Atomic layer deposition chemistry, mechanisms and related physical properties of high permittivity dielectric oxides.

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Introduction

Atomic layer deposition (ALD) is recognized as a gentle thin film growth technique suited for the deposition of ultrathin layers for advanced microelectronic applications such as gate dielectrics [1]. ZrO₂ and especially HfO₂ based dielectrics are herewith considered as the most prospective candidates for the next generation gate oxides. ZrO₂ is known as the material having higher permittivity (20-25) compared to HfO₂ (12-16) [2], whereas the HfO₂ has higher stability in contact to silicon [3]. ZrO₂ and HfO₂ can be grown by atomic layer deposition (ALD) via surface exchange reactions commonly occurring during alternate adsorption and hydrolysis of the metal precursors such as HfCl₄ and ZrCl₄ [4].

The chemical similarity between HfO₂ and ZrO₂ is recognized. In the work HfO₂ and ZrO₂ will be treated together, assuming and relying on the similarities of their precursor chemistries and considering the examples from particular precursor families examined as representatives for both HfO₂ and ZrO₂.

Our studies have been directed to the examination of alternative chemical routes to these oxides and measurements of basic physical properties of the resulting films. Since the precursor used should have low reaction barrier to react at low temperatures, be thermally stable, not to etch films or result in etching reaction products, the studies on precursors and related changes in ALD mechanisms [5] are the main target and issue of our research. In this paper, some comparative results obtained during the evaluation of the performance of precursor systems and film properties will be reported.

Results and discussion

Halides

Halides are the conventional solid Hf and Zr precursors suitable for ALD of dense polycrystalline HfO₂ and ZrO₂ films. Similar deposition time parameters as ALD cycle times can be used in the process for the two halide precursors, chlorides and iodides [6], resulting in comparable film growth rates (0.5-1.0 nm/cycle). Low vapour pressure necessitates rather high evaporation temperatures: for chlorides 150-160 °C (HfCl₄, ZrCl₄), and for iodides 190-195 °C (HfI₄) or 200-220 °C (ZrI₄). HfCl₄ and ZrCl₄ enable the growth of flat films over quite a wide temperature range of 160-900 °C [7,8]. High evaporation temperatures together with the ability of halides to bind water cause instabilities in the precursor partial pressure and particle transport in the reactor. Moreover, the surface reaction product HCl can poison the surface adsorption sites by reacting with functional OH-groups and block the sites against oncoming halide adsorption, causing profiled film thickness [9]. Significant thermal decomposition of HfCl₄ has not been observed in ALD reactor. At the same time, the weaker metal-iodide bond strength compared to the metal-chloride bond strength likely enables fast but slowly saturating adsorption of iodide, accompanied by slow release of iodine in addition to HI released during reactions with surface hydroxyls. This is supported by the monotonous long-term increase in the surface mass density during HfI₄ adsorption recorded by quartz crystal microbalances [10]. At higher temperatures exceeding 500 °C more intense decomposition takes place, causing significant thickness profiles.

The apparent refractive indexes and permittivities of the HfO₂ films grown from halide precursors have been similar, 2.03-2.10 and 12-16, respectively. For ZrO₂, it has been noticed that the effective permittivity increases with the growth temperature in the case of ZrCl₄ up to 22-23 above 300 °C [11], whereas the decrease in the permittivity from 22-24 to 13-14 has been observed in the case of ZrI₄ at growth temperatures ranging from 350 to 500 °C [12]. This can be connected to the decomposition of iodide on surface and intense crystallization with increasing void density. Naturally, the crystallization somewhat increases in the case of HfCl₄ as well, but the dispersion in the films grown in the temperature range of 500-600 °C has been less pronounced. In the case of both halide precursors, hysteresis in capacitance-voltage (C-V) curves tends to change its direction from counterclockwise to clockwise at
growth temperatures around 400-500 °C, likely indicating the increasing role for mobile ionic charge conduction along grain boundaries. Also the interface state density increases with growth temperature, approximately in the range of 2-8 x 10^{11} eV^{-1} cm^{2}.

