Atomic layer epitaxy—a valuable tool for nanotechnology?

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Abstract. Atomic layer epitaxy (ALE) is a surface controlled, self-limiting method for depositing thin films from gaseous precursors. In this paper the basic principle of ALE and its potentials for nanotechnology are introduced. From the point of view of nanotechnology the most important benefits of ALE are excellent conformality and easily realized subnanometre level accuracy in controlling film thicknesses, which are discussed in more detail with selected examples from thin-film technology. Studies on ALE preparation of laterally confined structures are also reviewed. The paper concludes with an outlook discussing the capabilities and challenges of using ALE in nanotechnology in depositing materials with one or several dimensions confined to the nanometre level.

1. Introduction

Atomic layer epitaxy (ALE) [1–3] is a special modification of the chemical vapour deposition technique for depositing thin films and related surface structures. The unique feature of ALE is the self-limiting film growth mechanism which gives it a number of attractive properties, like accurate and simple film thickness control, sharp interfaces, uniformity over large areas, excellent conformality, good reproducibility, multilayer processing capability, and high film qualities at relatively low temperatures.

Though the main efforts in ALE research have so far concentrated on 'conventional' thin-film applications [1–4], the above properties make ALE a technique also worthy of consideration for nanotechnology. In this paper, the basic principle of ALE together with its benefits and limitations will be introduced. The most important advantages of ALE with respect to nanotechnology will be discussed with some selected examples taken from ALE thin-film research. The few studies on using ALE in depositing materials with more than one dimension restricted to the nanometre level will be reviewed, and finally a brief future outlook of ALE in nanotechnology will be given.

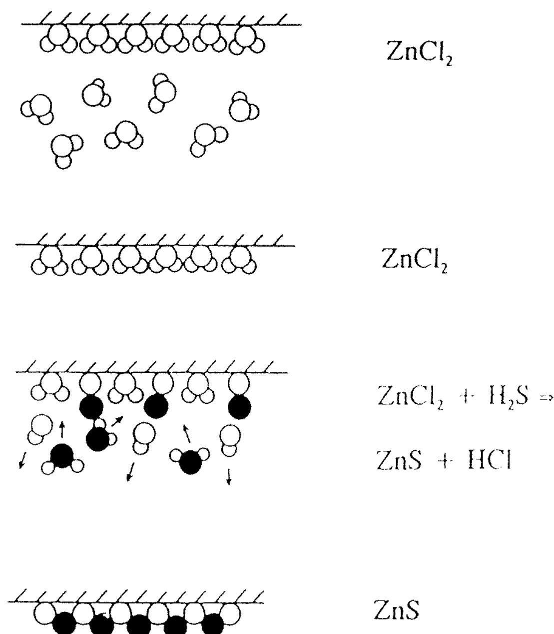

Figure 1. A schematic representation of the basic principle of the ALE process showing the growth of ZnS film from $ZnCl_2$ and H_2S.

2. ALE method

In ALE the reactant vapours are pulsed onto the substrate alternately one at a time, and between the reactant pulses the reactor is purged with an inert gas (figure 1) [1–3]. With a proper adjustment of the experimental conditions all the process steps are saturative, i.e. the precursors exposed on the surface chemisorb on it—or react with the surface groups—saturatively forming a tightly bound monolayer on the surface, and the subsequent purging step removes all the excess molecules from the reactor chamber. When the next precursor is dosed in, it will thus encounter only the surface monolayer with which it reacts, producing the desired solid product and gaseous by-products. Under such conditions the film growth is self-limiting, since the amount of solid deposited during one cycle is dictated by the amount of precursor molecules in the saturatively formed surface monolayer.

The advantageous consequences of the self-limiting growth mechanism are summarized in table 1. Further advantages of ALE arise from the separate dosing of the precursors and wide processing windows as also indicated

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Table 1. Characteristic features of ALE, their implications on the film growth and the consequent practical advantages.

Characteristic feature of ALE	Inherent implication for film deposition	Practical advantage
Self-limiting growth process	Film thickness is dependent only on the number of deposition cycles	Accurate and simple thickness control
	No need for reactant flux homogeneity	Large-area capability Large-batch capability Excellent conformality No problems with inconstant vaporization rates of solid precursors Good reproducibility Straightforward scale-up
	Atomic level control of material composition	Capability to produce sharp interfaces and superlattices Possibility to interface modification
Separate dosing of reactants	No gas phase reactions	Favours precursors highly reactive towards each other, thus enabling effective material utilization
	Sufficient time is provided to complete each reaction step	High-quality materials are obtained at low processing temperatures
Processing temperature windows are often wide	Processing conditions of different materials are readily matched	Capability to prepare multilayer structures in a continuous process

