

ATOMIC LAYER EPITAXY

Tuomo SUNTOLA

Microchemistry Ltd., Box 45, SF-02151 Espoo, Finland

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Contents

1. Introduction	266
2. The mechanism of the ALE process	268
2.1. Elemental reactants	269
2.1.1. Formation of a monolayer of element A	269
2.1.2. Purge time	272
2.1.3. Formation of a monolayer of element B	273
2.2. Compounds as the reactants	274
2.2.1. Metal halides and hydrides as reactants	274
2.2.2. Formation of a metal halide monolayer	274
2.2.3. Saturation of a metal halide monolayer	275
2.2.4. Reaction between a metal halide surface and a hydride reactant, formation of a monolayer B	276
2.2.5. Organometallic compounds as reactants	276
2.2.6. Monolayer formation	277
2.2.7. Re-evaporation of a monolayer during a purge sequence, effects of residual gas interaction	280
2.2.8. Reaction between a metal or a metal compound monolayer and a non-metal or a non-metal hydride	280
2.3. ALE process for elemental materials	282
2.4. The processing window of ALE	283
3. Equipment for the ALE process	284
3.1. System classification, open and closed systems	284
3.2. Vacuum systems	285
3.3. A lateral flow system with inert-gas valving	286
3.4. Inert-gas systems with moving substrate	287
4. Experimental	288
4.1. Gallium arsenide	288
4.1.1. Pioneering work on a TMG + AsH ₃ process	288
4.1.2. Introduction of a GaCl + AsH ₃ process	289
4.1.3. A model of photocatalysis in a TMG + AsH ₃ process	289
4.1.4. Further development of ALE processes of GaAs	289
4.1.5. Processes based on TMG + AsH ₃	290
4.1.6. Triethylgallium as a replacement for TMG	291
4.1.7. Gallium chloride (diethylgallium chloride) + arsine	293
4.1.8. Surface migration under ALE growth conditions	294
4.2. Other III–V compounds	295
4.2.1. AlAs	295
4.2.2. InP, GaP and InAs	295
4.2.3. Heterostructures of III–V compounds	296

<i>Atomic layer epitaxy</i>	263
4.3. II–VI single crystals	300
4.3.1. CdTe	300
4.3.2. ZnSe and ZnTe	301
4.3.3. ZnS	302
4.4. II–VI thin films, oxides and nitrides	302
4.5. ALE electroluminescent devices	304
4.5.1. ALE-EL thin film structure	304
4.5.2. ALE-EL devices	307
5. Summary	307
Acknowledgements	308
References	309

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This review discusses the development and present status of atomic layer epitaxy (ALE), a technology for growing layers of crystalline and polycrystalline materials one atomic layer at a time. Atomic layer epitaxy was originally developed to meet the needs of improved ZnS thin films and dielectric thin films for electroluminescent thin film display devices. Accordingly, early work on ALE was mainly carried out for thin films. During the 80s there has been a growing interest in applying ALE in the growth of single crystals of III–V and II–VI compounds and ordered heterostructures such as layered superalloys and superlattices. ALE has also been extended to the growth of elemental single crystals. A basic advantage of atomic layer epitaxy is in the increased surface control of the growth. This is achieved by combining a sequential reactant interaction with a substrate at a temperature which prevents condensation of individual reactants on the growing surface. This results in a stepwise process where each reactant interaction is typically saturated to a monolayer formation. Accordingly, the rate of the growth in an ALE process is determined by the repetition rate of the sequential surface reactions, and the thickness of the resulting layer is determined by the number of reactant interaction cycles. This self-controlling feature of atomic layer epitaxy ensures excellent uniformity of the thickness over large substrate areas even on non-planar surfaces. Owing to its principle of operation, ALE is especially suitable for producing layered structures of III–V and II–VI compounds. Superlattice structures of both these material groups have already been demonstrated. As a limiting case of superlattices, layered superalloys have also been grown. In ALE, chemical reactions producing a material, are divided into separate subreactions between a vapor and a solid surface, each of which results in a new atomic layer of the material. From the theoretical point of view ALE offers a unique link between theoretical and experimental chemistry by permitting direct observations of subreactions under conditions where the chemical environment is more precisely determined than in conventional continuous reactions.

1. Introduction

Atomic layer epitaxy is a method for producing thin films and layers of single crystals one atomic layer at a time utilizing a self-control obtained through saturating surface reactions. In conventional terminology, the term “epitaxy” has been used to describe the growth of single-crystal layers. An extension of the term epitaxy to also cover thin films in the case of atomic layer epitaxy is motivated through the original meaning of the expression “epitaxy”. It comes from the Greek language and means “on arrangement”. In ALE, a controlled “on arrangement” of atomic layers is obtained by sequentially controlled surface conditions.

Atomic layer epitaxy was originally developed to meet the needs of improved ZnS thin films and dielectric thin films for electroluminescent thin film display devices [1–3]. This goal was met, and it led to the commercial production of electroluminescent devices by Lohja Corporation in Finland. Because of this practical goal, the early development of atomic layer epitaxy was directed towards thin film processes which utilized large substrates. The selection of materials was limited to a few II–VI compounds and oxides. Scientific work on the mechanism of the growth was limited to the needs of practical processing of the thin films mentioned.

The basic mechanism of ALE, saturation of a monolayer onto the surface and a rate of growth that is proportional to the number of reaction cycles instead of to the time of the growth and the intensity of the material flux, was first proved simply by observing the growth per cycle with different dosing at different temperatures [1].

ALE is based on separate surface reactions between the growing surface and each of the components of the compound, one at a time. The components of the compound are supplied to the growing surface in vapor phase, either as elemental vapors or as volatile compounds of the elements. As a general introduction to the ALE process, fig. 1 summarizes the basic sequences of ALE in two alternative ways of producing ZnS. In each reaction there are sites for only one monolayer to make a bond with the original surface. A basic condition for a successful ALE

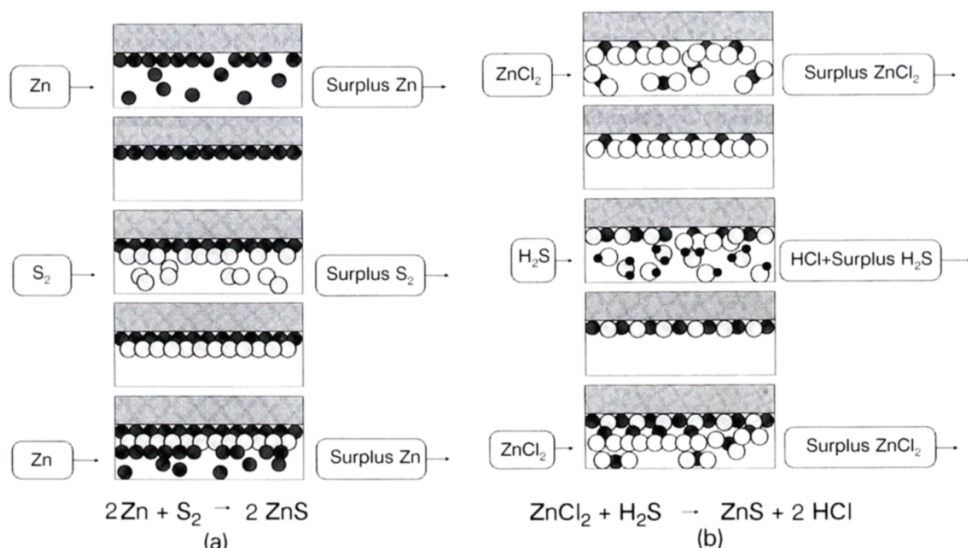


Fig. 1. ALE process for ZnS. (a) Zn and S as the reactants. (b) ZnCl₂ and H₂S as the reactants.

Table 1

Laboratories working on ALE, according to published papers. The list has been ordered according to the date of the first published paper of each laboratory. Laboratories marked with an asterix have not reported ALE processing, but describe the analysis of ALE thin films or single-crystal layers carried out in other laboratories

No.	Laboratory	Ref.
1	Lohja Co., Espoo, Finland	[1–9]
2	Tampere University of Technology, Tampere, Finland	[10–19]
3*	Helsinki University of Technology, Laboratory of Physics, Espoo, Finland	[20–34]
4*	Akademie der Wissenschaften der DDR, Zentralinstitut für Elektronenphysik, Berlin, DDR	[35]
5*	Institut für Festkörperphysik der Technischen Universität Berlin, Berlin, Germany	[36]
6*	Siemens AG, Munich, FRG	[37]
7	Helsinki University of Technology, Department of Chemistry, Espoo, Finland	[38–51]
8*	Joensuu University, Joensuu, Finland	[52–54]
9	Tohoku University, Sendai, Japan	[55–57]
10	{ Electrotechnical Laboratory, Ibaraki, Japan Tokai University, Kitakaname, Hiratsuka, Kanagawa, Japan	[58–68]
11	North Carolina State University, Raleigh, NC, USA	[69–78]
12	Research Development Co. of Japan, Semiconductor Research Institute, Sendai, Japan	[79–88]
13*	Standard Telecommunication Laboratories Ltd., Harlow, Essex, UK	[89,90]
14	NEC Co., Kawasaki, Japan	[91–105]
15	NTT Electrical Communications Laboratory, Musashino-shi, Tokyo, Japan	[106–115]
16	{ The Institute of Physical and Chemical Research, RIKEN, Saitama, Japan Hosei University, Tokyo, Japan Waseda University, Tokyo, Japan	[116–126]
17	Fujitsu Laboratories Ltd., Atsugi, Japan	[127–132]
18	Laboratoire Matériaux Exploratoire, L.C.R., Thomson C.S.F., Orsay, France	[133]
19	Rockwell International Science Center, Thousand Oaks, CA, USA	[134]
20	University of Southern California, Los Angeles, CA, USA	[135–138]
21*	The Wolfson Institute for Surface Engineering, Leeds University, Leeds, UK	[139]
22	Massachusetts Institute of Technology, Cambridge, MA, USA	[140]
23	McMaster University, Hamilton, Ontario, Canada	[141]
24	Tokyo Institute of Technology, Tokyo, Japan	[142–145]
25	Tokyo University of Agriculture and Technology, Tokyo, Japan	[146]
26	Philips Research Laboratories, Eindhoven, The Netherlands	[147]
27	Institut für Experimentalphysik, Johannes Kepler Universität, Linz, Austria	[148–150]
28	Hokkaido University, Sapporo, Japan	[151]
29	Changchun Institute of Physics, Changchun, China	[152]
30	Bell Communications Research Inc., Red Bank, NJ, USA	[153,154]
31	Purdue University, West Lafayette, IN, USA	[155]

process is that the binding energy of a monolayer chemisorbed on a surface is higher than the binding energy of subsequent layers on top of the formed monolayer. The temperature of the substrate is used as the primary controlling parameter. It is adjusted low enough to keep the monolayer on the surface until reaction with the following reactant takes place, but high enough to re-evaporate any of the subsequent layers or add-molecules on top of the monolayer. The control of a monolayer can further be influenced with the aid of a laser beam or other extra energy. The greater the difference between the bond energy of a monolayer and the bond energies of the subsequent layers, the better the self-controlling characteristics of the process.

In table 1 there is a list of laboratories working on ALE (according to published papers on ALE). The list has been ordered according to the date of the first published paper of each laboratory in the list.

Present interest in atomic layer epitaxy is primarily directed towards epitaxial growth of III-V and II-VI compounds, especially to layered structures, such as superlattices and superalloys. The use and development of ALE for these applications is motivated by the experimental and theoretical results according to which ALE

- (i) produces epitaxial layers at temperatures lower than those used in conventional epitaxial growth,
- (ii) is controllable to an accuracy of a single atomic layer because of saturated surface reactions.
- (iii) results in uniform layers over large areas, even on non-planar surfaces,
- (iv) makes it possible to study the chemical reactions associated with growth, in more detail than in conventional growth environments.

Atomic layer epitaxy has shown its commercial manufacturability in the production of electroluminescent display devices. In general, ALE is still very much in a developing state. Surface reactions used in ALE are not yet known in detail.

Excellent demonstrations of the potential of ALE for superlattice structures of both III-V and II-VI materials have been recently presented by Usui et al. [104] and Konagai et al. [144,145]. DenBaars et al. [135,137] have demonstrated a GaAs/(Al, Ga)As semiconductor laser with ALE grown GaAs layer.

2. The mechanism of the ALE process

The basic idea of ALE is the sequential surface reactions resulting in a saturating monolayer growth during each step. Most often the adsorption and desorption of atoms or molecules on a surface is described by the Langmuir model. In its simplest form, the Langmuir model [156] assumes that the adsorption of a molecule is not influenced by the presence of another adsorbed molecule. When restricting the analysis to the formation of bonds of one specific type at a time, this assumption can be accepted. It means that for each type of bond available for a certain molecule, we can define an activation energy for bond formation and an energy of desorption. For a second layer these energies will be different.

In a precise analysis of monolayer formation, the possible effects of the occupation of nearest-neighbor sites of the monolayer on the activation and desorption energies should also be considered.

The use of symbols in the following analysis is illustrated in fig. 2a. Activation and desorption energies and a pre-reaction state associated to surface reactions are often illustrated according to the Langmuir model, fig. 2b.

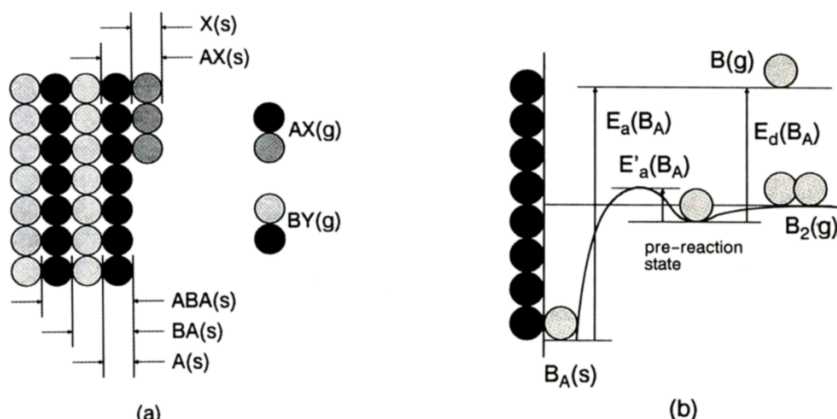


Fig. 2. (a) Use of symbols in the analysis of surface reactions. AB: compound of A and B; A: metal component of a compound; A(g): element A in gas phase; B: non-metal component of a compound; $B_n(g)$: non-metal component in gas phase as a multi-atom molecule; AX: compound of metal A used as a reactant for A, X denotes any additional part of the molecule of AX; BY: compound of non-metal B used as a reactant for B, Y denotes any additional part of the molecule BY; A(s): atoms A as surface atoms; AB(s): surface of compound AB with B as the surface atom; BA(s): surface of compound AB with A as the surface atom; BAX(s): reactant AX adsorbed on a B surface, surface atom is X, three atomic layers are encountered; ABAX(s): same as BAX(s), but four atomic layers are encountered; ABY(s): reactant BY adsorbed on an A surface, surface atom is Y, three atomic layers are encountered, etc. $E_a(A_B)$: activation energy of a reaction resulting in atom A to be bonded to a surface B(s); $E_a(AX_B)$: activation energy of a reaction resulting in molecule AX to be bonded to a surface B(s); $E(A_B)$: bond A–B energy; $E(AX_B)$: bond AX–B energy; $E_d(B_n)$: dissociation energy of a molecule B_n ; $E_a(B_A)$: activation energy of the chemisorption of B from a pre-reaction state on a surface A(s); $E'_a(B_A)$: bond energy of an atom B in a pre-reaction state on a surface A(s) (physisorption) which equals the desorption energy of a gas molecule B_n from a pre-reaction state on a surface A(s); $E(B_A)$: bond energy of an atom B on surface A(s) (chemical bond) which is equal to the desorption energy of a chemically bonded atom B from a surface A(s). (b) Langmuir model of surface energies for a gas molecule B_n .

