Atomic Layer Deposition of Oxide Thin Films with Metal Alkoxides as Oxygen Sources

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A chemical approach to atomic layer deposition (ALD) of oxide thin films is reported here. Instead of using water or other compounds for an oxygen source, oxygen is obtained from a metal alkoxide, which serves as both an oxygen and a metal source when it reacts with another metal compound such as a metal chloride or a metal alkyl. These reactions generally enable deposition of oxides of many metals. With this approach, an alumina film has been deposited on silicon without creating an interfacial silicon oxide layer that otherwise forms easily. This finding adds to the other benefits of the ALD method, especially the atomic-level thickness control and excellent uniformity, and takes a major step toward the scientifically challenging and technologically important task of replacing silica as the gate dielectric in the future generations of metal oxide semiconductor field effect transistors.

The continuous shrinkage of microelectronic devices during the past 30 years according to the predictions and guidance of the Moore's Law (*1*) has led to a situation in which the materials used since the beginning of the integrated circuit technology are approaching their fundamental limits (*2–4*). The replacement of aluminum with copper has already begun, and high- and low-permittivity dielectrics are being examined as substitutes for SiO_2. For example, the thickness of SiO_2 as the gate oxide in metal oxide semiconductor field effect transistors (MOSFET), the dominant device in today's integrated circuits, is projected to be scaled down to 1 nm by the year 2010 (*2*, *4*). The gate oxide capacitively couples the gate electrode to the channel region between the source and drain regions of the MOSFET. By applying a voltage on the gate electrode, the conductivity of the channel region may be controlled, and the transistor is thereby switched on and off. However, when thinned to 1 nm, which corresponds to only four to five atom layers, SiO_2 no longer serves as an insulator because of the tunneling current that runs through it (*3–5*). Therefore, alternative materials with a permittivity higher than that of SiO_2 (3.9) are needed to be able to use thicker gate dielectrics in achieving the required capacitances (*6*) without tunneling currents, and thereby continue the evolution toward higher integration densities.

The replacement of SiO_2 with high-permittivity dielectrics is a major challenge in which the basic research and the near-future needs of the semiconductor industry merge. To benefit from a high-permittivity substitute, it must be deposited on silicon in a way that an interfacial layer of SiO_2 only one or two molecular layers thick is formed. This requirement is illustrated by the concept of equivalent thickness d_{eq}, which is the thickness of such a SiO_2 layer that would give the same capacitance density C/A as the material under consideration, where C is the capacitance and A is the area of the capacitor. For a dielectric layer with a permittivity ε and thickness d, $d_{eq} = (\varepsilon_{SiO2}/\varepsilon)d = (3.9/\varepsilon)d$. High-permittivity dielectrics are required in realizing equivalent thicknesses of 1.0 nm and less. However, silicon has a high affinity toward oxygen, and therefore a thin interfacial SiO_2 layer is easily formed between silicon and the dielectric layer. In such a case, the resulting double-layer insulator structure corresponds to two capacitors in series, and the total equivalent thickness is a sum of the SiO_2 layer thickness and d_{eq} of the dielectric layer: $d_{eq,tot} = d_{SiO2} + d_{eq}$. Thus, every 0.1 nm of SiO_2 will be away from the thickness of the high-permittivity dielectric, thereby requiring a use of thinner layers with a concomitant risk of higher leakage currents. In other words, the interfacial SiO_2 layer sets the lower limit for the achievable $d_{eq,tot}$.

The interfacial SiO_2 layer may be formed by two mechanisms: (i) a reaction between silicon and the high-permittivity oxide and (ii) oxidation of the silicon surface during the oxide deposition. To avoid the first mechanism, oxides that appear to be thermodynamically stable in contact with silicon should be chosen, such as Al_2O_3 and ZrO_2 (*7*). To improve interface characteristics, some silicon may be incorporated to the high-permittivity oxide, thereby forming silicates (*8*). Another option is to use carefully tailored interface structures, like in the epitaxial structure grown by molecular beam epitaxy (MBE) in which one monolayer of strontium silicide was placed at the silicon-$SrTiO_3$ interface (*9*). However, there is major concern over whether this MBE-based approach can be scaled up to a cost-effective production. Avoiding the second possible mechanism for the interface layer formation, i.e., the oxidation of the silicon surface by the oxygen containing atmosphere during the film deposition, requires careful consideration of the deposition conditions, and will be focused on here.

