

PATENT SPECIFICATION

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(54) IMPROVEMENTS IN METHODS OF PRODUCING COMPOUND THIN FILMS ON SUBSTRATES

(71) We, INSTRUMENTARIUM OY, Elimäenkatu 22—24, 00510 Helsinki 51, Finland, a Finnish body corporate, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention concerns a method of producing solid-phase compound thin films of superposed layers by deposition upon a substrate from the gaseous phase.

Most important among the procedures of the prior art for producing compound thin films from the gaseous phase is vacuum evaporation, which is effected either directly using the respective compound as source or by simultaneous evaporation of different chemical element components from different sources. In the first instance the major drawback is decomposition of the compound into its components, making the stoichiometry of the film that is produced difficult to control, and the stoichiometry generally tends to change in the course of the evaporating process. When the evaporation is by simultaneous evaporation of different components, generation of a good stoichiometry implies close control of the components' evaporation rates, or selective back evaporation of the more readily evaporating component. As in evaporation from the compound, the nucleation properties and crystal structure of the film are inadequately controllable in simultaneous component evaporation.

When a single crystal substrate is used in the manner known in the prior art, the selective back evaporation may be made efficient enough to achieve the result that the growing film continues the crystal structure of the substrate. With regard to this previously known, Molecular Beam Epitaxy, reference is made to J. Vac. Sci. Technol., Vol. 10, No. 5, Sept./Oct. 1973. L. L. Chang et al.: "Structures Grown by Molecular Beam Epitaxy".

When the compound itself is used as source, the decomposition of the compound may be

reduced, as known in the prior art, with the aid of sputtering techniques, wherein the material to be transposed is detached from the source by means of ion bombardment. The best stoichiometry is usually attained in connection with sputtering techniques by means of so-called bias sputtering, which is comparable to the use of back evaporation.

One of the objects of the invention is to avoid or mitigate some of the drawbacks observed in procedures of the prior art.

A procedure employed in the method of the invention is termed "atomic layer epitaxy", abbreviated ALE.

The commercially most important groups of compound films are the II—VI and III—V binary compounds and combinations of those. This is mainly due to the semiconductor characteristics of these compounds. For successful semiconductor applications the crystalline structure of the films is of primary importance. For most applications this requirement is high enough to restrict the useful material to single crystals only which can be made by epitaxy on a single crystal substrate. The epitaxy of compound materials is relatively difficult, compared to the epitaxy of elementary materials such as silicon and germanium. This is mainly due to the higher complexity of the compound growth, which in the case of binary compounds and vapour phase epitaxy involves the existence of both the vapour and solid phases of the compound and both component elements. To obtain a good stoichiometry one must therefore have precise control of the arrival rates or partial pressures of the component elements as well as the temperature of the substrate.

For many applications it is desirable to have the semiconductor material in thin film form on a substrate which is not a single crystal, but combines the features of low price and possibility of producing extensive areas. Such applications where II—VI and III—V compounds are of high interest are, for instance, solar cells, several optoelectronic devices, imaging devices, and display devices. Extensive

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use of such devices has however been restrained by the poor quality of the semiconductor material obtained by deposition techniques of the prior art.

5 An unavoidable feature of known deposition methods used to obtain film deposition on non-single crystal substrates is formation of nuclei at the beginning of the film growth. The film does not gain a continuous structure until the single microcrystals (growing nuclei) touch each other. This generally occurs when the mean thickness of the film is about 100 Å. The resulting films have a polycrystalline (or in certain circumstances amorphous) structure. 10 The electrical characteristics of the films are strongly affected by the polycrystalline structure of the material. Not only the electrical characteristics of the films suffer from the poor structure of the materials, but also the chemical stability, which is a necessary condition for the technical use of the films. Both the electrical and chemical characteristics of the compound films are moreover strongly affected by deviations from stoichiometry, which are difficult to avoid in the deposition process. 15

