Chemical Vapor Deposition

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Essay

A Short History of Atomic Layer Deposition: Tuomo Suntola's Atomic Layer Epitaxy**

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Atomic layer deposition (ALD) is a thin film growth technique based on the repeated use of separate, saturating gas-solid reactions. The principle of ALD has been discovered twice; in the 1960s under the name "molecular layering" in the Soviet Union, and in the 1970s under the name "atomic layer epitaxy" (ALE) in Finland. In 2014, it is forty years since the filing of the worldwide patent on ALE as a method for the growth of compound thin films. This essay celebrates the fortieth anniversary of ALE-ALD, briefly telling the story of ALE as shared by its Finnish inventor, Dr. Tuomo Suntola. Initially, ALE was aimed at the growth of high-quality polycrystalline ZnS thin films for electroluminescent (EL) display panels. Gradually, the material selection of ALE increased, and the application areas were extended to photovoltaics, catalysis, semiconductor devices, and beyond. Fast, production-worthy ALE reactors were imperative for industrial success. The unprejudiced creation of new technologies and products with ALE, initiated by Dr. Tuomo Suntola and led by him until early 1998, are an integral part of the Finnish industrial history, the fruits of which are seen today in numerous applications worldwide.

Keywords: ALD, ALE, EL displays, History, ZnS

1. Introduction

ALD is a thin film growth method which belongs to the general class of CVD techniques, and which has become of worldwide importance. During the past decades, tremendous growth has been seen in the materials made by ALD,[1,2] applications,[3,4] and commercially available ALD equipment.[5] One of the key drivers for the success of ALD has been the microelectronics industry, which relies heavily on ALD for the down-scaling of device dimensions.[6] The growth is also seen in the rising number of attendants at international ALD conferences.[7]

ALD has been invented independently twice.[1,8–11] The more commonly acknowledged origin of ALD dates back to the "atomic layer epitaxy" technique originally developed for electroluminescent (EL) flat panel displays in Finland, starting in the 1970s.[8,12] The other origin is the "molecular layering" (ML) technique, initiated in the Soviet Union in the 1960s.[9,13] Over a hundred review articles have been published on ALD (see, e.g.,[1] and [2] and the references therein), nevertheless, the early days of ALD and the invention itself have not been adequately described in histories or scientific articles (neither ML nor ALE). For example: How did the concept develop in the inventor's mind? Which were the surrounding and conditions in which the invention was made? Was the invention a pure accident or was it the result of a more systematic approach? Regarding ML, the inventors, Prof. Aleskovskii and Prof. Kolt'sov, cannot now share their story with the rest of us and we have to rely on secondary sources.[13,14]

Regarding ALE, it is in 2014, forty years since the invention and since the first patent. The inventor, Dr. Tuomo Suntola, has recently shared his view on the early days in a presentation.[12] Through further getting answers to my numerous questions in private discussions, and also to questions that I did not know to ask, I have written up, in close collaboration with Suntola, this essay-formed history, which describes the historical development of ALD/ALE from one central viewpoint, from an inventor's viewpoint.

This work is focused on the historical developments of the ALE technique. It is about the invention, the birth of technology, and the success in industry. This is work made in the industry where the most significant demonstrations of

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[**] The author thanks Tuomo Suntola for sharing these and other details of the development of ALE and EL. It has been a great honor and privilege to work with him and to write this history. Writing this history was triggered by the parallel-running worldwide Virtual Project on the History of ALD (VPHA). Warmest thanks to Tuomo Suntola for his support for the VPHA, too. The author also acknowledges Tapio Alvesalo for checking the details related to NAPS, Dr. Marko Tuominen for the details related to ASM Microchemistry, Juhana Kostamo for the details related to Picosun, Prof. Victor Drozd for confirming the timing of Suntola's visit to Leningrad, Prof. Yukihiro Shimogaki and Prof. Markku Leskelä for identifying the second-left participant in the ALE-1 photograph, and Prof. David Cameron for polishing the language in this article. Funding by the Academy of Finland's Centre of Excellence in Atomic Layer Deposition (ALDCoE) is gratefully acknowledged.

success have not been scientific publications, but products. The significant material breakthroughs that there were, are indicated in the text, but typically there are no publications to cite, Suntola himself has been the source of the information. There have been many challenges in the way of ALE-EL development, and the great majority of them have not been related materials, but to ALE reactor design and to engineering aspects of the displays. This is by no means a covering review on the ALD/ALE field; for more comprehensive overviews on the scientific and materials aspects, other sources are recommended.[1,2,15–17]

The text is organized roughly as follows: Suntola's background and the environment in which the invention of ALE was made, are described first. Second comes the actual invention (1974) and the development of reactor prototypes, thin film EL display demonstrators, and production-worthy reactors. Suntola's stepping aside from EL business (1987) is described, and the initiation of Microchemistry Ltd., first with research on solar applications and catalysis, and soon with a focus on the commercialization of the ALE technology. To highlight the spreading of ALD research worldwide, an overview is given of worldwide ALE/ALD research by the year 1990. The moment of connection between ALE and ML is pointed out. A few less-known episodes related to the development of ALE are also shared. Finally, the new activities of Suntola after he stepped aside from an active role in ALD are described.

Originally, the story was written for the exhibition "40 Years of ALD in Finland – Photos, Stories",[18] as the essay celebrates the fortieth anniversary of ALD in Finland. General ALD history activities continue through the worldwide open voluntary effort called the Virtual Project on the History of ALD (VPHA).[19]

2. Background of the Invention

Tuomo Suntola was born in 1943 in Tampere, Finland. He went to school in Turku, Finland, and completed his Matriculation examinations (nation-wide examinations, which qualify to university studies) in 1962.

In 1963, Suntola started his studies on electrical engineering at Helsinki University of Technology (HUT-Teknillinen korkeakoulu, TKK, nowadays Aalto University). In 1967, he completed his Master's thesis ("diplomityö" in Finnish) on Schottky diodes for radar detectors (metal-semiconductor diodes for microwave frequencies).[20]

In the late 1960s, picosecond "Ovonic" switches, using amorphous chalcogenide compound thin films, were a hot research topic. Being an assistant teacher at HUT, Suntola proposed to Prof. Thor Stubb to investigate the picosecond switches more closely. Prof. Stubb gave him the green light for this study. After a few years thorough experimental and theoretical work, Suntola was able to find out the mechanism behind the switching phenomenon. Prof. Stubb saw that the solution was worth a doctoral thesis. (In short, the mechanism which was found is that the current concentrates into a thin filament, where the temperature rises above 700 °C, which makes the material highly conductive. For once a real postulate was defended in the thesis: one cannot expect wide technical use of the amorphous switches.) In a rapid schedule, Tuomo Suntola finished a licentiate's thesis[21] and a doctoral thesis[22] on the topic. In December 1971, Tuomo Suntola at the age of 28, became the youngest Doctor of Science in Technology from the Electrical Engineering department by that time.