ALD is a gas-phase thin-film deposition method that is unique because the film growth proceeds through self-limiting surface reactions (*10–13*). As a consequence, ALD offers excellent large-area uniformity and conformality (*14*) and enables simple and accurate control of film thickness and composition at an atomic layer level. All these characteristics make ALD an important film deposition technique for future microelectronics.

In ALD of oxides, one deposition cycle consists of an exposure to a metal precursor, a purge period, an exposure to an oxygen precursor, and another purge period. Typical metal precursors include halides, alkyls, alkoxides, and beta-diketonates, whereas water, hydrogen peroxide, ozone, and, in few cases, molecular oxygen has been used as an oxygen source (*10*). Oxide films made by ALD show good insulator properties, as evidenced by their use in commercial thin-film electroluminescent displays, and especially good insulators are obtained by constructing nanolaminate structures (*10*, *11*). The major problem in ALD of high-permittivity oxides on silicon is that only a monolayer of the metal compound lies on the silicon surface when it is exposed to the oxygen source for the first time. Under typical growth conditions, this monolayer does not protect the silicon against oxidation, and therefore a thin SiO_2 interface layer is easily formed.

We now show a chemical approach to ALD of oxides without the use of the common oxygen sources listed above, thereby making it possible to create sharp silicon–metal oxide interfaces with no interfacial silicon oxide layer (Fig. 1). Instead of using a separate oxygen source, two metal compounds are used such that at least one of them is an alkoxide $[M(OR)_n$, where M = metal and R = alkyl group] in which the oxygen of the ligand is directly bonded to a metal. In alkoxides, the metal-oxygen bonds are strong and short, implying multiple-bond character due to the π-bonding of the oxygen p-orbital to the metal d-orbital. Because oxygen is strongly bonded to metals that often have a higher free energy of oxide formation than SiO_2, it is reasonable to expect that metal alkoxides would be less oxidizing toward silicon than water, not to mention

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hydrogen peroxide or ozone.

Reactions of metal halides and alkoxides into oxides and alkyl halides are known from sol-gel processes under nonhydrolytic conditions, i.e., in absence of water (*15*, *16*)

$$\mathrm{M(OR)}_a + \mathrm{MX}_a \rightarrow 2\mathrm{MO}_{a/2} + a\mathrm{RX} \quad (1)$$

$$b\mathrm{M(OR)}_a + a\mathrm{M'X}_b \rightarrow M_b\mathrm{M'}_a\mathrm{O}_{(a+b)/2} + (a+b)\mathrm{RX} \quad (2)$$

where a and b are the oxidation states of the metals M and M′, respectively, and X represents a halide.

The metals in the two compounds may be either the same (Eq. 1) or different (Eq. 2), the latter resulting in the formation of mixed oxides. The reaction mechanism involves coordination of an oxygen atom of the alkoxy group to the metal center of the halide, followed by a nucleophilic cleavage of the O-R bond (*16*). Therefore, the cationic character of the alkyl group is important; the more stabilized the cleaving carbonium ion is, i.e., the more branched R is, the more facile the reaction is (*16*).

Reactions of metal alkoxides and halides in solutions at temperatures close to room temperature are slow, typically taking hours or days to reach equilibrim. But they are completed in seconds or minutes when carried out at 300°C in heptadecane or tricotylphosphine oxide, respectively (*17*). Therefore, the reactions appear promising for ALD where the achievement of high deposition rates requires that each monomolecular layer surface reaction step is completed in less than a second. The reactions may be accelerated by increasing the temperature, but an upper limit is set by the thermal self-decomposition of the alkoxides because the key feature of ALD, the self-limiting film growth, would then be ruined (*10*, *11*).

