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Atomic layer epitaxy

Tuomo Suntola

Microchemistry Ltd, Box 45, SF-02151 Espoo (Finland)

Abstract

Atomic layer epitaxy (ALE) is a surface-controlled process for thin film manufacturing, for formation of atomically controlled surfaces and for epitaxial growth of single crystals. It is based on the saturation of individual, sequentially performed surface reactions between the substrate and each of the reactants needed. The saturation mechanism of ALE sequences results in an inherent elimination of pinholes, conformal coating characteristics as well as in a thickness uniformity and homogeneity of the thin films produced. ALE is also an effective tool in a precise construction of superlattices, superalloys, tailored molecular structures and interface layers.

1. Introduction

Atomic layer epitaxy (ALE) is a surface-controlled process for thin film manufacturing and for epitaxial growth of single crystals [1]. It is primarily developed for compound materials, such as II–VI and III–V semiconductors, oxides and nitrides. It can be extended to certain covalent materials as well. ALE supports a precise construction of superlattices, superalloys, tailored molecular structures and interface layers.

The inherent surface control mechanism in ALE is based on the saturation of individual, sequentially performed surface reactions between the substrate and each of the reactants needed for the compound to be grown. The saturation mechanism makes the rate of growth proportional to the number of reaction cycles instead of to the intensity of the reactant flux or the time of the growth. The ALE process can be carried out either in vacuum or in an inert gas atmosphere. The surface control feature of ALE supports processing of large batches in small volumes, which is a key to a high production efficiency.

In producing thin films or epitaxial layers, the surface control results in reproducible physical characteristics with good homogeneity and thickness uniformity, in an effective step coverage and in a very low pinhole density, ALE is industrially applied in manufacturing of electroluminescent thin film displays.

2. Principle of operation

ALE can be performed in several different modes of operation depending on the type of material to be grown and the type of reactants used in the process. Basically, ALE has been developed for compound ma-

terials. With certain restrictions it can be applied, however, to elemental materials also.

In its simplest mode of operation, ALE is performed using the elements of the compound to be grown as the reactants. In this mode of operation the compound grows one full or partial monolayer in each reaction step as a result of an additive chemisorption. This mode of operation is applicable to several II–VI compounds (Fig. 1(a)).

An alternative way of performing ALE for compound materials is the use of compound reactants, each of which supplies one of the elements of the compound to be grown. The reaction between the vapour and the growing surface is an exchange reaction for at least one of the reactants (Fig. 1(b)).

For ALE of covalent materials a compound reactant is needed. A saturated monolayer of the reactant must be reduced to a monolayer of atoms of the covalent material before the next reaction step. The reduction can be done with a reducing surface reaction or with a pulse of extra energy to the surface (Fig. 2).

The characteristic feature of ALE in all operation modes is the saturation of each surface reaction, which makes the growth proceed incrementally, one reaction step at a time. The resulting thickness growth in a reaction step is dependent on the saturation density achieved in the reaction. For some III–V materials the saturation density has been observed to correspond to the density of atoms in a crystalline plane of the bulk material. This case is often referred to as “a full monolayer per cycle” growth. In most cases the saturation density has been observed to be less than a “full monolayer”, which refers to the important role of surface reconstruction in ALE growth steps. Use of large reactant molecules also reduces the saturation density of a monolayer.