In the early 1970s, semiconductor research was still young in Finland. VTT Semiconductor Laboratory had been established in 1964 as an integral part of Professor Thor Stubb's Electron Physics laboratory in the HUT. In the autumn of 1971, the Semiconductor Laboratory received its first industrial order, a task to develop a miniature solid-state humidity sensor for Vaisala Oy, a Finnish company specializing in meteorological instrumentation. Prof. Stubb assigned the challenge to Suntola a few months before Suntola had finished his thesis. To get off to a quick start, his colleague Tapio Wiik was assigned to make a pre-study on the state of the art in humidity sensing.

According to the pre-study, the most promising solutions demonstrated were capacitive devices made of porous aluminum oxide thin films or polymer foils. Suntola started to work on polymers; instead of using foils, he dissolved the polymer material and created a thin film on a solid substrate by vaporizing the solvent. The thin polymer film approach turned out to be successful and, with Jorma Antson, he completed the development by the end of 1973. Vaisala's instruments using the Humicap® sensor, based on the original patent by Suntola,[23] are still (2014) the world market leaders in humidity measurements (Fig. 1).

Since the late 1960s, beside his main work on technology, Suntola has been interested in the basis of physics, including antique metaphysics, eastern philosophy, and the philosophy of science in general. Suntola was also an active lecturer for INSKO, Insinöörijärjestöjen Koulutuskeskus, giving lectures on, for example, display technologies. All these, and especially the very successful humidity sensor, turned out to have an important impact on Suntola's later career.

3. 1974 - Initiation of the EL Development and the Invention of ALE

Late in 1973, Suntola was contacted by the top management of Instrumentarium Oy. At that time, Instrumentarium, originally a trading house importing medical instrumentation, was looking for possibilities for making their own products. They had established a small technology company, Datex Oy, that had introduced a novel bed-scale for weighing dialysis patients and a CO_2/CO meter for anesthesia control. When the key technical team of Datex left the company in late 1973, Suntola was invited to establish a research group directly under the management of Instrumentarium – with an open request to "suggest and find out something". Such an

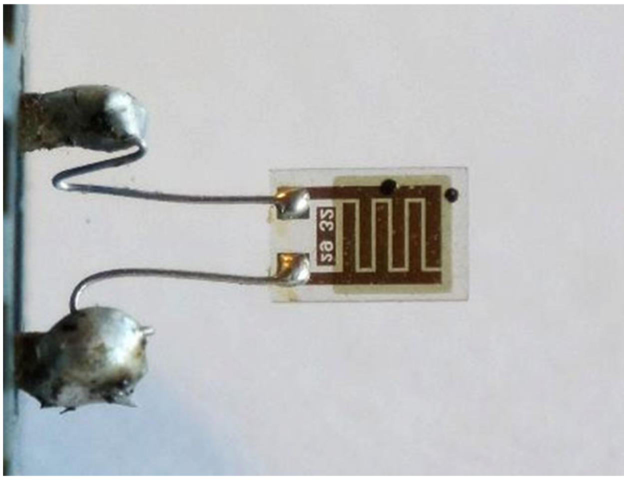

Fig. 1. A prototype of the Humicap® humidity sensor from 1973. The sensor was fully functional after 41 years when photographed in 2014 by Suntola. Published with permission of Tuomo Suntola (private collection).

unprejudiced suggestion was inspired by the success of the humidity sensor, already known to some industrialists.

In the beginning of 1974, Suntola and the small humidity sensor team moved from VTT to Instrumentarium (Ahertajantie 3, Tapiola, Espoo, Finland). First, Suntola made a market need/technology mapping study. The outcome from the mapping was that, in the interest area of Instrumentarium, sensor technologies are diversified into small unities, which makes it difficult to build a technology platform on such a basis. At the other end of an instrument the human interface, typically a display, is common to most instruments. There was an urgent need for flat panel displays which fit, e.g., in the beds of the patients and in small hospital rooms.

Suntola's proposal to Instrumentarium's management was to start working for two goals, for ion-selective sensors, and for flat panel displays. That was quite abstract for the management, and the CEO's comment after Suntola's presentation was: "I am still confused, but at a higher level" (in English, indeed). Anyway, Suntola got the approval to go on. Jorma Antson started the study on sensors and Suntola directed himself to solve the flat panel objectives.

A literature study on the state of the art in flat panel displays showed that EL had been tried in many ways, with limited success. Suntola concluded that successful manufacturing of thin film EL devices cannot be solved with conventional thin film technologies such as sputtering or vacuum evaporation. Based on his prior experience with amorphous thin films, Suntola reasoned that to get controlled properties, one has to have a well-controlled crystal structure in the thin films. To obtain a controlled material structure, "deposition", or material transfer, may not be sufficient – in principle, what is needed is to create conditions for the controlled build-up of the material layer.

The actual invention of ALE matured in early June 1974. Suntola describes it as follows: "We had still an empty laboratory with just tables and chairs and a Periodic Table of the Elements hanging on the wall. Looking at the Periodic Table, and thinking of the overall symmetry in nature, to me came the idea of "serving" the complementary elements of a compound sequentially, one at a time, onto a surface. Monoatomic layers may be obtained if the complementary elements make a stronger bond with each other than they do with their own kind of atoms".

Suntola decided to proceed in this direction. Once the basic idea of supplying elements to the surface in an alternated, cyclic manner had been conceived, active planning started. From the kinetic theory of gases, Suntola calculated the pressures and temperatures needed for the growth of zinc sulfide, the light-emitting material in a thin film EL display. He designed the equipment for testing the growth hypothesis applying standard vacuum components; a 12" T-piece formed the chamber – installations were built on the flanges on the top and the bottom of the T-piece. The

