Atomic layer deposition of HfO2 using HfCp(NMe2)3 and O2 plasma

Citation for published version (APA):

DOI:
10.1116/1.4972210

Document status and date:
Published: 01/01/2017

Document Version:
Publisher’s PDF, also known as Version of Record (includes final page, issue and volume numbers)

Please check the document version of this publication:
• A submitted manuscript is the version of the article upon submission and before peer-review. There can be important differences between the submitted version and the official published version of record. People interested in the research are advised to contact the author for the final version of the publication, or visit the DOI to the publisher’s website.
• The final author version and the galley proof are versions of the publication after peer review.
• The final published version features the final layout of the paper including the volume, issue and page numbers.
Link to publication

General rights
Copyright and moral rights for the publications made accessible in the public portal are retained by the authors and/or other copyright owners and it is a condition of accessing publications that users recognise and abide by the legal requirements associated with these rights.

• Users may download and print one copy of any publication from the public portal for the purpose of private study or research.
• You may not further distribute the material or use it for any profit-making activity or commercial gain
• You may freely distribute the URL identifying the publication in the public portal.

If the publication is distributed under the terms of Article 25fa of the Dutch Copyright Act, indicated by the “Taverne” license above, please follow below link for the End User Agreement:
www.tue.nl/taverne

Take down policy
If you believe that this document breaches copyright please contact us at:
openaccess@tue.nl
providing details and we will investigate your claim.
Atomic layer deposition of HfO$_2$ using HfCp(NMe$_2$)$_3$ and O$_2$ plasma

Akhil Sharma, Valentino Longo, Marcel A. Verheijen, Ageeth A. Bol and W. M. M. (Erwin) Kessels

Citation: J. Vac. Sci. Technol. A 35, 01B130 (2017); doi: 10.1116/1.4972210
View online: http://dx.doi.org/10.1116/1.4972210
View Table of Contents: http://avs.scitation.org/toc/jva/35/1
Published by the American Vacuum Society

Articles you may be interested in

- Plasma-assisted atomic layer deposition of HfNx: Tailoring the film properties by the plasma gas composition
  J. Vac. Sci. Technol. A 35, 01B129 (2016); 10.1116/1.4972208

- Low-temperature-atomic-layer-deposition of SiO$_2$ using various organic precursors
  J. Vac. Sci. Technol. A 35, 01B131 (2016); 10.1116/1.4972211

- Plasma-assisted atomic layer deposition of conformal Pt films in high aspect ratio trenches

- Tris(dimethylamido)aluminum(III): An overlooked atomic layer deposition precursor
  J. Vac. Sci. Technol. A 35, 01B128 (2016); 10.1116/1.4972469
Atomic layer deposition of HfO₂ using HfCp(NMe₂)₃ and O₂ plasma

Akhil Sharma
Department of Applied Physics, Eindhoven University of Technology, P.O. Box 513, 5600 MB Eindhoven, The Netherlands

Valentino Longo
Department of Applied Physics, Eindhoven University of Technology, P.O. Box 513, 5600 MB Eindhoven, The Netherlands and Philips Innovation Services, High Tech Campus 4, 5656 AE Eindhoven, The Netherlands

Marcel A. Verheijen
Department of Applied Physics, Eindhoven University of Technology, P.O. Box 513, 5600 MB Eindhoven, The Netherlands

Ageeth A. Bol and W. M. M. (Erwin) Kessels
Department of Applied Physics, Eindhoven University of Technology, P.O. Box 513, 5600 MB Eindhoven, The Netherlands

(Received 23 September 2016; accepted 29 November 2016; published 20 December 2016)

HfO₂ thin films were prepared by plasma-enhanced atomic layer deposition using a cyclopentadienylalkylamido precursor [HfCp(NMe₂)], HyALD™ and an O₂ plasma over a temperature range of 150–400 °C at a growth per cycle around 1.1 Å/cycle. The high purity of the films was demonstrated by x-ray photoelectron spectroscopy and elastic recoil detection analyses which revealed that by increasing the deposition temperature from 200 to 400 °C, the atomic concentrations of residual carbon and hydrogen reduced from 1.0 to <0.5 at. % and 3.4 to 0.8 at. %, respectively. Moreover, Rutherford backscattering spectroscopy studies showed an improvement in stoichiometry of HfO₂ thin films with the increase in deposition temperature, resulting in Hf/O ratio close to ~0.5 at 400 °C. Furthermore, grazing incidence x-ray diffraction measurements detected a transition from amorphous at the deposition temperature of 300 °C to fully polycrystalline films at 400 °C, consisting of a mixture of monoclinic, tetragonal, and cubic phases. Finally, the surface morphology and conformality of HfO₂ thin films studied by atomic force microscopy and transmission electron microscopy are also reported. © 2016 American Vacuum Society.

