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High-throughput growth of HfO$_2$ films using temperature-gradient laser chemical vapor deposition

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**Abstract:** The use of hafnia (HfO₂) has facilitated recent advances in combining uprated dielectric layers (UDLs) and environmental barriers (EBs) in supercomputers. However, an extremely low deposition rate limits further development and fabrication efficiency of HfO₂ films. In this study, high-throughput growth of HfO₂ films was realized via laser chemical vapor deposition using a laser spot with a gradient temperature distribution. In HfO₂ films fabricated by a single growth process, four regions with different morphologies could be discerned for deposition temperatures increasing from 1300 K to 1600 K: leaf-like, pyramid-like, bromeliad-like and pinecone-like. Two growth modes were observed for Regions I and II: Stranski-Krastanov and Volmer-Weber. Regions III and IV contained coexisting monoclinic and tetragonal HfO₂ grains with an in-plane boundary for m-HfO₂ (-110) {111} // t-HfO₂ (-111) {111}. The maximum deposition rate reached 362 μm/h, which was 10² - 10⁴ times higher than that obtained using existing deposition methods.

**Key words:** Laser chemical vapor deposition (LCVD); Temperature gradient; High-throughput growth; HfO₂ films; Microstructure; Growth mechanism.

1. **Introduction**

Supercomputers based on a combination of uprated dielectric layers (UDLs) and environmental barriers (EBs) offer the advantages of a compact size, adaptive integration, and massive parallelization [1]. Thus, corresponding advances are required in dielectric materials to passivate exposed surfaces against destabilization related to ion transport [2] and in barrier materials to protect core components against thermal shock or fluid erosion in harsh operating environments [3]. Processing studies have
shown that a traditional SiO$_2$ barrier layer with a thickness of over 50 μm sustained a weight loss of more than 70% after 500 cycles in a thermal-shock test [4], which does not meet the requirements of miniaturization and sustainability. In 2007, Intel Inc. announced that HfO$_2$, a high-k inorganic material with an ultrahigh melting point (3085 K) [5], a sufficient electrical breakdown field (3.9–6.7 MV/cm) [6], low thermal conductivity (~2.55 W·K$^{-1}$·m$^{-1}$), and four times the density (9.68 g/cm$^3$) of SiO$_2$ (2.26 g/cm$^3$) [7], as the most promising dielectric layer material to replace the traditional SiO$_2$ layer for a new generation of supercomputers [8].

Table 1. Comparison of deposition temperatures and rates of HfO$_2$ films grown using different methods.

