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Importance of precursor delivery mechanism for Tetra-kis-ethylmethylaminohafnium/water atomic layer deposition process

Shweta Tomer[a,b], Vandana[a,b,*], Jagannath Panigrahi[a,b], Ritu Srivastava[a,c], C.M.S. Rauthan[a,b]

[a] Academy of Scientific and Innovative Research (AcSIR), Ghaziabad 201002, India
[b] Photovoltaic Metrology Section, Advanced Materials and Device Metrology Division, CSIR- National Physical Laboratory, New Delhi 110012, India
[c] Photonic Materials Metrology Section, Advanced Materials and Device Metrology Division, CSIR- National Physical Laboratory, New Delhi 110012, India

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ABSTRACT

The present work investigates the importance of incorporating a boosting mechanism in an Atomic Layer Deposition (ALD) process for the delivery of a low vapour pressure precursor in the reaction chamber. Here we show that in the absence of the boosting mechanism, saturated growth was compromised and poor-quality films were obtained characterized by film non-uniformity and variable refractive index within the sample. We demonstrate that a boosting sequence of 0.5 s + 0.9 s with precursor bottle heating temperature of 120 °C was sufficient to produce good quality films showing saturated growth in our system. Furthermore, we demonstrate that for Tetra-kis-ethylmethylaminohafnium/water ALD process, the ALD window for hafnium oxide was found to be in the temperature range 300 °C–375 °C where the average growth per cycle and refractive index of the films deposited within the ALD window were found to be 1.16 Å/cycle and 2.00 respectively.

1. Introduction

The down-scaling of silicon-based devices gave a perspective to use materials other than the traditional silicon oxide, silicon nitrides as dielectric layers. Ever since; the implementation of metal-oxide based dielectric layers in silicon devices was considered and many new high-k materials like zirconium oxide, titanium oxide, tantalum oxide, hafnium oxide, aluminium oxide, aluminium doped zinc oxide, etc have been investigated [1–3]. Among these, hafnium oxide attracted researcher's interest due to its large energy bandgap E_g = 5.6–5.8 eV [1,4,5], high dielectric permittivity k = 16–25 [5,6], high refractive index n = 2-2.1 and high thermal stability (melting point ~2780 °C). It is a key dielectric used in many advanced silicon devices [7]. Its high thermodynamic stability in contact with silicon and high energy barriers for electrons and holes with respect to silicon (2.0 eV and 2.5 eV, respectively) [1,7,8] makes it a potential candidate for applications like high-k gate dielectric in MOSFETs, surface passivation of crystalline silicon solar cells among others [7,9–12]. The scaling of silicon devices to nanostructures has led to drastic increment in surface to volume ratio of the device. The high aspect ratio and critical structures increases the difficulty of depositing high quality conformal films on such structures. Atomic Layer Deposition (ALD) technique is a potential solution to this problem. It is a self-limiting, surface-controlled reaction process which has the capability to coat high aspect ratio structures with conformal material layers of high quality [3,13]. Its layer-by-layer growth enables to have precise control over the film thickness. Unlike other chemical vapour deposition techniques, the precursors are allowed in the reaction chamber in a sequential manner one at a time. This enables to have precise control over film composition. Consequently, ALD-grown materials find their applications over a wide range such as catalysts, electroluminescent displays, microelectronics, photovoltaics, etc. [3,14–16].

Film growth in an ALD process should be a saturated growth facilitated by suitable growth parameters dependent on precursor type and system design. There exist a range of deposition temperatures for a variety of precursors for which self-limiting, surface saturated reactions take place, such range of deposition temperatures constitute the 'ALD Temperature Window' or 'ALD Window' [3]. The self-limitation and saturation of a reaction depends on numerous factors, but are majorly affected by the (a) incoming precursor flux, (b) purging duration, (c) reaction kinetics of precursors with each other as well as with the substrate and (d) deposition temperature [3,17] (Fig. 1). A number of reports are available for ALD window of hafnium oxide film (HfO_x/Si system), Table 1 comprise of those studies particularly related to tetra-kis-ethylmethylaminohafnium (TEMAHf)/water process. It is clear from Table 1, the ALD window reported in different studies varied over a wide temperature range for same TEMAHf/water process. Also, the precursor heating temperature varies from 60 °C to 105 °C, most

* Corresponding author.
E-mail address: vandana1@nplindia.org (Vandana).