[http://dx.doi.org/10.1116/1.4972210]

I. INTRODUCTION

Atomic layer deposition (ALD) of high-k dielectric materials has been a subject of intensive research over the past years. Among such high-k oxides, hafnium oxide (HfO₂) has been considered largely for the application of high-k gate oxide in charge coupled devices owing to its high permittivity, fairly large band gap, and ability to form a thermodynamically stable interface with Si. The application of HfO₂ as a gate oxide material is not only limited to conventional Si based devices but also extending its horizons in novel nanomaterials based devices. For instance, Radisavljevic et al. have recently shown that by implementing HfO₂ as gate oxide for a field effect transistor device based on an emerging 2D-nanomaterial, molybdenum disulphide (MoS₂), the mobility could be drastically boosted owing to the suppression of coulombic scattering via dielectric screening. Furthermore, most recently, the application of a gate stack based on HfO₂/Al₂O₃/III-V (In₀.₅₃Ga₀.₄₇As) for metal-oxide-semiconductor capacitor devices has been demonstrated by Djara et al. These devices have a HfO₂/Al₂O₃ stack as gate oxide deposited by plasma enhanced ALD (PEALD) and show a low interface trap density (D_it). Additionally, HfO₂ also finds applications as a protective coating for microelectromechanical systems and as insulator for organic devices such as organic light emitting diode and organic field effect transistors.

ALD has been the method of choice for depositing thin films of HfO₂. The self-saturating nature of the ALD process enables atomic level control over thickness and uniformity and this makes ALD ideal for preparing ultrathin HfO₂ thin films. In particular, the much needed conformality over high aspect ratio structures in combination with the excellent uniformity over large surface areas and the pin-hole free nature of the ALD produced thin films makes ALD a befitting deposition process.

In ALD, the choice of precursor has a large effect on the quality and properties of the deposited thin films. This leads to a continuous effort in precursor synthesis aiming at improving temperature stability and/or reducing impurity concentrations in the resulting film depending on the final application. In literature, a number of Hf precursors have been implemented for HfO₂ ALD processes. The established ALD processes leave a room for improvement in terms of extension of operating conditions. In this contribution, we have investigated a novel precursor, HfCp(NMe₂), in combination with O₂ plasma which has yielded into a viable HfO₂ ALD process with a constant growth rate over the widest possible range of operating conditions such that it is suited for a multitude of applications. The details of the process investigated will be discussed in this paper. However, it is useful to systematically look at established ALD processes as listed in Table I, where a brief overview of efforts.

---

*© 2016 American Vacuum Society*
reported in literature focusing on detailed investigation of the ALD processes by using four different precursor groups for HfO2 thin films is given. The most frequently used precursor for HfO2 ALD is HfCl4 which is combined with H2O or O3 as oxygen source.2-15 However, the limitations associated with this precursor, such as corrosive byproducts and poor nucleation on H-terminated Si at high temperatures (≥300°C), make this precursor unfavorable for some specific applications like dynamic random-access memories and flexible electronics based on novel nanomaterials.10,22 In this context, another alternative is to employ a plasma enhanced ALD (i.e., O2 plasma as oxygen source) in combination with the same Hf precursor [Hf(Cp(NMe2)3] for growth of HfO2 thin films. It is well known that the use of plasma chemistry offers potential advantages like improved material properties, feasibility of lower deposition temperatures, and increased flexibility in process conditions.28

In the present study, we report the HfCp(NMe2)3 in combination with an O2 plasma process which yields a fairly high growth per cycle over a wide ALD temperature window (150–400°C) while retaining the high material properties. A detailed characterization of the HfO2 PEALD process has been carried out. The dependence of film growth rate on various parameters like growth temperature and duration of dose during the plasma enhanced ALD process has been studied. Furthermore, an elaborated material characterization elucidating the film structure and composition depending on growth temperature has been performed. Finally, in order to assert the potential of ALD to deposit conformally on 3D structures, the film conformity over high aspect ratio structures has also been demonstrated.