<table>
<thead>
<tr>
<th>Ref.</th>
<th>Method</th>
<th>Precursor</th>
<th>$T_{\text{dep}}$ (K)</th>
<th>$R_{\text{dep}}$ (μm/h)</th>
</tr>
</thead>
<tbody>
<tr>
<td>[9]</td>
<td>MOCVD</td>
<td>Cp$_2$Hf(NEt$_2$)$_2$</td>
<td>1273</td>
<td>$2.40 \times 10^{-1}$</td>
</tr>
<tr>
<td>[10]</td>
<td>MOCVD</td>
<td>(Cp$_2$CMe$_2$)HfMe$_2$</td>
<td>923</td>
<td>$7.20 \times 10^{-2}$</td>
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<tr>
<td>[11]</td>
<td>MOCVD</td>
<td>Hf(dmml)$_4$</td>
<td>973</td>
<td>$5.40 \times 10^{-2}$</td>
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<tr>
<td>[12]</td>
<td>TCVD</td>
<td>HfCl$_4$</td>
<td>473</td>
<td>$1.64 \times 10^{-3}$</td>
</tr>
<tr>
<td>[13]</td>
<td>ALD</td>
<td>Hf(NEt$_2$)$_4$</td>
<td>1373</td>
<td>$9.60 \times 10^{-3}$</td>
</tr>
<tr>
<td>[14]</td>
<td>ALD</td>
<td>HfO$^\circ$Bu(NEtMe)$_3$</td>
<td>623</td>
<td>$8.90 \times 10^{-2}$</td>
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<tr>
<td>[15]</td>
<td>ALD</td>
<td>Hf(NEtMe)$_4$</td>
<td>633</td>
<td>$1.01 \times 10^{-1}$</td>
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<tr>
<td>[16]</td>
<td>ALD</td>
<td>Hf(NEt$_2$)$_4$</td>
<td>1273</td>
<td>$8.64 \times 10^{-2}$</td>
</tr>
<tr>
<td>[17]</td>
<td>ALD</td>
<td>CpHf(NEt$_2$)$_3$</td>
<td>523</td>
<td>$7.20 \times 10^{-2}$</td>
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<tr>
<td>[18]</td>
<td>sol-gel</td>
<td>HfCl$_4$</td>
<td>873</td>
<td>$1.03 \times 10^{-3}$</td>
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<tr>
<td>[19]</td>
<td>sol-gel</td>
<td>HfCl$_4$</td>
<td>823</td>
<td>$2.07 \times 10^{-3}$</td>
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<tr>
<td>[20]</td>
<td>sol-gel</td>
<td>HfCl$_4$</td>
<td>873</td>
<td>$6.67 \times 10^{-3}$</td>
</tr>
<tr>
<td>[21]</td>
<td>RFMS</td>
<td>HfO$_2$ target</td>
<td>573</td>
<td>$7.50 \times 10^{-2}$</td>
</tr>
<tr>
<td>[22]</td>
<td>PLD</td>
<td>HfO$_2$ target</td>
<td>1173</td>
<td>$8.52 \times 10^{-1}$</td>
</tr>
<tr>
<td>This study</td>
<td>HT-LCVD</td>
<td>Hf(acac)$_4$</td>
<td>1300–1600</td>
<td>$4.68 \times 10^1$ ~ $3.62 \times 10^2$</td>
</tr>
</tbody>
</table>
Table 1 shows the deposition temperature ($T_{\text{dep}}$) and deposition rate ($R_{\text{dep}}$) measured for HfO$_2$ films grown using different methods, such as metal-organic CVD (MOCVD) [9-11], thermal CVD (TCVD) [12], atomic layer deposition (ALD) [13-17], sol-gel [18-20], radio frequency magnetron sputtering (RFMS) [21] and pulsed laser deposition (PLD) [22]. As a result of the extremely low deposition rate of HfO$_2$ films, only a few scholars have studied the growth of films with thicknesses below 100 nm over the last decade, such that HfO$_2$ films have not been exploited at the micron scale. Since 2012, our group has been developing LCVD [23] to significantly improve the CVD deposition rates, and we have been able to rapidly grow SiC [24], SiOC [25], AlN [26], LiAlO$_2$ [27], BaTi$_2$O$_5$ [28], and SmBa$_2$Cu$_3$O$_7$ [29] films at deposition rates 10-10$^4$ times higher than those of conventional CVD methods. Novel structures and growth mechanisms have been found using LCVD to grow films [30].

High-throughput growth offers a significant advantage toward improving the experimental efficiency in that multiple specimens are obtained from a single preparation. Advances in CVD need to be made to realize high-throughput growth, which is currently mainly achieved using physical vapor deposition (PVD) because of good uniformity, excellent step coverage, simple equipment, and convenient control of the film composition [31]. However, various factors in CVD processes, such as the growth temperature, pressures, and gas flow rates, need to be further investigated [32]. The presence of multiple variables and uncertainties in these variables result in an extended experimental time and deteriorate the repeatability of the entire process; hence, little pertinent research has been performed on high-throughput CVD.
We significantly shortened the experimental time by modifying the high-throughput LCVD (HT-LCVD) method by using a temperature-gradient preparation with credible measurement and repeatability, resulting in $10^2$ - $10^4$ times higher growth rates than other methods and the fabrication of multiple specimens per unit time. In this study, HfO$_2$ films were grown using a highly efficient HT-LCVD process. The morphologies, deposition rates and growth mechanisms of four novel microstructures were determined.

