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Photoassisted atomic layer deposition of oxides employing alkoxides as single-source precursors

Ville Miikkulainen,^{1,a)} Katja Väyrynen,^{1,b)} Kenichiro Mizohata,² Jyrki Räisänen,² Marko Vehkamäki,¹ and Mikko Ritala¹

¹Department of Chemistry, University of Helsinki, A.I. Virtasen aukio 1, FI-00560 Helsinki, Finland

²Department of Physics, University of Helsinki, Pietari Kalmin katu 2, FI-00560 Helsinki, Finland

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Photoassisted atomic layer deposition (photo-ALD) is a variant of an ALD process where photons of ultraviolet or visible range are utilized to supply energy to, and to modify, the ALD surface reactions. In this paper, the authors report photo-ALD processes for titanium, zirconium, hafnium, niobium, and tantalum oxides by employing the corresponding liquid, volatile metal alkoxides as precursors in a single-source approach, i.e., without any additional reactant. The ALD reactor was equipped with a light source delivering photons over a continuous spectrum between 190 and 800 nm in wavelength. The deposition sequence consisted of a precursor pulse, a purge, a photon exposure, and another purge. The process characteristics and film properties were explored. Nb₂O₅ and Ta₂O₅ films were amorphous, whereas TiO₂, ZrO₂, and HfO₂ showed an amorphous and polycrystalline structure, depending on the deposition conditions. With photo-ALD, area-selective deposition is realized by shadow masking. The character of the growth process, i.e., whether the chemistry is driven by photo-lytic or photothermal mechanism, is discussed based on deposition experiments with patterned substrates and optical filtering. Electrical characterization of photo-ALD HfO₂ shows promising dielectric properties. *Published by the AVS.* <https://doi.org/10.1116/1.5124100>

I. INTRODUCTION

Atomic layer deposition (ALD) is a thin film deposition technique based on alternately repeated, saturative, and irreversible gas-solid reactions on the surface of the solid substrate. Typically, ALD sequence is built on cyclic repetition of pulse and purge of two precursors so that the deposition reactions take place on the surface in a self-limiting manner. The digital nature of the deposition process enables accurate control over the film thickness by adjusting the number of deposition cycles.¹ The self-limiting and saturative reactions make ALD films extremely conformal and uniform over large area substrates. However, the advantageous property of ALD to deposit films uniformly everywhere turns into a challenge if the film is desired only on selected areas.

Many applications require lateral control of the deposited thin film. Selective-area ALD (S-ALD) can be realized by controlling the chemical interaction between the precursors and the substrate. This can be achieved (1) by the passivation of the substrate areas where film deposition is not wanted, (2) by activation of areas where film deposition is wanted, or (3) by using inherently selective deposition chemistries. The applicability of these approaches depends on the substrate and the surfaces where the S-ALD is considered as well as the ALD chemistries available for the film deposition.

Passivation layers used for S-ALD in approach (1) are typically self-assembled monolayers (SAMs) and polymers.²⁻⁴

Oxides nucleate readily on most surfaces, however, and especially SAMs suffer from degradation, and the selectivity is eventually lost when the S-ALD process is continued further. Furthermore, after S-ALD, the passivation layers need to be removed. Approach (2) by activation layers requires inherent differences in nucleation on areas in question, and this approach is at present mostly applicable for metal films that have a much higher nucleation preference on metallic surfaces than on others.^{5,6} With this approach for S-ALD, removal or etching of layers after S-ALD is not required. As a result, there are fewer processing steps in the manufacturing flow. In the most efficient approach for S-ALD (3), inherently selective ALD chemistry is employed on a substrate surface that contains different materials such as conductors and insulators, and the film grows solely on the desired material(s). This is realized by choosing an appropriate ALD chemistry for the targeted materials without any passivating or activating layers. This purely bottom-up processing of films reduces the overall process steps to the minimum, is self-aligned, and thus improves the device yield. Inherent selectivity is a very attractive approach for S-ALD, but due to the challenging control over the surface chemistry, mainly metals can be deposited selectively this way.⁷

Besides the methods listed above, S-ALD can be realized by photoassisted ALD (photo-ALD) where photons at ultraviolet (UV) or visible range supply energy to the deposition reactions. S-ALD can be realized simply by shadowing the areas where deposition is not wanted. While the resolution is not enough for the state of the art microelectronic devices, photo-ALD and shadow masks offer a promising approach to S-ALD for microelectromechanical systems and sensor applications to, e.g., protect contact areas or backsides of the