2.1. Elemental reactants

2.1.1. Formation of a monolayer of element A

At its simplest, an ALE process for making a compound AB is carried out by first supplying A atoms onto the surface of B as a monatomic vapor of A(g) and B atoms as a vapor $B_n(g)$. The exposure times of A and B are $t(A)$ and $t(B)$, respectively. The re-evaporation or purge times after A and B exposures are $t_1(A)$ and $t_1(B)$, respectively, fig. 3.

The surface temperature is assumed to be high enough to prevent condensation of A onto a formed A surface. A monolayer of A atoms on the surface of B atoms of compound AB is then formed through the reaction



Monatomic vapors need no decomposition energy for the surface reaction (1) to occur. The formation of a monolayer of atoms A(s) basically follows the hitting rate of atoms A(g) onto the surface B (without a pre-reaction state) according to the equation

$$d[A(s)]/dt = H_A \{1 - [A(s)]/N_0(A)\} - [A(s)] R(A_B); \quad (2)$$

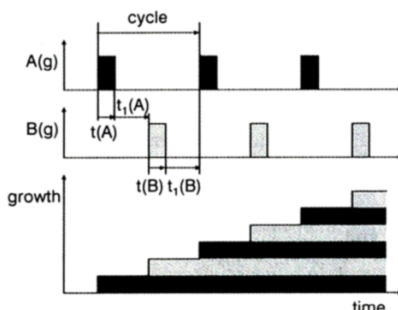


Fig. 3. Exposure and re-evaporation sequences of atoms A(g) and molecules B_n(g).

here H_A is the hitting rate of A(g) onto the surface per unit area,

$$N_0(A) = N_s(A) f_s(A_B), \quad (3)$$

where $N_s(A)$ is the density of atoms A in a monolayer on a surface B(s) in a given lattice direction of compound AB, $f_s(A_B)$ is the coverage of surface B with atoms A,

$$R(A_B) = R \exp[-E(A_B)/kT] \quad (4)$$

is the re-evaporation probability of an A atom from a B surface, R is a constant, $E(A_B)$ is the binding energy A–B (the desorption energy of A from a surface B), k is Boltzmann's constant and T is the temperature of the surface.

From (2) we have

$$[A(s)] = \frac{N_0(A)}{1 + R(A_B)N_0(A)/H_A} \{1 - \exp[-t/t_0(A)]\}. \quad (5)$$

Assuming a low re-evaporation rate of the monolayer

$$R(A_B) \ll H_A/N_0(A) \quad (6)$$

and letting $t = t(A)$, the surface occupation during the exposure of A can be expressed as

$$[A(s)] = N_0(A) \{1 - \exp[-t(A)/t_0(A)]\}, \quad (7)$$

where $t(A)$ is the exposure time of A(g) onto the surface and

$$t_0(A) = N_0(A)/H_A. \quad (8)$$

If the assumption (6) is not valid, the surface occupation $[A(s)]$ reaches the value shown by eq. (5) by letting $t = t(A)$.

$N_0(A)$ can be defined as the *saturation density* of surface atoms A on a surface B at a certain process temperature T , with the hitting rate H_A and exposure time $t(A)$. If $N_0(A)$ equals $N_s(A)$ on a surface, a *full monolayer saturation* is achieved. This is the most desirable surface occupation case, because it is needed for "a full monolayer growth/cycle".

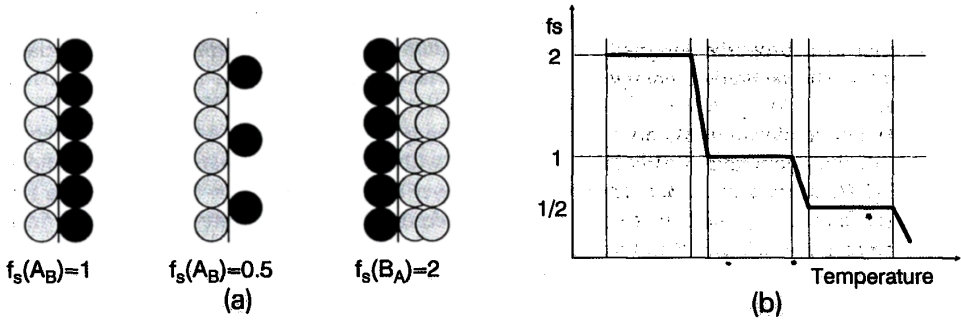


Fig. 4. (a) Left: $f_s(A_B) = 1$, atoms A form a complete monolayer; middle: $f_s(A_B) = 1/2$, a surface deformation results in a surface atom density of $1/2$ of the monolayer; right: $f_s(B_A) = 2$, a two-atomic molecule B_2 forms a monolayer. (b) Temperature dependence of surface layer filling factor f_s when $E_{1/2}(A_B) > E_1(A_B) > E_2(A_B)$.

In the analysis above, the desorption energy $E(A_B)$ was assumed to be independent of the surface coverage $f_s(A_B)$, which is not necessarily the case [157]. Fig. 4a illustrates surface configurations with filling factor $f_s(A_B) = 1/2$, $f_s(A_B) = 1$ and $f_s(A_B) = 2$ and desorption energies $E(A_B) = E_{1/2}(A_B)$, $E(A_B) = E_1(A_B)$ and $E(A_B) = E_2(A_B)$, respectively. Assuming $E_{1/2}(A_B) > E_1(A_B) > E_2(A_B)$, the Langmuir adsorption analysis results in a saturation $N_0(A) = N_0(A, T)$, i.e. the observed saturation density (filling factor at saturation) is a function of temperature, fig. 4b.

The characteristic feature of ALE, the saturation of a surface layer at a density $N_0(A)$ does not require the condition $f_s(A_B) = 1$. For a growth rate proportional to the number of cycles, it is essential that there exists a dominating surface configuration with a discrete binding energy $E(A_B)$. At different growth temperatures this dominating surface configuration might be different resulting in different growth/cycle ratios in the ALE growth [148].

The dose of A(g) can be defined as

$$D_A = t(A) H_A. \quad (9)$$

In order to make $[A(s)]$ approach $N_0(A)$, the condition $t(A) \gg t_0(A)$ must be satisfied:

$$D_A = t(A) H_A \gg N_0(A). \quad (10)$$

The hitting rate H_A and system characteristics are discussed in more detail in section 3. An important result is that for an open system, the hitting rate H_A at the growth surface can be expressed as defined by eq. (55) below:

$$H_A(\text{open}) = F_A f_s, \quad (11)$$

where F_A is the flux of A(g) from a source and f_s is a geometry factor of the system.

In a closed system the hitting rate is proportional to the partial vapor pressure of A(g) as defined by eq. (56)

$$H_A(\text{closed}) = p_A / (2\pi m_A kT)^{1/2}, \quad (12)$$

where p_A is the partial vapor pressure of A(g) and m_A is the mass of atom (molecule) A(g).

Eqs. (11) and (12) suggest that condition (10) can be reached with essentially smaller amount of material in a properly designed closed system than in an open system. This is especially important if the activation energy $E_a(A)$ of a surface reaction is high (resulting in a low reactivity).

In the above calculations, no attention has been paid to the possible effects of surface mobility during monolayer formation. Experiments with GaAs, in an enhanced mobility mode of MBE [107], show that by dosing only a “monolayer equivalence”, $D_A = N_0(A)$ of Ga, a full monolayer can be obtained. In this case, the temperature of the substrate has not been high enough to re-evaporate Ga from the Ga surface. Ga atoms migrate on the Ga surface until they are captured at a lattice site with a bond with As.

2.1.2. Purge time

A purge time is needed to ensure that reactants are not simultaneously present at the substrate surface.

If the dose D_A exceeds $N_0(A)$ at a temperature where condensation of A may take place, possible condensation on the formed A surface must be re-evaporated during the purge time. The re-evaporation rate of A atoms from an A(s) surface is

$$R(A_A) = R \exp[-E(A_A)/kT], \quad (13)$$

where $E(A_A)$ is the bond strength A–A(s) (the desorption energy of atom A from a surface of A atoms) and R is a constant.

If there is more than one layer of condensed A atoms, the re-evaporation rate remains constant. As soon as multilayers of condensation have re-evaporated, the re-evaporation reduces according to

$$d[AA(s)]/dt = [AA(s)] [1 - R(A_A)]. \quad (14)$$

Therefore,

$$[AA(s)] = [AA_0(s)] \{1 - \exp[-tR(A_A)/[AA_0(s)]]\}, \quad (15)$$

where $[AA_0(s)]$ is the density of the first condensed layer.

In practice, the processing temperature is kept high enough to prevent condensation, i.e. $R(A_A) > H_A$ during the exposure of A(g). In that case the necessary length of $t_1(A)$ is mainly a system parameter.

An unwanted effect that occurs during the purge time is the re-evaporation of a formed monolayer A(s) bonded to B. The surface occupation $[A(s)]$ ($[A(s)] \approx N_0(A)$ when $t = t(A)$) changes, owing to a re-evaporation of A(s) during the purge time, according to the equation

$$d[A(s)]/dt = -[A(s)] R(A_B), \quad (16)$$

so that

$$[A(s)] = N_0(A) \exp[-t_1(A) R(A_B)/N_0(A)]. \quad (17)$$

Under favorable ALE conditions, $R(A_B)$ is much less than $R(A_A)$. This minimizes the loss of A(s) monolayer and at the same time a high $R(A_A)$ prevents the formation of a condensate on AA(s).

2.1.3. Formation of a monolayer of element B

In the vapor phase, non-metallic elements generally appear as two- or multi-atomic molecules. When subjecting a vapor $B_n(g)$ onto an $A(s)$ surface, an activation energy must be exceeded for a reaction to occur. The final reaction can be assumed to occur through a pre-reaction state, e.g. the reaction rate is proportional to the occupation probability $P(B_A)$ of a pre-reaction state, fig. 2. As a first approximation it is assumed that for each bond site there is a pre-reaction state, which disappears as soon as a chemical bond has been formed.

$P(B_A)$ can be expressed in analogy to eq. (5) by replacing $R(A_B)$ with $R'(B_A)$ (the re-evaporation rate from a pre-reaction state). The occupation probability of a pre-reaction state can now be expressed as (for a single pre-reaction state $N_0(B) = 1$)

$$P(B_A) = \frac{1}{1 + R'(B_A)/H_B} \{1 - \exp[-t/t_0(B)]\}. \quad (18)$$

For a surface saturation we can assume that $t \gg t_0(B)$, which simplifies eq. (18) to

$$P(B_A) = \frac{1}{1 + R'(B_A)/H_B}, \quad (19)$$

where $R'(B_A)$, the re-evaporation probability of B_n molecules from a pre-reaction state on a surface $A(s)$, is given by

$$R'(B_A) = \exp[-E'(B_A)/kT]. \quad (20)$$

The coverage rate of a surface A with $B(s)$ can now be expressed in the form (for simplicity re-evaporation of chemisorbed B atoms is neglected)

$$d[B(s)]/dt = nH_B R_r(B_A) \{1 - [B(s)]/N_0(B)\}, \quad (21)$$

where $N_0(B) = N_s(B)f_s(B_A)$, H_B is the hitting rate of $B_n(g)$ molecules, $f_s(B_A)$ is the filling factor of B atoms on surface A,

$$R_r(B_A) = RP(B_A) \exp[-E_a(B_A)/kT] \quad (22)$$

is the reaction rate of B-A bond formation, R is a constant and $E_a(B_A)$ is the activation energy of B-A(s) bond formation (from a pre-reaction state).

The solution of eq. (21) can now be expressed in the form

$$[B(s)] = N_0(B) \{1 - \exp[-t(B)/t_0(B)]\}, \quad (23)$$

where $t(B)$ is the exposure time of $B_n(g)$ onto $A(s)$, and

$$t_0(B) = N_0(B)/2H_B R_r(B_A). \quad (24)$$

For compounds AB, the energy $E(B_A)$ is generally higher than the energy $E(A_B)$, i.e. non-metal surface atoms generally form a more stable surface than the metal atoms. This motivates the neglect of the re-evaporation of a $B(s)$ surface.

Condensation of $B_n(g)$, on the other hand, can be neglected as well. In general, as referred to in several papers on ALE, the critical component in ALE growth is the metallic component, whether it is used in elemental form or as a compound. The main concern in the non-metallic

component appears to be the activation energy $E_a(B_A)$ which might reduce the formation rate of a surface $B(s)$, eq. (23).

2.2. Compounds as the reactants

2.2.1. Metal halides and hydrides as reactants

In this section the ALE process for a compound AB is studied in the case where elements A and B are supplied onto the substrate as alternate exposures of compounds AX and BY. As in section 2.1, the elements A and B denote metallic and non-metallic components of a compound AB, respectively.

There might be different reasons for using compounds of the elements A and B as the reactants rather than elemental vapors of A and B. The most important reason is that for many metals the vapor pressure is low. It is difficult to prevent condensation of the element at low desirable substrate temperatures. This is especially true for group III elements.

The first reported ALE process using compound reactants [2] and exchange reactions, was zinc sulphide. ZnS was deposited through



An on-line mass-spectroscopic analysis by Hyvärinen et al. [9], indicated that ZnCl_2 stays on a sulphur surface until an exchange reaction with H_2S forms ZnS and releases HCl.

Owing to the sequential nature of the ALE process, reaction (25) should be described with separate reactions for each reaction step. In the following, a metal halide is denoted as AX and a non-metal compound, typically a hydride, as BY. Accordingly, the reaction during AX exposure onto a $B(s)$ surface can be expressed in the form



For eq. (26) the reaction of component B can now be expressed as



In (26) and (27) $\text{BAX}(s)$ denotes reactant AX adsorbed on a surface B. The surface atom is X, three atomic layers are encountered. $\text{AX}(s)$ is the same as $\text{BAX}(s)$, except that only two atomic layers are encountered.

In the case of eq. (26), some activation energy for the reaction might be needed owing to a deformation of the metal halide molecule on the surface.

In the gas phase, a ZnCl_2 molecule is a linear molecule with chlorine atoms at the opposite sides of the zinc atom. According to a quantum-chemical calculation by Pakkanen et al. [53], a ZnCl_2 molecule reacts readily with an S surface of ZnS and a chemical bond is formed between the Zn atom of the ZnCl_2 molecule and a sulphur atom of the surface. The chlorine atoms stay bonded to the zinc but are bent to an angle of 125.5° , fig. 5. While no decomposition occurs, these chlorine atoms result in a hindrance to the formation of a complete zinc coverage by occupying a share of the S surface.