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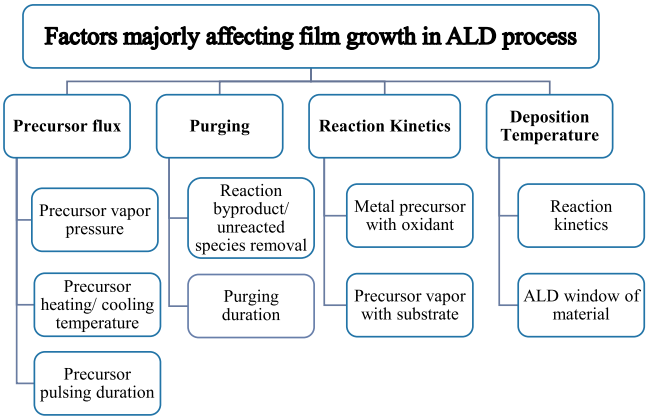

Fig. 1. A flowchart listing the four major factors affecting the film growth in an ALD process.

probably due to different precursor delivery systems used by different researchers. The dissimilarity among the precursor parameters and its direct influence on other ALD process parameters is evident from Table 1, film growth rate varies from 0.75 Å/cycle–1.4 Å/cycle. Another important aspect of ALD process is one ALD cycle duration which varies from 1.9 s to 26 s. Particularly for low vapour pressure precursors, such as TEMAHf, the precursor vapour does not possess sufficient kinetic energy at room temperature for them to reach the reaction chamber for controlled film growth and thus are usually heated at temperature higher than their vapourization temperature to boost the saturation reaction process. However, every precursor has a thermal breakdown temperature and if heated above this temperature, films of unwanted composition are obtained. This limits the scope of increase in precursor heating temperature and thus increase in precursor vapour energy. Thus, for effective delivery of low vapour pressure precursors, the presence of suitable precursor delivery system with optimised precursor process parameters is crucial. In the present study, the focus is to understand the importance of integrating boosting mechanism into the metal precursor delivery system. In the past studies, Hausmann et al. used a precursor delivery system, where two valves, empty valve and fill valve were used, separating different pressure regions lying between the precursor container and the reaction chamber; but did not explore the relation between the incoming precursor flux, the valve opening duration and eventually its effect on the ALD window [19]. The Hausmann's approach was followed by two different groups, viz. Hackley et al. [22] and Oh et al. [23]; but both the groups explored the potential chlorine-free precursors using special mechanism (termed as fixed volume approach) for effective delivery of low vapour pressure precursor. Here in this study, the immediate effect of boosting on the deposited film properties is studied along with deposition parameters optimisation for saturated film growth. Also, the ALD window of HfO_x/Si system is determined using optimised TEMAHf/water recipe.

2. Experimental

2.1. Sample preparation

In the present study phosphorus doped, Czochralski grown, (100) oriented single crystalline silicon substrates of thickness 325 μm were used. Each sample was quarter diced from a 100 mm diameter wafer. HfO_x thin films (100 ALD cycles) were deposited on silicon substrate using thermal Atomic Layer Deposition Technique (Model: R200, M/s Picosun, Finland). Before HfO_x deposition, the samples were cleaned in Piranha solution [4-parts H_2SO_4 (98% conc.) + 1-part H_2O_2 (30% conc.)] for 15 min to remove the present organic residues and metal contaminants, if any. The samples were then given a 2 min dip in 5% HF (48% conc.) in order to remove the native oxide formed during the

Table 1
Literature available for ALD deposited hafnium oxide film (HfO_x/Si system) with TEMAHf/water as precursors. The pulsing duration is TEMAHf pulse + purge + water pulse + purge.