2. Experimental Section

Fig. 1 shows the HT-LCVD apparatus that was constructed to fabricate HfO$_2$ films. An InGaAlAs beam-by-diode laser (wavelength: 808 nm, LHTC-200, ZK-LASER, China) was introduced into the chamber through a quartz-glass window and diverged by an optical lens (around 18 mm in diameter) to irradiate the entire substrate surface. The diode laser beam created a temperature-gradient distribution over the substrate surface. Fig. 2 shows vertical and stereo views of the temperature distribution during high-throughput growth. As $T_{\text{dep}}$ increased from 1300 K to 1600 K, four specific regions with different novel microstructures could be observed for several specimens fabricated by a single growth process. The temperature distribution was measured by an infrared pyrometer (CHINO IR-AH) and regulated by an infrared temperature-measurement program (OMRON, Japan). Fig. 3 shows the growth procedure. Si (100) single crystal wafers were cut into samples with dimensions of $10.0 \times 10.0 \times 0.5$ mm for use as substrates, which were placed on a heating stage in the chamber and preheated at 873 K for 5 min after evacuating the chamber to 5 Pa. The substrate holder was supported
by an alumina plate with a K-type thermocouple, which was used to monitor the
temperature of the heating stage. The precursor, Hf(acac)$_4$ (Aladdin Inc., Shanghai,
China), was vaporized at 493 K and carried into the vacuum chamber by Ar gas
(99.999%). Table 2 shows a summarization of deposition conditions used to prepare the
temperature-gradient HfO$_2$ films via HT-LCVD.

The crystalline phases were examined by the microarea X-ray diffraction (μ-XRD;
D8 DISCOVER, Bruker, Germany; 40 kV, 40 mA) with Cu $\text{K}_{\alpha2}$ radiation, whereby a
small region (0.4 mm in diameter) in the specimen was fingerprinted. The composition
of the microarea on the surface was detected by Raman spectroscopy (inVia. Renishaw,
633 nm He-Ne laser, UK). The surface and cross-section morphologies were
characterized by scanning electron microscopy (SEM, Quanta FEG 450, FEI, USA, at
20 kV). The microstructures were observed using double-beam electron microscopy
with focused ion beam processing (FIB, Helios NanoLab G3 UC, FEI, USA, at 20 kV)
and transmission electron microscopy (TEM, JEOL Ltd., Japan, JEM-2100F, at 200
kV).
Fig. 1. Schematic of the HT-LCVD apparatus.

Fig. 2. (a) Top view of the temperature distribution and (b) stereo view of four discernible regions.
Fig. 3. Diagram showing the evolution of temperature in HfO$_2$ films grown using HT-LCVD.

Table 2. Deposition Conditions

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Precursor:</td>
<td>Hf(acac)$_4$</td>
</tr>
<tr>
<td>Substrate:</td>
<td>Si (100)</td>
</tr>
<tr>
<td>Deposition temperature ($T_{\text{dep}}$):</td>
<td>1250-1600 K</td>
</tr>
<tr>
<td>Total pressure ($P_{\text{tot}}$):</td>
<td>200 Pa</td>
</tr>
<tr>
<td>Laser power ($P_L$):</td>
<td>100 W</td>
</tr>
<tr>
<td>Precursor vaporization temperature:</td>
<td>493 K</td>
</tr>
<tr>
<td>Pipe/gas nozzle temperature ($T_{\text{pip}}$):</td>
<td>573K</td>
</tr>
<tr>
<td>Deposition time ($t_{\text{dep}}$):</td>
<td>10 min</td>
</tr>
<tr>
<td>Ar carrier gas flow rate:</td>
<td>$1.67 \times 10^{-6}$ m$^3$ s$^{-1}$ (100 sccm)</td>
</tr>
<tr>
<td>Ar diluent gas flow rate:</td>
<td>$1.67 \times 10^{-6}$ m$^3$ s$^{-1}$ (100 sccm)</td>
</tr>
<tr>
<td>Nozzle diameter:</td>
<td>6.0 mm</td>
</tr>
<tr>
<td>Distance between nozzle and substrate:</td>
<td>15 mm</td>
</tr>
</tbody>
</table>
3. Results and Discussion

