Electronic Materials

Atomic Layer Deposition Chemistry: Recent Developments and Future Challenges**

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New materials, namely high-k (high-permittivity) dielectrics to replace SiO_2, Cu to replace Al, and barrier materials for Cu, are revolutionizing modern integrated circuits. These materials must be deposited as very thin films on structured surfaces. The self-limiting growth mechanism characteristic to atomic layer deposition (ALD) facilitates the control of film thickness at the atomic level and allows deposition on large and complex surfaces. These features make ALD a very promising technique for future integrated circuits. Recent ALD research has mainly focused on materials required in microelectronics. Chemistry, in particular the selection of suitable precursor combinations, is the key issue in ALD; many interesting results have been obtained by smart chemistry. ALD is also likely to find applications in other areas, such as magnetic recording heads, optics, demanding protective coatings, and micro-electromechanical systems, provided that cost-effective processes can be found for the materials required.

1. Introduction

Atomic layer deposition (ALD) has recently received much interest as a potential deposition method for advanced thin-film structures. However, ALD had already been developed and introduced worldwide with the name Atomic Layer Epitaxy (ALE) in the late 1970s.[1] The motivation for the development of ALD was the need for a deposition method for thin-film electroluminescent (TFEL) flat-panel displays. For such an application, high-quality dielectric and luminescent films are required on large-area substrates.[2] ALD is still used today in the industrial production of TFEL displays.[3] In the mid-1980s the applicability of ALD to epitaxial compound semiconductors was demonstrated, and great efforts were made in the preparation of III–V compounds in the late 1980s.[4] Due to the unfavorable chemistry between group III alkyl compounds and group V hydrides, no real benefits were achieved with ALD, compared to metal–organic vapor phase epitaxy (MOVPE) or molecular beam epitaxy (MBE). The renaissance of ALD began in the mid-1990s, with the interest focused on silicon-based microelectronics. Shrinking device dimensions and increasing aspect ratios in integrated circuits (IC) require the introduction of new materials and thin-film deposition techniques. ALD is considered as one deposition method with the greatest potential for producing very thin, conformal films with control of the thickness and composition of the films possible at the atomic level.

In the following the principles and characteristic features of the ALD method are presented. The comprehensive review made by the authors[5] covers the ALD literature to summer 2000. This minireview focuses mostly on more recent literature. Since the major part of the ALD research at the moment is focused on thin films needed in microelectronics, the recent achievements are mostly connected to this area.

2. The Principle of ALD

ALD is a special modification of chemical vapor deposition (CVD) with the distinct feature that film growth takes place in a cyclic manner. Normally one growth cycle consists

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[**] Throughout this Minireview, nomenclature common to the area of semiconductor materials science is employed. For example, group III elements are those of group 13 of the periodic table and group V elements are those of group 15. Hence, GaAs is an example of a III–V material.

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of four steps (Figure 1): 1) Exposure of the first precursor, 2) purge of the reaction chamber, 3) exposure of the second precursor, and 4) a further purge of the reaction chamber.[5] The growth cycles are repeated as many times as required for the desired film thickness. Depending on the process and the reactor being used, one cycle can take time from 0.5 s to a few seconds, and may deposit between 0.1 and 3 Å of film material. The cycle time depends particularly on the aggressiveness of the film-formation reaction. In ALD, in contrast to CVD, reactions with as negative a value of ΔG as possible are desired.[5] The film thickness obtained per cycle may depend on the size of the precursor molecule, because steric hindrance between large precursors limits the number of molecules capable to adsorb on the surface. With small molecules and elements as precursors, a full monolayer growth per cycle is possible. In addition, the number of adsorption sites at the surface also affects the amount of molecules adsorbed.

Figure 1. An ALD deposition cycle showing schematically the deposition of TiO_2 films from $TiCl_4$ and H_2O.