The dielectric quality of the films can be a consequence of the growth mechanism and influenced by the growth conditions. Also the properties of annealed films may remain affected by the sample history. The growth from metal halides commonly proceeds via reaction of halide with surface OH-groups. Depending on the density of OH-groups, the adsorbing molecule may react with one or two, sometimes three neighbouring hydroxyls [13]. The density of hydroxyls diminishes with increasing growth temperature [7,14,15]. Concurrently, the density of metal atoms in the adsorbed layers decreases together with the nucleation density and related layer homogeneity. Low process temperatures always lead to the incompleteness of the surface reactions, therewith to the oxygen vacancies [16] and enhanced impurity content [11]. This is due to the formation of chlorine-containing intermediate surface species, relatively stable at low substrate temperatures [17]. Oxygen vacancies are able to stabilize multiphase ZrO_{2-x} species, relatively stable at low substrate temperatures [17]. Formation of chlorine-containing intermediate surface species, relatively stable at low substrate temperatures [17]. Oxygen vacancies are able to stabilize multiphase ZrO_{2-x} species, relatively stable at low substrate temperatures [17]. Oxygen vacancies are able to stabilize multiphase ZrO_{2-x} species, relatively stable at low substrate temperatures [17]. Oxygen vacancies are able to stabilize multiphase ZrO_{2-x} species, relatively stable at low substrate temperatures [17]. Oxygen vacancies are able to stabilize multiphase ZrO_{2-x} species, relatively stable at low substrate temperatures [17]. Oxygen vacancies are able to stabilize multiphase ZrO_{2-x} species, relatively stable at low substrate temperatures [17].

Changes in phase content can also be related to changes in deposition mechanism. For instance, at temperatures below 300 °C the amount of surface hydroxyls is likely sufficiently high to ensure tetragonal symmetry of nucleating crystallites with nucleation density high enough favouring the formation of nanocrystalline, poorly ordered and amorphous phases. Referring back to some alternative chemical routes via analogous precursor systems, it may be recognized that the initial phase content in zirconia coatings is sensitive to the water/ligand ratio [22], whereby the increasing contribution of OH-groups or water vapor is responsible for the preferred stabilization of metastable (tetragonal) phases [23]. Such factors should be considered in ALD processes as well. In the ALD films, the impurity (H, OH, halide) concentration decreases towards higher growth temperatures and structure becomes more crystalline. The films consist of dominant monoclinic polymorph and often tend to show pronounced (111) orientation [7,24]. It has been found, that 300 °C is approximately the critical temperature, where the impurity (chlorine) concentration decreases below 0.5 at.%, the polycrystallinity is not yet too high to cause dramatic leakage and the effective permittivity achieves values measured and calculated for HfO_{2} (12-16) [6,25] and ZrO_{2} (20-25) [11]. Dielectric losses and leakage current become significant in the films grown at 600 °C and higher temperatures. The latter observation is consistent with earlier mentioned variations in polarization in ZrO_{2}. It is to be noted that the capacitance of HfO_{2} seemed to be less sensitive to the deposition temperature although the impurity content behaved in a way similar to that in ZrO_{2}.

In the case of ALD HfO_{2} [6,26], it is important to note that in the case of similar layer thickness stable stoichiometric monoclinic polymorph appears more eagerly, than in the case of ZrO_{2} which contains relatively stronger contribution from tetragonal phases [11,27]. The more homogeneous phase composition better corresponding to stoichiometric dioxide can thus be the plausible reason for higher dielectric stability.

In the ultrathin films, the crystallographic phase content of the HfO_{2} grown from HfCl_{4} tended to be more heterogeneous than in the films grown from HfI_{4} [6,28], i.e. more defective. Although the capacitance of the films has been quite comparable for the films grown from the two halide precursors, HfO_{2} grown from HfI_{4} tended to be dielectrically more stable and more pure than films grown from HfCl_{4} – the content of residual iodide ligand ions in the films is lower and the residues can be annealed out more easily compared to chloride [28]. The hysteresis in the capacitance-voltage curves has been wider in the case of HfCl_{4} compared to films processed from HfI_{4} [6,28]. Even if the metastable phases formed in artificial sandwiched dielectric structures could possess enhanced permittivity value [27], the variable stoichiometry and defective grain boundaries in single oxide layers in silicon enhance oxygen diffusion, violates the thermodynamic stability and enables the growth of interface layers of arbitrary physical quality between oxide and semiconducting substrate. The formation of interfacial SiO_{2} or HfSiO_{x} could not be completely avoided. It is still to be noted that the formation of interfacial SiO_{2} between Si and HfO_{2} may not be too intense in the case of low substrate temperatures. Very thin interfacial layers (0.3-0.8 nm) were obtained in the case of HfI_{4} and H_{2}O precursors at 300 °C [28]. The thickness of SiO_{2} still increased after annealing processes at 900 °C by 1.5-2 times.

