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CONTRIBUTING AUTHORS

<i>Thomas C. Arnoldussen</i>	<i>R. M. Osgood</i>
<i>E. Baer</i>	<i>C. J. Raub</i>
<i>J. J. Cassidy</i>	<i>Allan Rosenzweig</i>
<i>S. R. Coriell</i>	<i>Eva-Maria Rossi</i>
<i>G. F. Fulop</i>	<i>Herbert Schäfer</i>
<i>E. R. Gertner</i>	<i>Carleton H. Seager</i>
<i>H. H. Gilgen</i>	<i>R. F. Seierha</i>
<i>P. Haasen</i>	<i>D. M. Smyth</i>
<i>A. Hiltner</i>	<i>J. Stuke</i>
<i>Jaakko Hyvärinen</i>	<i>Tuomo Suntola</i>
<i>Lynn W. Jelinski</i>	<i>J. C. Swearingen</i>
<i>H. R. Khan</i>	<i>R. M. Taylor</i>
<i>L. C. Klein</i>	<i>K. N. Tu</i>
<i>J. Lipkin</i>	<i>R. Wagner</i>
<i>T. C. Lowe</i>	<i>Peter Williams</i>
<i>Egon Matijević</i>	<i>Alex Zunger</i>
<i>G. B. McFadden</i>	



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Stanford University

JOSEPH A. GIORDMAINE, *Associate Editor*
Bell Laboratories

JOHN B. WACHTMAN, JR., *Associate Editor*
Rutgers University

ANNUAL REVIEWS INC. 4139 EL CAMINO WAY PALO ALTO, CALIFORNIA 94306 USA



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ATOMIC LAYER EPITAXY

Tuomo Suntola and Jaakko Hyvärinen

Lohja Corporation, Electronic Display Division, Post Office Box 46,
SF-02201 Espoo, Finland

INTRODUCTION

So far, methods of thin film production have been methods of material transfer, where a compound is transferred from the source onto the substrate through a vapor phase. Regardless of the realization of the vapor phase, whether by heat energy (in vacuum evaporation), plasma energy (in sputtering) or by use of chemical compounds (in CVD), the substrate occurrence is similar in all these methods. It is dominated by nucleation, which means that neighboring molecules energetically seek the most favorable position relative to one another, thus forming microcrystals that in later phases control thin film growth. Due to this formation of microcrystals the film, especially at the beginning of the growth, contains uncontrolled crystal boundaries whose average density can be considerably below that of a bulk crystal. Efforts are often made to improve this condition subsequently, by heat treatment intended to reduce the defect density in the crystal structure.

In the atomic layer epitaxy (ALE) method the compound thin film immediately achieves its final crystal form through sequential surface reactions in which one element of the compound at a time reacts with the growing surface. This method is a self-controlled process that automatically "accepts" only one atomic layer at a time. It utilizes the ion bond nature of the II-VI, III-V, and oxide-nitride compounds, which typically produce a compound bond stronger than the mutual bonds of the elements present.

In the semiconductor industry the word epitaxy is used to mean growth that repeats the substrate structure. However, the literal translation of the Greek roots of the word is "on arrangement." Thus, the word can also be used in a wider sense, here to include the method described below.

THE FIRST PROOF OF THE ALE MECHANISM

The first experiments with ALE were made in 1974. The equipment was a modified vacuum evaporation apparatus able to produce separate surface reactions between the reactants and substrates. The substrates were placed in a carousel that rotated over zinc and sulphur sources in turn (Figure 1). ZnS was selected as the material in the original experiments because from the very beginning the goal was to create a production process for electroluminescent devices. Figure 2 illustrates another type of ALE reactor, where separation of reaction steps is accomplished by gas flow over immobile substrates. The reactants are injected into the reaction chamber in turn, and following each reaction are purged away by the carrier gas flow. The workings of the ALE mechanism were verified by studying growth rate as a function of vapor amount in separate reaction steps. When the vapor amount was sufficient to produce monolayer coverage, growth was saturated and surplus material had no effect (Figures 1, 2).

To study the mechanism more scientifically, ordinary MBE equipment was modified to work according to the ALE principle by addition of a proper shutter and temperature control (Figure 3) (1). The equipment was incorporated into a multitechnic electronic spectrometer in order to study the film grown, and to verify ALE reaction phases using Auger measurements (2).

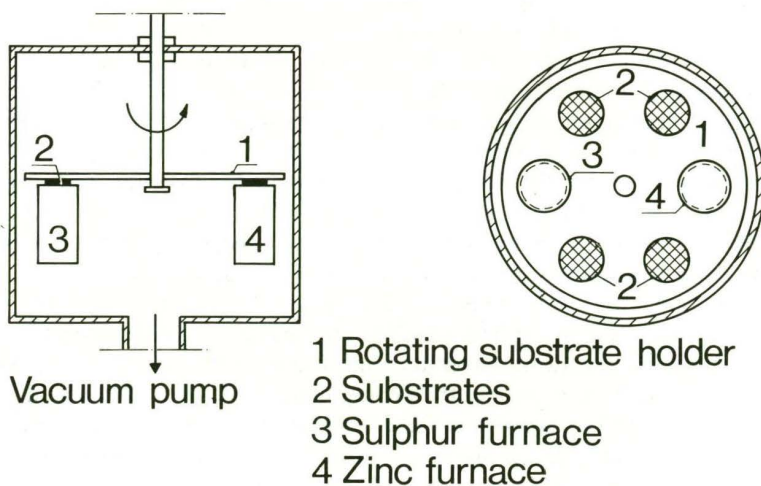


Figure 1 An early version of an evaporating ALE reactor used to grow ZnS. The separation of reaction steps is accomplished by the movement of substrates.