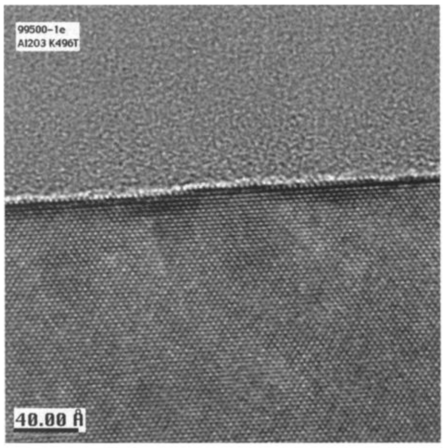

Fig. 1. High-resolution transmission electron microsope image of an interface between a silicon substrate and an Al_2O_3 film made from $AlCl_3$ and $Al(O^iPr)_3$ at 300°C.

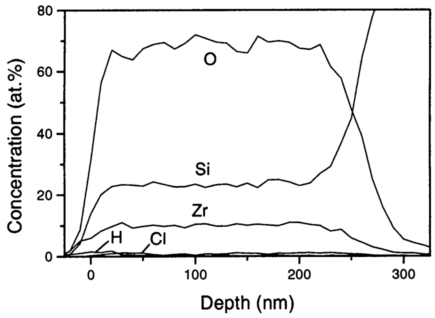

Fig. 2. Elemental depth profiles determined by TOF-ERDA for a Zr-Si-O film deposited from $ZrCl_4$ and $Si(O^nBu)_4$ at 500°C (^{n}Bu, *n*-butyl) at. %, atomic %.

Results of our experiments (*18*) on growing oxides by ALD with the use of only metal-containing precursors are summarized in Table 1. The results demonstrate that the metal chloride–metal alkoxide chemistry is effective, resulting in the growth of uniform films from various precursor combinations, provided that a threshold temperature is exceeded. The threshold temperature is lower when the alkyl group is more branched. For example, no film is obtained from the $AlCl_3$–$Al(OEt)_3$ combination at 300°C, whereas the $AlCl_3$–$Al(O^iPr)_3$ combination gives a deposition rate of 0.80 Å/cycle (^{i}Pr, isopropyl). Thus, like the solution-phase studies (*16*), the cationic character of the alkyl group is important also here. The deposition temperatures were chosen so that no thermal self-decomposition of the alkoxides occurred. This was verified experimentally by observing that no film growth occurred when only the alkoxide was pulsed into the reactor at a given temperature.

One remarkable result of this new chemical approach is the incorporation of silicon into oxide mixtures. Until now, no facile chemistry has been found for depositing SiO_2 by ALD. All the reported processes have been based on long reaction times of at least tens of seconds (*12*, *13*) and therefore have been far from cost-effective. With the current chemistry, large amounts of silicon were uniformly incorporated into Zr-Si-O mixtures (Table 1, Fig. 2), a material with a great potential for gate oxides (*8*). On the other hand, all the attempts so far to deposit binary SiO_2 have failed with this chemical approach. Also, this finding parallels the sol-gel studies in which reactions between $SiCl_4$ and $Si(OR)_4$ with primary or secondary R groups require metal chloride catalysts to proceed (*19*).

In the mixed-oxide films, the metal ratio often does not correspond to the ratio expected on the basis of Eq. 1, thereby implying that more complex overall reactions are involved. For example, the $HfCl_4 + Ti(O^iPr)_4$ combination leads to a metal ratio of Hf/(Hf+Ti) = 0.24 instead of the expected 0.50. This can be understood by the thermodynamically (*20*) facile etching reaction in which TiO_2 on the film surface is partially replaced by HfO_2

$$\mathrm{TiO_2(s)} + \mathrm{HfCl_4(g)} \rightarrow \mathrm{HfO_2(s)} + \mathrm{TiCl_4(g)}$$

$$\Delta G(300°\mathrm{C}) = -73\ \mathrm{kJ/mol} \quad (3)$$

where ΔG is the change in Gibb's free energy.

In general, the processes presented here result in higher deposition rates than those obtained in the conventional metal halide–water or metal alkoxide–water ALD processes (*10*). In these new processes, both precursor pulses deposit metal ions into the film, whereas in the conventional approach only one of the precursors deposits metal. Time-of-flight–elastic recoil detection analysis (TOF-ERDA) studies showed that the films deposited with this chemistry at 300°C and above contained less than 1 atomic % carbon and hydrogen. On the other hand, the films do contain some chlorine residues, typically 1 to 2 atomic %, and thus it is evident that the removal of the chlo-

Table 1. Summary of the film growth experiments. Me, methyl.

