Edited by Nicola Pinna and Mato Knez

Atomic Layer Deposition of Nanostructured Materials

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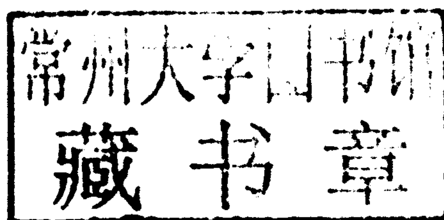

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Library of Congress Card No.: applied for

British Library Cataloguing-in-Publication Data
A catalogue record for this book is available from the British Library.

Bibliographic information published by the Deutsche Nationalbibliothek
The Deutsche Nationalbibliothek lists this publication in the Deutsche Nationalbibliografie; detailed bibliographic data are available on the Internet at http://dnb.d-nb.de.

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Typesetting Thomson Digital, Noida, India
Printing and Binding Fabulous Printers Pte Ltd, Singapore

Cover Design Grafik-Design Schulz, Fußgönheim

Printed in Singapore
Printed on acid-free paper

Print ISBN: 978-3-527-32797-3
ePDF ISBN: 978-3-527-63993-9
oBook ISBN: 978-3-527-63991-5
ePub ISBN: 978-3-527-63992-2
mobi ISBN: 978-3-527-63994-6

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Foreword

Atomic layer deposition (ALD) is a relatively new and low-temperature growth method capable of depositing a variety of thin films on virtually any substrate. Although it is a vapor-based technique like chemical vapor deposition (CVD), there are two main differences that make it a particularly powerful method for very thin and conformal film growth. First, precursor molecules react only with the surface (not with themselves) under deposition temperatures. Second, growth is achieved by sequential introduction of typically two precursors, separated by a thorough inert gas purge, so that different precursors are not present together in the gas phase. These characteristics are in fact responsible for generating much interest from researchers belonging to scientific areas that had thus far been considered unrelated, thus creating a stimulating interdisciplinary environment. These are gas-phase chemistry, surface science, solid-state chemistry, kinetics of thin film growth, and engineering of gas flow reactors.

The community that is responsible for the development of ALD came from *organometallic chemists*. They were responsible for identifying or synthesizing precursors capable of reacting at moderate temperatures with specific surface groups while remaining stable in the gas phase (no self-reaction), which is key for the ALD process. The challenge for this community has been to produce complementary precursors that react with complete ligand exchange at moderate temperatures, essential to grow pure films. Incomplete reactions lead to the incorporation of carbon or other impurities into the films.

Surface scientists have quickly been drawn to ALD because the process is based on surface reactions. As is now recognized, surface processes can be substantially different from gas-phase chemistry because the surface structure and steric interactions dramatically affect chemical reactions at surfaces. *In situ* characterization is therefore necessary to verify choices based on gas-phase chemistry and to quantify surface reactivity with precursors. Furthermore, it has now been shown in several instances that the substrate can also play an active role. Specifically, at typical process temperatures reactions with the substrate can take place, such as formation of SiO_2 during deposition of metal oxides on oxide-free Si substrates. Therefore, much thought is being given to developing diffusion barriers to prevent oxidation of and/or ion penetration into the substrate, including surface functionalization and

even self-assembled monolayers. Given the diversity of approaches and complexity of the mechanisms, the whole arsenal of surface techniques has been brought to bear: vibrational spectroscopy (infrared, Raman), electron spectroscopy (X-ray photoelectron, photoemission, Auger), ion scattering (Rutherford backscattering, medium- and low-energy ion spectroscopies), imaging (transmission electron microscopy, atomic and in some cases scanning tunneling spectroscopies), mass spectroscopy, and quartz crystal mass analysis. Much needed fundamental work continues to be performed as new precursors and systems (e.g., metal films) are considered.

Solid-state chemists and modelers are also engaged in ALD processes because the simple picture of alternative deposition of element A and element B to form an amorphous A_xB_y film is not strictly correct. Atoms A and B require substantial rearrangement and rebonding as their ligands are removed, which is not always consistent with layer-by-layer growth and is certainly more complicated than the simple ALD models typically presented. Kinetics play a central role. A striking example of complex, kinetically controlled surface mechanism is the agglomeration of metal atoms upon thin metal film deposition, making it virtually impossible to initiate a uniform thin metal film growth. A combination of measurements and advanced modeling is needed to develop a mechanistic understanding of the processes with some predictive power.

