Energetic Ions during plasma-enhanced atomic layer deposition and their role in tailoring material properties

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Energetic ions during plasma-enhanced atomic layer deposition and their role in tailoring material properties

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Abstract

Plasma-enhanced atomic layer deposition (PEALD) has obtained a prominent position in the synthesis of nanoscale films with precise growth control. Apart from the well-established contribution of highly reactive neutral radicals towards film growth in PEALD, the ions generated by the plasma can also play a significant role. In this work, we report on the measurements of ion energy and flux characteristics on grounded and biased substrates during plasma exposure to investigate their role in tailoring material properties. Insights from such measurements are essential toward understanding how a given PEALD process at different operating conditions can be influenced by energetic ions. Ion flux-energy distribution functions (IFEDFs) of reactive plasmas typically used for PEALD (O_2 , H_2 , N_2) were measured in a commercial 200 mm remote inductively coupled plasma ALD system equipped with RF substrate biasing. IFEDFs were obtained using a gridded retarding field energy analyzer and the effect of varying ICP power, pressure and bias conditions on the ion energy and flux characteristics of the three reactive plasmas were investigated. The properties of three material examples— TiO_x , HfN_x and SiN_x —deposited using these plasmas were investigated on the basis of the energy and flux parameters derived from IFEDFs. Material properties were analyzed in terms of the total ion energy dose delivered to a growing film in every ALD cycle, which is a product of the mean ion energy, total ion flux and plasma exposure time. The properties responded differently to the ion energy dose depending on whether it was controlled with RF substrate biasing where ion energy was enhanced, or without any biasing where plasma exposure time was increased. This indicated that material properties were influenced by whether or not ion energies exceeded energy barriers related to physical atom displacement or activation of ion-induced chemical reactions during PEALD. Furthermore, once ion energies were enhanced beyond these threshold barriers with RF substrate biasing, material properties became a function of both the enhanced ion energy and the duration for which the ion energy was enhanced during plasma exposure. These results have led to a better insight into the relation between energetic ions and the ensuing material properties, e.g. by providing energy maps of material properties in terms of the ion energy dose during PEALD. It serves to demonstrate how the measurement and control of ion energy and flux characteristics during PEALD can provide a platform for synthesizing nanoscale films with the desired material properties.

Supplementary material for this article is available [online](#)

Keywords: atomic layer deposition, plasma ALD, substrate biasing, ion energy flux, ion energy dose, RFEA, displacement energy threshold

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List of symbols

A_{eff}	effective ion sampling area at RFEA collector plate (mm^2)
A_{tot}	total ion sampling area at RFEA entrance orifices (mm^2)
e	elementary charge constant (C)
E_i	ion kinetic energy (eV)
$E_{i,\text{max}}$	maximum ion kinetic energy (eV)
$\langle E_i \rangle$	mean ion kinetic energy (eV)
$E_{i,\text{flux}}$	total ion kinetic energy flux ($\text{eV nm}^{-2} \text{s}^{-1}$)
$E_{i,\text{dose}}$	total ion kinetic energy dose per unit substrate area per ALD cycle (eV nm^{-2})
$\Delta E_{\text{LP-HP}}$	low and high energy peak separation in multimodal ion flux-energy distribution (eV)
$h_{\Gamma}(E_i)$	ion flux-energy distribution function ($\text{cm}^{-2} \text{s}^{-1} \text{eV}^{-1}$)
Γ_i	total ion flux ($\text{cm}^{-2} \text{s}^{-1}$)
I_C	ion current at RFEA collector plate (A)
J_C	ion current density at RFEA collector plate (A m^{-2})
J_{CPP}	ion current density measured using a capacitive planar probe (A m^{-2})
n_o	plasma density (cm^{-3})
$P_{\text{RF,bias}}$	RF bias power (W)
P_{ICP}	RF inductively coupled plasma power (W)
$\langle s \rangle$	time-averaged plasma sheath thickness (m)
t_p	duration of plasma exposure (s)
T_e	mean electron temperature (eV)
T_G	net transmission factor of RFEA grid stack
τ_i	ion transit time across a plasma sheath (s)
τ_{RF}	time period of RF bias signal (s)
V_{G2}	retarding voltage on ion discriminator grid of RFEA (V)
$\langle V_{\text{bias}} \rangle$	time-averaged substrate bias voltage (V)
V_p	plasma potential (V)
V_{sub}	substrate potential (V)
$\tilde{V}_{\text{RF,bias}}$	oscillation amplitude of time-varying RF bias signal (V)
$\tilde{V}_{\text{sh}}$	oscillation amplitude of time-varying sheath voltage (V)
ΔV_{sh}	potential across plasma sheath (V)

1. Introduction

Continuous downscaling of semiconductor technology nodes and emerging applications in nanotechnology exert rigorous demands on the techniques used in processing materials at the atomic level [1, 2]. It has become vitally important to retain

proper control over the growth of functional materials when they are deposited on substrates with nanoscale dimensions and three-dimensional (3D) geometries [3–5]. Atomic layer deposition (ALD) is a technique that has been widely adopted for synthesizing nanoscale films of a variety of materials [6]. It is a cyclic deposition process based on sequential and self-limiting precursor and co-reactant dose steps for growing films in a layer-by-layer fashion. These attributes confer excellent growth control that leads to uniform and conformal film deposition even on challenging substrate topographies. For materials that require low processing temperatures or for which thermally driven growth chemistries are not available, an energy-enhanced ALD method can be employed such as plasma-enhanced atomic layer deposition (PEALD) [7, 8]. In PEALD, a plasma is used during one of the reactant exposure steps of the cyclic deposition process. A plasma constitutes a mixture of highly reactive atomic and molecular neutrals (plasma radicals), photons, ions and electrons. The highly reactive species generated during plasma exposure can provide an alternate source of the energy required for film growth that is typically provided by substrate heating. While the contribution of highly reactive radicals towards film growth is a well-known feature of PEALD, the ions generated during plasma exposure can also play a significant role in the deposition process.

Ion-surface interactions are an inherent feature of plasma-enhanced processing techniques [9, 10]. Additional energy can be delivered to a material surface by the kinetic energy of ions impinging on the material. The extent to which ion-surface interactions can influence a material, during both deposition and etching, also depends on other factors such as the mass, reactivity, impingement rate (or flux) and dose (or net flux integrated over time) of ionic species incident on the film surface [9, 11–15]. Furthermore, the concurrent arrival of energetic ions and reactive radicals at a surface has been reported in the literature to bring about synergistic ion-radical processes during both deposition and etching [9, 10, 16]. Although the effects of ion-surface interactions have been investigated in great detail for plasma-enhanced chemical and physical vapor deposition together with plasma-based dry etching processes, very limited studies have been conducted on the role of ions during PEALD. Building upon our previous work [17, 18], we recently demonstrated how the material properties of oxides and nitrides (of Ti, Hf and Si) grown using PEALD on planar and 3D substrates can be tailored by implementing RF substrate biasing in a remote plasma ALD system [19, 20]. Specifically, an RF bias signal applied to the substrate table of the remote plasma system through a matching network (consisting of inductive and capacitive components) induces a negative time-averaged bias voltage, $\langle V_{\text{bias}} \rangle$, on the substrate. This increases the potential difference, and therefore, the electric field across the sheath region formed between the plasma and the substrate, which in turn accelerates ions toward the substrate in a direction perpendicular to its surface. As a result, the energy brought to a growing film surface by the impinging ions can be controlled by means of RF substrate biasing. This technique was demonstrated to significantly enhance the versatility of

PEALD processes by providing additional knobs—magnitude and duration of $\langle V_{\text{bias}} \rangle$ during plasma exposure—that enabled enhanced control over a wide range of material properties, relevant for numerous applications [19]. Based on these recent observations made in our previous work, it was concluded that controlling the magnitude of $\langle V_{\text{bias}} \rangle$ imparted ion energy control while varying the duration of $\langle V_{\text{bias}} \rangle$ during plasma exposure influenced the dose or fluence (i.e. particle flux integrated over time) of energetic ions impinging on a growing film [19]. While $\langle V_{\text{bias}} \rangle$ is an often known parameter given the relative ease with which it can be measured, the energy characteristic of ions also depends on the spatial and temporal variations of the electric field in the sheath region during RF substrate biasing. In order to better understand how any given PEALD process is influenced by ion-surface interactions, information on the energy and flux characteristics of ions impinging on a growing film surface under various plasma conditions is required. Such ion energy and flux characteristics are usually reported for plasma-based dry etching processes including the etch counterpart of PEALD, namely plasma-enhanced atomic layer etching (ALE) where so-called ALE windows have been identified for different materials as a function of the ion energy [21–23].

In this work, we measured ion energy and flux characteristics of reactive plasmas typically used for PEALD (O_2 , H_2 , N_2) in order to investigate their role in tailoring material properties. An O_2 plasma is generally employed for depositing oxides, an H_2 plasma can typically act as the reducing agent for growing metallic elements or conductive compounds (e.g. transition metal nitrides and carbides) while an N_2 plasma can be used as the co-reactant for synthesizing nitrides [8]. Ion flux-energy distribution functions (IFEDFs) of these plasmas were measured in a commercial remote plasma ALD system equipped with RF substrate biasing that allows for processing large area (200 mm) substrates. The accuracy of the measured datasets were initially benchmarked for inert Ar plasma exposures without and with RF substrate biasing. The effect of varying operating conditions (source power, pressure) and substrate configurations (grounded or biased) on the ion energy and flux characteristics of the three reactive plasmas were also investigated. The properties of three materials having a dielectric or conductive nature—namely TiO_x , HfN_x and SiN_x —grown using the three reactive plasmas in this ALD system, without and with substrate biasing, were analyzed as a function of the ion energy and flux parameters derived from IFEDFs. The results obtained herein provide experimental evidence for validating the conclusions made in our previous work (discussed above). The results of this work have also afforded a better understanding of the relation between energetic ion characteristics and the ensuing material properties, e.g. by providing energy maps of material properties in terms of the ion energy dose during PEALD. These findings can serve as practical guidelines for obtaining materials with the desired properties when growing nanoscale films using PEALD.

