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**(54) Title:** METHOD FOR DEPOSITION OF A METAL

**(57) Abstract**

A method for depositing a metal originating from a metal precursor upon a suitable substrate comprises transporting via a carrier gas precursor material, vaporized from said precursor, to said substrate, wherein said carrier is loaded at a certain temperature with said precursor material by flowing through a liquid which contains said precursor normally solid at said temperature.

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# METHOD FOR DEPOSITION OF A METAL

The invention relates to a method for depositing a metal originating from a metal precursor upon a suitable substrate comprises transporting via a carrier gas precursor material, vaporized from said precursor, to said substrate, for example carried out in a Metal Organic Chemical Vapour Deposition (MOCVD) process.

More in detail MOCVD is a process whereby thin films are fabricated, for use i.a in the electronics and opto-electronics industries generally comprising the following steps: introducing the vapours of at least one metal-organic compound - known as a precursor or metal precursor - into a reactor under conditions of pressure and temperature such that the aforesaid precursor vapours decompose to give in a reactor chamber a deposit of the desired material as a thin film on a substrate material. For example, in the case of the deposition of III-V semiconducting materials, vapours containing compounds of at least one element of Group III are mixed with those containing at least one element of Group V, and the resulting thin films deposited via this process consist of a III-V semiconducting material or alloys thereof. Examples of III-V materials which have been thus deposited include GaAs, AlAs, InP, and alloys thereof, that is, for example, materials such as $Al_xGa_{1-x}As$, $Ga_yIn_{1-y}P$, $Ga_xIn_{1-x}As_yP_{1-y}$, where x or y lie in the range 0 - 1, mostly referred to as ternary and quaternary alloys. In this context the indications III and V are conventionally used when elements from respectively Periodic Table elements Groups 3a and 5a, as defined in Handbook of Chemistry and Physics, 63rd edition, are concerned.

For the fabrication of devices with specific electronic properties it is necessary to control precisely the composition and thickness of the resulting layers grown by MOCVD and making up a layer arrangement, and this in turn requires accurate control of the amounts of precursor vapours entering the reactor. The manner by which dosimetry of the precursor vapours is controlled depends upon the physical state of the precursor at ambient temperature and one atmosphere pressure. For example, gases are stored in high pressure cylinders and the dosimetry into the reactor is usually controlled using a calibrated mass-flow controller. In contrast, solid and liquid precursors are usually placed in a vessel fitted with an inlet and an outlet such that well known carrier gases, such as there are $H_2$, He, Ar, $N_2$, can be passed through the vessel, thereby entraining the precursor vapours away for conduction to the reactor.

The normal vessel which is used in MOCVD is known as a "bubbler": a vessel fitted with an inlet tube which conducts carrier gas to the bottom of the precursor sample via a dip-tube, and an outlet which opens directly from the top of the vessel. The carrier gas is thereby passed through the precursor sample and therefore entrains some of the precursor vapour before being forced out of the bubbler at the top.

Using a bubbler arrangement to control the dosimetry of precursors into an MOCVD reactor requires accurate control of the flow of carrier gas through the bubbler in addition to reliable efficiency of entrainment of the precursor vapours in the carrier gas. As said above control of the carrier gas flow is normally achieved using a mass-flow controller. The efficiency of entrainment of precursor vapours, however, depends upon the contact achieved between the carrier gas and the surface of the condensed phase, as well as the actual evaporation coefficient $\alpha$ of the condensed phase itself. The evaporation coefficient is the ratio of the observed evaporation rate to that predicted by the kinetic theory of gases for a condensed phase in equilibrium with its vapour. For many organic compounds the value of $\alpha$ is close to unity, and the materials very rapidly attain their saturated vapour pressure. However, for materials which possess vapour phase compounds which are very different from that of the condensed phase, e.g. solid arsenic, then $\alpha$ may be several orders of magnitude less than unity.

Low evaporation coefficients may also be found for organometallic compounds which react with traces of oxygen and/or water to form oxide skins over the condensed phase which are relatively involatile and obstruct free evaporation of the precursor material itself. Many of the precursors used in MOCVD, particularly those used to deposit layers used in the electronics industry, react with even minute traces of oxygen and/or water to form involatile oxides.