According to the invention there is employed a method of producing a solid-phase compound film of superposed layers upon a substrate, comprising the steps of depositing the chemical element components of the compound film in sequence and one at a time from the gaseous phase, *in vacuo* or in an inert gas atmosphere, characterised in that the said components are deposited in layers upon one another in turn, each layer being of only single atomic thickness, this single atomic thickness being achieved by the procedure herein termed "atomic layer epitaxy." 20 (abbreviated to ALE) that is to say the sequence of elements is selected so that after deposition of the first layer each subsequent layer is deposited upon a preceding layer to which its atoms have a bond stronger than the bond between the atoms of the layer being deposited, and conditions as regards vapour pressures and temperature of the substrate and/or periods of chemical interaction are controlled so that except for the atoms bonded to atoms of the element of the preceding layer all the atoms of the element of the layer being deposited remain in or return to the gaseous phase. 25

The method of this invention embodies important features of epitaxy even when an amorphous substrate is used, resulting in a nucleation-free compound film which is highly oriented in the direction of film growth. An essential difference from other deposition methods is that the film growth proceeds stepwise, atomic plane by atomic plane resulting from a surface reaction between one component element in gas phase and the other as surface atoms in the growing compound film. 30 35 40 45 50 55 60 65

The deposition is "self-regulating" in the case where the temperature of the growing surface is kept high enough to prevent any deposition other than by the ALE procedure. For a binary film AB, where A presents an element of groups I, II, III and IV, and B an element of groups VII, VI and V, the reaction is cyclically repeated, i.e., gas A reacts with a B surface forming an A surface with A—B compound bindings, then the surface is subjected to gas B, where by the reaction between gas B and the A surface again forms B—A bindings and a B surface, which again is subjected to A gas, etc. 70 75

Owing to the powerful B—A bond produced on the surface, all A atoms which in addition hit the surface will immediately return to the gaseous phase if the temperature of the substrate is kept so high that the A—A bond is not strong enough to prevent the evaporation from the substrate of the unreacted element A. When in interaction with the gaseous phase of the element A, the film that is being grown can grow by only one atomic layer even if a number of atoms considerably exceeding that corresponding to a monatomic layer should impinge on the surface. After the surface to be grown has been in interaction with the gaseous phase of element A, it is next brought into interaction with the gaseous phase of element B, whereat the A atoms in the superficial layer of the film once again enter a strong bond B—A with the B atoms directly hitting it, and the surface is now coated with a single atomic layer of element B, the temperature of the substrate being so high that the B—B bond is unable to prevent the unreacted element B from returning to the gaseous phase. These alternating reaction steps are repeated until the required thickness of AB compound has been obtained. 80 85 90 95 100 105

When a glass substrate is used, the condition for initiation of the stepwise process is that one of the components of the compound has sufficient binding strength with oxygen atoms at the surface of the glass. This condition is directly fulfilled for most II—VI and III—V compounds, and in practice it can be fulfilled for all compounds suitable for ALE growth using intermediate atomic layers. 110 115

If the ALE method is used for epitaxy on single crystals, the lattice direction of the substrate must be appropriate.

Consider an instance in which there are deposited atomic layers of element A and element B, whereof element A usually belongs to one of the groups I, II, III or IV of the periodic system and element B belongs to one of groups VII, VI or V. Typical films produced by the method of the invention are I—VII, II—VI or III—V compounds or oxides. The element A in gaseous phase reacts with a surface of which the surface atoms are of element B, forming one single atomic layer of element A, owing to the powerful 120 125 130

B—A bond produced on the surface, while all A atoms which in addition hit the surface immediately return to the gaseous phase if in the prevailing conditions of substrate temperature and vapour pressure the A—A bond is not strong enough to prevent the back evaporation of the element A. Thus with the gaseous phase of the element A the film that is being grown achieves a thickness of only one atomic layer even if a number of atoms considerably exceeding that corresponding to a monatomic layer should impinge on the surface. After the deposition of element A, the surface is brought into interaction with the gaseous phase of element B, whereat the A atoms in the superficial layer of the film once again enter a strong bond B—A with the B atoms directly hitting it, and the substrate temperature and vapour pressure are controlled so that the surface is now coated with a single atomic layer of element B, the B—B bond being unable in these conditions to prevent the element B from returning to the gaseous phase. These alternating reaction steps are repeated until the required thickness of AB compound has been obtained.