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^{a)}Present address: School of Chemical Engineering, Aalto University, Kemistintie 1, FI-02150 Espoo, Finland; electronic mail: ville.miikkulainen@aalto.fi

^{b)}Present address: Beneq Oy, Olarinluoma 9, FI-02200 Espoo, Finland.

substrates. Due to the challenging ALD chemistry and construction of the photo-ALD reactors, there is only a limited number of papers reporting photo-ALD processes. The studied materials include GaAs, ZnO, Ta₂O₅, ZrO₂, BN, TiO₂, and Al₂O₃.^{8–20}

Metal alkoxides are a useful class of precursors for metal oxide photo-ALD. Lee *et al.* deposited Ta₂O₅ from tantalum ethoxide.¹⁵ They studied two process approaches utilizing a UV lamp with 185-nm emission. The single-source approach, using a process sequence of Ta(OEt)₅ purge irradiation, resulted in a growth rate of 0.26 Å/cycle, which increased to 0.37 Å/cycle when O₂ was used as a reactant during the irradiation. For both approaches, the growth rate was fairly constant within the 200–300 °C photo-ALD process window. Recently, we published a preliminary report on photo-ALD of oxides using the single-source approach.²¹ Lee *et al.* demonstrated ZrO₂ photo-ALD at a low deposition temperature of 20 °C from zirconium *tert*-butoxide.¹⁸ In their process approach, water was pulsed together with UV exposure (Xe lamp with the main emission peak at 254 nm). Their process is an example of enhancement of an existing ALD process with photons, as the metal precursor and water also deposit ZrO₂ without UV, even though at higher temperatures. Chalker *et al.* reported photo-ALD of TiO₂.²⁰ Titanium isopropoxide was employed as the titanium precursor and O₂ was fed during the UV exposure at a low deposition temperature of 60 °C. They used a deuterium lamp as the UV source with emission peaks at 125 and 160 nm. In addition to TiO₂, photo-ALD of Al₂O₃ was reported using trimethylaluminum as an aluminum precursor and O₂ fed simultaneously with the UV excitation. Interestingly, S-ALD was facilitated by masking, but with a poor feature resolution. That was concluded to result from the gas phase diffusion of photoexcited, reactive O₂ to the shadowed area contributing to the Al₂O₃ deposition there as well. Obviously, any gas phase photochemistry needs to be excluded if S-ALD is the target with photo-ALD.

Recently, Henke *et al.* reported flash-enhanced ALD (FEALD), an approach of the same type as photo-ALD.²² In FEALD, high-intensity pulsed visible-infrared light is employed to deliver short pulses of heat on the surface and thereby drive the surface reactions. The essential difference of FEALD from photo-ALD is that the light has longer wavelengths with the aim of heating the surface and actually avoiding photolysis. In photo-ALD, in turn, photolysis is the desired mechanism for facilitating reduced deposition temperatures and S-ALD. FEALD has been reported to deposit Si, Ru, and Al₂O₃.^{22,23}

In the present study, we report photo-ALD of several metal oxides employing metal alkoxides and the single-source approach, i.e., the alkoxide precursor serving as both the metal and oxygen source. Since the photochemistry takes place solely on the surface, this approach facilitates S-ALD by shadow masking. The key properties of the deposited metal oxides were studied, and the mechanisms of the growth processes were investigated. The films had mostly low levels of carbon and hydrogen impurities, and they showed interesting structural and promising electrical properties.

II. EXPERIMENT

A. Film deposition

Substrates for the film deposition were either 150 mm Si (100) wafers or coupons cut from them. A specially modified Picosun™ R-200 reactor was used for photo-ALD. An RC-800 series pulsed xenon discharge light source from Xenon Corporation was used as the light source. The lamp produces high-intensity pulsed light with a broad and continuous wavelength spectrum from 190 to 800 nm. The pulse energy was 207 J/pulse, as specified by the lamp's manufacturer. The pulsing frequency of the lamp was 5 Hz, if not otherwise stated. The typical duration of a single pulse from this lamp type is in the order of a few hundred microseconds. Behind the light emitting bulb, there is a reflector directing most of the emission toward the substrate, yet no well-defined focusing nor collimation is used. Due to these optical characteristics of the lamp, the whole photo-ALD reactor interior including the whole substrate is irradiated. The optical window between the reactor and the light source was made of fused silica (Finnish Specialglass) transmitting light down to 190 nm in wavelength. The window was purged with N₂ to prevent film deposition on it. No gate valve or other physical shutter is needed since the pulsing of light can be controlled and synchronized through the ALD reactor software. The substrate holder temperature was monitored with a thermocouple. The reactor pressure was in the order of 10 mbar during the operation. Schematics of the photo-ALD reactor are presented in Fig. 1.

