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D E C I S I O N
of 9 September 1999

Case Number: T 0832/96 - 3.4.3

Application Number: 90309106.4

Publication Number: 0416774

IPC: H01L 21/321

Language of the proceedings: EN

Title of invention:
A method of treating a sample of aluminium-containing material

Applicant:
Hitachi, Ltd.

Opponent:
-

Headword:
-

Relevant legal provisions:
EPC Art. 56

Keyword:
"Inventive step: yes, after amendment"

Decisions cited:
-

Catchword:
-

Case Number: T 0832/96 - 3.4.3

D E C I S I O N
of the Technical Board of Appeal 3.4.3
of 9 September 1999

Appellant: Hitachi, Ltd.
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Decision under appeal: **Decision of the Examining Division of the European Patent Office posted 24 April 1996 refusing European patent application No. 90 309 106.4 pursuant to Article 97(1) EPC.**

Composition of the Board:

Chairman: M. Chomentowski
Members: G. L. Eliasson
W. Moser

Summary of Facts and Submissions

I. The appellant (applicant) filed the European patent application No. 90 309 106.4 (publication No. 0 416 774) containing 18 claims. Independent claim 13 and dependent claim 14 of the application as filed read as follows:

"13. A method of etching a sample of aluminum-containing material using a halogen gas and treating the samples after the etching by effecting a corrosion prevention treatment using a plasma that has at least a hydrogen component and an oxygen component."

"14. A method according to claim 13, wherein the plasma having the hydrogen component and oxygen component is a plasma of a mixture of (i) any one of methanol (CH_3OH), ethanol (C_2H_5OH), acetone (CH_3 $COCH_3$), hydrogen (H_2) and methane (CH_4), and (ii) any one of oxygen (O_2), O_3 and N_2O."

During the examining procedure, the following prior art documents were particularly considered:

D1: VLSI Electronics Microstructure Science, vol. 8, edited by N.G. Einspruch et al, Academic Press, Inc., Orlando, USA, (1984), pages 318 to 323,

D2: EP-A-0 247 603,

D4: IBM Technical Disclosure Bulletin, Vol. 24, No. 11B, April 1982, H. R. Potts, "Plasma corrosion inhibition", page 6001, and

D5: Abstract of JP-A-62 04 31 32.

II. The application was refused by decision of the Examining Division on the grounds that the subject-matter of the submitted claim requests did not involve an inventive step.

Claim 1 of the main request, which was based on claim 13 of the application as filed, read as follows:

"1. A method of treating a sample having an aluminum-containing material covered with a patterned resist, comprising the steps of:

(i) etching said sample by means of a plasma having a halogen component which generates residual adhered materials containing said halogen and carbon; and

(ii) after step (i), performing a corrosion-prevention treatment by means of a second plasma containing simultaneously hydrogen and oxygen radicals which both react with said residual adhered materials to remove them, said second plasma not being a plasma formed from a mixture of CHF_3 and O_2."

The Examining Division took the following view:

The closest prior art for claim 1 of the main request was represented by D2, which concerns a method (Method II) of stripping a photo resist on an aluminium alloy which has been etched using a dry etch process with an etching gas containing chlorine, the stripping method using a plasma of a gas comprising oxygen and a fluorinated gas such as CF_4 or CHF_3. In said Method II,

a corrosion preventing treatment could be effected simultaneously with the step of stripping the photoresist.

In D2, there was another method (Method III) of the same type which used nitrogen and oxygen in the second plasma mixture.

The claimed method was distinguished from the known methods wherein the second plasma comprised a gas mixture of oxygen and either CHF_3 or nitrogen. Thus, the object of the invention could be seen in looking for an alternative gas mixture for a method of anti-corrosion treatment.

The skilled person would thus use a gas mixture comprising an oxygen component for stripping the resist and a second component for facilitating the removal of the chlorine compounds.

For this purpose of anticorrosion treatment, it was known, from *inter alia* D4, and also from D2, to use hydrogen, alone or in a mixture.

Thus, an obvious alternative to the examples of D2 of corrosion-prevention would consist of a plasma gas mixture containing both hydrogen and oxygen.

In particular, for the substitution of hydrogen for instance for the fluorinated gases of D2, there was a good expectation of a successful removal of chlorine compounds.