A conventional way to obtain reproducible dosimetry from a conventional MOCVD bubbler is to ensure that the carrier gas is saturated with the precursor vapour: the saturated vapour pressure of a material is fixed for a given temperature, so if it can be ensured that the carrier gas is saturated then the concentration of precursor therein will always be the same. It has been found that under the conditions of temperature, pressure and carrier gas flow rates, under which precursors for MOCVD are normally used, liquid precursors readily approach saturation to the extent that the dosimetry from a conventional bubbler is reproducible until the vessel is virtually empty; at least while the level of the liquid therein is above that of the bottom of the dip-tube of the carrier gas inlet, i.e. whilst the carrier gas still bubbles through the precursor.

For solid precursors, however, the pick-up from the bubbler is notoriously unreliable: frequently the carrier gas must be passed through the bubbler for a considerable time before the concentration of precursor in the outlet gas is stable. Moreover the final concentration attained has been observed to fluctuate throughout the usage of the source. This fluctuation may be either an increase or decrease in the efficiency of pick-up, and may be either a gradual or abrupt change. Those fluctuations can be ascribed to a number of phenomena such as, regrowth of crystals, migration of precursor material because of temperature gradients within the bubbler vessel, forming of channels, often called 'chimneys', within the precursor material, contamination of the surface of the sample by traces of impurities, and/or precursor structure varieties such as metastables.

One of the most problematic precursors which has been used is that of trimethylindium, $(CH_3)_3In$ (TMI). This material is a crystalline solid which melts at 89 °C, and is by far the most commonly used precursor for the deposition of indium-containing semiconducting thin films by MOCVD. The analogous aluminium and gallium compounds (TMA and TMG), which are, in turn, the most commonly used precursors for introducing those respective metals into semiconducting thin films, are both liquids at ambient temperature, having melting points of respectively 15 and -16 °C.

A clear indication of the variation in pick-up efficiency which has been observed for TMI is shown when the precursor is used to grow epitaxial layers of the above said ternary or quaternary alloys.

Epitaxial layers are layers of material deposited on a substrate material (which may or may not be the same material) such that there is no interruption of crystallinity at the interface. To satisfy this condition both the epitaxial layer and the substrate must have either similar crystal structures, or possess some special relationship between their crystal structures which makes continuity of crystallinity at the interface possible. It is frequently the case that for electronic devices the substrate material and the epitaxial layers must be single crystal. It is also frequently the case that both the epitaxial layer and the substrate possess the same crystal structure. In both cases a necessary condition for the obtention of a single-crystal epitaxial layer is that the dimensions of the lattice of both substrate and epitaxial layer are essentially identical, a situation known as lattice match. It is mainly under these circumstances that changes in the dosimetry from TMI are most readily noticed, and with the most disastrous results. It is frequently found that for the growth of lattice-matched ternary or quaternary epitaxial layers, numerous

MOCVD experiments are wasted, necessitating recalibration of the system to account for the variation found in the dosimetry of TMI.

Attempts to solve the problems encountered with the variable dosimetry from TMI have been manifold. Initially, growth was attempted using triethylindium, $(CH_3CH_2)_3In$ (TEI), which is a liquid at ambient temperature. However, its vapour pressure is much lower than that of TMI, and TEI tends to pre-react with some of the Group V precursors giving rise to an involatile material, thereby ruining compositional control by depleting indium species from the vapour phase; furthermore TEI is less thermally stable than TMI, thus giving rise to non-uniform deposition over the surface of the substrate.

Other liquid precursors which have been used include $(CH_3)_3In.NH[CH(CH_3)_2]_2$, $(CH_3)_2\overline{In(CH_2)_3N}(CH_3)_2$ or $(CH_3)_3In.P(CH_3)_2(CH_2CH_3)$, but all of these precursors possess much lower volatilities than TMI, thereby giving rise to growth rates of the epitaxial layers that are unacceptably low for most purposes.

Other attempts have involved using TMI but modifying the apparatus whereby it is introduced into the MOCVD reactor. For example, the bottom of the bubbler dip-tube may have been modified to spread the carrier gas more evenly throughout the bottom of the bubbler prior to it rising under buoyancy. The effect of this buoyancy, and its tendency to form the above said chimneys has been overcome by maintaining an essentially standard bubbler arrangement but reversing the flow of carrier gas. However, with such an arrangement the large linear velocities of carrier gas up the dip-tube blow small solid particles of precursor out of the bubbler.

From Japanese patent application published under number 01-265511 it is known to deposit TMI onto small spherical supports prior to packing into the bubbler. Although it could help to reduce the tendency for the average crystal size to increase with time, it is more likely to enhance lateral diffusion, and therefore, be similar in effect to modifications in the end of the dip-tube, as mentioned above.