The most common oxygen precursor used in halide ALD process has been H_{2}O, used together with halides in the most cases [1,6,7,15,18]. O_{2} does not react feasibly with chlorides at convenient ALD temperatures and pressures. O_{3} is to be used with chlorides, instead [29]. At the same time, iodide reaction chemistry, likely its ability to decompose at surfaces, makes it feasible for metal iodide to react either with H_{2}O [6] or with O_{2} [25,30]. Oxygen can also be released from hydrogen peroxide [10,12]. The iodide-O_{2} process works with reasonably high rate at temperatures exceeding 400 °C, depending on the oxygen partial pressure. The film crystallinity and capacitance-voltage behaviour are both dependent on the oxygen pressure, too. Due to the high growth temperatures and film polycrystallinity enabling oxygen diffusion, interface SiO_{2} growth (1-1.5 nm) has been unavoidable [25].
Deep level and capacitance transient spectroscopy studies [20] have demonstrated that increment in HfO₂ film thickness in the range of 3.5-10 nm has minor influence on the DIGS density. Consequently, crystallization upon thickness increment has similarly minor effect on defect density and the physical quality of the films is determined mainly by the properties of the interface layers in the range of first few nanometers grown. Due to the higher impurity contents in the vicinity of the substrate [31,32], higher disorder of the structure is assumed in the ultrathin films, consequently increasing the density of disorder-induced gap states [20,21]. At the same time, the films which were initially more intensely crystallized due to higher growth temperatures used (400-500 °C) have possessed higher defect concentrations. The water pulse length and partial pressure has some effect on the high-k film properties in the halide process, increasing the crystallinity and decreasing the oxide/semiconductor interface state density. Exploitation of variable water pressures increased from 3 Pa to 12 Pa also assisted in the increase of film density and reduction of trap density, which still remains in the order of $10^{11}-10^{12} \text{cm}^{-2}\text{eV}^{-1}$. At the same time, ion beam analysis has shown that apparent residual hydrogen content is not dependent on the water partial pressure applied in the process.

**Alternative oxygen-free precursors**

Another ALD route to the high-quality gate oxide materials is the exploitation of metal alkylamide precursors. The alkylamide precursors are proven to be capable to ensure completely conformal growth [33]. Similarly to the halides, alkylamides are not affected by strong metal-oxygen bonds and dense metal oxides can form at really low temperatures (150-300 °C) as a result of exchange reactions by breaking the relatively weak metal-nitrogen bond and replacing the alkylamide ligands by oxygen from water as the oxygen precursor.

The representative of hafnium alkylamide precursors has in our case been the hafnium tetrakis-ethylmethylamide, Hf[N(C₂H₅)(CH₃)]₄. This precursor is a liquid with water as the oxygen precursor. The suitable ALD temperatures range between 200 and 350 °C [34] enabling the growth of polycrystalline, preferably (200) and (020) oriented films. Higher growth temperatures possibly enhancing the decomposition may not be used. Partially due to the fact that both hafnium and oxygen precursors contain hydrogen, the content of residual hydrogen can become rather high, reaching 5-6 at.%, whereas in the case of halide process the content of hydrogen remains typically at 0.5-1.5 at.% when grown at 300 °C. Besides, carbon residues remain in the film due to the usage of this precursor. High impurity levels deteriorate the performance of capacitors fabricated using alkylamides [35]. On the other hand, the resulting films were very flat and possessed high refractive index with no essential interface layer as-deposited at around 250 °C [36]. In this way, 50-100 nm thick films of dominantly monoclinic phase [34] and 5-10 nm thick amorphous films [36] have been formed. In the ultrathin films with thickness lower than 10 nm, crystal growth became inhibited likely due to the low temperatures and high residual contents and the films remain amorphous. For comparison, in the case of halide precursors, crystal growth can be favoured also in 2-10 nm thick films [6,28]. The refractive indexes (2.03-2.08) and permittivities (13-15) of the films grown from alkylamide are similar to these in the films grown from halides. The capacitance-voltage curves are still influenced by the different nature of the defects, showing varying direction of the hysteresis. Clockwise hysteresis direction has been rather common for the films with high hydrogen content grown from alkoxides or alkylamides [36,37], referring to the increasing role for positively charged ionic (H⁺) transport. In the films with lower hydrogen content grown from halides counterclockwise hysteresis dominates [11,12], although the direction of hysteresis may change upon increase in growth temperature, related crystallinity and assumptional development of conductive grain boundaries.

Another well-behaving precursor is Cp₂Zr(CH₃)₂ (Cp=cyclopentadienyl) [38], reacting with either water or ozone. The resulting films grown at 350 °C have been highly crystallized possessing overwhelmingly monoclinic structure and contained very low amounts of residuals (< 0.1 at.%). Appreciably narrow hysteresis (ca. 50-100 mV) was often observed in capacitance-voltage characteristics as an indication of relatively low defect density already in as-deposited state. It is noteworthy that the exploitation of the cyclopentadienyl precursors (analogously to alkylamides) has resulted in growth rate *versus* growth temperature dependences with regions where the rate truly weakly depends on the temperature, i.e. the ALE window [39]. This is a promising feature regarding the expectational reproducibility of the film growth process and the resulting physical properties. Other precursor systems have virtually not shown any sign of ALD window apart from the low-temperature regions close to the reaction thresholds.