Metal precursors were titanium isopropoxide [97% Ti(OⁱPr)₄, Sigma-Aldrich], zirconium *tert*-butoxide [99% Zr(O^tBu)₄, Strem], hafnium *tert*-butoxide [99.9% Hf(O^tBu)₄, Strem], niobium ethoxide [99.9% Nb(OEt)₅, Strem], and tantalum ethoxide [99.99% Ta(OEt)₅, Strem], which were evaporated from a PicoHot™ source. The precursor source operates with the carrier gas loading and release principle to enable a more efficient precursor delivery from the source to the reaction chamber. During the source operation cycle, first,

Fig. 1. Schematics for photo-ALD reactor used in this study. Lamp-to-substrate distance is 255 mm.

the source container is loaded with a short carrier gas pulse, and then the precursor vapor together with the loaded carrier gas is released to the source line. Vanadyl isopropoxide [$\text{VO}(\text{O}^i\text{Pr})_3$, Sigma-Aldrich] was also tested as a photo-ALD precursor for vanadium oxide, but no conditions for controllable growth were found.

B. Film characterization

Film crystallinity and crystal phases were characterized by x-ray diffraction (XRD, Panalytical X'Pert Pro) with parallel beam optics and grazing incidence measurement geometry (incidence angle 1.0°). Scanning electron microscopy (SEM, Hitachi S-4800) was used for analyzing film morphology and, from the cross sections, film conformality. Film thicknesses were determined by UV-VIS reflectometry or x-ray reflection (XRR). For thickness analyses, films with 4000–5000 photo-ALD cycles were deposited to obtain samples with optimal thickness (12–160 nm) for XRR. Thinner samples were also analyzed by XRR with good fitting of the data. Estimated error in thickness values by XRR is less than 0.5 nm. XRR was also used for analyzing the densities of the deposited films. Time-of-flight elastic recoil detection analysis (ToF-ERDA) was used to characterize the composition of the films, including their elemental depth profiles. Dielectric properties of the oxide films were characterized by current-voltage (I-V) and capacitance-voltage (C-V) methods. A metal-insulator-metal capacitor structure was made by depositing a continuous platinum film as a bottom electrode on silicon by electron beam evaporation (EBE), a 50 nm photo-ALD HfO_2 as an insulator layer, and shadow-mask patterned EBE aluminum as a top electrode. The area per capacitor was $2.04 \times 10^{-7} \text{ m}^2$, as defined by the patterned top electrode.

III. RESULTS AND DISCUSSION

Photo-ALD processes were realized for TiO_2 , ZrO_2 , HfO_2 , Nb_2O_5 , and Ta_2O_5 with the single-source approach, i.e., without any additional oxygen source or other reactants besides the metal alkoxide that thus served as both the metal and oxygen source. The process sequence was 1.6 s alkoxide pulse–5 s purge–UV exposure–purge. The source temperatures for alkoxides, as reported below for each, were taken from optimized thermal ALD process conditions with water as the other reactant and are expected to provide saturative conditions in photo-ALD as well. The purge time right after the UV exposure was usually 0.1 s. Also, 1.0 s purge after the UV exposure was studied in the case of the Ta_2O_5 process, and no effect of that purge time to film uniformity or film thickness was found. Such a short purge time is reasonable in this case, considering that during the UV exposure, only volatile reaction products are released from the surface without feeding any precursor, in contrast to the conventional ALD precursor pulse. Purging of the released products only is much more efficient in this case compared to purging the products and, more importantly, the surplus of unreacted precursor vapor in conventional ALD. The pulsed precursor has

significantly higher concentrations in the gas phase than the released products, requiring long purge times. Also, any failure to purge out unreacted precursor molecules can lead to chemical vapor deposition type reactions during the next precursor pulse. In the case of photo-ALD, with, e.g., 30 flashes, the UV exposure time is 6 s at 5 Hz pulsing frequency, and the purging of the released products starts from the very first flash. Thereby, the effective purge time for UV exposure is much longer than the 0.1 s after the UV exposure.

