Comparison of thermal and plasma-enhanced atomic layer deposition of niobium oxide thin films

Citation for published version (APA):

Basuvalingam, S. B., Macco, B., Knoops, H. C. M., Melskens, J., Kessels, W. M. M., & Bol, A. A. (2018). Comparison of thermal and plasma-enhanced atomic layer deposition of niobium oxide thin films. *Journal of Vacuum Science and Technology A: Vacuum, Surfaces, and Films*, 36(4), [041503].
<https://doi.org/10.1116/1.5034097>

DOI:

[10.1116/1.5034097](https://doi.org/10.1116/1.5034097)

Document status and date:

Published: 01/07/2018

Document Version:

Accepted manuscript including changes made at the peer-review stage

Please check the document version of this publication:

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

[Link to publication](#)

General rights

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

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

If the publication is distributed under the terms of Article 25fa of the Dutch Copyright Act, indicated by the "Taverne" license above, please follow below link for the End User Agreement:

www.tue.nl/taverne

Take down policy

If you believe that this document breaches copyright please contact us at:

openaccess@tue.nl

providing details and we will investigate your claim.

Comparison of thermal and plasma-enhanced atomic layer deposition of niobium oxide thin films

Running title: Atomic layer deposition of niobium oxide

Running Author: Basuvalingam et al

DOI: [10.1116/1.5034097](https://doi.org/10.1116/1.5034097)

Saravana Balaji Basuvalingam, and Bart Macco

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

Harm C. M. Knoop

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

Oxford Instruments Plasma Technology, North end, Bristol BS49 4AP, United Kingdom

Jimmy Melskens, Wilhelmus M. M. (Erwin) Kessels, and Ageeth A. Bol^{a)}

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

^{a)} Electronic mail: a.a.bol@tue.nl

Niobium pentoxide was deposited using $t\text{BuN}=\text{Nb}(\text{NEt}_2)_3$ as niobium precursor by both thermal atomic layer deposition (thermal ALD) and plasma-enhanced atomic layer deposition (PE-ALD) with H_2O and O_2 plasma as co-reactants, respectively. The deposition temperature was varied between 150 °C and 350 °C in both ALD processes. Amorphous films were obtained in all cases. Self-limiting saturated growth was confirmed for both ALD processes along with high uniformity over a 200 mm Si wafer. The PE-ALD process enabled a higher growth per cycle (GPC) than the thermal ALD process (0.56 Å vs 0.38 Å at 200 °C, respectively), while the GPC decreases with increasing temperature in both cases. The high purity of the film was confirmed using Rutherford backscattering spectrometry (RBS), elastic recoil detection (ERD), and X-ray

photoelectron spectroscopy (XPS), while the latter technique also confirmed the Nb⁺⁵ oxidation state of the niobium oxide films. The thermal ALD deposited films were sub-stoichiometric due to the presence of oxygen vacancies (V_O), of which a more dominant presence was observed with increasing deposition temperature. The PE-ALD deposited films were found to be near stoichiometric for all investigated deposition temperatures.

I. INTRODUCTION

Niobium oxide has more than 15 polymorphs, making it a complex and an interesting material to investigate as the phase and stoichiometry of the material are directly dependent on the deposition technique and temperature.^{1,2} The phase and stoichiometry of niobium oxide strongly influence its material properties. Stoichiometric niobium oxide (Nb_2O_5) has a high-k dielectric (insulating) behaviour that has been used in various applications such as capacitors,^{3,4} insulators,⁵ and sensors.^{6,7} The slight deficiency in oxygen content (sub-stoichiometric) causes a transition from insulating to n-type semiconductor behaviour. This sub-stoichiometric conducting oxide can be used as an electron transport or passivating layer in solar cells,⁸ and also as a catalysts.⁹ Additionally, Nb_2O_5 can be sulfurized into 2D- NbS_2 at high temperature, which has both semiconducting and superconducting properties.^{10,11}

Nb_2O_5 has been synthesized adopting various techniques, such as sol-gel,¹² sputtering,¹³ e-beam evaporation,¹⁴ pyrolysis,^{15–17} chemical vapour deposition (CVD),¹⁸ pulsed laser deposition (PLD),⁶ and atomic layer deposition (ALD).^{3,19–29} Of aforesaid techniques, ALD has the advantage of achieving precise thickness control, conformality, and uniformity over a large area, which are valuable assets for most of the above-mentioned applications.³⁰ ALD is a cyclic process where in the first half-cycle the