Chemical engineers have played an important role in addressing the gas flow requirements that are much more stringent in ALD than in any other vapor-phase growth method. Indeed, the complete removal of one precursor gas before the other is introduced into the reactor requires that flow patterns are optimized such that the purge gas can efficiently remove all traces of the precursor gas. For industrial applications, uniform supply of precursor gas over large wafers also demands careful optimization of precursor delivery rates and flow.

The chapters in the first part of this book involve authors from this wide community and address many of the issues outlined above, including the growth of organic thin films. The focus of the book, however, is related to the extraordinarily diverse ALD-based applications that have emerged over the past few years. While the initial work was motivated by metal oxide film deposition for microelectronic applications (ALD was initially adopted by industry for the growth of high-k dielectrics, for instance), the ALD technique has begun to contribute to a wide range of systems. It is now used for sensor fabrication, fiber coating, and biomedical device fabrication, with a focus on highly structured material and nanomaterials. The second part of the book brings together a diversity of topics that underscore the value and importance of the ALD technique and foreshadows its growing popularity.

With such an explosion of applications and a growing community using ALD, it is clear that fundamental studies of ALD processes are needed to provide the necessary understanding for progress and success. This book is therefore a motivation for researchers in other fields to bring their discipline and expertise to critically evaluate and address the complex issues arising in all these applications. It constitutes an

excellent reference book for students and young scientists interested in ALD, and its applications and challenges. Much remains to be done, well beyond precursor development, to fully implement this powerful technique for the current and future applications.

Dallas, Texas
January 2011

Prof. Yves J. Chabal

Preface

Atomic layer deposition (ALD) is a coating technology that in the past two decades rapidly developed from a niche technology to an established method. The method itself is not too difficult to understand and apply. The basic requirements are a vacuum chamber, at least two reactive precursors, and valves for alternate dosing of the precursors, since the different precursors must never be present in the chamber at the same time. For most of the processes, one metal-containing chemical is used as metal source and subsequently reacted with another chemical, which is the source of, for example, oxygen, nitrogen, sulfur, and so on. The chemistry is normally very simple and often shows hydrolysis, oxidation, reduction, or an organic coupling reaction in the particular case of molecular layer deposition (MLD). There are some restrictions for the chemicals: One has to ensure that the precursors have a reasonably high vapor pressure in order to allow saturation of the chamber volume upon dosing and a good thermal stability to avoid decomposition prior to the next step. A further requirement is that the precursor must chemisorb onto the substrate to be coated. Once these preconditions are fulfilled, the coating process, consisting of alternating pulse and purge steps for each precursor, can be started. The timely separation of the precursors is necessary in order to achieve a saturation (self-termination) of the substrate surface with the precursor and thus to enable a very precise thickness control, which is normally on the angstrom scale. Since ALD is not a line-of-sight coating technology, even complicated 3D structures with not easily accessible surfaces (e.g., trenches, grooves, pores, aerogels, etc.) can be uniformly and conformally coated.

The chemistry used for ALD is often derived from the chemical approaches used for chemical vapor deposition (CVD) and one may argue that it is a modified form of CVD. This comparison is indeed correct as demonstrated from the fact that all ALD precursors can be used for CVD; however, not necessarily vice versa. On the other hand, (i) the timely separation of the precursors and the resulting film thickness control with the number of cycles instead of processing time, (ii) the often much higher compactness of the deposited films compared to CVD, and (iii) the exceptionally good step coverage make ALD an outstanding subset of CVD that surely deserves particular attention as an individual coating technology.

The rapid increase of popularity of ALD in the past two decades is clearly demonstrated by the number of articles published every year (Figure P.1). An almost