Fig. 4. μ-XRD patterns of different regions in HfO₂ film produced by the high-throughput growth process: (a) 1300K/I, (b) 1400K/II, (c) 1500K/III, (d) 1600K/IV, and (e) Si (100) substrate.

Fig. 4(a)–(d) displays the μ-XRD patterns of the 4 temperature regions in a HfO₂
film grown on Si (001) shown in Fig. 2, which were indexed with JCPDS data, No. 06-0318 (monoclinic HfO₂, P2₁/c) and No. 08-0342 (tetragonal HfO₂, P4₂/nmc). The (111) and (111) main peaks of m-HfO₂ at 2θ = 28.3° and 31.7°, respectively, were identified for all specimens. The patterns for Regions I (1300 K) and II (1400 K) showed no trace of t-HfO₂ peaks. At T_{dep} = 1400 K, m-HfO₂ exhibited a strong <002> orientation. The two diffraction peaks at 2θ = 34.6° and 72.7° corresponded to the (002) and (004) planes of m-HfO₂, respectively. The patterns for Regions III (1500 K) and IV (1600 K) exhibited two prominent peaks at 2θ = 30.1° and 35.1° corresponding to the (111) and (111) planes of t-HfO₂, respectively, indicating the coexistence of m- and t-HfO₂. Eq. (1) shows an approximate calculation formula that Luo et al. [33] developed to estimate the proportion of m-HfO₂, Cₘ, from µ-XRD patterns with high precision:

$$C_m \% = \frac{100}{1 + \frac{R_m}{R_t} \frac{I_t}{I_m}}$$  \(1\)

where Rₘ/Rₜ is the ratio of the standard diffraction coefficients of m- and t-HfO₂ and was calculated as 0.85 [6], Iₜ/Iₘ is the ratio of the main-peak diffraction intensities of the two phases corresponding to the m-HfO₂ (111) and t-HfO₂ (111) planes. Using Eq. (1), the proportion of m-HfO₂ in Regions III and IV was calculated as 82% and 74%, respectively, indicating a slight increase in the proportion of t-HfO₂ grains from 1500 K to 1600 K.
Fig. 5. Raman spectra for the four regions in the HfO$_2$ film.

Fig. 6. (a) FWHM of the m-HfO$_2$(111) XRD peak and (b) intensity ratio $\eta = I_{TO} / I_{LO}$ obtained from Raman spectra of four regions with $T_{dep}$ ranging from 1300 K to 1600 K.
Fig. 5 shows the Raman scattering spectra for the four regions with deposition temperatures of 1300-1600 K in a HfO$_2$ film. For Raman shifts from 100 to 800 cm$^{-1}$, the two characteristic peaks at ~129 cm$^{-1}$ and ~144 cm$^{-1}$ were ascribed to two acoustic phonon modes for transverse acoustic (T$_A$) and longitudinal acoustic (L$_A$) phonons of m-HfO$_2$ films, respectively. The intensity of the acoustic-phonon peaks increased remarkably with the film thickness [34]. Two characteristic bands appeared at approximately 494 cm$^{-1}$ and 572 cm$^{-1}$ for all samples that were ascribed to transverse optical (T$_O$) and longitudinal optical (L$_O$) phonons, respectively. For the crystal growth of m-HfO$_2$ films, the integral intensities of the L$_O$ bands were expected to increase with film qualities because the L$_O$ mode is allowed, whereas the T$_O$ mode is forbidden. Fig. 6(b) shows the intensity ratio between T$_O$ and L$_O$, $\eta$, that was used to evaluate the HfO$_2$ film quality. When $T_{\text{dep}}$ increased from 1300 K to 1600 K, the lowest $\eta$ was observed at 1400 K (Region II). A similar trend can be observed for the full width at half maximum (FWHM) of the m-HfO$_2$ (111) peaks in $\mu$-XRD patterns shown in Fig. 6(a). Tkachev et al. [35] analyzed the XRD patterns and Raman spectra of polycrystalline HfO$_2$ films with various grain sizes and found that $\eta$ for the Raman spectra decreased as the grain size increased. Hence, we inferred that the increase in the integral intensity of the HfO$_2$ film resulted from an increase in the proportion of large grains. For $T_{\text{dep}}$ above 1500 K (Regions III and IV), the four broad peaks (B$_1$ - B$_4$) at ~237, ~251, ~336, and ~382 cm$^{-1}$ in the spectra were ascribed to the interstitial tetragonal phase that retarded the lattice vibrations at the phase boundary [36]. The integral intensity of the broad B$_1$ - B$_4$ peaks increased with the proportion of t-HfO$_2$, consistent with the XRD patterns. The peaks
at 519 cm⁻¹ were assigned to the Si (100) substrates.