How the invention may be put into practice appears from the following description with reference to the accompanying diagrammatic drawings, in which:—

Fig. 1 represents a sectional view of an apparatus for effecting the method of the invention,

Fig. 2 is a view in section along the line II—II in Fig. 1,

Fig. 3 shows a sectional view of another apparatus for effecting the method of the invention,

Fig. 4 is a view in section along the line IV—IV in Fig. 3,

Fig. 5 shows an apparatus wherein the reaction chambers may be tightly sealed against vacuum, yet allowing axial movement of the substrate holder,

Fig. 6 shows an apparatus wherein the substrate is stationary, and

Fig. 7 shows a modification of the apparatus of Fig. 6, and wherein deposition occurs on both sides of the substrates and the reaction chamber can be evacuated, between reaction steps, through a valve.

Figures 1 and 2 illustrate a vacuum apparatus confined in a chamber 10, wherein substrates 14, on which films are being grown, are mounted on a disk 12 rotatable with the aid of a shaft 11. Below the disk 12 are vapour sources 13a and 13b, which are mutually isolated sectors and each of which is arranged to have in the prevailing conditions in the chamber 10 a desired vapour pressure of an elementary component of the film to be grown. When the disk 12 is rotated the substrates 14 are alternately placed in interaction with the vapours of elements A (13a) and B

(13b), whereby the growth of the film takes place according to the method of the invention, provided that the vapour pressures and the temperature of the substrate 14 required by the method are maintained.

The deposition can be terminated at any time desired, for example by reducing the temperature and/or increasing inert gas pressure in the chamber 10.

Figures 3 and 4 show a ring 12b which is rotatable with the aid of the shaft 11 and on the outer circumference of which the substrates 14 are mounted. The vapour sources 13a, 13b and 13c are placed radially around the ring 12b. The speed of rotation of the ring 12a is most appropriately between 1 and 20 r.p.s.

An apparatus wherein there is relative motion between the substrates 14 and the vapour sources 13 may also be accomplished if the substrates 14 are stationary and the vapour sources are moving. The apparatus may also be designed so that, for instance, the substrates 14 are affixed to an endless belt which carries the substrates past the vapour sources. Relative motion of substrates and vapour sources with reference to each other can be accomplished by various different devices.

The apparatus according to Figure 5 comprises a vacuum chamber 10 and separate reaction chambers 19a and 19b, where the substrates 14 can be moved in rotation, and vacuum-tightly sealed during each reaction. This arrangement allows better separation of the reaction steps from each other and smaller leakage of the reaction gases, but it is mechanically more complicated. Improved separation of the reaction steps may also be obtained with fewer mechanically moving parts, using the embodiment of Figures 6 and 7. Further according to Figure 5, the shaft 11a may also be moved in its axial direction. A means for carrying out both movements is illustrated schematically by the block 24. A block 23 represents schematically the motion control in question, and a block 22 similarly represents the control of the valves 15a and 15b. The sources of the different gases are indicated by reference numerals 20a and 20b. Reference numeral 21 refers to the sealing means in connection with the reaction chambers 19a and 19b. Deposition can be discontinued by closing the valves 15a and 15b, for example.

In the apparatus shown in Figure 6 the substrate is stationary on a base 12c, and it is kept at a suitable temperature with the aid of a heating member 17. The apparatus comprises two vapour sources 20a and 20b, which are alternately arranged to supply vapour to act on the substrate 14. This is accomplished with the aid of valves 15a and 15b fitted in pipes 16a and 16b, these valves opening/closing in alternation so that while one of the valves 15a or 15b is open the other valve 15b or 15a is closed. The means for

controlling the valves is schematically represented by a block 18 and a switch *k*. Deposition is discontinued if both the valves 15a and 15b are closed.

According to Figure 7 there are outside the reaction chamber 10, the sources 20a and 20b of different gases. The substrates 14 in the chamber 10 are held in their position by holding means 29 and 30.