<table>
<thead>
<tr>
<th>Precursor group</th>
<th>Hafnium precursor/oxygen source</th>
<th>Growth temperature range (°C)</th>
<th>Substrate(s) used</th>
<th>Growth per cycle (Å)</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Halides</td>
<td>HfCl4/H2O</td>
<td>500</td>
<td>Glass</td>
<td>0.5</td>
<td>12</td>
</tr>
<tr>
<td></td>
<td>HfCl4/H2O</td>
<td>300</td>
<td>Si</td>
<td>0.47–0.62</td>
<td>13</td>
</tr>
<tr>
<td>Alkylamides</td>
<td>Hf[NMeEt4]/H2O</td>
<td>150–325</td>
<td>Glass, SiO2/Si</td>
<td>0.9–1.5</td>
<td>17</td>
</tr>
<tr>
<td></td>
<td>Hf[NMe2Et]/H2O</td>
<td>50–500</td>
<td>Si</td>
<td>0.9</td>
<td>18</td>
</tr>
<tr>
<td></td>
<td>Hf[NMeEt4]/O3</td>
<td>120–300</td>
<td>SiO2/Si</td>
<td>0.8–1.1</td>
<td>19</td>
</tr>
<tr>
<td></td>
<td>Hf[NMe2Et]/H2O</td>
<td>300</td>
<td>Si</td>
<td>0.78</td>
<td>3</td>
</tr>
<tr>
<td></td>
<td>Hf[NMeEt4]/O2 plasma</td>
<td>230–350</td>
<td>Si</td>
<td>1.0</td>
<td>20</td>
</tr>
<tr>
<td>Cyclo-pentadienyls</td>
<td>Cp[HfMe3]/H2O</td>
<td>300–500</td>
<td>SiO2/Si</td>
<td>0.42</td>
<td>21</td>
</tr>
<tr>
<td></td>
<td>(CpMe2)Hf(OMe)Me/O3</td>
<td>350–500</td>
<td>SiO2/Si</td>
<td>0.5</td>
<td>22</td>
</tr>
<tr>
<td>Alkylamides + Cyclo-pentadienyls</td>
<td>Cp[Hf(NMe2)3]/H2O</td>
<td>305–410</td>
<td>SiO2/Si</td>
<td>0.23–0.36</td>
<td>23</td>
</tr>
<tr>
<td></td>
<td>Cp[Hf(NMe2)3]/O3</td>
<td>250–400</td>
<td>SiO2/Si</td>
<td>0.7–0.8</td>
<td>24</td>
</tr>
<tr>
<td></td>
<td>Cp[Hf(NMe2)3]/O2 plasma</td>
<td>150–400</td>
<td>SiO2/Si</td>
<td>1.1</td>
<td>This study</td>
</tr>
</tbody>
</table>

*Cp* last treated.

One of such a widely applied alternative precursor group for HfO2 ALD is alkylamide comprising metal–nitrogen bonds, namely Hf(NEtMe4) (TEMAH), Hf(NEt2)4, and Hf(NMe2)4 (Et = C2H5, Me = CH3).3-20 These alkylamide type precursors possess a high volatility and reactivity and yield a high growth per cycle (GPC) in combination with H2O or O3 as coreactants.17 However, they suffer from a limited thermal stability which can lead to a parasitic CVD component and might result into high impurity concentrations and poor film uniformity.25 In addition, Kukli et al. have demonstrated that the HfO2 ALD process using TEMAH in combination with H2O as oxygen source leads to an increment in GPC from 0.9 Å/cycle at 250°C to 1.5 Å/cycle at 325°C, indicating the decomposition of the precursor at temperatures ≥300°C.17