The HF-stripped Si surface is partially H-terminated and naturally heterogeneous. Intermittent storage and treatment in oxygen(air) can result in partial oxidation and island growth [40] regarding both SiO₂ and overlying ZrO₂(HfO₂). The surface heterogeneity may be reduced by pre-covering the Si surface with continuous SiO₂ layer or HF-etching with HF/alcohol solution, ensuring better surface coverage respectively with OH- or H-groups. Lower substrate temperatures provide the same tendency to more
homogeneous surfaces and slower de-hydroxylation of the substrate, ensuring more uniform, although often amorphous film growth. However, likely due to the necessity to oxidize the Si surface before the film growth with pre-determined rate or adsorption and reaction with OH-groups, that halide ALD process can suffer from delayed growth rate at the very beginning of the deposition process on hydrogen-terminated silicon [41]. The growth rate increases during the first tens of growth cycles and becomes constant after forming continuous solid oxide layer after oxidation of the silicon surface. The mechanism of the relative insensitivity of this precursor to the surface treatment is not yet clarified. The same phenomenon has been observed for another nitrogen containing precursor Hf(NO3)4, able to react with H2O and result in the HfO2 films at quite a low substrate temperatures at 180 ºC [42].

Precursors containing inherent oxygen

The ALD rate is determined by the reactivity of metal precursor towards water and enhanced by the ability of the metal precursor to decompose thermally at elevated temperatures. Despite the difference in the size of precursor molecules in the case of halide and alternative organometallic or metal-organic precursors, the larger size does not necessarily cause lower density of adsorbed molecules accompanied with lower growth rate per deposition cycle. However, differently from the metal halide based ALD, the growth from alkoxide or functionalized alkoxide based precursors has resulted in the growth of nanocrystalline ZrO2 [43,44] and HfO2 [37] with functionalized alkoxide based precursors has resulted in the halide based ALD, the growth from alkoxide or deposition cycle. However, differently from the metal molecules accompanied with lower growth rate per deposition cycle. However, differently from the metal alkoxide precursor to thermally decompose may also be considered as useful property assisting in the growth of amorphous films with the aid of O2 supply at relatively high temperatures above 350 ºC. At the same time, the halide and alkylamide precursors make the formation of the thin solid films possible strictly via surface exchange reactions between oxygen precursor and metal precursor ligands. No pyrolysis can be involved in the film growth process. This likely favours the formation of dense ionic compound matrix with metal-oxygen bonds formed and arranged after surface reactions corresponding to the lattice of the polymorph in growing surface layer. In the case of oxygen containing precursors, the process may be affected by the coordination chemistry and bond strength related to the already existing metal-oxygen bonds in the precursor molecules. This suppresses the surface migration and inhibits the well-defined oxide lattice formation upon thermally enhanced decomposition of precursor molecules.