Another well-known method has been to melt the precursor under a slow stream of carrier gas prior to use, as this has the effect of restoring the high surface area of the sample and filling in any chimneys it may also give rise to metastable polymorphs of higher volatility than the most stable form, but if performed prior to every MOCVD experiment then at least this effect would be reproducible. Although this procedure has been reported to have given relatively reproducible entrainment efficiency, it is an additional step in the MOCVD process, and could be dangerous in view of the low thermal stability of some precursors, such as TMI.

Yet another approach is to abandon the conventional bubbler and use a special diffuser unit. This consists of enclosing the precursor in a vessel fitted with a porous membrane through which the precursor can diffuse at a rate determined only by the porosity of the membrane and the vapour pressure of precursor. Such diffusion is essentially independent of the rate of flow of carrier gas flowing past the other side of the membrane. Using such a set-up the concentration of precursor in the carrier gas leaving the precursor unit is inversely proportional to the rate of flow of carrier gas, rather than the case of a conventional bubbler operating under ideal conditions wherein it should be independent of the flow rate. Therefore, such a method for controlling dosimetry is reliable until very high fractional use of the sample, but the computation of the carrier gas flows to achieve a given final concentration of precursor in the reactor is more complicated. The diffuser also suffers in that the membrane tends to become progressively blocked by the formation of oxides in the pores of the membrane due to contaminants in the carrier gas, with a concomitant reduction in the rate of diffusion through it.

From an article by B.R. Butler et al, 'Variations in TMI partial pressure measured by an ultrasonic cell on an MOVPE-reactor', J. of Cr.Gr. 94 (1989), 481-487, it is known to monitor the composition of the carrier gas leaving the bubbler which is held at constant temperature in an oil bath, thereby obtaining information about both the concentration of precursor therein and its stability with time. This has been achieved by measuring the speed of sound through the vapour by passing it through an ultrasonic cell. Such an apparatus could be made to operate such that the flow of carrier gas through the bubbler compensated variations in the efficiency of pick-up. However, it is also clear that such a set-up is relatively expensive and represents an additional complication to the MOCVD process.

Some further documents on supplying precursor material are known. For example in EP 342009, in JP 03037101, and in JP 03037102, formation of well-known YBaCuO-high temperature superconductor films is presented thereby applying CVD on Y-, Ba-, and Cu-containing organic compounds. In particular, after being heated and consequently being evaporated, said compounds are entrained to a substrate to be deposited. However, in order to vaporize such compounds more easily, solvents, for example THF, are added. After the solvent has formed an adduct with the above organic compounds, the vaporized adducts as a whole are entrained. Thus vaporization temperatures could be lowered. In US 4,716,130, InP layers having specific resistivities, accomplished by entraining adducts of indium containing organic compounds (e.g. TMI, TEI) and alkylphosphines in an MOCVD process, are obtained.

Therefore, it is a main object of this invention to provide a method for carrying out an MOCVD process whereby solid precursors may be used in conventional MOCVD bubblers whilst still giving reproducibility of entrainment efficiency that is found with liquid sources under similar conditions.

It is another object of this invention to provide a source of precursor vapour which possess substantially the same vapour pressure of the desired material as would the solid source itself.

Therefore in accordance with the invention the method as mentioned above further comprises loading said carrier gas at a certain temperature with said precursor material by flowing through a liquid, containing said precursor normally solid at said temperature, preferably applied in an MOCVD process, more preferably by employing a bubbler vessel.

In an advantageous embodiment of the present invention said precursor is in contact with said liquid, and more advantageously said precursor is dissolved in said liquid.

In a further embodiment of the present invention said liquid has a vapour pressure relatively low with regard to that of the precursor, in particular at least one order of magnitude lower, and said liquid being saturated with said precursor.

In a further advantageous embodiment of the present invention during said flowing a substantial amount of said precursor originally present remains undissolved. In particular at least 50 %w, preferably 65 %w, more preferably 80 %w remains undissolved. Furthermore during the usage at most 50 %w of said liquid is evaporated.

Further details of the invention will be described now by way of example in the following description.