To overcome this, an ALD process using the cyclopentadienyl (Cp = C5H5) precursor type was investigated. A higher thermal stability was achieved and ALD saturation was realized at a relatively high substrate temperature of 400°C.25 However, a lower GPC of ~0.5 Å/cycle was obtained when using Cp-precursors like (CpMe2)HfMe2 and (CpMe2)Hf(OMe)Me as compared to the alkylamides (~0.9 Å/cycle).19

With the aim of combining the benefits of both precursor types, precursors comprising both cyclopentadienyl and alkylamide type ligands have been investigated.23,24 A high thermal stability and high GPC attributed to cyclopentadienyl ligands and alkylamide ligands, respectively, have been demonstrated for both Hf and Zr based ALD processes.23,24,26 For ZrO2, this combined merit of high thermal stability and high growth per cycle has been manifested by using a chemically analogous precursor, i.e., CpZr(NMe2)3 in combination with H2O, where a growth per cycle of 0.8–1 Å/cycle in the temperature range of 120–350°C was obtained.26 However, a similar Hf precursor containing mixed cyclopentadienyl and alkylamide ligands, i.e., HfCp(NMe2)3 when applied in combination with H2O yielded a growth per cycle of only 0.23–0.36 Å/cycle in the temperature range of 305–375°C.23 Furthermore, Niinistö et al. have shown that the use of a stronger oxidant like O3 in combination with HfCp(NMe2)3 yields a higher growth per cycle (0.75 Å/cycle) in the temperature range of 250–350°C.24 The higher growth in the latter case might be attributed to the high reactivity of O3 at a relatively low temperature resulting in the efficient removal of the bulky Cp ligands.24 However, both with H2O or O3 as oxidizing agents, deposits have not been reported below 250°C, which might be necessary for HfO2 film deposition on temperature-sensitive substrates, in particular, for organic device applications and flexible electronics based on novel nanomaterials.10,27
II. EXPERIMENT

A. Film deposition

The HfO₂ thin films were deposited in an Oxford Instruments FlexAL™ ALD reactor on 100–200 mm Si wafers either with a native oxide layer or H-terminated as created by a hydrofluoric acid (HF)-last process (1% HF). The Hf precursor employed was HfCp(κNMe₂)₃, HyALD™, obtained from AirLiquide. The precursor was stored in a stainless steel canister and heated to 60 °C. At this temperature, the vapor pressure of the HyALD precursor is approximately 100 mTorr. For the precursor delivery to the deposition chamber a 100 sccm Ar (>99.999% purity) bubbling flow was employed. An Ar purge step with 100 sccm of Ar flow was applied after the precursor and plasma exposure steps. To avoid condensation of the precursor, the delivery lines were kept at 90 °C while the reactor walls were heated to 120 °C. As the oxidizing agent, an O₂ (>99.999% purity) plasma generated in an inductively coupled plasma source was used. The reactor pressure during the plasma step was 15 mTorr. The plasma power used was 400 W. The substrate stage was heated to temperatures in the range of 150–400 °C during the deposition processes. It is worth mentioning that there was a ~20%–25% difference between the set temperature value and the actual substrate temperature for the reactor employed in this work.

B. Film analysis

The thickness and the optical properties of the HfO₂ thin films were measured by spectroscopic ellipsometry (SE). Ex situ measurements (J.A. Woollam M2000D) were performed to determine the final thickness and the dielectric function in the 1.25–6.5 eV spectral range. The film thickness evolution during deposition was monitored by in situ measurements (J.A. Woollam M2000F, 1.25–5 eV).

To determine the elemental composition and the density of the films Rutherford backscattering spectroscopy (RBS) was used. Furthermore, elastic recoil detection (ERD) was employed to determine the hydrogen content in the films. Both RBS and ERD were performed using a 2 MeV ⁴He⁺ ion flux (Actec BV, The Netherlands). X-ray photoelectron spectroscopy (XPS) was also performed using a Thermo Scientific K-alpha spectrometer using monochromatic Al Kα x-ray radiation (hν = 1486.6 eV). XPS was used to quantify C and N contaminations in the films due to the higher sensitivity of XPS compared to RBS for these elements. For the XPS analysis, a 400 μm diameter spot was used, and photoelectrons were collected at a take-off angle of 60°. The samples were neutralized during the XPS analysis using an electron flood gun in order to correct for differential or non-uniform charging.