2. Experimental setup

A schematic of the experimental setup employing a remote plasma ALD system (Oxford Instruments FlexAL) is shown in figure 1. The reactor consisted of a radio-frequency (RF) power supply (13.56 MHz, up to 600 W) connected to a water-cooled copper coil wrapped around a cylindrical alumina tube to generate an inductively coupled plasma (ICP). For the specific FlexAL configuration, an additional external RF power supply (13.56 MHz, up to 100 W) was connected to the reactor table that allowed for substrate biasing during plasma exposure. Both RF power sources were in phase with each other and connected to the system via automated matching units consisting of inductive and capacitive components. The FlexAL system provides a readout for $\langle V_{\text{bias}} \rangle$ when applying an RF bias signal during plasma exposure. Additionally, an oscilloscope was connected to the reactor table via a high-voltage probe, shown in figure 1, from which sinusoidal RF bias voltage waveforms developing on the table could be measured. These oscilloscope measurements were used to independently verify $\langle V_{\text{bias}} \rangle$ readouts from the FlexAL system (within ± 5 V). A base pressure in the reactor chamber of $\sim 10^{-6}$ Torr was obtained using a turbo pump. A butterfly valve in front of the turbo pump controlled the effective pumping speed and functioned as an automated pressure controller.

A commercial gridded retarding field energy analyzer (RFEA) [24–27] from Impedans Ltd was placed on the reactor table for measuring IFEDFs during plasma exposures without and with substrate biasing. A schematic of the RFEA is shown in figure 1. It consisted of a series of grids (G1, G2 and G3) located beneath an array of ion sampling orifices with total ion sampling area (A_{tot}) of about 19 mm^2 and terminated by a collector plate (figure 1) [25, 28, 29]. The ions entered the RFEA through the sampling orifices facing the plasma. The first grid, G1, was electrically connected to the body of the RFEA and therefore, floated at the potential of the reactor table. Grid G1 consisted of apertures with a diameter of about $25 \mu\text{m}$ which is less than the Debye length encountered in the plasma conditions of this work ($> 100 \mu\text{m}$) [26], thus preventing any plasma from extending inside the analyzer. The second grid, G2, was biased with a positive voltage sweep with respect to the potential at G1 to provide a retarding potential barrier, V_{G2} , for the incoming positive ions. V_{G2} was swept from the average potential of G1 (corresponding to zero retarding potential) to about 50 V above plasma potential. At each step of the voltage sweep, only ions with energies greater than the energy barrier, eV_{G2} , formed at the discriminating grid G2 would be detected (e is the elementary charge constant). The third grid, G3, was biased about 60 V more negative than G1 to repel plasma electrons that may enter the RFEA and about 20 V more negative than the underlying collector plate. In other words, biasing the collector plate, C, 20 V more positive than G3 inhibits any secondary electrons that may be emitted from C. For each bias step applied to G2, the corresponding current at the collector plate, I_{C} , was recorded. This current arises from

Figure 1. Schematic of an Oxford Instruments FlexAL system equipped with substrate biasing. A radio-frequency power supply (RF-ICP) acts as the remote inductively coupled plasma generator. A second RF power supply (RF-Bias) connected to the reactor table enables substrate biasing. Both RF power supplies are connected to the system via automated matching units (AMU) consisting of inductive and capacitive components. An oscilloscope connected to the reactor table via a high-voltage probe allowed measurement of voltage waveforms developing on the substrate and a gridded retarding field energy analyzer (RFEA) mounted on the substrate table allowed measurement of the flux-energy distribution function of ions (IFEDFs) impinging on the substrate. The magnified schematic on the right illustrates features of the plasma sheath formed between an electropositive plasma (consisting of positive ions and negative electrons as the charged species) and the substrate leading to a directional flux of accelerated positive ions on the RFEA. A cross-section of the RFEA illustrates three grids (G1, G2, G3) and a collector plate (C) on which fixed and varying potentials were applied to determine IFEDFs.

ions that initially pass through the sampling orifices before successively passing through the three layers of partially transmitting planar grids. Dividing I_C measured at the RFEA collector plate with an effective ion sampling area, A_{eff} (discussed below and in RFEA calibration section in supplementary information, available online at stacks.iop.org/PSST/28/024002/mmedia), gives the ion current density at the collector, J_C , for each retarding voltage step applied to the discriminating grid G2 (i.e. $J_C = I_C/A_{\text{eff}}$). Taking the negative derivative of the J_C-V_{G2} characteristic measured using the RFEA results in the IFEDF. Note that RFEA measurements have been often reported in the literature using the term ion ion energy distribution function (IEDF) although IFEDF is a more accurate representation of such measurements. Recently, several works have addressed this issue in nomenclature by using the term IFEDF instead of IEDF to represent RFEA measurements [30–32]. As such, this work also uses the term IFEDF to represent the measurements conducted using a RFEA (see section on Deriving IFEDF from J_C-V_{G2} measurements in supplementary information).

The net transmission factor of the RFEA grid stack, T_G , is simply the proportion of incident ions at the entrance orifices that reach the collector plate after passing through all grids. The A_{eff} at the RFEA collector plate depends on the product of the aforementioned A_{tot} at the RFEA orifices and T_G (i.e. $A_{\text{eff}} = T_G \cdot A_{\text{tot}}$ where $0 < T_G < 1$). Several methods have been reported in the literature to calibrate a RFEA in order to determine T_G and the associated A_{eff} at the underlying collector plate [29, 33–36]. In this work, the RFEA was calibrated by comparing I_C measured at the RFEA collector with a reference ion current density, J_{CPP} , measured separately using a capacitive planar probe (CPP) [37]. The

calibration was performed for different plasmas at different operating conditions and yielded an A_{eff} of $0.39 \pm 0.09 \text{ mm}^2$ at the RFEA collector plate (see figure S1 and RFEA calibration section in supplementary information). The relative measurement uncertainty of $\pm 23\%$ arises from the calibration and includes the (non-systematic) measurement accuracy of the CPP. The A_{eff} at the collector expressed as a percentage of the A_{tot} at the entrance orifices yielded a T_G of about 2.1%. The aforementioned values for A_{eff} , its measurement uncertainty and T_G obtained from the calibration performed in this work were comparable to the corresponding values obtained from RFEA calibration reported in the literature (see RFEA calibration section in supplementary information) [34]. The values of J_C determined from the calibrated A_{eff} were used to derive parameters such as the ion flux, ion energy flux and kinetic energy dose of ions per unit substrate area per ALD cycle (discussed in the following section). The ion flux determined from the CPP calibrated J_C values obtained in our current work was comparable to the ion flux reported in our previous work measured in a similar FlexAL plasma ALD system under similar plasma conditions [38]. As a result, the uncertainty associated with the calibration technique implemented in this work was considered to be within acceptable limits. Furthermore, any systematic errors that were not included in the uncertainty but get incorporated in parameters derived using the calibrated J_C values were not expected to affect either the trends in material properties (as a function of the derived parameters), or the conclusions drawn on those trends.

When growing films in the FlexAL system using PEALD, the chamber wall temperature was set to 150°C while the substrate table (or stage) temperature was set between 300°C and 500°C . All substrates underwent a

Table 1. PEALD process conditions for the materials deposited with and without substrate biasing during plasma exposure.

Material	TiO _x	HfN _x	SiN _x
Precursor	TDMAT ^a	TDMACpH ^b	DSBAS ^c
Bubbler temperature (°C)	60	60	40
Precursor delivery	Bubbled with 100 sccm Ar	Bubbled with 100 sccm Ar	Vapor drawn
Stage temperature (°C)	300	450	500
Precursor dose time (ms)	200	4000	500
Precursor reaction step (s)	—	—	3
Precursor purge time (s)	3	2	2
Plasma gas	O ₂	H ₂	N ₂
Plasma gas flow (sccm)	100	100	100
Plasma pressure (mTorr)	9	30	11
RF-ICP power (W)	200	100	600
Plasma exposure time (s)	10	10	20
Plasma purge time (s)	3	4	3
$\langle V_{\text{bias}} \rangle$ or time-averaged substrate bias voltage (V)	0 to −254	0 to −210	0 to −103
Bias during plasma	All 10 s, Last 5 s	All 10 s	Last 10 s

^a TDMAT–Ti(NMe₂)₄.^b TDMACpH–CpHf(NMe₂)₃.^c DSBAS–SiH₃N(ⁱBu)₂.

30 min heating step prior to commencing deposition to ensure substrate temperature stabilization. The precursor delivery lines were heated to 70 °C to prevent precursor condensation. TiO_x, HfN_x and SiN_x films were deposited using PEALD cycles composed of sequential precursor dose, precursor purge, plasma exposure (without or with substrate biasing) and plasma purge steps. The precursors, plasma gases and other PEALD process conditions for depositing the three materials are shown in table 1, similar to that reported in our previous work [19]. Details regarding PEALD process conditions are further outlined in the supplementary information and the step sequences implemented without and with substrate biasing are shown in figure S2.