Besides the above explanations as to methods generally known with respect to this field of application of MOCVD it will be clear to those skilled in the art that when carrier gas is passed through a bubbler containing such a mixture, evaporation of the precursor to achieve a gas phase saturated with vapour from that precursor occurs both from the solution itself and from the surface of the excess solid precursor. This is in contrast with the case of only a solid precursor being present as then only the solid surface of the precursor acts as a source of precursor vapour. When vapour is derived from the solution then this solution becomes depleted in concentration of precursor and becomes unsaturated. However, the rate of evaporation usually employed in MOCVD experiments is so slow that this depletion is readily compensated by dissolution of more solid in the solution. Thus, the departure from a saturated solution does not appreciably change the partial pressure of precursor over this solution.

The partial pressure of precursor over such a system will remain constant and substantially equal to the vapour pressure of the pure solid precursor up until the time that the last solid precursor material has a dissolved in the solution. Thereafter, the system will exhibit a progressively lower partial pressure of precursor as the concentration of precursor in the solution reduces.

Advantageously, the amount of liquid present in the solid/liquid mixture should be such that the bottom of the bubbler dip-tube extends below its surface, thereby causing actual bubbling of carrier gas through the liquid. This would provide intimate contact between the carrier gas and the evaporating medium and would also cause agitation of the liquid surface, thereby breaking up any transitory semi-permeable oxide skins on the liquid surface. However, this need not necessarily be so, and simply the presence of a liquid film wetting the surface of each crystal of precursor has appeared to be sufficient to increase the evaporation efficiency such as to obtain reliable dosimetry of the solid precursor.

In general, the solvent used should be of low volatility to minimise its co-evaporation with the volatile precursor. In general, it may be simply a hydrocarbon of high boiling point in which the precursor dissolves. Many simple hydrocarbons are largely inert in the chemistry which occurs during MOCVD. However, the exact nature of the optimal solvent depends upon the chemical nature of the solid precursor and the material which is to be deposited in the MOCVD process.

For those skilled in the art it is clear that it is most advantageous to use the method in accordance with the invention at a temperature at which the precursor is normally used, Thus, for example TMI is processed at around ambient temperature.

Besides the above, some precursors like TMI are known to form Lewis acid-Lewis base adducts with organic compounds containing heteroatoms of Groups V and VI of the Periodic Table, notably with amines, phosphines, arsines, ethers, thioethers etc. Some of these adducts - those involving amines and phosphines - are volatile and have been used as precursors of the Group III component in MOCVD of III-V materials. The amine or phosphine moiety is inert in the process over a very wide range of conditions. Therefore, it is highly unlikely that amines or phosphines present in the source bubbler will adversely affect the properties of indium-containing materials. Furthermore, some of these adducts in the liquid state are good solvents for additional TMI, so it can be seen that such adducts would also be suitable solvents for the system described in this invention.

Other Lewis bases may give rise to deleterious incorporation of impurities in the grown layers owing to the presence of heteroatoms within the Lewis base itself; for example, oxygen could be incorporated from ethers. However, this does not entirely preclude their use, as the ether may be relatively inert in the MOCVD process, and/or its partial pressure in the vapour leaving the bubbler could be so vanishingly small that it causes no problem.

The use of such an adduct employed in this invention, because of the formation of an adduct between the precursor and the solvent compound, usually substantially lowers the volatility of the latter advantageously. In contrast, the volatility of a solvent which acts entirely as a solvent will not be greatly affected by the addition of the precursor, except to the extent of some lowering of its vapour pressure which results from its being diluted with solute.

Advantageously the above mentioned hydrocarbons have melting points below ambient temperature and boiling points of at least 150 °C, more advantageously of at least 200 °C. In an advantageous embodiment of the invention the liquid used as solvent is a straight-chain or branched aliphatic or aromatic hydrocarbon containing a least 12 carbon atoms.

A number of Lewis bases are known which upon treatment with TMI give mixtures which are liquid at ambient temperature, some of which, as mentioned above, are volatile and have been used as MOCVD precursors themselves. For the purposes of this invention, it is advantageous for the adducts to be relatively involatile, of which adducts of TMI with $[CH_2N(CH_2CH_3)]_3$ or $[CH_3O(CH_2)_2O(CH_2)_2]_2O$ (tetraglyme), which are also liquid at around ambient temperature, have been found to be so. The following examples illustrate the obtention of systems which give more reliable dosimetry from TMI held in a conventional bubbler.

