Plasma-assisted atomic layer deposition of HfNx: tailoring the film properties by the plasma gas composition

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Plasma-assisted atomic layer deposition of HfN_x : Tailoring the film properties by the plasma gas composition

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The authors synthesized HfN_x ($x \geq 1$) thin films by plasma-assisted atomic layer deposition at stage temperatures of 350–450 °C by using the high-thermal-stability $\text{CpHf}(\text{NMe}_2)_3$ monomer as Hf precursor and either H_2 plasma or N_2 plasma as coreactant. Most notably, the selection of the plasma gas composition enabled us to tune the film properties: films fabricated using N_2 plasma led to the formation of highly resistive and amorphous Hf_3N_4 films ($6 \times 10^2 \Omega \text{cm}$), while the use of the strongly reducing H_2 plasma generated conductive (resistivity of $6 \times 10^{-1} \Omega \text{cm}$) films with the signature of the δ -HfN *fcc* crystal structure. Via x-ray photoelectron spectroscopy, the authors observed that the use of the H_2 plasma facilitates the reduction of the oxidation state of Hf from Hf^{4+} to Hf^{3+} . This result was corroborated by the simultaneous increase in the free carrier absorption observed in the infrared range via spectroscopic ellipsometry. The δ -HfN_x films fabricated via the present route are promising as highly reflective back contacts for thin films solar cells, Cu diffusion barriers, and as a gate metal for metal–oxide–semiconductor capacitors, provided that the resistivity values can be further decreased by suppressing the formation of the resistive Hf_2ON_2 impurity phase and grain-boundary scattering of the charge carriers. © 2016 American Vacuum Society.

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I. INTRODUCTION

Transition metal nitrides are of great interest for semiconductor devices owing to their low electrical resistivity and excellent oxygen¹ and copper^{2–4} diffusion barrier properties. Two envisioned applications are the combination of HfO_2 with HfN as gate dielectric and gate metal in a MOS configuration as reported by Yu *et al.*^{1,5} and HfN as back reflector electrode for copper-indium-gallium-selenide solar cells, due to its high reflectivity (>85%) in the low energy photon region ($1 \text{ eV} \leq E \leq 2.4 \text{ eV}$) for semi-infinite films.^{6–8} Both applications require low resistivity of HfN layers ($\rho = 10^{-4}$ – $10^{-5} \Omega \text{cm}$).⁹

Low resistivity epitaxial single crystal *fcc* δ -HfN films have been developed by physical vapor deposition with a resistivity of $1.42 \times 10^{-5} \Omega \text{cm}$ for a thickness of 650 nm.¹⁰ Moreover, chemical vapor deposition (CVD) of δ -HfN_x at a stage temperature of 800 °C employing alkylamide Hf precursor and *N,N*-dimethylhydrazine as reducing agent led to a grain size of $\sim 170 \text{ nm}$ and a resistivity of $1 \times 10^{-3} \Omega \text{cm}$ for a film thickness of $\sim 1 \mu\text{m}$.¹¹ An increase in the stage temperature was shown to increase the film conductivity and was attributed to an increase in crystallinity and grain size.¹¹ In the same work, NH_3 was demonstrated to yield nonconductive Hf_3N_4 films marking the requirement of a highly

reducing coreactant (*N,N*-dimethylhydrazine) to obtain the conductive δ -HfN_x films.¹¹

Many of the applications mentioned above require conformal films on 3D structured surfaces with precise thickness control. Supreme thickness controllability and conformality achieved by atomic layer deposition (ALD) has been demonstrated on high surface area materials such as silica gel^{12–15} and nanopowders.^{16–18} Some works on ALD of HfN_x have already been reported in the literature^{19–21} and are summarized in Table I. Becker *et al.* reported the growth of insulating Hf_3N_4 films by employing tetrakis(ethylmethylamino)hafnium (TEMAH) as the precursor and NH_3 as the coreactant in a thermal ALD process, demonstrating the low reduction potential of NH_3 .¹⁹ Note that thermal decomposition of TEMAH was observed at a stage temperature above 250 °C.¹⁹ On the other hand, low resistivity δ -HfN_x films ($2.3 \times 10^{-3} \Omega \text{cm}$) were obtained by Consiglio *et al.* using Ar- H_2 mixed plasma and the same precursor (TEMAH) in a plasma-assisted ALD processes.²⁰ Using TDMAH, similar results were also reported by Kim *et al.* with a N_2 - H_2 mixed plasma yielding a resistivity of $6.7 \times 10^{-3} \Omega \text{cm}$ for 14 nm film.²¹ These studies demonstrate the requirement of highly reducing H_2 plasma species to achieve the conductive *fcc* δ -HfN phase.^{20,21}

