

Invited

Atomic Layer Epitaxy

Tuomo Suntola

Lohja Corporation

P.O.B. 46, SF-02201 Espoo 20, Finland

Atomic Layer Epitaxy (ALE) is a process for growing high quality compound thin films either on amorphous or single crystal substrates. It is carried out by separate surface reactions, which each produce a self-balanced monolayer on the surface to be grown. The ALE method has been developed primarily for growing thin films for electroluminescent display devices but it may prove usable also in other thin film applications.

1. ALE process

The ALE process^{1,2)} is carried out stepwise by separate surface reactions so that the surface to be grown is exposed sequentially to the vapourized elements of the compound, either as such or in form of a volatile compound of the elemental component in question. This means that growing of a film of typical thickness, i.e. 0.1 - 1 microns, requires thousands of separate surface reactions. In practice, these reaction steps can be carried out in 0.5 - 3 seconds and thus the growth times of typical films are several hours. A simplified description of the ALE process is in Fig. 1, which illustrates the growth of zinc sulphide, firstly from its elements zinc and sulphur and secondly, through exchange reactions from zinc chloride and hydrogen sulphide.

The serial picture visualizes the progress of the ALE process without paying attention to the surface conditions of the process, e.g. the filling factor of the surface, the stability of each surface condition, the mechanism of an exchange reaction etc. All these factors depend on the material to be grown, on its crystal structure and on the reactant used. In the case of zinc sulphide it has been noted that the ALE process produces typically hexagonal ZnS, though the growth temperature is no more than 300 - 500°C. When

Fig. 1a ZnS growth from the elements, zinc and sulphur

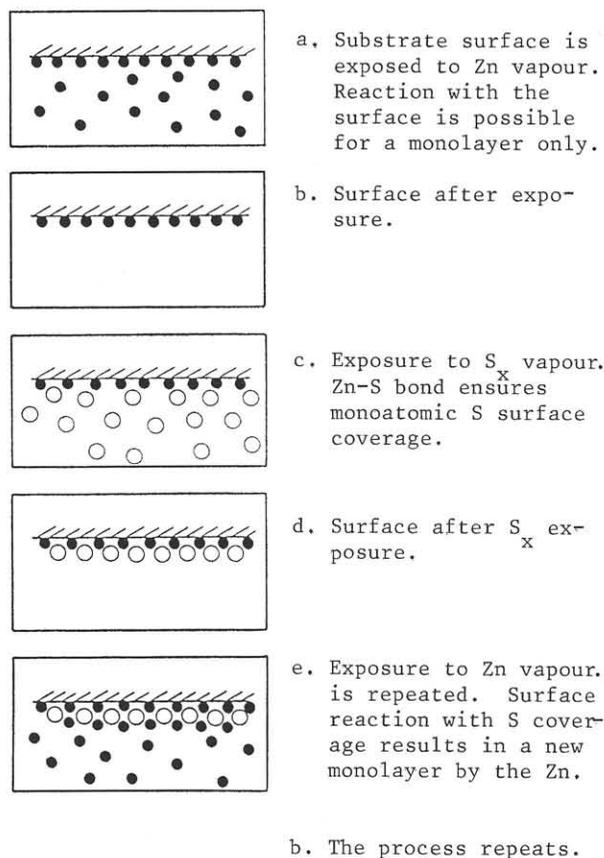
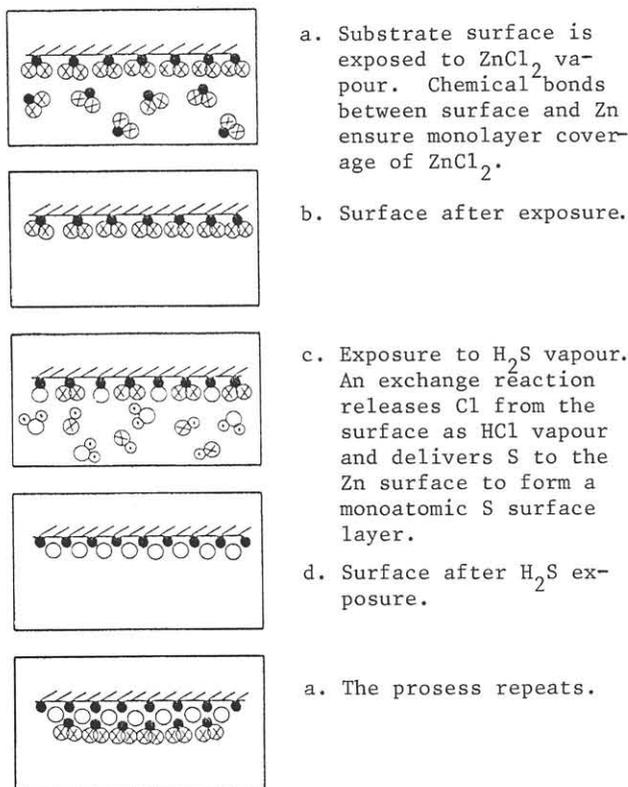