Ideally each exposure and purge step in ALD is complete. The precursor molecules chemisorb or react with the surface groups saturatively, and after the formation of the chemisorbed layer no further adsorption takes place. Under these saturative reaction conditions the film growth is self-limiting; that is, the amount of film material deposited in each reaction cycle is constant. The self-limiting growth mechanism brings several advantages to ALD: 1) Film thickness depends only on the number of reaction cycles, which makes the thickness control accurate and simple; 2) unlike CVD, there is less need of reactant flux homogeneity, which gives large area (large batch and easy scale-up) capability, excellent conformality (Figure 2) and reproducibility, and simplifies the use of solid precursors. Separate dosing of the precursors prevents gas-phase reactions, which allows the use of highly reactive precursors and gives enough time for each reaction step to reach completion. This results in pure films being deposited at relatively low temperatures. The ALD processing window is often wide, which makes the process insensitive to small changes in temperature and precursor flows, and allows the processing of different materials to multilayer structures in a continuous process (Figure 3).[6]

Figure 2. Cross-sectional SEM images for a 300-nm Al_2O_3 film (a) and a 14-nm TiN film (b) deposited on a patterned silicon substrate.

3. Precursors

ALD precursors may be gases, volatile liquids, or solids. The vapor pressure must be high enough for effective mass transportation; all solid, and some liquid precursors need to be heated. Thanks to the self-limiting growth, demands for the evaporation rates to remain constant are more relaxed

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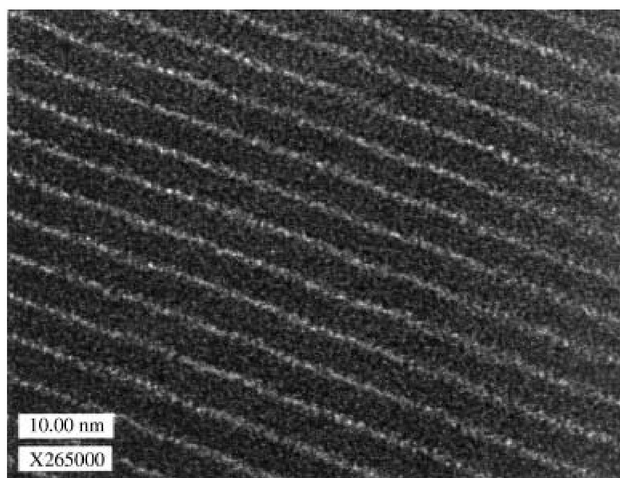

Figure 3. Cross-sectional TEM image of a $Zr_xSi_yO_z$–$Zr_xTi_yO_z$ nanolaminate.

than in CVD, thus making it easier to use solid precursors. The challenging task of pulsing precursors evaporated at high temperatures is solved by inert-gas valving.[5,7] The precursors must be thermally stable at the growth temperature. Decomposition would destroy the self-limiting growth mechanism and the related advantages. In some applications, such as protective coatings, slightly thermally unstable precursors can be acceptable if their decomposition is slow (compared to the pulsing sequence times), and makes only a small contribution to the overall growth. The precursors must adsorb or react with the surface sites, such as hydroxyl groups on oxide surfaces (Figure 1). The type of adsorption, molecular or dissociative, and reaction mechanisms have recently been extensively studied in situ with quartz-crystal microbalance and mass spectrometric measurements. Different mechanisms have been found for different precursors.[5]

Typical metal precursors used in ALD are halides, especially chlorides, alkyl compounds, and alkoxides. Organometallic compounds, such as cyclopentadienyl complexes and alkyl and silyl amides have gained more attention recently.[6] The nonmetal precursors used are: water, hydrogen peroxide, and ozone for oxygen; hydrides for chalcogens; ammonia, hydrazine, and amines for nitrogen; hydrides for group V elements.[5]

4. ALD in Microelectronics

In microelectronics, ALD is studied as a potential technique to deposit high-k (high permittivity) gate oxides, high-k memory capacitor dielectrics, ferroelectrics, and metals and nitrides for electrodes and interconnects. In high-k gate oxides, where the control of ultrathin films is essential, ALD is only likely to come in to wider use at the 45-nm technology.[8] In metallizations, conformal films are required; currently it is expected that ALD will be used in mainstream production at the 65-nm node. In dynamic random access memories (DRAMs), the conformality requirements are even higher and ALD is the only method that can be used when feature sizes become smaller than 100 nm.[8]