Refs.	Metal precursor (TEMAHf) delivery system	ALD window	Growth per cycle (Å/cycle)	Pulsing duration (s)
Kukli et al. [18]	Evaporated from an open boat heated at 60 °C	200 °C –250 °C*	0.90*	0.4s + 0.5s + 0.5s + 0.5s
Haussmann et al. [19]	Empty valve, fill valve and precursor reservoir enclosed in an oven heated to 75 °C[b]	-	0.93	(1s + 1s) + 5s + 0.5s + 5s
Deshpande et al. [20]	Quartz open boat type reservoir heated to 80 °C kept in a thermostat SS vessel[b]	300 °C –350 °C	1.40	4s + 8s + 0.8s + 12s
Gieraltowska et al. [21]	-	130 °C –140 °C	1.40	-
Liu et al. [13]	Container heated to 75 °C - 95 °C	200 °C - 370 °C	0.75	0.8s - TEMAHf 0.1s - water/ozone
Hackley et al. [22]	Fixed volume approach described by Hausmann. Container heated to 105 °C.	200 °C–275 °C	1.20	-
N K Oh et al. [23]	Container heated to 60 °C	200 °C –300 °C	0.90	(0.5s + 4.5s) + 10s + 1.2s + 10s

*Hafnium oxide on borosilicate glass.
[b] TDMAHf used.

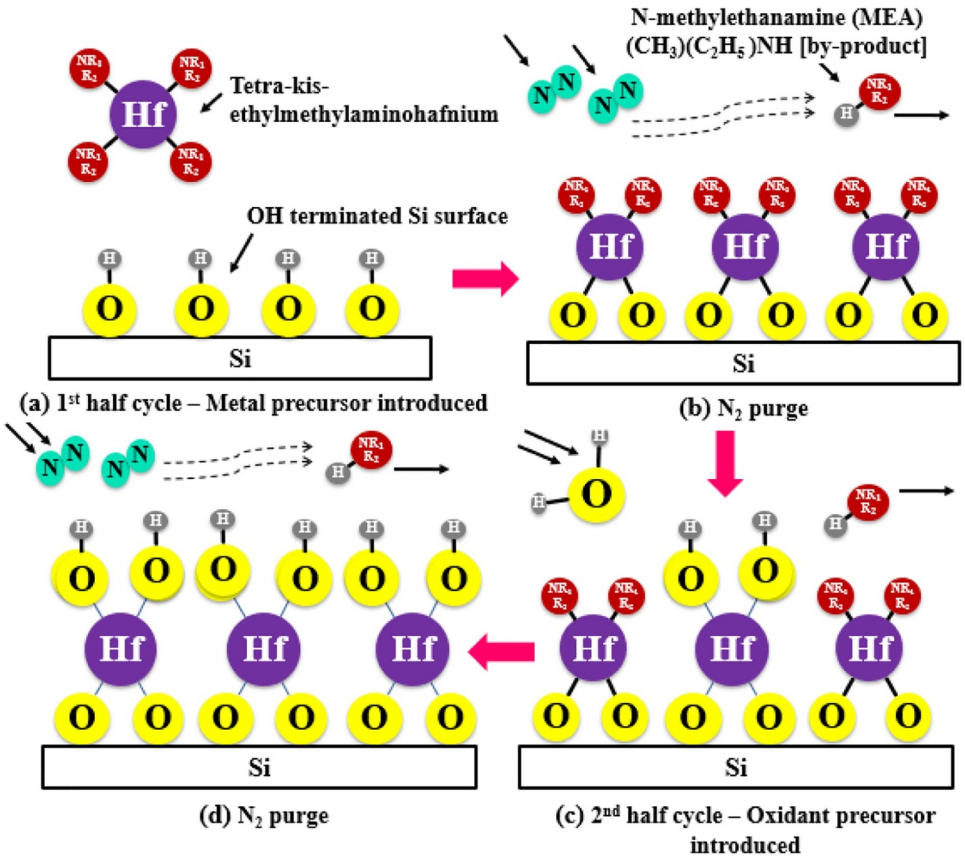

Fig. 2. One ALD cycle for HfO_x deposition using TEMAHf and H_2O as metal precursor and oxidant respectively. Where NR_1R_2 is the methlyethylamine ligand attached to Hf and MEA (N-methylethanamine) is the reaction byproduct.

cleaning process. The samples were then carefully transferred to the ALD chamber which was pre-heated to the substrate temperature.