The extent of Hf^{4+} reduction (in the precursor) to Hf^{3+} (in the film) by H_2 plasma species was not specifically addressed, and thus far, a comprehensive study of the influence of variable plasma conditions and gas composition on

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TABLE I. Overview of HfN_x film properties as reported for some ALD processes using several metal precursors and coreactants. The selected reports are chosen in order to highlight the importance of reductive H₂ plasma essential to fabricate δ -HfN_x *fcc* phase.

Hf precursor	Coreactant	Stage temperature (°C)	N/Hf	C (at. %)	O (at. %)	Resistivity (Ω cm)	GPC (nm/cycle)	References
TEMAH Hf[N(CH ₃)(C ₂ H ₅) ₂] ₃	NH ₃	200	1.3	0.5	5	$>10^2$	0.11–0.12	19
TEMAH Hf[N(CH ₃)(C ₂ H ₅) ₂] ₃	15 s Ar + H ₂ plasma	250	1	10.1	2.2	2.3×10^{-3}	0.12	20
TDMAH Hf[N(CH ₃) ₂] ₃	60 s H ₂ + N ₂ plasma	175	0.6	21	2	6.7×10^{-3}	0.085	21

the chemical, microstructural, and optical material properties of HfN_x thin films is lacking. Furthermore, the deposition of the HfN_x films has been limited to rather low temperatures due to the thermal self-decomposition of the used homoleptic alkylamide precursors for Hf. Fortunately, the alkylamide precursor chemistry can be tailored by replacing one of the original ligands with a cyclopentadienyl ligand (Cp = C₅H₅). In such heteroleptic precursors, the Cp functional group imparts high thermal stability to the precursor, thus enabling a larger temperature window while minimizing precursor decomposition.²²

In this contribution, we studied the effect of plasma gas composition for the plasma-assisted ALD of HfN_x at 350 and 450 °C by adopting a thermally stable novel heteroleptic metal precursor tris(dimethylamino)cyclopentadienylhafnium [CpHf(NMe₂)₃] [TDMACpH] and using it together with H₂ or N₂-fed plasma as the coreactant. In particular, a detailed study on the influence of plasma gas composition on the optoelectronic, chemical, and microstructural properties is presented. The material properties were shown to fundamentally depend on the plasma composition: highly resistive ($\rho = 6 \times 10^2 \Omega$ cm) amorphous Hf₃N₄ films are obtained by using N₂ plasma, whereas use of highly reducing H₂ plasma enables synthesis of conductive ($\rho = 6 \times 10^{-1} \Omega$ cm) δ -HfN_x films. Using x-ray photoelectron spectroscopy (XPS), these improved film properties for the H₂ plasma are shown to stem from a large increase in Hf³⁺/(Hf³⁺ + Hf⁴⁺) fraction. In addition, the factors limiting the film conductivity were identified and quantified.

II. EXPERIMENT

A. Film deposition

HfN_x thin films of ~50 nm in thickness were deposited on 100 mm Si(100) substrates with 450 nm SiO₂ using an Oxford Instruments FlexAL ALD reactor,^{23,24} equipped with

an inductively coupled remote plasma (ICP) source with an alumina dielectric tube. The deposition chamber of the ALD reactor was pumped down by a turbomolecular pump to a base pressure of 1.6×10^{-6} Torr before every deposition and thereafter the substrate was transferred to the chamber from the load-lock. The stage temperature was controlled in the range 350–450 °C, and the reactor walls were maintained at 145 °C during all the depositions. Note that via spectroscopic ellipsometry (SE), a substrate temperature of 270 and 340 °C was measured for a stage temperature 350 and 450 °C, respectively.²³

The Hf precursor TDMACpH (Air Liquide, >99.99% purity) was placed in a stainless steel container kept at 60 °C and bubbled by an Ar flow of 100 sccm. During the precursor dosage, an Ar flow rate of 100 sccm was also injected from the ICP chamber in order to suppress the deposition on the ICP tube, thereby setting up the chamber pressure of 200 mTorr as illustrated in Fig. 1. Furthermore, during the plasma exposure, N₂ (>99.999% purity, working pressure ~12 mTorr) or H₂ (>99.999% purity, working pressure ~30 mTorr) was first introduced into the chamber, and thereafter, the plasma was ignited for the desired exposure time. The excess precursor, reaction byproducts, and plasma species were purged with Ar at 200 sccm with full valve opening. The ALD step sequence is presented in Fig. 1, including the optimum exposure times for the N₂ and H₂ plasma cases.