2.2.2. Formation of a metal halide monolayer

An analysis of the formation of a metal chloride monolayer can be made according to eqs. (18)–(24) where a pre-reaction state and an activation energy of chemisorption is assumed. The

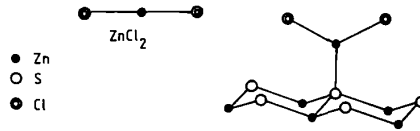


Fig. 5. Reaction of a ZnCl_2 molecule on a sulphur surface of ZnS according to the cluster model by Pakkanen et al. [53].

formation rate of an $\text{AX}(\text{s})$ surface is

$$d[\text{AX}(\text{s})]/dt = H_{\text{AX}} R_r(\text{AX}_\text{B}) \{1 - [\text{AX}(\text{s})]/N_0(\text{AX})\}, \quad (28)$$

where

$$N_0(\text{AX}) = N_s(\text{A}) f_s(\text{AX}_\text{B}), \quad (29)$$

$N_s(\text{A})$ is the density of atoms A in a monolayer on a surface B(s) in a given lattice direction of compound AB, $f_s(\text{AX}_\text{B})$ is the filling factor of molecules AX on the surface (and is a function of surface configuration and the size of the AX molecule),

$$R_r(\text{AX}_\text{B}) = RP(\text{AX}_\text{B}) \exp[-E_a(\text{AX}_\text{B})/kT] \quad (30)$$

is the probability of reaction (26) for a molecule $\text{AX}(\text{g})$ from a pre-reaction site, $P(\text{AX}_\text{B})$ is the occupation probability of a pre-reaction state of AX (refer to eq. (20)) and $E_a(\text{AX}_\text{B})$ is the activation energy of reaction (26).

In a more precise analysis, $E_a(\text{AX}_\text{B})$ cannot be assumed to be constant but rather is a function of the occupation state of surface B with $\text{AX}(\text{s})$. The activation energy of bonding to “a nearly empty” surface may be different from the activation energy of bonding to a “nearly filled surface”.

The solution of eq. (28) can be expressed as

$$[\text{AX}(\text{s})] = N_0(\text{AX}) \{1 - \exp[-t(\text{AX})/t_0(\text{AX})]\}, \quad (31)$$

where $t(\text{AX})$ is the exposure time of $\text{AX}(\text{g})$ onto surface B(s) and

$$t_0(\text{AX}) = N_0(\text{AX})/H_{\text{AX}} R_r(\text{AX}_\text{B}). \quad (32)$$

Re-evaporation of AX from surface B, which has been neglected during the monolayer formation in eq. (31), is determined by the strength of the bond B-AX, $E(\text{AX}_\text{B})$.

In spite of the higher vapor pressure of ZnCl_2 as compared to elemental Zn, a Zn atom in the ZnCl_2 molecule makes a stronger S- ZnCl_2 bond on the S surface than a Zn atom on an S surface, i.e. on a sulphur surface $E(\text{AX}_\text{B}) > E(\text{A}_\text{B})$.

2.2.3. Saturation of a metal halide monolayer

A necessary condition for saturation of the surface reaction (26) is that the condensation of the metal halide is prevented. In a detailed analysis of the re-evaporation criteria, one should consider the substrate temperature, dosing of the reactant in question, and purge time, eqs. (13)–(15).

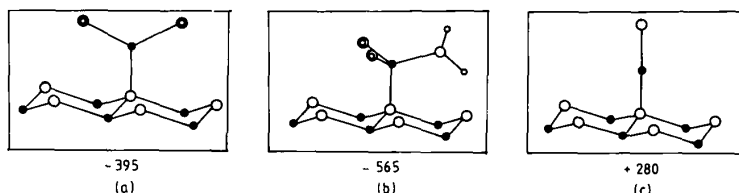


Fig. 6. Exchange reaction $\text{ZnCl}_2 + \text{H}_2\text{S} = \text{ZnS} + 2\text{HCl}$ calculated for a ZnCl_2 molecule independently chemisorbed to a S atom of a ZnS(s) surface [53]. (a) A single ZnCl_2 molecule on a ZnS surface. (b) H_2S bonded to the ZnCl_2 molecule. (c) ZnS-Zn-S after an exchange reaction.

The vapor pressure of a metal halide is typically higher than the vapor pressure of the corresponding metal itself. However, only in very few cases is the vapor pressure of a metal halide high enough to allow room-temperature valving of the halide vapor.

2.2.4. Reaction between a metal halide surface and a hydride reactant, formation of a monolayer B

In ALE processes utilizing a metal halide reactant, a hydride of the non-metal component has been used as the second reactant. The halogen in a halide monolayer is released through reaction with the hydrogen of the non-metal hydride.

According to ref. [53], for an individual ZnCl_2 molecule on a ZnS(s) surface, the $\text{ZnS(s)-ZnCl}_2\text{-H}_2\text{S}$ structure is energetically more favorable over an exchange reaction releasing the two HCl molecules. On a saturated monolayer of ZnCl_2 , a $\text{ZnCl(s)-H}_2\text{S}$ structure is probably less favorable, fig. 6.

In the following, the non-metal hydride is described as BY, with Y referring to 1 to n hydrogen atoms. Following the same formalism as that used in deriving eq. (23), the formation of a B(s) surface, according to reaction (27), can be expressed as

$$[\text{B(s)}] = N_0(\text{B}) \{ 1 - \exp[-t(\text{BY})/t_0(\text{BY})] \}, \quad (33)$$

where $t(\text{BY})$ is the exposure time of BY(g) onto the surface AX(s) ,

$$t_0(\text{BY}) = N_0(\text{B})/H_{\text{BY}}R_r(\text{BY}_{\text{AX}}), \quad (34)$$

H_{BY} is the hitting rate of BY(g) onto AX(s) ,

$$R_r(\text{BY}_{\text{AX}}) = RP(\text{BY}_{\text{A}}) \exp[-E_a(\text{BY}_{\text{AX}})/kT] \quad (35)$$

is the reaction rate of BY-A bond formation, $P(\text{BY}_{\text{A}})$ is the occupation probability of a pre-reaction state and $E_a(\text{BY}_{\text{AX}})$ is the activation energy of reaction (27) (from a pre-reaction state).

In the case of a complete exchange reaction, the formed B surface is identical with the B monolayer formed in the reaction of the elements A and B. Accordingly, the considerations of the re-evaporation of a formed monolayer B are the same as those made in section 2.1.3.

The vapor pressure of non-metal hydrides is typically high and condensation of BY does not occur in normal ALE conditions.

2.2.5. Organometallic compounds as reactants

Organometallic compounds are attractive alternatives as reactants in an ALE process owing to their high vapor pressure. Further, there is a large amount of information available on many

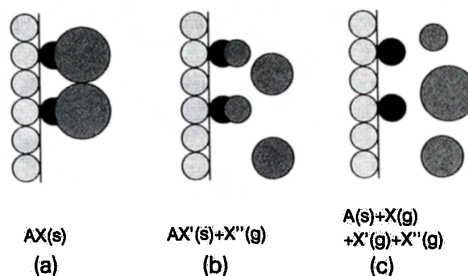


Fig. 7. Reaction alternatives of an organometallic compound $AX(g)$ and a non-metallic surface. (a) No decomposition of AX occurs. (b) Partial decomposition of AX . (c) Complete decomposition of AX .

important organometallic compounds because of their wide use in the chemical vapor deposition (CVD) technology.

An ALE process using an organometallic compound as a reactant for the metal component is less understood than some of the halide processes. In the papers regarding ALE utilizing organometallic reactants, there are indications of surface reactions resulting in a non-decomposed organometallic surface species [80], partly decomposed organometallic surface species [57,73] and fully decomposed organometallic reactants, resulting in a surface of metal atoms [130], fig. 7. Photoexcitation from a laser [57,117–119] or a UV lamp [83] has also been used to accelerate a desirable decomposition of an organometallic reactant in an ALE process.

When an organometallic reactant is used for the metal component of a compound, the reactant for the non-metal component most often is a non-metal hydride. An ALE process using organometallic reactants and hydrides as reactants can be made with equipment utilizing gas sources and room-temperature valving. Vacuum systems in the case of utilizing chemical beam epitaxy (CBE) and MOCVD systems at atmospheric pressure or low pressure (10–100 mbar) have been used. The carrier gas used in MOCVD systems is generally hydrogen.

In a comparison between using nitrogen versus hydrogen as the carrier gas in the TMG + AsH_3 reaction, no difference in the surface reactions could be observed [136]. However, we cannot exclude a possible reaction between surface species and the H_2 carrier gas.

2.2.6. Monolayer formation

The formation of a monolayer of the metal component is discussed in three cases:

- (a) no thermal decomposition of the reactant on surface B;
- (b) partial thermal decomposition of the reactant on surface B;
- (c) complete thermal decomposition of the reactant resulting in an atomic metal monolayer.

(a) $AX(g)$ does not decompose on surface B, fig. 7a. The surface reaction for the formation of a monolayer with organometal AX on a surface of atoms B can be expressed as



Formally, eq. (36) equals eq. (26), and the monolayer saturation can be expressed by eq. (33).

In case (a), one must assume a complete exchange reaction in connection with the reaction between $BY(g)$ and the formed monolayer surface $AX(s)$. Otherwise, an additional reaction resulting in the necessary decomposition of $AX(s)$ is required, as shown in fig. 8.

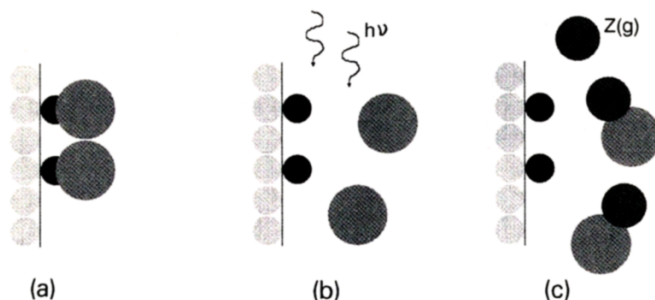


Fig. 8. (a) Surface after AX(g) reaction if no inherent decomposition occurs. (b) Complete decomposition of AX(s) by photoexcitation. (c) Complete decomposition of AX(s) by an extra reaction with a gas Z(g).

Especially in the low-temperature III-V processes, the monolayer AX(s) formation occurs according to (36) [80]. In order to make the AX(s) surface reactive to BY(g), a separate decomposition of the AX(s) surface is made by using a laser beam or UV light from a Hg lamp, fig. 8b. The reaction (36) is now completed with a reaction



X' (g) and X'' (g) denote different decomposition results of X.

If the additional energy, $h\nu$, is given simultaneously with the AX(g) exposure, one must assume that the conditions are not favorable to reactions



or



If reaction (38) or (39) occurs, a monolayer saturation does not occur owing to continuous condensation of A(s). This will not occur if the vapor pressure of A(g) is high enough to cause evaporation of A from an A(s) surface, which is not usually the case with group III metals.

In the case of simultaneous exposure of AX(g) and light on the surface B(s), there must be a difference in the activation energies of reactions (37) and (38) or (39)

$$E_a(\text{AX}_B, h\nu) < E_a(\text{AX}_A, h\nu), \quad (40)$$

$$E_a(\text{AX}_B, h\nu) < E_a(\text{AX(g)}, h\nu), \quad (41)$$

so that (37) occurs while (38) and (39) are suppressed. This situation can also be described as a photodecomposition of AX(g), catalysed by surface B(s).

No risk of the formation of a condensate AA(s) exists if the extra energy $h\nu$ is given as a separate photoexcitation sequence after the saturation of a monolayer BAX(s) (and after the exposure of AX(g)). Because the molecule AX(g) may be large compared to a lattice site of A(s), the surface saturation density in this case might remain low.

The extra energy needed to decompose a surface molecule AX(s) may also be given in the form of a reactive gas Z(g), fig. 8c. A carrier gas in a CVD-type growth system may serve this

purpose. If this is the case, the activation of the decomposition of $AX(g)$ occurs continuously during the exposure of $AX(g)$. Once again the decomposition



must occur while the reactions



and



must not occur: this implies that we need a gas $Z(g)$ which reacts with $AX(g)$ only when catalysed by the surface $B(s)$.

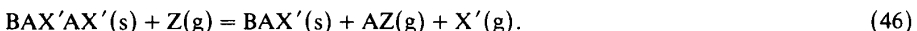
If a gas $Z(g)$ is exposed to a $BAX(s)$ surface as a separate reaction sequence, the problem of undesirable decomposition is avoided in the same way as in the case of applying photoexcitation as a separate reaction step after the formation of a saturated $BAX(s)$ surface.

When using an ALE process in the growth of elemental materials, the procedure of applying a separate decomposition sequence after the formation of a saturated $BAX(s)$ surface can also be used. Takahashi et al. [113] demonstrated an ALE process of germanium by first forming a monolayer of $Ge(C_2H_5)$ at about $300^\circ C$. They subsequently increased the substrate temperature up to about $400^\circ C$, causing the thermal desorption of C_2H_5 radicals from the surface. Owing to a temperature change after each reaction sequence, the process is slow but does yield epitaxial Ge at a low deposition temperature.

(b) $AX(g)$ decomposes partly on $B(s)$. A partial decomposition, fig. 7b, of $AX(g)$ results in a surface $BAX'(s)$, that can be expressed as



Necessary conditions for a $BAX'(s)$ monolayer saturation are: (1) $AX'(s)$ is formed through a catalytic effect of the surface $B(s)$ on the $AX(g)$, or (2) $AX'(s)$ is formed through a thermal decomposition of $AX(g)$ at the substrate temperature, but $AX'(g)$ is volatile enough to re-evaporate when formed on an $AX'(s)$ monolayer or in the gas phase, or (3) a carrier gas or a separate gas $Z(g)$ is able to pick up $AX'(s)$ selectively from an $AX'(s)$ surface (but not from a $B(s)$ surface):



In principle there are many possible variations that could result in the effect of eq. (46).

Once a saturated monolayer of $AX'(s)$ is formed: (1) it must be further decomposed through an additional decomposition step, as in the case (a) or (2) the reaction of $AX'(s)$ with the hydride $BY(g)$ must be an exchange reaction corresponding to the reaction of a hydride on a metal halide surface as in reaction (27).

If a molecule $AX'(s)$, formed as a result of a partial decomposition $AX(g)$, is small enough, a full monolayer density $[AX'(s)] = N_s(A)$ can be obtained. It is suggested by Nishizawa et al. [56,80,84] that a Ga atom + one methyl group fulfils this condition and could be a possible result of a partial decomposition of $Ga(CH_3)_3$.

(c) $AX(g)$ decomposes thermally into $A(s) + X(g)$, fig. 7c. The decomposition reaction is



Necessary conditions for a monolayer saturation are now applied to $A(s)$ in the same way as the conditions applied to $AX'(s)$ in the previous case (b): (1) the decomposition (45) occurs only on a $B(s)$ surface, or (2) if the decomposition of $AX(g)$ occurs in the gas phase or on the surface $A(s)$, then $A(g)$ must be sufficiently volatile to prevent multilayer condensation of $A(s)$, or (3) a carrier gas or a separate etching gas $Z(g)$ removes extra $A(s)$ condensed on an $A(s)$ surface.

Kodama et al. [132] suggest that TMG is selectively decomposed on an As surface of GaAs into metallic Ga. Using high flow speed in a H_2 carrier at 100 mbar, they also demonstrated a nice saturation of the Ga surface. Nishizawa et al. [57] suggest a complete decomposition of TMG above 520 °C. Under their high-vacuum conditions, a poor saturation of the Ga surface was achieved, which suggests a rapid surface decomposition of the TMG.