Precursors	Temperature (°C)	Growth rate (Å/cycle)	Metal ratio	Chlorine residues (atomic %)
$AlCl_3 + Al(OEt)_3$	400	0.7		2.6
	300	No growth		
$AlCl_3 + Al(O^iPr)_3$	300	0.8		2.0
$AlMe_3 + Al(O^iPr)_3$	300	1.3		
$AlMe_3 + Ti(O^iPr)_4$	300	No growth		
$AlCl_3 + Ti(OEt)_4$	300	No growth		
$AlCl_3 + Ti(O^iPr)_4$	300	2.3	Al/(Al+Ti) = 0.80	4.0
$ZrCl_4 + Al(OEt)_3$	400	0.45	Zr/(Zr+Al) = 0.28	1.8
	300	No growth		
$HfCl_4 + Al(OEt)_3$	400	0.6	Hf/(Hf+Al) = 0.33	1.0
	300	No growth		
$ZrCl_4 + Ti(O^iPr)_4$	300	1.2	Zr/(Zr+Ti) = 0.45	0.8
$HfCl_4 + Ti(O^iPr)_4$	300	0.5	Hf/(Hf+Ti) = 0.24	0.8
$TaCl_5 + Ta(OEt)_5$	275	0.5		2.0
$ZrCl_4 + Si(OEt)_4$	500	0.5	Zr/(Zr+Si) = 0.39	1.5
	350	No growth		
$ZrCl_4 + Si(O^nBu)_4$	500	1.3	Zr/(Zr+Si) = 0.30	0.8
	250	0.7	Zr/(Zr+Si) = 0.53	8.3
$SiCl_4 + Si(O^nBu)_4$	500	No growth		
$SiCl_4 + Si(OEt)_4$	500	No growth		

rides is more difficult than that of the alkoxo ligands. Nevertheless, the permittivities of these films are only slightly lower than those of the corresponding materials deposited by the conventional ALD processes, and their leakage current properties are nearly identical (*21*). For removal of the chloride residues, proper postdeposition annealing conditions must be looked for in which the chlorides are replaced by oxygen but the underlying silicon is not yet oxidized. In contrast, the use of metal iodides with weaker binding energies than the chlorides offers a potential way to decrease the halide residues. Yet another scheme might be to use this new process only for the interface formation and then continue with the conventional ALD processes, which leave fewer residues.

Whereas the reactions between the halides and alkoxides were known from the solution studies, the success of depositing Al_2O_3 from aluminium isopropoxide and trimethyl aluminium was more surprising. Most likely this reaction mechanism involves formation of *tert*-butane

$$Al(CH_3)_3 + Al(OCH(CH_3)_2)_3 \rightarrow Al_2O_3 + 3\ CH_3CH(CH_3)_2 \qquad (4)$$

The most important finding related to this ALD chemistry is that there is no interfacial silicon oxide layer between the silicon substrate and an Al_2O_3 film (Fig. 1). Before depositing this film, the silicon surface was etched with a dilute aqueous HF solution to remove the native oxide and to leave the surface hydrogen terminated. Whether the thin light zone at the interface is real or is an artifact is impossible to distinguish. However, even if the interface does have oxidized silicon, it is only one monolayer thick and, thus, represents an atomic-level interface between Al_2O_3 and Si, which is oxidized only from its topmost layer. The absence of a thicker interfacial layer implies that ALD with the use of alkoxides as oxygen sources is a viable technique for gate oxide deposition for the future-generation integrated circuits. The other requirements for the gate oxide deposition method, i.e., accurate thickness control and uniformity over the large silicon wafers, are inherently fulfilled by ALD because of its self-limiting film growth process.

