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

**Citation for published version (APA):**
https://doi.org/10.1116/1.5034097

**DOI:**
10.1116/1.5034097

**Document status and date:**
Published: 01/07/2018

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

**Please check the document version of this publication:**

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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. The phase and stoichiometry of niobium oxide strongly influence its material properties. Stoichiometric niobium oxide (Nb$_2$O$_5$) has a high-k dielectric (insulating) behavior that has been used in various applications such as capacitors, insulators, and sensors. The slight deficiency in oxygen content (substoichiometric) causes a transition from insulating to n-type semiconductor behavior. This substoichiometric conducting oxide can be used as an electron transport or passivating layer in solar cells, and also as a catalysts.

Additionally, Nb$_2$O$_5$ can be sulfurized into 2D-NbS$_2$ at high temperature, which has both semiconducting and superconducting properties. Nb$_2$O$_5$ has been synthesized adopting various techniques, such as sol-gel, sputtering, e-beam evaporation, pyrolysis, chemical vapor deposition (CVD), pulsed laser deposition, and atomic layer deposition (ALD). Of aforesaid techniques, ALD has the advantage of achieving precise thickness control, conformity, and uniformity over a large area, which are valuable assets for most of the abovementioned applications. 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 coreactant 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 Nb$_2$O$_5$ has previously been demonstrated employing various precursors with either H$_2$O or O$_3$ as coreactant. ALD of Nb$_2$O$_5$ was first demonstrated using Nb(OEt)$_5$ as the precursor with H$_2$O as coreactant. In this process, Kukli et al. observed stoichiometric growth of Nb$_2$O$_5$ film with a growth per cycle (GPC) of 0.30 Å. Later, for this process, more literature has appeared reporting similar low GPC. Furthermore, this precursor has low volatility and decomposes when maintained above 100 °C. In the case of halide based precursors, NbI$_5$ with O$_3$ plasma was successfully demonstrated to result in Nb$_2$O$_5$, and also NbF$_5$ with H$_2$O was demonstrated, but in the latter case, Nb$_2$O$_5$ film started to etch at higher temperatures resulting in no growth or nonuniform growth. Also in the case of NbCl$_5$ with H$_2$O, reproducibility problems were reported due to nonuniform growth. Recently, Lee et al. demonstrated a niobium oxide ALD process using NbF$_5$ as a precursor with H$_2$ plasma as coreactant to form niobium metal, which was followed by a super-cycle with O$_3$ as a coreactant to form a substoichiometric niobium oxide. In this process, the stoichiometry of the oxide film was controlled by varying the number of super cycles. Blanquart et al. demonstrated that ALD processes involving the amino-based precursors $^{1}$BuN=Nb(NEt)$_3$ and

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

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(Received 9 April 2018; accepted 29 May 2018; published 18 June 2018)

Niobium pentoxide was deposited using $^{1}$BuN=Nb(NEt)$_3$ as niobium precursor by both thermal atomic layer deposition (ALD) and plasma-enhanced atomic layer deposition (PE-ALD) with H$_2$O and O$_2$ plasma as coreactants, respectively. The deposition temperature was varied between 150 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, elastic recoil detection, and x-ray photoelectron spectroscopy, while the latter technique also confirmed the Nb$^{+5}$ oxidation state of the niobium oxide films. The thermal ALD deposited films were substoichiometric 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. Published by the AVS. https://doi.org/10.1116/1.5034097


\[ ^{1}\text{BuN}=\text{Nb}(\text{NEt}_2)_3 \]

attained a GPC of \( \sim 0.45\ \text{Å} \) when used with either \( \text{H}_2\text{O} \) or \( \text{O}_3 \) as coreactants. While \( ^{1}\text{BuN}=\text{Nb}(\text{NEt}_2)_3 \) appears to be the more commonly used ALD precursor in recent times, substoichiometric growth of \( \text{Nb}_2\text{O}_5 \) with this precursor has been reported by using both \( \text{H}_2\text{O} \) and \( \text{O}_3 \) as coreactants individually.\(^{4,8} \) It was also observed that films deposited with \( \text{O}_3 \) as coreactant had higher contamination levels compared to the case where \( \text{H}_2\text{O} \) was used as coreactant.