2.2. ALD of hafnium oxide using TEMAHf and water

Atomic Layer Deposition technique is based on the series of sequential pulsing of metal precursor and the oxidant vapours where each precursor pulse is separated by an inert gas purging step to remove any unwanted or un-reacted species from the previous precursor pulse. For ALD of HfO_x, TEMAHf (Sigma Aldrich, product number- 553123, vapour pressure: 0.01 hPa at 78 °C) was used as the metal precursor and Deionised water (DI H_2O, vapour pressure: 31.73 hPa at room temperature) as the oxidant. One complete ALD cycle consist of one TEMAHf pulse, a nitrogen purge, followed by one DI H_2O pulse, and again a nitrogen purge (Fig. 2). TEMAHf is a low vapour pressure precursor thus, in the present study, a boosting mechanism is used to ensure that sufficient TEMAHf precursor vapours are available in the reaction chamber during film growth. This mechanism involves the high-pressure state built up in precursor bottle prior to execution of metal pulse and at the end of each metal pulse this state is rebuilt to make it ready for next ALD cycle. The type of active surface sites available on the substrate majorly govern the reaction kinetics of the precursor with the substrate surface. An –OH terminated surface was chosen as it proves to be ideal for the growth of HfO_x film when using TEMAHf and water as precursors, also such surface has shown good surface passivation properties [24]. Table 2 gives the details of the parameters varied in this study.

2.3. Ellipsometry analysis: film thickness and refractive index determination

The thickness and refractive index of the film are extracted using Variable angle spectroscopic ellipsometry (VASE, model: M2000, M/s J.A. Woollam Co. Inc., USA). The measurement is carried over a spectral range of 245 nm–1000 nm. For this, a quartz tungsten halogen and a deuterium lamp were used. A beam of diameter 3 mm is made incident on the sample at four different angles viz. 50°, 60°, 70° and 80°. The choice of incidence angle varies according to the optical constant of the sample and is chosen in the vicinity of Brewster's angle of the substrate. The values reported represent the mean of the measurements taken at three different points, in order to account for in-homogeneity of the film. VASE finds its applications over wide range of materials [25]. The key feature is that it measures the change in polarisation of

Table 2
Parameters varied for optimizing TEMAHf/ water process. Only one parameter was varied at a time, other parameters were kept constant; constant values are given in bold.

TEMAHf heating temperature (P_1)	Master-fill (P_2)	Pre-empty (P_3)
120 °C	0 s	0.1 s
	0.4 s	
	0.6 s	
	0.9 s	
	1.2 **s**	0.3 s
85 °C	1.6 s	**0.5 s**

Table 3
Details of the fitted parameters of the optical model: Cauchy layer/Si, for HfO_x film deposited at substrate temperature 300 °C, 100 ALD cycles. Where A_n, B_n and C_n are Cauchy parameters and MSE is the mean squared error.

	Thickness, d (nm)	A_n	B_n	*C_n	MSE
Cauchy parameters	11.691 ± 0.005	1.974 ± 0.007	0.008 ± 0.002	0	2.757

*fixed parameter

light when reflected from a surface. This change in polarisation is written as:

$$\rho = \frac{r_p}{r_s} = \tan(\Psi)e^{i\Delta} \quad (1)$$

where r_s and r_p are the Fresnel's reflection coefficients of sample for s (perpendicular to plane of incidence) and p(in the plane of incidence) polarised light; Ψ and Δ are measurement parameters accounting for change in amplitude and phase of the incident light wave respectively [25,26]. As VASE is an indirect method of extracting the optical constants and thickness of the thin film, based on fitting of experimental data with the modelled data, usually the quality of fit is given by a maximum likelihood estimator which is a positive quantity and tends to zero when the experimental data approaches or exactly matches the modeled data. In the present study, Mean Squared Error (MSE) shall be used as the maximum likelihood estimator given as:

$$MSE = \sqrt{\frac{1}{2N-M}\sum_{i=1}^{N}\left[\left(\frac{\psi_i^{\mathrm{mod}} - \psi_i^{\mathrm{exp}}}{\sigma_{\psi,i}^{\mathrm{exp}}}\right)^2 + \left(\frac{\Delta_i^{\mathrm{mod}} - \Delta_i^{\mathrm{exp}}}{\sigma_{\Delta,i}^{\mathrm{exp}}}\right)^2\right]} \quad (2)$$

where N is the number of (Ψ, Δ) pairs, M is the number of variable parameters in the model and σ is the standard deviation on the experimental data points [25,26]. In the present study, the system measurement range is from 245–1000 nm (i.e. 1.24–5.06 eV) which doesn't cover the bandgap region of hafnium oxide (E_g = 5.6–5.8 eV) and hence the films must be transparent for the entire range. The optical modelling of transparent films can be done using a simple Cauchy layer. Thus, in the present study, films are modelled using Cauchy layer/Si. Table 3 gives the values of the fitted parameters for film deposited at substrate temperature of 300 °C. Fig. 3 shows good fit between modelled and the experimental data.