The reaction chamber 10 is filled with the element gases in rotation, using the valves 15a and 15b, and the chamber 10 is evacuated between consecutive deposition steps, with the aid of a valve 26. The walls of the reaction chamber 10 may become covered with the compound simultaneously with the growth on the substrates 14, which will be covered on both sides. A block 28 represents the means for actuating the valve 26, and a block 25 represents its control means.

Some theoretical background to facilitate appreciation of the invention follows. Assume that there exist conditions in which in one source the element A is in equilibrium between its solid phase and its vapour pressure P_A at temperature T_A (or if T_A exceeds melting point of A, equilibrium prevails between the liquid and gaseous phases). The corresponding situation for element B obtains in a second source.

In the case of a self-balancing ALE procedure the substrate temperature T_0 is kept higher than the source temperatures T_A and T_B , which means that the A and B vapours do not condense on the substrate. In the case where the A atoms form a solid compound with oxygen, with binding energy high enough to prevent decomposition, the substrate will be covered by a monatomic layer of A atoms with A—O bonds. The coverage of the surface with A atoms can be described by the equation:—

$$dP_A = \frac{\mu_A \alpha_{AO}}{N_s} (1 - P_A) : dt$$

$$P_A = 1 - e^{-\frac{\mu_A \alpha_{AO}}{N_s} : t_{AO}} \quad (1)$$

where

P_A = relative surface area covered with A atoms

μ_A = collision density of A atoms with the surface, which has the form (according to kinetic gas theory)

$$\mu_A = \frac{P_A}{\sqrt{2} \cdot m k T} \left[\frac{\text{atom}}{\text{cm}^2} \right] \approx \frac{10^{20}}{[\text{torr}]} \left[\frac{1}{\text{cm}^2 \text{s}} \right]$$

N_s = density of surface atoms

$$N_s \approx 10^{15} \text{ 1/cm}^2$$

t_{AO} = interaction time of the surface with O atom and reacting gas A [s]

α_{AO} = surface reaction probability, of atom A with O atom surface, corresponding to the "sticking coefficient" in conventional deposition methods.

The surface reaction probability α is a complex function of the temperature of the reaction surface and the pressure of the reacting gas. It varies widely with different elements and compounds formed. For monatomic gases α has been found to be higher than for biatomic or multiatomic gases.

From equation (1) it can be found that the relative coverage of the surface with A atoms approaches unity asymptotically with increasing time of interaction.

A significant benefit of the ALE growth is that the vapour pressure of the forming compound has its minimum just in the growth direction, the strongest possible bonds occurring perpendicular to the surface.

If the B atoms form a solid compound with oxygen with high binding energy, the substrate in interaction with the B source will be covered with B atoms exactly as described for the interaction between it and the A atoms and the glass surface. For B type elements this is not generally the case, which means that the surface of the substrate glass will remain unchanged during its interaction with B vapour.

In the next reaction step the substrates covered with a monatomic layer of A atoms are placed in interaction with the source of B atoms in gas phase. The surface will be covered with B atoms according to equation (1), again forming a monatomic layer of B atoms with A—B compound bond. The conditions valid for the vapour pressures of said monatomic B layer with A—B bonds and B atoms on this layer, with B—B bonds, differ by many orders of magnitude, resulting in an extremely selective back evaporation of the B atoms lacking compound bonds.

By repeated reaction steps in rotation, the surface of the substrates will be covered by a layer structure



where the first O stands for the surface atom layer of the substrate and the following A—B layers form a highly oriented film of com-

pound AB. In the case of perfect coverage in each reaction step the total thickness of the film is determined by the number of rotations and the lattice constant of the compound.

5 Using several sources with different elements $A_1...A_m$, $B_1...B_n$, layer structures containing compound combinations, such as superlattices, heterojunctions, etc., may be grown.

10 The conditions for ALE growth, as described, may be defined by the terms of equation (1). For a full coverage as described above the conditions

$$\alpha_{AO} \mu_A t_{AO} \gg N_s$$

$$\alpha_{AB} \mu_A t_{AB} \gg N_s$$

15 and

$$\alpha_{BA} \mu_B t_{BA} \gg N_s$$

(2)

must be provided.