4.1. Gate Oxides

Deposition of the high-k oxides Al_2O_3, ZrO_2, and HfO_2 has been the most widely examined area of ALD during the past few years. The motivation for this work comes from the detrimentally high tunneling currents through the currently used SiO_2 metal–oxide semiconductor field-effect transistor (MOSFET) gate dielectric, when it is downscaled to a thickness of about 1.0 nm and below for device generations in the near future.[9] When a high-k oxide is used, the gate dielectric can be made physically thicker for the required capacitance density, thus lowering the tunneling current. A convenient measure for the capacitance density is the equivalent oxide thickness ($EOT = d_{\text{high-k}}\,k_{SiO2}/k_{\text{high-k}} = 3.9(d_{\text{high-k}})/k_{\text{high-k}}$), and for future devices with high-k-based dielectrics this should be 1.0 nm or less. However, silicon is easily oxidized from its surface and a thin interface layer of SiO_2 or a mixture of SiO_2 and the high-k oxide is easily formed, which adds to the overall EOT. On the other hand, the Si–SiO_2 interface is commonly recognized as the best semiconductor–insulator interface. Therefore, to achieve an EOT of less than 1.0 nm with good electrical characteristics, a very thin, one-to-two monolayer thick interfacial SiO_2 layer should preferably be left between the silicon and the high-k oxide. Controlling such a thin SiO_2 layer is very challenging (Figure 4).

ALD high-k gate oxide research has mainly focused on three basic systems: $Al(CH_3)_3/H_2O$, $ZrCl_4/H_2O$, and $HfCl_4/H_2O$. These systems have all yielded good results in an EOT range of 1–2 nm,[9] but scaling the EOT down further is difficult and requires careful attention to the pretreatment of the silicon surface. Despite many efforts, better processes than those mentioned above have not been found. The lowest EOT should be achievable by using native-oxide free, hydrogen-terminated silicon as the starting surface. However,

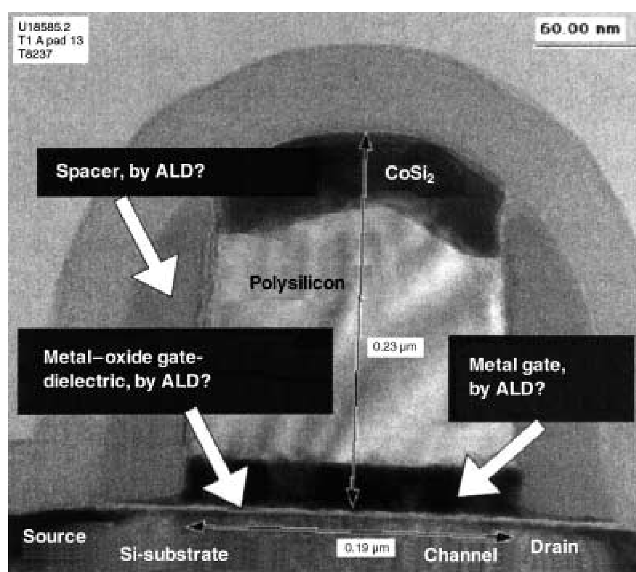

Figure 4. A cross-sectional TEM image of a MOSFET (channel length = 0.19 µm) showing three application areas where ALD films could be used. See text for details.

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nucleation on this surface, particularly for ZrO_2 and HfO_2, is poor and results in inhomogeneous microstructure, thereby preventing their direct application on hydrogen-terminated surfaces.[10] More work is needed to tailor the interface to an optimum level. Alternative chemistry developed for the ALD of oxides involves the use of metal alkoxides as oxygen sources, which react with other metal compounds, most often chlorides.[11,12] Because oxygen atoms are bound to the metal centers in the alkoxides, they oxidize silicon less strongly than water, which results in a sharp interface. Unfortunately, these processes leave a somewhat higher content of chloride residue ($\approx$1 atom %), as compared with the conventional metal chloride–water processes.

Progress in the application of high-k gate oxides has been somewhat slower than what was assumed a few years ago. The problem is the high-k materials themselves rather than the ALD processing.[8] Direct contact with silicon often degrades electron and hole mobility in the MOSFET channel region and the interaction with the polysilicon top electrode may create charges which shift the threshold voltage.