2.2.7. Re-evaporation of a monolayer during a purge sequence, effects of residual gas interaction

In section 2.1.2, the effects of re-evaporation of a formed monolayer were discussed for the case of an ALE process using elements A and B as reactants. Analogous considerations apply to a monolayer $A(s)$ or $AX(s)$ formed through the use of a compound reactant. The re-evaporation rate for a metallic monolayer is controlled by the binding energy $E(A_B)$, eq. (4). For a monolayer of $AX(s)$ or $AX'(s)$, the re-evaporation is controlled by the binding energies $E(AX_B)$ and $E(AX'_B)$, respectively.

During a purge sequence, a formed monolayer is subjected to a loss of surface atoms through re-evaporation. On the other hand, the surface layer is continuously subjected to the interaction of residual gases in the reaction chamber. The effect of each residual gas atom or molecule should be handled according to the concepts developed for the reactants. The effect of a residual gas is dependent on the type of substrate surface the gas encounters. A specific residual gas that is harmful for a metal surface might be inert for a non-metal surface. The effect of residual gases might therefore be quite different depending on the type of surface obtained through different types of partial decompositions of a compound reactant.

A reaction between a residual gas molecule and a surface may result in residual gas adsorption or the re-evaporation of a surface atom from the monolayer through a chemical reaction with the residual gas molecule. The number of atomic collisions with a surface by a gas having a vapor pressure of 10^{-10} mbar is about $10^{10} \text{ cm}^{-2} \text{ s}^{-1}$. A ppm contribution to monolayer could be formed in 1/10 of a second under such conditions.

2.2.8. Reaction between a metal or a metal compound monolayer and a non-metal or a non-metal hydride

In most published papers on ALE using organometallic compounds as reactant, a non-metal hydride, such as AsH_3 , has been used to form the metal monolayer. An exception of this concept is a process based on gallium diethylchloride ($GaDECl$) and As as the reactants [103]. A H_2 carrier was used in that study [103], which does not exclude the presence of AsH_3 together with As_4 .

The advantage of using non-metal hydrides as a reactant is their high vapor pressure which makes pulsed dosing easy. The major disadvantage of such hydrides is their extreme toxicity, which makes the handling and the system more complex. Also, elemental materials are generally available in a higher purity than the hydrides.

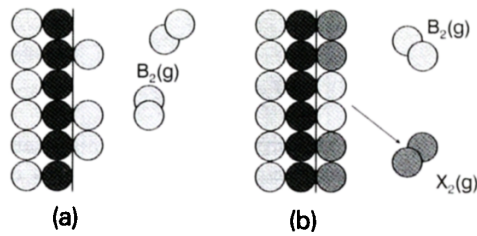


Fig. 9. Reaction alternatives between an elemental non-metal reactant $B_n(g)$ and an $A(s)$ or $AX(s)$ surface. (a) $B_n(g)$ on an $A(s)$ surface. (b) $B_n(g)$ on an $AX(s)$ surface.

In the ALE process of III–V compounds, the effect of hydrogen in the reactant molecule is not clear. The group V elements are volatile enough to fulfil a condition of monolayer saturation even if the reactant is the element itself or if a thermal decomposition of the group V hydride occurred before a surface reaction with a group III surface.

For an elemental reactant $B_n(g)$, when formed by a thermal decomposition



or when supplied to the reaction directly as an elemental vapor $B_n(g)$, a direct surface reaction with a metal surface, fig. 9a, can be formulated as



In case of a metal compound surface $AX(s)$ or $AX'(s)$, the reaction with an elemental non-metal vapor $B_n(g)$, fig. 9b, has the form



In the case of a group V hydride reactant $BY_3(g)$, fig. 10, reactions corresponding respectively to (49) and (50) can be expressed as



or

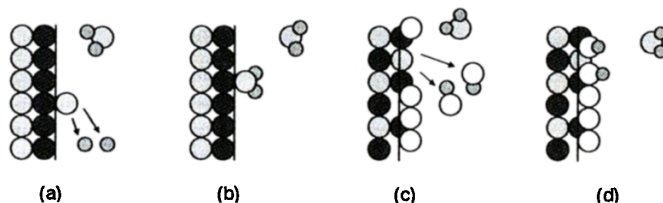
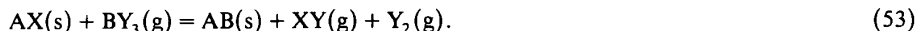


Fig. 10. Reaction alternatives between a non-metal hydride and a surface of $A(s)$ or $AX(s)$. (a) Hydride decomposes on an $A(s)$ surface. (b) Hydride chemisorbs on an $A(s)$ surface without decomposing. (c) Hydride makes an exchange reaction with $AX(s)$ surface. (d) Hydride chemisorbs on an $AX(s)$ surface forming an $AXBY(s)$ structure [53].

and



There is no direct reference to the possibility of forming a non-metal surface covered by an atomic layer of hydrogen, as indicated in eq. (52). This possibility cannot, however, be fully excluded as stated in a quantum-chemical calculation for a H_2S reaction on a ZnCl_2 surface by Pakkanen et al. [53].

In the literature on organometallic ALE processes, there are very few comments on the role of group V reactions. In almost all work on III–V compounds, AsH_3 has been used as the group V reactant and the group V reaction is stated to be “less critical” than the reaction forming the metallic monolayer. Additionally, there are very few comments on a possible role of a H_2 carrier gas on the reactions of a metal or a non-metal reactant.

One factor that clearly makes the group V reaction “less critical”, is the high (or fairly high) vapor pressure of the group V elements, which ensures the saturation of the surface reaction to one atomic layer. Also, a non-metal surface in general seems to be more “natural” for an AB compound.

2.3. ALE process for elemental materials

It is clear from the discussion in sections 2.1 and 2.2 that with suitable precautions the ALE process can also be applied to elemental materials such as metals or covalent semiconductors. The first reference to that possibility was given by Goodman and Pessa [90]. They suggested an exchange reaction of a chloride + hydride for the processing of silicon



Comparison of (54) with the criteria for monolayer saturation derived in section 2.2, shows that this reaction could be used for an ALE process of silicon. The problem in this case is associated with the thermodynamically unfavorable exchange reaction between a SiCl_4 surface and SiH_4 gas.

In principle, an ALE process for an elemental material could be constructed from a first sequence of a metal compound that fulfils the criteria of monolayer saturation, a second sequence completing a decomposition of the metal compound into a monolayer of metal atoms, and a volatile decomposition result that re-evaporated during a purge sequence before the next exposure of the metal compound. The decomposition can be activated by a reducing gas or extra energy in form of light exposure or elevated temperature as in ref. [113], fig. 11.

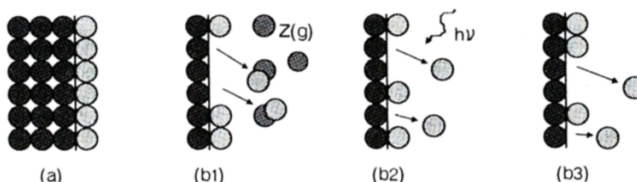


Fig. 11. Alternatives for an ALE process for the growth of elemental materials. (a) Sequence 1: monolayer formation of a metal compound. (b1) Sequence 2: decomposition of a monolayer AX(s) into metal monolayer A(s) + a gaseous product XZ(g) using a chemical reaction. (b2) Alternative sequence 2 with photon interaction. (b3) Alternative sequence 2 using increased temperature [113].

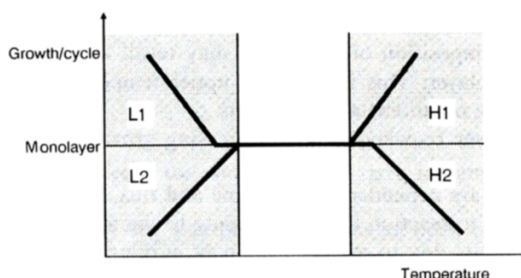


Fig. 12. A processing window of the ALE process. A full monolayer saturation $f_s = 1$ for both reactants is assumed. Limiting mechanisms in the different areas of the chart are: (L1) condensation of a reactant occurs; (L2) activation energy of a necessary reaction is not exceeded; (H1) decomposition of a reactant results in a non-evaporating surface layer on a monolayer; (H2) re-evaporation of a formed monolayer occurs.

There are established techniques for the epitaxy of elemental materials, in particular silicon [158]. An advantage of applying the ALE process to silicon could be a decreased epitaxial temperature, which is desirable for the manufacturing of any low-dimension devices where abrupt doping profiles are needed. Furthermore, the ALE process has inherent characteristics of a conformal growth owing to the monolayer saturation which results in a thickness uniformity over large areas and controlled step coverage.

2.4. The processing window of ALE

As a summary of the considerations in sections 2.1–2.3, a processing window of fig. 12 can be constructed to the ALE process.

The temperature behavior of the rate of growth in monolayer units per cycle gives a first indication of the limiting mechanisms of an ALE process.

Lower limits of the substrate temperature

- (L1) The temperature of the substrate must be high enough to prevent condensation of any of the reactants. This also applies to all decomposition products of the reactants. If condensation results on a desired monolayer, there might be a chance of converting the condensation into volatile constituents through a reaction with an extra gas interaction or with photoexcitation. This is a way of widening the processing window.
- (L2) In several types of surface reactions there is an activation energy to be exceeded. Extra energy, such as photoexcitation, may help in exceeding the activation energy.

The ALE temperature window

Full monolayer saturation:

- All bonding sites, corresponding to the number of atoms in a crystal plane, are occupied. A growth rate of one lattice unit/cycle is observed.

Most important mechanisms for saturation densities below unity:

- Compound reactants; reactant molecule is oversized to the bond site – a decreased saturation density and growth rate is observed.
- Surface reconstruction may decrease the saturation density.
- Bond strength of an adsorbed surface atom is higher when nearest-neighboring sites are unoccupied – a decreased saturation density is observed at a high process temperature.

Saturation density above unity:

- Undecomposed molecules form a monolayer.

Upper limits of the substrate temperature

- (H1) An undesirable decomposition of a reactant may result in decomposition products that condense on a monolayer. This is a typical upper temperature limiting mechanism for GaAs processes using organometallic reactants.
- (H2) If a formed monolayer re-evaporates, a decreasing growth/cycle versus temperature is observed.

The temperature limits are dependent on the time and flux density of the reactant used for each sequence. Limits due to reaction thresholds relate to the total dose of a reactant (per unit area of the substrate), limits due to re-evaporation of surplus reactant or formed monolayer relate to the purge times used.

The characteristic feature of ALE is the control of growth by the number of reaction sequences, which is due to saturation of a monolayer at a certain saturation density in each reaction step. Depending on the nature of the surface and the reactant used, the monolayer may correspond to the theoretical number of atoms in one lattice plane or it may be a fraction or multiple of that number. As long as the saturation predominates the formation of a surface atom layer, the characteristic feature of ALE, growth that is proportional to the number of cycles, occurs. Especially for superlattice structures, it is most desirable to find reactants and process conditions that result in ALE growth with full monolayer saturation.

3. Equipment for the ALE process

3.1. System classification, open and closed systems

Equipment used for the ALE process can be classified according to their characteristic features such as working pressure (vacuum, low-pressure inert gas, atmospheric inert gas), method of arranging the pulsing needed in ALE (moving substrate or valved sources) or according to the types of sources (hot source [MBE-type], cool source [CVD-type]).

When related to the mechanism of the growth and to some of the specific features of the ALE process, such as the material utilization efficiency and a saturation of a monolayer, a useful classification of the growth apparatus can be made to closed and open systems, fig. 13.

In an open system, such as a MBE vacuum system, the walls of the vessel are cold and the pumping speed is high, which means that molecules re-evaporated from the substrate are captured either by the walls or by the vacuum pump. The reactants are fed to the substrate surface as focused beams without collisions with the walls of the vessel. This means that each

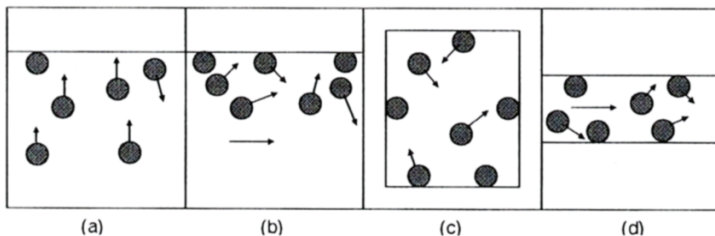


Fig. 13. Classification of ALE growth systems. (a) Open system. (b) Semi-open system. (c) Closed system. (d) Semi-closed system.

reactant molecule hits the substrate surface only once, and the hitting rate at the substrate, H , is described by

$$H = Ff_s, \quad (55)$$

where F is the material flux from the source, and f_s is a system parameter describing the spreading of the material flux.

A cold-wall MOCVD-type system can be classified as an open or semi-open system, where the probability of multiple collisions to the substrate is generally small.

An ideal closed system is a closed hot-wall box where the reactant is dosed through a valve. In a closed system, each reactant molecule either makes a permanent bond with a surface or continues to hit the surfaces until a permanent bond is formed. All the walls of a closed system act as the substrate surface. The hitting rate of a reactant in a closed system can be expressed in terms of the partial pressure of the reactant:

$$H = p/(2\pi mkT)^{1/2}, \quad (56)$$

where p is the partial pressure of the reactant and m is the mass of the molecule.

The gas flow system of ref. [2] can be classified as a semi-closed system, fig. 13. While the thermal velocity of molecules at a typical growth temperature approaches 1000 m s^{-1} , the velocity of the transport gas is typically one or two orders of magnitude less. This means that the reactant molecules travelling in the channel between the substrates make multiple collisions with the substrate surfaces like a vapor in a closed system.

3.2. Vacuum systems

The first experiment of an ALE growth was made in 1974 using the apparatus shown in fig. 14 [1]. It is a high-vacuum system with a rotating substrate holder for necessary sequencing. Mechanical tolerances between the substrate holder and the sources were minimized to a fraction of a millimeter in order to minimize the leak of the source materials to the surrounding vacuum. Each source chamber formed a semi-closed vapor environment which made it possible to test the occurrence of a monolayer saturation at high hitting intensities.

Most ALE work on III-V compounds is made in a MBE-type vacuum system equipped with gaseous sources and valving. The system may be equipped with an in-situ RHEED system for direct observation of the surface atom configurations [59,107], other surface analysis arrangements or arrangements for optical excitation of the growing surface [82], fig. 15.

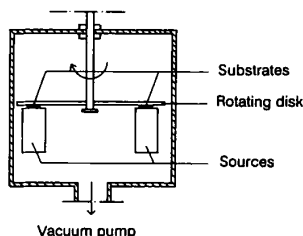


Fig. 14. ALE reactor used in the first demonstration of the ALE process in 1974. Hot-wall sources with a tight tolerance against the substrate disc form semiclosed reaction zones [1].

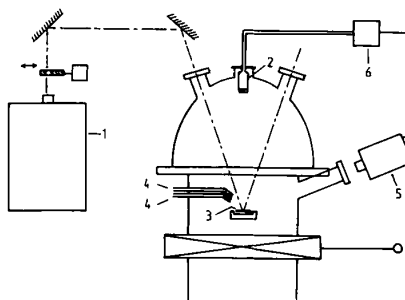


Fig. 15. A MBE-type ALE reactor equipped with organometallic gas inputs and photoexcitation means [82]. (1) Laser, (2) lamp, (3) substrate, (4) gas admittance nozzles, (5) pyrometer, (6) temperature controller.