20 In cases with p_A and p_B directly in interaction with the reacting surface, as in Figs 1, 2, 3, 4, 5 and 7, the source temperatures T_A and T_B are linked with μ_A and μ_B by equations

$$\mu_A = f(p_A) = f(T_A)$$

(3)

$$\mu_B = f(p_B) = f(T_B)$$

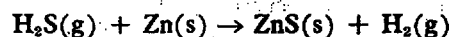
25 To ensure perfect back evaporation of the elements having no compound bond, which is mandatory in a self-balancing ALE process, the substrate temperature T_0 must be sufficiently far above the temperatures T_A and T_B . The upper limit of T_0 is in principle determined by the vapour pressure of the compound.

30 In practice, however, when a glass substrate is used, the upper limit of T_0 is generally determined by the softening point of the substrate glass. It should be noted that the lattice direction of the growing surface in ALE growth most efficiently minimizes the vapour pressure of the compound. This has been established e.g. in connection with CdSe growth, which has been carried out at $T_0 > 500^\circ\text{C}$ without any detectable back evaporation of the compound.

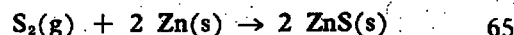
35 It is obvious that ALE growth is obtainable with several types of growing equipment. The essential features are the source and substrate temperatures, and stepwise interactions between the substrate and the element vapours of the compound in rotation. Especially the 40 II—VI compound group offers great freedom in equipment design, due to the high vapour pressure of II and VI elements.

45 In ALE growth the interaction with a component vapour may also be obtained by using a gaseous compound of the element which decomposes on the reacting surface, in analogy with the practice of chemical vapour deposition. This kind of reaction may be accom-

lished e.g. with H_2S , instead of S_2 . The corresponding surface reactions in the case of 60 ZnS growth are



in the case of H_2S , corresponding to the reaction



for pure S_2 gas. According to the ALE principle the reactions are only possible as long as free $\text{Zn}(\text{s})$ surface atoms are available. The ALE procedure can be performed with the aid of sputter-type deposition of the component elements. In this case there is an inert gas or plasma present in the reaction steps.

When applying equation (1) to a substrate surface which is only partially formed of the atoms which react with the gas atoms in question, the equation is to be applied only to the active portion of the surface. If an AB compound is grown using partial surface coverage in each or one of the process steps, the equation (1) may be modified to read

$$P_A = P_B^* - e^{-\frac{\mu_A \alpha_{AB}}{N_s} \cdot t_{AB}} \quad (4)$$

for A atom reaction steps and

$$P_B = P_A^* - e^{-\frac{\mu_B \alpha_{BA}}{N_s} \cdot t_{BA}} \quad (5)$$

for B atom reaction steps, where P_B^* and P_A^* represent the relative surface area covered by B and A atoms before the A and B reaction steps, respectively.

The partial coverage of one component element is of special importance when growing compound films with low vapour pressure elements or with compounds which contain different amounts of the component elements. An important example of the first-mentioned is the growth of III—V compounds on a substrate which cannot be heated to temperature T_0 high enough to ensure perfect back evaporation of the unreacted group III elements. In such a case the surface reaction between group V surface atoms and group III gaseous atoms is limited to cause only partial coverage of group III atoms to ensure the absence of super-numerary group III atoms on the surface. The group V gas reaction with the surface partially covered with group III atoms can be made perfect enough to ensure the oriented nucleation-free ALE growth of the compound.

Another important case in which partial surface reaction steps have to be used in the growth of dioxides of elements which also have stable or relatively stable monoxides. The growth of tin dioxide by ALE technique is an illustrative example. In order to form SnO₂, instead of SnO, the interaction of Sn vapour with the O surface is restricted to cause Sn coverage of a few per cent only. The O₂ interaction, effected by means of O₂ plasma, ensures the maximum number of oxygen atoms to be bonded with Sn atoms, thus causing the dioxide growth. A strong indication for use of ALE growth in such instances, too, has emerged from the observation that the SnO₂ layer on a glass plate shows electrical conductivity in the plane of the surface starting from 10 Å SnO₂ thickness. The conductivity shows no tunnelling effects, which is proof that the film has a continuous crystal structure. Such films are physically extremely firm and chemically resistant, which is in fact true for all compound films made by ALE techniques, no matter whether with perfect or partial coverage of the reacting surface in the individual reaction steps.