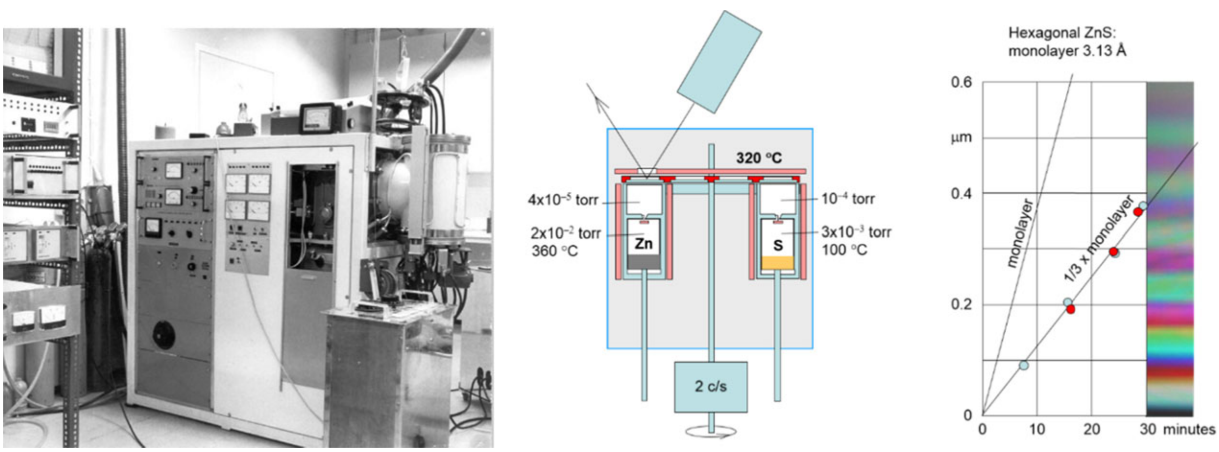

Fig. 2. Left: The ALE reactor was built in the T piece on right of the pumping unit. Middle: It consisted of a rotating carousel holding the substrates, and the sources for the reactants. Windows in the top flange allowed observation of the interference color of the film building up in the course of the process. Right: By comparing the color to an interference color map the increase in thickness could be monitored during the process. Photo and schemes from Suntola's collections; published with permission of Tuomo Suntola (private collection).

design was completed in June 1974 and the drawings were sent to the in-house mechanical workshop (Fig. 2).

The equipment operated under a low pressure of about 10^{-6} Torr. The sources for elemental Zn and S, reasonably isolated from the vacuum environment, were heated to obtain the desired vapor pressures. The equipment can be classified as a hybrid ALE-PVD system. Due to its low vapor pressure, the Mn dopant was added by evaporation from an open source. (The option of evaporation and sputtering was long retained in the high-vacuum reactors for "partial ALE" of oxides.) The first reactor had a window in the top flange, which facilitated following the development of the thickness during the process by observing interference colors on the glass substrate.

The first growth experiments were made in August-September 1974. Cycle time in the rotating carousel reactor was 2 cycles s^{-1}. The very first experiment was successful; a film was observed to grow – not, however at the expected rate, one monolayer in a cycle, but only a third of a monolayer in a cycle. It took quite some time before it was understood how the surface rearrangement accounted for the less-than-monolayer growth.

The films were analyzed by X-ray diffraction (XRD) at Helsinki University of Technology, and first of course, by look and feel. The first impression was that the films were mechanically harder than films made by conventional methods (evaporation or sputtering). The X-ray studies showed that the ALE-grown ZnS film had a hexagonal crystalline structure, in contrast to evaporated or sputtered ZnS films that had a cubic crystalline structure. It was also noticed that the films were hydrophobic; a water droplet rolled on them. (Interestingly, the films made later from $ZnCl_2/H_2S$ were, in contrast, hydrophilic, a water droplet did not roll on them.)

Early ZnS(Mn) samples showed faint EL light with direct DC excitation. The level of Mn doping was $0.1 - 1.0\%$. The indium tin oxide transparent electrodes were made in the carousel reactor by "semi-ALE" by sputtering the metal components.

Tuomo Suntola decided to call the new growth technology "atomic layer epitaxy". Epitaxy originates from Greek, and means on-arrangement. It was meant to emphasize the surface control feature of the process – to make a distinction with traditional source-controlled deposition methods such as evaporation and sputtering.

The ALE invention was protected by an international patent.[8] The priority date of the patent comes from the Finnish application, filed on November 29, 1974. The patent was applied for, and granted, in more than twenty countries, including the United States, Japan, and the Soviet Union. In the study of the prior art, the closest reference found was a German patent from the mid-1950 s, describing vacuum evaporation of compound materials from the components of the compound in a carousel system, much like ALE in the first reactor. The essential feature of ALE, the saturation of the surface reactions was not, however, claimed in the patent.

Hearings related to the patent were organized in several countries, including the United States, Japan, and the Soviet Union. The patent hearing in Moscow in 1977 or 1978 Suntola describes as memorable. Suntola went there alone. Two local attorneys, well acquainted with the application, assisted him to defend the work. The hearing took about two hours. The discussion was mainly focused on the generality and broadness of the claims. No critical prior art, neither from the USSR nor from other countries, was presented by the examiners. The patent was granted as applied.

In hindsight, in 2014, Tuomo Suntola concludes that the 1974 patent was successfully formulated; it covered the basic ALE concept well. In fact, no infringements were reported during the whole lifetime of the patent. Suntola thinks that the main reason for that was that ALE was regarded as too slow and complex for any practical use. The first patent focused on ALE from elemental reactants, however the option of using compound reactants (H_2S) was mentioned, which slightly limited the formulation of the second important patent applied in early 1979.[24]

4. Steps Toward Practical Processing of EL Displays

The performance of the early EL demos made with high-vacuum reactors was far from sufficient. Also, it became obvious that a high-vacuum system would not be production-worthy; the source had to be in line-of-sight to the substrate, and up-scaling would be limited. Also, the use of chemically aggressive materials, possibly needed in full-ALE oxides in a high vacuum reactor, was dubious. The ALE process itself was encouraging, but it was understood that there was still a long way to go. It was realized that the basic work needed had limited motivation in the small research team in a medical instrumentation trading company. In 1978, the ALE-EL project, with the personnel and the facility, was sold to the building material company Lohja Oy. Lohja had recently started the production of TV sets and was looking for opportunities for further growth in electronics.

The transfer to Lohja allowed a substantial increase in the resources for the development. One of the new tasks triggered was a study of the possible replacement of the high-vacuum equipment with more compact flow-type reactors allowing the use of volatile reactants and a batch-type arrangement of the substrates, effectively utilizing the self-control feature of ALE.

Suntola recalls that the decision to switch from elemental reactants to compound reactants was not easy. "We did not have the necessary understanding of the chemistry, also, we did not have experience in working with aggressive chemicals such as chlorides and H_2S." First, a simple, glass tube reactor was constructed for the experiments. The very first experiment for a chloride process was tried by combining $ZnCl_2$ and elemental S, then by adding H_2 flow over the heated sulfur source. The experiments were not successful.

An abrupt change occurred when a H_2S gas bottle was acquired and coupled to the reactor thus enabling the real $ZnCl_2 + H_2S$ process. In the memorable first $ZnCl_2 + H_2S$ run the walls of the reactor tube were evenly covered with a strictly uniform film – with a "starting profile" essentially steeper than in the ZnS processes based on elemental reactants – thus telling about the high reactivity of the reactants.

In the famous picture (Fig. 3), Sven Lindfors is sitting next to the glass tube ALD reactor used for the successful demonstration of the $ZnCl_2/H_2S$ process. What is missing in the picture is Arto Pakkala and his first reaction to the success: "That's it!" ("Siinä se on!" in Finnish.) Pakkala was right; the ALE-EL development was immediately switched to chloride processes, and to the design of a new generation of inert gas reactor.