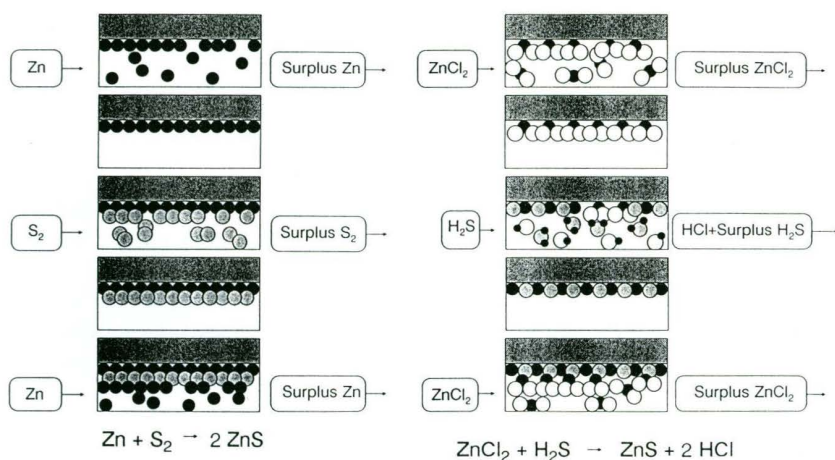


Fig. 1. Sequences of ALE process for ZnS using (a) elemental reactants (exposure to zinc vapour, chemisorption of zinc monolayer, purge of zinc surplus exposure to S₂ vapour, chemisorption of sulphur, purge of S₂ surplus, exposure to zinc vapour etc.) and (b) compound reactants (exposure to ZnCl₂ vapour, chemisorption of ZnCl₂, purge of ZnCl₂ surplus, exposure to H₂S, exchange reaction resulting in solid ZnS and HCl, purge of HCl and surplus of H₂S, exposure to ZnCl₂ vapour etc.).

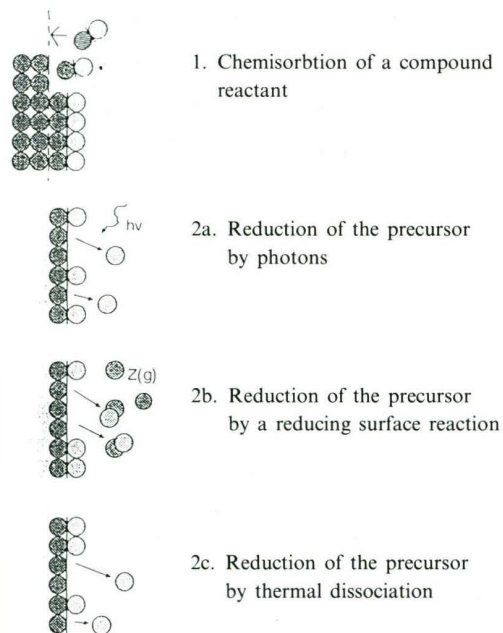


Fig. 2. Alternative ALE sequences for elemental materials.

In contrast with the demands of reactants in chemical vapour deposition (CVD) processes, optimal reactants in ALE should react aggressively with each other, *i.e.* the activation energy of desirable surface reaction should be low. In CVD the uniformity of thickness is very much reliant on a high reaction threshold, which also is needed to avoid gas phase reactions. In ALE, gas phase reactions between reactants are automatically eliminated by the sequencing of reactants, and thickness uniformity results from the saturation mechanism. High reactivity assures efficient saturation and a high mate-

rial utilization factor. For a uniform saturation it is also important that the reactants used are stable at the processing temperature. Undesirable decomposition results of the reactants may be a major source for impurities in the resulting thin films.

3. Applications

3.1. Atomic layer epitaxy of single crystals

3.1.1. Motivation

The objectives are to achieve high precision tailored structures and low temperature epitaxy of covalent single crystals, and to elucidate the science of crystal growth and surface chemistry.

The main part of recent research activity on ALE is directed at the growth of III-V single crystals, focusing on obtaining a complete full monolayer control in the growth of the material. Other important processing demands are low impurity level and doping into p-type or n-type material at controlled conductivity levels. For superlattice structures and abrupt doping profiles a low processing temperature and reasonable process time are desirable features. A special demand for processes combining layers of different compounds is that non-desirable chemical interactions between the compounds must be avoided. Owing to the incremental nature of growth, ALE has a specific potential in the manufacturing of layered microstructures and superlattices.

3.1.2. Gallium arsenide—an example of atomic layer epitaxy of III-V single crystals

The main features reported in the development of an ALE process for GaAs can be listed as follows.

3.1.2.1. Elemental gallium as the gallium reactant (migration enhanced epitaxy). The main problem in using elemental gallium as the reactant is the poor desorption of gallium from a gallium surface (low vapour pressure of gallium). It has been compensated by applying a precise dose of gallium to fill the arsenic surface with a monolayer [2]. A uniform filling of gallium sites on an arsenic surface is enhanced by a high surface mobility of gallium on a gallium surface. The surface mobility of free gallium atoms on an arsenic surface results in a two-dimensional nucleation which makes the gallium atoms gather at the edges of an already-formed gallium island rather than stay at a random position on an arsenic surface.

An advantage of this migration enhanced epitaxy is that problems with impurities from complex reactants can be avoided. A disadvantage is that the non-critical dosing of reactants as well as self-controlled saturation have been lost.