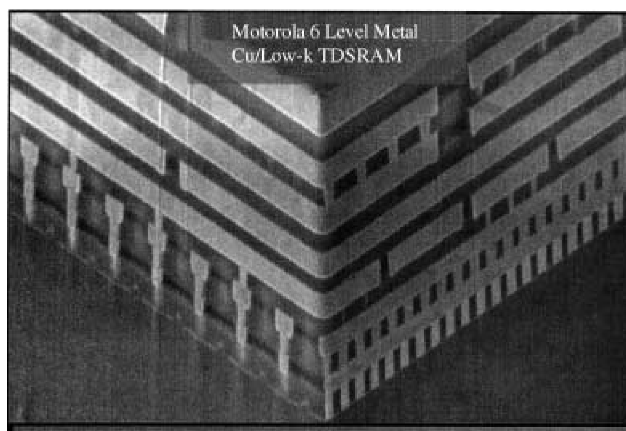

Figure 5. Focused ion beam (FIB) cross section through a six-layer Cu/low-k dielectric interconnect metallization. Here ALD could be used for depositing thin metal or metal nitride barrier layers (not resolved in the image) encapsulating the copper wires (bright features) as well as depositing seed layers for Cu electroplating.

4.2. DRAM Capacitors

The development of DRAM capacitor dielectrics has been similar to that of gate dielectrics: SiO_2 has dominated thus far, but is likely to be phased out in the near future. The DRAM capacitors will be three dimensional, thus requiring good conformality, but permittivity values above 200 will still be required, and thus the candidate materials are different from those explored for MOSFET gate dielectrics. The most extensively studied candidate has been $(Ba,Sr)TiO_3$. Due to the high conformal requirements of DRAM applications, ALD is a very promising method, although ternary and quaternary compounds are very challenging for chemical thin-film deposition techniques. Totally new ALD chemistry has been developed for $SrTiO_3$ and $BaTiO_3$ using strontium and barium cyclopentadienyl compounds, [Ti(O*i*Pr)$_4$], and water as precursors.[13] A permittivity of 180 was measured for $SrTiO_3$ and 165 for $BaTiO_3$ when films thicker than 200 nm were post-deposition annealed, but when the film thickness was decreased to 50 nm, the permittivity decreased to only 100.

4.3. Transition-Metal Nitrides

Transition-metal nitrides, such as TiN and TaN find potential use both as metallization barriers and as gate metals. Metallization barriers are needed on one hand to avoid Cu diffusion into the surrounding insulators and the silicon substrate and, on the other hand, to prevent Cu contamination by elements diffusing from the insulators (Figure 5). Metal gates (Figure 4), in turn, will be needed to eliminate the EOT-increasing effect of the depletion layer capacitance in the presently used polysilicon gate electrodes. The most studied ALD nitride process has been that where TiN is deposited from $TiCl_4$ and NH_3. Films with low resistivity ($<200\,\mu\Omega\,cm$) and excellent conformality are obtained with this process at 400 °C (Figure 2b).[14] The process is not ideal, however, because of the modest reactivity of ammonia, the halide residue content, the modest deposition rate and, most importantly, the fact that the HCl formed as a byproduct in the process causes pitting of copper.[14] Many alternative titanium precursors have been studied but an ideal solution for the TiN process has not yet been found. Simultaneously, ALD chemistry has been developed for TaN and WN_x materials, which are more demanding to prepare than TiN since they require stronger reduction. In the deposition of TaN a three-precursor process ($TaCl_5/Zn/NH_3$) using Zn as a reducing agent has given the best results.[15] The use of zinc, however, is not accepted in microelectronics applications, and therefore alternative reducing agents, such as trimethylaluminum,[16] dimethylhydrazine,[17] and *tert*-butylamine[18] have been studied with varying success. Plasma enhancement offers new possibilities for the ALD of TaN and other transition-metal nitrides. TaN has been deposited using *tert*-butylimidotris(diethylamido)tantalum, [$(Et_2N)_3$Ta=N*t*Bu], and hydrogen radicals as precursors.[19] The process takes place at low temperature (260 °C), has a good growth rate (0.8 Å/cycle), but needs long hydrogen plasma exposure times (30 s). Another plasma-enhanced ALD process for TaN uses $TaCl_5$ together with hydrogen and nitrogen plasma.[20] The N/Ta ratio was controlled from 0.3 to 1.4 by varying the nitrogen partial pressure, which indicated that the process was not completely self-limited. However, the films had a low resistivity of 350 $\mu\Omega$ cm. WN is an alternative barrier material, which has been deposited from WF_6 and NH_3 with a rate of 0.42 Å/cycle at 350 °C.[14] In a high-vacuum chamber and with longer exposure times, the same process resulted in a much higher deposition rate of 2.55 Å/cycle.[21] Some copper pitting was observed also in this process, however.[14] Recently, a new process utilizing WF_6, NH_3, and $B(C_2H_5)_3$ was reported for depositing WC_xN_y (atomic composition: W 57 %, C 30 %, N 13 %).[22] A resistivity of 600–900 $\mu\Omega$ cm was measured for 7-nm films of this material. Unlike TiN and WN_x, WC_xN_y barriers deposited by ALD do not show Cu pitting voids in dual-damascene (Figure 6) copper metallization nor passiva-