The chloride processes for the ZnS and the dielectrics allowed the build-up of the whole EL structure, dielectric/ZnS(Mn)/dielectric, in one process. The proper choice of chlorides allowed the running of the process at a constant temperature. The temperature limits, however, were tight – the upper limit was set by the soda glass used as the substrate and the lower limit by the vapor pressure of the manganese chloride. Sodium diffusion from the substrate was stopped by an ALE-grown Al_2O_3 diffusion barrier.

In the high-vacuum reactors, the separation of the ALE sequences was based on the motion of the substrates between the fixed sources. In an inert gas reactor there was a need for high-speed valves capable of valving aggressive gases for thousands of times at the source temperatures. The chemically inert high-speed valving problem was solved by inert gas valving based on controllable blocking and transporting of the inert gas flows between the sources and the reaction chamber. The new reactors allowed uninterrupted processing of the whole EL structure comprising the stack of the first dielectric layer/the zinc sulfide(Mn) layer/the second dielectric layer. The production capability of the inert gas reactor was based on batch processing and the inherent self-control feature of ALE. Processing of a full EL structure was typically an overnight process without human oversight in the facility. A batch of 20–30 pieces of 100 mm × 200 mm substrates was stacked back-to-back in a reaction chamber of only a few liters.

The inert gas reactor and the basic processes for the ALE-produced EL displays were protected by the 2nd international ALE patent,[24] with the priority date Feb 28, 1979 of the Finnish application. Also, the ALE dielectric layers are documented in the patent.

The dielectric strength of the ALE dielectrics, above $4\,MV\,cm^{-1}$ (nowadays close to $10\,MV\,cm^{-1}$), was observed to be far better than ever reported for conventionally produced thin films. In fact, it turned out that the role of ALE was even more important for the properties of the dielectrics than for the light-emitting ZnS(Mn) layer in the EL display.

ALE-produced EL displays showed outstanding electrical and optical characteristics. The high dielectric strength of the dielectrics, with an intrinsic pinhole-free feature, allowed effective excitation of the light-emitting ZnS(Mn) layer. Due to the hexagonal crystalline structure of the ALE-produced ZnS, the color of the light emitted was a beautiful yellow; it was less orange than the EL devices based on sputtered ZnS with a cubic crystalline structure. The fully transparent structure allowed a black background layer resulting in an outstanding contrast even in bright ambient light. Figure 4 shows reactors used for early ALE-produced EL prototypes.

Later, the single oxide dielectrics were replaced by multilayer oxides such as an aluminum-titanium oxide nanolaminate (ATO). In the ATO, the evolution of crystallinity in the TiO_2 layer is interrupted by amorphous Al_2O_3 films. In the flow reactor, the doping of the ZnS layer

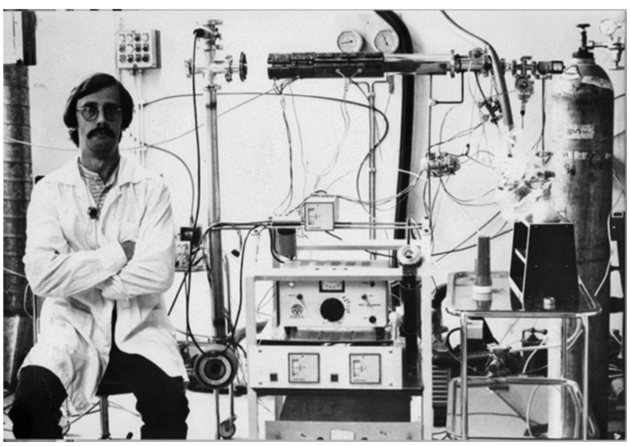

Fig. 3. Sven Lindfors in 1978 next to the flow-type ALD reactor in which the successful $H_2S/ZnCl_2$ process was demonstrated. Photo from Suntola's collections; published with permission of Tuomo Suntola (private collection).

Fig. 4. Arto Pakkala operates reactors used for early ALE-EL prototypes. Photo from Suntola's collections; published with permission of Tuomo Suntola (private collection).

Chemical Vapor Deposition

with manganese was carried out by supplying manganese chloride with every 50th zinc chloride pulse.

5. 1980 - The First Public Disclosure of a Thin Film (TF)-EL Display

In the 1970s, the ALE-EL development was carried out in strict confidence – until the first disclosure at the Society for Information Display (SID) conference in San Diego, California, in April 29 to May 1, 1980 (Fig. 5).[25] There were about 1000 people present. The presentation of the revolutionary EL display was given by an unknown person (Suntola), coming from an unknown country (Finland). In addition to the overhead slides, Suntola had an EL demonstration box with him. The demo had such a high contrast that the EL light was well visible to the audience even in the bright projector light. The presentation was a great success – Suntola had not realized before this, how much their EL technology was ahead of all the competitors.

After the SID presentation, Lohja Oy got about 3000 to 4000 requests for products. Two persons were hired to go through the requests. "What a tragedy, wasted marketing", says Suntola – "we had neither the production line constructed nor the product developed". The demand for flat panel displays, however, was confirmed.

6. Commercialization of ALE-EL

In 1983, the pilot production of TF-EL displays started in Lohja, the Kunnarla plant (Kaivurinkatu 5, Lohja, Finland).

The first real proof-of-concept of the ALE-EL displays was the large information boards installed in the departure hall at Helsinki-Vantaa airport in 1983.

Final testing of the alternatives for dielectric layers in the thin film structure – Al_2O_3, ATO (aluminum–titanium oxide nano-laminate) or Ta_2O_5 – was carried out in a prototype board installed in an underground cave under the airport (Fig. 6). Test modules with ATO dielectrics showed the best performance and reliability. In fact, the reliability of the panels turned out to be outstanding; in the final installations in the departure halls, the large information boards were running continuously for 15 years, day and night, without a single character module being replaced.

Year 1983 was financially favorable for Lohja. Also, there was much EL enthusiasm in the air. The same year, the Finnish government offered remarkable tax reductions for production investments completed by summer 1984. Lohja utilized the opportunity, and a large EL production facility with high-level cleanrooms was built in Espoo, Olarinluoma. The schedule was extremely challenging, but the building (Fig. 7) was finished on time.

The schedule for the construction of the production machines and the final development of the main product, a data display module with integrated high-voltage drivers, was at least as challenging as the new building. The production of the data modules started gradually in the Olarinluoma facility in 1985, and distribution channels were opened in the USA and in some other major industrialized countries (Fig. 8). Lohja's electronics activities were reorganized from a research unit to a business unit. The Display Electronics division got an experienced business-oriented manager, Antti Piippo, who was invited to Lohja from Aspo Oy. Suntola continued as the Chief Scientist with a mandate to look for new application areas for the ALE technology.