3.1.2.2. Trimethylgallium or triethylgallium as the reactant for gallium. Problems with trimethylgallium (TMG) and triethylgallium (TEG) can be connected to a modest difference between desirable and non-desirable surface reactions and decomposition reactions. An advantage of using TMG or TEG as a reactant in the ALE process is that they both have a high vapour pressure and that they can be dosed from an MOCVD source. Early work on ALE of GaAs was made in high vacuum conditions using TMG and arsine as the reactants [3, 4]. Without laser irradiation, almost no saturation was observed. However, when the same reaction was carried out in a hydrogen stream, a full monolayer saturation was observed over a wide temperature range [5–7].

Laser irradiation seems to widen the processing window both in the case of hydrogen flow and in the case of vacuum [8]. Nishizawa *et al.* [9] reported a TEG process with UV irradiation from a mercury lamp showing the same type of changes in the processing characteristic as obtained in a hydrogen flow. The main problem in the ALE process for GaAs using TEG or TMG as the gallium reactant seems to be carbon as an impurity in the resulting epitaxial layer.

3.1.2.3. Gallium chloride as the reactant for gallium. A way to avoid the problem of using carbon-containing reactants in ALE of GaAs and also to avoid the problem of low vapour pressure of elemental gallium is the use of GaCl as the gallium reactant [10]. Processing was carried out in an atmospheric-pressure hydrogen flow system, and saturation was observed between 400 and 600 °C. Usui *et al.* [11] reported a delta-doped field effect transistor based on ALE GaAs. When measured in terms of carrier concentration, GaAs layers made

using GaCl as the gallium reactant show acceptable impurity levels. No analysis of possible chlorine concentration in the epitaxial layers have been presented.

3.2. Atomic layer epitaxy of thin films

3.2.1. Motivation

The main aims were as follows: good crystallinity in polycrystalline films; high density, and good chemical stability in amorphous films; homogeneous reproducible thin films over large areas; precise stoichiometry of compound films; low pinhole density and an effective conformal coating; tailored adhesion and interface layers; sandwich structures of different materials in one process; cost-effective processing.

A need for high quality thin films for electroluminescent displays was the original motivation for the development of ALE. The term “high quality” mainly refers to desirable characteristics in the target product and does not necessarily have a precise physical meaning. In applications where a high electric field is applied across a thin film, a high dielectric strength, uniformity and low pinhole density are important features. In some other applications, electron mobility and crystallinity of the thin film material are more important features. It is yet another question of how these demands relate to the chemical and physical structure of the material and how the structure relates to processing parameters.

3.2.2. Electroluminescent panel—an example of atomic layer epitaxy for a large-area thin film application

An electroluminescent structure consists of a sandwich of several thin films (starting from the substrate glass): ion barrier (ALE)—transparent electrode dielectric layer (ALE)—light-emitting layer dielectric layer (ALE)—back electrode—passivation (ALE)—a back cover glass laminated on top of the thin film structure (Fig. 3). As indicated, with the exception of the electrode layers, ALE is used to process all the other necessary thin films.

3.2.3. Ion barrier

ALE electroluminescent thin film structures are made on soda glass. There is a need for an ion barrier layer on top of the substrate glass to prevent penetration of sodium from the substrate to the thin film structure. According to the results of Hamilo *et al.* [12], an ALE Al₂O₃ ion barrier layer of 80 nm is enough to block sodium at 500 °C (test time, 70 h).

3.2.4. Atomic layer epitaxy of ZnS in electroluminescent devices

In ZnS thin films made for electroluminescent devices [13], ALE produced hexagonal columnar polycrystalline material with the *c* axis in the direction of

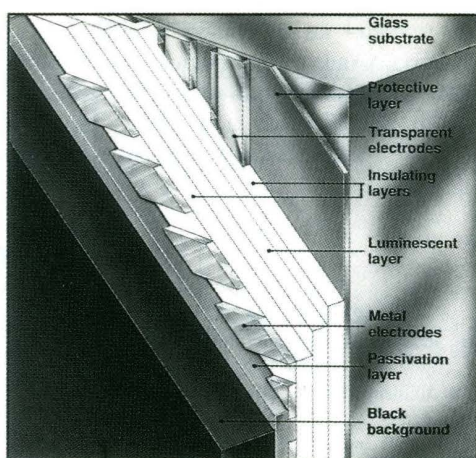


Fig. 3. Structure of an ALE electroluminescent thin film device.