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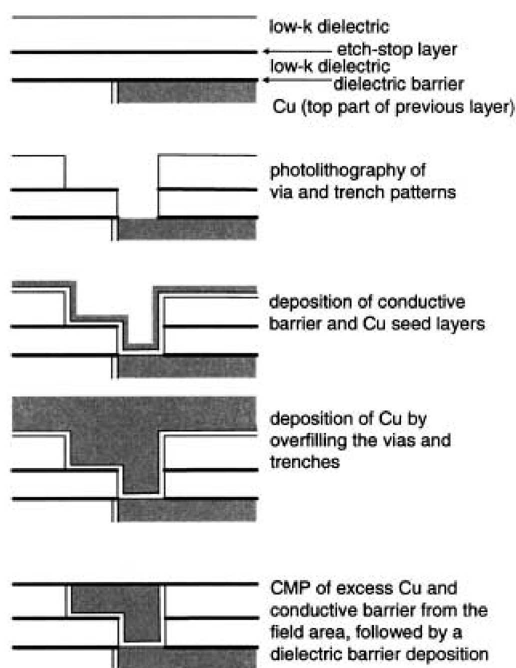

Figure 6. Dual-damascene process flow for the fabrication of copper interconnects. This approach was developed because the dry etching of copper is difficult because of a lack of suitable volatile copper compounds. In the damascene process, copper patterning into wires and via plugs is realized by dry etching appropriate trench and via patterns into the dielectric film, then filling these with copper, and finally removing the excess copper by chemical mechanical polishing (CMP).

tion blistering, and is the best ALD barrier material reported so far.

4.4. Metal Films

An interest in metal ALD has several motivations: 1) Cu interconnects and W plugs, or at least Cu seed layers for Cu electrodeposition and W seeds for W CVD, 2) Ti and Ta for Cu interconnect barriers, 3) noble metals for ferroelectric random access memory (FRAM) and DRAM capacitor electrodes, and 4) high- and low-workfunction metals for dual-gate MOSFETs. Metals have been quite problematic for ALD techniques; most trials to employ metal CVD chemistry in ALD have been unsuccessful. The reasons for these difficulties are thought to be related to a lack of an appropriate mechanism by which metal precursors can adsorb on metal surfaces that do not contain reactive sites, such as hydroxyl groups in the oxide processes, and the low reactivity of the common reducing agent H_2. George et al.[23] demonstrated that tungsten may be deposited from WF_6 and Si_2H_6. Based on detailed mechanistic studies, the overall reaction was suggested to be that which is displayed in Equation (1).

$$WF_6 + Si_2H_6 \rightarrow W + 2\,SiHF_3 + 2\,H_2 \quad (1)$$

Amorphous films, free of silicon and fluorine, could be deposited at a rate of 2.5 Å/cycle. The noble metals Ru and Pt have been deposited from the organometallic precursors $[Ru(C_5H_5)_2]$ and $[CH_3C_5H_4Pt(CH_3)_3]$ and oxygen.[24] A key feature of the growth mechanism is that oxygen atoms remain adsorbed on the Ru and Pt surfaces after the oxygen pulse and the following purge sequence. When the organometallic compounds are exposed on the surface, the oxygen atoms oxidize part of the hydrocarbon ligands to carbon oxides and water. The remaining ligands and hydrocarbon fragments are oxidized during the next oxygen pulse, which also reforms the adsorbed oxygen-atom layer. The films were pure and had resistivities of 10–20 μΩ cm. It is quite apparent that this kind of ALD chemistry is applicable to all noble metals capable of catalyzing the dissociation of molecular oxygen.