precursor is dosed into the reaction chamber and followed by a purge step, and in the second half-cycle the co-reactant is dosed which is followed by a second purging step. The purge steps are there to avoid CVD reactions in the gas phase and on the surface. ALD of Nb₂O₅ has previously been demonstrated employing various precursors with either H₂O or O₃ as co-reactant. ALD of Nb₂O₅ was first demonstrated using Nb(OEt)₅ as the precursor with H₂O as co-reactant.¹⁹ In this process, Kukli *et. al*¹⁹ observed stoichiometric growth of Nb₂O₅ film with a growth per cycle (GPC) of 0.30 Å. Later, for this process more literature has appeared reporting similar low GPC.^{23,27} Furthermore, this precursor has low volatility and decomposes when maintained above 100 °C. In case of halide based precursors, NbI₅ with O₂ plasma was successfully demonstrated to result in Nb₂O₅,²⁸ and also NbF₅ with H₂O was demonstrated, but in the latter case Nb₂O₅ film started to etch at higher temperatures resulting in no growth or non-uniform growth.³ Also in case of NbCl₅ with H₂O reproducibility problems were reported due to non-uniform growth.²⁹ Recently, Lee *et. al*²⁶ demonstrated a niobium oxide ALD process using NbF₅ as precursor with H₂ plasma as co-reactant to form niobium metal, which was followed by a super-cycle with O₃ as co-reactant to form sub-stoichiometric niobium oxide. In this process, the stoichiometry of the oxide film was controlled by varying the number of super cycles. Blanquart *et. al*²² demonstrated that ALD processes involving the amino-based precursors ^tBuN=Nb(NEt₂)₃ and ^tBuN=Nb(NMeEt)₃ attained a GPC of ~0.45 Å when used with either H₂O or O₃ as co-reactants. While ^tBuN=Nb(NEt₂)₃ appears to be the more commonly used ALD precursor in recent times, sub-stoichiometric growth of Nb₂O₅ with this precursor has been reported by using both H₂O and O₃ as co-reactants individually.^{4,8} It was also observed that films deposited with O₃

as co-reactant had higher contamination levels compared to the case where H₂O was used as co-reactant.

Although sub-stoichiometric growth of Nb₂O₅ has been reported, it has not been studied in detail. More specifically, a direct ALD process for Nb₂O₅ with both high GPC and good film quality along with stoichiometric film growth has not been reported in the literature. O₂ plasma is a well-known co-reactant with a higher reactivity than H₂O and often gives rise to a higher GPC along with improved film quality and also reduced reactant purge times.³¹ Therefore, in this work plasma-enhanced ALD (PE-ALD) of Nb₂O₅ using ^tBuN=NB(NEt₂)₃ with O₂ plasma and thermal ALD of Nb₂O₅ using H₂O as co-reactants are investigated and both processes are compared. From here on, the thermal process with H₂O as co-reactant will be referred to as thermal ALD, whereas the plasma process with O₂ plasma as co-reactant will be referred to as PE-ALD. The GPC along with film properties, such as stoichiometry, purity, and optical constants are determined by employing various analysis techniques on the films deposited by both processes and are discussed and compared in detail.

II. EXPERIMENTAL DETAILS

A. *Atomic layer deposition*

An Oxford Instruments Plasma Technology FlexAL ALD reactor was used for both thermal ALD and PE-ALD. This reactor was equipped with a remote inductively-coupled plasma source (ICP, 13.56 MHz) and the base pressure of the system was 10⁻⁶ Torr. The reactor was a warm wall reactor where wall temperature can be regulated between room temperature and a maximum temperature of 145 °C, independently. The warm wall temperature lead to longer residence time for reactant and product in the

reactor so needed longer purge time in comparison to hot wall reactor (wall and table temperature are same) to avoid parasitic CVD reaction.³² The similar system has been used for depositing Al₂O₃ by both thermal ALD and PE-ALD.³³ More details about the reactor can be found in the literature.³⁴ The metal-organic precursor (tert-butyldimido)-tris (diethylamino)-niobium “BuN=Nb(NEt₂)₃” (TBTDEN, 98% pure) was obtained from STREM chemical, Inc. The precursor was held in a stainless steel bubbler at 65 °C and was bubbled with Ar (99.999%, 100 sccm). The precursor supply line was maintained at 80 °C to avoid precursor condensation. The chamber wall was maintained at 145 °C for all investigated table temperatures. In the first half-cycle BuN=Nb(NEt₂)₃ was used as precursor, and the pressure was maintained at 80 mTorr for both the thermal ALD and PE-ALD processes using an automated pressure controller (APC). Ar (150-300 sccm) was employed as purge as well as carrier gas in both processes. The pressure was maintained at 80 mTorr in the second half-cycle of the thermal ALD process, using H₂O in the vapour phase as co-reactant. In the PE-ALD process O₂ plasma (100 sccm) was used as co-reactant and the pressure during the second half-cycle was maintained at 10 mTorr. The ICP RF power was set to 200 W. The films were deposited at various table temperatures between 150 °C and 350 °C in both thermal ALD and PE-ALD processes. All depositions were conducted on Si substrates with a native oxide (SiO₂, ~2 nm).

The optimized ALD recipes used are shown in Figure 1. They have a precursor dose time of 6 s, whereas the precursor purge time is 5 s in the thermal ALD process and 2 s in the PE-ALD process. The co-reactant, H₂O in thermal ALD is dosed for 200 ms, while O₂ plasma in PE-ALD is dosed for 4s. Here, thermal ALD has an additional step to hold H₂O for 4 s. The co-reactants purge time is 42 s in the former and is 3 s in the latter

process. Note that the co-reactant O_2 gas in PE-ALD is switched off before the purge step and only Ar is flown. The optimization of both ALD processes are discussed in detail in the Sec. III A.

FIG. 1. (Color online) Schematic sketch of the standard recipe used for a) thermal ALD and b) PE-ALD of niobium oxide.