A. Tantalum oxide

$\text{Ta}(\text{OEt})_5$ was evaporated at 140°C in a PicoHot™ source. First, the saturation of the film growth with respect to UV exposure was demonstrated, as illustrated in Fig. 2. The growth rate saturates at $0.12 \text{ \AA/cycle}$ with 30 flashes. The growth rate is lower than that reported by Lee *et al.* ($0.26 \text{ \AA/cycle}$ both at 220 and 260°C) for the same precursor in photo-ALD, most likely due to different UV emissions employed. Our lamp has a broad spectrum from 190 to 800 nm, whereas Lee *et al.*¹⁵ utilized a lamp with 185 nm emission. The lamp or emission details were not, however, described in their paper, but it is evident that the different spectra lead to different photochemistry and thereby result in different growth rates of Ta_2O_5 . Growth rates of both photo-ALD processes are lower than the growth rate in the corresponding thermal ALD process with water as the oxygen source ($0.4 \text{ \AA/cycle}$).²⁴ This can be explained by larger steric hindrances between $\text{Ta}(\text{OEt})_5$ adsorbates in photo-ALD, whereas in the thermal process, some of the ligands may be released in reactions with hydroxyl groups already during the $\text{Ta}(\text{OEt})_5$ adsorption. Two consecutive pulses of $\text{Ta}(\text{OEt})_5$ in place of one deposited the same thickness of Ta_2O_5 confirming saturation with respect to $\text{Ta}(\text{OEt})_5$.

Growth rate as a function of deposition temperature was studied for accessing the feasible temperature range for the process. At 200°C , the growth rate was $0.075 \text{ \AA/cycle}$, and at 150°C , $0.035 \text{ \AA/cycle}$. This temperature dependence differs from the study reported by Lee *et al.*¹⁸ where the growth rate

Fig. 2. Photo-ALD Ta_2O_5 growth rate as a function of UV flashes at a deposition temperature of 245°C (5 Hz pulsing frequency).

FIG. 3. Ta_2O_5 film thickness as a function of the number of photo-ALD cycles at the deposition temperature of 245°C , with 30 UV flashes (5 Hz pulsing frequency) per cycle.

remained constant, $0.24 \text{ \AA/cycle}$, over the temperature window between 200 and 300°C . The different growth rates likely stem from the different UV employed for the photo-ALD processes. The film thickness increased linearly with the number of photo-ALD cycles (Fig. 3).

The key fundamental question related to the growth mechanism in photo-ALD is whether the process is driven by electronic transitions (photolytic mechanism) or heat generated by the light absorption in the substrate (photothermal mechanism). To study the photon interaction mechanism, two experiments were performed. In the first setup, the Ta_2O_5 film was deposited on an Si substrate with pillared structures. The Si pillars were perpendicular to the surface and parallel to the UV flux. The resulting film is illustrated in Fig. 4. It is evident that the film thickness at the bottom of the structure is the same as on planar silicon (45 nm by XRR, Fig. 3), but on

the vertical surfaces, the film is significantly thinner. If the mechanism was photothermal, the heat generated by the photon absorption would be expected to be isotropically conducted throughout the pillars resulting in the same film thickness on the horizontal and vertical surfaces. This type of an approach was recently reported by Henke *et al.* when they deposited several materials by FEALD employing a photon source with emission in the visible and infrared range.^{22,23} In FEALD, infrared radiation is employed to heat the substrate (photothermal deposition), whereas in photo-ALD, UV radiation is employed to electronically excite the surface species (photolytic deposition). In contrast to our approach, FEALD aims to thermalize surface reactions with the heat delivered by the intense visible and, especially, infrared light. Based on the high thermal conductivity of silicon, Henke *et al.* concluded that there should be no difference in temperature down to at least $6 \mu\text{m}$ in patterned silicon. In our case, however, it appears from Fig. 4 that there is a distinct difference within a few hundred nanometers from the pillar tops as we compare the film thicknesses on the bottom and on the vertical walls.