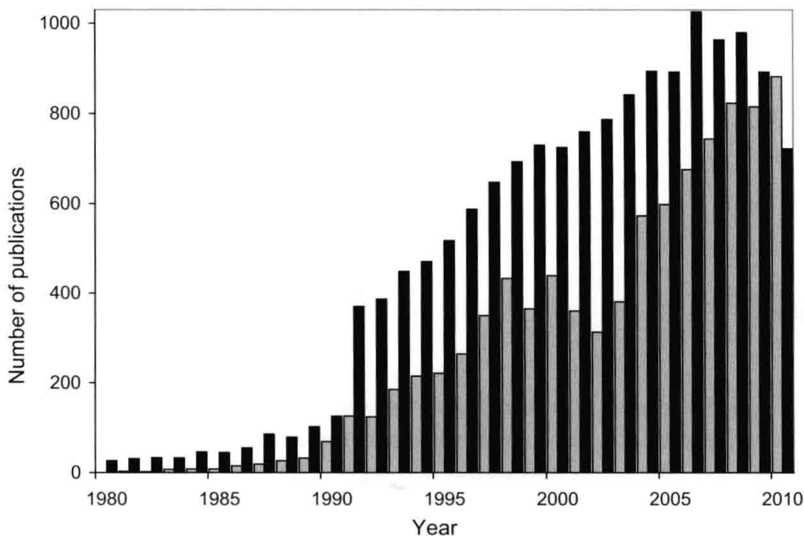

Figure P.1 Number of articles per year published on ALD (gray bars) and CVD divided by five (black bars). *Source*: Web of Science accessed on December 20, 2010.

linear increase is observed, reaching a maximum of around 900 articles published in 2010. Although the number of articles per year is around five times larger, a similar trend can be observed for CVD. The only difference is that since 2004 the number of papers has remained somehow constant. The development of publications related to ALD promises a bright future for research and development.

The book is divided in two parts: the first part (Chapters 1–7) deals with all the basic aspects of the technique, while the second part focuses on ALD-based nanostructured materials and their fields of application (Chapters 8–17).

The introductory chapter, written by J. Niinistö and L. Niinistö is an introduction to ALD and its development since its discovery in 1976. The following two chapters describe theoretical modeling of ALD processes (Chapter 1) and step coverage (Chapter 2). Chapter 3 describes the precursors used in ALD and their requirements. Chapter 4 describes the soft chemistry routes to oxides and the comparison of the chemistry taking place in ALD and in solution. Chapter 5 introduces molecular layer deposition, which is equivalent to ALD for the deposition of hybrid organic–inorganic thin films. The features and the relevance of low-temperature processes are discussed in Chapter 6. Chapter 7 describes the plasma-enhanced ALD.

The second part of the book (Chapter 8) starts with the applications of ALD in microelectronics; these are without any doubt the reasons why ALD became so popular nowadays. Chapter 9 introduces area-selective ALD and shows how it can be used for the formation of nanopatterns. Chapters 10, 11, and 14 describe the coatings of high aspect ratio nanostructures, nanoparticles and nanowires, and carbon nanotubes. Chapters 12 and 13 describe the coatings of soft materials such as polymers and biological materials. Chapter 15 describes the coating of

nanostructures for optical applications such as opals. Chapter 16 describes the fabrication and properties of multilayers or nanolaminates. Finally, Chapter 17 discusses the challenges ALD is currently facing and possible novel directions and applications.

The book is structured in such a way to fit both the need of the expert reader (due to the systematic presentation of the results at the forefront of the technique and their applications) and the ones of students and newcomers to the field (through the first part detailing the basic aspects of the technique).

Halle, Germany
December 21, 2010

Dr. Mato Knez
Prof. Dr. Nicola Pinna

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Introduction: Basic Features and Historical Development of Atomic Layer Deposition

Jaakko Niinistö and Lauri Niinistö

1 Introduction

Atomic layer deposition (ALD) has gained wide interest as an advanced thin film growth technique for various applications in modern technology. The strength of the method relies on its unique growth process where alternate, self-limiting surface reactions of the precursors, separated by inert gas purging, form a growth cycle whereupon thin, up to one atomic layer of material is grown. Precise thickness control can be achieved by repeating the growth cycle a desired number of times. The unique growth mode leads to perfectly conformal films [1–4].

The ALD technology was developed and patented almost 40 years ago in Finland by Suntola and coworkers [5]. The goal in the early development of the ALD technology was strictly application-oriented, namely, the need to develop flat panel displays for mass production. However, the breakthrough of the technology was driven by the semiconductor industry some 10 years ago and industrial applications for ALD are now emerging.

This chapter describes briefly the basic principles of the ALD method, including the benefits and limitations. As it is quite interesting to understand how the ALD technology has evolved over the years, a short historical perspective to ALD technology is also given. In addition, we try to emphasize the development of the ALD community, and novel processes and applications studied by a large number of research groups in industry and academia. Especially, answer is sought for the question: Which research areas of ALD were in main focus in the past and which seem to be emerging in the future?