B. Film analysis

SE was employed to monitor the ALD growth every ten ALD cycles. Pseudodielectric functions were determined in the photon energy range of 0.75–5.0 eV by employing a visible and near-infrared rotating compensator ellipsometer (J.A. Woollam, Inc., M2000U) fitted to two optical viewports on the reactor. Subsequently, a model was set up for HfN films

FIG. 1. (Color online) Time sequence for two complete ALD cycles of HfN_x based on (a) N₂ plasma and (b) H₂ plasma. Time intervals are not drawn to scale.

on SiO₂ (450 nm)/c-Si substrates. In addition to the HfN_x film thickness, key material parameters such as optical resistivity and optical bandgap could be extracted by parametrizing the complex dielectric function $\varepsilon = \varepsilon_1 + i\varepsilon_2$.^{25,26}

High resistivity Hf₃N₄ with an N/Hf ratio of 1.3 behaves as an insulator,²⁷ for which the imaginary dielectric function (ε_2^{T-L}) can be described by a Tauc-Lorentz relation²⁶

$$\varepsilon_2^{T-L}(E) = \begin{cases} \frac{AE_oC(E - E_g)^2}{(E^2 - E_o^2)^2 + C^2E^2} \cdot \frac{1}{E}; & (E > E_g) \\ 0; & (E \leq E_g), \end{cases} \quad (1)$$

where A is the peak amplitude, E_o is the natural transition energy, E_g is the band gap, C is the full width half maximum (FWHM) of the ε_2 peak, and E represents the photon energy. Then, once the imaginary part is known, the real part of the dielectric function (ε_1^{T-L}) can be deduced using the Kramers–Kronig relation

$$\varepsilon_1^{T-L}(\omega) = 1 + \frac{2}{\pi}P \int_0^\infty \frac{\omega' \varepsilon_2(\omega')}{\omega'^2 - \omega^2} d\omega', \quad (2)$$

where P is the Cauchy principle value, ω' is the complex angular frequency, and ε_2 is the imaginary dielectric function as defined above.

On the other hand, the resistivity of the epitaxial *fcc* δ -HfN thin films can be as low as 14.2 $\mu\Omega\text{cm}$ (Ref. 10) and can be modeled by a combinatorial approach using one Drude and two Lorentz oscillators as described by Hu *et al.*⁷ In our case, due to the coexistence of two phases, δ -HfN_x ($x \leq 1$) and Hf₂ON₂, the dielectric function can be modeled using one Drude, one Lorentz, and one Tauc-Lorentz oscillator

$$\begin{aligned} \varepsilon(E) &= \varepsilon_1(E) + i\varepsilon_2(E) \\ &= \varepsilon_\infty - \frac{\overbrace{E_p^2}^{\text{Drude}}}{E^2 - i\Gamma_D E} + \frac{\overbrace{SE_0^2}^{\text{Lorentz}}}{E_0^2 - E^2 + iE\Gamma} \\ &\quad + \underbrace{\varepsilon_1^{T-L} + i\varepsilon_2^{T-L}}_{\text{Tauc-Lorentz}}, \end{aligned} \quad (3)$$

where ε_∞ represents transitions at higher energy which are not accounted in Lorentz oscillators, E_p is plasma energy, and Γ_D is the damping factor for Drude oscillator. The Lorentz oscillator is centered at E_o which corresponds to the resonance frequency, while S indicates the strength of the oscillator and Γ is the damping factor for the Lorentz oscillator.

The deposited films were analyzed by XPS using a ThermoScientific K-Alpha KA1066 system equipped with a monochromatic Al K α ($h\nu = 1486.6\text{ eV}$) source in order to determine the composition of the HfN_x layers. The films were first sputtered for 500 s by 200 eV Ar⁺ ion gun prior to taking high resolution (pass energy = 50 eV) scans, in order to exclude the surface oxidation and adventitious carbon.