Example 1

To 100 g of TMI was added 140 g of hexadecane and the mixture was allowed to stand overnight at ambient temperature. After this time 3 g of the TMI had dissolved in the hexadecane (as the molar solubility of TMI in hexadecane is 0.03:1 at 25 °C) thereby forming a slush of TMI in 143 g of liquid phase. The total contents were transferred to a bubbler conventionally used in MOCVD (the bubbler was held on a temperature of 25 °C whereas the flow rate of the carrier gas was 200 standard $cm^3$/minute), and used as a source of indium which gives reproducible dosimetry until > 80 % of the original sample of TMI is consumed.

Example 2

In the following example, for reason of comparison, especially with respect to the depletion performance of the method of the invention, in addition to the experiment carried out in accordance with the invention, results of an experiment on solid TMI are presented.

Some 70 g TMI and 12.7 g N,N-dimethyldodecylamine were added to a cylindrical stainless steel bubbler. The contents were held at 30 °C (as the molar solubility of TMI in dmda is 1.80:1 at this temperature), whereas 53 g of the solid remained undissolved. Then Pd-diffused hydrogen was used as carrier gas to entrain the TMI away. It was found that under a continuous carrier gas flow of 500 standard $cm^3$/minute, a stable output (i.e. concentration of TMI vapour in the exiting carrier gas) could be obtained from this source until around only 5 g of solid remained. This was compared with the output from a conventional solid source which initially consisted of 50 g TMI in a similar vessel. Under identical conditions of flow and temperature a progressive depletion in the output was observed after only 23 g had been consumed, even if the source was allowed to rest intermittently e.g. to achieve saturation once again.

Example 3

To 100 g of TMI was added 5 g of 1,3,5,-triethylhexahydro-1,3,5-triazine, $[CH_2N(CH_2CH_3)]_3$, and the mixture was allowed to stand overnight at 25 °C. After this time 14 g of the TMI had dissolved in the amine (as the molar solubility of TMI in $[CH_2N(CH_2CH_3)]_3$ is 3.0:1 at this temperature) thereby forming a slush of TMI in 19 g of liquid phase. This slush was then used as an indium source for MOCVD, as described in Example 1.

Example 4

To 100 g of TMI was added 2.0 g tetraglyme and the mixture was allowed to stand overnight at 25 °C. After this time some 6.6 g of TMI had dissolved in the tetraglyme (as the molar solubility of TMI in tetraglyme is 4.6:1 at this temperature) thereby forming a slush of TMI in 9.6 g of liquid phase. The slush was then used as an indium source for MOCVD, as described in Example 1.

From the foregoing description various modifications of the present invention will be apparent to those skilled in the art. Such modifications are also within the scope of the present invention.

CLAIMS

1. A method for depositing a metal originating from a metal precursor upon a suitable substrate, the method comprising transporting via a carrier gas precursor material, vaporized from said precursor, to said substrate, characterized in that said carrier gas is loaded at a certain temperature with said precursor material by flowing through a liquid containing said precursor normally solid at said temperature.

2. Method as claimed in claim 1, wherein said precursor is in contact with said liquid.

3. Method as claimed in claim 1 or 2, wherein said precursor is dissolved in said liquid.

4. Method as claimed in claims 1-3, wherein said liquid has a vapour pressure relatively low with regard to that of the precursor.

5. Method as claimed in claim 4, wherein said vapour pressure is at least one order of magnitude lower than that of the precursor.

6. Method as claimed in any one of the foregoing claims, wherein said liquid is saturated with said precursor.

7. Method as claimed in any one of the foregoing claims, wherein during said flowing a substantial amount of said precursor originally present remains undissolved.

8. Method as claimed in any one of the foregoing claims wherein during said flowing at most 50 %w of said liquid is evaporated.

9. Method as claimed in any one of the foregoing claims, wherein said method is applied in a Metal Organic Chemical Vapour Deposition (MOCVD) process.

10. Method as claimed in any one of the foregoing claims, wherein said liquid is contained in a bubbler vessel.

11. Method as claimed in any one of the foregoing claims, wherein said carrier gas is supplied through a dip-tube and said liquid is supplied to a level whereby said dip-tube extends below said level.

12. Method as claimed in claim 1, wherein said temperature is ambient temperature.

13. Method as claimed in any one of the foregoing claims, wherein the precursor is trimethylindium.

14. Method as claimed in any one of the foregoing claims, wherein the liquid is a hydrocarbon having a melting point below ambient temperature and a boiling point of at least 150 °C.

15. Method as claimed in claim 14, wherein the liquid has a boiling point of at least 200 °C.

16. Method as claimed in claim 14, wherein the liquid is a straight-chain or branched aliphatic or aromatic hydrocarbon containing at least 12 carbon atoms.