2 Basic Features of ALD

ALD processes and their possible as well as industrial applications have been reviewed numerous times in the past and even very extensive reviews have been published. [1, 6, 7] ALD is a special variant of the well-known chemical vapor

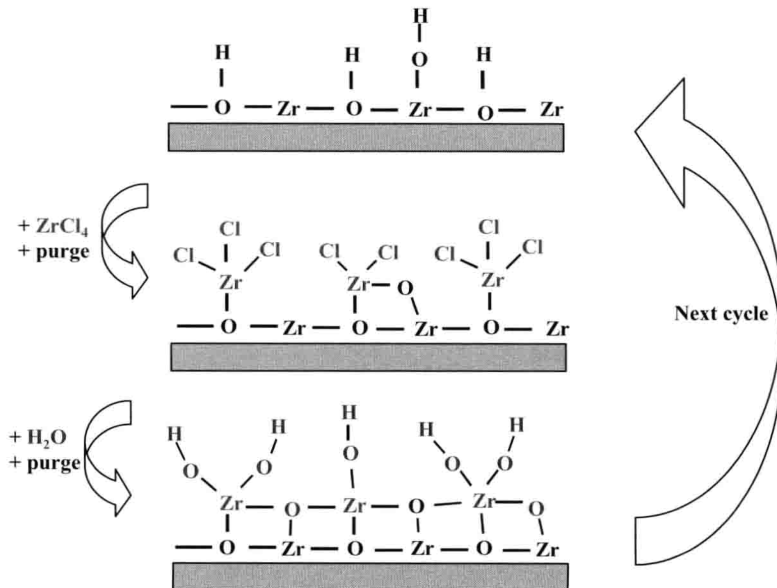

Figure 1 Sketch of a typical ALD growth cycle leading to ZrO_2 from $ZrCl_4$ and H_2O precursors. Reproduced with permission from ref. [3].

deposition (CVD) method. However, the differences between ALD and CVD are obvious. Whereas in CVD the precursors react at the same time on the surface or in the gas phase and precursors can decompose, in ALD the highly reactive precursors react separately by saturating surface reactions without self-decomposition. The method is surface controlled rather than process parameter controlled as in the case of CVD. In ALD the growth process proceeds in a cyclic manner and can be described as follows (exemplified with Figure 1).

An ideal ALD growth cycle is characterized by

- exposure of substrate surface to pulse of the first gaseous precursor;
- chemisorption of the first precursor onto the substrate;
- inert gas purge;
- introduction of the second precursor;
- surface reaction to produce the thin film;
- inert gas purge to remove gaseous reaction by-products.

In order to achieve a surface saturative ALD-type process, the growth rate has to be independent of the precursor dose provided that the dose is sufficiently large so that all the available surface sites have been occupied (Figure 2a). In other words, the precursor decomposition leading to a CVD-type growth mode should be avoided.

Often, but not always, a region with a constant deposition rate, also known as ALD window, is observed [2, 8, 9]. The ALD window certainly is not a requirement for an ALD-type growth mode, but it is a desirable feature that leads to the reproducibility of the film growth. Especially, if a ternary material is to be deposited, overlapping ALD

windows of the constituent binary processes offer a good starting point for the development of a ternary process. The observed growth rates *vs.* temperature in ALD processes are shown in Figure 2b.

2.1 Limitations and Benefits of ALD

Compared to CVD, the deposition rate in ALD is rather low: An ALD cycle requires some time, typically few seconds, and the resulting thickness after one cycle is ideally one monolayer but in practice, due to steric effects, only a distinct factor of a monolayer. On the other hand, in modern technology the required film thickness is often from a couple of nanometers up to few tens of nanometers, thus the low growth rate is not seen as severe problem any more. In addition, large batch processing is a rather straightforward way to increase throughput [10].

Another limitation often considered is the limited materials selection, that is, the available materials that can be grown effectively by ALD. Several technologically interesting materials such as Si, Ge, Cu, multicomponent oxide superconductors, and many transition metals are lacking effective and production-worthy processes. However, the list of available processes [1, 6] is expanding continuously and process development through precursor chemistry is increasingly studied by many research groups, in academia and the chemical industry. In addition, with plasma processing the materials selection is likely to be increased [11].