In semi-open systems, such as MBE equipment, the reactant vapor is generally directed to the substrate as a focused beam with nearly uniform flux intensity over the substrate. MBE of CVBE (chemical vapor beam epitaxy) equipment is usable for ALE growth provided that each source is equipped with shutter or valving means. An advantage of a vacuum system is that it can be equipped with in-situ analysis of the growing film. A MBE system is generally equipped with a fixed substrate holder and sources with mechanical shutters. For processes utilizing organometallic compounds as reactant, an external gas source system is needed.

3.3. A lateral flow system with inert-gas valving

The lateral flow system of fig. 16 [2] utilizes an inert-gas flow in several functions: in the transport of reactants, in preventing the pump oil from entering the reaction zone, in valving the sources, and in ensuring the separation of the reaction sequences by purging the reaction zone between subsequent reactions. Inert-gas valving can be performed at a high-temperature zone which is very difficult with any mechanical valves, especially when corrosive chemicals such as chlorides are concerned. Inert-gas valving is based on blocking inert-gas flows in the feeding tube between a source and the reaction chamber.

In a lateral flow system, such as the semi-closed system of fig. 16, the front end of the substrate receives a higher flux density than the down-stream end of the substrate. A uniform growth rate in a lateral flow system occurs as long as the saturation mechanism of the monolayer formation predominates.

A lateral flow system makes it possible to observe the type of growth (CVD-mode or ALE-mode) simply by observing the longitudinal thickness profile of the layer grown. The steepness of the thickness profile in the CVD-mode is a function of the partial vapor pressures of the reactants and also of the activation energy of the surface reaction in question, eq. (30).

A lateral flow system effectively utilizes the saturation mechanism of a monolayer formation obtained in ALE. Owing to a multi-collision exposure of the reactants, characteristic of a

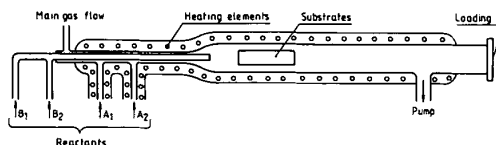


Fig. 16. ALE reactor utilizing inert gas as a carrier [2].

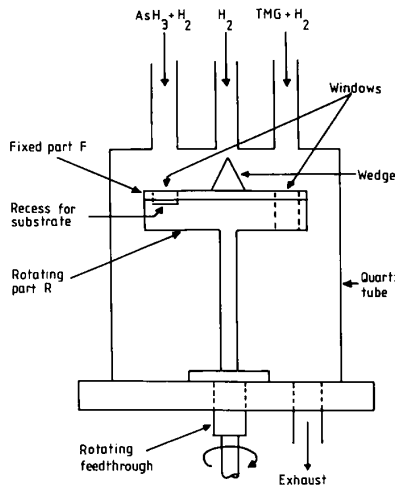


Fig. 17. A system with a rotating substrate holder in a hydrogen flow [73].

semi-closed system, the material utilization efficiency is high. This requires reasonable reactivity of the reactants and conditions where precautions of monolayer saturation are fulfilled.

3.4. Inert-gas systems with moving substrate

In vacuum systems, as well as systems utilizing an inert-gas flow, the sequencing can be performed with a moving substrate instead of valved sources. A system with a rotating disk in a hydrogen gas flow used by Tischler and Bedair [73] is shown in fig. 17. The rotating disk ensures a fast operation (~ 3 s/cycle) and the gas flow ensures an effective separation of the reactant flows and reaction sequences.

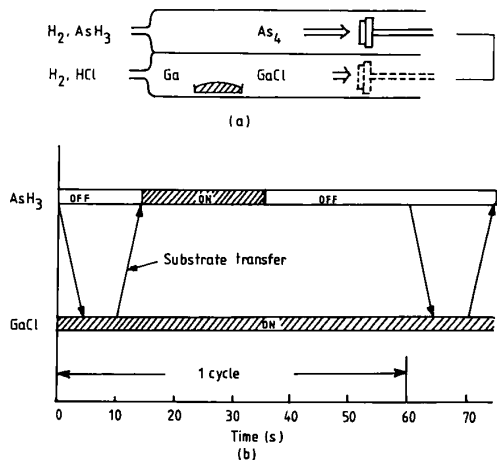


Fig. 18. A double-tube system [94].

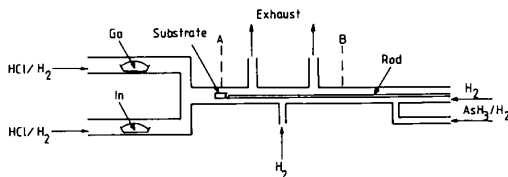


Fig. 19. A system with horizontally moving substrate. Mixing of the different reactant zones is prevented by blocking inert-gas flows [146].

Usui et al. [94] used a reactor with different source tubes and substrates moving sequentially from one source flow to the other. Usui's construction also allows the use of hot sources (i.e. reactants with low vapor pressure), fig. 18. Koukitu et al. [146] used an inert-gas system (fig. 19) where the substrate is moved horizontally between the reaction zones.

4. Experimental

4.1. Gallium arsenide

4.1.1. Pioneering work on a TMG + AsH₃ process

An ALE process of GaAs was first reported by Nishizawa et al. [80] in 1985. The process (called molecular layer epitaxy) was based on trimethylgallium (TMG) and arsine as the reactants. The equipment used was a high-vacuum system with valved inlet for gaseous reactants. The system was also equipped with optical ports for photoexcitation. Monolayer saturation to 0.22–0.23 nm/cycle was obtained at a temperature of 500 °C. Sequence for TMG was 4 s and for AsH₃ 20 s. Purge or evacuation sequence was 20 s for both reactants.

Saturation was observed to be quite insensitive to AsH₃ dosing, whilst increased AsH₃ dosing improved the film quality. Increased arsine and decreased TMG reduced the observed carrier density of the p-type GaAs layers. Irradiation with a Hg lamp was also observed to improve the visual quality of the layers – it decreased the carrier density and enhanced the growth at temperatures below 500 °C. A more detailed study of photostimulation effects in the ALE of GaAs is given by Nishizawa et al. [82].

At about the same time with Nishizawa's work in 1985, Bedair et al. [69] published their results on ALE of GaAs and AlAs. In the GaAs process, Bedair also used TMG and arsine as the reactants. The equipment used was a MOCVD-type system with a rotating disk for sequencing the reactant interactions. The apparatus operated at atmospheric pressure. H₂ was used as a carrier gas. The H₂ stream also acted as a diffusion barrier between the different reactant streams. A complete cycle was carried out in about 10 s. Monolayer saturation was observed in a temperature range of 560–600 °C.

In a later paper [73] on the same experimental arrangement, fig. 17, Tischler and Bedair report monolayer saturation over a wide temperature range, 450–700 °C. Sequencing was faster than in the earlier experiments, a full cycle was completed in 2.6 s which corresponded to 0.3 s interactions with both the TMG and the arsine flux. Tischler and Bedair suggest a surface selective decomposition of TMG as the mechanism of monolayer saturation. TMG was assumed to decompose partly or fully on an As surface but not on a formed Ga surface. The observed temperature range of saturated monolayer formation, 450–700 °C is more than reported for any other experimental arrangement for a TMG + AsH₃ reaction.

4.1.2. Introduction of a $\text{GaCl} + \text{AsH}_3$ process

The first report of an ALE process for GaAs using GaCl and AsH_3 as the reactants was given by Usui and Sunakawa [94]. The apparatus used was a double-tube system enabling ALE processes with low vapor pressure reactants, fig. 18. The system was operated at atmospheric pressure with hydrogen as the carrier gas. GaCl was formed in one of the source tubes by letting a HCl gas interact with a metallic gallium source kept at a temperature of 780°C . Reactant sequencing was realized by moving the substrate from one source stream to the other. The GaCl exposure time was 6 s and the exposure time of AsH_3 20 s. A full cycle including the substrate transfer was 60 s.

Usui and Sunakawa [94] assumed that AsH_3 was decomposed into elemental As₄ before encountering the substrate. Saturated monolayer growth was observed at temperatures between 400 and 600°C on differently oriented substrates. They also observed that, as a consequence of the monolayer saturation, the ALE process produced very uniform layers in masked (with SiO_2) areas of a substrate.

4.1.3. A model of photocatalysis in a $\text{TMG} + \text{AsH}_3$ process

A model of a photocatalytic mechanism in a laser-assisted ALE process of GaAs using TMG and AsH_3 as the reactants was suggested by Doi, Aoyagi and Namba [117,118]. The experimental work was performed using high-vacuum equipment with MOCVD source arrangements. Exposure and evacuation sequences were 1 s each, resulting in a cycle time of 4 s. Photoexcitation of the substrate surface was synchronized to the TMG exposure. The light source used was a cw Ar ion laser. No “temperature window” of saturated growth was observed without laser irradiation. With irradiation, saturated monolayer growth was observed in a temperature window from 365 to 430°C . Doi et al. concluded that TMG was decomposed under laser excitation on an As surface into Ga atoms, whereas such decomposition did not occur on a Ga surface.

4.1.4. Further development of ALE processes of GaAs

The early work on the ALE of epitaxial GaAs was directed towards demonstration of a stepwise growth mechanism. In further development of the ALE of GaAs, more attention has been paid to a better understanding of the growth mechanisms and the characteristics of the resulting material. Table 2 summarizes the development of GaAs ALE processes according to the reactants used. Numbers in the table refer to the laboratory in question. The number of each laboratory is the same as in table 1.

Most ALE development on III–V compounds aims at a process which is able to produce material suitable for high-speed electronic devices and semiconductor lasers. Necessary material characteristics are well-controlled carrier density, high carrier mobility and abrupt doping profiles at an accuracy of atomic layers. In devices based on quantum wells, it is also necessary to combine thin layers of materials with an accuracy of single atomic layers. As a limiting case of superlattice structures, a further object is the processing of superalloys, e.g. tailoring of complex compounds using single atomic layers as the building blocks.

Some of the inherent features of ALE fit well the basic demands of the III–V targets mentioned above since:

- gas-phase reactions are eliminated by sequencing;
- two-dimensional nucleation results in an increased surface mobility which leads to a lower growth temperature;
- lowered growth temperature decreases interdiffusion and helps in obtaining abrupt interfaces;

Table 2
Laboratories working on various ALE processes of GaAs. Laboratory numbering is the same as in table 1; laboratory names are repeated for convenience of the reader. Reactant abbreviations used are TMG, trimethylgallium; TEG, triethylgallium; DEGaCl, diethylgallium chloride

	Ga	Ga + H ₂	GaCl	TMG	TEG	DEGaCl
AsH ₃	-	-	14	9	9	14
			25	11	12	
				12	15	
				16	16	
				17	17	
				20	18	
As	15	-	14	-	-	-
AsCl ₃	-	9	-	-	-	-
		12				

9 Tohoku University, Sendai, Japan [55-57].
11 North Carolina State University, Raleigh, NC, USA [69,70,72-78].
12 Research Development Co. of Japan, Semiconductor Research Institute, Sendai, Japan [55-57,79-88].
14 NEC Co., Kawasaki, Japan [92-99,101-103,105].
15 NTT Electrical Communications Laboratory, Musashino-shi, Tokyo, Japan [106-112,114,115].
16 The Institute of Physical and Chemical Research, RIKEN, Saitama, Japan [116-124,126].
17 Fujitsu Laboratories Ltd., Atsugi, Japan [127,129,130,132].
18 Laboratoire Matériaux Exploratoires, L.C.R., Thomson C.S.F., Orsay, France [133].
20 University of Southern California, Los Angeles, CA, USA [135-138].
25 Tokyo University of Agriculture and Technology, Tokyo, Japan [146].

- monolayer saturation makes the control of the process easier and more reproducible;
 - areal uniformity, step coverage and sidewall epitaxy are direct consequences of the monolayer saturation.
- Problems met in the early experiments of III-V (mainly GaAs) ALE are:
- chemistry of the processes is not understood in necessary depth for optimizing the process conditions; the limiting factors of the processing windows are not fully understood;
 - as a consequence of the unknown chemistry, problems with impurities from the reactants (such as carbon or chlorine) have not been solved.
- Table 3 contains data on the reported processing window of ALE processes on GaAs.

4.1.5. Processes based on TMG + AsH₃

Fig. 20 summarizes published growth rates/temperature curves of TMG GaAs processes. It can be seen that in most processes carried out without photoexcitation, there is a very narrow or even no processing window [80,117], fig. 20a. In these cases, a monolayer saturation has been observed at 500 °C (when the growth rate curve passes one monolayer/cycle) for both TMG and AsH₃ reactions. For the same reaction, when carried out in a reactor with fast reactant interactions in a high-speed hydrogen flow followed by an efficient hydrogen purge, a substantially wider processing window has been observed by Tischler and Bedair [72,73] in an atmospheric system with rotating substrate holder in a hydrogen stream and Ozeki et al. [130] in a system called pulsed jet epitaxy, fig. 20b. Ozeki et al. also report fairly low carrier densities in GaAs made by the pulsed jet mode.

A comparison of the growth behavior shown by curves of figs. 20a and 20b and a schematic presentation of the limits of a processing window, fig. 12, indicates that an undesired

Table 3
Observed temperature ranges of monolayer saturation for various GaAs processes

Substrate	Plane	ML/cycle	<i>T</i> range (°C)	Reagents	Ref.
GaAs	100	0.8	500 ^{a)}	TMG + AsH ₃	[80]
GaAs:Cr	100	1	275–430 ^{a)}	TEG + AsH ₃	[88]
GaAs	100	~1	450–600	GaCl + As + H ₂	[94]
	511	<1			
	211	1–1.2	390–550		
	111 A	~1			
	111 B	~1	390–550		
	110	<0.6			
GaAs:Si	100	3.9	500 ^{a)}	TMG + AsH ₃	[118]
GaAs:Cr–O	100	2.5–3.2	500 ^{a)}		
GaAs:Zn	100	2.5	500 ^{a)}		
GaAs:Si	100	1	365–430 ^{a)}	TMG + AsH ₃	[117]
GaAs	100	1	340–370 ^{a)}	TEG + AsH ₃	[122]
GaAs	100	~1	450–700	TMG + AsH ₃	[73]
	111 B	~1			
GaAs	100	1	400–600	GaCl + AsH ₃	[101]
	111 B	1	450–600	DEGaCl + AsH ₃	
GaAs	100	1		TMG/TEG + AsH ₃	[127]
	110	1			
	111 B	1			
		1	440–560	TMG + AsH ₃	[130]
GaAs	110	~1	445	TMG + AsH ₃	[137]
	100	1	445	TMG + AsH ₃	[136]

^{a)} Photoassisted reaction.

decomposition of the TMG (resulting in condensation on a monolayer as in the curves of fig. 20a has been avoided in the cases of fig. 20b.

Curves in fig. 20c illustrate the influence of laser irradiation on a TMG + AsH₃ ALE process. Laser irradiation has been observed to shift the growth/cycle curves to a lower temperature by about 50 °C. Also, there is some widening in the processing window, in particular the lower temperature limit is decreased.

One of problems in a TMG + AsH₃ system is carbon contamination originating from reaction by-products of trimethylgallium. The origin of carbon contamination has been discussed in detail by Mochizuki et al. [129]. In accordance with observations by other authors, Mochizuki et al. observed a connection between the carbon concentration and the dose of TMG. Also, carbon concentration decreases with increasing AsH₃ dosing. It is further suggested that the reaction resulting in carbon contamination occurred between a TMG molecule and a Ga surface. Lowest carbon concentrations were obtained in growths resulting in less than a monolayer coverage of Ga.