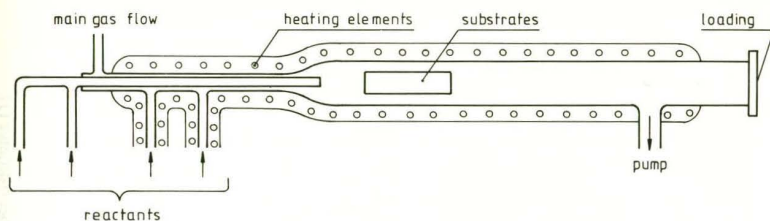


Figure 2 Schematic diagram of a gas flow-type ALE reactor.

The Auger spectra on the right in Figure 4 show that after ZnCl_2 exposure there is chloride on the surface (*lower figure*), which stays there until the surface is exposed to H_2S (*upper figure*). The spectrum on the left demonstrates that the final surface has no chloride atoms or other impurities. (The oxygen and boron peaks originate from the substrate.)

ALE PROCESS

In order to give a comprehensive description of the general features of the ALE process, it is convenient to study the ZnS ALE process as an example (3, 3a, 4).

The growth of ZnS with ALE is illustrated schematically in Figure 5. The growth from the two elements, Zn and S_x , is shown in Figure 5a. Figure 5b shows the thin film growth from the combination of the compounds ZnCl_2 and H_2S . The process path is the following: The substrate with oxygen atoms (glass or oxide thin film surface) is exposed to Zn (A1) or ZnCl_2 (B1) vapor, a bond is formed between Zn and O atoms, and extra Zn or ZnCl_2 is swept away. The Zn or ZnCl_2 surface is then exposed to S_x (A3) or H_2S (B3) vapor. The Zn-S bond ensures monoatomic S surface coverage. An exchange reaction releases chlorine from the surface in the form of HCl vapor, and delivers S to the Zn surface to form the monoatomic S surface layer. Then the process is repeated.

This process has certain exceptional features when compared to conventional thin film techniques: (a) the growth rate is not dependent on the rate of the reactions, provided that the dose in each reaction step is high enough to give full monolayer coverage. Accordingly, growth is uniform over large areas, and no thickness monitoring is needed because thickness is determined by the number of reaction steps. (b) The relatively high substrate temperature results in re-evaporation from the surface of any loosely bonded atoms. Together with the lack of vapor phase reactions, this results in highly stable and stoichiometric film. (c) Nucleation phenomena

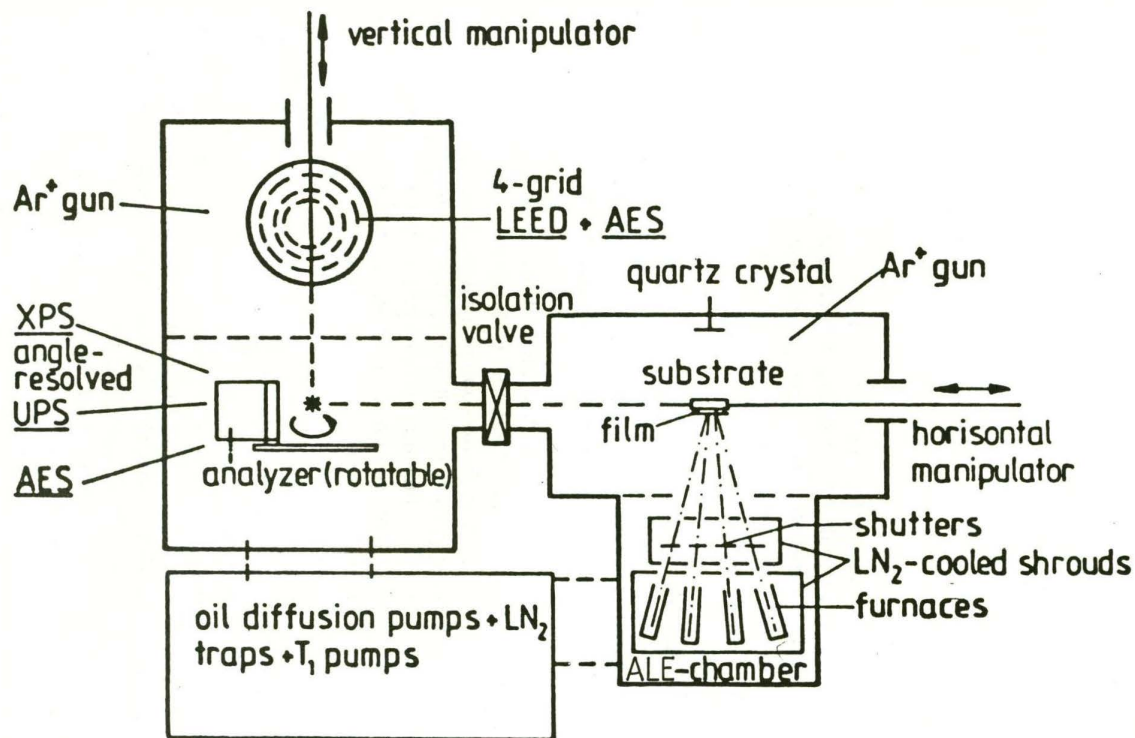


Figure 3 Schematic diagram of the modified MBE-ALE reactor, incorporated into a multitechnic electron spectrometer (1).

