.2$ Wcm⁻²; (2) T200S7: $t_l = 200$ μs, $\langle S_d \rangle = 7.3$ Wcm⁻²; (3) T200S18: $t_l = 200$ μs, $\langle S_d \rangle = 18$ Wcm⁻² and (4) T200S54: $t_l = 200$ μs, $\langle S_d \rangle = 54$ Wcm⁻². All films were composed of an interlayer with the Si substrate followed by a nano-columnar structure layer. Thus, the results show that the reactive gas flow control can be used to deposit vertically homogeneous films (without any multilayered structure which could hypothetically result from the O₂ flow pulsing). Decreasing $\langle S_d \rangle$ and t_l , was found to reduce the width of the columns, increase the thickness of the grain boundaries and thickness of the interlayer. Films prepared with a large t_l (T200S54, T200S18 and T200S7) exhibited a m-HfO₂ structure, while that with a smaller t_l (T100S7) exhibited a mixture of m- and o-HfO₂ phases. The hardness of

films was 13.4-17.6 GPa with those of a monoclinic structure possessing the highest hardness (17.0-17.6 GPa). The films exhibited a refractive index of 2.02-2.11 and an extinction coefficient between 0.1×10^{-3} and 1×10^{-3} (both at a wavelength of 550 nm). The highest refractive index was achieved for films T200S54 and T200S18 that exhibited denser microstructures with atomically sharp and tightly interlocking grain boundaries.

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Figure captions

Figure 1

Waveforms of the magnetron voltage, U_d , and the target current density (over total area of the target), J_t , for $\langle S_d \rangle = 18 \text{ Wcm}^{-2}$ and $t_f = 200 \text{ } \mu\text{s}$ with the pulse-averaged target power densities $S_{da} = 150 \text{ Wcm}^{-2}$ and 190 Wcm^{-2} relating to the minimum and maximum values of the oxygen partial pressure, p_{ox} , respectively, during preparation of the T200S18 film (Table 1). The pre-selected critical value of $p_{ox} = 0.07 \text{ Pa}$ determining the switching-on and switching-off of the oxygen flow rate $\Phi_{ox} = 10 \text{ sccm}$ in this case is marked by dots.

Figure 2

Non-contact AFM 3D images of HfO₂ films (a) T200S54, (b) T200S18, (c) T200S7 and (d) T100S7.

Figure 3

XRD patterns of the T200S54, T200S18, T200S7 and T100S7 film. The dotted and solid lines indicate the 2θ positions of the monoclinic HfO₂ and orthorhombic HfO₂ phase, respectively.

Figure 4

(a), (b) Plan-view TEM image, (c), (d) SAED pattern of the T200S54 and T200S18 film, respectively.

Figure 5

(a), (d) Cross-section TEM image of the HfO₂ film taken from T200S54 and T200S18, respectively. (b), (e) SAED pattern taken from the HfO₂ film in T200S54 and T200S18, respectively. (c), (f) Cross-section TEM image of the film/Si interface in T200S54 and T200S18, respectively.

Figure 6

(a), (b) Plan-view HRTEM image of T200S54 and T200S18 film, respectively.

Figure 7

(a), (b) Cross-section HRTEM image of the HfO_2 film and film/Si interface in T200S54, respectively. (c) Magnified cross-section TEM and (d) HRTEM image of the interface between the HfO_2 columnar structure and the interlayer in T200S18.

Figure 8

(a), (b) Plan-view TEM image for T200S7 and (b) T100S7, respectively. (c) SAED pattern of the T100S7 film in a plan-view TEM foil. (d) Comparison of SAED pattern for the T200S7 and T100S7 film.

Figure 9

Plan-view HRTEM image for (a) T200S7 and (b) T100S7 film.

Figure 10

(a, c) and (b, d) Cross-section TEM image and SAED pattern of the HfO_2 film from T200S7 and T100S7, respectively. (e) and (f) TEM image of the film/Si interface for T200S7 and T100S7, respectively.

Figure 11

(a) Cross-section HRTEM image of the HfO_2 film in T200S7. (b) and (c) HRTEM image of the interface between HfO_2 columnar structure and HfO_2 interlayer in T200S7. (d) HRTEM image of the interface between the HfO_2 interlayer and Si in T100S7.

Figure 12

(a) Variation of column width in the HfO_2 thin films as a function of voltage pulse duration, t_l , and target power density, $\langle S_d \rangle$. (b) Variation of column width with $(t_l \langle S_d \rangle)^{1/2}$.

Figure 13

Variation of n_{550} with column width and interlayer thickness.

Table 1. Deposition parameters and material characteristics of HfO₂ films: voltage pulse duration, t_l , deposition-averaged target power density, $\langle S_d \rangle$, pulse-averaged target power density, S_{da} , pulse-averaged magnetron voltage, U_{da} , deposition rate, a_D , substrate temperature, T_s , texture structure, crystal structure, column width, interlayer thickness, hardness, H , effective Young's modulus, E^* , and extinction coefficient, k_{550} , and refractive index, n_{550} , of the films at a wavelength of 550 nm.

Film No.	t_l (μ s)	$\langle S_d \rangle$ (Wcm ⁻²)	S_{da} (Wcm ⁻²)	U_{da} (V)	a_D (nm/min)	T_s (°C)	Texture structure	Crystal structure	Column width (nm)	Interlayer thickness (nm)	H (GPa)	E^* (GPa)	k_{550} (10 ⁻³)	n_{550}
T200S54	200	54	490-630	750	345	≤ 155	no	m-HfO ₂	46	10	17.6	176.8	1.0	2.11
T200S18	200	18	150-190	535	95	≤ 130	yes	m-HfO ₂	38	55	17.5	176.5	0.3	2.07
T200S7	200	7.3	45-80	430	30	≤ 90	yes	m-HfO ₂	24	60	17.0	176.0	0.2	2.02
T100S7	100	7.2	90-150	510	25	≤ 80	yes	m+o-HfO ₂	21	60	13.4	162.0	0.1	2.02

Table 2. List of the d-spacing of the m-HfO₂, o-HfO₂, and the measured values from the SAED patterns of the T200S54, T200S18, T200S7 and T100S7.

m-HfO ₂		T200S54 / T200S18		T200S7		T100S7		o-HfO ₂	
h k l	d (Å)	Diff. Ring	d (Å)	Diff. Ring	d (Å)	Diff. Ring	d (Å)	d (Å)	h k l
1 0 0	5.050	1	5.02	1	5.02	1	5.10	5.007	1 0 0
0 1 1	3.676	2	3.71						
1 1 0	3.612			2	3.62	2	3.64	3.616	1 1 0
-1 1 1	3.146	3	3.15	3	3.10	3	<u>3.15</u>		
						4a	2.96	2.942	1 1 1
1 1 1	2.825	4	2.83	4	2.79	4b	<u>2.83</u>		
0 2 0	2.584	5	2.59	5	2.55	5	2.56	2.529	0 0 2
0 1 2	2.332	6	2.33	6	2.31				
						6	2.22	2.258	2 1 0 / 1 0 2
-1 2 1	2.165	7	2.18	7	2.16				
1 2 1	2.052	8	2.03			7	2.04	2.062	2 1 1
1 1 2	2.012			8	2.01				
-1 2 2	1.793			9	1.79	8	1.82	1.818	0 2 2

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6

Figure 7

Figure 8

Figure 9

Figure 10

Figure 11

(a)

(b)

Figure 12

Figure 13