In case of a photolytic mechanism, the photon exposure depends on the angle of incidence and would lead to anisotropic growth. Film thickness would, in other words, have an angular dependence on the incoming photon direction, as is the case in the present study supporting the photolytic mechanism over the photothermal one.

In the second experiment, to obtain further information on the growth mechanism, photo-ALD of Ta_2O_5 was done with 1-mm thick soda lime and borosilicate glass slides above the silicon substrate to block the short end wavelengths from the lamp emission. The slide-to-substrate distance was around 0.5 mm. Soda lime and borosilicate glasses have cutoff wavelengths at around 300 and 350 nm, respectively. It was found that both glass slides effectively block the photo-ALD of Ta_2O_5 as no film was deposited on the area under the glasses. From this finding, we can first conclude that apparently the emission between 190 and 350 nm in wavelength is responsible for the photo-ALD of Ta_2O_5 . Accordingly, most of the emission spectrum has no contribution to the photo-ALD. If the photo-ALD process was driven by a photothermal mechanism, one would expect only a modestly thinner film under the glass slides since most of the spectrum delivering heat for the deposition reactions is transmitted onto the substrate. The findings from the experiments with pillared silicon and optical filtering with glass slides allow us to deduce that a photolytic mechanism is more plausible than a photothermal one.

Area-selective deposition of Ta_2O_5 on a 150-mm Si wafer was realized by photo-ALD employing a set of two aluminum masks placed 0.3 mm above the wafer resulting in a University of Helsinki emblem (Fig. 5). It should be again noted that the spatial resolution does not allow transistor-level patterning, at least with this relatively crude mask setup, but could be used for protecting the metal contact areas, for example. The purpose of the area-selective deposition experiment here is to provide a proof-of-concept, and optimization of the mask would improve the spatial resolution of the Ta_2O_5 features. As qualitatively analyzed by energy-dispersive X-ray spectroscopy line scanning

FIG. 4. Cross section SEM on photo-ALD Ta_2O_5 film (245°C , 4000 cycles, 30 flashes, 5 Hz pulsing frequency) deposited on Si with a pillared structure: (a) overview, (b) close-up of the bottom of the structure, (c) cut ALD-coated Si pillar, and (d) close-up of the Si pillar.

FIG. 5. Selective deposition of Ta_2O_5 by photo-ALD (245 °C, 30 flashes, 5 Hz pulsing frequency) deposited in two successive depositions with (a) two shadow masks on (b) 150-mm Si wafer. Substrate to wafer distance was 0.3 mm. Diameter of both masks was 150 mm. Photograph obtained with a digital camera in normal laboratory light.

across the edges of the areas of the selectively deposited Ta_2O_5 , the horizontal scale from full film thickness to no film deposited was in the order of tens of micrometers.

The densities of photo-ALD Ta_2O_5 films at all studied deposition temperatures (150, 200, and 245 °C) were 7.7 g/cm^3 , which is below the density of crystalline, orthorhombic Ta_2O_5 , 8.2 g/cm^3 , as expected for an amorphous material. Thermal ALD Ta_2O_5 films are amorphous too.²⁴ The densities of photo-ALD Ta_2O_5 films appear to be at the same level as the densities of Ta_2O_5 films deposited by conventional thermal ALD from $\text{Ta}(\text{OEt})_5$ combined with water or ozone: Kim *et al.*²⁵ reported density values of 7.30 and 7.85 g/cm^3 for films deposited at 300°C with water and ozone, respectively, as measured by XRR as in our case. Kukli *et al.*²⁴ determined film density by comparing optical thickness to RBS-derived thickness, and they found that the $\text{Ta}(\text{OEt})_5\text{-H}_2\text{O}$ process deposits Ta_2O_5 films with a density close to 8.2 g/cm^3 at 325°C , but the density was 11% less for the films deposited at 250°C .

The total impurity content in the photo-ALD Ta_2O_5 film is 8.6 at. % (Table I), which is somewhat higher than for thermal ALD Ta_2O_5 from $\text{Ta}(\text{OEt})_5$ and H_2O by Matero *et al.* They reported TOF-ERDA data with less than 2.6 at. % of carbon and hydrogen.²⁶ These findings show that our setup for photo-ALD provides an efficient system for deposition of high-quality films, also selectively by shadow masking.