Samples were continuously subjected to an electron flood gun during measurements in order to compensate for the charging. The sensitivity factors used for different elements in order to determine the chemical composition of HfN_x films were obtained from the ThermoScientific Avantage library.²⁸

The crystallinity of the films was studied by grazing-incidence x-ray diffraction. The experiments were conducted with a PanAlytical X'pert PRO MRD diffractometer operated at the incidence angle of 0.5° and using a Cu K α ($\lambda = 1.542\text{ Å}$) x-ray source. The sheet resistance values (R_s) of HfN_x films deposited on 450 nm SiO₂/Si were determined by *four-point* probe measurements, using a Keithley 2400 SourceMeter and a Signaton probe. Electrical resistivity (ρ) at room temperature could subsequently be calculated using the film thickness deduced from SE modeling. The surface morphology was studied by scanning electron microscopy (SEM) using a ZeissSigma Nanolab operating at an acceleration voltage of 2 kV.

III. RESULTS AND DISCUSSION

A. ALD process with N₂ plasma

The saturation of the growth-per-cycle (GPC) was studied at a stage temperature of 350 °C by systematically varying the process parameters, i.e., TDMACpH dose, TDMACpH purge, N₂ plasma exposure, and N₂ plasma purge (Fig. 2). Note that for all the depositions, a typical linear growth with no nucleation delay as a function of the number of ALD cycles was retrieved from *in situ* SE (Fig. 1, supplementary material).⁴⁰

During the variation of the TDMACpH dosing time, the N₂ plasma exposure was set to 20 s. Saturation of the GPC to a value of 0.038 nm/cycle was attained after 2 s of TDMACpH dosing [Fig. 2(a)], and hence, a TDMACpH pulsing of 4 s was adopted for subsequent experiments. Purging of the unreacted species and reaction byproducts was found to be fast, as 1–2 s were already sufficient to obtain saturated growth [Figs. 2(b) and 2(d)].

On the other hand, a peculiar decrease in the GPC with the increase in the N₂ plasma exposure was observed [Fig. 2(c)]. A very similar decrease in the GPC as a function of N₂ plasma exposure during the ALD of SiN_x was reported by Knoops *et al.*, attributed to the decrease in the C at. %.²³ In our case, closer inspection via XPS revealed a relative decrease in the C at. % from 13 at. % for 5 s of N₂ plasma exposure to 7 at. % for 20 s of exposure (Table II). It should be emphasized that C in the film results from either the redeposition of the ligands that are dissociated in the plasma if the gas residence time is long²⁴ or from the incomplete removal of ligands by the N radicals. In order to verify whether the redeposition is indeed occurring at $T_s = 350\text{ °C}$, the gas residence time was systematically varied in a limited range (0.10–0.14 s) by adding Ar to the total gas flow during the plasma step (only for this experiment) (Table I, supplementary material) and its effect on the GPC and C at. % was studied in a similar fashion as reported by Knoops *et al.*²⁴ A constant GPC and C at. % was obtained for 20 s of plasma exposure even for short residence time (0.10 s). This result

FIG. 2. GPC for the ALD process using N₂ plasma as the coreactant as a function of (a) TDMACpH dose, (b) TDMACpH purge, (c) N₂ plasma exposure time, and (d) N₂ plasma purge. On the basis of these results, a dosage sequence of 4-2-20-2 s was established for the ALD process with N₂ plasma. The gray lines serve as a guide to the eye.

suggests that the residual C of 7 at. % is due to the incomplete removal of the ligands at $T_s = 350^\circ\text{C}$.

The decomposition of TDMACpH was observed at a stage temperature above 360°C for the thermal ALD process of HfO₂ with H₂O.²⁹ In our case, the self-limiting ALD obtained at a stage temperature of 350°C (substrate temperature = 270°C) suggests that we are well below the thermal decomposition temperature of TDMACpH. Subsequently, the stage temperature was raised to 450°C , which corresponds to a substrate temperature of 340°C as concluded from SE.²⁹ An increase in the stage temperature to 450°C enabled complete removal of C (Table III), while maintaining a constant GPC of 0.038 nm/cycle for 20 s N₂ plasma exposure. This result corroborates that the 7 at. % residual C obtained at $T_s = 350^\circ\text{C}$ is a result of incomplete removal of ligands by N radicals.