In the mid-1980s in Finland, the technologically unique achievement had created wide publicity for the EL project which, together with the big investments into the development and production, had piled up enormous expectations

Fig. 5. SID representative and Tuomo Suntola and his key colleagues, (from left to right) Jorma Antson, Sven Lindfors, and Arto Pakkala, who received the 1980 SID Outstanding Paper Award for the EL work. The Award was handed to the group at the following year SID conference in 1981. Photo from Suntola's collections; published with permission of Tuomo Suntola (private collection).

Fig. 6. Dr. Ralf Graeffe inspects the display modules in the test assembly in Helsinki-Vantaa airport underground cave in 1983. Photo from Suntola's collections; published with permission of Tuomo Suntola (private collection).

Fig. 7. Picture: Olarinluoma plant in 2014, photographed by Tuomo Suntola. EL production continues, operated by Beneq Oy since 2012. Published with permission of Tuomo Suntola (private collection).

Fig. 8. Tuomo Suntola (right) and Ulf Ström, the managing director of Finlux Inc., responsible for marketing the ALE-EL panels in the USA. Photo from Suntola's collections; published with permission of Tuomo Suntola (private collection).

and pressures on its commercial success. Following Sharp in Japan and Planar in the US, Lohja became the third EL manufacturer in the world. Lohja's product was superior, but the start-up of the production in Olarinluoma was delayed, and the growth of the EL business was slower than expected.

In 1990, Lohja's EL business was sold to its American competitor, Planar Inc. The Finnish EL activity, Planar International, became a subsidiary of the US Planar. ALE showed its superiority in the manufacturing of the EL panels; in a few years all EL production of Planar was concentrated in the Olarinluoma plant. Gradually, other flat panel display technologies, first of all liquid crystal technology supplemented with thin film transistor active matrix, took over from the EL technology which suffered from the high driving voltage, about 200 VAC, and the lack of full color capability. EL displays remained a specialized device for demanding environments such as extreme temperatures or exposure to high mechanical shocks. In 2012, Planar's EL plant in Olarinluoma was acquired by Beneq Oy, who continue the production of the ALE-EL panels as the only commercial manufacturer in the world (2014).

The major developments made on the driving circuitries and the associated manufacturing technology for the EL panels under Ahti Aintila had created unique knowhow and experience, such as advanced fine-line printed circuit board technology (Fig. 9a) and tape automated bonding (TAB) of integrated circuits (Fig. 9b). After leaving Lohja microelectronics division in late 1984, Ahti Aintila worked for several companies developing further microelectronics production technologies. In 1991, Aintila established Picopack Oy for producing smart cards and other products utilizing the TAB technology.

When EL manufacturing was sold to Planar Inc. in 1990, the microelectronics division of Lohja was separated as an independent company, Elcoteq Oy. Antti Piippo and his closest colleagues bought Elcoteq in 1991. Elcoteq was an important contract manufacturer, e.g., to Nokia during the fast growth of the mobile phone markets. The structural changes in the electronics industry led to the bankruptcy of Elcoteq in 2011.

7. 1987–1998 Microchemistry Ltd.

In the mid-1980s, the national oil company Neste Oy had established a corporate venture unit, Neste Advanced Power Systems (NAPS), to study and develop business possibilities

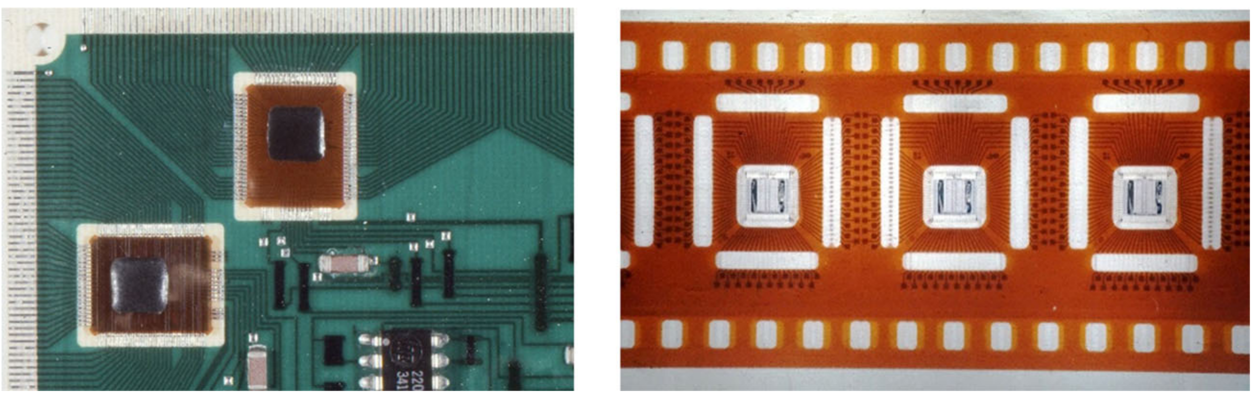

Fig. 9. A corner of the EL panel circuit board with high voltage IC drivers (left) and the film carrying the ICs to be bonded (right). Images from Suntola's collections; published with permission of Tuomo Suntola (private collection).

in the emerging field of renewable energy solutions. Based on the success of ALE in the EL technology in Lohja, the head of the venture team, Tapio Alvesalo, saw the technological potential of applying ALE for the manufacturing of thin film solar panels, and suggested research activity on this topic at Neste. In 1987, Tuomo Suntola was offered the chance to set up Microchemistry Ltd, as a subsidiary of Neste, for the development of ALE-based solar panels. Suntola also saw the possibility of applying ALE to heterogeneous catalysis, which complemented the objectives decided for the new research unit.

After a pre-study, the ALD solar panel research was directed towards cells based on CdTe thin films. Lohja's EL production reactors were considered too big and slow for effective solar cell research. As the first task in Microchemistry, Tuomo Suntola and Sven Lindfors designed a quick, compact research reactor for photovoltaic (PV) development. The outcome was the F-120 reactor which also became the first commercial ALD reactor. The F-120 (Fig. 10) was optimized for fast cycling and easy operation and maintenance.

The work on CdTe thin film cells brought with it a lot of expertise and insight into PVs, i.e., not only in CdTe cells but more broadly in PV technologies and renewable energy systems in general. In 1990, NAPS acquired a factory in France producing solar panels based on amorphous silicon (a-Si) thin films. Microchemistry got the challenge of working on the development of the production process and the improvement of the low conversion efficiency (3 to 4%) of the a-Si panels. Some improvement in the initial efficiencies of the panels was obtained. It turned out, however, that the increase in the efficiency was lost over six months use of the panel. A useful improvement, however, was the reaction injection molding techniques used for encapsulating the a-Si modules. As the market segment of a-Si panels remained very limited, NAPS withdrew from the French factory and the a-Si technology in 1997.