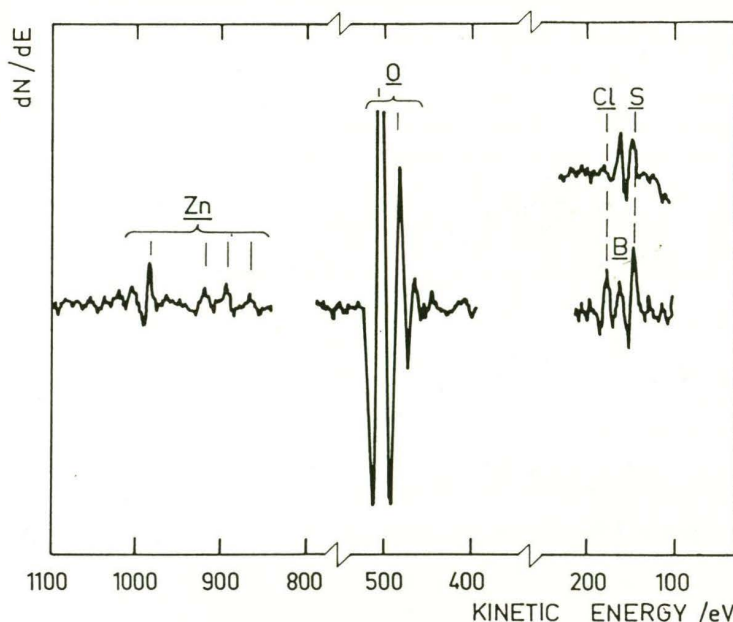


Figure 4 Auger electron spectra that show the surface exchange reactions that give rise to the growth of a ZnS film in ALE (2).

are apparently modified to allow only two-dimensional nucleation, ensuring very uniform layers even in ultra-thin structures. This is of high interest in making compound combinations, i.e. superlattices. Next, we discuss some details that affect the ALE ZnS process parameters.

Substrate

Because ALE was originally developed to produce electroluminescent (EL) displays, glass has been the major substrate material. Ordinary soda-lime glass limits the process temperature to a 500°C maximum, because higher temperatures cause alkali metal out-diffusion, and deformation of the material itself. The process temperature can be raised as high as 650°C if a higher quality substrate material, such as Corning 7059, is used.

Dosing of Reactants

The partial pressures of the reactants in the reaction chamber must be high enough to cause a monolayer to form in a reasonable length of time. If we assume the sticking coefficient is equal to one, and the surface state density

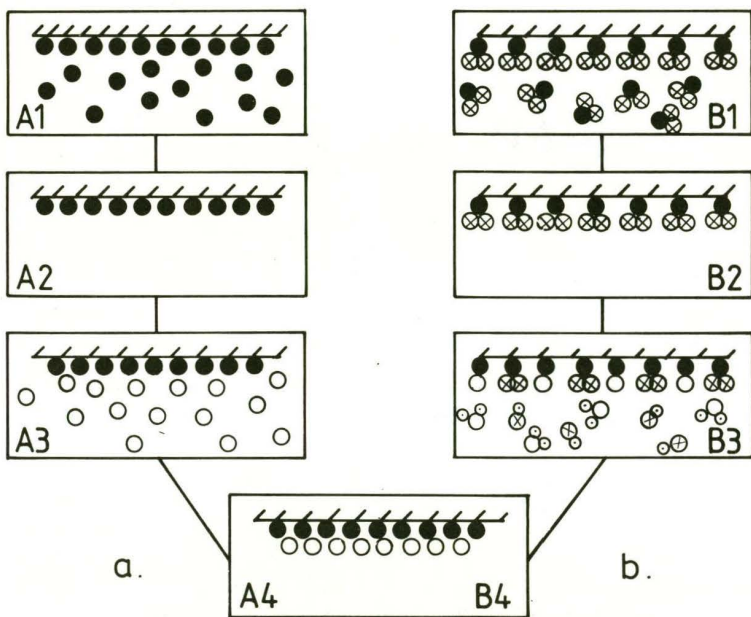


Figure 5 ALE sequences for ZnS when using (a) Zn and S_x, and (b) ZnCl₂ and H₂S as reactants.

is 10^{15} cm^{-2} , we can estimate that the minimum partial pressure for ZnCl₂ and Zn should be about 10^{-3} mbar, at 450°C. On the other hand, the partial pressure has to be considerably lower than the vapor pressure of the reactant at any given process temperature because even slight condensation of the reactant would ruin the growth mechanism. The vapor pressures of ZnCl₂ and Zn at 450°C are 3 mbar and 0.5 mbar, respectively. Those of H₂S and S are so high they need not be considered in this respect.

From the above information we can deduce that a suitable partial pressure range for a dose pulse of ZnCl₂ is 0.001–0.3 mbar, and 0.001–0.05 mbar for Zn. This is the most exceptional feature of ALE: The intensity of the reactant pulse can vary several decades without influencing the thin-film growth, as long as there is enough material for full coverage.

In the case of ZnS it is unimportant whether the compound ZnCl_2 or the element Zn is used as the reactant because their vapor pressures are quite close to each other. But Al_2O_3 , for example, cannot be grown from Al and O_2 at reasonable temperatures. However, when AlCl_3 and H_2O are used as reactants the temperature can vary between 200 and 600°C. ZnCl_2 and H_2S are also especially suitable reactants because they are not too expensive, reactive, or poisonous, all important practical properties.

Chemisorption of ZnCl_2

The chemisorption of ZnCl_2 by a ZnS surface is a complicated quantum chemical problem, and extensive calculations are required to get even qualitative information. This work is being done at the University of Joensuu, Finland, by Pakkanen with interesting preliminary results. The role of chemisorption in temperature dependence of growth rate is illustrated in Figure 6, in which it is assumed that condensation never happens.

When the temperature is below T_A only physisorption occurs, and the

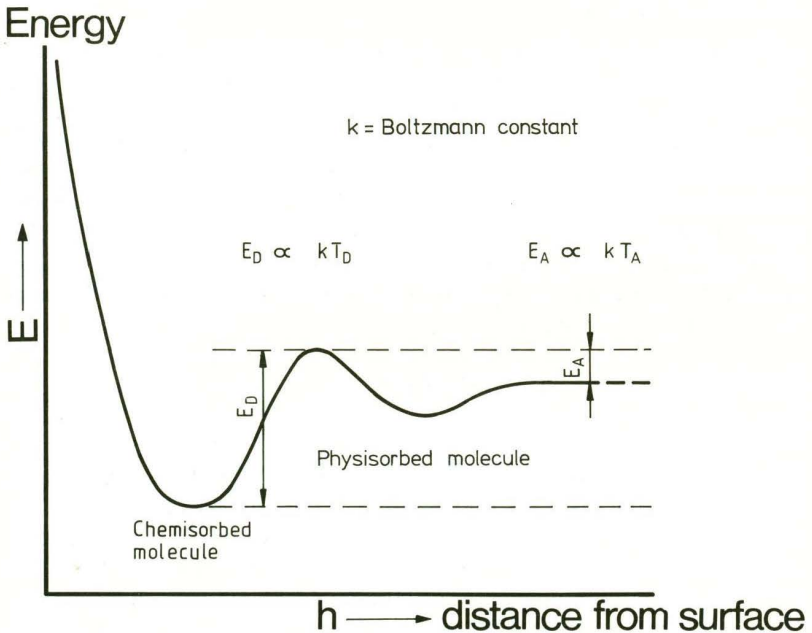


Figure 6 Potential energy for activated chemisorption with physical molecular adsorption.