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18. The films were deposited in a flow type F-120 ALD reactor (Microchemistry, Espoo, Finland) operated under a pressure of about 10 mbar. Nitrogen was used as a carrier and as a purging gas. The compounds $Al(CH_3)_3$ and $Si(OEt)_4$ were evaporated in external sources and led into the reactor through a solenoid valve. The other compounds were evaporated inside the reactor at temperatures that correspond to a vapor pressure of about 0.1 mbar. The source vapors were pulsed onto the substrates by means of inert gas valving. Glass and silicon were used as substrates. Film thicknesses were evaluated from transmission spectra, and elemental analyses were carried out at the accelerator laboratory in Helsinki by TOF-ERDA with the use of 53-MeV $^{127}I^{10+}$ ions as projectiles.
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21. For comparison with the conventional ALD processes, the dielectric properties were mainly measured with In_2O_3:Sn-insulator-Al capacitor structures because that was the standard procedure in earlier studies. The insulators were made 100 to 200 nm thick so that the measured permittivity and leakage reflect the properties of the film bulk rather than the interfaces in these specific capacitors. For an Al_2O_3 film made by the new process from $AlCl_3$ and $Al(O^iPr)_3$, a permittivity of 7.5 and a leakage current density of 10^{-7} A/cm^2 at an electric field of 2.0 MV/cm were measured. The corresponding values for an Al_2O_3 film made by the conventional ALD process from $Al(CH_3)_3$ and H_2O were 8.2 and 10^{-6} A/cm^2 for the permittivity and the leakage current density, respectively. Likewise, Ta_2O_5 made from $TaCl_5$ and $Ta(OEt)_5$ had a permittivity of 20 to 24, whereas the conventional processes result in permittivities of 24 to 25 (Et, ethyl). The leakages in these films were on equivalent levels. The $Zr_{0.45}Ti_{0.55}O_2$ film deposited at 300°C with the new chemistry was partly crystallized and had a high permittivity of 43, but, like the high permittivity materials in general, it possessed a rather high leakage current of 10^{-6} A/cm^2 at an electric field of 0.2 MV/cm. In contrast, when deposited at 250°C, the film was completely amorphous, had a permittivity of 17, and had a greatly reduced leakage such that the level of 10^{-6} A/cm^2 was achieved with an electric field of only 1 to 2 MV/cm. However, with this material, no direct comparison to the conventional ALD processes can be made.
22. Supported by the Academy of Finland and the Finnish National Technology Agency (TEKES).

6 December 1999; accepted 24 February 2000

Nanometer-Size α-PbO_2–Type TiO_2 in Garnet: A Thermobarometer for Ultrahigh-Pressure Metamorphism

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A high-pressure phase of titanium dioxide (TiO_2) with an α-PbO_2–type structure has been identified in garnet of diamondiferous quartzofeldspathic rocks from the Saxonian Erzgebirge, Germany. Analytical electron microscopy indicates that this α-PbO_2–type TiO_2 occurred as an epitaxial nanometer-thick slab between twinned rutile bicrystals. Given a V-shaped curve for the equilibrium phase boundary of α-PbO_2–type TiO_2 to rutile, the stabilization pressure of α-PbO_2–type TiO_2 should be 4 to 5 gigapascals at 900° to 1000°C. This suggests a burial of continental crustal rocks to depths of at least 130 kilometers. The α-PbO_2–type TiO_2 may be a useful pressure and temperature indicator in the diamond stability field.

Coesite or diamond inclusions in garnet are important indicators of ultrahigh-pressure (UHP) metamorphism [above 2.5 to 2.7 GPa for the production of coesite (*1*)] in orogenic belts such as the western Alps (*2*), the Kokchetav Massif in Kazakhstan (*3, 4*), Dabie Shan in central China (*5*), the western Gneiss Region in Norway (*6*), and recently the Saxonian Erzgebirge in Germany (*7*). UHP metamorphism is important to our understanding of continental collision zones and the mantle dynamics attending subduction (*1*). For example, the source rocks in the Kokchetav Massif (*4*) and the Saxonian Erzgebirge (*7*) are acidic crustal rocks, and as such they imply burial to the mantle depths before exhumation to the surface. In general, inclusions larger than several micrometers in diameter can be identified using optical microscopy, Raman probe, or electron probe microanalysis, as well as methods for polishing thin rock sections to quanti-

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