TABLE I. Elemental composition (at. %) of photo-ALD oxide films as measured by TOF-ERDA.

Material	TiO_2	ZrO_2	HfO_2	Nb_2O_5	Ta_2O_5
$T_{\text{dep}} (^\circ\text{C})$	225	150	150	245	250
M	34.3	29.5	28.6	28.4	25.0
O	64.7	61.3	66.8	67.3	66.4
C	0.08	2.6	1.6	1.2	1.4
H	0.9	6.3	2.7	3.2	7.2
F	—	0.3	0.3	—	—
Cl	0.07	—	—	—	—
Stoich.	$\text{TiO}_{1.9}$	$\text{ZrO}_{2.1}$	$\text{HfO}_{2.3}$	$\text{Nb}_2\text{O}_{4.7}$	$\text{Ta}_2\text{O}_{5.3}$

B. Niobium oxide

Photo-ALD process was studied for Nb_2O_5 analogously to Ta_2O_5 . Evaporation temperature for $\text{Nb}(\text{OEt})_5$ was 130°C . Deposition experiments were done at temperatures between 180 and 245°C . The growth rate increases as a function of deposition temperature, as illustrated in Fig. 6. The growth rate varies between 0.03 and $0.09 \text{ \AA/cycle}$, which is notably lower than in thermal ALD with $\text{Nb}(\text{OEt})_5$ and water ($0.3 \text{ \AA/cycle}$).²⁷

X-ray diffraction demonstrated that the films were amorphous, similar to their thermal ALD analog.²⁷ It is also evident that the film density, as determined by x-ray reflection, increases as a function of deposition temperature. The densities of the photo-ALD Nb_2O_5 films are unexpectedly high and range from 4.75 to 5.10 g/cm^3 (Fig. 6). These values are all above the density of crystalline, monoclinic Nb_2O_5 (4.60 g/cm^3) but closer to the density of orthorhombic Nb_2O_5 (4.98 g/cm^3) but still clearly below the density of NbO_2 (5.90 g/cm^3). The observed densities here are also higher than densities between 3.9 and 4.5 g/cm^3 reported for thermal ALD Nb_2O_5 by Blanquart *et al.*²⁸ The high density is in line with the stoichiometry derived from the TOF-ERDA composition in Table I: the film is slightly oxygen deficient ($\text{Nb}_2\text{O}_{4.7}$). This may indicate that Nb has partially reduced from +V to +IV; however, analysis beyond the scope of this

FIG. 6. Photo-ALD Nb_2O_5 growth rate and film density as a function of deposition temperature (60 UV flashes, 12.5 Hz pulsing frequency).

FIG. 7. Photo-ALD Nb₂O₅ growth per cycle as a function of number of UV flashes at 225 °C (12.5 Hz pulsing frequency).

FIG. 8. Photo-ALD TiO₂ growth rate as a function of deposition temperature (30 UV flashes, 5 Hz pulsing frequency).

study by x-ray photoelectron spectroscopy or x-ray absorption spectroscopy is required to confirm the Nb reduction.

In the case of Nb₂O₅, contrary to Ta₂O₅, the growth does not saturate as a function of number of flashes, as seen in Fig. 7. This might stem from the Nb reduction mechanism suggested by the high density of the deposited material, which also possibly changes as a function of flashes similar to what was seen for deposition temperature; yet, this finding calls upon more detailed studies to reveal the underlying mechanism. Considering the low growth rate of photo-ALD compared to thermal ALD with Nb(OEt)₅, it is also likely that in photo-ALD, surface reactions are not efficient enough to remove all the ligands within the studied range of UV exposure.

C. Titanium dioxide

Titanium dioxide photo-ALD was studied employing Ti(OⁱPr)₄ as a precursor evaporated at 60 °C. The film growth was studied as a function of temperature (Fig. 8) and number of UV flashes (Fig. 9). The temperature window for thermal ALD with Ti(OⁱPr)₄ and water as reactant in this photo-ALD reactor is 150–300 °C.

At 200 and 225 °C, the growth rates are close to each other, but at 245 °C, the growth rate is notably higher. Similar to the Nb₂O₅ photo-ALD process discussed above, it was found that the film growth does not fully saturate as a function of UV flash count (Fig. 9). These growth rates of below 0.1 Å/cycle are lower than has been reported for thermal ALD with Ti(OⁱPr)₄ and water (0.3 Å/cycle).²⁹ Also similar to Nb₂O₅, the stoichiometry of the TiO₂ film is oxygen deficient (Table I). The films were pure with 1% of total impurity content (Table I).