B. Analysis techniques

The film growth was monitored *in-situ* using a J.A. Woollam Co., Inc. M2000U rotating compensator spectroscopic ellipsometer (SE), over a photo energy range of 1.2 eV to 5 eV. CompleteEASE software was used to model the optical constants of the deposited film. The model consisted of a Si substrate, native oxide SiO_2 , and Nb_2O_5 layers. The latter layer was modelled by employing two Tauc-Lorentz oscillators. More details on the SE technique and SE modelling can be found in literature.³⁵

The elemental composition and valence band spectra were determined by X-ray photoelectron spectroscopy (XPS) using a Thermo Scientific KA1066 spectrometer employing monochromatic Al $K\alpha$ ($h\nu = 1486.6$ eV) X-ray radiation. Rutherford backscattering spectrometry (RBS) and elastic recoil detection (ERD) measurements with a 1.9M eV He^+ beam source were conducted by Detect 99 B.V. Eindhoven, The Netherlands to determine the composition and the mass density of the films. RBS was

performed with two detectors at scattering angles of 150° and 170° . The hydrogen content was obtained in the same setup using ERD with the detector at a recoil angle of 30° . Grazing incidence X-ray diffraction (GI-XRD) measurements were performed to study the crystallinity of the film with a PANalytical X'Pert Pro MRD analyser, using a Cu K α ($\lambda = 1.54 \text{ \AA}$) X-ray source.

III. RESULTS AND DISCUSSION

A. ALD film growth

Films with a target thickness of $\sim 30 \text{ nm}$ were deposited on the starting substrate for both ALD processes at various deposition temperatures between 150°C and 350°C using the optimized ALD recipe shown in Figure 1. The film thickness for the initial 500 ALD cycles as-determined by *in-situ* SE is shown in Figure 2 as a function of the number of ALD cycles for all investigated deposition temperatures in both ALD processes. As clear from the figure, a linear ALD growth behaviour is observed without any nucleation delay at all deposition temperatures for both processes. The GPC was observed to decrease with increasing deposition temperature in both cases.

FIG. 2. (Color online) Thickness of Nb_2O_5 films as a function of the number of ALD cycles measured using *in-situ* SE for deposition temperatures between 150°C and 350°C , for both thermal ALD (a) and PE-ALD (b) processes.

The self-limiting saturated growth behaviour was confirmed for both the thermal ALD and the PE-ALD processes at a deposition temperature of 200 °C, as shown in Figure 3. In thermal ALD, as seen in Figure 3 (a-d), $t\text{BuN}=\text{Nb}(\text{NEt}_2)_3$ precursor saturation was observed at 6 s exposure time when the H_2O exposure was fixed at 200 ms. The precursor purge with Ar (300 sccm) was observed to saturate at 5 s. The second half-cycle by using H_2O as co-reactant saturated at 200 ms of exposure time. In the subsequent step, the APC valve was closed, to make sure that H_2O reacts with all adsorbed precursor sites uniformly. Reducing the duration of this step to less than 4 s resulted in poor thickness uniformity over an area of 200 mm diameter (as discussed later). In the following step, by fully opening the APC valve, Ar (300 sccm) was used to purge away remaining co-reactants and by-products. This purge step saturated at 35 s. In comparison to the literature (where hot wall reactor was used),²² the co-reactant purge step needed longer time to reach saturation due to slow desorption of H_2O from the reaction walls (warm wall at 145 °C), which would otherwise result in parasitic CVD reactions.

FIG. 3. Saturation curves: GPC as a function of precursor (TBTDEN as Nb precursor), purge (Ar) and co-reactant flow time at 200 °C for both thermal ALD (a-d) and PE-ALD (e-h) processes with H₂O and O₂ plasma as co-reactants, respectively. The error bars indicate the fitting error in the SE measurements.

In PE-ALD, as shown in Figure 3 (e-h), precursor saturation was observed at 6 s exposure time similar to thermal ALD when the co-reactant O₂ plasma exposure time was fixed at 6 s. The Ar precursor purge (300 sccm) saturated at 1 s. In the next step, O₂ plasma (100 sccm) was used as co-reactant and saturation occurred at 2 s. The following co-reactant purge step saturated at 3 s. Note that this step was much shorter compared to the purge step in the thermal ALD process, because O₂ molecules are purged away

rapidly in comparison to the slow desorption of H₂O in the thermal ALD process. At 200 °C, the GPC was ~ 0.56 Å, which is higher in comparison to the thermal ALD process (~ 0.38 Å). Therefore, PE-ALD with O₂ plasma as co-reactant enables a significantly shorter process time through both an enhanced GPC and a strongly reduced purge time.

FIG. 4. (Color online) Growth per cycle (GPC_{SE}) measured using *in-situ* SE (left vertical axis) and deposited Nb atoms per nm² (GPC_{RBS}) measured using RBS (right vertical axis) for both the thermal ALD (open symbols) and the PE-ALD (close symbols) processes at various deposition temperatures between 150 °C and 350 °C.