The N₂ plasma process generated films with a high resistivity of $6 \times 10^2 \Omega\text{cm}$ for a film thickness $\sim 45\text{ nm}$ at $T_s = 450^\circ\text{C}$, measured via *four-point* probe. A closer inspection via XPS revealed a relatively high N/Hf ratio of 1.6 ± 0.03 (Table III). XPS was further used to study the oxidation state

fraction $\text{Hf}^{3+}/(\text{Hf}^{3+} + \text{Hf}^{4+})$. In Fig. 3(a), the Hf 4f spectrum is presented: the Hf 4f_{7/2} peak centered at low binding energy of 14.9 eV is attributed to the Hf–N bond in $\delta\text{-HfN}$. This peak is assigned as Hf^{3+} , corresponding to the presence of the Hf^{3+} oxidation state (Table IV).³⁰ It should be noted that the spin orbit coupling of Hf 4f give rise to a doublet: Hf 4f_{7/2} and Hf 4f_{5/2}, which is utilized in the peak deconvolution.

Kang *et al.* reported a Hf 4f_{7/2} peak shift to a higher binding energy of 16.0 eV due to the presence of O and the formation of HfN_xO_y.³¹ Moreover, Arranz *et al.* reported the Hf 4f_{7/2} peak to be centered at 16.0 eV in the case of highly resistive Hf₃N₄ phase.³² In both the above cases, the Hf 4f_{7/2} peak at 16.0 eV corresponds to the Hf^{4+} oxidation state. Correspondingly, in our case, the Hf 4f_{7/2} peak at 16.0 eV has been assigned to Hf^{4+} although the demarcation of the individual contributions of either Hf₃N₄ or HfO_xN_y is not possible due to overlap of the peaks (Table IV). In Fig. 3(c), the O 1s XPS spectrum is presented which consists of a small peak at 530.8 eV,³³ corresponding to the Hf–O bond formation and a broad Hf 4s overlapping feature at 535.5 eV (Table IV). As a result of the formation of the Hf–O bond, the Hf oxidation state increases to +4. Altogether, it can be concluded that the N₂ plasma process yielded films with a low relative Hf^{3+} fraction of 0.35 ± 0.02 (Table III). The small peak area of Hf–O bond accounts for only $\sim 2\text{ at. \%}$ [O] in the films, suggesting that the low Hf^{3+} fraction is primarily related to the low reduction potential of N₂ plasma.

The results of the x-ray diffraction studies were in line with the XPS studies. The N₂ plasma process generated amorphous films as no crystalline peak was observed (Fig. 4). Moreover, only a broad feature was seen at $2\theta = 33.6^\circ$. Wang

TABLE II. GPC and C at. % as a function of N₂ plasma exposure for the HfN_x films prepared at $T_s = 350^\circ\text{C}$. The carbon content is retrieved via XPS and the GPC is obtained via SE. The corresponding error bars are indicated in the first row.

N ₂ plasma exposure (s)	Thickness (nm)	GPC (nm/cycle)	C (at. %)
5	17.2	0.043 ± 0.003	13.0 ± 0.5
10	16.0	0.040	10.0
15	15.2	0.038	8.2
20	15.2	0.038	7.0

TABLE III. Properties of the ALD HfN_x films prepared using TDMACpH [CpHf(NMe₂)₃] for different deposition conditions. The chemical composition is determined by XPS, the resistivity by *four-point* probe and the thickness and GPC via SE. The corresponding error bars are indicated in the first row. The errors for the resistivity are less than 3% of their value.

Plasma condition	Stage temperature (°C)	N/Hf	C (at. %)	O (at. %)	$\frac{\text{Hf}^{3+}}{\text{Hf}^{3+}+\text{Hf}^{4+}}$	Resistivity (Ω cm)	GPC (nm/cycle)	Thickness (nm)
20 s N ₂	350	1.5 ± 0.1	7.0 ± 0.5	2.0 ± 0.3	0.37 ± 0.02	7 × 10 ²	0.038 ± 0.003	35
20 s N ₂	450	1.6	0	2.0	0.35	6 × 10 ²	0.038	45
10 s H ₂	450	1.0	0	15.3	0.59	6 × 10 ⁻¹	0.04	63
30 s H ₂	450	1.0	0	20.2	0.53	5 × 10 ⁻¹	0.04	33

et al. reported the presence of a broad feature at $2\theta = 33.5^\circ$ for N-rich HfN_{1.39} films.³⁴ Hence for our films, the broad feature was attributed to over-stoichiometric HfN_{1.6}, thus corroborating the XPS results.