Fig. 1b ZnS growth from the compounds $ZnCl_2$ and H_2S



using elements the growth rate can approach the growth rate of the simple model illustrating the coverage of the whole surface. However, the most stable growth condition shows a lower filling factor indicating some kind of intermediate states to formate the final ZnS-S bonds. When using zinc chloride and hydrogen sulphide the surface is covered by one third of the theoretical zinc amount because the chlorine atoms occupy a major part of the surface. For ZnS the exchange reaction process can be carried out in a wider substrate temperature range than the process using elements. This indicates, that the surface conditions in the different steps of the growth will be more stable when using compound source materials. On the basis of theoretical quantum chemical studies it seems possible that the exchange reaction would occur in cycles of three sequential surface reaction steps.³⁾

2. Experimental studies of the surface reactions

Surface-physical measurements in the steps of the ALE growth have been carried out at the Tampere University of Technology by ass. prof. Markus Pessa and x-ray diffraction measurements at the Helsinki University of Technology by ass. prof. Turkka Tuomi and Dr. Veli-Pekka Tanninen. To study the exchange reactions the surface was exposed alternately to short pulses of $ZnCl_2$ and H_2S . After each pulse Auger electron spectra were measured.⁴⁾ Fig. 2 shows a series of Auger spectra, which clarify the growth mechanism of the ZnS film. The two spectra on the right reveal how the ZnS film grows stepwise as the surface is subsequently exposed to $ZnCl_2$ pulse (lower spectrum) and to a H_2S pulse (upper spectrum). The large range spectrum shows that the final surface is free from chloride and other impurities.

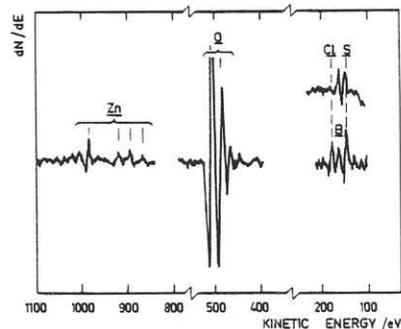


Fig. 2 Stepwise growth of a ZnS film, as studied by Auger spectroscopy. A chloride surface (lower spectrum on the right) has reacted with a H_2S pulse yielding HCl vapour and a solid layer² of S (upper spectrum). Oxygen and boron lines originate from a glass substrate and disappear for thicker films.

3. ZnS films grown on an amorphous substrate

Fig. 3 shows the x-ray diffraction patterns of ZnS films grown at a) $350^\circ C$ and b) $500^\circ C$.⁵⁾ In the diffraction pattern a) of the low temperature sample we see high diffused background intensity and broad reflections. These appear-

ances mean that the crystallization in the film is not perfect and the crystal size is very small.

Instead, in the high temperature pattern b) the background intensity is relatively small and the reflections are narrow. The line positions of cubic 3C phase and hexagonal 2H phase are marked on the figures a) and b), respectively. From the diffraction patterns we conclude that the films grown at 500°C by ALE are mainly hexagonal. This is somewhat surprising, because the cubic to hexagonal phase transition temperature is reported to be 960 to 1250 °C. The substrate on which the ZnS layer was grown was found to affect both the orientation and the background intensity. Dielectrics, like Al₂O₃, seemed to be better in this respect in comparison with for example slightly crystalline SnO₂.⁵⁾

The thinnest samples 10 nm, corresponding to some 20 atomic layers, were found to be extremely well oriented with the hexagonal c-axis perpendicular to the surface of the substrate.