In both thermal ALD and PE-ALD processes, the effect of deposition temperature on the film growth was studied by varying the deposition temperature between 150 °C and 350 °C. The growth per cycle (GPC_{SE}) was determined by calculating the slope for the last 100 cycles of the *in-situ* SE data shown in Figure 2. In both processes, the GPC_{SE} was observed to decrease with increasing deposition temperature, as shown in Figure 4. In thermal ALD, the GPC_{SE} decreases from 0.38 Å to 0.20 Å for temperatures ranging from 150 °C to 350 °C, whereas in PE-ALD the GPC_{SE} lowers from 0.58 Å to 0.45 Å. The growth per cycle (GPC_{RBS}) in terms of number of Nb atoms deposited per nm² per ALD cycle was calculated from RBS data by dividing the measured Nb atoms/nm² by the

number of ALD cycles, see Figure 4 (right vertical axis). GPC_{RBS} decreases from 0.75 to 0.5 Nb atoms/nm² in the case of thermal ALD and from 1.1 to 0.8 Nb atoms/nm² in the case of PE-ALD when increasing the deposition temperature from 200 °C to 350 °C, which yields a similar trend when compared to GPC_{SE} . This evidently indicates that a decrease in GPC with increasing deposition temperature can be traced to reduced adsorption of Nb precursor per cycle at higher deposition temperatures. Similar behaviour has been previously observed in both thermal ALD as well as PE-ALD of Al₂O₃,^{33,36} where a decrease in GPC with increasing deposition temperature has been associated with thermally activated dehydroxylation reaction that reduce the concentration of surface –OH reactive sites. As the niobium oxide ALD processes are likely similar to that of Al₂O₃, the decrease in GPC with increasing deposition temperature is probably also due to thermally activated dehydroxylation reaction of surface –OH reactive sites.

For deposition temperatures of 200 °C and below, we observed a GPC of ~0.55 Å in our PE-ALD process, which is higher than previously reported values. Kulki *et. al*¹⁹ and Liu *et. al*²⁷ reported a GPC of ~0.3 Å using Nb(OEt)₅ precursor with H₂O as co-reactant, while Blanquart *et. al*²² reported a GPC of ~0.4 Å and ~0.45 Å with H₂O and O₃ as co-reactants, respectively using the same precursor ^tBuN=Nb(NEt₂)₃. Generally, it appears that the GPC of the PE-ALD process is higher than the thermal ALD process for all investigated deposition temperatures. Therefore, it appears that an O₂ plasma is a more effective oxidant than H₂O as co-reactant such that it allows more Nb precursor molecules to adsorb on the surface per cycle. An extension of the Blanquart *et. al* work was reported by Tomczak *et. al*²⁴ on the reaction mechanism using *in-situ* analysis techniques for the same precursor ^tBuN=Nb(NEt₂)₃ with D₂O and O₃ as co-reactants. In

case of the D₂O process, it was observed that -NET₂ ligands reacted with the surface -OH reactive sites during the first half cycle, while the remaining ligands were exchanged during the second half cycle. The above mentioned reaction mechanism could also be speculated here for the thermal ALD of Nb₂O₅ with H₂O. In case of the O₃ process, it was speculated by Tomczak *et. al* that no -OH reactive sites were formed and all ligands were exchanged during the second half cycle. The above reaction mechanism could also be speculated here for the PE-ALD of Nb₂O₅ with O₂ plasma. However, in this case, the enhanced GPC observed with O₂ plasma could not be explained with this mechanism, as a lower GPC of ~0.45 Å was observed with O₃. Similar to other material systems, surface -OH reactive sites could be formed in an O₂ plasma, which could explain the enhanced GPC observed for PE-ALD of Nb₂O₅.³⁷ Similar behaviour was also observed for Al₂O₃ where PE-ALD with O₂ plasma shows higher GPC than thermal ALD with H₂O.^{33,36} Thus, alternatively, similar to the reaction mechanism of Al₂O₃ with O₂ plasma.³⁸ It could also be hypothesized that a ligand react with surface -OH reactive site in the first half cycle, while the remaining ligands react with O₂ plasma species forming -OH surface groups, and H₂O, CO_x, NO_x by-products.

FIG. 5. (Color online) Thickness uniformity contour plot obtained using *ex-situ* SE mapping on (a) the thermal ALD and (b) the PE-ALD grown film over a 200 mm Si wafer at 200 °C. The white arrow shows the position of the precursor inlet as well as the flow direction above the wafer in the reactor. The exhaust is directly below the wafer stage in the reactor.

The uniformity of both thermal ALD and PE-ALD films were determined using *ex-situ* SE by mapping a ~20 nm thick film over a 200 mm diameter Si wafer, see Figure 5. The thickness non-uniformity was calculated by dividing the difference between the maximum and the minimum thickness by the average thickness. The non-uniformity in the thermal ALD grown film was around $\pm 3.3\%$, whereas in the PE-ALD grown film it was around $\pm 4.4\%$. In case of thermal ALD (Figure 5a), the decline in thickness was observed from the upper left to the bottom right. This non-uniformity in thickness was considered to originate from both the precursor and H₂O flow direction. In case of PE-ALD (Figure 5b), the higher thickness was observed in the middle of the wafer. Here, the non-uniformity was attributed to a non-uniform distribution of O₂ plasma over a 200 mm diameter substrate³⁹ as well as the precursor flow direction. Although the uniformity is fair for both processes, it may be further improved by increasing the H₂O dose or hold time in case of thermal ALD and by increasing the O₂ plasma dose time in case of PE-ALD process, and also by further optimizing precursor dose time in both the cases.

B. Film characterization

Self-limiting growth of Nb₂O₅ was shown for both thermal ALD and PE-ALD in the Sec. III A. In this section, the material properties of the Nb₂O₅ films of ~30 nm thickness are discussed, utilizing various analytical techniques, to study their composition, density, and optical properties.