growth rate is a very sensitive function of temperature and of the time between reactant pulses. In most cases, T_A has no practical meaning because the condensation temperature and the minimum partial pressure requirement preemptively fix the minimum process temperature.

The temperature range between T_A and T_D is the actual ALE growth range because between these levels the molecules can adsorb, but will not be desorbed from the surface. This temperature range is considerably narrower for a Zn surface than for a ZnCl_2 surface, as shown in growth rate experiments. The chlorine surface seems to reduce the vapor pressure of the chemisorbed layer, even though the bulk vapor pressure of ZnCl_2 is higher than that of Zn. When the temperature exceeds T_D , about 400°C for Zn and about 550°C for ZnCl_2 , the growth rate decreases and once again becomes a very sensitive function of temperature and time between reactant pulses.

Pakkanen's calculations for ZnCl_2 and hexagonal (002) ZnS surfaces indicate that the chemisorbed ZnCl_2 is stable at 450°C , and that bonds are formed between the S atoms of the surface and the Zn atoms of the ZnCl_2 molecules. The chlorine atoms protrude from the surface, occupying so much space that only one third of the S atoms are covered by ZnCl_2 molecules (this has also been verified by growth rate experiments).

Exchange Reaction

The reduction in free energy upon going from the reactants to the products is a necessary, but not a sufficient condition, which tells nothing about the reaction path, which is of primary importance in the study of ALE reaction steps. In order to gain further insight into the growth mechanism one must solve the wave functions of the surface and the reactants. Pakkanen has approached this problem, and has been able to qualitatively predict some reaction paths. It appears likely that the exchange reactions occur in cycles of three sequential surface reaction steps to form a full lattice unit. Gas-phase mass spectrometer analyses are being made in an attempt to distinguish the reaction steps.

MATERIALS MADE BY ALE

ZnS-Mn

The crystalline structure of ZnS film grown by ALE has been studied with X-ray diffraction (5–8) at the Helsinki University of Technology by Professors Tuomi and Tanninen. Figure 7 shows the X-ray diffraction patterns of ZnS-Mn films grown from ZnCl_2 and H_2S at (a) 350°C and (b) 500°C (5). In the diffraction pattern of the low temperature sample (a), there is a high diffuse background intensity and broad diffraction lines. In the high temperature pattern (b) the background intensity is relatively low and

the lines are narrow, which indicates a good crystalline structure. The line positions of the cubic 3C phase and hexagonal 2H phase are marked in parts (a) and (b) of Figure 7, respectively. The diffraction patterns indicate that the films grown at 500°C with ALE are mainly hexagonal. This is somewhat surprising because the cubic to hexagonal phase transition temperature has been reported as 960–1250°C. Even the thinnest samples were extremely well oriented, with the hexagonal *c*-axis perpendicular to the surface of the substrate. This tendency continues up to at least 500 nm, and is a beneficial feature from the standpoint of electroluminescence (EL) efficiency.

The substrate material also influences the texture of the thin film. The highest degree of orientation appears in films deposited onto a Ta₂O₅ buffer layer about 50 nm thick, grown on a glass substrate. A slightly crystalline SnO₂ buffer layer, on the other hand, lowers the degree of orientation. The mean grain diameter for a 400 nm thick ZnS-Mn layer is about 90 nm, according to X-ray analysis. It is interesting to compare these

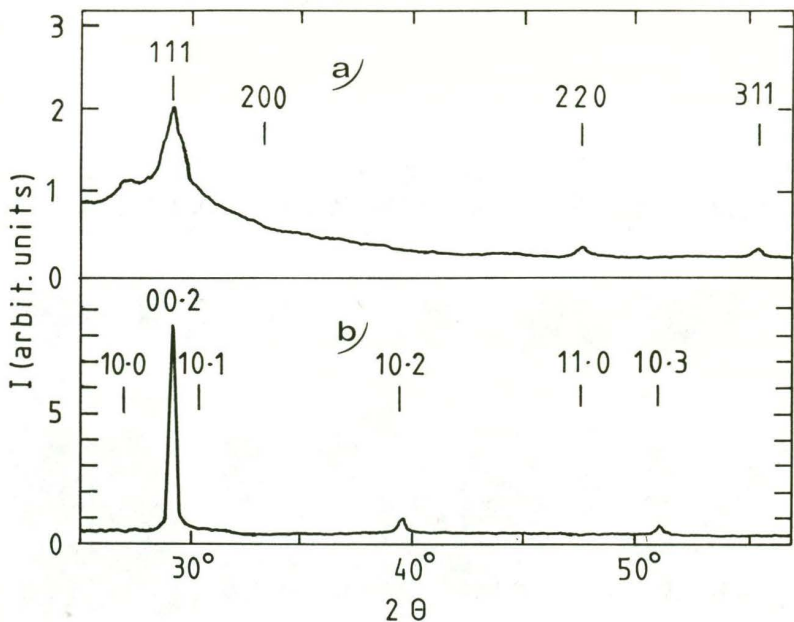


Figure 7 X-ray diffraction patterns of ZnS films grown at (a) 350°C, and (b) 500°C. The line positions marked in (a) and (b) refer to the cubic 3C phase and to the hexagonal 2H phase, respectively (5).

results to transmission electron microscope (TEM) photographs of cross-sections of ZnS ALE films (Figure 8) (9). The agreement of X-ray diffraction and TEM results suggests that the columnar grains are made up of single crystals. The thickness of poor crystallinity regions of ZnS-Mn films has been estimated to be 35–50 nm, using both X-ray analysis (8) and electrooptical measurements (10, 11). This is about one third of the values reported in experiments using conventional deposition methods. The mean grain diameter and the thickness of the poor crystallinity region (the so-called dead layer) are both important factors in EL efficiency.