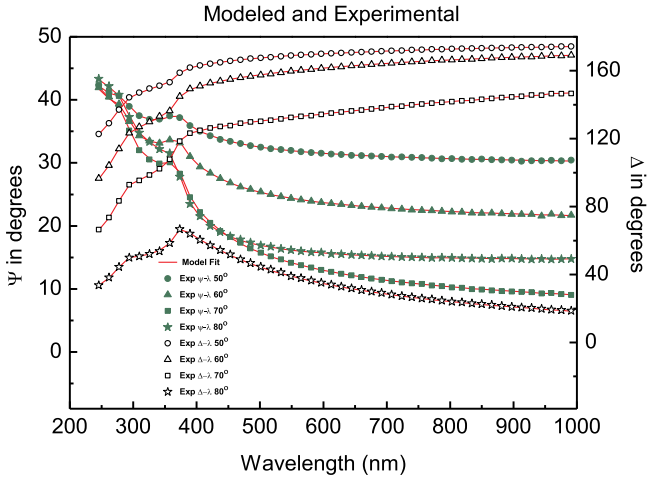

Fig. 3. Experimental (symbols) and fitted (solid line) Ψ (psi), Δ (delta) vs. wavelength curve measured at four different angles of incidence (50°, 60°, 70° and 80°) for HfO_x /Si structure. The experimental data is fitted using Cauchy layer/Si optical model (only every tenth measurement point is plotted for better visibility).

3. Results and discussion

3.1. Boosting sequence

A number of precursors are available for ALD film growth, which have varied range of vapour pressure and therefore a suitable mechanism for their effective delivery to the reaction chamber is important to have saturated ALD thin film growth. TEMAHf is a low vapour pressure precursor and needs to be heated to realize sufficient vapour pressure. However, this temperature should not exceed its thermal breakdown temperature of 140 °C [27]. In the present study, boosting mechanism is adopted for effective delivery of the TEMAHf precursor vapours into the reaction chamber. Fig. 4 is the schematic representation of the pulsing and the boosting sequences. A boosting sequence has two stages (a) Pre-Empty stage: most of the precursor is delivered into the reaction chamber during this stage with gas flow of 50 sccm. Film growth takes place majorly during this stage, (b) Master-fill stage: high pressure carrier gas (600 sccm) fills into the precursor bottle and the chamber. The metal pulse length regulates the duration for which the corresponding pneumatic ALD valve is opened. The boosting sequence time is kept 0.1 s longer (pre-empty: 0.5 s, master-fill: 0.9 s) than the TEMAHf pulse time (1.3 s). As the pulsing begins, ALD valve opens and pre-empty stage is executed for the specified time (0.5 s). For the remaining pulse time (0.8 s if pulse cycle is 1.3 s long) master-fill stage is executed. Although during the master-fill stage itself the precursor bottle is filled with high pressure gas preparing it for the next pre-empty stage, the last 0.1 s is just to ensure that while ALD valve closes, the precursor bottle is filled with high-pressure carrier gas enabling next pre-empty stage effective execution. Thus, TEMAHf pulse length depends on two factors: pre-empty and master-fill durations, while one ensures all active surface sites are saturated the other ensures the precursor vapour pressure in the precursor bottle is suitable for the next cycle. Before optimizing the TEMAHf pulse length and obtaining the ALD window, these two parameters along with the precursor heating temperature were optimized.