Fig. 10. The F-120 reactor. The heavy bars on each side of the reactor were meant to let the researcher lean and ponder while looking at the progress of the process. Photo from Suntola's collections; published with permission of Tuomo Suntola (private collection).

The top achievement in the ALE-CdTe cell development in Microchemistry was a test cell with 14% conversion efficiency, which in the early 1990s was among the highest efficiencies reported for thin film cells. The advantage of ALE on the CdTe cell, however, was marginal over the less expensive, robust technologies, and therefore a decision was made not to enter into production scale with ALE-CdTe cells.

One of the successful side paths in the PV research in Microchemistry was the development of new testing techniques for the PV panels. Jaakko Hyvärinen constructed a fast and handy solar simulator that measured the *I-V* characteristics of the panel in response to a single flash of a xenon lamp. The method and the equipment turned out to be a success; after the PV activity in Microchemistry and NAPS, Jaakko Hyvärinen established Endeas Oy to produce and sell the "Quicksun" simulators.

The work on ALE catalysts brought highly desired chemistry expertise into Microchemistry. Aimo Rautiainen and Eeva-Liisa Lakomaa were the first chemists in the team. Several ALD catalysts were successfully demonstrated and, importantly, the work had a major impact on the understanding of the surface chemistry in the ALE process. Several doctoral dissertations were produced: Marina Lindblad (1992), Suvi Haukka (1993), Arla Kytökivi (1997). Co-operation with the experienced catalyst researchers in Neste Central Research laboratories was initially hampered by the barrier between traditional methods and the novel ALE approach, which turned thinking from moles to molecules. Once the initial suspicions about ALE were overcome, the co-operation became very fruitful and ALE also served as an effective tool for studying the catalytic surfaces at the atomic level.

8. Microchemistry Focuses on ALE

When Microchemistry Ltd. was established in 1987, the ownership was divided between Neste and Lohja as 80%/20%. Lohja's ALE patents were licensed to Microchemistry for PV and catalyst applications only. When Lohja's EL activity was sold to Planar in 1990, Neste bought Lohja's share of Microchemistry, and soon the ALE license was extended to cover the manufacturing and sales of ALE reactors and the ALE technology for any use not covered by Lohja's EL patents.

Suntola had seen the large potential of ALE from the very beginning of the invention, especially in semiconductor manufacturing. The knowhow in the ALE process and the reactors, not disclosed in the patents, had been kept strictly confidential throughout the development and commercialization of the EL technology. The new situation offered Microchemistry the possibility to start working on ALE and the reactors for new applications.

As a first step, the F-120 was offered for research purposes. Next step was the design of the F-450 reactor which enabled processing of silicon wafers, and glass substrates up to 450 mm × 450 mm size. Samples of 8" silicon wafers with aluminum oxide layer were processed in an F-450 prototype, and computer-generated pictures of the commercial version were produced for a product brochure and a full-size exhibition booth wall. The new product was covered with a new patent portfolio, now assigned to Microchemistry.

Since the SID conference in 1980,[25] and from numerous other conferences and meetings, Suntola had contacts with key people in the display and semiconductor fields. Thanks to the confidence acquired with ALE-EL Suntola was offered the possibility of a visible introduction of ALE in the MRS 1994 Annual Meeting in Boston.[26] The talk "ALE for Semiconductor Applications" was complemented by Microchemistry's ALE booth (Fig. 11) in the exhibition held parallel to the conference.

The Boston MRS presentation demonstrated the excellent uniformity and conformal coating characteristics of ALE technology (Fig. 12). Based on the measurements of the refractive index, the high density of the Al_2O_3 films was also introduced. Actual 8" wafers were shown at the exhibition booth.

Gradually, major semiconductor manufacturers and equipment manufacturers became interested in the technology. The uniformity, conformal coating, and the highly repeatable material characteristics obtained with ALE were more and more acknowledged and appreciated. There were still doubts about the production efficiency of the process. The main doubts, however, were cast over the unknown equipment manufacturer from an unknown country. When a representative of a major semiconductor manufacturer expressed their interest in the ALE reactor, he stated that, in general, they do not do business with companies with the annual turnover less than 100 million dollars.

Fig. 11. Microchemistry's ALE booth at the MRS 1994 Annual Meeting in Boston. In the picture (left) Heli Vaara, assistant to (right) Tuomo Suntola. Photo from Suntola's collections; published with permission of Tuomo Suntola (private collection).

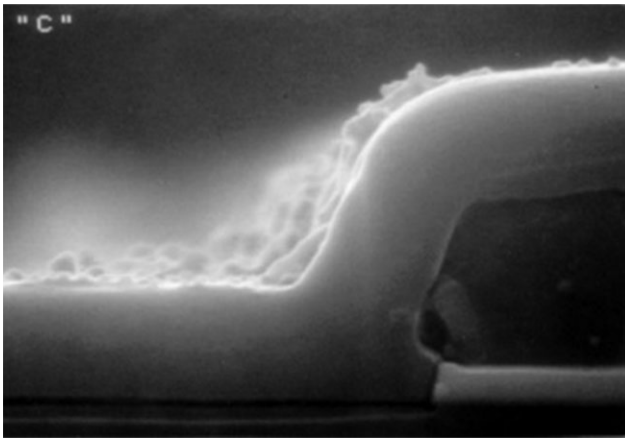

Fig. 12. Demonstration of the conformality of the ALE-produced Al_2O_3 passivation layer at the edge of a contact pad in an integrated circuit. From Tuomo Suntola's slides at Boston MRS 1994; published with permission of Tuomo Suntola (private collection).

The introduction of ALE technology and the Microchemistry reactors was continued in several exhibitions in the US, Europe, and Japan. In addition, samples were delivered and Suntola gave presentations in many universities and research institutes. Gradually, ALE became a subject in materials research conferences, and specific ALE conferences were organized. The increased activity generated new demonstrations of the special material properties obtained by ALE.

Obviously, ALE reactors and business with semiconductor manufacturers could not be considered as a natural business area in an oil company. This was also realized by the real actors in the field; Microchemistry was approached by several major semiconductor equipment manufacturers with proposals of co-operation or acquisition.

In 1997, as a part of a larger rearrangement in Neste Oy, Microchemistry was devoted to ALE technology and the reactor business only, and the PV and catalyst research activities were taken under Neste's Central Research. Suntola was offered a Research Fellow's position in Neste, and a business-oriented managing director, Matti Ervasti, was invited to take care of Microchemistry and the further ALE business development.