3. Material property characterization

The substrates used for depositing films with and without substrate biasing were single side polished (SSP) c-Si (100) wafers having a thin native oxide layer (~1.5 nm) for dielectric materials and SSP c-Si (100) wafers having a thick thermal oxide layer (~450 nm) for conductive materials. Film thicknesses between ~20 and ~80 nm were deposited for material characterization on these substrates. The optical properties and film thickness of the deposited layers on c-Si substrates were measured by means of spectroscopic ellipsometry (SE) using a J A Woollam M2000D rotating compensator ellipsometer (1.2–6.5 eV). For TiO_x films deposited with and without substrate biasing, the optical model used consisted of a silicon substrate, ~1.5 nm native oxide and the deposited layer parameterized using two Tauc-Lorentz oscillators [18, 39]. For HfN_x, different models were used for the films deposited with and without biasing, as reported previously by Karwal *et al* [20, 40]. The optical model used for the films grown without biasing consisted of a silicon substrate, ~450 nm thermal oxide and the deposited layer

parameterized using one Drude, one Lorentz and one Tauc-Lorentz oscillator [40]. The HfN_x films deposited with biasing were parameterized using one Drude and two Lorentz oscillators [20]. For SiN_x films deposited with and without substrate biasing, the optical model used consisted of a silicon substrate, ~1.5 nm native oxide and the deposited layer parameterized with a Cauchy dispersion relation [41, 42]. The mass density of TiO_x and SiN_x films were analyzed using x-ray reflectometry performed using a Bruker AXS D8 Advance system in the grazing incidence geometry with a Cu K α x-ray source (radiation wavelength of 0.154 nm) [43]. The residual stress of TiO_x films were determined by means of wafer-curvature measurements at room temperature. A KLA-Tencor FLX 2320 system was used to determine the curvature of 3 inch double side polished c-Si (100) wafers before and after deposition of the films. Based on the difference in curvature, the residual stress of the films deposited with and without substrate biasing was calculated using the Stoney equation [18, 43]. A sign convention was used where positive values represented tensile and negative values represented compressive residual stress. The chemical composition and oxidation state of elements present in HfN_x films were characterized using x-ray photoelectron spectroscopy (XPS). The XPS measurements were performed using a ThermoScientific K-Alpha KA1066 system equipped with a monochromatic Al K α ($h\nu = 1486.6$ eV) source. The crystallinity of TiO_x and HfN_x films deposited on planar c-Si substrates was analyzed using grazing incidence x-ray diffraction (XRD). The measurements were performed in a PANalytical X'pert PRO MRD with a Cu K α x-ray source (radiation wavelength of 0.154 nm) operated at an incidence angle of 0.5°. Electrical sheet resistance measurements of conductive HfN_x films deposited on c-Si substrates with ~450 nm thermal oxide were performed at room temperature using a Signatone four-point probe in combination with a Keithley 2400 Source Measurement Unit that acted as both current source and

Figure 2. (a) Ion flux-energy distribution function (IFEDF), $h_T(E_i)$, and (b) the product of the IFEDF and ion energy, $h_T(E_i) \times E_i$, as a function of the ion kinetic energy, E_i , for an Ar plasma at an ICP power, P_{ICP} , of 200 W and pressure of 9 mTorr in case of a grounded substrate (i.e. without biasing). The inset in (a) shows the ion collector current density versus retarding grid voltage (J_C-V_{G2}) characteristic measured using the calibrated RFEA, the negative derivative of which yields $h_T(E_i)$. The area under $h_T(E_i)$ allows determination of the total ion flux, Γ_i , while the high energy peak edge corresponds to the maximum kinetic energy of ions, $E_{i,max}$, impinging on the grounded substrate. The area under $h_T(E_i) \times E_i$ allows determination of the total ion energy flux, $E_{i,flux}$, while the ratio of $E_{i,flux}$ and Γ_i gives the mean ion energy, E_i .

voltage meter. The electrical resistivity was obtained from the slope of the generated $I-V$ curve and the film thickness deduced from the SE measurements. For investigating wet-etch rates (WERs) of SiN_x , the films were first deposited with and without substrate biasing during PEALD on coupons containing high aspect ratio trench nanostructures (width ~ 100 nm, height ~ 450 nm, $\text{AR} = 4.5:1$) and analyzed with cross-sectional transmission electron microscopy (TEM). Coupons containing these trench nanostructures were prepared and provided by Lam Research [42]. A JEOL 2010F ultrahigh-resolution scanning TEM at 200 kV (Nanolab Technologies) was employed to obtain cross-sectional images of the deposited films. A detailed outline on sample preparation for TEM imaging has been outlined in our previous work [19, 42]. The deposited film thickness was measured at planar and vertical regions of several trench nanostructures in the sample by counting pixels in the TEM image. To perform wet-etch treatments, coupons containing the trench nanostructures with the deposited films were dipped in a dilute hydrofluoric acid solution ($\text{HF}:\text{H}_2\text{O} = 1:100$) for 30 s. Two samples for TEM cross-sectional imaging were prepared from the same coupon, one before and one after the chemical wet-etch treatments. TEM measurements were conducted across several trench nanostructures of the same as-deposited and post wet-etch samples. The WERs were determined by comparing the as-deposited and post wet-etch film thicknesses on the trench nanostructures.

4. Results and discussion

4.1. Inert Ar plasma without and with RF substrate biasing

Figure 2(a) shows the IFEDF, $h_T(E_i)$, as a function of the ion kinetic energy, E_i , for an Ar plasma ignited at an ICP power,

P_{ICP} , of 200 W and pressure of 9 mTorr for a grounded reactor table (i.e. without RF substrate biasing). The inset shows the J_C-V_{G2} characteristic from which the IFEDF was determined using

$$h_T(E_i) = -\frac{1}{e^2} \cdot \frac{dJ_C}{dV_{G2}}, \quad (1)$$

where e is the elementary charge constant. The E_i brought to a substrate by ions accelerated across a collisionless plasma sheath is determined by the sheath potential, ΔV_{sh} , which is the difference between the plasma potential, V_p , and the substrate potential, V_{sub} . These parameters are related by the following well-known expression

$$E_i = e\Delta V_{sh} = e(V_p - V_{sub}). \quad (2)$$

The IFEDF consisted of a narrow mono-modal or single peaked feature which is a typical attribute of inductively coupled discharges exposed to a grounded substrate [44–46]. For a purely inductively coupled discharge over a grounded substrate, V_p is constant and $V_{sub} = 0$ V, resulting in the flux-energy distribution of ions impinging on the substrate to have a mono-modal feature around eV_p . For the practical inductive discharges over grounded substrates used in this work, the width of the mono-modal feature arises due to fluctuations in the plasma potential caused by parasitic capacitive coupling between the ICP coil and the discharge (in the absence of Faraday shielding), ion collisions in the presheath and/or the energy resolution of the RFEA [24, 44–46]. The low energy tail in the IFEDF in figure 2(a) indicated that a relatively small number of argon ions underwent collisions while traversing the plasma sheath. As such, the formation of a nearly collisionless sheath between the plasma and the grounded

substrate can be assumed at the low pressure of 9 mTorr (discussed more later in this section). The high energy edge of the IFEDF at about 20 eV corresponded to the maximum energy of ions, $E_{i,max}$, impinging on the grounded substrate (figure 2(a)). The total flux of ions, Γ_i , impinging on the substrate is given by the area under the IFEDF [26, 31, 32] such that

$$\Gamma_i = \int_0^\infty h_\Gamma(E_i) dE_i \quad (3)$$

which resulted in a Γ_i of about $3 \times 10^{14} \text{ cm}^{-2} \text{ s}^{-1}$ for the grounded Ar plasma in figure 2(a). The mean energy of ions, $\langle E_i \rangle$ (figure 2(a)), impinging on the grounded substrate can be determined from the ratio of the total ion kinetic energy flux, $E_{i,flux}$, and the Γ_i . The $E_{i,flux}$ can be obtained from a plot of the product of the IFEDF and the ion energy, i.e. $h_\Gamma(E_i) \times E_i$, as a function of E_i shown in figure 2(b) [46]. The area under $h_\Gamma(E_i) \times E_i$ allows determination of the $E_{i,flux}$ such that [47, 48]

$$E_{i,flux} = \int_0^\infty (h_\Gamma(E_i) \times E_i) dE_i \quad (4)$$

For the inductive Ar plasma exposure on a grounded substrate shown in figure 2, the $E_{i,flux}$ was about $44 \text{ eV nm}^{-2} \text{ s}^{-1}$. Using equations (3) and (4), the expression for $\langle E_i \rangle$ becomes [31, 32, 46].

$$\langle E_i \rangle = \frac{E_{i,flux}}{\Gamma_i} = \frac{\int_0^\infty (h_\Gamma(E_i) \times E_i) dE_i}{\int_0^\infty h_\Gamma(E_i) dE_i} \quad (5)$$

which yielded a $\langle E_i \rangle$ at around 15 eV in figure 2(a). The total ion kinetic energy dose imparted to the substrate by the impinging ions, $E_{i,dose}$, during plasma exposure can be obtained from the product of $E_{i,flux}$ and plasma exposure time, t_p , such that

$$E_{i,dose} = E_{i,flux} \times t_p \quad (6)$$

Therefore, a t_p of 10 s using an Ar plasma on a grounded substrate shown in figure 2 yielded an $E_{i,dose}$ of about 440 eV nm^{-2} .