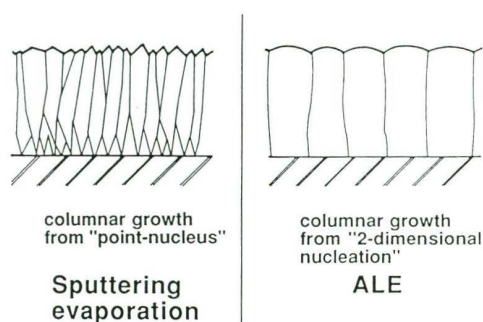


Fig. 4. Comparison of basic nucleation mechanisms for sputtered or evaporated and ALE thin films.

growth. Sputtering and electrogun evaporation of ZnS generally produces the cubic form of ZnS. A transmission electron microscopy picture of the cross-section of the ALE ZnS thin film shows that the columns have their final diameter directly from the starting surface, which is an indication of a two-dimensional nucleation mechanism (Fig. 4). Good crystallinity in a ZnS layer is essential for a good light conversion efficiency. ALE electroluminescent structures show excellent light conversion efficiency even when the thickness of the ZnS film is reduced to 100 nm, which is an indication of good crystallinity also close to the starting surface [13].

3.2.5. Dielectric layers

In electroluminescent thin film structures the quality of dielectric layers is at least as important as the quality of the light-emitting ZnS layer. For dielectric layers in electroluminescent devices the key characteristics are a high dielectric constant and a high dielectric strength. The dielectric strength is basically a material characteristic. In practice the dielectric strength obtained is strongly process related and correlates with the bulk density of the thin film and the density of pinholes.



Fig. 5. Effect of saturated surface coverage on pinhole formation under microcontamination particles.

ALE is able to produce thin films of $\text{Al}_x\text{Ti}_y\text{O}_z$ with dielectric strengths as high as 6 MV cm^{-1} measured over the whole large-area display panels [14]. The measurement is made without any pre-burning, which shows that ALE produces the dielectric layers without any pinholes.

3.2.6. Elimination of pinholes

The mechanism of "no pinholes on a non-perfect substrate" is a consequence of the effective conformal coating characteristic of the ALE. Because of the saturation of the surface in each reaction step, ALE builds a conformal packaging around the microcontamination particles and thereby prevents the formation of weak points in the film (Fig. 5). In an electroluminescent structure the elimination of pinholes is essential also in the ion barrier and in the passivation layers.

3.2.7. Sandwich structure in one process

ALE makes it possible to grow the whole sandwich structure of dielectric–semiconductor–dielectric in one process. This is a major advantage in production. It is also an advantage in the control of the interfaces between the dielectric layers and the ZnS layer.

3.3. Atomic layer epitaxy of porous materials

3.3.1. Motivation

The aims are to obtain tailored heterogeneous catalysts and to determine the science of surface chemistry.

The coating of a porous substrate can be considered as an extreme case of conformal coating. Porous high surface area substrates (carriers) are widely used in the preparation of heterogeneous catalysts. ALE serves as a novel approach to preparing heterogeneous catalysts both by atomic tailoring of the surface of the porous carrier and by a bond-selective filling of desirable active species on the tailored surface.

3.4. Atomic layer epitaxy processing equipment

Two main approaches in ALE processing equipment are molecular beam epitaxy (MBE)-type of high vacuum systems and CVD-type inert gas systems. In scientific work, vacuum systems give more freedom for *in situ* observation and analysis of the growing surface.

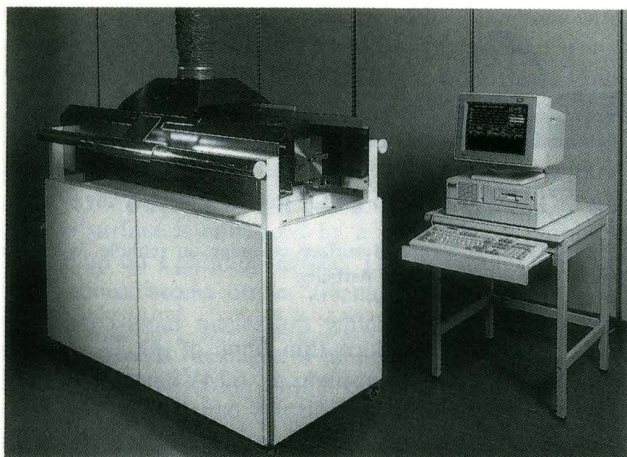


Fig. 6. ALE reactor F-120 by Microchemistry Ltd. The reactor is primarily designed for two 50 mm × 50 mm substrates. Typical processing speed of F-120 reactor is 0.8 s cycle⁻¹ (injection pulses of reactants, 0.2 s each; purge sequences, 0.2 s).