Fig. 7. SEM images of cross-sections and surfaces of HfO₂ films obtained using the high-throughput growth process with insets showing similarity of morphologies to well-known structures.

Fig. 8. Schematic model for the growth of <002>-oriented grains in Region II showing (a) atomic nodes and (b) pyramid-like exposed surface.
Fig. 7 shows SEM micrographs of the cross-section and surface for Regions I to IV of the HfO$_2$ film as $T_{\text{dep}}$ increased from 1300 K to 1600 K. Measurements taken from the cross-sectional SEM micrographs (Fig. 7(a)–(d)) show that the thickness increased from 7.8 μm to 60.3 μm, corresponding to calculated growth rates of 46.8–362.0 μm/h. The surface SEM images show four morphologies in the as-deposited film: leaf-like (Fig. 7(i)), pyramid-like (Fig. 7(j)), bromeliad-like (Fig. 7(k)) and pinecone-like (Fig. 7(l)). The cross-sectional micrographs show the leaf-like structure (Region I) formed at 1300 K had a columnar microstructure. Aggregates of fine grains were arrayed in random lines on the film surface. The cross-sectional micrographs show the pyramid-like structure (Region II) formed at 1400 K was composed of $<002>$-oriented columnar grains. Fig. 7(n) shows a pyramidal faceted morphology corresponding to the (111), ($\bar{1}$11), (1$\bar{1}$1), and ($\bar{1}$ $\bar{1}$ 1) planes of m-HfO$_2$, with a parallel texture at the surface of (002)-oriented m-HfO$_2$ grains. Fig. 8(a) shows atomic nodes with a twofold rotational symmetry, which is the typical morphology of the P$\overline{2}_1$/c space group. Javier Sanz et al. calculated lower surface energies for the m-HfO$_2$ (111) and (1$\bar{1}$11) planes than the (100) and (010) planes based on Born-Oppenheimer molecular dynamics (BOMD) simulations [37]. Lower surface energies usually correspond to exposed surfaces, as shown in Fig. 8(b). The cross-section micrographs show that the bromeliad-like structure (Region III) formed at 1500 K consists of crystal clusters. At the surface, the crystal clusters are aggregates of vertical bundles that are decorated allover with fine grains, presumably resulting from the coexistence of m- and t-HfO$_2$. The cross-sectional
micrographs show the pinecone-like structure (Region IV) formed at 1600 K exhibits a porous microstructure. The surface morphology is similar to that of Region III, except that the grain size increases from ~200 nm to ~500 nm with increasing temperature, with a wavy texture at the surface. The morphologies corresponded to XRD patterns ranging from random (Region I) to highly oriented (Region II) and back to random (Regions III and IV) with increasing temperature.