The crystal structure of ZnS-Mn films grown with ALE has also been studied by investigating the fine structure of the Mn^{2+} transitions: ${}^6\text{A}_1 \rightarrow {}^4\text{E}_1$, ${}^6\text{A}_1 \rightarrow {}^4\text{T}_2$, and ${}^4\text{T}_1 \rightarrow {}^6\text{A}_1$ (12). The position of the zero-phonon lines indicates that the structure is predominantly hexagonal, a result also supported by the magnitude of the decay time of the emission. To the best of our knowledge, zero-phonon lines of the Mn^{2+} transitions have never been observed in ZnS-Mn thin films before. It is also remarkable that the zero-phonon lines were seen in the excitation spectrum, ${}^6\text{A}_1 \rightarrow {}^4\text{E}_1$ and ${}^6\text{A}_1 \rightarrow {}^4\text{T}_2$, since even the broad band characteristics of the excitation spectrum have not been observed in ZnS-Mn thin films.

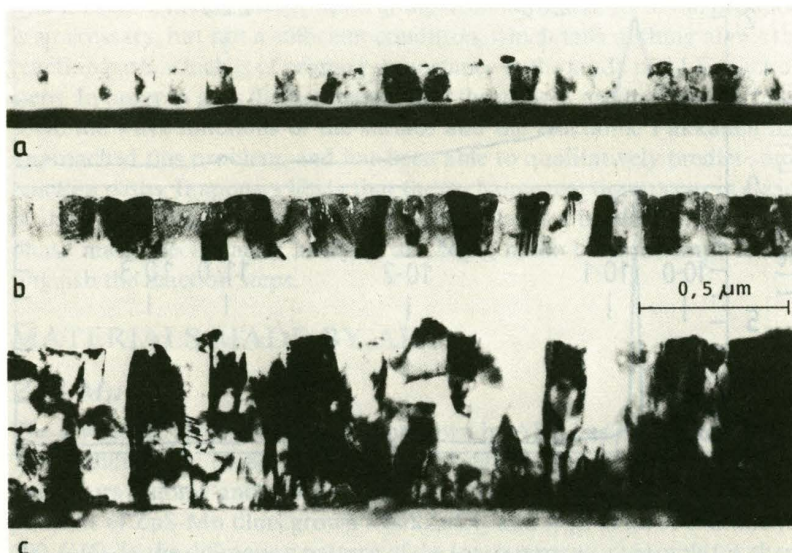


Figure 8 TEM picture of ALE ZnS-Mn films of different thicknesses: (a) 120 nm, (b) 220 nm, and (c) 580 nm (9).

Recently, ZnS has been grown by replacing ZnCl_2 with zinc acetate, $\text{Zn}(\text{CH}_3\text{COO})_2$ (13), which has made it possible to lower the deposition temperature to about 300°C . The crystalline size of the films is about 30 nm, and they have an extremely well oriented cubic phase (14). Note that all the above-mentioned films were grown on amorphous substrates.

Oxides

ALE has also been used to grow some oxides, mainly those used in EL devices. Pessa studied the ALE surface exchange reactions with the Ta_2O_5 process, and showed that the growth mechanism is similar to that of ZnS, illustrated in Figure 4 (2).

ALE Al_2O_3 is utilized in EL displays as an ion barrier, dielectric, and passivation film (Figure 12). It has been studied with flame photo analysis

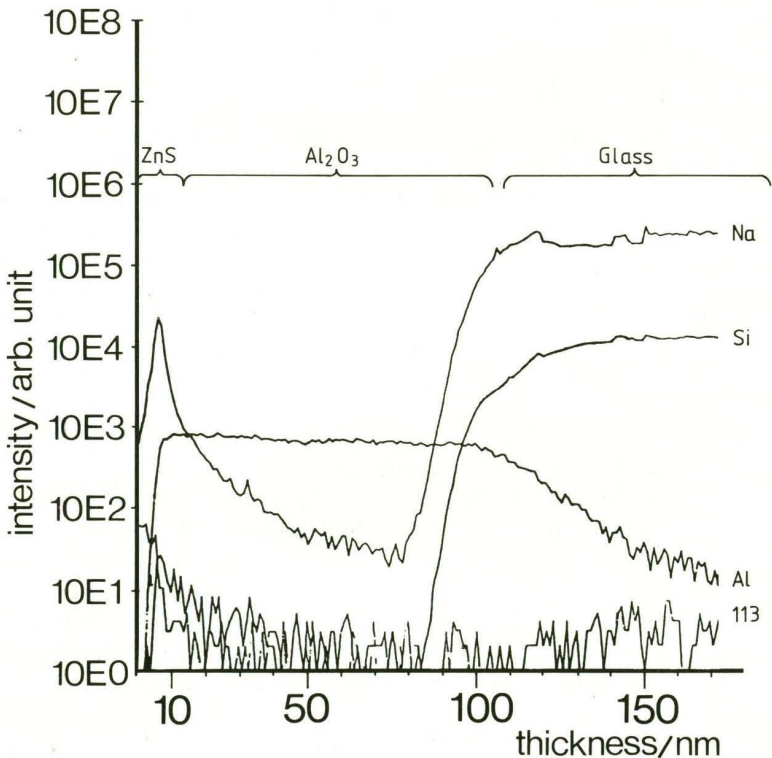


Figure 9 SIMS depth profile showing the distribution of sodium, silicon, and aluminum in Al_2O_3 and ZnS films grown on soda-lime glass (15).

and secondary ion mass spectrometry (SIMS) as an ion barrier (15). The results show that amorphous Al_2O_3 grown by ALE is an efficient ion barrier against sodium diffusion (Figure 9). An Al_2O_3 layer 50 nm thick eliminates the influence of the high sodium concentration of the glass material, even when subjected to severe heat treatment conditions.