Grazing incidence x-ray diffraction (GI-XRD) was employed to determine the crystalline phases of the HfO₂ thin films. The XRD analysis was performed on a Panalytical X’Pert PRO MRD employing Cu Kα (1.54 Å) radiation with an incidence angle of 0.5° with respect to the substrate plane. Atomic force microscopy (AFM) was used to investigate the surface morphology of the films. The AFM scans were performed in tapping mode with a NT-MDT Solver P47 microscope using a TiN coated Si tip (NSG10/TiN, NT-MDT). Cross-sectional TEM analysis was performed using a JEOL ARM 200 operated at 200 kV. For this, the HfO₂ film was coated with a SiO₂/Pt film stack as a protective layer and subsequently prepared using a standard FIB lift-out TEM sample preparation scheme.

The conformality of HfO₂ ALD process was determined on substrate coupons with high-aspect-ratio (HAR) nanostructures. These HAR nanostructures were created by etching SiO₂ grown by PECVD into the Si wafer. The SiO₂ nanostructures were then coated with a SiNx layer deposited by high-temperature CVD, onto which a SiO₂ thin film was deposited using ALD. The HfO₂ sample was coated with a layer of spin-on epoxy to fill the remaining gaps in the trenches in order to protect the film from curtaining damage during the subsequent lift-out FIB sample preparation.

III. RESULTS AND DISCUSSION

A. ALD growth

The ALD process was characterized by monitoring the GPC by in situ SE analysis. The influence of dose steps was investigated by varying the duration of the precursor step, the O₂ plasma step and the purge steps between each half cycle. Figures 1(a)–1(d) show the GPC values obtained at a substrate temperature of 250 °C when varying the HyALD and O₂ plasma exposure steps [Figs. 1(a) and 1(c), respectively] and purge times after the precursor dose and the plasma exposure step [Figs. 1(b) and 1(d), respectively]. The GPC showed a clear saturation behavior for both the precursor and the plasma half cycles resulting in a GPC value of ~1.1 Å/cycle. The Ar purge after the HyALD dose showed a negligible influence on the GPC [Fig. 1(b)]. Also, when no purge step was applied after the precursor dose step, the GPC value did not show a remarkable change. By supplying O₂ during all ALD steps, including the precursor dose, it was verified that the HyALD precursor does not react with the molecular oxygen in the process space investigated, thus excluding the presence of a parasitic CVD component.

The duration of the purge step applied after the plasma step showed however an influence on the growth, in particular a higher GPC was recorded with a decreasing purge time. This is likely caused due to a parasitic CVD growth component due to chemical reactions between the by-products after the plasma step (i.e., H₂O) and the HyALD precursor when low purge times are employed. On the basis of the results in Fig. 1, to guarantee a genuine saturation behavior of precursor and purge steps, a precursor/purge/plasma/ purge sequence of 5/2/8/5 s was chosen in this work.

The influence of the substrate temperature on the GPC was also determined. Figure 2(a) shows the thickness evolution of HfO₂ films deposited at substrate stage temperatures ranging between 150 and 400 °C as obtained from in situ SE. For all temperatures studied, the films showed a linear growth trend without growth delay as expected for a typical O₂ plasma ALD process. Figure 2(b) shows the
GPC values as calculated from Fig. 2(a), corresponding to the studied substrate stage temperatures and the average number of Hf atoms deposited per ALD cycle as determined from RBS measurements. As mentioned above, the high thermal stability of HfCp(NMe₂)₃ allows to explore a larger temperature window. The GPC value remains constant at around 1.1 Å/cycle for the whole range of substrate stage temperatures from 150–400 °C signifying the decomposition-free deposition.