Fig. 9. Effect of $T_{\text{dep}}$ on $R_{\text{dep}}$ and crystal phase of HfO$_2$ films prepared using HT-LCVD, MOCVD, TCVD and ALD.
Fig. 9 shows a dependence of deposition rates ($R_{dep}$) on inverse deposition temperatures ($T_{dep}^{-1}$) of HfO$_2$ films grown using HT-LCVD, showing the presence of crystal phases (monoclinic, tetragonal or amorphous) and precursors, and the results are compared against those in the literature. To improve the measurement accuracy, the HfO$_2$ film was divided into eight specimens fabricated at 1250-1600 K using a single growth process. The $R_{dep}$ of the HfO$_2$ film prepared by HT-LCVD reached a maximum of 362 μm/h at $T_{dep} = 1600$ K, which was $10^2$-$10^4$ times higher than that obtained using existing methods, such as MOCVD [9-11], TCVD [12] and ALD [13-17]. Using the infrared temperature-measurement program, the microstructure of the HfO$_2$ film was found to change from columnar to cluster-like at approximately 1420 K. A phase transition temperature above 1300 K was measured at atmospheric pressure [6]. Lin C et al. [38] reported that enhanced EB coatings could be prepared by increasing the microstructure transition temperature. Considering the ultrahigh melting point (3085 K) of HfO$_2$, EB failure could result from by the phase transition.

The Arrhenius equation was used to calculate the activation energies ($E_a$) of the specimens as 100-220 kJ/mol in the curved regions of the energy surface over the range of 1250–1400 K (Regions I and II) and 80 kJ/mol in the linear part of the energy surface at $T_{dep} = 1400–1600$ K (Regions III and IV). The deposition rates in the curved regions were correlated with controlling kinetic mechanisms of deposition processes [i.e., the chemical reaction regime (CRR) or the mass transfer regime (MTR)], where the transition from CRR to MTR is normally induced by an increase in temperature [39]. Loumagne et al. [40] suggested that the transition from the CRR to the MTR increases
the supersaturation of the grains. In Regions I and II, the slope of the Arrhenius equation decreased from 220 kJ/mol to 100 kJ/mol, indicating a transition from the CRR to the MTR domain. A higher $E_a$ was determined in the range of 1250–1400 K for LCVD than for other methods. Akihiko Ito et al. attributed this high $E_a$ to the breakage of precursor bonds by laser phonons in LCVD [41]. Therefore, an increase in the number of active radicals over the growing surface increased $R_{dep}$.

![Cross-section TEM images of Regions I and II in m-HfO$_2$.](image)

Fig. 10. Cross-section TEM images of Regions I and II in m-HfO$_2$.

Fig. 10 shows cross-section TEM images of the leaf-like and pyramid-like specimens. The bright-field (BF) image of Region I shows columnar grains with a variety of
orientations. The selected area electron diffraction (SAED) pattern exhibited in Fig. 10(b) was indexed to a set of well-defined (002) sites along the zone axis of [110]. Application of Vander Drift’s evolutionary selection model [39] to the high-resolution (HR) TEM image revealed exposed surfaces along the [\(\bar{1}11\)] or [002] directions, which explained why the fastest growing crystallographic plane overlaid the other growing planes. Komiyama et al. [43] developed a model for the CRR or MTR controlling mechanisms of the CVD processes by assuming Langmuir-type adsorption of the reactants. The leaf-like structure formed at 1300 K was associated with CRR, and \(R_{\text{dep}}\) was expressed as given in Eq. (2):

\[
R_{\text{dep}} = k_r N_{hkl} V
\]

where \(k_r\), \(N_{hkl}\), and \(V\) represent the reaction-limited rate coefficient, atomic density of the \((hkl)\) plane, and molar volume of HfO\(_2\), respectively. In a finite region, \(R_{\text{dep}} \propto N_{hkl}\).