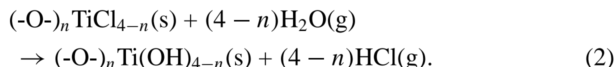
in table 1. Altogether these characteristics constitute a long list of benefits in the last column of the table, thus suggesting ALE to be an almost ideal tool for thin-film deposition. However, there is one major disadvantage which has greatly limited the use of ALE: the slowness of the film growth. Since each cycle consists of four separate steps (figure 1), and the outcome of one cycle is at best one monolayer—and quite often a submonolayer—the film growth evidently takes time. Nonetheless, by proper reactor and precursor design this limitation can be compensated for. In flow-type reactors which have closely spaced substrates and are operated in the millibar pressure range with plug-like flow conditions [1], both reaction and purging steps can be completed within 0.1–0.2 s, provided that the precursors exhibit high reactivity towards each other. Therefore, deposition rates up to about 500 nm h^{-1} may be achieved. Although these deposition rates are still rather low, high productivities can be realized by making use of the large-batch processing capability of ALE. For example, the largest ALE reactors used in industrial manufacturing of thin-film electroluminescent (TFEL) displays accommodate 82 glass substrates with dimensions of 155×265 mm^2 [4]. Therefore, while evaluating the potential of ALE, the productivity should be carefully distinguished from the deposition rate.

The term ALE is usually used generally for the deposition technique outlined above, irrespective of whether the resulting films are epitaxial, polycrystalline or amorphous. The selection of materials deposited by ALE is extensive, covering compound semiconductors, oxides, nitrides and also some elements (table 2) [1–4]. It must be noted, however, that some of these processes are far from being ideal. For example, SiO_2 can be deposited by ALE but the pulse times needed to realize the reactions are very long [5–7], and thus the process is useful only for very thin films deposited in a few cycles only. More detailed reviews on ALE processes and related chemical aspects can be found in [1–3].

At this stage it must be emphasized that figure 1 is only schematic, the real processes being often much more complicated [2, 3]. In many cases no molecular chemisorption takes place but the incoming precursors react with the functional groups on the surface [2, 6–14]. For example, in the growth of metal oxides from the corresponding chlorides and water, the metal chloride, for example $TiCl_4$, binds to the surface by undergoing an exchange reaction with the surface hydroxyl groups [8, 9]:

$$n(\text{-OH})(s) + TiCl_4(g) \rightarrow (\text{-O-})_n TiCl_{4-n}(s) + n HCl(g) \quad (1)$$

where $n = 1$–3 depending on the temperature and spatial distribution of the hydroxyl groups. The following water pulse changes the surface back to a hydroxylated one:



$$(\text{-O-})_n TiCl_{4-n}(s) + (4-n)H_2O(g) \rightarrow (\text{-O-})_n Ti(OH)_{4-n}(s) + (4-n)HCl(g). \quad (2)$$

Another simplification of figure 1 is the impression that the self-limiting film growth would always proceed smoothly in a layer-by-layer manner. First, because of steric limitations, caused in particular by large ligand groups like thd (= 2, 2, 6, 6-tetramethyl-3, 5-heptanedionato) but also by smaller ligands like halides, the density of metal ions in the chemisorption monolayer is often too low for a full monolayer deposition [2, 15]. Another potential reason for the less than monolayer per cycle deposition rate is the limited number of surface groups which the precursor has to react with to become firmly bonded (cf equation (1)). Secondly, atomic force microscopy studies [16–20] have shown that the ALE growth of polycrystalline films involves nucleation stages similar to those of other film deposition methods, and thus the film deposition does not proceed completely smoothly but leads to roughening of the surface. Entirely smooth film growth may be expected only when the film is amorphous [13, 14, 21] or epitaxial [22], though even then some roughening may occur.

Table 2. Thin-film materials deposited by ALE including all the films deposited in epitaxial, polycrystalline or amorphous form.