Although substoichiometric growth of \( \text{Nb}_2\text{O}_5 \) has been reported, it has not been studied in detail. More specifically, a direct ALD process for \( \text{Nb}_2\text{O}_5 \) with both high GPC and high-quality and also reduced reactant purge times.\(^{31} \) Therefore, in this work, plasma-enhanced ALD (PE-ALD) of \( \text{Nb}_2\text{O}_5 \) using \( ^{1}\text{BuN}=\text{Nb}(\text{NEt}_2)_3 \) with \( \text{O}_2 \) plasma and thermal ALD of \( \text{Nb}_2\text{O}_5 \) using \( \text{H}_2\text{O} \) as coreactants are investigated and both processes are compared. From here on, the thermal process with \( \text{H}_2\text{O} \) as coreactant will be referred to as thermal ALD, whereas the plasma process with \( \text{O}_2 \) plasma as coreactant 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 \( 10^{-6} \text{Torr} \). The reactor was a warm wall reactor where the wall temperature can be regulated between room temperature and a maximum temperature of \( 145 \text{°C} \), independently. The warm wall temperature leads to a longer residence time for the reactant and product in the reactor so needed a 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 \( \text{Al}_2\text{O}_3 \) 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-butylimido)-tris (diethylamino)-niobium \( ^{1}\text{BuN}=\text{Nb}(\text{NEt}_2)_3 \) (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 \( ^{1}\text{BuN}=\text{Nb}(\text{NEt}_2)_3 \) 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 \( \text{H}_2\text{O} \) in the vapor phase as coreactant. In the PE-ALD process, \( \text{O}_2 \) plasma (100 sccm) was used as coreactant 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 and 350°C in both thermal ALD and PE-ALD processes. All depositions were conducted on Si substrates with a native oxide (\( \text{SiO}_2 \), \( \sim 2 \text{nm} \)).

The optimized ALD recipes used are shown in Fig. 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 coreactant, \( \text{H}_2\text{O} \) in thermal ALD is dosed for 200 ms, while \( \text{O}_2 \) plasma in PE-ALD is dosed for 4 s. Here, thermal ALD has an additional step to hold \( \text{H}_2\text{O} \) for 4 s. The coreactant purge time is 42 s in the former and is 3 s in the latter process. Note that the coreactant \( \text{O}_2 \) gas in PE-ALD is switched off before the purge step and only Ar is flown. The optimization of both ALD processes is discussed in detail in Sec. III A.

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 1.2–5 eV. COMPLETEASE software was used to model the optical constants of the deposited film. The model consisted of a Si substrate, native oxide \( \text{SiO}_2 \), and \( \text{Nb}_2\text{O}_5 \) layers. The latter layer was modeled by employing two Tauc-Lorentz oscillators. More details on the SE technique and SE modeling can be found in literature.\(^{35} \)

The elemental composition and valence band (VB) spectra were determined by x-ray photoelectron spectroscopy (XPS) using a Thermo Scientific KAI066 spectrometer employing monochromatic Al K\( _\text{α} \) (\( h\nu = 1486.6 \text{eV} \)) x-ray radiation. Rutherford backscattering spectrometry (RBS) and elastic recoil detection (ERD) measurements with a 1.9 MeV He\( ^+ \) beam source were conducted using 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 analyzer, using a Cu K\( _\text{α} \) (\( \lambda = 1.54 \text{Å} \)) 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 and 350°C using the optimized ALD recipe shown in Fig. 1. The film thickness for the initial 500 ALD cycles as-determined by in situ SE is shown in Fig. 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 behavior 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.

The self-limiting saturated growth behavior was confirmed for both the thermal ALD and the PE-ALD processes at a deposition temperature of 200 °C, as shown in Fig. 3. In thermal ALD, as seen in Figs. 3(a)–3(d), \( ^{1}BuN\equiv Nb\left(NEt_{2}\right)_{3} \) precursor saturation was observed at 6 s exposure time when the \( H_{2}O \) 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 \( H_{2}O \) as coreactant saturated at 200 ms of exposure time. In the subsequent step, the APC valve was closed, to make sure that \( H_{2}O \) 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 coreactants and by-products. This purge step saturated at 35 s. In comparison to the literature (where the hot wall reactor was used),\(^{22}\) the coreactant purge step needed longer time to reach saturation due to slow desorption of \( H_{2}O \) from the reaction walls (warm wall at 145 °C), which would otherwise result in parasitic CVD reactions.

In PE-ALD, as shown in Figs. 3(e)–3(h), precursor saturation was observed at 6 s exposure time similar to thermal ALD when the coreactant \( O_{2} \) plasma exposure time was fixed at 6 s. The Ar precursor purge (300 sccm) saturated at 1 s. In the next step, \( O_{2} \) plasma (100 sccm) was used as coreactant and saturation occurred at 2 s. The following coreactant purge step saturated at 3 s. Note that this step was much shorter compared to the purge step in the thermal ALD process, because \( O_{2} \) molecules are purged away rapidly in comparison to the slow desorption of \( H_{2}O \) in the thermal ALD process. At 200 °C, the GPC was \(~0.56 \text{ Å}\), which is higher in comparison to the thermal ALD process \((~0.38 \text{ Å})\). Therefore, PE-ALD with \( O_{2} \) plasma as coreactant enables a
significantly shorter process time through both an enhanced GPC and a strongly reduced purge time.