The use of radicals has introduced many new possibilities for metal ALD, as compared with just thermally activated processes. Titanium and tantalum, for example, are such electropositive elements that their deposition without additional activation is apparently impossible at reasonable temperatures. But by using highly reactive hydrogen radicals generated in a remote plasma discharge these metals have been deposited from the corresponding chlorides.[25] Reasonable deposition rates, resistivities, and step coverages have been reported for these metal films, and the barrier performance in separating copper and silicon was better than that of sputtered tantalum with a similar thickness. Even aluminum has been deposited at low temperatures with a good growth rate (1.5 Å/cycle) by a hydrogen-plasma-enhanced ALD process using trimethylaluminum as an aluminum precursor.[26] Nickel films have been deposited indirectly by first making the oxide and reducing that with hydrogen[27] or hydrogen radicals.[28]

Despite some initial reports[29] on copper ALD this metal has remained quite problematic. Recently, it was shown that copper seed layers may be formed indirectly by first depositing a copper oxide film using $[Cu(thd)_2]/O_3$ (thd = 2,2,6,6-tetramethyl-3,5-heptanedionate) as precursors and then reducing CuO to metallic copper with alcohols, aldehydes, or carboxylic acids.[30] It has also been shown that copper may be deposited from $[Cu(acac)_2]$ (acac = acetylacetonate) using hydrogen radicals from an upstream microwave plasma discharge.[31] The films deposited on glass were quite rough, however, and had resistivities of 14 μΩ cm when 30-nm thick.

5. Recent Discoveries

The increasing interest in ALD over the last few years has resulted in some interesting new innovations. The results show clearly that the key issue in ALD is proper chemistry. With smart thermal-activated chemistry, it has been possible to develop new processes and new film materials grown by ALD. A good example of this development is the discovery of Gordon et al., who deposited SiO_2 with a small amount of Al_2O_3 at an exceptionally high growth rate (12 nm/cycle) from tris(*tert*-butoxy)silanol activated by trimethylaluminum.[32] A low growth temperature (250 °C) was employed and yielded materials with complete conformality in trenches with an aspect ratio of 70:1. The proposed mechanism relies on a polymerization reaction where silanol molecules insert into Al–O bonds. The chains that are formed may then crosslink

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via the decomposition of *tert*-butyl groups and the elimination of isobutene and *tert*-butanol. Though this deposition rate is too high for gate dielectric applications, the process may find applications for ALD-grown SiO_2 in spacers (Figure 4) and trench insulators between transistors, multilayer optical filters, planar waveguides, protective layers, and microelectromechanical system (MEMS) devices.

The deposition of tungsten films from tungsten hexafluoride and disilane is another example of the new smart chemistry.[23] Non-noble metals are difficult to prepare in thermally activated processes, but it is possible with a suitable combination of precursors. The new chemistry introduced for high-k gate oxides that utilizes metal alkoxides as oxygen sources is also showing the importance of chemistry in ALD processes.[11]

The use of a third component in an ALD cycle of binary compounds opens up many possibilities. The use of bases to catalyze the reaction $SiCl_4 + 2H_2O \rightarrow SiO_2 + 4HCl$, and reductive pulses in the preparation of nitride films represent some existing examples.[15,33] The third component may introduce a new element into the film, as is in the serendipitous case of WC_xN_y, where improved barrier properties and process integration were obtained.