The high film resistivity of the films (6 × 10² Ω cm) is also reflected in the dielectric functions, obtained via the modeling of the spectroscopic ellipsometry data using a single Tauc-Lorentz (T-L) oscillator centered at 3.86 eV [Fig. 5(a)]. The Tauc-Lorentz behavior of the ϵ_2 is in-line with earlier reported optical studies for Hf₃N₄ resistive phase in the given photon energy range.²⁷ Furthermore, the Tauc-Lorentz oscillator gives a band-gap of 2.26 eV which further corroborates the insulating properties of the material.

Altogether, the high resistivity of the films prepared with the N₂ plasma process is attributed to a relative over-stoichiometric HfN_{1.6} phase with a small Hf³⁺ fraction, given the fact that the films only contain trace amounts of C and O as impurities. Furthermore, a low O content of 2 at. % is believed to be obtained for the N₂ plasma process due to

the presence of a small Hf³⁺ fraction. In order to form an Hf–O bond, the oxidation state of Hf should increase from +3 to +4. Since a small Hf³⁺ fraction of 0.35 ± 0.02 is obtained due to the low reduction potential of the N₂ plasma, the films are less susceptible to be oxidized by O.

B. ALD process with H₂ plasma

In the case of the H₂ plasma process, the GPC increased with the increase in plasma exposure using TDMACpH dosing of 4 s and a saturated GPC of 0.04 nm/cycle was obtained for a plasma exposure of 10 s or longer (Fig. 6). Langereis *et al.* reported a soft-saturation in the GPC for the ALD of TaN_x using pentakis(dimethylamino)tantalum and H₂ plasma,³⁵ where the GPC continued to slightly increase after attaining a saturation for a plasma exposure of 5 s. This increase in the GPC after saturation is primarily attributed to the change in the N/Ta ratio with plasma exposure.³⁵ XPS studies of the HfN_x films revealed that the N/Hf ratio is

FIG. 3. (Color online) Hf 4f XPS spectra depicting the peak deconvolution for (a) ~45 nm HfN_x deposited using the N₂ plasma at T_s = 450 °C and (b) ~63 nm HfN_x deposited using 10 s H₂ plasma exposure at T_s = 450 °C. The shaded blue area represents Hf⁴⁺ fraction whereas the golden represent Hf³⁺ fraction. The deconvoluted O 1 s spectra for (c) N₂ plasma and (d) H₂ plasma. The shaded blue area represents Hf–O bond.

TABLE IV. Corresponding XPS peak assignment, binding energies and full width half maximum for the Hf and O spectral lines used to deconvolute the peaks.

Spectral line	Peak assignment	Binding energy (eV)	FWHM (eV)	References
Hf 4f _{7/2}	Hf ⁴⁺	16.0	1.6	31 and 32
Hf 4f _{5/2}	Hf ⁴⁺	17.8	1.6	31 and 32
Hf 4f _{7/2}	Hf ³⁺	14.9	1.6	34
Hf 4f _{5/2}	Hf ³⁺	16.7	1.6	34
O 1s	HfO _x	530.8	1.9	33

consistent with the increase in plasma exposure whereas the material properties change due to an increase in the O at. % with the plasma exposure. The O content increased from 15.3 to 20.2 at. % as the H₂ plasma exposure was increased from 10 to 30 s, respectively (Table III). Note that the O in the film can result from either the ingress of H₂O or O from the reactor background during the deposition, or from the postdeposition oxidation of the films which might arise due to potentially low film density. In order to demarcate the source of O in the HfN_x films, a thin layer of dense SiN_x (~10 nm) was deposited on top of the HfN_x film (~30 nm) *in situ*, following the same recipe as reported by Andringa *et al.* for the deposition of gas/moisture barrier layers.³⁶ A decrease in the O content to 10.2 at. % was observed for the HfN_x films prepared with 10 s H₂ plasma exposure and SiN_x capping layer implying that the O primarily incorporates during the deposition itself. This can occur due to the background H₂O and/or O₂ (reactor base pressure = 1.6×10^{-6} Torr) in the reactor which can get incorporated during the film growth for the complete cycle time, depending on the reactivity of the growing surface. Quite remarkably, an increase in the Hf³⁺/(Hf³⁺ + Hf⁴⁺)