Therefore, the subject-matter of claim 1 of the main

request did not involve an inventive step.

The auxiliary requests concerned either combinations of claims of the main request or combinations with additional features, and the subject-matter of these claims were thus considered to be obvious as well.

III. The applicant lodged an appeal against this decision, paid the corresponding fee and filed a statement setting out the grounds of appeal.

IV. In the annex to the summons for oral proceedings, which had been requested auxiliarily by the appellant, the Board of Appeal drew additionally attention to the following prior art documents cited in the European Search Report:

D17: IBM Technical Disclosure Bulletin Vol. 22, No. 8A, January 1980, C. Crimi et al., "Etching of aluminum and aluminum-copper alloys", page 3196, and

D18: EP-A-0 140 201.

V. During the oral proceedings of 9 September 1999, the appellant filed a new text of the application consisting of the following documents:

Claims: Nos. 1 to 6;

Description: Pages 1 to 4, 4a, 5 to 16;

Drawings: Sheets 1/2 to 2/2 (Figures 1 to 6).

Present claim 1 is the only independent claim of the set of 6 claims and, as compared to claim 1 having formed the basis of the decision under appeal, specifies that, in step (i), the halogen component is chlorine and the residual adhered material comprises chlorine, aluminium, carbon and hydrogen, and that, in step (ii), the second plasma contains radicals which are chiefly hydrogen and oxygen radicals which both react with the residual adhered materials; moreover, the disclaimer about CHF_3 has been deleted. Present claim 1 reads as follows:

"1. A method of treating a sample having an aluminium-containing material with a patterned resist, comprising the steps of:

(i) etching said sample by means of a plasma having a chlorine component which by the etching generates residual adhered materials containing chlorine, aluminium, carbon and hydrogen; and

(ii) after step (i), performing a corrosion-prevention treatment by means of a second plasma containing radicals which are chiefly hydrogen and oxygen radicals, said second plasma being such that both said hydrogen and oxygen radicals react with said residual adhered materials so as to remove them."

Moreover, the application has been amended, in particular by deleting Figures 7 to 10 and description passages, *inter alia* the pages 17 to 26.

VI. The appellant requests that the decision under appeal be set aside and that a patent be granted on the basis

of said application documents, and he submits the following arguments in support of his request:

Plasma etching of aluminium-containing wiring with a plasma post-etch process for performing a corrosion-prevention treatment is known from document D2. Although the second plasma of the known Method I and Method II contain radicals such as hydrogen (in CHF_3) and oxygen, said second plasma is in fact based on a fluorine containing plasma and results in the forming of a passivation layer on the sidewalls of the etched aluminium, and not in a step whereby the adhered residual material is removed by the mechanism proposed in the present application, where the plasma components are "chiefly" oxygen and hydrogen radicals which react with said residual materials. The relevance of document D2 is accidental because there is only one example of said methods including both oxygen and hydrogen (in CHF_3), all the examples of mixtures being in fact based on fluorine-containing plasma gas mixtures. The same remark applies to document D18.

Another method is known from document D2, i.e. Method III, wherein a combination of oxygen and a nitrogen-containing gas is used in the corrosion-prevention plasma for the same purpose. The utilization of hydrogen in addition to, or as a substitute for, nitrogen in such a mixture is not obvious because:

- the teaching of document D4 is very short and does not provide enough information about the effect of the "forming gas (hydrogen/nitrogen)" and of its constituents for the mentioned corrosion prevention; and

- the method of document D5 is for removing the organic resist on a silicon substrate, and not for the treatment of aluminium-containing wiring or for corrosion prevention, so that the skilled person had no incentive to combine document D5 with document D2.

Therefore, the subject-matter of claim 1 involves an inventive step.

Reasons for the Decision

1. The appeal is admissible.

2. *Admissibility of the amendments*

Present claim 1 is based on independent claim 13 of the application as filed; it is restricted to

- chlorine for the halogen gas in the plasma of the etching step (i), to

- materials generated by the etching which are residual adhered materials containing chlorine, aluminium, carbon and hydrogen, and to

- chiefly hydrogen and oxygen radicals, whereby both said hydrogen and oxygen radicals react with the particular residual adhered materials resulting from the etching step so as to remove them, for the second plasma for the corrosion prevention treatment having at least a hydrogen component and

an oxygen component,

respectively.