At that time there was already a clear indication of the commercial potential of ALE. Microchemistry had sales representatives in the US, Japan, and South Korea, and several reactors had been delivered to customers. The most

Fig. 13. ALD reactor F-1000 by Microchemistry Ltd. for coating big batches of 500 mm × 500 mm substrates. Photo from Suntola's collections; published with permission of Tuomo Suntola (private collection).

impressive contract consisted of several large ALE reactors capable of handling big batches of 500 mm × 500 mm substrates (Fig. 13).

The original name of the process, atomic layer epitaxy, met continuous resistance among semiconductor people who had devoted the term epitaxy to meaning single crystal growth only. The practical choice was to accept the reality and change the process name to atomic layer deposition (ALD).

In 1999, Microchemistry with all its personnel, ALE expertise, and the patent portfolio was sold to the Dutch company ASM. The ALE activity continued as ASM Microchemistry in Finland. After a few years, ASM moved the ALE reactor manufacturing to their plant in Phoenix, Arizona. ASM's activity in Finland was focused on ALE research, at present in a close connection with the Inorganic Chemistry Laboratory of the University of Helsinki. As a consequence, highly experienced reactor designers were freed. Sven Lindfors, the closest co-worker to Suntola in ALE reactor design since 1975, set up Picosun Oy with Kustaa Poutiainen in 2004. In 2005, Beneq Oy was founded, and Pekka Soininen started the ALE reactor activity in the company.

9. Spread of ALE by Year 1990

9.1. ALE in Japan

After the successful SID conference, Suntola was invited to give a presentation on ALE at the International Conference on Vapor Growth and Epitaxy 5, in San Diego, California in 1981.[27] The presentation was not a big success; there was very little scientific information available on the ALE-grown material. Furthermore, the use of the term "epitaxy" for non-single-crystal thin films offended the "silicon guys" in the audience.

An outcome from the 1981 San Diego conference, however, was that the seeds were laid for ALE research in Japan. Professor Jun-ichi Nishizawa from Japan was among the participants, and he realized the significance of ALE. Nishizawa started to investigate the possibility of ALE growth of GaAs in his laboratory in Japan. Professor Nishizawa initially renamed ALE as "Molecular Layer Epitaxy" (MLE), thereby making a distinction with Suntola's original work. Ten years later he admitted that it was one and the same technique.

Nishizawa introduced his MLE-grown GaAs at the 16th International Conference on Solid State Devices and Materials, in Kobe, Japan, 1984. Suntola was invited to give a general talk on ALE at the conference.[28] The conference was successful, Suntola gave the talk to a room overfull of people. Japanese TV was also present, and Suntola was interviewed about ALE.

Suntola recalls that the Japanese group III-V materials activity in the mid-1980s was the most visible research effort on ALE. One of the most impressive demonstrations, introduced by Nippon Electric Company (NEC), was the InGaP-GaAs-InGaP superlattice, where the GaAs layer is obtained by applying 11 ALE cycles (Fig. 14).

According to Suntola, most of the Japanese works on the group III-V materials were carried out in ultra-high vacuum MBE equipment modified to operate in the ALE mode. In some experiments laser irradiation was used to enhance the process.

9.2. ALE in the USA

In the 1980s, Professor Bedair and his group in North Carolina State University demonstrated the ALE of GaAs

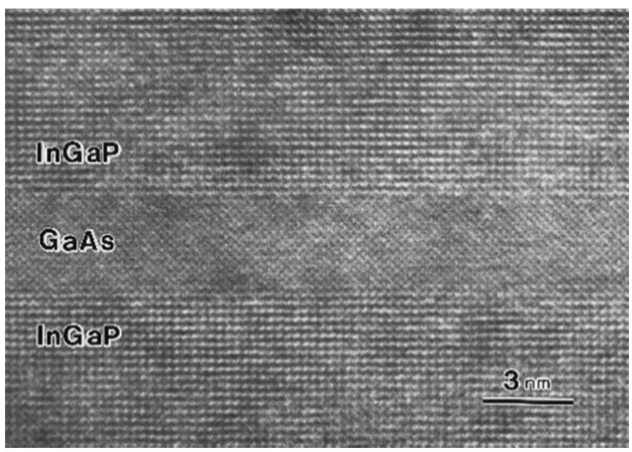

Fig. 14. InGaP-GaAs-InGaP superlattice by NEC, where the GaAs layer is obtained by applying 11 ALE cycles (the center layer in the picture). Picture from Suntola's collections; published with permission of Akira Usui and Tuomo Suntola (private collection).

in a CVD system, where sequencing of the reactants was obtained with a fast rotating disk. Prof. DenBaars and his group in the University of Southern California, Los Angeles, demonstrated the ALD of GaAs in an atmospheric metal-organic (MO)CVD system.

9.3. First ALE Conferences in Finland

In 1984, the first specific ALE conference, the "First Symposium on Atomic Layer Epitaxy",[29] was organized in Espoo, Finland, by VTT Semiconductor Laboratory upon the initiation by Professor Lauri Niinistö. In the late 1970s, Suntola had contacted Lauri Niinistö, the professor of inorganic and analytical chemistry at HUT, asking for scientific consultation on ALE chemistry and luminescent materials. The challenge was well received by Prof. Niinistö, and a fruitful, long-lasting co-operation was started.

The preface of the proceedings of the First Symposium on Atomic Layer Epitaxy states:

> "This proceedings contains the invited papers presented at the First Symposium on Atomic Layer Epitaxy, held on December 13-14, 1984 in Espoo. Most of the papers have been devoted to this novel growth method. Related growth techniques, methods of layer characterization and potential applications account for the rest of the content. The contributions represent the growing number of research groups active in this area in Finland…". [30]

The first International Symposium on Atomic Layer Epitaxy was held in Espoo, June 11–13, 1990.[30] The conference chair was Professor Lauri Niinistö (Fig. 15).

Fig. 15. Participants at the ALE-1 conference dinner in Herttoniemi, Helsinki, restaurant Vanha Mylly: Ms. Erja Nykänen, HUT; Dr. Yoshinobu Aoyagi, RIKEN; Dr. Tuomo Suntola, Microchemistry Ltd.; Prof. Lauri Niinistö, HUT; Prof. Jun-ichi Nishizawa, Semiconductor Laboratory, Sendai; Prof. Salah Bedair, North Carolina State University. Photo from Suntola's collections; published with permission of Tuomo Suntola (private collection).

9.4. ALE in Otaniemi (Espoo), Helsinki, and Joensuu, Finland

The strict confidentiality regarding the ALE reactors and the process knowhow resulted in severe limitations to the co-operation with universities. The first reactor supplied to the HUT in the early 1980s, to Professor Niinistö's laboratory, was placed in a locked room accessible only to authorized operators and researchers, however this early co-operation served as the start for extensive ALE activity in HUT and a seed to the presently vital ALE activities headed by Professors Markku Leskelä and Mikko Ritala, as the Finnish Centre of Excellence in Atomic Layer Deposition, in the Laboratory of Inorganic Chemistry in the University of Helsinki.