FIG. 4. (Color online) GI-XRD spectra for the HfN_x films prepared by various ALD processes: (black) the N₂ plasma process and (green and red) the H₂ plasma process with varying exposure times. The powder δ -HfN_x and Hf₂ON₂ XRD spectra are shown for comparison.

fraction to 0.59 ± 0.02 was observed via XPS for 10 s of plasma exposure as compared to the N₂ plasma process [Fig. 3(b)]. Due to the increased Hf³⁺ oxidation state fraction as compared to the N₂ plasma process, the electrical resistivity decreased from $6 \times 10^2 \Omega \text{ cm}$ prepared with the N₂ plasma process to $6 \times 10^{-1} \Omega \text{ cm}$ for 63 nm thick film prepared with 10 s H₂ plasma exposure.

The x-ray diffractogram revealed the development of the conductive δ -HfN *fcc* structure for the H₂ plasma process, in line with the decrease in electrical resistivity and the results from the XPS studies (Fig. 4). Moreover, a shift in the peak position was observed for δ -HfN pattern when compared with the powder spectrum, as a result of the incorporation of O. In addition, a new peak could be discerned at $2\theta = 31^\circ$ for 30 s H₂ plasma exposure. This peak can be attributed to the (222) reflection of the resistive, cubic Hf₂ON₂ structure (Fig. 4),³⁴ in-line with the XPS study suggesting Hf–O bond formation.

Although a polycrystalline δ -HfN *fcc* conductive phase is obtained, an electrical resistivity of $6 \times 10^{-1} \Omega \text{ cm}$ is rather high. In order to obtain more insight into the electrical properties, modeling of the SE data was performed. The dielectric function could be fitted with one Drude, one Lorentz oscillator centered at 1.41 eV, and one Tauc-Lorentz oscillator centered at 4.88 eV, as shown in Fig. 5(b). The Tauc-Lorentz oscillator reveals a band-gap of 2.7 eV which is higher as compared to 2.26 eV for the N₂ plasma process. This increase in the optical bandgap most probably arises due to the presence O in the form of Hf–O bonds. The simultaneous presence of the Tauc-Lorentz and the Drude

FIG. 5. (Color online) Imaginary dielectric function ϵ_2 for (a) (blue) the resistive Hf₃N₄ films prepared by the N₂ plasma process obtained via parameterization of the spectroscopic ellipsometric data using one Tauc-Lorentz oscillator, and (b) (golden) the conductive δ -HfN ($x \leq 1$) films prepared by the H₂ plasma process obtained via parameterization using one Drude, one Lorentz, and one Tauc-Lorentz (T-L) oscillator.

FIG. 6. GPC for the ALD process using H₂ plasma as the coreactant as a function of H₂ plasma exposure time. The gray line serves as a guide to the eye.

contributions indicates the synthesis of a mixed phase material composed of both conductive and resistive domains. The presence of the Drude absorption signifies the presence of free electrons contributing to the conductivity.³⁷ The optical resistivity can be deduced from the Drude absorption using

$$\rho = \frac{\Gamma_D}{\epsilon_o \cdot \omega_p^2}, \quad (4)$$

where Γ_D is the damping factor for the Drude oscillator, ϵ_o is the permittivity of free space, ω_p is the plasma frequency, and ρ is the resistivity of the deposited films as determined by SE. By using this equation, we obtained an optical resistivity of $5 \times 10^{-3} \Omega \text{ cm}$ —a value that is notably lower than the electrical resistivity value obtained via the *four-point* probe. The discrepancy between optical and electrical resistivity signifies prominent grain boundary (GB) scattering which dictates the electrical conductivity of the films.³⁷ In the simplified case with O in the films existing only in the Hf₂ON₂ lattice, 15 at. % O for 10 s H₂ plasma exposure would imply 75 at. % of Hf₂ON₂ and 25 at. % HfN. This result contradicts the Hf³⁺ fraction of 0.59 ± 0.02 , signifying that only a fraction of O exits in the Hf₂ON₂ lattice. Therefore it is expected that O is primarily bonded to Hf on the defect sites such as grain boundaries which can lead to prominent GB scattering. Furthermore, Hf–O bond formation would warrant an increase in the oxidation state of Hf to +4 which subsequently quenches the free electron density and limits the conductivity.