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 and 350°C. The growth per cycle (GPCSE) was determined by calculating the slope for the last 100 cycles of the in situ SE data shown in Fig. 2. In both processes, the GPCSE was observed to decrease with increasing deposition temperature, as shown in Fig. 4. In thermal ALD, the GPCSE decreases from 0.38 to 0.20 Å for temperatures ranging from 150 to 350°C, whereas in PE-ALD the GPCSE lowers from 0.58 to 0.45 Å with H2O and O2 as coreactants, respectively, using the same precursor 1BuN=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 coreactant 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. on the reaction mechanism using in situ analysis techniques for the same precursor 1BuN=Nb(NEt2)3 with D2O and O3 as coreactants. 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 the case of the O3 process, it was speculated by Tomczak

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

![Fig. 4. (Color online) Growth per cycle (GPCSE) measured using in situ SE (left vertical axis) and deposited Nb atoms per nm2 (GPCRBS) 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 and 350°C.](image)
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 Nb$_2$O$_5$ with O$_2$ plasma. However, in this case, the enhanced GPC observed with O$_2$ plasma could not be explained with this mechanism, as a lower GPC of ~0.45 Å was observed with O$_3$. Similar to other material systems, surface –OH reactive sites could be formed in an O$_2$ plasma, which could explain the enhanced GPC observed for PE-ALD of Nb$_2$O$_5$. Similar behavior was also observed for Al$_2$O$_3$ where PE-ALD with O$_2$ plasma shows higher GPC than thermal ALD with H$_2$O. Thus, alternatively, similar to the reaction mechanism of Al$_2$O$_3$ with O$_2$ plasma. It could also be hypothesized that a ligand reacts with surface –OH reactive site in the first half cycle, while the remaining ligands react with O$_2$ plasma species forming –OH surface groups, and H$_2$O, CO$_x$, NO$_x$ by-products.

The uniformity of both thermal ALD and PE-ALD films was determined using ex situ SE by mapping a ~20 nm thick film over a 200 mm diameter Si wafer (see Fig. 5). The thickness nonuniformity was calculated by dividing the difference between the maximum and the minimum thickness by the average thickness. The nonuniformity in the thermal ALD grown film was around ±3.3%, whereas in the PE-ALD grown film, it was around ±4.4%. In the case of thermal ALD [Fig. 5(a)], the decline in thickness was observed from the upper left to the bottom right. This nonuniformity in thickness was considered to originate from both the precursor and H$_2$O flow direction. In the case of PE-ALD [Fig. 5(b)], the higher thickness was observed in the middle of the wafer. Here, the nonuniformity was attributed to a nonuniform distribution of O$_2$ plasma over a 200 mm diameter substrate as well as the precursor flow direction. Although the uniformity is fair for both processes, it may be further improved by increasing the H$_2$O dose or hold time in the case of thermal ALD and by increasing the O$_2$ plasma dose time in the case of PE-ALD process, and also by further optimizing precursor dose time in both the cases.

B. Film characterization

Self-limiting growth of Nb$_2$O$_5$ was shown for both thermal ALD and PE-ALD in Sec. III A. In this section, the material properties of the Nb$_2$O$_5$ 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 and 350 °C. The O/Nb ratio in Table I shows that the thermal ALD deposited films are substoichiometric with all values being below 2.5 and the O/Nb ratio. The number of deposited Nb atoms/nm$^2$ 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. —, no data.

<table>
<thead>
<tr>
<th>Process</th>
<th>Deposition temperature (°C)</th>
<th>GPC$_{SE}$ (Å)</th>
<th>Refractive index $n_g$ (eV)</th>
<th>$E_g$ (eV)</th>
<th>GPC$_{RBS}$ (at. nm$^{-2}$ cycle$^{-1}$)</th>
<th>Mass density (g cm$^{-3}$)</th>
<th>O/Nb ratio (at. %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Thermal ALD</td>
<td>150</td>
<td>0.39</td>
<td>2.35</td>
<td>3.47</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td></td>
<td>200</td>
<td>0.37</td>
<td>2.37</td>
<td>3.45</td>
<td>0.75</td>
<td>4.35</td>
<td>2.36</td>
</tr>
<tr>
<td></td>
<td>300</td>
<td>0.25</td>
<td>2.40</td>
<td>3.43</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td></td>
<td>350</td>
<td>0.21</td>
<td>2.46</td>
<td>3.36</td>
<td>0.50</td>
<td>4.98</td>
<td>2.22</td>
</tr>
<tr>
<td>PE-ALD</td>
<td>150</td>
<td>0.56</td>
<td>2.36</td>
<td>3.47</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td></td>
<td>200</td>
<td>0.55</td>
<td>2.36</td>
<td>3.47</td>
<td>1.08</td>
<td>4.11</td>
<td>2.48</td>
</tr>
<tr>
<td></td>
<td>300</td>
<td>0.47</td>
<td>2.36</td>
<td>3.47</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td></td>
<td>350</td>
<td>0.44</td>
<td>2.36</td>
<td>3.47</td>
<td>0.87</td>
<td>4.10</td>
<td>2.49</td>
</tr>
</tbody>
</table>
Nb ratio decreases when raising the deposition temperature from 200 to 350 °C. The substoichiometric (Nb₂O₅₋ₓ) nature of the films can be linked to oxygen vacancies, 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.