3.2. Precursor heating temperature (P_1 varied; P_2 and P_3 kept constant; Table 2)

The incoming precursor flux is most influential parameter when discussing thin film growth. To obtain saturated film growth, it is imperative that the incoming precursor flux is sufficient to react and

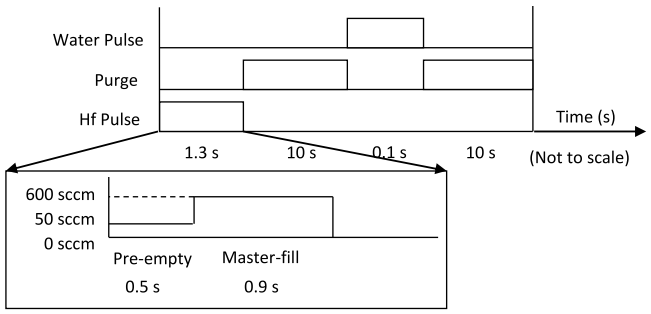

Fig. 4. Schematic representation of pulsing sequence for one ALD cycle. The boosting sequence is shown in an expanded box. The mentioned pulse lengths are the final optimized durations.

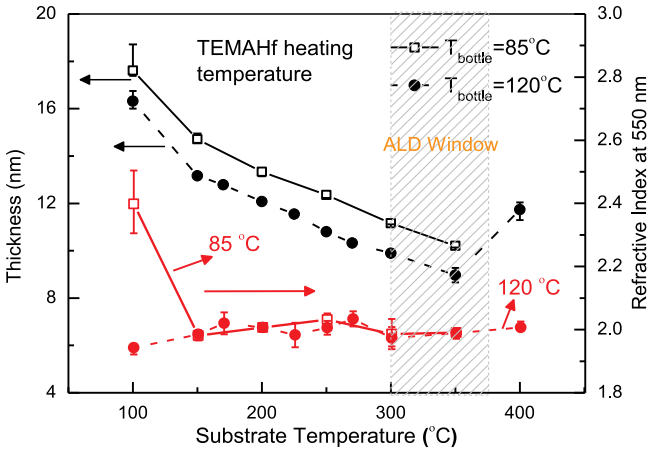

Fig. 5. Film thickness (black) and refractive index (red) versus substrate temperature curve obtained at two different TEMAHf heating temperature of 120 °C (circles) and 85 °C (squares). The vertical bars represent the dispersion in the values at different points on the sample. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

saturate all the present active surface sites on the substrate. If the precursor flux is less, then saturation of the active surface sites is compromised resulting into non-uniform, unsaturated film growth and if the precursor flux is more, then the excess vapour harms the particle trap present and diminishes its lifetime. The flux can significantly be controlled by the temperature to which the low vapour pressure precursor is heated. The precursor heating temperature varies from 60 °C to 105 °C for different studies listed in Table 1 and it can be deduced that with increasing bottle heating temperature, for some studies, the ALD window was observed to be broader and shifted towards higher temperature region; for e.g. Kukli et al. obtained their ALD window from 200 °C to 250 °C, keeping bottle temperature at 60 °C [18]. While, Liu et al observed a broader ALD window for their process varying from 200 °C to 370 °C, keeping precursor heating temperature in the range of 75 °C–95 °C [13]. On the contrary, Hackley et al kept the precursor heating temperature at 105 °C and obtained a narrow parabolic shaped window with a minimum at 250 °C [22]. This implies that the precursor heating temperature along with precursor delivery system has direct influence on the nature of the ALD curve. To assess its dependence an experiment was performed. The film thickness and refractive index of the films deposited at different substrate temperature were plotted for two different TEMAHf heating temperatures and the obtained ALD windows were compared (Fig. 5). The ALD window constitute those particular range of substrate temperatures for which the film thickness/growth rate is constant. In the past, our group had demonstrated good surface passivation properties of the ALD deposited hafnium oxide thin films, where TEMAHf was heated to a temperature of 120 °C [10]. Hence the two temperatures chosen were 120 °C and 85 °C. It is conclusive from Fig. 5 that the ALD window for both the TEMAHf heating temperature occur in the same region, 300 °C–375 °C. The growth per cycle within the ALD window for both TEMAHf heating temperatures (~1 Å/cycle and 1.1 Å/cycle) matches well with the previously reported growth rate (see Table 1). Observing the deposited film thickness curve (Fig. 5), entire curve corresponding to the films deposited at lower TEMAHf heating temperature have shifted upwards by a constant factor. This constant factor is an indication of the change in the incoming precursor flux. This is due to as the precursor temperature regulates the number of precursor vapours generated, reducing the precursor temperature reduces the thermal energy of the precursor thus reducing the precursor vapour flux. Less precursor vapour flux causes less precursor vapours per active surface site and hence saturation of the substrate surface is compromised leading to non-uniform, unsaturated film growth. Therefore, it may be concluded that at low TEMAHf heating temperature saturated ALD growth is compromised. Thus, TEMAHf heating temperature of 120 °C is considered suitable for saturated growth to take place and the same value was used for further studies.