17. Method as claimed in claim 14, wherein the liquid is hexadecane.

18. Method as claimed in claim 1-13, wherein the liquid is formed by addition of a Lewis base.

19. Method as claimed in claim 18, wherein the Lewis base is N,N-dimethyldodecylamine.

20. Method as claimed in claim 18, wherein the Lewis base is 1,3,5-triethylhexahydro-1,3,5-triazine.

21. Method as claimed in claim 18, wherein the Lewis base is tetraglyme.

22. Method for depositing a metal precursor on a suitable substrate substantially as described in the description with reference to the Examples 1-4.

23. Layer arrangement containing at least one layer obtained by using the method as claimed in any one of the foregoing claims.

# INTERNATIONAL SEARCH REPORT

International Application No PCT/EP 92/01744

**I. CLASSIFICATION OF SUBJECT MATTER** (if several classification symbols apply, indicate all)[6]

According to International Patent Classification (IPC) or to both National Classification and IPC

Int.Cl. 5 C23C16/44; C30B25/14; C30B25/02; C23C16/30

**II. FIELDS SEARCHED**

Minimum Documentation Searched[7]

| Classification System | Classification Symbols |
|---|---|
| Int.Cl. 5 | C23C ; C30B |

Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched[8]

**III. DOCUMENTS CONSIDERED TO BE RELEVANT**[9]

| Category ° | Citation of Document, [11] with indication, where appropriate, of the relevant passages [12] | Relevant to Claim No.[13] |
|---|---|---|
| X | EP,A,0 022 349 (THE BRITISH PETROLEUM COMPANY LTD.)<br>14 January 1981<br>see page 8, line 16 - line 36<br>--- | 1-3,6,9,<br>12,23 |
| A | JOURNAL OF APPLIED PHYSICS<br>vol. 66, no. 3, 1 August 1989, WOODBURY, NY, USA<br>pages 1185 - 1189 , XP39851<br>K.A.SALZMAN ET AL. 'POINT OF USE ARSINE GENERATION FOR ORGANOMETALLIC VAPOR-PHASE EPITAXIAL GROWTH'<br>see page 1187, left column, line 16 - line 54; figure 1<br>--- | 4,5,7,8,<br>10,11 |
| A | US,A,4 734 999 (M.FUJISAWA ET AL.)<br>5 April 1988<br>see column 3, line 37 - column 4, line 2<br>---<br>-/-- | 13-17 |

° Special categories of cited documents : [10]

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"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

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**IV. CERTIFICATION**

1

| Date of the Actual Completion of the International Search | Date of Mailing of this International Search Report |
|---|---|
| 21 OCTOBER 1992 | 24. 11. 92 |
| **International Searching Authority** | **Signature of Authorized Officer** |
| EUROPEAN PATENT OFFICE | EKHULT H.U. |

| III. DOCUMENTS CONSIDERED TO BE RELEVANT (CONTINUED FROM THE SECOND SHEET) | | |
|---|---|---|
| Category ° | Citation of Document, with indication, where appropriate, of the relevant passages | Relevant to Claim No. |
| A | CHEMISTRY OF MATERIALS<br>vol. 3, no. 2, 1 March 1991, WASHINGTON, DC, USA<br>pages 225 - 242 , XP246429<br>P. ZANELLA ET AL. 'ORGANOMETALLIC PRECURSORS IN THE GROWTH OF EPITAXIAL THIN FILMS OF GROUPS III-IV SEMICONDUCTORS BY METAL-ORGANIC CHEMICAL VAPOR DEPOSITION'<br>see page 239, right column, line 4 - line 20<br>----- | 18-22 |

# ANNEX TO THE INTERNATIONAL SEARCH REPORT ON INTERNATIONAL PATENT APPLICATION NO. EP 9201744 SA 62743

This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report.
The members are as contained in the European Patent Office EDP file on 21/10/92
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| Patent document cited in search report | Publication date | Patent family member(s) | Publication date |
|---|---|---|---|
| EP-A-0022349 | 14-01-81 | CA-A- 1139160 | 11-01-83 |
| | | JP-A- 56025961 | 12-03-81 |
| | | US-A- 4297150 | 27-10-81 |
| US-A-4734999 | 05-04-88 | JP-A- 63011598 | 19-01-88 |



For more details about this annex : see Official Journal of the European Patent Office, No. 12/82