Al_2O_3 has a reasonable dielectric strength by itself (Figure 10a) (16), but essential improvement has been achieved using an Al_2O_3 - TiO_2 mixture dielectric (Figure 10b). Even better breakdown properties have been demonstrated for a $\text{Ta}_x\text{Ti}_y\text{O}_z$ -mixed dielectric (17). Although most of the bibliographic entries that concern EL devices in general concentrate on properties of the emissive layer, the importance of the other layers must not be forgotten (Figure 12). These layers are of key importance as far as stability and reliability of the device are concerned (16).

Work is also being done at Lohja Corporation with In_2O_3 - SnO_2 (ITO) to be used as a transparent conductor in displays. Resistivity of 1.6×10^{-4} ohm cm, with a transmission of more than 80%, has been reproducibly demonstrated over a substrate area of 150 mm $\times$ 250 nm.

CdTe - $\text{Cd}_{1-x}\text{Mn}_x\text{Te}$

Some ALE experiments using single crystal substrates have been performed at the Tampere University of Technology by Pessa (18–22). In these experiments, ALE has been used to grow CdTe and $\text{Cd}_{1-x}\text{Mn}_x\text{Te}$ epitaxial layers on single crystal substrates. The growth apparatus (Figure 3) was a MBE reactor modified to work according to the principles of ALE, and elements were used as reactants. He found that generally the ALE process was considerably less sensitive to furnace and substrate temperature variations than an ordinary MBE process would be. Proper substrate preparation was clearly essential for the success of ALE growth. Pessa found by low energy electron diffraction (LEED) and ultraviolet photoelectron spectroscopy (UPS) analyses that in most cases the surface of an overlayer possesses a better ordered structure than the surface of the substrate. The LEED patterns improve as the film grows thicker (up to at least 50 nm), which indicates a gradual elimination of surface imperfections during growth.

Pessa also found that some of the CdTe overlayers grown on nonpolar CdTe (110) surfaces exhibited intrinsic surface states that indicate high structural quality in the film. Recently, heteroepitaxial growth of CdTe on GaAs has been achieved, which may offer a viable alternative to expensive CdTe wafers.

Figure 11 (*upper portion*) shows an ALE-grown CdTe - $\text{Cd}_{0.6}\text{Mn}_{0.4}\text{Te}$ multiquantum well heterostructure, with a rectangular potential of 0.58-electron volt depth located at the conduction band minimum. The width of

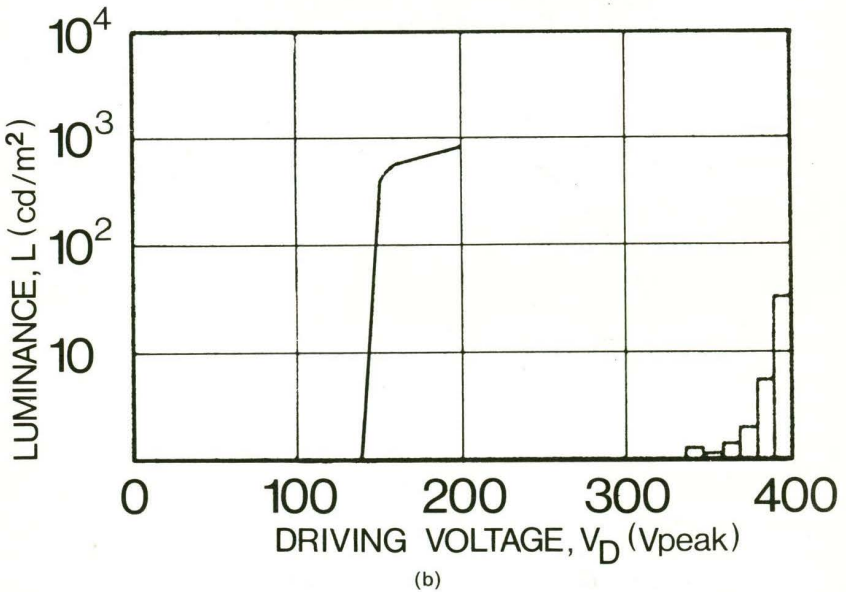
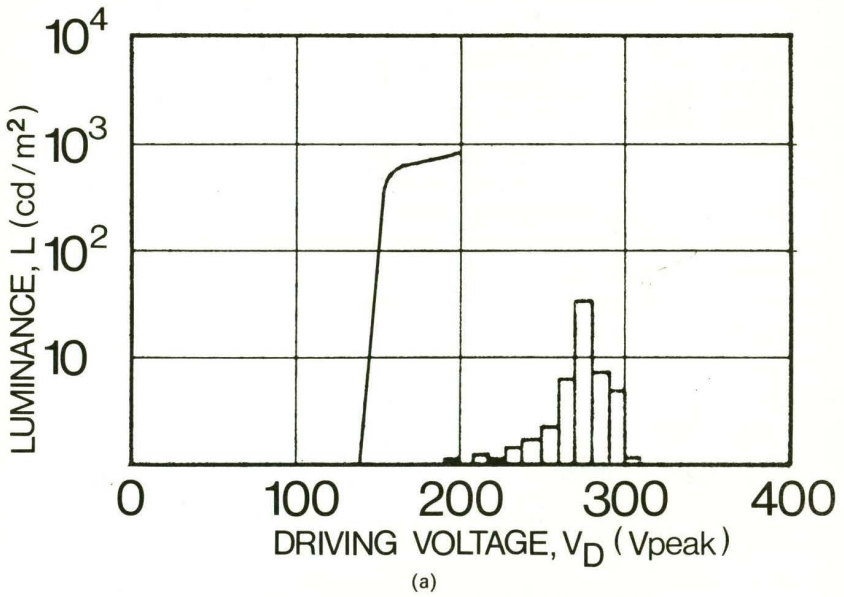