When a sinusoidal RF voltage signal is applied to the substrate table through a matching network during plasma exposure, a negative average or DC offset voltage is induced on the substrate such that the net flux of ions and electrons impinging on it is zero over one RF cycle. The negative DC offset or time-averaged substrate bias voltage ($V_{sub} = -\langle V_{bias} \rangle$) can be increased by increasing the amplitude of the time-varying RF bias signal, $\tilde{V}_{RF,bias}$, applied to the substrate table. This can be visualized in figure 3(a) which shows the RF bias voltage waveforms induced on the substrate in an Ar plasma as a function of time, measured using an oscilloscope (see also figure S3 in supplementary information). The oscillating waveforms were observed to have a time period, τ_{RF} , of about 74 ns, corresponding to the applied bias frequency of

13.56 MHz. $\langle V_{bias} \rangle$ can be controlled by varying the RF bias power, $P_{RF,bias}$, applied to the reactor table. This was observed in figure 3(b) which shows $\langle V_{bias} \rangle$ as a function of $P_{RF,bias}$. The plot shows a deviation from an ideally linear trend suggesting that the applied $P_{RF,bias}$ was not dissipated entirely by accelerating ions across the plasma sheath. For remote ICP reactors employing RF substrate biasing, it has recently been reported that some of the bias power may be consumed in heating electrons near the substrate, which affects plasma density and consequently ion current [49–52]. This together with other effects such as power dissipation across resistive losses at the substrate or in the matching network can contribute to the nonlinear trend in $\langle V_{bias} \rangle$ versus $P_{RF,bias}$.

A plot of Γ_i as a function of $P_{RF,bias}$ has also been shown in figure 3(b) where a slight increase in Γ_i to $4.7 \times 10^{14} \text{ cm}^{-2} \text{ s}^{-1}$ was observed on increasing $P_{RF,bias}$ to 20 W. Further increase in $P_{RF,bias}$ did not change Γ_i . The values of Γ_i have been determined using equation (3) for IFEDFs obtained in the Ar plasma without and with RF substrate biasing. Figure 3(c) shows the IFEDFs while figure 3(d) shows the products of the IFEDFs and the corresponding ion energies for Ar plasma without and with RF substrate biasing. The narrow mono-modal distributions in the plots for a grounded substrate became broad bi-modal distributions with RF substrate biasing. They illustrate how $\langle E_i \rangle$, $E_{i,max}$ and $E_{i,flux}$ scale as a function of $\langle V_{bias} \rangle$ (see also figure S4 in supplementary information), which effectively demonstrates how E_i characteristics can be controlled by varying the magnitude of $\langle V_{bias} \rangle$. The difference between $\langle E_i \rangle$ and $E_{i,max}$ was also observed to increase linearly with $\langle V_{bias} \rangle$. This was also observed for the case of reactive plasmas (discussed in the following sections) which were studied to show how a growing film surface during PEALD with RF substrate biasing can get exposed to a range of ion energies significantly exceeding $\langle E_i \rangle$. As a result, values for the $\langle E_i \rangle$ often calculated using equation (2) with easily measurable values of $\langle V_{bias} \rangle$ may not be representative of the actual energies of ions impinging on a growing film surface. This serves to highlight the importance of measuring IFEDFs as they provide information beyond just the $\langle E_i \rangle$, which is essential for investigating the relation between energetic ion characteristics and the properties of materials grown with or without RF substrate biasing during PEALD (discussed in the following sections). The width of the bi-modal distributions in terms of the low and high energy peak separation, ΔE_{LP-HP} , is generally used in the literature as a means of quantifying the spread in the energy of ions impinging on the substrate. Various analytical models have been developed to measure ΔE_{LP-HP} . The model developed by Benoit-Cattin and Bernard [53] states that

$$\Delta E_{LP-HP} = \frac{4e\tilde{V}_{sh}}{\pi} \left(\frac{\tau_{RF}}{\tau_i} \right), \quad (7)$$

where $\tilde{V}_{sh}$ is the amplitude of the time-varying sheath voltage formed under RF biasing and is approximately given by $\tilde{V}_{RF,bias}$ [25, 26, 54] (obtainable from oscilloscope measurements in figure 3(a)), while τ_i is the ion transit time across the sheath

Figure 3. (a) Substrate voltage waveforms as a function of time measured using an oscilloscope in an Ar plasma at 200 W ICP power, P_{ICP} , and 9 mTorr pressure without (i.e. grounded) and with RF substrate biasing. It illustrates the development of instantaneous substrate bias voltages (bottom axis) and negative time-averaged substrate bias voltages, $\langle V_{bias} \rangle$, with respect to ground (top axis) for the corresponding RF bias powers, $P_{RF,bias}$. (b) $\langle V_{bias} \rangle$ and total ion flux, Γ_i , as a function of the applied $P_{RF,bias}$ where Γ_i was determined from measurements conducted using a calibrated retarding field energy analyzer (RFEA). (c) Ion flux-energy distribution function (IFEDF), $h_T(E_i)$, and (d) product of the IFEDF and ion energy, $h_T(E_i) \times E_i$, as a function of the ion kinetic energy, E_i , for the Ar plasma without and with RF substrate biasing measured using the calibrated RFEA. The mean ion energy, $\langle E_i \rangle$, maximum ion energy, $E_{i,max}$ and total ion energy flux, $E_{i,flux}$, for the corresponding $\langle V_{bias} \rangle$ are indicated.

[55]. Equation (7) states that the bi-modal IFEDFs become broader (i.e. ΔE_{LP-HP} increases) with increase in $\tilde{V}_{sh}$ and/or a decrease in τ_i . This was demonstrated in figure 3(c) where ΔE_{LP-HP} can be inferred to increase with $\langle V_{bias} \rangle$, and hence with $\tilde{V}_{sh}$ (see also figure S5 in supplementary information), similar to the trend reported by Hayden *et al* [25]. Furthermore, no significant low energy tails were observed for the bi-modal IFEDFs in figure 3(c), which suggested that ions traversed the plasma sheaths formed with RF substrate biasing without undergoing significant ion-neutral charge-exchange collisions [26, 36]. This was corroborated by calculating time-averaged sheath thicknesses, $\langle s \rangle$, for the investigated Ar plasmas using the expression for a collisionless Child-Langmuir sheath [55]

where values of $\langle s \rangle$ up to 6 mm were obtained with RF substrate biasing (see figure S6 and equations S6 and S7 in supplementary information). This indicated that the sheath thicknesses evolving as a function of $\langle V_{bias} \rangle$ were less than the ion mean free path (~ 8 mm for Ar plasma at ~ 10 mTorr [26]), thereby confirming the formation of nearly collisionless plasma sheaths.

The values of ΔE_{LP-HP} measured in this work for an RF biased inductive Ar plasma were used to calculate τ_i using equation (7). The magnitude of the calculated values of τ_i , ranging from ~ 400 ns to ~ 300 ns (see figure S7 in supplementary information), and the trend in those values as a function of $\tilde{V}_{sh}$ were comparable to those reported by Wen *et al* [54] who used a Monte-Carlo model to calculate τ_i for an

inductive Ar plasma at similar conditions. This indicated that the ion energy ($\langle E_i \rangle$, ΔE_{LP-HP}) and voltage ($\langle V_{sh} \rangle$, $\langle V_{bias} \rangle$) characteristics measured using the RFEA and oscilloscope, respectively, were of a reasonable accuracy.

4.2. Reactive plasmas for PEALD without and with RF substrate biasing

Materials synthesis with PEALD often makes use of gases such as O₂, H₂, N₂, etc, for generating reactive species in the plasma exposure step, which enable or contribute towards film growth. Although these gases are all diatomic molecules, the properties of the plasmas generated using these gases can be quite different owing to the difference in mass (32, 28 and 2 for O₂, N₂ and H₂ molecules), molecular dissociation energy (5.2, 9.8 and 4.5 eV for O=O, N≡N and H-H bonds) [56], ionization energy (12.1, 15.4 and 15.6 eV for creating O₂⁺, N₂⁺ and H₂⁺ ions) [57], ion species composition, etc. For the pressures investigated in this work, diatomic O₂⁺, N₂⁺ and triatomic H₃⁺ species have been reported to be the dominant ions in remote inductively coupled O₂, N₂ and H₂ plasmas, respectively [36, 58, 59]. The energy and flux of these ions generated in the respective plasmas will depend on all the aforementioned factors in a non-trivial manner, but are primarily determined by the plasma density, n_o , and the mean electron temperature, T_e . These two plasma properties are usually controlled by varying P_{ICP} and the discharge pressure. Therefore, the energy and flux characteristics of ions generated in remote inductively coupled O₂, H₂ and N₂ plasmas, without and with RF substrate biasing, have been investigated for different P_{ICP} and pressure conditions. Figures 4 and 5 show the IFEDFs obtained in O₂, H₂ and N₂ plasmas without and with RF substrate biasing during the respective plasma exposures. Figure 4 shows the effect of varying P_{ICP} (for a constant pressure) while figure 5 illustrates the effect of a change in pressure (for the same P_{ICP}) as a function of $\langle V_{bias} \rangle$ induced on the substrate by the corresponding $P_{RF,bias}$ (a grounded substrate has been indicated by $\langle V_{bias} \rangle = 0$ V for which $P_{RF,bias} = 0$ W). Some common trends were observed for all three discharges without and with substrate biasing upon individually varying P_{ICP} and pressure which will first be presented. It will be followed by a discussion on trends that were more unique for the individual plasmas.