ALE activities were also initiated in the Semiconductor Laboratory of VTT Technical Research Centre of Finland in mid-1980s. Initial focus was on group III-V materials.

Theoretical work on ALE was free of the limitations created by the confidentiality of the technology. Fruitful co-operation with Professor Tapani Pakkanen in the University of Joensuu (Finland) resulted in a quantum chemical analysis of the ZnS growth, finally completed by Marina Lindblad in her doctoral thesis in Microchemistry Ltd., in 1992.

9.5. Early ALE in Tampere, Finland

In 1973, before Suntola had started the work leading to ALE and EL, he was invited to give lectures on semiconductor physics in Tampere University of Technology (TUT). Suntola was nominated as a docent in TUT, and he continued to give the lectures every second Friday for a couple of years. In 1975, after the early results in the EL project, Suntola encouraged the small TUT group to work on ALE of the group III-V semiconductors. The challenge was taken by M. Ahonen, who at that time was a graduate student. In 1978, Markus Pessa was nominated as the professor of physics in TUT. He took care of the lectures on semiconductor physics and directed a vital research activity on the group III-V materials, using the conventional MBE technology. Pessa's work led to effective GaAs laser technology and successful industrial activities in optoelectronics.

9.6. Pioneering Work in the Soviet Union

When Suntola, for his 1989 review paper,[16] mapped known laboratories working on ALE, there was no information on the Soviet group that had been studying "molecular layering". In 1990 at the ALE-1 conference,[30] Dr. Victor Drozd invited Suntola to visit the University of Leningrad (at present St. Petersburg) to meet Prof. Aleskovskii. Suntola travelled to Leningrad in August 1990, where Aleskovskii presented his works dealing with oxide

Chemical Vapor Deposition

layer build-up based on saturated surface reactions, just as in the ALE process. The discussion confirmed that the essence of ALE had been independently discovered by the Aleskovskii group. Suntola was impressed by the deep understanding of the surface chemistry related to the molecular layer build-up. Samples or applications using molecular layering were not shown, neither was the equipment used for the experimentation.

10. Little-known Episodes of ALE Research

There are many "episodes" in the ALE-EL development that have remained more or less unknown.

ALE became limitedly known after Suntola's first public conference presentations. Among some experts in conventional thin film technologies, ALE technology was seen as weird and most probably useless. A German professor, a well-known thin film expert, sent a letter to Suntola, where he proved, based on his experiments, that the ALE mechanism is impossible. At this time, ALE-EL displays were already in pilot production, so Suntola did not respond. Later, when Suntola met the professor at a conference, the doubts were settled.

In the early 1980s, the ALE-EL technology was licensed to France. First contacts were made at the SID conference in 1980. The big French state-owned company CGE became interested and contacted Lohja in order to discuss a license for the technology. The discussions led to an agreement, and an ALE-EL license was granted in 1983 (now to Sintra Alcatel due to local arrangements between French state-owned companies). An ALE reactor capable of handling 450 mm $\times$ 450 mm substrates was delivered to France as part of the license arrangement.

Suntola tells that Lohja had a high-level meeting in New York with a big American semiconductor manufacturer in 1982. Lohja offered the company an ALE license for semiconductor applications, possibly to be used for thin gate electrodes and for passivation layers. The advantages of ALE were told to be excellent thickness uniformity, controllable dielectric constant, extremely high dielectric strength, and the conformal coating characteristic, already proven with the EL devices. It turned out that the advantages of ALE were not understood; the then existing technologies were seen to fulfill the needs. In the early 1980s this was certainly true. The time was not yet right for ALE.

It is interesting to know that, in addition to the EL patents, Suntola also had a patent on Liquid Crystal Displays (LCDs).[31] The patent "Method for generating electronically controllable color elements and color display based on the method", which was applied for in 1985 and granted in 1990, was meant to guarantee a technology for full color display in the case that full colors are not achieved with the EL. Suntola's concern about the color limitation with the EL became true (three-color displays with red, green, and yellow were achieved by filtering the wide-band yellow emission of ZnS(Mn), but full-color displays with blue remained unsuccessful), but the sequential color concept in Suntola's patent has not yet been taken into use.

11. Epilogue

When handing Microchemistry Ltd. over to his successor, Matti Ervasti, in the beginning of 1998, Suntola left behind his active role in ALE, now renamed as ALD. Seeds had been sown, and the technology had matured ready for success.

As a research fellow in Neste, now in Fortum Oyj, after the fusion of the state oil company Neste and the electric utility company IVO, Suntola worked for long-term research and global energy issues, with the main emphasis on renewable energies. He was a member of the World Energy Council, and served as the attorney of Fortum Foundation until part-time retirement in 2000, and full retirement in the beginning of 2004. In the same year, Suntola joined Picosun Oy, first as the scientific adviser and, since 2007, as a board member.

The year 2004 brought a delightful surprise to Suntola in the form of the European SEMI Award 2004 *"Honoring the Pioneer in Atomic Layer Deposition Techniques … that paved the way for the development of nanoscale semiconductor devices"*. The Award was handed to Suntola at the Munich Electronics Show 2004 (Fig. 16). The founders of Picosun Oy, Sven Lindfors and Kustaa Poutiainen, accompanied Suntola to Munich to participate in the Award Ceremony. When receiving the award, Suntola expressed his acknowledgements to his many co-workers with whom he shares the honor brought by the Award. Also, he saw the Award as recognition of the importance of the often invisible

Fig. 16. The European SEMI Award was awarded to Suntola (right) at the Munich Electronics Show 2004 by Stanley Myers, the President & CEO of SEMI (USA) (left). Photo from Suntola's collections; published with permission of Tuomo Suntola.

long-span efforts behind the progress of science and technology.

In the biography on his www-page[32] Suntola states: "*Considerations of the philosophy of science and the foundations of physics have been a source of inspiration throughout my career, both in technological developments and the search of a holistic view of physical reality*".

Since the mid-1990s, with early roots extending to the late 1960s, Suntola has worked on a holistic picture of reality published in 2011 in the book "The Dynamic Universe – toward a unified picture of physical reality". [33] For linking his philosophical and theoretical considerations to the historical development, he worked on the book "The Short History of Science – or the long path to the union of metaphysics and empiricism", published in 2012.[34]

As of 2014, Suntola continues as a board member of Picosun Oy, the chairman of the Physics Foundations Society, and a board member and a frequent lecturer in the Finnish Society for Natural Philosophy.

Suntola reminds us that the success of ALE-ALD development became possible through the contribution of many highly competent and motivated people, and he wishes to express his gratitude to all of them — equally to those mentioned by name in this history, and to the large majority not mentioned. "*It looks like our long run led rather to a start than to a completion – I am deeply impressed by the huge advance that has followed in the ALD technology and the scope of its applications*".

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