Examples

Known techniques and apparatus can be employed in effecting the method of the invention.

Example 1.

ALE growth for ZnS has been effected with following values of system parameters:

Substrate material: Corning (Registered Trade Mark) Glass 7059—substrate temperature 320° C, the total bombardment of Zn-atoms during one interaction between the surface and Zn vapour about 5×10^{15} atoms/cm², which was measured with a quartz/crystal rate monitor, corresponding to an effective Zn vapour pressure of about 10⁻³ torr and equilibrium temperature of about 290° C for the Zn source—equilibrium temperature of the S source 100° C, corresponding to a vapour pressure of about 10⁻² torr and total bombardment of S₂ molecules of about 5×10^{16} molecules/cm².

For a ten minutes process the film thickness was about 0.27 μm, for processes of 20 and 30 minutes the thicknesses were about 0.54 μm and 0.80 μm respectively.

The film structure was examined by etching techniques.

Examples 2.

ALE growth of SnO₂ layers on Corning (Registered Trade Mark) Glass 7059 substrates has been effected as follows:

The substrate temperature 300° C
The total amount of Sn atoms bombarded

during one interaction with Sn source about 0.6×10^{14} atoms/cm²
oxygen source is of plasma type with 10–100 mTorr total pressure and 40mA plasma current. The total amount of O₂⁻ ions bombarded being $\sim 7 \times 10^{14}$ ions/cm² during the interaction with the plasma source.
with speed rotation 1 rotations per second this process gives a growth of SnO₂ film to 600Å in 25 minutes.

Example 3.

ALE growth of GaP-layers on Corning Glass 7059 substrates has been effected as follows:

the substrate temperature $\sim 300^\circ \text{C}$
the total amount of Ga atoms bombarded during the interaction with Ga source $\lesssim 10^{15}$ atoms/cm²
the total amount of P molecules (most probably P₄) bombarding the surface during the interaction with Phosphorus vapour is about 5×10^{15} atoms/cm²
a 0.25 μ film was grown with these parameters of substrate and sources in 25 minutes.

Example 4.

ALE growth of ZnS has been effected with following system parameters:

substrate Corning (Registered Trade Mark) glass 7059
substrate temperature $\sim 470^\circ \text{C}$
temperature of Zn-source $\sim 390^\circ \text{C}$
temperature of S-source $\sim 120^\circ \text{C}$
interaction time of the Zn-source 6 seconds
interaction time of the S-source 2 seconds

With a 140 min. process the film thickness was 0.12 μm.

Experiments with ALE growth have established the fact that the theoretical growth speed cannot be exceeded but approached asymptotically with increased time (or pressure) of interaction at each reaction step.

Selective etching of the ZnS films made by ALE techniques has been performed with the aid of an etchant containing 60 parts H₃PO₄, 5 parts by weight HNO₃ and one part by weight HF at room temperature. The etching speed was from 10 μm/s to 150 μ/s in the direction of the surface for 0.1 to 0.7 μm thick ZnS film whilst no etching effect could be detected in the direction perpendicularly to the surface plane. Etching of ALE-SnO₂ films has been possible only by electrochemical methods.

WHAT WE CLAIM IS:—

1. A method of producing a solid-phase compound film of superposed layers upon a substrate, comprising the steps of depositing



Another important case in which partial surface reaction steps have to be used in the growth of dioxides of elements which also have stable or relatively stable monoxides. The growth of tin dioxide by ALE technique is an illustrative example. In order to form SnO_2 , instead of SnO , the interaction of Sn vapour with the O surface is restricted to cause Sn coverage of a few per cent only. The O_2 interaction, effected by means of O_2 plasma, ensures the maximum number of oxygen atoms to be bonded with Sn atoms, thus causing the dioxide growth. A strong indication for use of ALE growth in such instances, too, has emerged from the observation that the SnO_2 layer on a glass plate shows electrical conductivity in the plane of the surface starting from 10 Å SnO_2 thickness. The conductivity shows no tunnelling effects, which is proof that the film has a continuous crystal structure. Such films are physically extremely firm and chemically resistant, which is in fact true for all compound films made by ALE techniques, no matter whether with perfect or partial coverage of the reacting surface in the individual reaction steps.