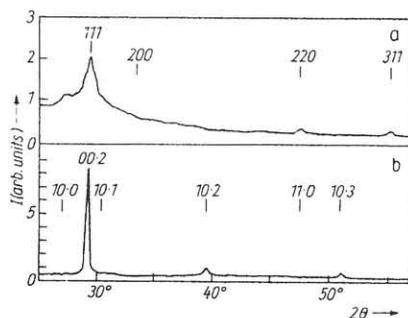


Fig. 3 X-ray diffraction patterns of ZnS films grown at a) 350 and b) 500 °C. The line positions of cubic 3C phase and hexagonal 2H phase are marked on the figures a) and b), respectively.

From the point of EL efficiency this is very interesting feature because the efficiency is reported to be larger with field applied in the parallel direction than for example in the perpendicular one.⁶⁾

Fig. 4 shows the mean grain diameter parallel to film surface versus distance from bottom interface for ALE and EBE films.⁷⁾ Average crystallite sizes of 30 nm for the 680 nm thick EBE film and 90 nm for the 580 nm thick ALE film are estimated.^{5,7)} The contrast between the estimations and Fig. 2 is due to the large number of small grains in the so called dead layer in EBE films. Dead layer is considerably thinner in ALE films. This is believed to be the main reason why ALE films have twice the EL efficiency of EBE films.⁷⁾

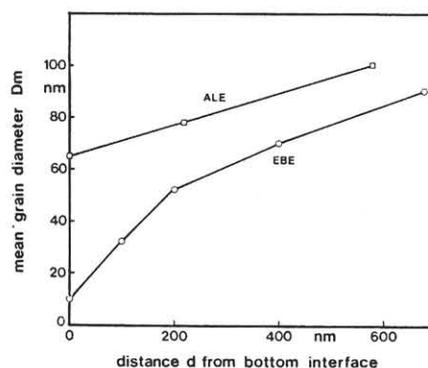


Fig. 4 Mean grain diameter parallel to film surface versus distance from bottom interface for ALE and EBE films.

Busse et al.⁸⁾ have been able to measure the energy of the zero-phonon lines of the transition ${}^6A_1 \rightarrow {}^4E_1$, ${}^6A_1 \rightarrow {}^4T_2$ and ${}^4T_1 \rightarrow {}^6A_1$ within the 3d-shell of Mn²⁺ in ALE ZnS:Mn films. This is exceptional in thin films grown on an amorphous substrate and indicates a good crystalline structure of the ZnS:Mn layer grown by ALE. The location of the ZPLs is closer to the lines of Mn²⁺ on hexagonal sites than to the lines corresponding to cubic sites, which is in agreement with the x-ray diffraction measurements.

4. Atomic Layer Epitaxy on CdTe single crystal substrates

Some experiments of ALE applied to single crystals have been made at the Tampere University of Technology by Markus Pessa. In these experiments ALE has been used to grow CdTe, $\text{Cd}_x\text{Hg}_{1-x}\text{Te}$ and $\text{Cd}_x\text{M}_{1-x}\text{Te}$ epitaxial layers on CdTe substrates. (9,10,11,12) Growth apparatus was a modified MBE reactor made to work according to the principles of ALE and elements were used as reactants. It was found that the ALE process was considerably less sensitive to furnace and substrate temperature control than an ordinary MBE process.

The crystal structure of the films and the substrate were studied by LEED. LEED picture proved that the surface structural quality of the layers is higher than that of the substrate. ALE process seems to be able to heal the defects and irregularities of the substrate in grown layers. The depth profiling of the ternary films reveals no appreciable interdiffusion effects. This observation is encouraging because it implies that multilayer structures with sharp interfaces may be grown.

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