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 and 350 °C for both the thermal ALD [(a) and (b)] and the PE-ALD [(c) and (d)] processes. All the XPS spectra shown in Fig. 6 were calibrated by setting the carbon C–C bond peak to 284.8 eV in the C1s XPS spectra. In the Nb3d spectrum, as seen in Figs. 6(a) and 6(c), the doublet Nb3d⁵/₂ and Nb3d₃/₂ components are located at ~207.4 and ~210.2 eV, respectively. This corresponds to the Nb⁺⁵ oxidation state with the spin-split orbital components (between Nb3d⁵/₂ and Nb3d₃/₂) of Δ ~ 2.8 eV. An additional doublet at ~1.5 eV toward lower binding energy (BE) at ~205.9 eV is attributed to the Nb⁺⁴ oxidation state. In the O1s spectrum, the peak centered 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 Fig. 6(d) shows that the metal oxide peak center is located at 530.3 eV for both temperatures. In the Nb3d spectrum, the Nb3d₅/₂ component peak center 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 NbO₂ composition. In the case of thermal ALD, for the 200 °C film the Nb3d₅/₂ component peak center shifts to 207.4 eV along with a further broadening (FWHM = 1.23 eV) and a similar shift in the metal oxide peak center to 530.5 eV was observed. The broadening of the FWHM and shift in peak center to higher binding energies have previously been associated with oxygen vacancies in the film. For the 350 °C film, the Nb3d₅/₂ 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 Nb3d₃/₂ 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 substoichiometric nature of thermal ALD deposited Nb₂O₅₋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 350 °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.

XPS 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 Fig. 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 (Eᵥₐ) and Fermi level (Eₓ), as seen in Fig. 7(b), whereas in the PE-ALD films no such trap states were observed. The localized trap states between Eᵥₐ and Eₓ have previously also been observed in various other materials, such as Ta₂O₅ (Ref. 41 and 42) and TiO₂ (Ref. 43) where it was attributed to the presence of oxygen vacancies. The number of trap states...
observed in the thermal ALD films increases with the 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 O₂ plasma compared to H₂O 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.

The refractive index data (at 2.1 eV) shown in Table I were obtained from ex situ SE measurements. In the 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 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 the 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⁺⁺⁺ oxidation states in the films. As the bulk density of niobium oxide at Nb⁺⁺⁺ oxidation state (NbO₂) is higher than it is at the Nb⁺⁺ oxidation state (Nb₂O₅), the presence of small fraction of Nb⁺⁺ 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 the deposition temperature, which is consistent to other observations.

The absorption coefficient 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: (αhv)¹/² ~ (hv – E₀), where α is the absorption coefficient, hv is the photon energy, E₀ 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 [(αhv)¹/² vs hv] was estimated by extrapolating the linear region of the curve to zero absorption. The tail region below the optical band gap (linear region) in Fig. 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 the case of thermal ALD films, the band gap was ~3.5 eV as shown in Table I, but a small shift toward lower band gap was observed with increasing deposition temperature corresponding to oxygen vacancies present 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

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**Fig. 7.** (Color online) Valence band spectra for (a) thermal ALD and (c) PE-ALD films deposited at temperatures between 150 and 350 °C. Plot (b) shows a magnified part of the inset shown in (a).
oxygen vacancies in the films was further confirmed by a widening of the tail region toward 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 coreactants, respectively. The self-limiting saturated growth was confirmed for both processes at 200 °C, respectively. The self-limiting saturated growth was confirmed for both processes at 200 °C, and the deposition temperature did not have any effect on the optical band gap of the films.

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 IOPT, UK, for the assistance with uniformity measurements. This work was supported by the European Research Council (Grant Agreement No. 648787). The work of author J. Melskens was supported by the Netherlands Organisation for Scientific Research under the Dutch TTW-VENI Grant No. 15896.

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 and 350 °C.