During the recent years, many research groups have been studying growth characteristics during the early stages of growth in order to understand the growth mechanism and to better control the growth process (Figure 2). In many cases, poor nucleation has been observed that can lead to rough surfaces and in the case of many metals a discontinuous film when the thickness is only couple of nanometers. Also, in the case of high-*k* dielectric growth on bare silicon can suffer from inhibited growth and it can be difficult to obtain a sharp interface without a mixed interfacial layer between the material and the Si substrate [12, 13]. Such process-specific deviations are not characteristic to the method itself, but rather the precursor

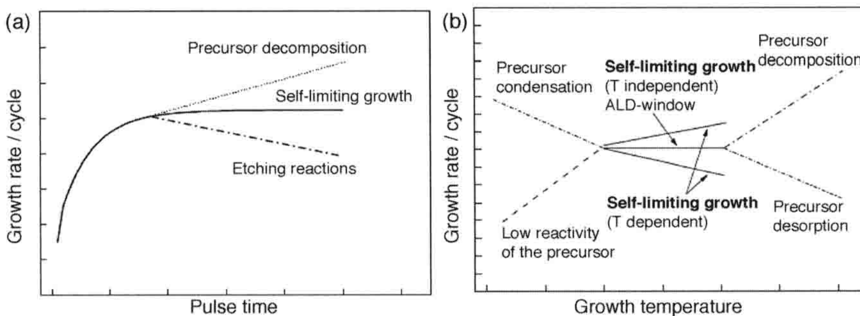

Figure 2 Growth per cycle as a function of the pulse time (a) and temperature (b) for different growth modes.

chemistry should be considered as one of the reasons. Other deviations related to precursor chemistry include reactive by-products that could etch the growing film or readsorb on the surface. Even small partial decomposition of the precursor can change the growth mechanism substantially. However, it should be noted that some applications can tolerate some of these deviations and "an ideal ALD growth" is not always needed.

The list of advantages of ALD is long. The characteristic feature of ALD, the self-limiting growth mode, leads to a precise control of the film thickness, a large area capability, and uniformity also in batch processes as well as to a good reproducibility. The excellent conformality is the main feature that distinguishes ALD from other thin film deposition methods and possible applications related to that are numerous. Separate dosing of highly reactive precursors allows production of high-quality materials (e.g., pinhole-free materials) at relatively low temperatures. The growth temperatures can often be reduced using, for example, plasma-generated radicals. Further benefits include the possibility to produce multilayer structures and the straightforward doping.

2.2
The Impact of Precursor Chemistry

As noted previously, a successful ALD process relies on the underlying chemistry. The alternately introduced precursors undergo saturative surface reactions. Thermal decomposition of the applied precursor destroys this self-limiting growth mode and thus the thermal stability of the precursor is the key issue in the ALD process. Naturally, being a vapor-phase method, ALD requires sufficient volatility of the precursors. Fast and complete reactions are mandatory; first of all, precursors must adsorb or react with the surface sites and these intermediates must be reactive toward the other precursor, for example, H_2O in the case of many oxide processes. To maintain film uniformity, precursor molecules or reaction by-products should not etch the growing film.

In general, volatile metal-containing ALD precursors can be divided into five categories: elements (only Zn and Cd), halides, oxygen-coordinated precursors (alkoxides and beta-diketonates), true organometallics (carbon-coordinated precursors, such as alkyls and cyclopentadienyls), and nitrogen-coordinated precursors (alkylamides, silylamides, and acetamidinates). For nonmetal precursors, hydrides are most widely used. Many successful oxide processes apply water as an oxygen source. Usually O_2 is found too inert in thermal ALD but it is used as a radical source in plasma-enhanced ALD and, for example, in growth of noble metals. Ozone has gained increasing interest as a powerful oxygen source and some industrial oxide processes rely on the use of ozone. The other most commonly used nonmetal precursors include H_2 and NH_3, also as a radical source. For sulfide film growth, H_2S should be mentioned.

As the precursor chemistry is extremely important factor in ALD processing, more detailed description on different aspects is given elsewhere in this book.

3 Short History of the ALD Technology

The purpose of the development of ALD technology in the 1970s by T. Suntola and coworkers was to meet the needs of producing improved thin films and structures based thereupon for thin film electroluminescent (TFEL) flat panel displays. The first Finnish patent application was filed in November 1974 and the first US patent was granted in 1977 [5]. The name of the technology then was named by T. Suntola as atomic layer epitaxy (ALE). The word epitaxy can be translated as "on arrangement" and thus Dr. Suntola used this broad definition even though usually ALD is used to grow nonepitaxial films. Until the end of the twentieth century, the method was mostly called ALE, which was not universally accepted because mostly polycrystalline and amorphous films are deposited rather than single crystalline growth on single crystalline substrate. Other names were used as well, for example, atomic layer CVD. For the past 15 years, the term ALD became generally accepted.