Hole densities (due to carbon contamination) measured in GaAs made by using a TMG + AsH₃ process range from 10¹⁴ to 10²⁰ cm⁻³.

4.1.6. Triethylgallium as a replacement for TMG

The first report of replacing TMG with TEG was given by Kobayashi et al. [106]. High-flow-rate hydrogen was used as a carrier, and reactant injection time was 1 s for each reactant. Small AsH₃ partial pressure was maintained even during the TEG injection. Reasona-

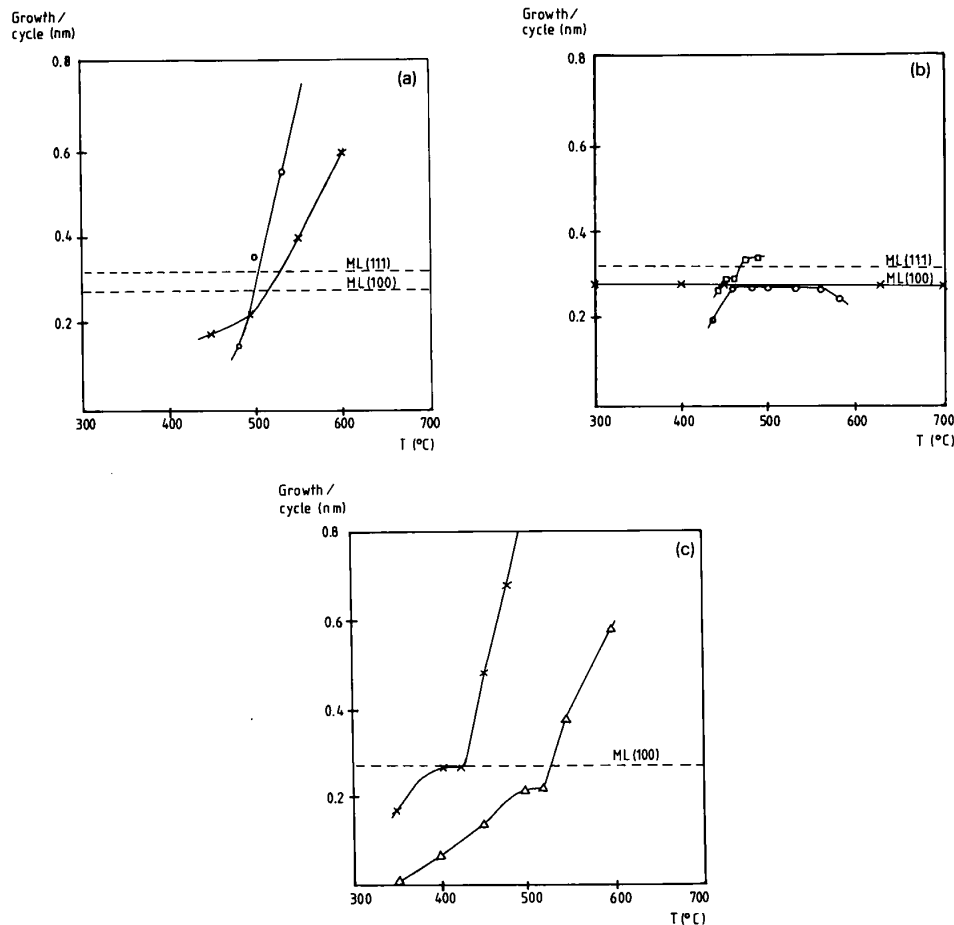


Fig. 20. Growth/cycle versus temperature characteristics of a TMG+AsH₃ ALE GaAs process. (a) No laser irradiation. (○, ref. [117]; ×, ref. [80].) (b) No laser irradiation, short reactant injection, effective purge with a hydrogen stream. (○, ref. [130]; ×, refs. [73,78]; □, ref. [136].) (c) Effect of laser on the curves in section (a). (×, ref. [117]; △, ref. [57].)

ble monolayer saturation was observed at temperatures from 450 to 600 °C. In analogy with the high H₂ flow rate results with TMG, the processing window of the “flow rate modulated epitaxy” with TEG appears at a substantially higher temperature than other TEG processes, fig. 21.

In the other TEG processes of fig. 21a, without photoexcitation, there is practically no flat area in the growth/cycle curve at all. Even with laser excitation, a processing window is narrow, followed by rapid condensation of undesired decomposition results at an increased temperature.

A drastic improvement in the process window has been reported by Nishizawa et al. [88]. The improvement was obtained by using UV irradiation from a Hg lamp, fig. 21b. Nishizawa et

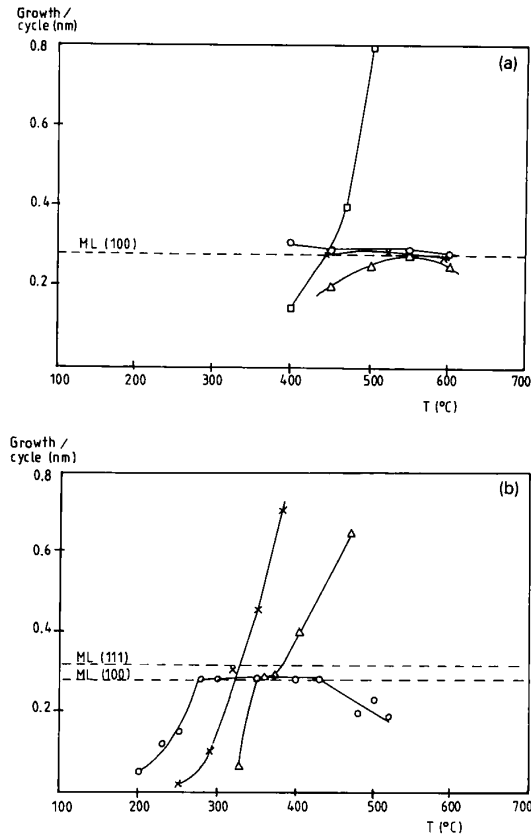


Fig. 21. Processing windows observed in ALE processes for GaAs using TEG (or DEGaCl) and AsH_3 as the reactants. (a) No photoexcitation. (×, GaCl [101]; ○, DEGaCl [101]; □, refs. [119,122]; △, ref. [106].) (b) Photoexcitation by laser or Hg lamp (UV). (×, ref. [82]; ○, ref. [88]; △, ref. [119].)

al. also report of highly improved control of the carrier concentrations of both n- and p-type GaAs.

4.1.7. Gallium chloride (diethylgallium chloride) + arsine

Mori et al. [105] have reported further developed forms of halide + hydride processes for GaAs. A precise monolayer saturation was observed between 450 and 600 °C in a DEGaCl (diethylgallium chloride) + AsH_3 process. The equipment used was a multitube MOCVD system with moving substrate. The conduction type of the resulting GaAs was found to change from p-type to n-type with increasing temperature. In the p-type material, carbon was identified as the main acceptor impurity. In n-type samples grown at 600 °C a carrier concentration of $1.1 \times 10^{15} \text{ cm}^{-3}$ was measured at 77 K.

As an alternative to using arsine, Sasaoka et al. [103] also reported a process where elemental As is used. As_4 vapor was generated in a source tube by heating elemental arsenic to 400 °C. The As_4 vapor was transferred to the substrate by pulsed H_2 flow through the source tube. No

arsine formation is reported. Carbon contamination in the resulting GaAs was observed to be lower than in the GaAs obtained with a process using $\text{DEGaCl} + \text{AsH}_3$. Obvious advantages of elemental As compared to arsine are a lowered toxicity and better purity. A precondition for the use of elemental arsenic is a hot source and a hot valving system.

4.1.8. Surface migration under ALE growth conditions

The good crystallinity obtained in an ALE process of GaAs at a relatively low growth temperature is generally regarded as a consequence of increased surface mobility of the reactants or decomposition results of the reactants.

The effect of surface migration or the surface mobility in ALE-type surface conditions, where only one of the components of a compound is on the surface at a time, has been studied by Horikoshi et al. [107] using a method they call migration-enhanced epitaxy. They dosed elemental Ga and As one after the other on a GaAs substrate as in the ALE process. However, while using elemental Ga, a condition of saturating surface reaction cannot be achieved at the growth temperature because of the low vapor pressure of Ga. The MEE process therefore does not meet the criteria of an ALE process but combines some of the features of MBE and ALE.

Ga has been dosed to correspond to one full monolayer in one process step. The experiment was carried out in a MBE-type system, and thus the use of on-line RHEED measurement during the film formation was possible.

According to Horikoshi et al. [107], there is rapid migration of Ga atoms both on Ga and As surfaces. Molecules of As migrate rapidly on an As surface but on Ga surface As molecules decompose catalytically into As atoms and easily form stable bonds with Ga atoms. As has high vapor pressure itself, which means that an As monolayer is formed as in an ALE growth condition, fig. 22.

Migration-enhanced epitaxy is a compromise between ALE and MBE. On one hand, it utilizes the possibility of MBE to use reactants with a low vapor pressure and, on the other, it utilizes ALE-type surface conditions, which enhances the surface mobility by preventing random formation of compound molecules. The use of elemental reactants is a straightforward way to avoid some of the problems connected with carbon contamination from metalorganic reactants. A drawback of MEE is the need to control the Ga component. Horikoshi et al. [107] observed that owing to a tendency of island formation at the edges of a newly forming atomic layer, there is a “self-flattening effect” which allows certain deviation from a precise dosing.

Horikoshi et al. [110] report photoluminescence measurements of AlGaAs–GaAs single quantum wells grown by migration-enhanced epitaxy at 300 °C. The PL spectra of the AlGaAs–GaAs structure showed a more efficient PL emission than corresponding samples produced by conventional MBE at a temperature of 580 °C.

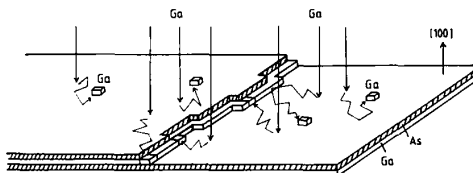


Fig. 22. Development of Ga monolayer on As surface of GaAs.

4.2. Other III–V compounds

4.2.1. AlAs

There are very few precise data on the AlAs process. Ozaki et al. [125] observed monolayer saturation in a laser-assisted growth in a triethylaluminium + arsine process at 350 °C. By calculating the surface coverage as a function of TEA dosing, Ozaki et al. [125] concluded that TEA behaves like a dimer supplying two Al atoms of each TEA molecule to the As surface. For a saturated monolayer growth, one should be able to eliminate the thermal decomposition of the TEA.

DenBaars et al. [137] observed a monolayer saturation with trimethylaluminium (TMA) and arsine at 460 °C in an atmospheric pressure MOCVD system.

Ozeki et al. [127] report partial saturation (saturates with respect to AsH₃ dosing but not with respect to TMA) of 2 or 3 monolayers per cycle at 500 °C depending on the crystal plane of the substrate. They suggest that a surface selective decomposition of trimethylaluminium on an As surface may occur in a ratio of two or three aluminium atoms per As surface atom. On the other hand, they state that there is no monolayer saturation with respect to TMA dosing but that the growth per cycle increases monotonously with increasing TMA dosing.

Table 4 summarizes the referred publications on ALE-type process (including processes where only partial saturation occurs) of AlAs. All published ALE processes of AlAs use trimethylaluminium (TMA) or triethylaluminium (TEA) as the reactants. The citation of work carried out at NTT refers to migration-enhanced epitaxy using elements, which does not fulfil the criteria of monolayer saturation of elemental aluminium.

4.2.2. InP, GaP and InAs

Sakuma et al. [131] report ALE process for InP using trimethylindium (TMI) and PH₃ as the reactants. A saturation of 0.5 monolayers per cycle is observed at 350 °C. No precracking of PH₃ was performed. The saturation with respect to TMI dosing was observed to diminish gradually with increasing temperature, until a linearly increasing growth with increased TMI dosing resulted at 600 °C.

Table 4
Publications on ALE on AlAs with various reactants. Reactant abbreviations used are TMA, trimethylaluminium and TEA, triethylaluminium

	Al	TMA	TEA
AsH ₃	–	11	9
		14	12 ^{a)}
		17	15
		20	16
As	15 ^{b)}	–	–

9 Tohoku University, Sendai, Japan [86].
11 North Carolina State University, Raleigh, NC, USA [69].
12 Research Development Co. of Japan, Semiconductor Research Institute, Sendai, Japan [86].
14 NEC Co., Kawasaki, Japan [92].
15 NTT Electrical Communications Laboratory, Musashino-shi, Tokyo, Japan [107,109–112,114].
16 The Institute of Physical and Chemical Research, RIKEN, Saitama, Japan [125].
17 Fujitsu Laboratories Ltd., Atsugi, Japan [127,128].
20 University of Southern California, Los Angeles, CA, USA [137].
^{a)} In cooperation with 9.
^{b)} MEE.

Table 5

Publications on ALE on InP with various reactants. Reactant abbreviations used are TMI, trimethylindium and TEI, triethylindium

	InCl	TMI	TEI
P	14	–	–
PH ₃	–	17	18

14 NEC Co., Kawasaki, Japan [93,99,101,104].

17 Fujitsu Laboratories Ltd., Atsugi, Japan [131].

18 Laboratoire Matériaux Exploratoires, L.C.R., Thomson C.S.F., Orsay, France [133].

Table 6

Publications on ALE on GaP with various reactants

Reactant	GaCl	DEGaCl
P	14	–
PH ₃	–	14

14 NEC Co., Kawasaki, Japan [99,101].

Table 7

Publications on ALE on InAs with various reactants

	InCl	TEI
As	11	–
AsH ₃	14	11

11 North Carolina State University, Raleigh, NC, USA [70–72,74–77].

14 NEC Co., Kawasaki, Japan [99,101].

In a N₂ carrier gas, Sakuma et al. [131] observed that a monolayer saturation occurs at 380 °C. The difference may be due to the smaller chemical activity of N₂ with respect to H₂, or more probably to the different thermal properties of the N₂ gas resulting in different thermal conditions at the substrate surface.

In all reports on GaAs using AsH₃ as the reactant for As, it was stated that the reactivity of AsH₃ is high and As surface saturates very effectively. In the ALE process of InP, Sakuma et al. [131] observed that the saturation of the PH₃ surface reaction occurs relatively slowly with respect to PH₃ dosing, which indicates a moderate rather than a high reactivity.

Tables 5, 6 and 7 summarize the reactants used in ALE processes for InP, GaP and InAs, respectively.

Table 8 summarizes some published data on monolayer saturation of ALE single-crystal epitaxy on III–V materials other than GaAs.

ALE of InP, GaP and InAs as a component in heterostructures has been reported by Usui and Sunakawa [104], Tischler and Bedair [71,72] and Razeghi et al. [133], see table 9 below.

4.2.3. Heterostructures of III–V compounds

Controlled growth of one atomic layer at a time is an ideal opportunity for making layered superalloys and superlattice structures, fig. 23.

For a practical process, it is desirable to have a processing temperature that fits the processing window of each of the components of the heterostructure. Also, the interface reactions must be chemically favorable.