As observed previously for the case of Ar plasma, implementing substrate biasing during the three reactive plasmas led to the appearance of bi-modal features in the IFEDFs whose widths increased with $\langle V_{bias} \rangle$. At a constant pressure, the area under IFEDFs increased with increase in P_{ICP} (figure 4). It is known that at higher P_{ICP} , more power is coupled into the plasma that increases the collision frequency between electrons and neutral plasma species resulting in a higher ionization rate [38]. This increases n_o which leads to a higher Γ_i impinging on the substrate, thereby enhancing the area under IFEDFs (see equation (3) and figure 4). Note that for H₂ plasmas, increasing P_{ICP} led to a much larger increase in the area under IFEDFs compared to O₂ or N₂ plasmas, which indicated significantly higher plasma densities at the higher P_{ICP} for H₂ plasmas. This could arise from the H₂

Figure 4. Effect of varying ICP power, P_{ICP} , on the ion flux-energy distribution functions, $h_i(E_i)$, of (a) O₂, (b) H₂, and (c) N₂ plasmas with RF substrate biasing at a pressure of 9 mTorr. All plots have the same scale for the horizontal and vertical axes to facilitate comparison. The negative time-averaged substrate bias voltages formed by the applied RF bias powers are indicated in the legends.

plasmas undergoing a transition from capacitive to inductive mode, also reported in the literature as the *E to H mode transition* which is a hallmark of ICP discharges [60, 61]. A characteristic feature of this transition is the significant jump in n_o as P_{ICP} is increased from a low to a high value [60, 61]. Furthermore, the IFEDFs of H₂ plasmas showed some other unique trends compared to O₂ or N₂ plasmas, which will be addressed at the end of this section. For a fixed P_{ICP} , increasing pressure led to a decrease in the area under IFEDFs, narrower IFEDF widths (i.e. lower ΔE_{LP-HP}), leftward shift of IFEDFs (i.e. lower $\langle E_i \rangle$, $E_{i,max}$) and a lower

Figure 5. Effect of varying pressure on the ion flux-energy distribution functions, $h_I(E_i)$, of (a) O_2 , (b) H_2 , and (c) N_2 plasmas with RF substrate biasing at an ICP power, P_{ICP} , of 600 W. All plots have the same scale for the horizontal and vertical axes to facilitate comparison. The insets in (a) and (c) depict $h_I(E_i)$ for O_2 and N_2 plasma, respectively, at 30 mTorr with a scaled vertical axis for better illustration. The negative time-averaged substrate bias voltages formed by the applied RF bias powers are indicated in the legends.

$\langle V_{bias} \rangle$ for the same $P_{RF,bias}$ (figure 5). The n_o (and therefore Γ_i) has been reported to increase in a remote ICP system with a planar/spiral coil configuration when P_{ICP} is kept constant and the pressure is raised [44, 59]. However, the spatial properties of plasma parameters in remote downstream ICP systems with an upper source chamber driven by a cylindrical coil configuration and a lower expansion chamber near the substrate can be quite complicated [24, 62–65]. The substrate

table, and hence the location at which RFEA measurements were conducted, lies at the end of the expansion chamber where n_o has been reported to decrease with pressure for a constant P_{ICP} [38, 62, 63]. This has been attributed to a reduced out-diffusion of charged particle species from the plasma source at elevated pressures that lowers Γ_i at the substrate [38, 62, 63], which could explain the diminished areas under the IFEDFs. Furthermore, a reduced Γ_i induces a larger $\langle s \rangle$ which leads to a longer τ_i (see equations (S6)–(S8) in supplementary information). The longer τ_i together with a lower $\tilde{V}_{sh}$ (due to a lower $\langle V_{bias} \rangle$) could contribute towards the narrower widths (i.e. lower ΔE_{LP-HP}) observed for the IFEDFs. It is known that at higher pressures, the electron mean free path is reduced leading to more electron-neutral collisions and hence, a lower T_e [29, 66]. As a result, ΔV_{sh} is lowered owing to the dependence of both V_p and $\langle V_{bias} \rangle$ on T_e [66] which can therefore, account for the shift in IFEDFs to lower $\langle E_i \rangle$ and $E_{i,max}$.

For O_2 plasma at a constant pressure, increasing P_{ICP} led to a slight shift of the IFEDFs to lower energies when the substrate was grounded or biased with a low $P_{RF,bias}$ of 4 W. This could be due to a lower T_e at the higher P_{ICP} condition as observed in previous work [38], which could lead to a lower V_p [8]. However, the shift in IFEDF at the two P_{ICP} values decreased as the $P_{RF,bias}$ applied to the substrate was increased to 20 W. This suggested that the relatively small influence of P_{ICP} on V_p during O_2 plasmas diminished when the substrate was biased using high $P_{RF,bias}$, which may be speculated to arise from the previously mentioned electron heating effects in inductive discharges with RF substrate biasing recently reported in the literature [49–52]. Further investigation is needed to better ascertain these effects which lies beyond the scope of this work. On the other hand, for H_2 plasma at a constant pressure, increasing P_{ICP} leads to wider IFEDFs together with a significant shift in IFEDFs to higher energies for both grounded and biased substrates compared to O_2 plasma. This could be due to a combination of several possible factors discussed herein. The broader IFEDFs suggested an increase in $\tilde{V}_{sh}$ and/or decrease in τ_i . As mentioned before, the IFEDF width in case of an ICP exposed to a grounded substrate can arise from parasitic capacitive coupling between the ICP coil and the discharge in the absence of electrostatic shielding [36, 58]. Therefore, the plasma potential can have an oscillating RF component superimposed on it. The amplitude of this RF component can increase when the supplied power (i.e. P_{ICP}) was increased [58] from 200 W to 600 W at a fixed pressure leading to an increase in $\tilde{V}_{sh}$. Furthermore, for the pressures investigated in this work, H_2 plasmas are known to have an ion composition where H_3^+ has been reported to be the dominant ion [36, 58]. The mass of H_3^+ is lower than that of ions generated in the other plasmas in this work. In addition, since the plasma densities in H_2 plasmas were observed to be significantly higher at 600 W P_{ICP} , thinner $\langle s \rangle$ could form over the substrate in H_2 plasmas compared to those formed in other plasmas. The combined effects of a thinner $\langle s \rangle$ and lower ion mass may therefore, lead to a comparatively lower τ_i (see equation (S3) in supplementary information). The shift in IFEDFs to higher energies at a higher P_{ICP}

Table 2. Crystalline phase composition, refractive index and mass density of titanium oxide films deposited at a stage temperature of 300 °C without and with RF substrate biasing during O₂ plasma exposure at 200 W ICP power and 9 mTorr. The time-averaged substrate bias voltage, $\langle V_{\text{bias}} \rangle$, plasma exposure time, t_p , bias duration during t_p , mean ion energy, $\langle E_i \rangle$, maximum ion energy, $E_{i,\text{max}}$, total ion energy flux, $E_{i,\text{flux}}$, and total ion energy dose per unit substrate area per ALD cycle, $E_{i,\text{dose}}$, for each film are indicated. Any associated measurement uncertainties are given in the first row.

$\langle V_{\text{bias}} \rangle$ (V)	t_p (s)	Bias during t_p (s)	$\langle E_i \rangle$ (eV)	$E_{i,\text{max}}$ (eV)	$E_{i,\text{flux}}$ (eV nm ⁻² s ⁻¹)	$E_{i,\text{dose}}$ (eV nm ⁻²)	Crystal phase	Ref. index	Mass density (g cm ⁻³)
0	10	—	19	27	38	380	Anatase	2.47 ± 0.03	3.7 ± 0.2
0	108	—	19	27	38	4100	Anatase	2.39	3.3
−152	10	All 10	161	204	429	4290	Anatase + Rutile	2.51	4.1

suggested an increase in T_e , which is contrary to the trend for O₂ plasma as reported in our previous work [38]. Godyak *et al* [67] have reported on the unusual increase in T_e with P_{ICP} at low pressure (1 and 10 mTorr) and attributed this to an increase in electron–electron collisions at the higher n_o obtained from increasing P_{ICP} . Similarly, the higher n_o of an H₂ plasma at 600 W P_{ICP} at the low pressure of 9 mTorr could allow for more electron–electron collisions resulting in the elevation of T_e with P_{ICP} . Another factor reported by different authors in the literature which could play a role at low pressure is gas heating by ion–neutral collisions during ion acceleration in the presheath by the plasma ambipolar potential [67–72]. This can lead to a lower gas density, which in turn can increase the electron mean free path and hence, T_e . Further investigation is required to verify these effects which lies beyond the scope of this work. In case of N₂ plasma at constant pressure, no comparable shifts in IFEDFs were observed with increase in P_{ICP} , which suggested that T_e was relatively unaffected by P_{ICP} in N₂ plasma [73].

4.3. Role of energetic ions on properties of materials deposited without and with RF biasing

The effects of ion energy and flux characteristics on material properties of films deposited using PEALD without and with substrate biasing are discussed herein. Three materials, namely TiO_x, HfN_x and SiN_x grown using reactive O₂, H₂ and N₂ plasmas, respectively, discussed in the previous section have been used as case studies.