II–VI compounds	ZnS, ZnSe, ZnTe, $ZnS_{1-x}Se_x$
	CaS, SrS, BaS, $SrS_{1-x}Se_x$
	CdS, CdTe, MnTe, HgTe, $Hg_{1-x}Cd_xTe$, $Cd_{1-x}Mn_xTe$
II–VI based TFEL	ZnS:M (M = Mn, Tb, Tm), CaS:M (M = Eu, Ce, Tb, Pb)
phosphors	SrS:M (M = Ce, Tb, Pb, Mn, Cu)
III–V compounds	GaAs, AlAs, AlP, InP, GaP, InAs
	$Al_xGa_{1-x}As$, $Ga_xIn_{1-x}As$, $Ga_xIn_{1-x}P$
Nitrides	
Semiconductors/Dielectric	AlN, GaN, InN, SiN_x
Metallic	TiN, TaN, Ta_3N_5, NbN, MoN
Oxides	
Dielectric	Al_2O_3, TiO_2, ZrO_2, HfO_2, Ta_2O_5, Nb_2O_5, Y_2O_3, MgO, CeO_2,
	SiO_2, La_2O_3, $SrTiO_3$, $BaTiO_3$
Transparent conductors/	In_2O_3, In_2O_3:Sn, In_2O_3:F, In_2O_3:Zr, SnO_2, SnO_2:Sb, ZnO,
Semiconductors	ZnO:Al, Ga_2O_3, NiO, CoO_x
Superconductors	$YBa_2Cu_3O_{7-x}$
Other ternaries	$LaCoO_3$, $LaNiO_3$
Fluorides	CaF_2, SrF_2, ZnF_2
Elements	Si, Ge, Cu, Mo
Others	La_2S_3, PbS, In_2S_3, $CuGaS_2$, SiC

Even if the film growth does not proceed in the ideal manner depicted in figure 1, the advantages listed in table 1 are still valid. In the following, two of these, considered as the most important ones with respect to nanotechnology, will be discussed in more detail.

3. Conformality

Excellent conformality is inherent to ALE, provided that the precursor doses and pulse times are sufficient for reaching the saturated state at all surfaces and no extensive precursor decomposition takes place. The conformality of ALE has been verified with trench structures having dimensions relevant to semiconductor devices (figure 2) [23–25]. In addition, it has been shown that by ALE one can tailor the pore size of alumina membranes [26]. The excellent conformality ensures also that small defects and impurities on the starting surface will not form point defects to the films but rather will be uniformly encapsulated. This is of vital importance in depositing high-quality insulators for TFEL devices [1] and dense corrosion protection coatings [27].

Even more demanding conformality requirements have been successfully met in processing porous substrates, like porous silica and alumina powders [8–12], and porous silicon layers [28, 29]. Because the time needed to transport precursors into and out of the nanometre size pores is long, usually only a few ALE deposition cycles have been applied. Therefore, these ALE processes have been used just to modify the surfaces of the porous substrates rather than to deposit a thin film onto them. Nevertheless, in all cases a uniform distribution through the nanoporous substrate has been confirmed.

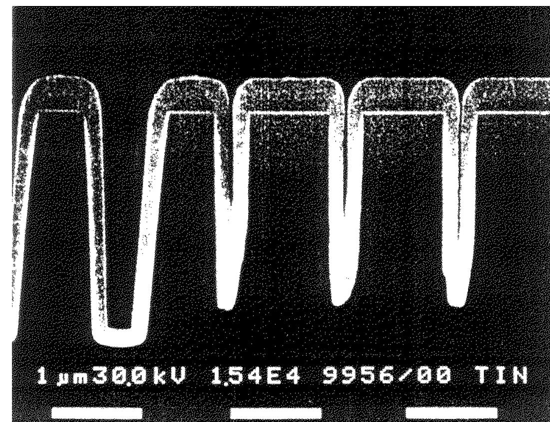


Figure 2. Cross-sectional scanning electron microscopy image of about 160 nm TiN film deposited on patterned silicon wafer. On the top surface of the substrate there is a 100 nm thermal SiO_2 layer which should be distinguished from the TiN film.

4. Subnanometre level accuracy in thickness control

Film thickness control in ALE is easily and simply realized with the aid of the number of deposition cycles applied because during each cycle exactly the same amount of material is deposited. The most sophisticated examples of the monolayer accuracy in the film thickness control are found from the most well-defined growth systems, i.e. epitaxial superlattices [1, 30, 31]. For example, Mori *et al* [30] have deposited superlattices of the type $(InAs)_1(GaAs)_5$, i.e. one InAs monolayer between five GaAs monolayers, and confirmed the structure by x-ray diffraction and cross-sectional transmission electron microscopy.

The convenience in thickness control applies also to non-epitaxial films, though the accuracy is then usually somewhat poorer than the one monolayer in the growth of superlattices. For example, optical multilayers have been made by ALE for both visible [32] and soft x-ray [33, 34] wavelength ranges. The optical components made for the visible range reproduced accurately the spectral responses calculated for the designed multilayer structures, indicating that both the thicknesses and optical properties of the films were well controlled [32]. These components consisted of polycrystalline ZnS and amorphous Al_2O_3 layers with thicknesses of 62 and 86 nm, respectively.