The effect of the temperature on the composition and quality of the films was determined using RBS. The RBS measurements were performed on both thermal ALD and PE-ALD deposited films at 200 °C and 350 °C. The O/Nb ratio in Table 1 shows that the thermal ALD deposited films are sub-stoichiometric with all values being below 2.5

and the O/Nb ratio decreases when raising the deposition temperature from 200 °C to 350 °C. The sub-stoichiometric ($\text{Nb}_2\text{O}_{5-x}$) nature of the films can be linked to oxygen vacancies,¹ and the further decline in O/Nb ratio at 350 °C indicates an increase in the number of oxygen vacancies with increasing deposition temperature. In the case of PE-ALD deposited films, the O/Nb ratio was ~2.5 illustrating the near stoichiometry of the films. All the deposited films show no traces of impurities in the films other than hydrogen. The carbon detection limit was relatively high at 10 at.% and it was detected only on the surface due to exposure to atmosphere. Around 3 at.% of H was detected using ERD in all the films and it was observed to decrease with temperature for both ALD processes.

TABLE I. Material properties of thermal ALD and PE-ALD deposited niobium oxide thin film at various temperatures between 150 °C and 350 °C, as determined from SE, RBS and ERD measurements. All films were ~30nm thick and the GPC was calculated from the last 100 cycles by *in-situ* SE. The refractive index (at 2.1 eV) and the Tauc band gap were also determined from SE. The number of deposited Nb atoms/nm² per ALD cycle and the O/Nb ratio were determined by RBS. The mass density was calculated using both RBS and thickness from SE. The H content was determined by ERD. The typical error range is indicated in the first row.

Process	Deposition Temperature (°C)	GPC _{SE} (Å)	Refractive Index	E _g (eV)	GPC _{RBS} (at. nm ⁻² cycle ⁻¹)	Mass Density (g cm ⁻³)	O/Nb ratio	H (at. %)
Error		±0.03	±0.03	±0.03	±0.04	±0.1	±0.05	±0.1
Thermal ALD	150	0.39	2.35	3.47	-	-	-	-
	200	0.37	2.37	3.45	0.75	4.35	2.36	3.38
	300	0.25	2.40	3.43	-	-	-	-
	350	0.21	2.46	3.36	0.50	4.98	2.22	1.97
PE-ALD	150	0.56	2.36	3.47	-	-	-	-
	200	0.55	2.36	3.47	1.08	4.11	2.48	2.9
	300	0.47	2.36	3.47	-	-	-	-
	350	0.44	2.36	3.47	0.87	4.10	2.49	2.37

-: no data

XPS measurements were performed to determine the composition and also to further assess the quality of the films. Depth profiling of the films by means of sputtering with Ar⁺ ions was performed to avoid surface impurities, but it resulted in preferential sputtering of O over Nb atoms and caused reduction of Nb⁺⁵ to lower oxidation state.

Therefore, spectra acquired before sputtering were used to estimate the chemical states. Figure 6 shows the Nb3d and O1s core level XPS spectra of the films deposited at 200 °C and 350 °C for both the thermal ALD (a & b) and the PE-ALD (c & d) processes. All the XPS spectra shown in Figure 6 were calibrated by setting the carbon C-C bond peak to 248.8 eV in the C1s XPS spectra. In the Nb3d spectrum, as seen in Figure 6 (a & c), the doublet Nb3d_{5/2} and Nb3d_{3/2} components are located at ~207.4 eV and ~210.2 eV, respectively. This corresponds to the Nb⁺⁵ oxidation state with the spin-split orbital components (between Nb3d_{5/2} and Nb3d_{3/2}) of $\Delta \sim 2.8$ eV. An additional doublet at ~1.5 eV towards lower binding energy (BE) at ~205.9 eV is attributed to the Nb⁺⁴ oxidation state.⁴⁰ In the O1s spectrum, the peak centred around 530-531 eV corresponds to metal oxide O-Nb bonds and a second peak at ~532 eV to O-H bonds or other surface species originating from ambient exposure after deposition.

In the case of PE-ALD films, the O1s spectrum in Figure 6d shows that the metal oxide peak centre is located at 530.3 eV for both temperatures. In the Nb3d spectrum, the Nb3d_{5/2} component peak centre was observed at 207.3 eV (FWHM=1.17 eV) for both temperatures, along with a negligible presence of the Nb⁺⁴ oxidation state. This confirms the near stoichiometry of the films with Nb₂O₅ composition. In the case of thermal ALD, for the 200 °C film the Nb3d_{5/2} component peak centre shifts to 207.4 eV along with a further broadening (FWHM = 1.23 eV) and a similar shift in the metal oxide peak centre to 530.5 eV was observed. The broadening of the FWHM and shift in peak centre to higher binding energies have previously been associated with oxygen vacancies in the film⁴¹. For the 350 °C film, the Nb3d_{5/2} peak FWHM further increases to 1.36 along with an additional 0.1 eV shift to 207.5 eV. The O1s metal oxide peak also further shifts to

530.8 eV indicating an increase in oxygen vacancies. Additionally, the second Nb3d_{5/2} peak corresponding to the Nb⁺⁴ oxidation state is also significant at this temperature in the thermal ALD case, in contrast to the PE-ALD film. This confirms the presence of oxygen vacancies and supports the RBS measurements with the suggested sub-stoichiometric nature of thermal ALD deposited Nb₂O_{5-x} films. From the deconvolution of the Nb3d peaks of the thermal ALD films, it is estimated that ~7% of the total Nb3d originates from the Nb⁺⁴ oxidation state for the 200 °C film, whereas at 350 °C this increases to ~12%. Carbon was only observed at the surface for all the deposited films, and its concentration was reduced to a negligible amount (identical to RBS measurements) after depth profiling. No other impurities were detected by XPS both before as well as after sputtering.