4.3.1. Titanium oxide (TiO_x) grown with O₂ plasma. Table 2 compares the material properties of three TiO_x films deposited on planar substrates at 300 °C for two films grown without and one film grown with RF substrate biasing during the O₂ plasma exposure step of PEALD. An $\langle E_i \rangle$ of 19 eV was measured for both films deposited without biasing ($\langle V_{\text{bias}} \rangle = 0$ V) and had a corresponding $E_{i,\text{max}}$ of 27 eV and $E_{i,\text{flux}}$ of 37 eV nm⁻² s⁻¹. Keeping E_i constant at the grounded substrate configuration and increasing $E_{i,\text{dose}}$ from 380 to 4100 eV nm⁻² by increasing t_p from 10 to 108 s, respectively (as per equation (6)), led to a decrease in refractive index and mass density of TiO_x. Grazing incidence XRD patterns revealed that both films grown without any biasing had a crystalline composition consisting of predominantly anatase

TiO_x (see figure S8 in supplementary information). This is similar to the observations reported by Schindler *et al* [74] who obtained predominantly anatase TiO_x when the films were deposited with 60 and 180 s O₂ plasma exposure steps (without any biasing) in a remote PEALD system. However, when t_p was kept constant at 10 s and $E_{i,\text{dose}}$ was increased to 4290 eV nm⁻² by enhancing E_i with RF substrate biasing (−152 V $\langle V_{\text{bias}} \rangle$) applied for a bias duration of 10 s during the 10 s t_p such that $\langle E_i \rangle$ reached 161 eV (table 2), both refractive index and mass density increased in contrast to the trends discussed above. The XRD pattern for this biased condition revealed a mixed phase crystalline content consisting of anatase and rutile TiO_x (see also figure S8 in the supplementary information). This is in agreement with the observations reported in our previous work for TiO_x deposited with substrate biasing where the higher refractive index and mass density were attributed to the presence of the denser rutile phase [19]. These results demonstrate how material properties of TiO_x respond differently to the $E_{i,\text{dose}}$ depending on whether it is controlled by enhancing E_i with RF substrate biasing, or by increasing t_p without any biasing during O₂ plasma exposure. Similar effects have been reported in the literature where increasing E_i from 20 to 100 eV at a fixed incident flux ratio of ions to atoms had different effects on material properties compared to increasing the incident flux ratio of ions to atoms at a fixed E_i of 20 eV [75, 76].

The results of this work indicated the presence of an E_i threshold at or above a lower limit of 27 eV given by $E_{i,\text{max}}$ measured for a grounded substrate in O₂ plasma, which the ions impinging on a growing TiO_x film must overcome to form the denser and more optically refractive rutile phase. This threshold generally refers to the energy barrier for displacing atoms from their equilibrium positions [66, 77, 78] and is proportional to the binding energy of the material, which is an average energy dependent on the specific position of material atoms (e.g. surface or bulk atom) [23]. Typical values reported in the literature as thresholds for displacing surface atoms range from ~20 to ~50 eV [66, 77, 78]. The corresponding values typically reported for displacing sub-surface (or bulk) atoms lie between ~40 and ~100 eV since they have a comparatively higher coordination number and are therefore, more strongly bound than surface atoms [77–79]. When E_i lies above atom displacement thresholds, ions impinging on a target material are known to transfer their

energy by interacting with the nuclei and electrons of the material [9, 77, 78]. For E_i up to ~ 1 keV and comparable masses of incident ions and target material atoms, energy transfer has been reported to occur predominantly through elastic nuclear interactions [9, 15, 77]. Inelastic electronic interactions become significant for $E_i \gg 1$ keV and for a large mass difference between the impinging ions and target material atoms [15, 77, 80]. In this regard, for E_i up to a few hundred eV obtained for oxygen ions impinging on TiO_x with substrate biasing, energy transfer could be considered to occur mainly through elastic nuclear interactions. Such interactions can initiate collision cascades through so-called recoil implantation (i.e. forward sputtering of knock-on atoms generated by ion-surface interactions) and/or incident ion implantation [77, 81, 82], which leads to atomic scale heating [83]. Therefore, the cascades represent a localized volume of material at a high temperature (i.e. *hot spot*) [82, 84] where atoms are simultaneously in motion and undergo collisions that can break and reform bonds in the surface and sub-surface regions of the material undergoing ion bombardment [66, 77]. The mobile atoms continue to undergo further collisions until their energy drops below the thresholds needed to displace other atoms from their equilibrium positions, at which point the remaining energy gets dissipated as thermal vibrations [82, 83]. The anatase to rutile phase transformation of TiO_x has been reported in the literature to be a reconstructive process involving the breaking and reforming of bonds, in contrast to other phase transformation processes where the original bonds are distorted but retained without being broken [85]. In this regard, the ions impinging on a growing TiO_x film surface during O_2 plasma exposure could provide the energy needed to break and reform bonds as long as E_i lies above the thresholds for displacing atoms. An alternative view could be that the local temperature spike induced by energetic ion-surface interactions enhance surface and bulk atom diffusion processes by mimicking high temperature deposition environments generally required to form rutile TiO_x [77, 82]. Furthermore, it has been reported that when impinging ions originate from a reactive plasma (e.g. O_2 plasma), additional processes can occur simultaneously whereby reactive plasma radicals (e.g. O atoms) can diffuse to the surface and chemisorb at dangling bonds formed at the surface by the incident energetic ions [16]. The concurrent arrival of energetic ions and radical species at a surface during either material etching or deposition has been reported in the literature to lead to synergistic ion-radical processes [9, 10, 16]. Such processes typically consist of physical momentum transfer and chemical reaction components that yield unique characteristics, e.g. significantly enhanced etch rates during Si etching or the interplay between sp^2 and sp^3 bonds during $\alpha\text{-C:H}$ deposition [9, 10, 16, 86]. In this regard, synergistic ion-radical processes during O_2 plasma exposure with substrate biasing could play a role in the anatase to rutile phase transformation of TiO_x obtained in this and previous work by PEALD [17–19].

Figures 6(a)–(c) shows TiO_x material properties—refractive index, mass density and residual stress—as a function of E_i given in terms of $\langle E_i \rangle$ and $E_{i,\text{max}}$ obtained for

the corresponding $\langle V_{\text{bias}} \rangle$ applied during plasma exposure. Although $\Delta E_{\text{LP-HP}}$ is generally used in the literature as an indicator for the spread in E_i delivered to a substrate by the impinging ions, figure 6(a) illustrates how the spread can also be inferred from the difference between $E_{i,\text{max}}$ and $\langle E_i \rangle$. The horizontal bars in figure 6(a) indicate that the substrate was exposed to a range of E_i between $\langle E_i \rangle$ and $E_{i,\text{max}}$ that widens with increase in the corresponding $\langle V_{\text{bias}} \rangle$, as discussed in the previous section. It highlights the importance of measuring IFEDFs that reveal how the actual E_i delivered to a growing material can be greater than the $\langle E_i \rangle$ and also allows determination of energy maps during deposition (see below). In our previous work, it was observed that the same $\langle V_{\text{bias}} \rangle$ applied for a different duration (or duty cycle) during t_p induced differences in the variation of material properties for TiO_x grown using PEALD with RF substrate biasing [19]. On the basis of these results, it was suggested that varying the duration of $\langle V_{\text{bias}} \rangle$ during plasma exposure can lead to a change in the dose or fluence (i.e. particle flux integrated over time) of energetic ions impinging on a growing film. This was concluded to provide an additional route for tailoring material properties besides varying the magnitude of $\langle V_{\text{bias}} \rangle$ to control the E_i delivered to a growing film [19]. Figures 6(a) and (b) show that $\langle V_{\text{bias}} \rangle$ applied for the entire duration of the 10 s t_p causes the refractive index and mass density of TiO_x to demonstrate a two-stage behavior as a function of E_i : initial rise to a peak at $\langle E_i \rangle$ of 161 eV followed by a gradual fall with further increase in $\langle E_i \rangle$. When $\langle V_{\text{bias}} \rangle$ was applied for a duration of 5 s in the last half of the 10 s t_p , a similar behavior was observed for the refractive index and mass density but with peaks at a higher $\langle E_i \rangle$ of 230 eV. A parallel trend was observed for the residual stress of the films in figure 6(c). The stress changed from tensile to compressive on applying $\langle V_{\text{bias}} \rangle$ with a peak in compressive stress at $\langle E_i \rangle$ of 161 eV and 230 eV for bias durations of 10 s and 5 s, respectively, during the t_p of 10 s. The shift in peak positions suggested that when TiO_x was deposited with RF substrate biasing where E_i exceeded the atom displacement thresholds (i.e. $E_i >$ lower limit of 27 eV $E_{i,\text{max}}$ for a grounded substrate), the resulting material properties were influenced by several factors. These include the magnitude of E_i and the duration for which E_i was enhanced with RF substrate biasing during t_p . Figures 6(d)–(f) show the three aforementioned TiO_x properties as a function of $E_{i,\text{dose}}$ during plasma exposure with $\langle V_{\text{bias}} \rangle$ spanning the entire duration and last half (5 s) of the 10 s t_p . This plot also shows a similar two-stage behavior of the refractive index, mass density and compressive stress of TiO_x films with a peak occurring at an $E_{i,\text{dose}}$ of $\sim 3800 \text{ eV nm}^{-2}$. It effectively demonstrates how the material properties of TiO_x films become a function of both E_i and the bias duration during t_p when E_i is enhanced beyond the atom displacement thresholds (i.e. $E_i >$ at least 27 eV) with RF substrate biasing. The results shown in figures 6(d)–(f) validate the conclusions derived in our previous work where controlling the dose of energetic ions during PEALD with RF substrate biasing was suggested as an additional route (besides controlling ion energies) for tuning material properties [19]. A similar relation was reported recently for the etch counterpart of

Figure 6. (a) Refractive index, (b) mass density and (c) residual stress of titanium oxide films deposited at a stage temperature of 300 °C expressed as a function of the kinetic energy of ions, E_i , impinging on the substrate during O_2 plasma exposure using 200 W ICP power at a pressure of 9 mTorr. The solid square denotes film growth using an O_2 plasma exposure time, t_p , of 10 s without biasing while the rest of the symbols denote film growth with RF substrate bias spanning the entire duration (10 s, solid symbols) and last half (5 s, hollow symbols), respectively, of the t_p . Each non-square symbol denotes a particular mean ion kinetic energy, $\langle E_i \rangle$, for the corresponding negative time-averaged substrate bias voltage, $\langle V_{bias} \rangle$, during the O_2 plasma step. The horizontal bars represent the range of E_i between $\langle E_i \rangle$ and maximum ion energy, $E_{i,max}$, that a substrate is exposed to for the corresponding $\langle V_{bias} \rangle$. (d) Refractive index, (e) mass density and (f) residual stress of the same films expressed as a function of the total kinetic energy dose of ions per unit substrate area per ALD cycle, $E_{i,dose}$, during O_2 plasma exposure without and with RF substrate biasing. The symbols represent the same parameters as before (indicated in the legend). All the lines serve as a guide to the eye.