In the multilayers made for the soft x-ray range the layers must be only a few nanometres thick. Therefore the

requirements on the film thickness accuracy and interface smoothness are more stringent than in the visible range optics. Nevertheless, in good agreement with the calculations, Kumagai *et al* [33] achieved, with an ALE-made multilayer structure, a high reflectance of over 30% at a wavelength of 2.734 nm and an incidence angle of 71.8° from the surface normal. The multilayer consisted of 20 pairs of amorphous Al_2O_3 and TiO_2 layers and had a layer-pair thickness of 4.43 nm. Multilayers with even lower layer-pair thicknesses of 3.2 nm have also been made from the same materials [35]. Ishii *et al* [34] prepared soft x-ray multilayer mirrors from AlP and GaP layers deposited on GaP substrate with a rate of exactly one monolayer per cycle. A multilayer consisting of 50 bilayers of $(AlP)_{22}(GaP)_{13}$ had a maximum reflectance of over 10% at a wavelength of about 17 nm and an incidence angle of 35° from the surface normal.

Another study where the accurate thickness control of ALE was found to be of great importance was the preparation of nanolaminate dielectric films [36–38]. The motivation for making such nanolaminate structures was to develop insulators with high permittivity and low leakage current. Ta_2O_5 has a relatively high permittivity of about 25 but it is very leaky. In the nanolaminates Ta_2O_5 was combined with other insulators, like ZrO_2 or HfO_2, into a stack of thin (2.5–15 nm) layers (figure 3) with a dramatic improvement in leakage current properties and only a small decrease of the permittivity. It is believed that in the nanolaminates localized weak points in one sublayer are counterbalanced by the adjacent layers, thus restricting leaky channels extending through the entire nanolaminate structure. However, in addition, it was observed that the dielectric properties of the nanolaminates could be tailored further by adjusting the sublayer thicknesses. These changes are thought to arise from changes in the structure and size of the crystallites in the ZrO_2 or HfO_2 sublayers as suggested by x-ray diffraction. Therefore, in achieving the optimized dielectric properties reproducibly over large-area substrates, the accurate film thickness control and large-area uniformity give ALE an advantage over other techniques.

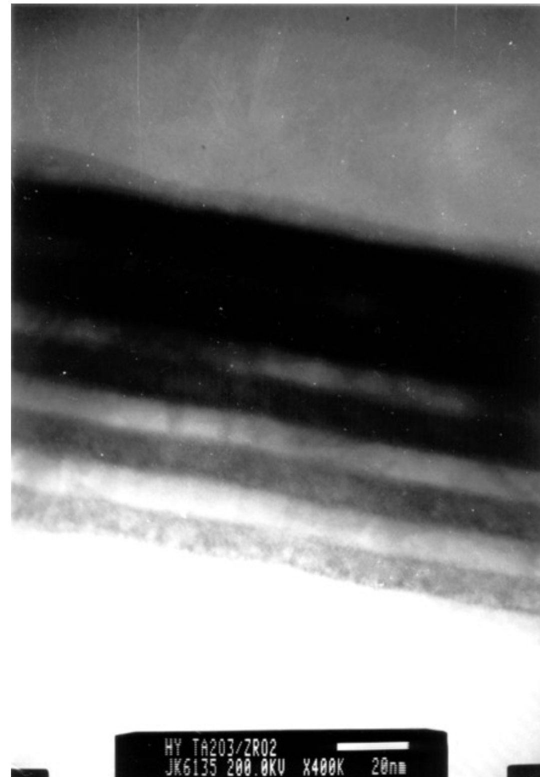


Figure 3. Cross-sectional transmission electron microscopy image of a nanolaminate structure consisting of alternate 10 nm thick Ta_2O_5 and ZrO_2 layers.

5. ALE deposition of laterally confined structures

The above examples selected from thin-film research demonstrated that with ALE it is straightforward to confine one dimension of the deposit, i.e. film thickness, into the nanometre range. Preparation of structures with two or three dimensions on the nanometre level is, however, obviously much more complicated.

Two-dimensionally confined quantum wires have been deposited by making use of a crystallographic selective ALE process [39–41]. V-shaped grooves etched on (100) GaAs substrate have (111) planes as their inclined sidewalls, while at the bottom the (100) surface is exposed. By controlling the purge time after AsH_3 or PH_3 exposure it is possible to adjust the GaAs or GaP deposition to occur anisotropically on the (100) facet only, or isotropically on both facets. About 10 nm high and 35 nm wide nearly rectangularly shaped GaAs quantum wires embedded between $GaAs_{1-x}P_x$ upper and lower barriers were prepared by depositing first $GaAs_{1-x}P_x$ isotropically on both the bottom and sidewalls of the V-shaped grooves, followed by an anisotropic deposition of GaAs on the bottom only, and finishing with isotropic $GaAs_{1-x}P_x$ [39, 40]. It has also been demonstrated that the laterally confined wire-like deposits may consist of $(GaAs)_m(GaP)_n$ short-period superlattices [41].