At relatively lower temperatures (150–200 °C), the GPC value is relatively higher compared to the higher temperatures. This can be attributed to a higher incorporation of impurities combined with a lower density of the films for lower deposition temperatures. This hypothesis was confirmed by the elemental composition analysis carried out by XPS and RBS as reported in Table II. The film densities were obtained through the combined RBS and SE analysis, and the stoichiometric ratios for Hf/O were determined from the RBS areal density values for Hf and O, respectively. As reported in Table II, the Hf/O ratio increased with increasing deposition temperature and an excellent stoichiometric value close to ~0.5 was achieved at 400 °C. The over-stoichiometric films (i.e., oxygen rich) obtained at lower deposition temperatures might be attributed to the formation of hydroxyl impurities. The hydroxyl impurities are directly related to the H content which decreased with the increasing deposition temperature. Furthermore, the N and C levels were below 1 and 2 at. % irrespective of the deposition temperature. The corresponding XPS depth profile spectra for the films deposited at the substrate stage temperature of 400 °C are shown in Fig. 1 of the supplementary material. The low N and C levels obtained are a clear merit, as in earlier work the performance of devices with HfO₂ has clearly shown to degrade with increasing impurity levels. Moreover, as will be shown in Sec. III B, the degree of crystallinity increases for higher deposition temperatures.

**Fig. 1.** (Color online) GPC values as a function of (a) HfALD dose; (b) Ar purge time after precursor dose; (c) O₂ plasma exposure; and (d) purge time after the plasma step. The substrate temperature during the process was 250 °C. The dashed lines serve as a guide to the eyes.

**Fig. 2.** (Color online) (a) Film thickness as a function of number of ALD cycles with temperature ranging between 150 and 400 °C. The thickness values have been obtained from in situ SE. (b) GPC values corresponding to the studied substrate stage temperatures and the average number of Hf atoms deposited per ALD cycle as determined from RBS measurements.
TABLE II. Elemental composition of HfO2 films as determined by RBS, ERD and XPS. The typical corresponding errors for Hf/O ratio, density values and H content are mentioned. The Tauc band gap values (E_g) are obtained from SE measurements; a dash (—) means not measured.

<table>
<thead>
<tr>
<th>Substrate stage temp. (°C)</th>
<th>H/O content from RBS</th>
<th>Density from RBS (g/cm³)</th>
<th>H content from ERD (at. %)</th>
<th>E_g (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>150</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>5.5</td>
</tr>
<tr>
<td>200</td>
<td>0.46 ± 0.03</td>
<td>8.7 ± 0.1</td>
<td>3.4 ± 0.2</td>
<td>5.5</td>
</tr>
<tr>
<td>250</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>5.5</td>
</tr>
<tr>
<td>300</td>
<td>0.48 ± 0.03</td>
<td>9.0 ± 0.1</td>
<td>1.4 ± 0.1</td>
<td>5.4</td>
</tr>
<tr>
<td>350</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>5.3</td>
</tr>
<tr>
<td>400</td>
<td>0.49 ± 0.03</td>
<td>9.3 ± 0.1</td>
<td>0.8 ± 0.1</td>
<td>5.5</td>
</tr>
</tbody>
</table>

As mentioned above, the GPC obtained in this work (1.1 Å/cycle) is considerably higher than the previously reported values in the literature when using HfCp(NMe2)3 in combination with H2O (0.23–0.36 Å/cycle) or O3 (0.75 Å/cycle) as oxidizing agents. This can likely be attributed to the creation of a higher density of reactive surface sites for precursor adsorption owing to the higher reactivity of plasma species. It is also worth mentioning that the usage of plasma cursor adsorption owing to the higher reactivity of plasma creation of a higher density of reactive surface sites for precursor adsorption.

This is corroborated by the fact that HfCp(NMe2)3 in combination with H2O (30 s)23 as compared to post-O2 plasma purge time (5 s) in this work which therefore increases the net ALD throughput.

B. Optoelectronic properties and crystallinity

The optical properties of HfO2 films have been analyzed by ex situ SE. Cauchy and B-spline models were used for obtaining the dielectric functions in the fully transparent and absorbing regions, respectively. Figure 3 shows the dielectric function, i.e., the real (ε1) and imaginary (ε2) part of the dielectric function as a function of photon energy measured by ex situ SE. The sharp features at a growth temperature of 400 °C indicate the polycrystalline structure of the film. The transition from smooth to sharp dielectric function for films grown at 400 °C can be observed in the inset.

The optical properties of HfO2 films have been analyzed by ex situ SE. Cauchy and B-spline models were used for obtaining the dielectric functions in the fully transparent and absorbing regions, respectively. Figure 3 shows the dielectric function, i.e., the real (ε1) and imaginary (ε2) part of the dielectric function as a function of photon energy measured by ex situ SE. The sharp features at a growth temperature of 400 °C indicate the polycrystalline structure of the film. The transition from smooth to sharp dielectric function for films grown at 400 °C can be observed in the inset.