In the regular hydrolysis process, such as taking place in reactions between alkoxide based metal precursors and water, metal-oxide bond is broken and replaced by the oxygen from oxygen precursor. As suggested, this is less favoured due to strong oxygen bond and resulting films are of rather low density. The oxygen in the metal precursor is a component of the ligand and leaves substrate surface in refractive index values and undergo well-defined crystal growth, differently from the films obtained with alkoxide based precursors, such as propanolate complexes of hafnium, Hf(OC(CH3)2CH2OCH3)4 [37,46] or butoxides of zirconium [44]. In the case of alkoxide based precursors, the film growth becomes possible via pyrolysis by pulsing the metal precursor alone into the reactor without intermediate hydrolysis steps [37,44], although with considerably lower growth rate. Thus, these compounds suffer from the ability to thermally decompose already at relatively low temperatures around 300 ºC with consequences such as thickness nonuniformities, high hydrogen and carbon contents (4-6 at.% ) and/or low refractive index values (< 1.95). Another precursor, hafnium hydroxylamide, Hf[ON(CH2)2]4, has enabled the growth of the films in a rather narrow temperature range around 300 ºC, because lower temperatures do not enable the reactions with appreciable rate and higher temperatures cause too intense decomposition [47]. It is still to be noted that the properties of films obtained using oxygen containing precursors can be improved using remote plasma oxidation [46,48] or just post-deposition annealings [47]. The C-V curves of the films prepared in alkoxide process at 300-350 ºC have shown considerably larger instabilities, expressed by variable hysteresis and features attributable to interface and bulk trap distributions. Stable C-V behaviour appears in the films grown at higher temperatures, where the thickness profile has already became pronounced. The ability of Hf or Zr alkoxide precursor to thermally decompose may also be considered as useful property assisting in the growth of amorphous films with the aid of O2 supply at relatively high temperatures above 350 ºC [49]. At the same time, the halide and alkylamide precursors make the formation of the thin solid films possible strictly via surface exchange reactions between oxygen precursor and metal precursor ligands. No pyrolysis can be involved in the film growth process. This likely favours the formation of dense ionic compound matrix with metal-oxygen bonds formed and arranged after surface reactions corresponding to the lattice of the polymorph in growing surface layer. In the case of oxygen containing precursors, the process may be affected by the coordination chemistry and bond strength related to the already existing metal-oxygen bonds in the precursor molecules. This suppresses the surface migration and inhibits the well-defined oxide lattice formation upon thermally enhanced decomposition of precursor molecules.
the form of alcohol-based compounds as reaction products. It is possible to use, in oxide growth, an alternative approach and let the alkoxide-based precursor react with some halide, such as ZrI4, HfI4 or HfCl4 [50,51]. In this case, nucleophilic attack between oxygen and halogen-metal bond occurs and metal-oxygen-metal bonds are formed on the basis of oxygen in the metal precursor newly bound to the metal from halide. The reaction products now comprise chloro- or iodoalcohols [52]. The resulting films can now consist of combinations of metals from variable alkoxides and halides. In this way, for instance, ZrO2 films can be grown from Zr-ethoxide and chloride [50]. Moreover, this approach allows straightforward deposition of zirconium silicates [50] or hafnium silicates [51], while the growth of latter compounds occurs with resulting hafnon stoichiometry.

Conclusions and outlines:

It is quite a challenging task to select the most appropriate ALD precursor system. If the well-established growth should proceed in the widest temperature range, chloride could be chosen as precursor. If the maximum purity is the target, iodides should be considered. Highest conformality of the growth and the highest density at the lowest growth temperatures could be obtained with alkylamides. Conformality, density and structural uniformity requirements are all well met by cyclopentadienyl-based precursors. Alkoxide-based precursors seem to be a class of precursors resulting in amorphous or nanocrystalline films. However, obligatory post-deposition thermal or plasma treatments might provide reproducible densification of the films and annealing out the impurities also from the films obtained in alkoxide process.

It can be noted that despite different precursor chemistries, the resulting effective permittivity of HfO2 films has been quite insensitive to the process, typically varying between 12 and 16. Structural differences between strongly polycrystalline, dominantly monoclinic, HfO2 grown from halides, nanocrystalline low-density monoclinic HfO2 grown from alkoxide based precursors and amorphous or monoclinic films grown from alkylamides have not caused obvious structure-related diversities in permittivity, although refractive indexes were clearly dependent on the growth mechanisms. Even the high hydrogen content in the films obtained from alkoxide process did not have dramatic effect on the net permittivity value. It could be suggested, that the monoclinic structure most often dominating in HfO2 films determines the polarizability and resulting capacitance of the material layer.

It the case of ZrO2 films the situation looks somewhat different from that of HfO2. Even the halide processes otherwise resulting in most dense and crystallized films have resulted in capacitor structures with permissitivity value varying between 13 and 22 with changes in structure and purity. Optimum film density and permittivity has been reached at established process temperature (300 °C). Structure of ZrO2 films seems to be relatively strongly affected by the process conditions and includes more pronounced contributions from metastable (e.g. tetragonal) phases compared to HfO2. Also in the thick films obtained in alkoxide-based process, the phase formed was not identified as monoclinic, but rather remained undetermined. Unexpectedly high apparent permittivity (25-33) was likely dependent on the high hydrogen content and interface polarizability, sometimes also assigned to the electronic properties of tetragonal ZrO2.

Based on comparative analysis and the results obtained under similar conditions, we could temporarily state that a good ALD precursor for the deposition of HfO2 and ZrO2 should not contain internal oxygen bound to the metal. This seems to be valid especially for the deposition of these two oxides – in the case of other oxides such as Ta2O5, TiO2 and Nb2O5 oxygen containing precursors such as alkoxides can result in the growth of films with acceptable density and uniformity. For HfO2 or ZrO2, halides, alkylamides and cyclopentadienyls might be preferred, whereby the final selection between these groups could be made taken into account the conformality and purity requirements in particular process.

References:


