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D E C I S I O N
of 18 May 2001

Case Number: T 0713/96 - 3.4.3

Application Number: 90300967.8

Publication Number: 0381456

IPC: H01L 21/205

Language of the proceedings: EN

Title of invention:

Vapor-phase growth of epitaxial crystals

Applicant:

Sumitomo Chemical Company Limited

Opponent:

-

Headword:

Arsenic trihydride/SUMITOMO

Relevant legal provisions:

EPC Art. 56

Keyword:

"Inventive step (no)"

Decisions cited:

T 0495/91

Catchword:

-



Case Number: T 0713/96 - 3.4.3

D E C I S I O N
of the Technical Board of Appeal 3.4.3
of 18 May 2001

Appellant: Sumitomo Chemical Company Limited
5-33, Kitahama 4-chome
Chuo-ku
Osaka-shi
Osaka 541-0041 (JP)

Representative: Dixon, Donald Cossar
Gee & Co.
Chancery House
Chancery Lane
London WC2A 1QU (GB)

Decision under appeal: Decision of the Examining Division of the
European Patent Office posted 22 March 1996
refusing European patent application
No. 90 300 967.8 pursuant to Article 97(1) EPC.

Composition of the Board:

Chairman: R. K. Shukla
Members: G. L. Eliasson
M. J. Vogel

Summary of Facts and Submissions

I. European patent application No. 90 300 967.8 was refused in a decision of the examining division dated 22 March 1996. The ground for the refusal was that the subject matter of claim 1 according to each of the main, first and second auxiliary requests lacked an inventive step having regard to the prior art documents

D1: Journal of Crystal Growth, vol. 93, 1988, pages 543 to 549; and

D2: Journal of Crystal Growth, vol. 89, 1988, pages 131 to 136.

II. The reasoning in the decision for the finding of lack of inventive step can be summarized as follows:

- (a) Document D1 discloses a vapor-phase epitaxial growth method of forming e.g. GaAs using arsenic trihydride (arsine) as an arsenic source. It is moreover reported in document D1 that germanium and silicon impurities were found in the grown GaAs layers. Arsenic trihydride is suggested as a possible source of germanium.
- (b) The method of claim 1 differs from that of document D1 in that arsenic trihydride is purified by distillation so as to have a volatile impurity concentration of not more than 1.5 molar parts per billion on a germanium tetrahydride conversion.
- (c) Since document D1 teaches that germanium or silicon impurities in the arsenic trihydride source affect the resistivity of the grown GaAs

layers, the skilled person faced with the task of producing high-purity GaAs layers would attempt to purify the arsenic trihydride to the required degree of purity. The skilled person would consider distillation for this purpose, since distillation is considered the most basic purification method, known from e.g. document D2, and the boiling points of arsenic trihydride and the most probable germanium compound, germanium tetrahydride, are sufficiently different.

III. The appellant (applicant) lodged an appeal on 21 May 1996, paying the appeal fee on 22 May 1996. A statement of the grounds of appeal was filed on 24 July 1996 together with a copy of a prior art document

D3: D. F. Shriver and M. A. Drezdson, "The Manipulations of Air-Sensitive Compounds", Second Edition (John Wiley & Sons, New York, 1986), pages 7 to 13.

Oral proceedings were requested in case the Board intended to dismiss the appeal.

IV. At the oral proceedings held on 18 May 2001, the appellant requested that the decision under appeal be set aside and a patent be granted on the basis of one of the following requests:

Main request:

Claims: 1 to 4 filed with the letter dated
23 November 1994
5 to 10 filed with the letter dated
11 January 1996

Description: pages 1 to 7 and 9 to 33 as filed
page 8 filed with the letter dated
23 November 1994

Drawings: sheets 1/9 to 9/9 as filed with the
letter dated 6 February 1990

Auxiliary request:

Claims: 1 to 6 filed during the oral proceedings
of 18 May 2001

Description and Drawings as for the main request.

V. Claim 1 in accordance with the main request reads as follows:

"1. A vapor-phase epitaxial growth method for producing a semiconductor for a field effect transistor, the semiconductor being a compound of an element of Group III, IV or V containing arsenic, by vapor-phase epitaxial growth using arsenic trihydride as an arsenic source, wherein said arsenic trihydride is purified by distillation and has a volatile impurity concentration of not more than 1.5 molar parts per billion on a germanium tetrahydride conversion."