Ternary and quaternary compounds needed for the preparation of ferroelectric oxides are apparently the greatest challenge for ALD. There are two major issues: Ferroelectric oxides contain several cations whose stoichiometry must be accurately controlled. Second, for some of these elemental cations, such as lead, bismuth, and also to some extent strontium, there is no good ALD binary oxide process available. One solution for controlling the cation stoichiometry is to employ bimetallic complexes where the cations are present in the same ratio as in the desired film. $SrTa_2O_6$ has been deposited from such a precursor ($[SrTa_2(OEt)_{10}(dmae)_2]$; dmae = *N,N*-dimethylaminoethoxide) using either water[34] or oxygen plasma[35] as the other precursor. Currently, the addition of bismuth to this film is being studied with an aim to obtain the ferroelectric $SrBi_2Ta_2O_9$. A large amount of work is still required for controlled ALD processes for ferroelectrics.

Radical enhancement has opened new possibilities for developing ALD processes for materials which have remained outside the capabilities of thermally activated chemistry. Illustrative examples of this are the successful depositions of titanium, tantalum, and aluminum metals. Besides materials completely new to ALD, radical enhancement will also offer alternative, apparently lower temperature routes for those materials which have so far been deposited by traditional ALD processes. Radical enhancement is also likely to assist in keeping precursor chemistry relatively simple, however, one obvious drawback of the radical enhanced processes is the need for a more complicated reactor design.

High-surface-area substrates have been a subject of ALD studies because of their importance in heterogeneous catalysis, and because they offer plenty of materials for detailed chemical characterization.[36] Some good results have been obtained from depositions on porous silicon, for example.[37] Slow precursor transportation makes the processes very slow, but as there are no other viable alternatives, ALD is and will remain an important method for deposition on porous materials and holes.

Selective ALD is a very attractive concept but also very challenging. With self-assembled monolayers (SAMs) as passivation agents, ZrO_2 was recently deposited selectively for $Cu/ZrO_2/Si$ capacitors.[38] The patterning of spin-coated octadecyl tetrachlorosilane (OTS) was achieved by microcontact printing.

6. The Limitations of ALD

The major limitation of ALD is its slowness; usually only a fraction of a monolayer is deposited in one cycle. Typically deposition rates are 100–300 $nm\,h^{-1}$. Therefore it is not very practical to grow micrometer-thick films by ALD. The slow growth rate can be compensated by processing large batches of substrates in one process, as is done in TFEL production. In microelectronics, however, single-wafer processing is preferred. Fortunately the films needed for future-generation ICs are very thin and thus the slowness of ALD is not such an important issue.

Although the selection of film materials grown by ALD is wide,[5] many technologically important materials (Si, Ge, Si_3N_4, several multicomponent oxides, certain metals) cannot currently be deposited by ALD in a cost-effective way. Only a small number of groups have been studying new ALD precursors and processes and this has limited the development of the technique.

ALD is a chemical technique and thus there is always a risk of residues being left from the precursors. The impurity content of the films depends on the completeness of the reactions. In typical oxide processes where metal halides or alkyl compounds are used together with water as precursors, impurities found in the films are at the 0.1–1 atom% level. The carrier gas is also an important source of impurities, as has been exemplified, for example, with oxygen-sensitive AlN films. In physical vapor deposition (PVD) methods the environment is much cleaner due to the high vacuum used and the lack of precursor compounds with unwanted elements.

Because of their unique impurity background, ALD-grown materials may have different properties than those made by PVD, for example. This has been seen in transition-metal nitride films, where small variations in composition markedly affects the electrical properties.[8] Also microstructure and morphology of ALD films may differ from PVD films. Therefore the ALD materials have to be characterized thoroughly before use. Post-deposition treatments, particularly high-temperature annealing under varied atmospheres, form an important part of this research as they may have both beneficial and adverse effects on purity and microstructure.

7. Future Aspects

Despite the achievements made over recent years, many challenges still remain for the future development of ALD in

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microelectronics applications. Basic research on precursor chemistry and film deposition will remain important, especially when expanding the application of ALD to new materials and devices, for example, to ferroelectric oxides for nonvolatile memories. Integration of the ALD processes and materials to the overall process flow forms another important area of the research, and this should be properly addressed during the early stages of the process development.

The intense research into using ALD in microelectronics has brought the technique wider publicity. As the general awareness of ALD has increased, an interest in its usage in other potential application areas has also increased. Such areas include insulator layers in magnetic write–read heads, MEMS, and a number of demanding applications in optics and protective coatings. It is evident that in the future, research into ALD will expand further.

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