FIG. 6. (Color online) Nb3d and O1s XPS spectra for both the thermal ALD (a & b) and the PE-ALD (c & d) deposited films at 200 °C and 350 °C.

XPS valence band (VB) studies were performed on both the thermal ALD and the PE-ALD deposited films to further confirm oxygen vacancies observed in the films, see Figure 7. The Fermi level ($BE = 0$ eV) was calibrated by measuring the Fermi edge of gold. In thermal ALD films, trap states were observed between the valence band maximum (E_{VB}) and Fermi level (E_F), as seen in Figure 7b, whereas in the PE-ALD films no such trap states were observed. The localized trap states between E_{VB} and E_F have previously also been observed in various other materials, such as Ta_2O_5 ,^{41,42} and TiO_2 ,⁴³ where it was attributed to the presence of oxygen vacancies. The number of trap states observed in the thermal ALD films increases with deposition temperature and could therefore be correlated with oxygen vacancies in the film, confirming observations from both the RBS and the XPS measurements. The trap states were not observed for films grown at temperatures below 300 °C contrary to the previous measurements. Presumably, the trap state density was too low to be detected by the XPS system used. The higher reactivity of the O_2 plasma compared to H_2O with the precursor can be speculated to be the reason for obtaining stoichiometric films with no significant amount of oxygen vacancies in the PE-ALD process.

FIG. 7. (Color online) Valence band spectra for (a) thermal ALD and (c) PE-ALD films deposited at temperatures between 150 °C and 350 °C. Plot (b) shows a magnified part of the inset shown in (a).

The refractive index data (at 2.1 eV) shown in Table 1 were obtained from *ex-situ* SE measurements. In case of PE-ALD films, the refractive index at 2.36 does not vary with the deposition temperature. Similarly, the mass density of both 200 °C and 350 °C films is 4.1 g/cm³ around 90% of the Nb₂O₅ bulk density. Based on the literature, the bulk density is 4.5 g/cm³ for Nb₂O₅ and 5.9 g/cm³ for NbO₂.¹³ This is typical for ALD grown amorphous films to have lower density than bulk density. In case of thermal ALD films, the refractive index increases from 2.35 to 2.46 with increasing deposition temperature. Likewise, the mass density increases from 4.35 g/cm³ at 200 °C to 4.98 g/cm³ at 350 °C. Interestingly thermal ALD films have higher density than PE-ALD films at all temperatures, and for 350 °C film the density was apparently higher than the bulk density of Nb₂O₅. This increase in density could potentially be explained by relating to the presence of oxygen vacancies in the form of Nb⁺⁴ oxidation states in the films. As the bulk density of niobium oxide at Nb⁺⁴ oxidation state (NbO₂) is higher than it is at the

Nb^{+5} oxidation state (Nb_2O_5) presences of small fraction of Nb^{+4} oxidation state would increase the density of the films. This also explains the density of the 350 °C film above the bulk density as the oxygen vacancies in the film increases with deposition temperature, which is consistent to other observations.

FIG. 8. (Color online) Tauc plot determined from the absorption coefficient measured by *ex-situ* SE for (a) thermal ALD and (b) PE-ALD films deposited at temperatures between 150 °C and 350 °C.

The absorption co-efficient was obtained from *ex-situ* SE measurements. GI-XRD measurements revealed that all films deposited by thermal ALD and PE-ALD are amorphous regardless of the deposition temperature. Based on the absorption coefficient data, the optical band gap of the films can be determined using the Tauc equation: $(\alpha h\nu)^{1/2} \sim (h\nu - E_g)$, where α is the absorption coefficient, $h\nu$ is the photon energy, E_g is the optical band gap, and the exponent ‘1/2’ corresponds to the allowed indirect transition in the amorphous film.^{44,45} The optical band gap from the Tauc plot $((\alpha h\nu)^{1/2}$ vs $h\nu$) was estimated by extrapolating the linear region of the curve to zero absorption. The tail region below the optical band gap (linear region) in Figure 8 is most likely due to localized states and trap states (from defects) between the valence and conduction bands, as were also observed from XPS. In case of thermal ALD films, the band gap was ~3.5 eV as shown in Table 1, but a small shift towards lower band gap was observed with increasing deposition temperature corresponding to oxygen vacancies presence in the

film. Lee *et. al*²⁶ also observed a similar reduction in band gap for niobium oxide films with increasing oxygen vacancies. Along with this reduction, the influence of oxygen vacancies in the films was further confirmed by a widening of the tail region towards the lower photon energy into the band gap. In case of PE-ALD films, the optical band gap was 3.5 eV, and the deposition temperature did not have any effect on the optical band gap of the films.