Figure 10 Luminance versus voltage, and voltage distributions for a structure with Al_2O_3 (a), and $\text{Al}_2\text{O}_3/\text{TiO}_2$ (b) dielectrics.

the interface has been studied by depositing very thin overlayers of CdTe onto a $\text{Cd}_{0.6}\text{Mn}_{0.4}\text{Te}$ barrier film, and measuring the Auger signals of Mn, Cd, and Te (Figure 11, lower portion). The solid curves in the figure represent the behavior of Mn and Cd peak-to-peak intensities relative to the Te peak-to-peak intensity. These calculations are based on the assumption that the junction is sharp, i.e. no interdiffusion of Mn or other grading effects take place in the interface region, and CdTe grows layer by layer, at the rate of one monolayer per pulse. The excellent fit of the

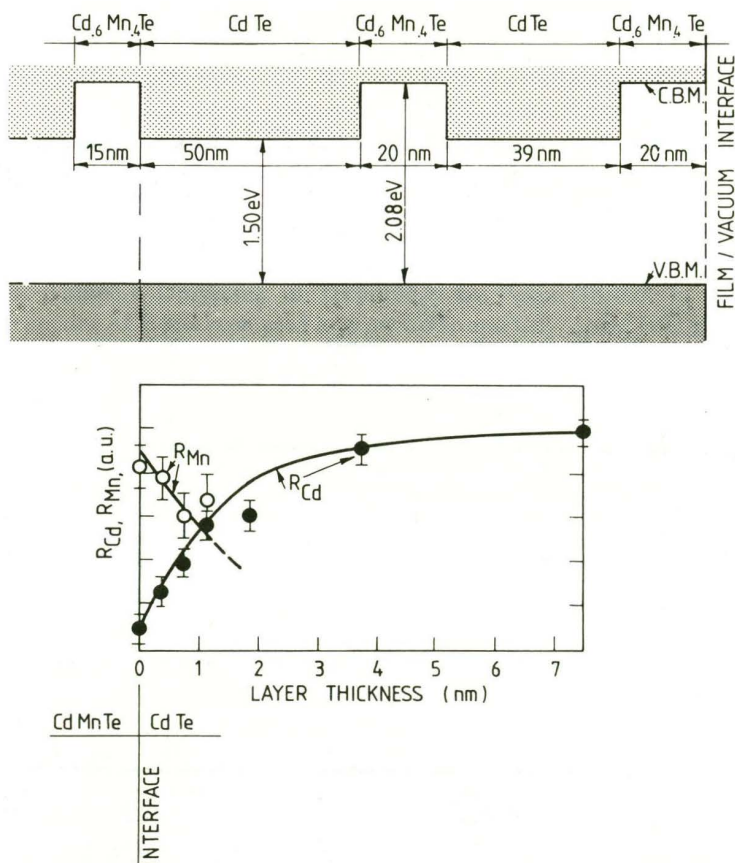


Figure 11 Schematic real-space energy band diagram of a $\text{Cd}_{0.6}\text{Mn}_{0.4}\text{Te}$ -CdTe quantum well heterostructure grown with ALE. The lower panel represents a study of the interface at the position indicated by the vertical line (22).

calculated curve and the measured points indicates that the interface is atomically sharp.

ALE EL DEVICES

In Figure 12 we have a cross-section of an ALE EL device. The substrate, ordinary soda-lime glass, acts as a mechanical support for the thin film structure, and forms a viewing window. It is passivated against possible ion diffusion from the substrate by an ion barrier layer of Al_2O_3 , grown with ALE. The transparent front electrode is indium tin oxide (ITO) made by sputtering. On both sides of the emitting layer there are dielectric layers of mixed Al_2O_3 - TiO_2 grown with ALE. The light-emitting layer is polycrystalline zinc sulphide doped with manganese (ZnS-Mn), also grown with ALE. The back electrode can be either sputtered ITO or aluminum, depending on the application. The structure is protected by a passivation layer of Al_2O_3 grown with ALE. To increase contrast, black printing is applied on top of the passivation layer.

The light emission originates from the internal transition of Mn centers excited by energetic electrons. To obtain the necessary excitation energy, electrons are accelerated in an electric field on the order of 2×10^6 V/cm, which is capacitively coupled to the ZnS-Mn layer by dielectrics from an ac power source. In this high-voltage field the ZnS lattice begins to ionize, which leads to significant electron multiplication. The role of the dielectrics is to prevent current runaway. Figure 13 shows brightness and internal efficiency versus voltage at two different frequencies. Brightness is linearly related to the current until the maximum point of the efficiency curves. Figure 14 shows a half page matrix-display module for personal computers that has an internal structure very similar to that shown in Figure 12.

SUMMARY

We have reviewed the general principles and some detailed factors of the ALE process, and have also placed much emphasis on the properties of thin films grown with ALE. It is well recognized that before we can make full use of ALE the surface reactions must be understood more precisely than they are currently. However, the results obtained so far have shown the power of the basic idea.