Examples

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For a ten minutes process the film thickness was about $0.27 \mu\text{m}$, for processes of 20 and 30 minutes the thicknesses were about $0.54 \mu\text{m}$ and $0.80 \mu\text{m}$ respectively.

The film structure was examined by etching techniques.

Examples 2.

ALE growth of SnO_2 layers on Corning (Registered Trade Mark) Glass 7059 substrates has been effected as follows:

The substrate temperature 300°C
The total amount of Sn atoms bombarded

during one interaction with Sn source about 0.6×10^{14} atoms/ cm^2
oxygen source is of plasma type with 10–100 mTorr total pressure and 40mA plasma current. The total amount of O_2^- ions bombarded being $\sim 7 \times 10^{14}$ ions/ cm^2 during the interaction with the plasma source
with speed rotation 1 rotations per second this process gives a growth of SnO_2 film to 600 Å in 25 minutes.

Example 3.

ALE growth of GaP-layers on Corning Glass 7059 substrates has been effected as follows:

the substrate temperature $\sim 300^\circ\text{C}$
the total amount of Ga atoms bombarded during the interaction with Ga source $\lesssim 10^{15}$ atoms/ cm^2
the total amount of P molecules (most probably P_4) bombarding the surface during the interaction with Phosphorus vapour is about 5×10^{15} atoms/ cm^2
a 0.25μ film was grown with these parameters of substrate and sources in 25 minutes.

Example 4.

ALE growth of ZnS has been effected with following system parameters:

substrate Corning (Registered Trade Mark) glass 7059
substrate temperature $\sim 470^\circ\text{C}$
temperature of Zn-source $\sim 390^\circ\text{C}$
temperature of S-source $\sim 120^\circ\text{C}$
interaction time of the Zn-source 6 seconds
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With a 140 min. process the film thickness was $0.12 \mu\text{m}$.

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Selective etching of the ZnS films made by ALE techniques has been performed with the aid of an etchant containing 60 parts H_3PO_4 , 5 parts by weight HNO_3 , and one part by weight HF at room temperature. The etching speed was from $10 \mu\text{m/s}$ to $150 \mu\text{m/s}$ in the direction of the surface for 0.1 to $0.7 \mu\text{m}$ thick ZnS film whilst no etching effect could be detected in the direction perpendicularly to the surface plane. Etching of ALE- SnO_2 films has been possible only by electrochemical methods.

WHAT WE CLAIM IS:—

1. A method of producing a solid-phase compound film of superposed layers upon a substrate, comprising the steps of depositing



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the chemical element components of the compound film in sequence and one at a time from the gaseous phase, *in vacuo* or in an inert gas atmosphere, characterised in that the said components are deposited in layers upon one another in turn, each layer being of only single atomic thickness, this single atomic thickness being achieved by the procedure herein termed "atomic layer epitaxy" (abbreviated to ALE) that is to say the sequence of elements is selected so that after deposition of the first layer each subsequent layer is deposited upon a preceding layer to which its atoms have a bond stronger than the bond between the atoms of the layer being deposited, and conditions as regards vapour pressures and temperature of the substrate and/or periods of chemical interaction are controlled so that except for the atoms bonded to atoms of the element of the preceding layer all the atoms of the element of the layer being de-

posited remain in or return to the gaseous phase.

2. A method according to Claim 1, wherein after the formation of a layer of single atom thickness upon part of the surface upon which deposition is occurring the temperature of the said surface does not prevent further condensation upon the said surface of the component being deposited, but the deposition is discontinued (for example by removal of the source material) prior to the formation of the respective layer over the whole of said surface.

3. A substrate carrying a compound film of superposed layers when produced by a method according to either one of the preceding Claims.

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