A SEM image shown in Fig. 7(a) reveals a lateral grain size of $(24.5 \pm 2.5) \text{ nm}$ for 63 nm thick film prepared with 10 s H₂ plasma exposure. This grain size increases with thickness due to the grain growth as apparent from the cross-sectional image [Fig. 7(b)]. The small grain size obtained via SEM, together with the formation of resistive Hf–O bond further corroborates prominent grain-boundary scattering of the free electrons.

Altogether, H₂ plasma is capable of efficiently reducing the Hf⁴⁺ oxidation state to Hf³⁺, which is required to generate the conductive δ -HfN *fcc* structure. However, a limited

FIG. 7. (a) Top-view and (b) cross-sectional SEM image for approximately 63 nm HfN_x film deposited by 10 s H₂ plasma exposure at T_s = 450 °C. The images reveal a V-shaped grain growth mechanism (Ref. 38).

conductivity is obtained due to the prominent grain-boundary scattering. Therefore, in order to further improve the conductivity of the HfN_x films (10^{-4} – $10^{-3} \Omega \text{ cm}$), either the O should be reduced which would therefore promote the presence of the Hf³⁺ fraction^{20,21} and/or the grain size has to be increased.

IV. CONCLUSIONS

A plasma-assisted ALD process for HfN_x thin films has been introduced and investigated using a novel metal precursor CpHf(NMe₂)₃ and a N₂ or H₂ plasma as the coreactant. The growth-per-cycle and the material properties, such as chemical composition, electrical resistivity, optical properties, and crystal structure, were presented in light of the reducing character of the chosen plasma gas. In the case of the N₂ plasma, the films grown at stage temperatures of 350 and 450 °C showed a growth-per-cycle of 0.038 nm/cycle. An increase in the stage temperature from 350 to 450 °C led to a decrease in carbon content from 7 at. % to below the XPS detection limit, for the N₂ plasma process. However, the N₂ plasma was found inefficient in reducing the Hf⁴⁺ oxidation state to Hf³⁺, leading to high resistivity values of $6 \times 10^2 \Omega \text{ cm}$.

The process employing H₂ plasma as the coreactant yielded conductive stoichiometric, *fcc* δ -HfN films. For this process, a higher Hf³⁺/(Hf³⁺ + Hf⁴⁺) fraction of 0.59 was obtained which can be attributed to the high reduction potential of H₂ plasma species. The H₂-plasma based process markedly improved the electrical resistivity down to a value of $6 \times 10^{-1} \Omega \text{ cm}$. We identified two predominant reasons for the yet limited conductivity. First, the presence of O, up to 15 at. % was observed for 10 s H₂ plasma exposure: O induces the formation of the resistive Hf₂ON₂ impurity phase. Second, prominent grain-boundary scattering as concluded from the discrepancy between the optical in-grain resistivity ($5 \times 10^{-3} \Omega \text{ cm}$) and the electrical intergrain

resistivity ($10^{-1} \Omega \text{cm}$) values accompanied with the small grain size of $(24.5 \pm 2.5) \text{ nm}$.

In light of the results obtained in this study, we have demonstrated that the low $\text{Hf}^{3+}/(\text{Hf}^{3+} + \text{Hf}^{4+})$ fraction is a bottleneck for the film conductivity, which is attributed to either the low reduction potential of the N_2 plasma or high O content in the case of H_2 plasma process. In the case HfN_x films reported earlier,^{20,21} very low O at. % can justify the realization of conductive δ -HfN films with low resistivity. Furthermore, the presence of high C at. % leading to formation of Hf-C (Table I) would not increase the resistivity, since Hf-C is a conductive phase.³⁹ In conclusion, highly reducing coreactant is entailed in order to obtain conductive δ -HfN *fcc* crystal system. The Hf^{3+} oxidation state has a high affinity toward O, and therefore, reduction of O impurity content is a requirement to further lower the resistivity of the films.

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