3.3. Boosting parameters and metal precursor pulse optimization (P_1 kept constant; P_2 , P_3 varied; Table 2)

Fig. 6 shows the film thickness and refractive index variation with respect to master-fill and TEMAHf pulse lengths. In Fig. 6(a), the pre-empty pulse length was kept constant at 0.5 s [10]. The master-fill pulse length of 0 s represents the case where only the pre-empty stage of 0.5 s is executed, i.e. the precursor is delivered to the reaction chamber without using the boosting mechanism. The poor film thickness and huge variations in the refractive index at different points of the sample for such deposition conditions shows the unsaturated growth of the film. Further, on increasing the master-fill pulse length to 0.4 s and beyond, thereby incorporating boosting into the deposition cycle, saturated film growth is achieved. Fig. 6(b) shows the thickness and refractive index variation with respect to TEMAHf precursor pulse length. TEMAHf pulse durations of 0.2 s and 0.5 s were obtained without the master-fill stage; i.e. only pre-empty stage was executed. The unsaturated film growth is highlighted by the poor film thickness and non-uniformity in the film. As TEMAHf pulse length is increased from 0.5 s to 0.8 s (master-fill introduced) a significant increase in film thickness is seen. Also, the dispersion in refractive index values reduced significantly. This can be explained as, heating the precursor to a high temperature of 120 °C while might have increased the precursor flux, but without the master-fill the probability of all the precursor vapours reaching the reaction chamber and reacting with the substrate surface reduces. The incoming high-pressure gas carries the low-pressure precursor vapour into the reaction chamber and boosts the film growth. This clearly marks the importance of incorporating boosting mechanism for effective delivery of low vapour pressure precursor. The refractive indices of the films deposited without boosting mechanism are higher than films deposited with booster. This is because insufficient TEMAHf vapours caused increased interaction of oxidant with silicon surface atoms causing a silicon rich film to be formed. Fig. 6 (a) and (b) collectively conclude that master-fill duration of 0.9 s corresponding to metal pulse length of 1.3 s are sufficient for a self-limiting saturating reaction to take place as increasing the duration further showed no significant change in the film properties. An experiment of varying the pre-empty duration was also conducted. Since we have already got good passivation properties with pre-empty fixed to 0.5 s, the option of increasing it further was negated and reducing it further directly implied reducing the flux. The film properties degraded as expected. Hence pre-empty duration of 0.5 s, master-fill duration of 0.9 s corresponding to TEMAHf pulse length of 1.3 s (Fig. 6, encircled in blue) are used for further studies.

3.4. ALD window of HfO_x (P_1, P_2 and P_3 kept constant; Table 2)

Now that the boosting parameters and the hafnium pulse length are optimized, the ALD window for TEMAHf/ water process was obtained. Fig. 7 shows the ALD window for the process (shaded region). At low substrate temperatures, thicker films with poor refractive index were deposited. This may be attributed to both or either of the two reasons (a) condensation of precursor vapours, and (b) removal of precursor molecules by purging due to small reaction thermal energy. At high substrate temperatures, the sudden increase in film thickness after 375 °C is due to thermal decomposition of the reactants. High energy causes the reactants to decompose and films of unwanted stoichiometry are grown which might have led to increased thickness. The ALD window for TEMAHf/ water process lies from 300 °C to 375 °C substrate temperatures. The average growth per cycle of the deposited film was