VI. Claim 1 in accordance with the auxiliary request reads as follows:

"1. A vapor-phase epitaxial growth method for producing a semiconductor for a field effect transistor, the semiconductor being a compound of an

element of Group III, IV or V containing arsenic, by vapor-phase epitaxial growth using arsenic trihydride as an arsenic source and trimethyl gallium as a source of the Group III element, wherein said arsenic trihydride is purified by distillation and has a volatile impurity concentration of not more than 0.2 molar parts per billion on a germanium tetrahydride conversion, and wherein the growth is carried out using amounts of arsenic trihydride and trimethyl gallium to provide an As/Ga ratio of from 20 - 80 to obtain a grown crystal having a carrier concentration of not more than $1 \times 10^{14}/\text{cm}^3$."

VII. The appellant presented essentially the following arguments in support of his requests:

- (a) According to the established case law, an objective definition of the problem to be solved by the invention should normally start from the problem described in the contested patent (cf. *Case Law of the Board of Appeal of the European Patent Office, 3rd Edition*, pages 114 to 116, OJ EPO Special Edition 1999, page 20, and T 495/91, referred in EPOR (1995), pages 516 to 524). One of the few exceptions to this Rule arises when prior art previously unknown to the applicant is revealed in e.g. the official search report. In the present case, however, document D1 which has three of the inventors as co-authors, was known to the applicant at the time the application in suit was filed but was not considered relevant for the problem the application in suit addresses.
- (b) It was known in the prior art that a vapor-phase epitaxial growth method using arsenic trihydride

as an arsenic source was not capable of producing semiconductor layers of high purity, since the impurity concentration of the semiconductor layers varied from one lot of arsenic trihydride source to the other. Therefore, the vapor-phase epitaxial growth method was not suitable for producing high purity layer which are required in e.g. GaAs field effect transistors.

In the pursuit of eliminating the variation in impurity concentration of ultra-pure semiconductors produced using vapor-phase epitaxy, the inventors were faced with the following questions:

- (1) what impurities were involved;
- (2) how much of each impurity was present;
- (3) which technique is suitable for purifying the arsenic trihydride gas; and
- (4) deciding to what degree the impurities should be reduced.

The inventive merit of the present invention is seen as a combination effect of finding answers to all the above four questions.

- (c) In document D1, the impurity concentration of GaAs layers grown by vapor phase epitaxy was found to vary depending on which container of arsenic trihydride was used, and it was confirmed that Si and/or Ge impurities were present in arsenic trihydride. Although the importance of removing the Si and Ge impurities from arsenic trihydride

is highlighted in document D1, other impurities such as oxygen, carbon and zinc are mentioned as well. Moreover, document D1 does not contain any suggestion to use distillation. Instead, a ternary Ga-In-Al melt is used for the purpose of removing oxygen impurities from arsenic trihydride (cf. D1, page 544, right hand column). Thus, document D1 fails to indicate the solution to any of the questions (1) to (4) above.

- (d) Document D2 discloses a method of purifying trimethyl indium (TMI) by distillation. For arsenic trihydride, on the other hand, it is taught to use a Ga-In-Al melt of similar type as that disclosed in document D1 for removing oxygen and water (cf. D2, page 132, left hand column, lines 20 to 24). Therefore, the skilled person would not find any information in document D2 that distillation might be useful for purifying arsenic trihydride.

- (e) The common knowledge regarding distillation technique which reduces impurity content from a value in the range of several tens of percent to one in the range of several percent is not useful for the present case, where extremely high purity is demanded. Reference is made to document D3 for conventional distillation equipment.

Reasons for the Decision

1. The appeal complies with Articles 106 to 108 and Rule 64 EPC and is therefore admissible.

2. *Inventive step - Main request*

2.1 Document D1 is a research Article investigating the role of residual impurities in GaAs and AlGaAs grown by Metal Organic Vapor Phase Epitaxy (MOVPE) using trimethyl gallium (TMG) and arsenic trihydride. Before the arsenic trihydride gas is brought to the reaction chamber for growing undoped GaAs, the arsenic trihydride is purified in a melt of Al:In:Ga to remove oxygen impurities (page 544, right hand column, first paragraph). The electron concentration of the grown samples was measured, and it was found that the electron concentration varied depending on which arsenic trihydride gas cylinder was used (page 545 "Results 3.1"; Table 4). The variation in electron concentration was found to be due to the presence of germanium and silicon donors (impurities). Since the same source of TMG was used for all the experiments, the authors concluded that the germanium and silicon impurities must have been contained in arsenic trihydride (page 546, left hand column, lines 1 to 7). This result therefore confirmed conjectures made in earlier publications that arsenic trihydride may contain germanium impurities (cf. page 543, right hand column, first paragraph; references 5 and 6). It is concluded in document D1 that most of the donor impurities, such as Ge and/or Si, is carried into the system by the arsenic trihydride gas, and therefore the reduction of shallow donor impurities, such as Ge and/or Si, in arsenic trihydride, is considered by the authors of document D1 to be the most important issue in order to achieve better GaAs layers by MOVPE using arsenic trihydride (cf. page 546, right hand column, second paragraph).