The above-mentioned patents showed the basis of reactor and process technology of ALD. It should be noted that in Russia, V. Aleskowski and others had published papers in Russian language about "molecular layering," describing alternate surface reactions characteristic to ALD. This work has been reviewed extensively by R. Puurunen earlier [6]. Here we focus on the development of ALD technology, especially reactor and process development for various applications.

3.1 ALD Reactor Development

The strength of T. Suntola's work inventing the ALD technology is clearly based on the development of feasible reactors for the processing. The aim of the first patent by Suntola and Antson was to describe a method for producing compound thin films using pure elements as reactants. The reactor configuration is shown in Fig. 3. In a rotating substrate reactor, the substrates are moved from one precursor flux to another and thus high-speed valving of pulses is not needed. This kind of concept is getting more interest again when roll-to-roll ALD or spatial ALD reactors are being developed.

Usually ALD reactors are based on valving the precursors and purges into the reaction chamber. Pulsing of the precursors separately, especially if the precursor has high vapor pressure, is simple with pneumatic or solenoid valves. Thus, it is possible to use CVD reactors as ALD reactors and many ALD reactor configurations are modified pulsed CVD reactors. The development of an inert gas valving system in early 1980s can be considered as a breakthrough for introducing low-pressure precursors. This invention led to the introduction of first commercial ALD research-scale reactors few years later. The reaction chamber and thus ALD reactors can be roughly divided into cross-flow (traveling-wave) or perpendicular-flow (e.g., showerhead) type reactors. The benefit of the cross-flow reactor is the higher throughput, and both precursor pulsing and inert gas purging are fast. However, the film thickness uniformity can be difficult to control, as CVD-type growth components may be present. Thus, careful optimization of the gas flow dynamics

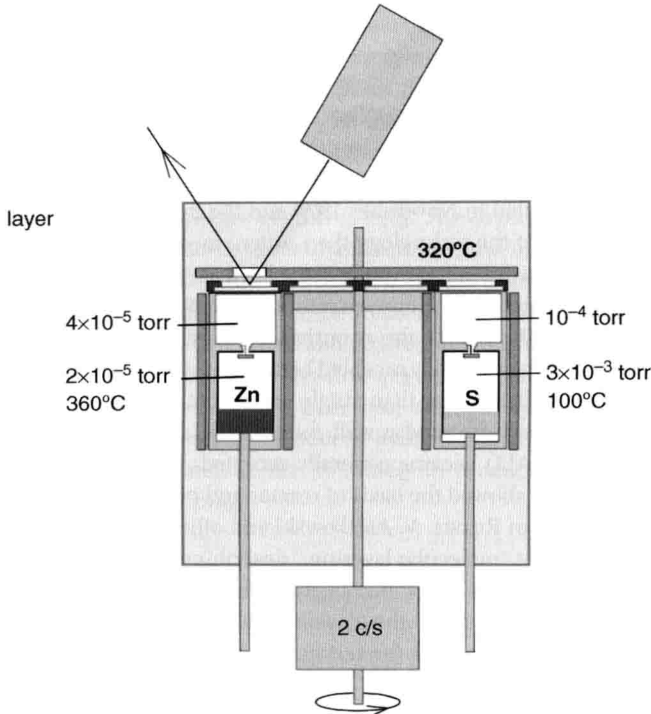

Figure 3 An early reactor configuration. Courtesy of Tuomo Suntola.

is needed. Batch reactors were introduced in the 1990s to overcome the major limitation of ALD technology, the low throughput. Currently, large batch reactors are used for various applications in volume production [14]. Carefully optimizing the configuration with multiple flow channels, it is possible even to reach nearly as fast cycle times as in single-wafer systems.

As the plasma became popular giving additional energy in CVD processing, the first reports of plasma-enhanced ALD became available in the late 1990s [15]. Many reactor manufacturers are introducing their PEALD reactors into the market. Using remote hydrogen plasma, for example, can overcome some problems related to ALD of transition metals. It should be noted that the PEALD techniques can be roughly divided to two categories, direct and remote PEALD. Among those, remote PEALD has gained wider interest, as mainly radicals are reaching the growing film during plasma exposure and ion bombardment can be avoided.

3.2
The Early Years – ALE

As mentioned earlier, TFEL displays were the key issue when inventing ALD technology. The research in ALE (the definition used originally) was focused on

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