The GPC obtained in this work (1.1 Å/cycle) is considerably higher than the previously reported values in the literature when using HfCp(NMe2)3 in combination with H2O (0.23–0.36 Å/cycle) or O3 (0.75 Å/cycle) as oxidizing agents. This can likely be attributed to the creation of a higher density of reactive surface sites for precursor adsorption owing to the higher reactivity of plasma species.

This is corroborated by the fact that HfCp(NMe2)3 in combination with H2O (30 s)23 as compared to post-O2 plasma purge time (5 s) in this work which therefore increases the net ALD throughput.
The GI-XRD patterns obtained in this work are remarkably similar to the ones reported by Niinistö et al.,24 for the HfO2 ALD process employing the same precursor, HfCp(NMe2)3, and O3 as the oxidizing agent. In their work, Niinistö et al. showed a similar temperature dependence of the HfO2 film crystallinity with a clear transition from amorphous to crystalline films at a deposition temperature of 300°C. The difference in temperature between this work and the one reported by Niinistö et al. at which this transition could be observed is imputed to a ~20%–25% difference between the set stage temperature value and the actual substrate temperature for the reactor employed in this work.32 It can be concluded that the crystallization temperature of HfO2 films is rather independent of the oxygen source used in combination with HfCp(NMe2)3 during the ALD process. However, the usage of a plasma-assisted ALD process may open the possibility for tuning of the crystalline phase by ion bombardment by employing substrate biasing during processing.33 which is the object of further investigation.

Figure 5 shows a cross-sectional TEM image of a ~32 nm HfO2 film deposited at 400°C on H-terminated Si substrate. The full Si/HfO2 (32 nm)/SiOx (~100 nm)/Pt stack is shown in Fig. 5(a). The HfO2 film shows a sharp interface with the underlying Si substrate, while an interface with higher roughness was formed with the overlying protective SiOx layer due to the crystalline HfO2 grains. A close inspection of Fig. 5(b) reveals the presence of an amorphous SiO2 layer at the Si/HfO2 interface. The amorphous nature of the Si substrate is imputed to damage caused by the focused ion beam used during sample preparation. The TEM image shows that the HfO2 film is fully crystalline which is in line with the GI-XRD analysis. Furthermore, individual HfO2 grains can be identified [Fig. 5(b)] with an average lateral grain size of ~20–30 nm.

C. Surface morphology

The AFM scans over an area of 500 × 500 nm² for the ~32 nm thick HfO2 films (300 ALD cycles) deposited at 200, 300, 350, and 400°C are depicted in Figs. 6(a), 6(b), 6(c), and 6(d), respectively. The root-mean-square (RMS) roughness values obtained from 2 × 2 μm² AFM scans of the same samples are indicated in Figs. 6(a)–6(d). For the film deposited at 200°C, a very smooth surface (RMS = 1.29 nm) with very few randomly distributed singular features was obtained [see Fig. 6(a)]. The higher substrate temperature of 300 and 350°C yielded an increase in density and size of these singular features as depicted in Figs. 6(b) and 6(c). The RMS roughness values also showed an increment with increasing deposition temperature from 200 to 350°C. AFM scans of the HfO2 sample deposited at 400°C revealed a slightly different film morphology with a decreased RMS roughness value compared to the film deposited at 350°C [Fig. 6(d)]. On the basis of the obtained morphology, it can be argued that the singular features observed might be associated with the increasing degree of crystallinity with the increase in deposition temperature from 200 to 350°C resulting in a transition from amorphous to polycrystalline films as shown before in Figs. 3 and 4 corresponding to the SE and GI-XRD analyses. Furthermore, the lower RMS roughness value obtained at 400°C might be attributed to the full crystallization obtained already during the deposition process leading to a laterally homogeneous and smooth HfO2 thin film, which is also supported by TEM image (Fig. 5).