The natural stacking sequence of the m-HfO\(_2\) unit cell with P\(_{2_1}\)/c symmetry lies along the \([\bar{1}11]\) direction, in agreement with the XRD patterns. As there was insufficient energy for the system to reach the equilibrium state at a low temperature, supersaturation of m-HfO\(_2\) grains led to lattice distortion of the \((\bar{1}11)\) planes and a variety of orientations in Region I. The overall growth process could be considered an extension of the Stranski-Krastanov (SK) growth mode [43] for a two-dimensional (2D) thin film to a finite 3D case.

The SAED in Fig. 10(e) for Region II was indexed to a set of (002) sites along the zone axis of [110]. The HRTEM image showed exposed surfaces corresponding to the \((1\bar{1}1)\) and \((\bar{1}11)\) planes of m-HfO\(_2\). The distinct pyramid-like structure formed at 1400
K was associated with MTR, and $R_{dep}$ was expressed using Eq. (3):

$$R_{dep} = k_s \eta_{hkl} V$$

(3)

where $k_s$ and $\eta_{hkl}$ represent the adsorption-limited rate coefficient and sticking probability for the $(hkl)$ plane, respectively. For Langmuir-type adsorption, the stacking sequence transforms into the multiple-layer inclusions of other polytypes [43]. The *pyramid-like* structure was formed by the Volmer-Weber (VW) island growth mode [44] and provided many adsorption sites, making [002] the fastest growing direction. The faster-growing grains covered the slower-growing grains, such that the grains along the fastest [002] growing direction survived and dominated the entire thickness.

**Fig. 11.** Cross-section TEM images of Regions III and IV in m/t-HfO$_2$. 

![Fig. 11](image-url)
Fig. 11 shows the cross-section TEM images of the bromeliad-like and pinecone-like specimens composed of monoclinic (yellow) and tetragonal (bright green) grains. When the deposition temperature exceeded 1500 K, growth deviated from the equilibrium state again via the Volmer-Weber (VW) island growth mode [44], and the increase in the concentration of activated molecules resulted in an increase in the supersaturation of the grains. The HRTEM images showed the in-plane boundary for m-HfO$_2$(110){111}//t-HfO$_2$(111){111}. Falkowski et al. found a similar structure in m/t-ZrO$_2$ along the O-[010]/M-[010] direction by modeling the field-induced phase transition [45]. The self-vanishing defects at the interface induced the migration of {111} planes, such that no distinct interface between the two phases of HfO$_2$ could be observed.

4. Conclusion

In this study, high-throughput HfO$_2$ films were deposited on Si (100) substrates via HT-LCVD using Hf(acac)$_4$ as a precursor. The maximum deposition rate of 362 μm/h was $10^2 \sim 10^4$ times higher than that obtained using existing CVD methods. The HfO$_2$ films obtained using a single growth process could be divided into four regions corresponding to increasing $T_{\text{dep}}$ from 1300 K to 1600 K, with orientations ranging from random to highly oriented and back to random. The leaf-like region formed at 1300 K was associated with CRR and was a nonequilibrium state that could be modeled by extending the Stranski-Krastanov growth mode on a two-dimensional (2D) thin film to a finite 3D case. The columnar grains in the pyramid-like region formed at a $T_{\text{dep}}$ of 1400 K exhibited a strong <002> orientation that was associated with the transition
from CRR to MTR. In Region II, a Volmer-Weber growth mode resulted in faster-growing grains covering slower-growing grains, whereby grains survived along the fastest growing direction. As the temperature rose to 1500 K, the concentration of activated molecules increased, resulting in an increase in the supersaturation of the grains. Regions III (bromeliad-like, 1500 K) and IV (pinecone-like, 1600 K) consisted of coexisting monoclinic and tetragonal phases, with an in-plane boundary for m-HfO$_2$ \((\vec{1}10)\) \(\{111\}\) // t-HfO$_2$ \((1\overline{1}1)\) \(\{111\}\).

Conflict of interest

The authors declare that they have no conflict of interest.

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