IV. SUMMARY AND CONCLUSIONS

Nb₂O₅ thin films were deposited by both a thermal ALD and a PE-ALD process with H₂O and O₂ plasma as co-reactants, respectively. The self-limiting saturated growth was confirmed for both processes at 200 °C and a high uniformity over a 200 mm Si wafer was obtained. All the films were of high quality with no detectable contamination apart from a H content of ~3 at.%. The PE-ALD process showed higher growth per cycle than the thermal ALD process due to enhanced Nb adsorption. The effects of deposition temperature were studied by varying the temperature between 150 °C and 350 °C in both processes. From RBS, XPS and SE the thermal ALD films were found to be sub-stoichiometric due to the presence of oxygen vacancies which observed to be more dominantly present in the film with increasing deposition temperature. The PE-ALD films were near stoichiometric in the entire investigated deposition temperature range. This work shows that the composition, density and sub-band gap states of Nb₂O₅ can be controlled by choosing the ALD process and processing temperature. This is advantageous for many applications in which Nb₂O₅ can be used, such as solar cells, microelectronic devices, and sensors.

ACKNOWLEDGMENTS

The authors acknowledge Jeroen van Gerwen and Christian van Helvoirt for their technical assistance. Saurabh Karwal, Alfredo Mameli and Shashank Balasubramanyam for the valuable suggestions and Aileen O'Mahony from OIPT, UK for the assistance with uniformity measurements. This work was supported by the European Research Council (grant agreement number: 648787). The work of author J. Melskens was supported by the Netherlands Organisation for Scientific Research under the Dutch TTW-VENI Grant 15896.

- ¹ C. Nico, T. Monteiro, and M. P. F. Graça, *Prog. Mater. Sci.* **80**, 1 (2016).
- ² R. A. Rani, A. S. Zoolfakar, A. P. O'Mullane, M. W. Austin, and K. Kalantar-Zadeh, *J. Mater. Chem. A* **2**, 15683 (2014).
- ³ T. Blomberg, C. Wenger, C. Baristiran-Kaynak, G. Ruhl, and P. Baumann, *Microelectron. Eng.* **88**, 2447 (2011).
- ⁴ H. García, H. Castán, E. Perez, S. Dueñas, L. Bailón, T. Blanquart, J. Niinistö, K. Kukli, M. Ritala, and M. Leskelä, *Semicond. Sci. Tech.* **28**, 55005 (2013).
- ⁵ N. Alimardani, J. M. McGlone, J. F. Wager, and J. F. Conley, *J. Vac. Sci. Technol. A* **32**, 01A122 (2014).
- ⁶ M. E. Gimon-Kinsel and K. J. Balkus, *Micropor. Mesopor. Mat.* **28**, 113 (1999).
- ⁷ A. Kohli, C. C. Wang, and S. A. Akbar, *Sensor. Actuat. B-Chem.* **56**, 121 (1999).
- ⁸ W. L. Hoffeditz, M. J. Pellin, O. K. Farha, and J. T. Hupp, *Langmuir* **33**, 9298 (2017).
- ⁹ H. Cui, G. Zhu, Y. Xie, W. Zhao, C. Yang, T. Lin, H. Gu, and F. Huang, *J. Mater. Chem. A* **3**, 11830 (2015).
- ¹⁰ W. Hu, Y. Mi, D. Tian, Y. Zhao, Z. Liu, K. Yao, and Y. Zhu, *Mater. Chem. Phys.* **109**, 184 (2008).

- ¹¹ H. Simchi, T. N. Walter, T. H. Choudhury, L. Y. Kirkley, J. M. Redwing, and S. E. Mohney, *J. Mater. Sci.* **52**, 10127 (2017).
- ¹² N. Özer, D. -G. Chen, and C. M. Lampert, *Thin Solid Films* **277**, 162 (1996).
- ¹³ E. Çetinörgü, B. Baloukas, O. Zabeida, J. E. Klemberg-Sapieha, and L. Martinu, *Appl. Optics* **48**, 4536 (2009).
- ¹⁴ D. -D. Zhao, Q. -Y. Cai, Y. -X. Zheng, J. -B. Zhang, S. -D. Yang, L. Yang, Z. -H. Liu, R. -J. Zhang, S. -Y. Wang, and L. -Y. Chen, *J. Phys. D Appl. Phys.* **49**, 265304 (2016).
- ¹⁵ M. T. Duffy, C. C. Wang, A. Waxman, and K. H. Zaininger, *J. Electrochem. Soc.* **116**, 234 (1969).
- ¹⁶ R. Romero, J. R. Ramos-Barrado, F. Martin, and D. Leinen, *Surf. Interface Anal.* **36**, 888 (2004).
- ¹⁷ R. Romero, E. A. Dalchiele, F. Martín, D. Leinen, and J. R. Ramos-Barrado, *Sol. Energ. Mat. Sol. C.* **93**, 222 (2009).
- ¹⁸ J. -P. Masse, H. Szymanowski, O. Zabeida, A. Amassian, J. E. Klemberg-Sapieha, and L. Martinu, *Thin Solid Films* **515**, 1674 (2006).
- ¹⁹ K. Kukli, M. Ritala, M. Leskelä, and R. Lappalainen, *Chem. Vapor Depos.* **4**, 29 (1998).
- ²⁰ J. P. Correa-Baena, L. Steier, W. Tress, M. Saliba, S. Neutzner, T. Matsui, F. Giordano, T. J. Jacobsson, A. R. Srimath Kandada, S. M. Zakeeruddin, A. Petrozza, A. Abate, M. K. Nazeeruddin, M. Grätzel, and A. Hagfeldt, *Energ. Environ. Sci.* **8**, 2928 (2015).
- ²¹ A. Guerrero, G. Garcia-Belmonte, I. Mora-Sero, J. Bisquert, Y. S. Kang, T. J. Jacobsson, J. -P. Correa-Baena, and A. Hagfeldt, *J. Phys. Chem. C* **120**, 8023 (2016).
- ²² T. Blanquart, J. Niinistö, M. Heikkilä, T. Sajavaara, K. Kukli, E. Puukilainen, C. Xu, W. Hunkes, M. Ritala, and M. Leskelä, *Chem. Mater.* **24**, 975 (2012).