ALD employing energetic and directional ion bombardment, namely anisotropic ALE [22, 87]. Berry *et al* [22] reported that the rate of material removal during anisotropic plasma ALE becomes a function of both the ion energy and the duration of energetic ion exposure (hence, the ion energy dose) when the ion energy lies above the threshold for surface atom displacement. Note that Berry *et al* [22] employed an inert Ar plasma with substrate biasing to remove target materials, where energetic inert ions created volatile etch products through purely physical momentum transfer. In contrast, this work utilized a reactive O_2 plasma with substrate biasing to deposit TiO_x , where energetic ions and reactive radicals created stable (or non-volatile) deposition products through both physical momentum transfer and chemical reaction components (discussed above). The results of this work signify that thresholds related to material atom displacement are parameters relevant not only for plasma ALE [23, 87] but also for plasma ALD carried out under the influence of energetic ions.

Figures 6(d)–(f) can also be interpreted as an energy map of TiO_x properties in terms of the $E_{i,dose}$ during PEALD when E_i is enhanced beyond atom displacement thresholds (of at least 27 eV) with RF substrate biasing. An $E_{i,dose}$ of ~ 3800 eV nm $^{-2}$ obtained with RF substrate biasing serves as a transition point between regimes that yield different trends in material properties as a function of $E_{i,dose}$. The first $E_{i,dose}$ regime consisted of an increase in refractive index and mass density together with a change in crystalline composition from a predominantly anatase to a mixed anatase and

rutile phase, which could be due to the formation of the denser rutile phase with substrate biasing as discussed above. This regime also showed a change in the residual stress from tensile to compressive. This was attributed to the formation of oxygen rich TiO_x films (O/Ti ratio > 2) with substrate biasing in our previous work [19], where the excess oxygen could be present as interstitial species that induce compressive stress [81, 88, 89]. The second $E_{i,dose}$ regime yielded a decrease in refractive index and mass density together with compressive stress relaxation. This was attributed to the incorporation of voids in the film microstructure and amorphization in our previous work [19], together with the onset of plastic deformation that could take place under highly energetic ion bombardment [15, 81, 90]. The results shown in figures 6(d)–(f) (and in figures 7(a)–(c) and 8(a)–(c) in the next sections) illustrate how an energy map of material properties in terms of the $E_{i,dose}$ during PEALD can serve as a basis for growing nanoscale films with the desired material properties.

4.3.2. Hafnium nitride (HfN_x) grown with H_2 plasma. Figure 7 shows an energy map of HfN_x material properties [20, 40], that includes the resistivity, Hf^{3+} fraction and oxygen content, in terms of the $E_{i,dose}$ during PEALD at 450 °C without and with $\langle V_{bias} \rangle$ during H_2 plasma exposure. For the two films deposited without biasing ($\langle V_{bias} \rangle = 0$ V), an $\langle E_i \rangle$ of 20 eV was measured together with a corresponding $E_{i,max}$ of 28 eV and $E_{i,flux}$ of 10 eV nm $^{-2}$ s $^{-1}$. For a fixed E_i at the grounded substrate configuration, increasing $E_{i,dose}$ from ~ 600 to

Figure 7. (a) Resistivity, (b) Hf^{3+} fraction, and (c) oxygen content of hafnium nitride films deposited at a stage temperature of 450 °C expressed as a function of the total kinetic energy dose of ions per unit substrate area per ALD cycle, $E_{i,dose}$, during H_2 plasma exposure using 100 W ICP power at a pressure of 30 mTorr. The solid and crossed squares denote film growth using a plasma exposure time, t_p , of 10 s and 30 s, respectively, without any biasing while the rest of the symbols denote time-averaged substrate bias voltages, $\langle V_{bias} \rangle$, applied for the entire t_p of 10 s. Each non-square symbol denotes a particular $\langle V_{bias} \rangle$.

~ 1800 eV nm $^{-2}$ by a three-fold increase in t_p from 10 s to 30 s, respectively, led to a very small decrease in resistivity that essentially remained in the same order of magnitude. It was accompanied by a decrease in the Hf^{3+} fraction (by 0.06 ± 0.02) and an elevation in the film oxygen content (by about 5.0 ± 0.7 at%). Grazing incidence XRD patterns for these films revealed peaks corresponding to cubic hafnium oxynitride, or Hf_2ON_2 (see figure S9 in supplementary information) confirming the presence of the high oxygen impurity content measured in these two films. This was attributed to the incorporation of oxygen in the film mainly during deposition due to background water present in the $\sim 10^{-6}$ Torr vacuum environment of the PEALD system, as addressed in previous work conducted by Karwal *et al* [40]. However, when t_p was kept constant at 10 s and $E_{i,dose}$ was increased to ~ 7400 eV nm $^{-2}$ by increasing E_i with RF substrate biasing (-95 V $\langle V_{bias} \rangle$ applied for a bias duration of 10 s, during a 10 s H_2 t_p) such that $\langle E_i \rangle$ reached 109 eV, a drastic reduction of the film resistivity by about two orders of magnitude was observed (figure 7(a)). This was accompanied by a significant increase in Hf^{3+} fraction (by about 0.20 ± 0.02 , figure 7(b)) and decrease in the film oxygen content (by about 8.0 ± 0.7 at%, figure 7(c)). Note that the change in the Hf^{3+} fraction and film oxygen content on increasing $E_{i,dose}$ through an increase in E_i with RF substrate

Figure 8. (a) Refractive index (b) mass density and (c) wet-etch rate of silicon nitride films deposited at a stage temperature of 500 °C expressed as a function of the total kinetic energy dose of ions per unit substrate area per ALD cycle, $E_{i,dose}$, during N_2 plasma exposure using 600 W ICP power at a pressure of 12 mTorr. The solid and crossed squares denote film growth using a plasma exposure time, $E_{i,dose}$, of 20 s and 80 s, respectively, without any biasing while the rest of the symbols denote time-averaged substrate bias voltages, $\langle V_{bias} \rangle$, applied for the last half (10 s) of the 20 s t_p . Each non-square symbol denotes a particular $\langle V_{bias} \rangle$.

biasing (at a constant t_p) was the exact opposite of the trends observed upon increasing $E_{i,dose}$ through an increase in t_p (at constant E_i for a grounded substrate). Increasing $E_{i,dose}$ by enhancing E_i with RF substrate biasing led to a two-stage behavior in resistivity and Hf^{3+} fraction, concurrent with the trends reported in previous work as a function of $\langle V_{bias} \rangle$ [20]. The resistivity decreased to a minimum and Hf^{3+} fraction reached a peak at an $E_{i,dose}$ of $\sim 12 \times 10^3$ eV nm $^{-2}$. The film oxygen content, however, showed a monotonic decrease to levels below the instrument detection limit (< 2 at%) as $E_{i,dose}$ was enhanced by means of RF substrate biasing. XRD patterns of the films deposited with biasing revealed peaks corresponding to face-centered-cubic hafnium mononitride (see figure S9 in supplementary information) [20]. As outlined in previous work reported by Karwal *et al* [20], the significant drop in resistivity and corresponding jump in Hf^{3+} fraction with RF substrate biasing could arise from the drastic reduction in film oxygen content. It could also contribute toward the formation of the more conductive face-centered-cubic hafnium mononitride films. Increasing $E_{i,dose}$ beyond $\sim 12 \times 10^3$ eV nm $^{-2}$ by enhancing E_i with RF substrate biasing led to a comparatively small increase in resistivity and a similar decline of the Hf^{3+} fraction. This was speculated to arise from an increase in film hydrogen content and associated

Hf–H bonds for $\langle V_{\text{bias}} \rangle$ beyond -130 V, as explained in previous work reported by Karwal *et al* [20].