2.2 The method of claim 1 thus differs from that of document D1 in that the arsenic trihydride gas is purified by distillation and has a volatile impurity concentration of not more than 1.5 molar parts per billion (molppb) on a germanium tetrahydride conversion, whereas in document D1 no purification by distillation is carried out, and consequently the volatile impurity concentration is not below the claimed limit.

2.3 The method of document D1 has the disadvantage that the conductivity of the GaAs layers grown using highly purified TMG and various sources of arsenic trihydride was not constant.

The technical problem thus addressed by the application in suit relates to producing high-purity layers of III-V semiconductor compounds for a field effect transistor by vapor-phase epitaxial growth using arsenic trihydride.

2.3.1 The above problem is the same as stated in the application as filed (cf. the application as published, page 3, lines 41 to 47). Therefore, the arguments given by the appellant relating to the case law on the formulation of the technical problem is not relevant, since no reformulation of the technical problem is necessary, despite the fact that the closest prior art document D1 was not cited in the application as filed (cf. item VII(a) above).

2.4 Since document D1 teaches that the reduction of germanium and/or silicon impurities in arsenic trihydride is the most crucial issue for achieving better GaAs layers by MOVPE using arsenic trihydride,

the skilled person faced with the above-mentioned technical problem would take on the task to purify the arsenic trihydride gas. Thus, he first has to decide what degree of purity of the arsenic trihydride gas is desirable, and then choose a technique for purification which would attain the desired degree of purity.

- 2.5 The desired degree of purity of the arsenic trihydride is dictated by the requirements on the performance of the device to be formed using vapor-phase epitaxy. From the discussion of the prior art in the application as filed, and document D1, it follows that it was well-known in the art that the impurity concentration of the buffer layer of a GaAs field effect transistor should be at the most $1 - 2 \times 10^{14} \text{ cm}^{-3}$ in order to allow an optimum device performance (cf. the application as published, page 2, lines 51 to 54; D1, Table 4 "Electronic properties" where even lower impurity concentrations in samples S8, S9, and S11 are disclosed). A similar requirement applies for the undoped channel layer of other field effect devices, such as HEMTs, in order to obtain a high carrier mobility (cf. application, page 2, lines 26 to 43; D1, abstract; page 543, "Introduction", first paragraph). Therefore, the skilled person faced with the task of improving the vapor-phase epitaxial method known from document D1 so that high-purity layers suitable for GaAs field effect transistors can reliably be formed, would consider a method that is capable of producing GaAs layers which consistently have an impurity concentration of at most $2 \times 10^{14} \text{ cm}^{-3}$.

In claim 1, the purity of the arsenic trihydride gas is expressed in terms of germanium tetrahydride conversion, since it was not possible to directly

measure the impurity concentration in the gas itself. Instead, the purity of the gas is determined by growing a semiconductor using the arsenic trihydride gas as arsenic source, measuring the carrier concentration of the semiconductor crystal, and finally, with the aid of Figure 2 of the application in suit, the measured carrier concentration is translated into the amount of germanium tetrahydride which would have been added to pure arsenic trihydride in order to grow a semiconductor crystal with the same impurity concentration. For example, it follows from Figure 2 of the application in suit that an impurity concentration of $2 \times 10^{14} \text{ cm}^{-3}$ in GaAs corresponds to a value well below 1.5 molar parts per billion of germanium tetrahydride conversion, whereas an impurity concentration of $7 \times 10^{13} \text{ cm}^{-3}$ corresponds to about 0.2 molar parts per billion.

It should also be pointed out, that the means of expressing the impurity concentration in terms of germanium tetrahydride conversion does not make any distinction whether the impurities are in form of germanium or silicon compounds.

Since $1 - 2 \times 10^{14} \text{ cm}^{-3}$ or less is a common requirement for the undoped layer of a GaAs field effect transistor, the corresponding, claimed purity range of less than 1.5 parts per billion on germanium tetrahydride conversion would be considered by the skilled person as a matter of routine.

- 2.6 As to the choice of technique for obtaining the above chosen degree of purity, it is evident to the skilled person that the ternary melt of Al:In:Ga used in the method of document D1 to remove oxygen from the arsenic

trihydride gas is not adequate for removing Ge and/or Si compounds, since these compounds evidently remain in the gas after it has been passed through the melt. Therefore, the skilled person would have to seek a method for further purifying arsenic trihydride.

2.7 Document D2 discloses the use of a vacuum distillation apparatus for purifying the source compounds to be used in MOCVD growth of III-V compounds, in particular for purifying trimethyl indium (cf. Figure 1; abstract). It is furthermore pointed out in document D2 that fractional distillation is one of the classical laboratory and large scale methods for purifying volatile reagents (cf. D2, page 132, left hand column, penultimate paragraph).