The agglomeration observed in the beginning of ALE deposition of polycrystalline materials [16–20] suggests that if only very few deposition cycles were applied, one would obtain nanoparticles rather than a continuous film. Such particles could be subsequently capped with a film with a low tendency towards agglomeration. In fact, with such a process CdSe dots with a uniform diameter of about 40 nm and height of 10 nm have been deposited on ZnSe(111) [42].

The most sophisticated three-dimensionally confined structures prepared by ALE are $In_{0.5}Ga_{0.5}As$ quantum dots which already during their deposition became laterally surrounded by an $In_{0.1}Ga_{0.9}As$ barrier [43–46]. Such structures were self-formed when alternate InAs and GaAs deposition cycles were applied. The dots were about 10 nm in height, had flat surfaces, and their areal coverage was 5–10%. With an increase of InAs/GaAs deposition cycles from 9 to 30 the in-plane diameter increased linearly from 20 to 32 nm and the photoluminescence (PL) emission peak wavelength shifted correspondingly from 1.17 to 1.3 μm [44]. The PL emission wavelength of the quantum dots could also be controlled by the composition of the adjacent buffer layers [45]. The PL emission peaks were narrow, 30–40 meV full width at half maximum, thus indicating good uniformity of the ALE deposited quantum dots [44–46]. The self-formation mechanism of the quantum

dots is not thoroughly understood, however, but they are believed to form as compositional non-uniformities during two-dimensional growth. It remains to be seen whether similar structures comprising quantum dots embedded in the surrounding barrier layer can be made of other materials as well.

6. Outlook

With ALE it is straightforward to deposit structures with one dimension confined to the nanometre level. The most sophisticated of such structures are epitaxial superlattices with layer thicknesses down to one monolayer, but also non-epitaxial structures with only a few nanometre layer thicknesses have been made for soft x-ray mirrors and nanolaminate dielectrics. Furthermore, the thickness accuracy is well preserved up to thicknesses of about 100 nm, at least. The conformality and large-area uniformity of ALE also make it possible to deposit well-controlled films on large-area, complex-shaped substrates. In the most extreme cases, the substrates may be nanoporous. Thus, whatever the application requiring highly conformal deposits with accurately controlled thicknesses, ALE will be a viable choice.

Preparation of two- or three-dimensionally confined structures has so far been realized by making use of crystallographic selectivity and agglomeration or self-formation, respectively. The quantum dot preparation is less controlled in the sense that it is not possible to affect their exact location. Further improvements in the preparation of laterally confined structures might be achieved by combining ALE with sophisticated patterning techniques. The patterning could be done not only after ALE deposition of a continuous layer but also before the ALE process, to create a patterned starting surface for surface selective ALE. Though ALE usually shows poor surface selectivity, some exceptions exist: the crystallographic selectivity [39–41] discussed above, deposition of GaAs and $In_{1-x}Ga_xP$ selectively on GaAs in the presence of SiON or SiO_2 [23, 31], and deposition of copper from $Cu(thd)_2$ and H_2 where the growth surface needs to be activated with platinum [47]. Whether further selective processes can be found remains to be examined.

On the other hand, as far as the authors know, no systematic studies have been performed on chemical passivation of surfaces against ALE growth. One approach might be to react the active surface sites, such as hydroxyl groups, with a compound which would form new surface groups inert to further reactions in the ALE process. For example, the well known silylating agents could be used for this purpose. Once uniformly passivated, the starting surface could be patterned by desorbing or decomposing the passivating groups with an electron beam, for instance. However, a detailed study of this approach is needed to evaluate its potential for selective ALE deposition of nanomaterials.

Nanoporous substrates already have by themselves more than one dimension in the nanometre range. The success of ALE in uniform modification of the inner surfaces of nanoporous materials has been demonstrated both with powders and nanoporous silicon surface layers. This is clearly a field where ALE can contribute a lot to nanotechnology.

ALE evidently has a lot of potential benefits for nanotechnology. Fruitful testing and exploitation of these benefits will require contributions from both ALE and nanotechnology researchers. Hopefully this paper assists in judging the possibilities of ALE and in providing visions of its use in nanotechnology.

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