Similar to the Ta₂O₅ process, the UV lamp emission wavelength region contributing to the TiO₂ photo-ALD was studied by placing slides of soda lime and borosilicate glasses above the substrate to filter off the emission below

350 nm. It was found that no TiO₂ was deposited on areas shadowed by the glasses. The effective wavelength region was thus concluded to be 190–350 nm for photo-ALD of TiO₂. As for Ta₂O₅, this speaks for the photolytic over the photothermal mechanism.

The crystalline phase of the photo-ALD TiO₂ films was somewhat unexpected considering the deposition temperature range used. The films were either amorphous or crystalline in the rutile phase, as seen in Fig. 10. It is also evident that the number of UV flashes has an effect on the crystalline phase: at 225 °C, the films deposited with 20 and 30 flashes show no distinct crystalline features but the film deposited with 40 flashes shows the rutile phase clearly. This change may be caused either by a better completion of the reactions allowing the higher purity film to crystallize or by photoinduced crystallization. The density of a film deposited at 245 °C, as determined by XRR, was 4.1 g/cm³,

FIG. 9. Photo-ALD TiO₂ growth per cycle as a function of number of UV flashes at 225 °C (5 Hz pulsing frequency).

FIG. 10. X-ray diffractograms of TiO_2 deposited at various temperatures and with different flash counts (5 Hz pulsing frequency).

which is much closer to the bulk density of the rutile (4.23 g/cm^3) than the anatase (3.78 g/cm^3) phase. Typically, ALD TiO_2 films deposit as amorphous or crystalline anatase phase at temperatures below about 300°C .¹ The rutile phase has been reported for ALD TiO_2 films at high deposition temperatures or for rutile-structured or other lattice-matching substrates. In photo-ALD, the unique reaction mechanism, high density, and slight oxygen deficiency in TiO_2 appear to promote the rutile phase formation. At this stage, the reaction mechanism remains to be studied in future experiments, but it obviously is largely different from those in typical thermal ALD processes. This is an interesting finding from the microelectronics application point of view keeping in mind that rutile TiO_2 has a high dielectric constant up to 160. Oxygen deficiency is expected to result in high leakage current density. Leakage current can be suppressed by nanolaminating TiO_2 films with an amorphous material such as Al_2O_3 or by postdeposition annealing in oxygen. However, with the novel photo-ALD approach presented here, dense and very pure rutile TiO_2 can be deposited area-selectively at a low temperature.

D. Zirconium and hafnium dioxide

Zirconium and hafnium *tert*-butoxides [$\text{Zr}(\text{O}^i\text{Bu})_4$ and $\text{Hf}(\text{O}^i\text{Bu})_4$] were employed in the experiments on photo-ALD of ZrO_2 and HfO_2 , respectively. Both precursors were evaporated at room temperature. Film growth was studied at 150°C and 245°C employing 5000 photo-ALD cycles. At 150°C , the growth rates of both oxides were below 0.1 Å/cycle , and at 245°C , the growth rates were 0.25 and 0.32 Å/cycle for ZrO_2 and HfO_2 , respectively. XRD analysis of the films deposited at 245°C showed (Fig. 11) that ZrO_2 is mostly in the cubic phase, while minor amounts of the monoclinic phase cannot be fully excluded due to the overlapping reflections. The HfO_2 film, in turn, is monoclinic. Broadness of the reflections from both materials indicates that the crystallite size is small compared to the common ALD HfO_2 and ZrO_2 films at a thickness range of over 100 nm . It is

FIG. 11. XRD on photo-ALD: (a) ZrO_2 and (b) HfO_2 films deposited at 245°C with 5000 cycles.

moreover noteworthy that ZrO_2 shows a cubic phase for such a thick film of 125 nm , as this phase is usually found only in very thin ALD films. The cubic phase is typically transformed into the tetragonal and then to the monoclinic phase as ZrO_2 film is deposited thicker.¹ Most likely, the small crystallite size stabilizes the tetragonal phase in the photo-ALD ZrO_2 as it does in thin thermal ALD ZrO_2 films. The fundamentally different mechanism of the photo-ALD compared to the thermal ALD apparently promotes the formation of nanocrystalline materials that is favorable to the tetragonal phase.