High vacuum systems are usable for small-area thin films rather than for large-area thin films.

3.4.1. Atomic layer epitaxy reactors using inert gas flow

ALE reactors used on an industrial scale are based on inert gas transport and valving of the reactants [15]. Substrates are placed in a cassette back to back with active surfaces facing gas flow spacings of a few millimetres each. This type of construction effectively utilizes the saturation of surface reactions in ALE. An inert gas flow through the flow spacings of the substrate cassette transports travelling waves of reactants across the active surfaces of the substrates. Owing to the saturation, uniform monolayers are formed on the whole active surfaces of the substrates.

A demonstration of the importance of the surface saturation in the ALE is a comparison of thickness profiles of CdS thin films made in the CVD mode and in ALE in an F-120 reactor (Fig. 6) (made by Microchemistry Ltd) under similar processing conditions when the temperature, reactants and flow conditions are considered. In F-120, there is a cassette for two substrates of 50 mm × 50 mm and a flow spacing of 1 mm between the active surfaces of the substrates (Fig. 7). In the CVD mode the 0.1 s pulses of the reactants, cadmium and S₂ are given simultaneously to the substrate with a repetition cycle time of 0.6 s. A short growth distance and strong thickness profile in the direction of the carrier gas flow indicate a high reactivity between the reactants (Fig. 8(a)). In the ALE mode the reactant pulses of 0.1 s are given in sequence with a 0.2 s purge sequence between the subsequent reactant pulses (cycle time of 0.6 s as in the case of the CVD mode). Satura-

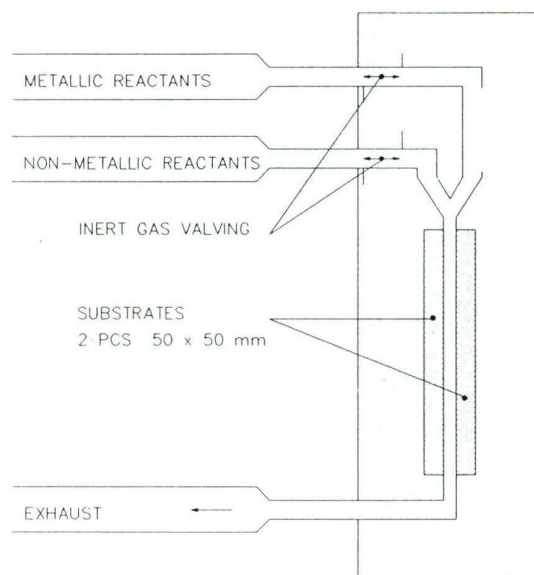


Fig. 7. Gas flow channels in F-120 reactor. Metallic and non-metallic reactants are supplied in different channels into the reaction zone, which is formed by a 1 mm spacing between two substrates.

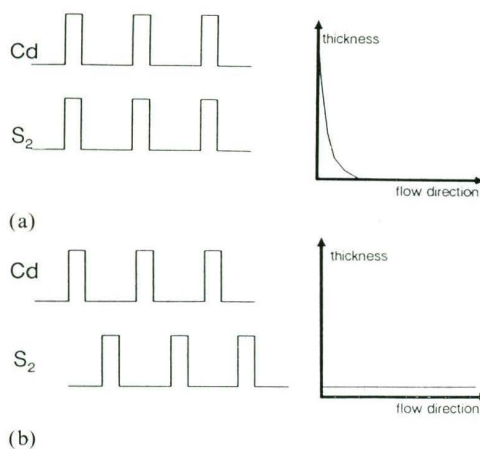


Fig. 8. Thickness profiles demonstrated in F-120 reactor for CdS in (a) the CVD mode (simultaneous feeding of the cadmium and S₂ pulses) and (b) the ALE mode (one-at-a-time feeding of the cadmium and S₂ pulses).

tion is effective and a uniform thickness is observed over the whole substrate area (Fig. 8(b)). Saturation density in this case is about a third of full monolayer density.

Summary

Atomic layer epitaxy (ALE) is an effective way of producing high quality thin films especially of compound materials. ALE is a surface-controlled, sequentially proceeding process. The saturation mechanism of

ALE sequences results in an inherent elimination of pinholes, conformal coating characteristics as well as in thickness uniformity and homogeneity of the thin films produced. ALE is a cost-effective thin film process applicable on an industrial scale.

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