As mentioned in the introduction, ALE was invented to grow thin films used in EL displays. This application set special requirements of thickness uniformity, dielectric strength, and chemical stability over large areas. ALE has proved its suitability for this purpose, and it is also likely that it can be used to grow very high quality single crystal layers. The preliminary work

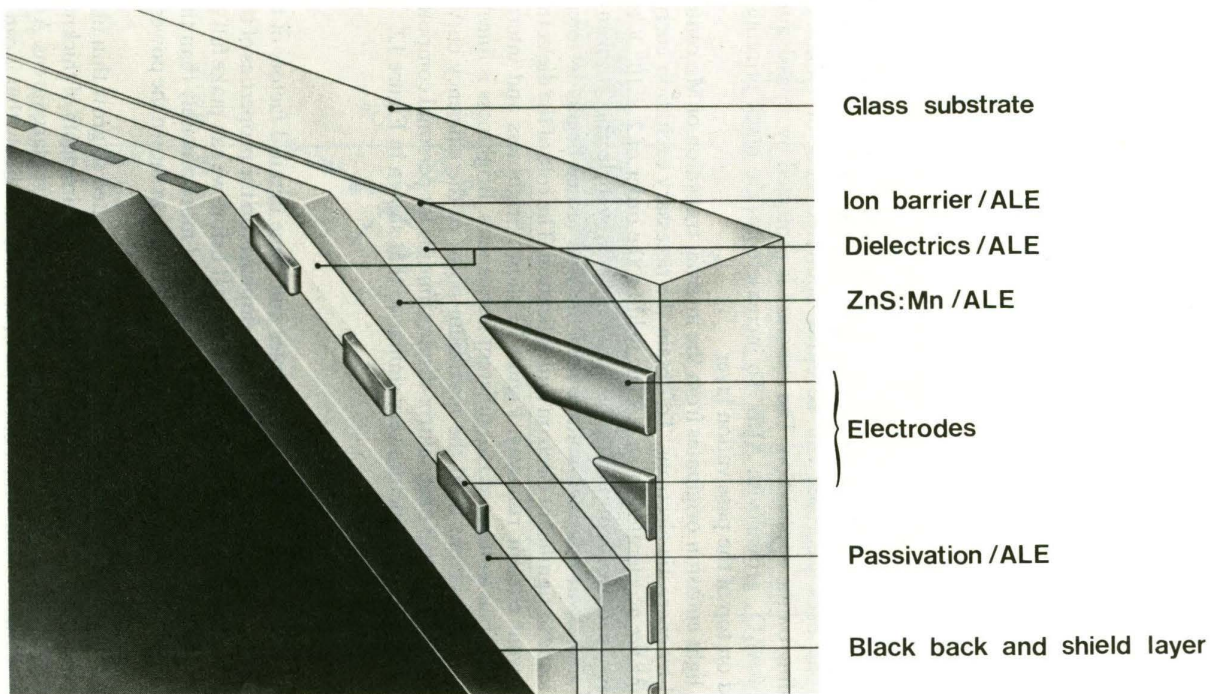


Figure 12 Structure of an ALE EL cell.

of demonstrating the viability of this use has been done by Pessa with II-VI compounds, and recently by Nishizawa of Tohoku University, Japan, with GaAs. Nishizawa uses photoenergy to overcome a reaction threshold that would otherwise require too high a temperature for the GaAs material itself. The use of extra energy in the form of light emission or plasma can make new reactant compounds possible at lower temperatures, and can widen the selection of materials that can be grown with ALE.

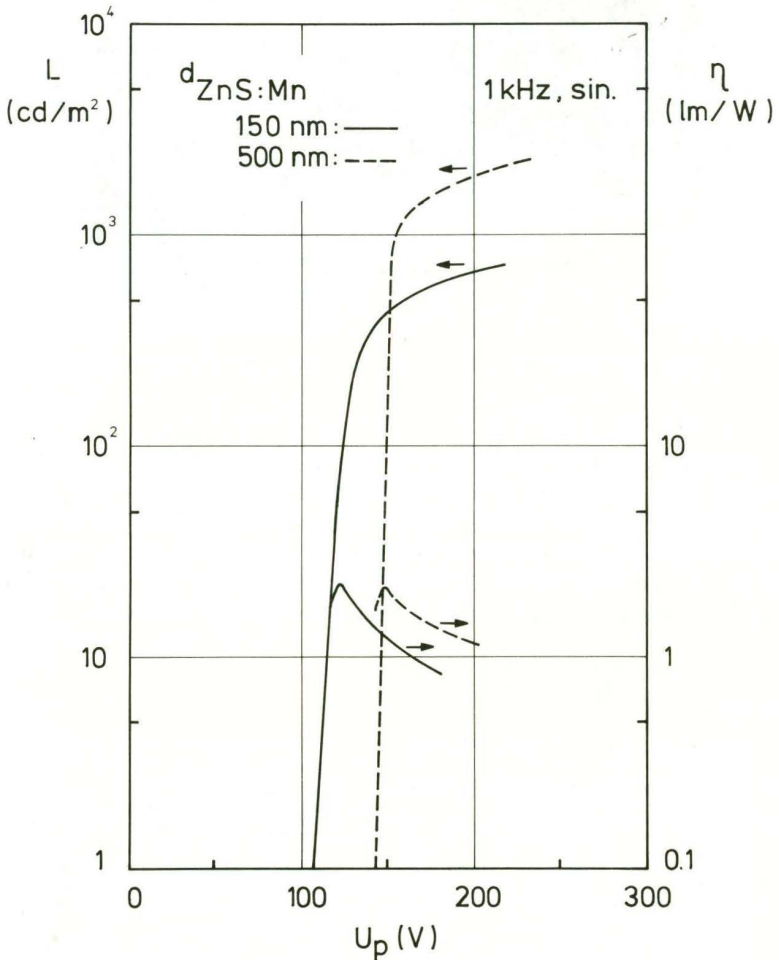


Figure 13 Luminance and luminous efficiency versus excitation voltage, measured in two ac thin film structures of different ZnS-Mn layer thicknesses.



Figure 14 Half page matrix display module for personal computers.

One very special feature of ALE is the opportunity it gives scientists to control the composition of films on the atomic scale, and in the growth direction. This allows the preparation of new combinations of materials, heterostructures, and quantum well structures (polycrystalline or amorphous). This feature, combined with the ability to grow high quality films over large areas, may eventually give rise to brand-new products.

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