- ²³ A. Brodie, P. De Cecco, C. Bevis, J. R. Maldonado, R. Bhatia, E. Deguns, and G. Sundaram, *ECS Transactions* **33**, 101 (2010).
- ²⁴ Y. Tomczak, K. Knapas, M. Sundberg, M. Leskelä, and M. Ritala, *Chem. Mater.* **24**, 1555 (2012).
- ²⁵ T. Blanquart, K. Kukli, J. Niinistö, V. Longo, M. Heikkilä, M. Ritala, and M. Leskelä, *ECS Solid State Lett.* **1**, N1 (2012).
- ²⁶ S. -H. Lee, J. -D. Kwon, J. -H. Ahn, and J. -S. Park, *Ceram. Int.* **43**, 6580 (2017).
- ²⁷ J. Liu, Y. Xu, Q. Sun, H. Lu, and D. W. Zhang, *Mater. Lett.* **65**, 2182 (2011).
- ²⁸ M. Rooth, K. Kukli, and A. Hårsta, *Proc. Electrochem. Soc.* **2005-09**, 598 (2005).
- ²⁹ K. -E. Elers, M. Ritala, M. Leskelä, and E. Rauhala, *Appl. Surf. Sci.* **82–83**, 468 (1994).
- ³⁰ H. C. M. Knoop, S. E. Potts, A. A. Bol, and W. M. M. Kessels, *Handbook of Crystal Growth* **III**, 1101 (2015).
- ³¹ H. B. Profijt, S. E. Potts, M. C. M. van de Sanden, and W. M. M. Kessels, *J. Vac. Sci. Technol. A* **29**, 50801 (2011).
- ³² G. B. Rayner and S. M. George, *J. Vac. Sci. Technol. A* **27**, 716 (2009).
- ³³ J. L. van Hemmen, S. B. S. Heil, J. H. Klootwijk, F. Roozeboom, C. J. Hodson, M. C. M. van de Sanden, and W. M. M. Kessels, *J. Electrochem. Soc.* **154**, G165 (2007).
- ³⁴ S. B. S. Heil, J. L. van Hemmen, C. J. Hodson, N. Singh, J. H. Klootwijk, F. Roozeboom, M. C. M. van de Sanden, and W. M. M. Kessels, *J. Vac. Sci. Technol. A* **25**, 1357 (2007).
- ³⁵ E. Langereis, S. B. S. Heil, H. C. M. Knoop, W. Keuning, M. C. M. van de Sanden, and W. M. M. Kessels, *J. Phys. D Appl. Phys.* **42**, 73001 (2009).
- ³⁶ S. E. Potts, G. Dingemans, C. Lachaud, and W. M. M. Kessels, *J. Vac. Sci. Technol. A* **30**, 21505 (2012).

- ³⁷ S. E. Potts, H. B. Profijt, R. Roelofs, and W. M. M. Kessels, *Chem. Vapor Depos.* **19**, 125 (2013).
- ³⁸ E. Langereis, M. Bouman, J. Keijmel, S. B. S. Heil, M. C. M. Van de Sanden, and W. M. M. Kessels, *ECS Transactions* **16**, 247 (2008).
- ³⁹ K. -E. Elers, T. Blomberg, M. Peussa, B. Aitchison, S. Haukka, and S. Marcus, *Chem. Vapor Depos.* **12**, 13 (2006).
- ⁴⁰ Z. Weibin, W. Weidong, W. Xueming, C. Xinlu, Y. Dawei, S. Changle, P. Liping, W. Yuying, and B. Li, *Surf. Interface Anal.* **45**, 1206 (2013).
- ⁴¹ K. V Egorov, D. S. Kuzmichev, P. S. Chizhov, Y. Y. Lebedinskii, C. S. Hwang, and A. M. Markeev, *ACS Appl. Mater. Inter.* **9**, 13286 (2017).
- ⁴² M. V. Ivanov, T. V. Perevalov, V. S. Aliev, V. A. Gritsenko, and V. V. Kaichev, *J. Appl. Phys.* **110**, 24115 (2011).
- ⁴³ S. Wang, L. Zhao, L. Bai, J. Yan, Q. Jiang, and J. Lian, *J. Mater. Chem. A* **2**, 7439 (2014).
- ⁴⁴ J. Tauc, R. Grigorovici, and A. Vancu, *Phys. Status Solidi* **15**, 627 (1966).
- ⁴⁵ S. Balasubramanyam, A. Sharma, V. Vandalon, H. C. M. Knoop, W. M. M. Kessels, and A. A. Bol, *J. Vac. Sci. Technol. A* **36**, 01B103 (2018).