Table 8
Referenced data on monolayer saturation of III–V compounds other than GaAs

Material	Substrate	ML/cycle	T(°C)	Reagents	Ref.
AlAs	AlAs 100	2	500	TMA + AsH ₃	[127]
	AlAs 111 B	2	500		
	110	3	500		
	100	1	460	TMA + AsH ₃	[138]
InAs	GaAs 100	~ 1	480	TMI + AsH ₃	[71]
	InAs 111 B	~ 1	450	InCl + AsH ₃	[101]
GaP	GaP 100	<1	450	GaCl + PH ₃	[101]
InP	InP 100	1	450	InCl + PH ₃	[101]
	InP : Fe	0.5	350	TMI + PH ₃	[131]
	InP : Sn		350		

Superalloys of III–V compounds make it possible to tailor the energy band of the compound. An ordered superalloy structure of figs. 23a and 23b can be made by alternate sequencing of the III or V group components, respectively, see fig. 24a. Ratios other than 1 : 1 of the alternating component can be achieved by proportional sequencing or proportional dosing, figs. 24b–24d.

Alternate and proportional sequencing allow the utilization of the monolayer saturation characteristic of ALE. This results in a self-control of the mixing ratio of the superalloy.

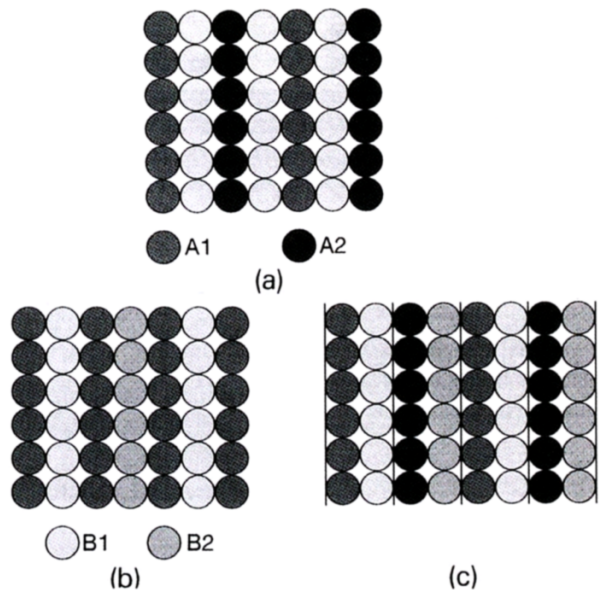


Fig. 23. Layered heterostructures. (a) A_1A_2B superalloy; one non-metal component, two alternating metal components. (b) AB_1B_2 superalloy; one metal component, two alternating non-metal components. (c) $(A_1B_1)_1(A_2B_2)_1$ superlattice.

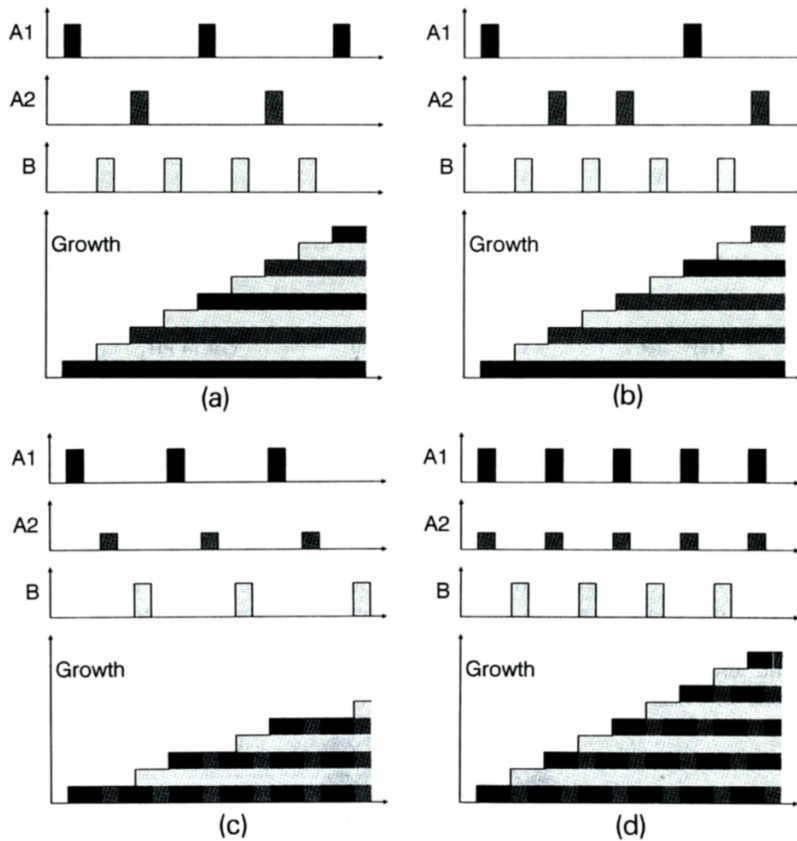


Fig. 24. (a) Alternate sequencing resulting in an A_1A_2B (1:1) superalloy ($= (A_1)_{1/2}(A_2)_{1/2}B$). (b) Proportional sequencing, resulting in an A_1A_2B (1:2) superalloy ($= (A_1)_{1/3}(A_2)_{2/3}B$). (c) Proportional dosing by sequential exposures. (d) Proportional dosing by simultaneous exposures.

Structures obtained with alternate and proportional sequencing are layered superalloys and they can be regarded as limiting cases of superlattices. Proportional dosing does not involve a self-control of the mixing ratio.

Usui and Sunakawa [104] compared InGaP superalloys made by alternate sequencing and by proportional (simultaneous) dosing of GaCl and InCl. The measured photoluminescence spectra from the sample produced by alternate sequencing showed one strong, narrow emission peak at 640 nm, whereas the sample made by simultaneous dosing showed two broad and weaker emission peaks.

Delta doping is a limiting case of a layered superalloy. A successful FET structure using Se-delta-doped GaAs was reported by Usui and Watanabe [98]. A high transconductance was measured. Kobayashi et al. [108] report planar doping with a $\text{SiH}_4 + \text{Ga(s)}$ which resulted in 10^{13} cm^{-2} Si density TEG + AsH_3 .

Control of the mixing ratio of a superalloy using proportional dosing by sequential exposures provides that the first exposure is not saturated or that the second exposure results in

Table 9
ALE superalloys and superlattices of III–V compounds

Superalloy material		Superlattice structure	Ref.
proportional dosing	alternate proportional/ sequential dosing		
$\text{Al}_x\text{Ga}_{1-x}\text{As}$ $x \approx 0.35$	$\text{Al}_x\text{Ga}_{1-x}\text{As}$ $x \approx 0.35$	AlGaAs/GaAs	[86]
	$\text{Al}_{0.25}\text{Ga}_{0.75}\text{As}$	n-AlGaAs/GaAs	[109]
	$\text{Al}_{0.5}\text{Ga}_{0.5}\text{As}$		[110,114]
	$\text{Al}_{0.3}\text{Ga}_{0.7}\text{As}$	GaAs–AlAs alternate layers	[111]
	$\text{Al}_x\text{Ga}_{1-x}\text{As}$ $\text{Al}_{0.46}\text{Ga}_{0.54}\text{As}$	GaAs–AlAs alternate layers	[128] [92]
$\text{In}_x\text{Ga}_{1-x}\text{As}$ $0 < x < 0.43$			[71,72]
	$\text{In}_{0.5}\text{Ga}_{0.5}\text{As}$	GaAs–InAs alternate layers	[76]
	$\text{In}_{0.5}\text{Ga}_{0.5}\text{As}$	InP–GaP alternate layers	[104]
$\text{In}_x\text{Ga}_{1-x}\text{As}$			[146]
		ZnSe/ZnTe alternate layers	[58]
		ZnSe/ZnTe alternate layers	[144,145]

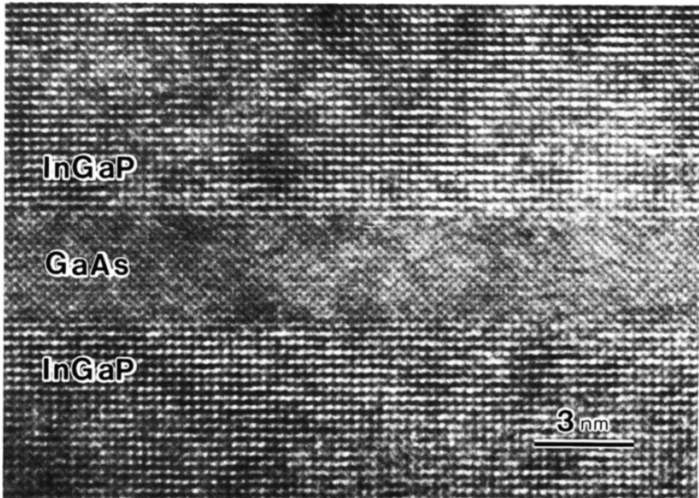


Fig. 25. TEM picture of an InGaP/GaAs(11 cycles)/InGaP single quantum well. Sample by H. Sunakawa and A. Usui, TEM picture by N. Igarashi and K. Ishida (NEC).

a direct reaction even on the saturated first monolayer. Proportional dosing makes it possible to control the mixing ratio continuously, a self-controlling mechanism of the mixing ratio does not occur.

Table 9 summarizes published III–V superalloys according to the classification of fig. 23. Superlattice structures are also included.

Fig. 25 is a high-resolution TEM picture of a InGaP/GaAs/InGaP single quantum well with 11 cycles of GaAs between the InGaP layers.

4.3. II–VI single crystals

A specific feature of II–VI compounds compared to III–V compounds is that the vapor pressure of the elements is higher, which makes it possible to use the elements themselves as the reactants in an ALE process. Unfortunately, also the vapor pressures of the compounds are higher or more precisely, the evaporation rates of both group II and group VI elements from the surface of the compound are higher than the evaporation rates of group III and group V elements, respectively.

4.3.1. CdTe

The first report on ALE of a single-crystal II–VI material (in fact the first report on *any* ALE single crystal) was given by Pessa et al. [12]. The material processed was CdTe and the substrate used was a (110) face of a CdTe single crystal. The system used was a MBE-type high-vacuum system. The system was equipped with Knudsen-cell sources and mechanical shutters for sequencing. For in-situ analysis, the system was equipped with analyzers of X-ray photoelectron spectrum (XPS), low-energy electron diffraction (LEED), Auger electron spectrum and angle-resolved UV photoemission spectrum [10]. Source temperatures for Cd and Te were 290–350 °C and 370–450 °C, respectively. The substrate temperature was 270–280 °C. The growth rate was estimated to be close to one monolayer per cycle (the growth rate was estimated by observing the attenuation of the Mo Auger signal from the substrate holder being coated with a CdTe thin film). The grown layer continued the crystalline structure of the substrate.

In ref. [14], Herman et al. report ALE growth of a $\text{Cd}_{1-x}\text{Mn}_x\text{Te}$ layered superalloy. With a simultaneous proportional dosing of Cd and Mn, the Mn/Cd ratio was controlled between $x \approx 0.15$ and $x \approx 0.40$. Formation of metallic Mn clusters was prevented by a low rate of Mn flux used. Theoretical considerations of the ALE growth mechanism were presented by the same authors in ref. [19].

Faschinger et al. [148] used a (111) BaF_2 substrate in the ALE of CdTe. In the substrate temperature range of 200 to 400 °C, several saturation levels of a monolayer have been observed, fig. 26a. With the re-evaporation times used, the lower limit of a monolayer saturation observed at 252 °C corresponded well to a value calculated from the actual re-evaporation times used and the vapor pressure data of tellurium. Faschinger et al. estimate further that a theoretical upper limit of the monolayer saturation, based on the vapor pressure of bulk CdTe, should be 360 °C.

The observed plateaus of the growth/cycle versus temperature curve in fig. 26 indicate that there are surface configurations of either Cd or Te surfaces where the bonding energy is higher than that of a full monolayer. Faschinger also concluded that a second layer of tellurium on a tellurium monolayer is more strongly bonded than subsequent layers, which have the bond strength of bulk tellurium.

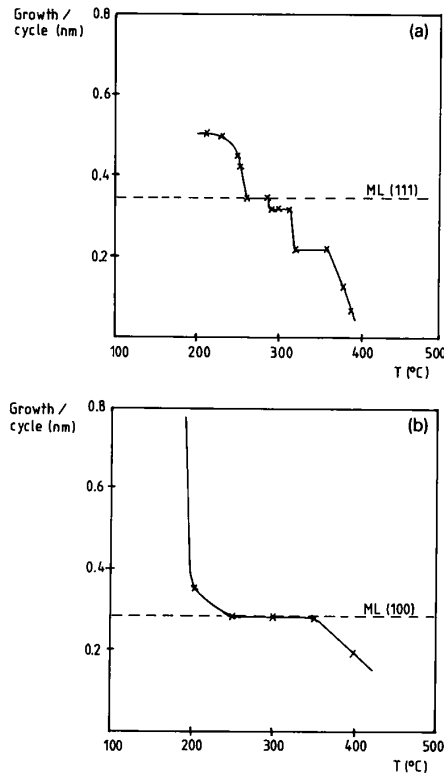


Fig. 26. Growth/cycle versus temperature characteristics of (a) CdTe [148]; (b) ZnSe [144] made by ALE using elemental Cd, Te, Zn and Se as the reactants.

4.3.2. ZnSe and ZnTe

Yao and co-workers [58–68] have made extensive studies on ALE of ZnTe and ZnSe. The apparatus used is a MBE-type high-vacuum system, equipped with Knudsen-cell-type sources for elemental Zn, Se and Te. Special emphasis has been placed on in-situ observation of the growth using continuous monitoring of a reflection high-energy electron diffraction (RHEED) pattern of the growing surface. In ref. [58] Takeda et al. report on the ALE process of ZnTe and ZnSe on a (001) GaAs surface. The evolution of RHEED patterns for ZnTe in an ALE growth at 230 °C indicated an improvement in the surface smoothness in the course of the growth, which the authors see as a change from a three-dimensional nucleation mechanism to a two-dimensional nucleation after a growth of about 100 monolayers.

A superlattice structure $(\text{ZnSe})_4(\text{ZnTe})_4$ was reported in the same paper [58] and was started with the ALE process on a ZnSe buffer layer on the GaAs substrate in order to have a two-dimensional nucleation dominant. The periodicity of the structure was observed with X-ray diffraction techniques, which indicated the existence of the four successive monolayers of ZnTe and ZnSe.

In ref. [68], Yao et al. state that a two-dimensional mode of growth is more dominant in an ALE of ZnSe when started on an As-stabilized GaAs surface than when started on a Ga-stabilized surface.

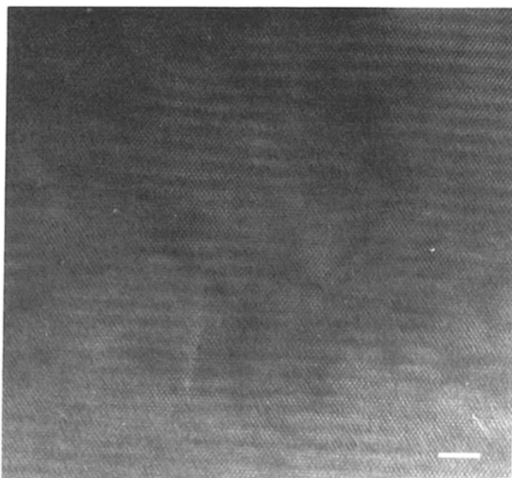


Fig. 27. TEM picture of an ALE $(\text{ZnSe})_4-(\text{ZnTe})_2$ superlattice, from Konagai et al. [144]. The length of the bar is 40 Å.