The densities of both of these materials, as studied by XRR, were unexpectedly low considering the typical values obtained for thermal ALD films. The measured densities for the photo-ALD HfO_2 were 6.7 and 7.7 g/cm^3 at 150 and 245°C , respectively. For comparison, a density of

FIG. 12. SEM micrographs on photo-ALD: (a) ZrO_2 and (b) HfO_2 films deposited at 245 °C with 5000 cycles.

9.23 g/cm^3 has been reported for the HfO_2 deposited from alkylamide precursors and water.³⁰ The photo-ALD ZrO_2 showed a similar trend: its density was 4.2 and 4.6 g/cm^3 at 150 and 245 °C, respectively. These values are likewise lower than the ones reported for the thermal ALD ZrO_2 deposited from alkylamide precursors and water (5.85 g/cm^3).³⁰ Top-view SEM (Fig. 12) shows that both films are rough, and considering the small crystallite size and low density observed by the x-ray characterization, the films are likely porous. Also, ZrO_2 film has cracks between some of the crystallites that could be an indication of, e.g., crystalline phase changes in

the course of deposition. These are the most plausible causes for the low density, as the impurity levels are low (Table I) and the films are polycrystalline.

From the microelectronic application point of view, ZrO_2 and HfO_2 are important materials for high-k dielectrics. After briefly aging the film with a 5 V bias, a stable capacitance of 420 pF was observed for the test capacitor at 10 kHz frequency with a dielectric loss of 0.022. Dielectric constant calculated from these values was 11.6, which compares reasonably well to the values between 12 and 17 reported for HfO_2 films deposited from Hf alkoxides and water by thermal ALD.³¹ During aging, there was a clear hysteresis, but after aging, the hysteresis was negligible, which is anticipated for our metal-insulator-metal test structure with no expected polarization. Considering the nanocrystalline and seemingly porous structure of the film, this is a promising result and calls for further optimization of the photo-ALD HfO_2 and ZrO_2 processes for improved properties for these films. Importantly, the possibility to deposit these high-k thin film materials area selectivity opens up new application possibilities.

IV. SUMMARY AND CONCLUSIONS

The present study provides a proof-of-concept for depositing titanium, zirconium, hafnium, tantalum, and niobium oxides from the corresponding volatile metal alkoxides by photo-ALD with a single-source approach. The main findings are summarized in Table II. The resulting films are of high purity and mostly dense when compared to the films deposited by thermal ALD with water as another reactant. Regarding the mechanism of the photo-ALD processes, the surface chemistry was concluded to be driven by electronic transitions rather than heat delivered by photons, i.e., the deposition process appears to be photolytic rather than photothermal. Moreover, we showed that the photolytically effective wavelength range in our experimental setup is 190–350 nm. As the photochemistry takes place on the surface only, not in the gas phase, area-selective growth can be realized by shadow masking. We successfully demonstrated this, yet the feature resolution was limited due to the simple mask design and uncollimated light source. Even if this approach does not allow device-level patterning, it could be used for protecting contacts or the backside of the wafer from the film growth. The exploratory results presented here serve as an opening for more detailed studies in the interesting and emerging field of photo-ALD.

TABLE II. Summary of the main findings from this study.

Material	Precursor	Deposition temperatures studied (°C)	Growth rate range (Å/cycle)	Crystallinity/crystalline phase	Material property anomalies found
Ta_2O_5	$\text{Ta}(\text{OEt})_5$	150–245	0.035–0.12	Amorphous	None
Nb_2O_5	$\text{Nb}(\text{OEt})_5$	180–245	0.03–0.09	Amorphous	Oxygen deficient, high density
TiO_2	$\text{Ti}(\text{O}^i\text{Pr})_4$	200–245	0.06–0.12	Amorphous/rutile	Oxygen deficient, rutile phase, high density
ZrO_2	$\text{Zr}(\text{O}^i\text{Bu})_4$	150–245	0.1–0.25	Cubic (monoclinic)	Cubic phase
HfO_2	$\text{Hf}(\text{O}^i\text{Bu})_4$	150–245	0.1–0.32	Monoclinic	Low density

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