This effect was also confirmed for thicker films as depicted in Figs. 6(e) and 6(f) with 500 × 500 nm² AFM scans of ~80 nm HfO2 films deposited at 250 and 400°C, respectively. The RMS roughness values of these two films are also indicated in Figs. 6(e) and 6(f). The increase in RMS as a function of layer thickness of the samples grown at 400°C can be explained by grain coarsening, i.e., increase in (lateral) grain size as a function of film height. The film deposited at 250°C shows higher surface roughness compared to the one deposited at 400°C, most likely because of coalescence of individual crystalline grains at 400°C in the top part of the layer.
D. Conformality

The conformality of the above HfO₂ ALD process was determined by depositing a ~20 nm thick HfO₂ film over HAR nanostructures with varying aspect ratio (0.6–9) at a deposition temperature of 250 °C. Figure 7 shows a cross-sectional TEM image of the HAR trench structures conformally covered with the HfO₂ film. It should be noted that the deposition conditions for this purpose were kept the same as implemented for the planar Si substrates. A comparison of the HfO₂ film thickness on the side walls and planar areas of the nanostructures shows that the HfO₂ films had a conformality of 79% and 72.2% for aspect ratios of 3 and 7.3, respectively. A further optimization of the precursor conditions could improve the conformal deposition of HfO₂ films on nanostructures.

Fig. 6. (Color online) AFM scans with a scan area of 500 × 500 nm of the ~32 nm HfO₂ films (300 ALD cycles) deposited at (a) 200 °C, (b) 300 °C, (c) 350 °C, and (d) 400 °C. An increase in amount of the crystallites can be detected from 200 to 400 °C indicating enhanced crystallinity with increase in substrate stage temperature. Similar AFM scans of thicker ~80 nm HfO₂ (750 ALD cycles) films deposited at (e) 250 °C and (f) 400 °C show higher roughness.

Fig. 7. (Color online) (Left) Cross-sectional transmission electron microscopy image of a conformal HfO₂ layer deposited on high aspect ratio nanostructures by ALD at 250 °C using HfCp(NMe₂)₃ and O₂ plasma. (Right) A close up of trench structures with varying aspect ratios shows the conformal HfO₂ thin film.
dose and plasma conditions is required to exclude the recombination- or diffusion-limited regimes being the limiting factors for the step coverage.34

IV. SUMMARY AND CONCLUSIONS

In this study, a plasma enhanced atomic layer deposition process for the deposition of HfO2 thin films using a hafnium precursor [HiCp(NMe2)3] comprising cyclopentadienyl-alkylamido ligands in combination with O2 plasma has been evaluated. The growth characteristics clearly show the high thermal stability and high growth rate of the used precursor combined with O2 plasma yielding a high GPC value of ~1.1 Å/cycle over a wide ALD temperature range of 150–400 °C. High purity HfO2 thin films were obtained even at fairly low deposition temperatures with carbon and hydrogen residual impurity contents below 2 and 3.5 at. %, respectively, for the whole range of substrate stage temperature investigated. A high substrate stage temperature of 400 °C resulted in fully crystalline, predominantly monoclinic as-deposited HfO2 thin films with a high refractive index and a smooth surface. It was also found that the HiCp(NMe2)3 in combination with O2 plasma requires shorter ALD cycle time relatively as compared to the ALD process using H2O as oxidizing agent and therefore plasma requires shorter ALD cycle time relatively as compared to the ALD process using H2O as oxidizing agent and therefore the plasma-enhanced ALD process offers a promising and viable method complementary to the thermal ALD process for producing high quality HfO2 thin films.

ACKNOWLEDGMENTS

The authors gratefully acknowledge Cristian van Helvoirt for technical assistance, Harm Knoop, Vincent Vandalon for fruitful discussion and Lam Research for providing substrates with HAR trench structures. The authors would like to acknowledge AirLiquide for providing the Hf precursor. They would also like to acknowledge W. Keuning and B. Barcones for the FIB sample preparation and Solliance Solar Research for funding the TEM facility. One of the authors (W. M. M. Kessels) would like to acknowledge “Gravitation project” for making this research work possible. This work is part of the Research Centre for Integrated Nanophotonics (NWO-578467), which is partly financed by the Netherlands Organization for Scientific Research (NWO).

31See supplementary material at http://dx.doi.org/10.1116/1.4972210 for XPS depth profile plot and Tauc Plot for bandgap value extraction.