Similar to the case of TiO_x , these results demonstrate how the material properties of HfN_x deposited using an H_2 plasma respond differently to the $E_{i,\text{dose}}$ depending on whether it is controlled by enhancing E_i with RF substrate biasing, or by increasing t_p without any biasing during plasma exposure. They again indicated the presence of an E_i threshold at or above a lower limit of 28 eV given by $E_{i,\text{max}}$ measured for a grounded substrate in H_2 plasma, which the ions impinging on a growing HfN_x film surface must exceed to form highly conductive and oxygen impurity free hafnium mononitride. The results also allow identification of regimes characterized by different trends in material properties (resistivity and Hf^{3+} fraction) as a function of increasing $E_{i,\text{dose}}$ obtained by enhancing E_i beyond (at least) 28 eV with RF substrate biasing. The transition point between regimes could be considered to lie in the vicinity of the aforementioned $E_{i,\text{dose}}$ value of 12×10^3 eV nm $^{-2}$ (figure 7). For the case of TiO_x , the thresholds were speculated to be related to synergistic oxygen based ion-radical processes involving both physical momentum transfer and chemical reaction components. The thresholds involving synergistic hydrogen based ion-radical processes are bound to be related primarily to the chemical reaction component and associated activation energy barrier involving removal of oxygen species from a hafnium oxynitride surface. This arises from the significantly lower mass of hydrogen plasma species that leads to a large mass difference between the incident hydrogen ions and target hafnium oxynitride atoms. As discussed previously, this renders physical momentum transfer processes through elastic nuclear interactions [15, 78, 80] highly unlikely. Based on recent experimental investigations reported in the literature [91–93], the kinetic energy of the lighter hydrogen ions impinging on the significantly heavier hafnium oxynitride atoms is quite likely transferred through inelastic electronic interactions [15, 77, 80]. Energy transfer through such interactions do not contribute to physical displacement of hafnium oxynitride atoms but could play a role in facilitating chemical reactions between the oxygen species at the film surface and the concurrently arriving hydrogen plasma radicals. Chemical reactions activated by such ion-induced processes could remove oxygen species from the hafnium oxynitride surface, which eventually leads to the formation of hafnium mononitride. The exact nature and mechanisms of these processes that induce changes in material composition and associated properties are currently being investigated on the basis of theoretical modeling and will be reported in a subsequent publication [94].

4.3.3. Silicon nitride (SiN_x) grown with N_2 plasma. Figure 8 shows an energy map of SiN_x material properties [42], that includes the refractive index, mass density and WER, in terms of the $E_{i,\text{dose}}$ during PEALD at 500°C without and with $\langle V_{\text{bias}} \rangle$ during N_2 plasma exposure. An $\langle E_i \rangle$ of 19 eV was measured for the two films deposited without any biasing ($\langle V_{\text{bias}} \rangle = 0$ V) together with a corresponding $E_{i,\text{max}}$ of 29 eV

and $E_{i,\text{flux}}$ of 35 eV nm $^{-2}$ s $^{-1}$. For a fixed E_i at the grounded substrate configuration, increasing $E_{i,\text{dose}}$ from ~ 700 to ~ 2800 eV nm $^{-2}$ by a four-fold increase in t_p from 20 s to 80 s did not cause any significant change in refractive index and WER while the mass density increased slightly by 0.1 g cm $^{-3}$. The high refractive index and mass density of these two films confer excellent wet-etch resistance in dilute hydrofluoric acid. This accounts for the insignificant WER values of 0 ± 1 nm min $^{-1}$ measured at planar surface regions of films deposited on 3D trench nanostructures (see figure S10 in supplementary information). However, when t_p was kept constant at 20 s and $E_{i,\text{dose}}$ was increased to ~ 2600 eV nm $^{-2}$ by increasing E_i with RF substrate biasing (-94 V $\langle V_{\text{bias}} \rangle$) applied for the last 10 s of a 20 s N_2 t_p) such that $\langle E_i \rangle$ reached 113 eV, a monotonic decrease was observed in refractive index and mass density. This was accompanied by a drastic increase in WER to about 36 ± 1 nm min $^{-1}$. These results again indicated the presence of an E_i threshold at around 29 eV given by $E_{i,\text{max}}$ measured for a grounded substrate in N_2 plasma. The data suggests that ions impinging on a growing SiN_x film during N_2 plasma exposure should not exceed this threshold if the aim is to form a dense and wet-etch resistant material. The monotonic trends in material properties of SiN_x on increasing $E_{i,\text{dose}}$ by increasing E_i with RF substrate biasing were unlike the two-stage trends observed previously for TiO_x and HfN_x . In those cases, material properties improved on increasing $E_{i,\text{dose}}$ up to a certain level with RF substrate biasing before being degraded, whereas SiN_x degraded instantly on increasing $E_{i,\text{dose}}$ with biasing. Changes in other properties of SiN_x due to energetic ion bombardment during N_2 plasma exposure reported in our previous work include formation of nitrogen rich films (N/Si ratio > 1.33) together with a significant increase in the film oxygen and carbon impurity content [19]. The excess nitrogen could be speculated to get incorporated as N–N bonds [95] in the material and/or N_2 gas bubbles [15, 96], as reported in the literature for films subjected to energetic ion bombardment. The film impurity content could be incorporated from species of dissociated ligand fragments and background impurities formed during plasma exposure. This was reported as the redeposition effect by Knoops *et al* [97] for PEALD of SiN_x using a Si precursor with two amino ligands (BTBAS). Although using DSBAS was shown to lower the redeposition effect in our previous work owing to it having one less amino ligand [42], ionized species of dissociated ligand fragments formed in the plasma step can impinge on a growing film surface with a higher E_i when implementing RF substrate biasing. These factors could contribute towards degrading SiN_x by decreasing its refractive index, density and wet-etch resistance. An analogous decrease in etch resistance was recently reported for SiN_x films having a low density and high impurity content formed upon treatment with energetic helium and/or hydrogen ions [95, 98, 99]. Similar to the case of TiO_x and HfN_x , these results demonstrate how the properties of SiN_x films deposited using N_2 plasma behave differently as a function of the $E_{i,\text{dose}}$ depending on whether it is controlled by enhancing E_i with RF substrate biasing, or by increasing t_p without any biasing during plasma exposure.

They suggest that N_2 plasma exposure on a grounded substrate yields optimum SiN_x material properties as long as $E_{i,dose}$ is not enhanced with substrate biasing (i.e. $E_i < 29$ eV $E_{i,max}$ for a grounded substrate), which would otherwise induce degradation of those properties.

5. Conclusions

Ion flux-energy distributions functions (IFEDFs) of reactive O_2 , H_2 and N_2 plasmas were measured using a gridded RFEA in a commercial 200 mm remote plasma ALD system without and with RF substrate biasing. These measurements were used to derive ion energy and flux characteristics to investigate their role in tuning the properties of films deposited by plasma ALD using the aforementioned plasmas. The properties of three materials having a dielectric or conductive nature—namely TiO_x , HfN_x and SiN_x —were analyzed as a function of the ion energy and flux parameters derived from IFEDFs measured for the reactive plasmas on grounded and RF biased substrates. Material properties were investigated in terms of the total ion kinetic energy dose imparted to a growing film in every plasma ALD cycle ($E_{i,dose}$), which was determined from the product of the mean ion kinetic energy, the total ion flux and the plasma exposure time. The properties were found to behave differently as a function of the $E_{i,dose}$ depending on whether it was controlled by enhancing the ion kinetic energy (E_i) with RF substrate biasing, or by increasing the plasma exposure time (t_p) without any biasing. This showed that material properties during plasma ALD were influenced by whether E_i lied within or beyond certain energy thresholds. These are related to energy barriers involving physical displacement of material atoms or activation of an ion-induced chemical reaction component. A lower limit for these energy thresholds was obtained (at ~ 30 eV) from the maximum E_i measured in the IFEDFs for grounded substrates. When a grounded substrate was used in the plasma exposure step, E_i delivered to a growing film by the impinging ions was observed to lie below the aforementioned E_i thresholds. For this substrate configuration, increasing $E_{i,dose}$ by increasing t_p at a constant E_i resulted in (a) TiO_x films remaining in the anatase phase with a comparatively low density and refractive index, (b) HfN_x films with higher oxygen impurity content and lower Hf^{3+} fraction while their resistivity remained comparatively unchanged, (c) SiN_x films retaining high refractive indices and mass densities with negligible WERs.

For RF biased substrates during plasma exposure, E_i can exceed thresholds for physical relocation of material atoms or for activation of ion-induced chemical reactions. Increasing $E_{i,dose}$ by increasing E_i with RF biasing at constant t_p yielded a two-stage behavior in TiO_x and HfN_x material properties while those of SiN_x showed a monotonic trend. The TiO_x films gradually transformed from anatase to rutile while their refractive index and mass density initially increased followed by a gradual decline. For HfN_x , the films went from cubic hafnium oxynitride to face-centered-cubic hafnium mononitride while their conductivity and Hf^{3+} fraction initially increased significantly followed by a slight decline. SiN_x

films monotonically degraded to a lower mass density and refractive index while undergoing a significant increase in WERs. Additionally, material properties of TiO_x grown with RF substrate biasing, where E_i was enhanced beyond the aforementioned thresholds, were found to become a function of both the enhanced E_i and the duration for which E_i was enhanced during t_p . These findings validated the conclusions made in our previous work where controlling the dose of energetic ions impinging on a growing film by varying the bias duration was suggested as an alternative route for tuning material properties. In addition, the results of this work shed light on the relation between the characteristics of energetic ions and the ensuing material properties, e.g. by providing energy maps of material properties in terms of the $E_{i,dose}$ during plasma ALD. They demonstrate how the quantification and control of ion energy and flux characteristics during plasma ALD serve as a means for obtaining nanoscale films with the required material properties. Finally, the results of this work signify how energy thresholds related to material atom displacement or activation of ion-induced chemical reactions are parameters relevant not only for plasma ALE [23, 87], but also for plasma ALD performed under the influence of energetic ions. Further investigation for better determination of such thresholds at $E_i < 100$ eV can be carried out by implementing tailored bias voltage waveforms, which are known to provide mono-energetic ions (having narrow, mono-modal IFEDFs) during plasma exposure with substrate biasing [100].

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