2.8 The skilled person seeking to remove the shallow donor impurities in arsenic trihydride would therefore consider distillation as one suitable method, in particular since the use of distillation in document D2 is carried out under similarly stringent purity requirements as the method according to claim 1.

Moreover, as also pointed out in the decision under appeal, the boiling points of arsenic trihydride and the most probable germanium compound, germanium tetrahydride, are sufficiently distinct from each other that there is a reasonable expectation of success when using distillation for removing the germanium and/or silicon impurities.

2.9 The arguments of the appellant are not convincing for the following reasons:

2.9.1 The appellant argued that the skilled person making an

endeavour to solve the above problem would inevitably have to address the following four questions: (1) establishing what impurities are involved; (2) determining the concentrations of the impurities; (3) finding a technique for purifying the arsenic trihydride (cf. item VII(b) above); and finally (4) deciding to what degree the impurities should be reduced. Document D1 would, according to the appellant, not be able to aid the skilled person in any of these aspects. The inventive merit was also seen to lie in a combination effect of addressing the above questions.

In this connection as already discussed above, document D1 teaches that Ge and/or Si impurities in arsenic trihydride are considered to be the main sources for the lot-to-lot variation in electrical conductivity. Moreover, the document also discloses results of an analysis of the type of impurities as well as their concentration in GaAs samples (cf. Table 4 and Figure 1 with accompanying text). Thus, document D1 provides information as to the impurities (Si and/or Ge in arsenic trihydride) (question (1)); and their concentrations (question (2)).

As to the questions (3) and (4) referred to above, question (3) is entirely determined by the requirements of the device to be produced using the vapor-phase epitaxial growth method, and the choice of purification technique (question (4)) depends on the required degree of purity, since a particular technique for purification may only be useful in a certain range of purity.

The Board also cannot see any unexpected combination effect arising from addressing the above questions (1)

to (4), since, document D1 answers the questions (1) and (2), and the remaining issues (3) and (4) are considered to be within the routine expertise of the skilled person employing the well-established purification technique.

- 2.9.2 The appellant argued that the skilled person would not consider the distillation of document D2, since distillation is only disclosed therein for trimethyl indium, and for arsenic trihydride, a ternary melt of Al:In:Ga is recommended for the cleaning (cf. items VII(d) and (e) above).

These arguments cannot be followed, since firstly the trimethyl indium purified in the process of document D2 has to meet the same criteria for purity in order to be useful as raw material for the growth of high-quality semiconductor layers (cf. D2, section 6. "Summary"). Therefore, the skilled person would expect that distillation of the type known from document D2 would have the potential to purify arsenic trihydride as well to the required degree of purity.

Secondly, as mentioned under item 2.6 above, a ternary melt of Al:In:Ga is not effective for removing germanium and/or silicon impurities, but is used to remove oxygen and water from the arsenic trihydride gas (cf. D1, page 544, right hand column, first paragraph; D2, page 132, left hand column, second paragraph).

- 2.10 For the foregoing reasons, in the Board's judgement, the subject matter of claim 1 according to the main request does not involve an inventive step within the meaning of Article 56 EPC.

3. *Inventive step - auxiliary request*

3.1 With respect to the method according to the main request, Claim 1 according to the auxiliary request contains the further features that (i) trimethyl gallium is used as a source of the Group III element; (ii) the volatile impurity concentration is not more than 0.2 molar parts per billion on a germanium tetrahydride conversion; and (iii) the ratio of arsenic trihydride and gallium tetrahydride is between 20 and 80 to provide a GaAs layer having an impurity concentration of not more than 10^{14} cm^{-3} .

3.2 Document D1 discloses values of the ratio of arsenic trihydride to trimethyl gallium between 30 and 80 (cf. Table 4). As seen from Figure 2 of the application in suit, the limit 0.2 molar parts per billion on a germanium tetrahydride conversion corresponds to an impurity concentration in GaAs of not more than 10^{14} cm^{-3} . Since a impurity concentration of less than 10^{14} cm^{-3} still lies within what is commonly required for GaAs field effect transistors (cf. item 2.5 above), the additional features (i) to (iii) do not contribute to an inventive step.

3.3 Therefore, in the Board's judgement, the subject matter of claim 1 according to the auxiliary request does not involve an inventive step within the meaning of Article 56 EPC.

4. Thus, the appellant's main and auxiliary requests do not meet the requirement of inventive step according to Articles 52(1) and 56 EPC.

Order

For these reasons it is decided that:

The appeal is dismissed.

The Registrar:

The Chairman:

M. Beer

R. K. Shukla