Konagai et al. [144] report a drastic improvement in the interface abruptness in ALE ZnSe–ZnTe strained-layer superlattices (SLSSs) compared to a corresponding structure made by MBE. The growth system used was a MBE-type high-vacuum system with Knudsen cells as the sources. Elements were used for the main components of the II–VI compounds. For n-type doping of ZnSe, Zn was replaced with ZnCl_2 . The observed growth rate per cycle characteristics is shown in fig. 26b. A monolayer saturation occurs in the temperature range of 250–350 °C. A mirror-like surface was obtained in samples made in the monolayer saturation conditions. At 280 °C, a monolayer saturation was obtained for both ZnTe and ZnSe. ZnSe samples doped with ZnCl_2 showed n-type conductivity.

In ref. [144], Konagai et al. also report an ordered superalloy or “monolayer superlattice” $(\text{ZnSe})_1-(\text{ZnTe})_1$. The PL emission from an ordered ZnSeZnTe superalloy was much stronger than that from a mixed $\text{ZnSe}_{0.5}\text{Te}_{0.5}$ crystal. Fig. 27 shows a TEM picture of an ALE $(\text{ZnSe})_4-(\text{ZnTe})_2$ superlattice produced by Konagai et al.

4.3.3. ZnS

The only work on ZnS single crystal found in the survey of this review was reported by Nelson [134]. ZnS and ZnSe single crystals were grown on (100)- and (110)-oriented GaAs. X-ray analysis of the grown layers indicated that they were good-quality epitaxial layers in the same orientation as the GaAs substrate.

Table 10 summarizes ALE single-crystal works on II–VI compounds. In all listed works of table 10, elements of the compounds have been used as the reactants.

4.4. II–VI thin films, oxides and nitrides

Early development of ALE was primarily made with thin films of ZnS and dielectric oxide materials for use in electroluminescent devices. Materials and structures used in thin film electroluminescent devices are discussed in detail in section 4.5. In this section, we summarize

Table 10
Substrate materials and temperature range of monolayer saturation in publications on ALE of II–VI single crystals

Compound	Substrate	ML/cycle	<i>T</i> range (° C)	Reagents	Ref.
ZnS	GaAs	1	300–400	Zn + S	[134]
	100; 110				
ZnSe	GaAs	1	275–375	Zn + Se	[134]
	100; 110				
ZnSe	GaAs	1	280	Zn + Se	[61]
	001				
ZnSe	GaAs	1	250–350	Zn + Se	[144]
ZnSe	GaAs	1	280	Zn + Se	[145]
	001				
ZnTe	glass	0.7	340–400	Zn + Te	[10]
ZnTe	GaAs	1	200–400	Zn + Te	[61]
	001				
ZnTe	InP	1	280	Zn + Te	[145]
CdTe	CdTe	1	267–277	Cd + Te	[12]
	110				
CdTe	BaF ₂	1	260–285	Cd + Te	[148]
	111	~ 0.85	285–315		
		~ 0.6	315–360		
CdMnTe	CdTe		267	Cd + Te	[18]
	111				

Table 11
II–VI thin films oxides and sulphides produced by ALE

Compound	Substrate	ML/cycle	<i>T</i> range (° C)	Reagents ^{a)}	Ref.
ZnO	glass		290–360	Zn acetate + H ₂ O	[41]
ZnS	glass	0.7	320–470	Zn + S	[1]
ZnS	glass	0.3	450	ZnCl ₂ + H ₂ S	[2]
ZnS	glass	0.9	290–360	Zn acetate + H ₂ S	[39,41]
CaS	glass			Ca(thd) ₂ + H ₂ S	[46]
SrS	glass			Sr(thd) ₂ + H ₂ S	[46]
BaS	glass			Ba(thd) ₂ + H ₂ S	[46]

^{a)} thd = 2,2,6,6-tetramethyl-3,5-heptanedionato.

Table 12
Oxide thin films produced by ALE

	Reactants				
	AlCl ₃	Al-alkoxides	TiCl ₄	TaCl ₅	InCl ₃ and SnCl ₄
H ₂ O	1		1	1	1
	7				
alcohol	7	7			
phenol	7				
O ₂		7			

1 Lohja Co., Espoo, Finland [1,2,4,5],
7 Helsinki University of Technology, Department of Chemistry, Espoo, Finland [51].

Table 13
Nitride thin films produced by ALE

	Reactants			
	TiCl ₄	NbCl ₅	TaCl ₅	MoCl ₅
NH ₃	7	7	7	7

7 Helsinki University of Technology, Department of Chemistry, Espoo, Finland [48].

published data of ALE processes of II–VI thin films in the form of table 11 and some oxide and nitride thin films in tables 12 and 13. All data in tables 11–13 refer to work on ALE of polycrystalline or amorphous thin films.

4.5. ALE electroluminescent devices

Electroluminescent (EL) devices have a long development history extending back to 1936 when the Frenchman Destriau [159] observed light generation in some solid materials when excited with a high electric field.

The first attempt to utilize the phenomenon in a commercial application was made by Sylvania, USA, in the 50s. The product was a guide light to be used in dark ambient. The technology used was a powder technique, where the active material was mixed in a binder and “painted on a substrate”. Light emission and also lifetime characteristics of the devices were modest and the production was stopped.

New interest in EL arose in the mid 60s, this time based on thin film technology. When the light-emitting ZnS(Mn) film was put between two dielectric layers, it was possible to report considerable brightness with an ac excitation and promising lifetime characteristics [160–162]. These promises triggered the development of ALE technology in 1974 as a new approach to handle the growth of compound thin films in a more precise and controllable way.

4.5.1. ALE-EL thin film structure

The structure of a double-insulator EL device is presented in fig. 28 [163]. In an operation condition, there is an electric field of about $2 \times 10^6 \text{ V cm}^{-1}$ placed across the structure of two dielectric layers and a ZnS layer, of a total thickness less than 1 μm . Owing to the high electric stress and large surface area, the demands on the quality of the thin films in an EL display panel are extremely high. In an EL device, the ZnS material is in polycrystalline form, and the dielectric layers are polycrystalline or amorphous depending on the material used.

The substrate material in the ALE-EL device of fig. 28 is soda glass. Sodium migration from the substrate to the thin film structure can be prevented with an Al₂O₃ layer made by ALE using the reaction



The resulting Al₂O₃ layer is amorphous. The capability of ALE Al₂O₃ to act as an ion barrier has been analyzed in ref. [4]. Test samples used had an Al₂O₃ layer of 80 nm and a soda glass substrate and a ZnS layer of 350 nm on top of the Al₂O₃ layer. The determination of the sodium concentration was made by SIMS. A heat treatment of 70 h at 500 °C did not result in detectable increase of sodium in the Al₂O₃/ZnS interface. Out of 31 different ion barrier types tested, the ALE Al₂O₃ ion barrier gave the best result.

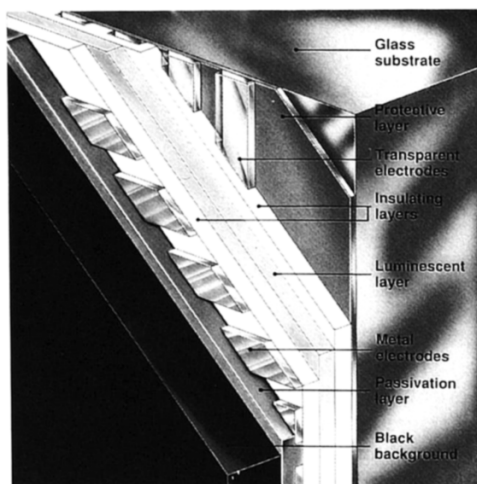


Fig. 28. A double-insulator EL structure produced by the ALE technique.

There are published data for processes and characteristics of aluminium oxide, tantalum oxide and titanium oxide as well as mixtures of those as the dielectric layers of a double-insulator electroluminescent device [2,8]. Processes are based on a metal chloride + H_2O reaction, corresponding to eq. (57). In a thin film electroluminescent device, the most important characteristic is a high dielectric strength. A comparison of the dielectric strengths of Al_2O_3 and a mixed $Al_xTi_yO_z$ dielectric is given in ref. [8].

In a thin film device, at least as important as an inherent dielectric strength of a material is the dielectric strength observed in a large-area device. The large-area strength is strongly influenced by weak points or pinholes related to a microcontamination or to inhomogeneities in the substrates. In an ALE process, a surface is overdosed by a reactant in each reaction sequence in order to achieve a monolayer saturation. This means that microcontamination particles and partly covered substrate areas also receive the same coverage as the flat areas. Instead of becoming shaded as in conventional deposition methods, a substrate area under a contamination particle takes on the same thickness and strength as the non-disturbed areas of the surface, fig. 29.

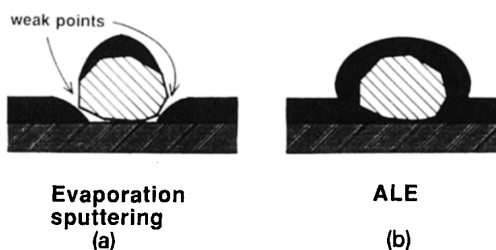


Fig. 29. "Packaging" of microcontamination in an ALE process. (a) In conventional deposition techniques a contamination particle shades the surface resulting in weak points in the shaded areas. (b) In an ALE process, the surface is saturated for each monolayer. Shaded areas receive the same thickness as the non-shaded areas.

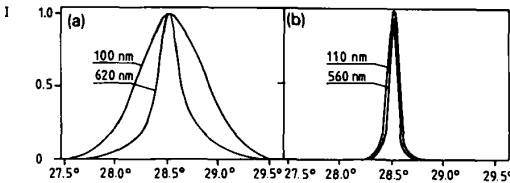


Fig. 30. Normalized X-ray diffraction line profiles [25]. (a) Evaporated ZnS; 111 profiles for samples of 100 nm and 620 nm thickness. (b) ALE ZnS; 00.2 profiles for samples of 110 nm and 560 nm thickness.

The light-emitting layer of the EL structure of fig. 28 is ZnS doped with Mn. A ZnS layer, when made using the ALE process on an amorphous substrate, has a polycrystalline, predominantly hexagonal (wurtzite), structure [26]. Films grown at a temperature of about 500 °C have a high degree of specific orientation with the *c* axis perpendicular to the substrate. In fig. 30 there is a comparison of measured X-ray diffraction peaks of ZnS made by vacuum evaporation and ALE, taken from Tanninen [25]. ZnS films made by vacuum evaporation generally have a cubic polycrystalline structure. The comparison is made between the 111 profiles of the evaporated samples of two thicknesses and the 00.2 profiles of ALE samples of about the same thicknesses.

- As a result of the X-ray study, we can observe that
- ALE grown ZnS prefers the hexagonal crystalline structure (in ALE for some thin films grown at a temperature of 350 °C, a predominantly cubic form has been observed) [50];
 - ALE produces highly oriented films even at small thicknesses.

In EL thin films, good crystallinity results in a high power efficiency of light generation. In favorable surface conditions, a monolayer saturation in an ALE process results in two-dimensional nucleation rather than a three-dimensional one that is dominating in conventional deposition techniques. In thin films where two-dimensional nucleation dominates, a columnar growth occurs from the beginning of the film formation. This minimizes a dead layer, i.e. a zone of poor crystallinity at the beginning of the growth. The approximately same width of peaks in fig. 30b for samples of different thicknesses is an indication of a small dead layer.

In EL films the term “dead layer” refers to a poor light conversion efficiency of a zone with poor crystallinity. The luminance as a function of the thickness of the thin film is studied in ref.

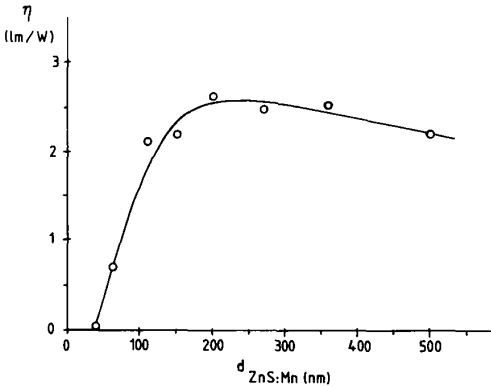


Fig. 31. Light conversion efficiency of ALE-EL thin films as a function of thickness of the ZnS layer [163].



Fig. 32. Information boards using ALE-EL modules at Helsinki International Airport.

[163]. Fig. 31 indicates that the light conversion efficiency (in lumen W^{-1}) of ALE-EL films stays nearly constant to a thickness of about 100 nm.

Because of the hexagonal crystalline structure of the ALE ZnS(Mn) films, the peak wavelength of emitted light of an ALE-EL device is slightly different from that of an EL device based on a vacuum evaporated or sputtered ZnS(Mn) film. The shift of wavelength is from 585 nm, typical of a device with a cubic ZnS(Mn) layer, to 580 nm, which changes the color of the display from orange yellow to a bright yellow.

The EL structure of fig. 28 has a passivation layer of ALE Al_2O_3 as a protection against the ambient.

4.5.2. ALE-EL devices

Fig. 32 shows two of the four large information boards installed at Helsinki International Airport in March 1983 [164]. They consist of 3000 ALE-EL modules totalling 6.5 m^2 of light-emitting thin film area. The boards operate 24 h day^{-1} at a brightness of 115 cd m^{-2} . Based on a statistics of 50 000 h of continuous operation the mean time between failure for a thin film module is more than $2 \times 10^6 \text{ h}$. The degradation of brightness is shown in fig. 33.

Fig. 34 shows a “Finlux 640.400” data display panel based on ALE-EL technology.

5. Summary

This review of the status of atomic layer epitaxy has been written with emphasis on the mechanism and growth conditions of ALE. ALE is a method of making ordered material

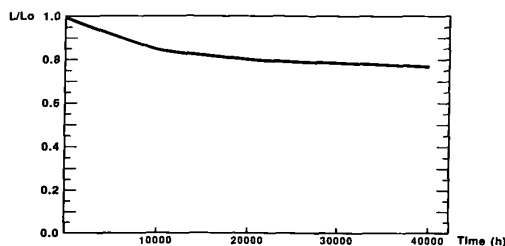


Fig. 33. Degradation of brightness of the ALE-EL board of fig. 32.



Fig. 34. Finlux 640.400 flat panel display.

structures at an atomic scale. An increased degree of order in a material structure has been obtained by an increased order in the micro-environment of the growth. In ALE, an increased order in the micro-environment of the growth is created by sequencing the growth phenomenon; the formation of each atomic layer is completed through a saturated surface reaction before a pile-up of the next atomic layer is allowed.

Many of the inherent potentials of ALE have been confirmed by experimental work:

- Crystal quality obtained with ALE is high when estimated through X-ray diffraction analysis, photoluminescent spectra and electrical and optical properties of the material.
- An epitaxial temperature resulting in good crystallinity is lowered in comparison to conventional processes. This is explained by increased surface mobility of reactant molecules or atoms in ALE conditions.
- Abrupt material interfaces and layer structures can be tailored with atomic accuracy.
- Monolayer saturation results in a precise thickness control of a grown layer over large areas and different shapes of a substrate.

A precisely known environment of reactions in an ALE process is a challenge to a deeper understanding of chemical reactions. In this respect, ALE may build a link between theoretical and experimental chemistry and serve as a tool for surface chemistry at an atomic scale.

The capability of atomic layer epitaxy as a method for producing high-quality material has been proved by efforts in many laboratories, and commercial production of ALE-EL thin film electroluminescent display panels. The increasing research activity and the promising results especially in tailored compounds and microstructures for quantum effect electronic devices suggest that most of the realization of the potential and use of ALE still lies ahead.

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