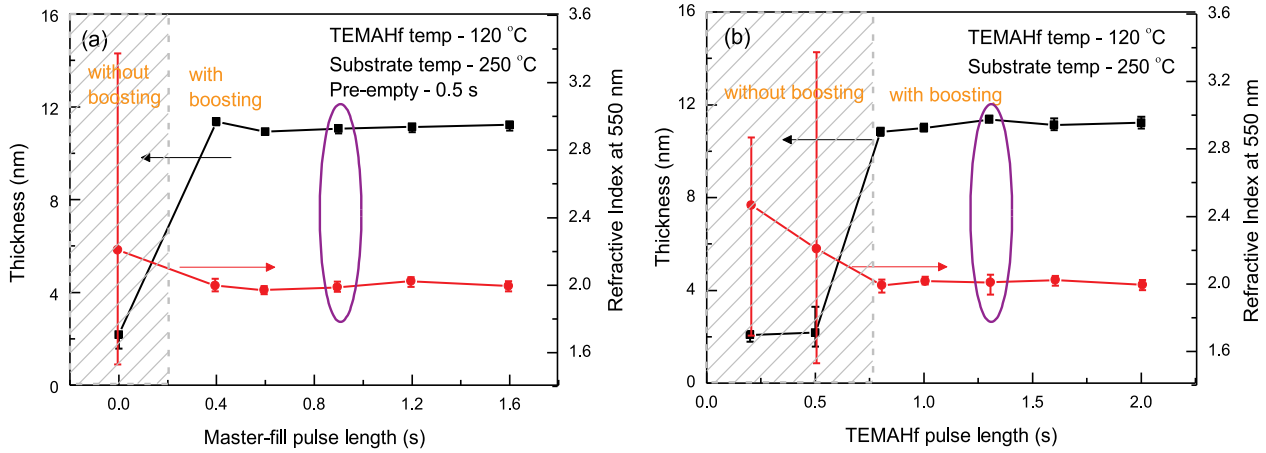

Fig. 6. Film thickness (black) and refractive index (red) variation with (a) master-fill pulse length and (b) TEMAHf pulse length. For Master-fill length of 0 s and TEMAHf pulse lengths below 0.8 s, the films are deposited without boosting mechanism (shaded area). The vertical bars represent the dispersion in the values at different points on the sample. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

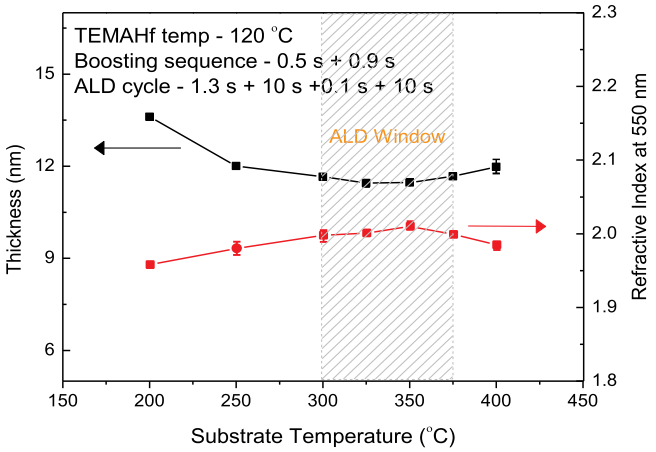

Fig. 7. ALD window (shaded region) of HfO_x/ Si system obtained using optimized TEMAHf/ water recipe. The window lies between 300 °C to 375 °C. The vertical bars represent the dispersion in the values at different points on the sample.

found to be 1.16 Å/cycle. The refractive index for films deposited within ALD window was found to be 2.00.

4. Conclusion

The present work highlights the importance of incorporating a boosting mechanism in an ALD process for the delivery of a low vapour pressure precursor in the reaction chamber. Hafnium oxide thin films were deposited on silicon substrate using Thermal Atomic Layer Deposition technique using TEMAHf (tetra-kis-ethylmethylamino-hafnium) and water as the metal precursor and oxidant, respectively. The thickness and refractive index profiles of the deposited films were obtained by fitting the ellipsometry data using a simple Cauchy/Si optical model. We observed that without the boosting sequence, saturated growth of the material layer was compromised and poor-quality films were obtained characterized by film non-uniformity and variable refractive index within the sample. We demonstrated that a boosting sequence of 0.5 s + 0.9 s (pre-empty + master-fill) with TEMAHf bottle heating temperature of 120 °C is sufficient to produce good quality films showing saturated growth rate. Furthermore, we demonstrated that for TEMAHf/ water ALD process, the ALD window for hafnium oxide was found to be in the temperature range 300 °C–375 °C where the average growth per cycle and refractive index of the films deposited within the ALD window were found to be 1.16 Å/ cycle and 2.00, respectively.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper. The authors declare the following financial interests/personal relationships which may be considered as potential competing interests.

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