These features are based on the application as filed (see page 9, line 35 to page 11, line 28), whereby, for a particular example of a mixture of the second plasma such as claimed in dependent claim 14 of the application as filed, it is explained that the hydrogen radicals react with the chlorine component (Cl) in the residual adhered matter (Al, Cl, C, H, etc..) to form hydrogen chloride (HCl) which volatilizes or forms H_2O to dissolve the elute chlorine component contributing presumably to removing the residual chlorine component which is a cause of corrosion to the wiring film containing aluminium. It is to be noted that it is derivable from the end of the cited passage and from the whole content of the application as filed (see for instance Figure 5) that, although the particular example of mixture mentioned here above is for simultaneously removing of the corrosive material and the resist, the process, however, is not restricted to such a simultaneous procedure.

The further amendments concern the adaptation of the dependent claims and of the description and drawings to the new claim 1.

Therefore, in the Board's judgement, the present application satisfies the requirement of Article 123(2) EPC that a European patent application may not be amended in such a way that it contains subject-matter extending beyond the content of the application as filed.

3. *Clarity of the claims*

The feature of present claim 1 that the hydrogen and oxygen radicals of the second plasma are such that both said radicals react with the particular residual adhered materials resulting from the etching step so as to remove them is a functional feature. It is to be noted in this respect that it is further specified in the claim that said second plasma contains radicals which are chiefly hydrogen and oxygen radicals. As convincingly argued by the appellant, this allows to distinguish the subject-matter of present claim 1 in particular from the method using CHF_3 and O_2 taught in document D2 (see page 5, lines 7 to 10; see also page 2, lines 35 to 38) in that, in said known method,

- there is a substantial proportion of fluorine radicals, and it is thus not a mixture of chiefly hydrogen and oxygen radicals, and in that,

- it is specified that plasma-processing a substrate in a fluorinated gas such as CHF_3 results in replacing the residual chlorine atoms by the fluorine atoms produced in the etching plasma, a stable aluminium fluoride (AlF or AlF_3) being thus formed over the aluminium surface to prevent the chlorine component from reacting with the water contained in the air, so that there is no removing of the residual chlorine.

It is also to be noted that particular examples of the plasma gas components are mentioned in the present description and in dependent claim 3, and that original examples which did not correspond to the present text

of claim 1 have been deleted.

Therefore, the Board is satisfied that present claim 1 correctly defines the matter for which protection is sought and is clear in the sense of Article 84 EPC.

4. *Novelty*

The subject-matter of present claim 1 does not form part of the state of the art and is therefore new in the sense of Article 54 EPC.

5. *Inventive step*

5.1 Methods (Method I and Method II) of treating a sample having an aluminium-containing material with a patterned resist are known from document D2 (see page 3, lines 1 to 17; page 3, line 27 to page 4, line 14; page 5, lines 7 to 10), said methods comprising:

(i) etching said sample by means of a plasma having a chlorine component which by the etching generates residual adhered materials containing chlorine; and

(ii) after step (i), performing a corrosion-prevention treatment by means of a second plasma containing radicals such as hydrogen (in CHF_3) and oxygen, said second plasma being such that both the hydrogen and oxygen radicals react with said residual adhered materials.

However, as already set forth above with respect to the

clarity of the claims, and contrary to the method of present claim 1, these particular methods of document D2 are not such that the radicals contained in the second plasma are chiefly hydrogen and oxygen radicals and, indeed, in the known gas mixture which comprises gases such as CHF_3 and O_2, fluorine has an important function. Moreover, CHF_3, which is mentioned as one of a plurality of substitutes for CF_4, is the only fluorine containing gas mixture comprising hydrogen atoms, and is thus of accidental relevance.

Moreover, as also set forth above, the known gas mixture of the second plasma results in replacing the residual chlorine atoms by the fluorine atoms produced in the etching plasma, a stable aluminium fluoride (AlF or AlF_3) being thus formed over the aluminium surface to prevent the chlorine component from reacting with the water contained in the air, so that said plasma is not for removing the residual chlorine in the sense of the application in suit.

5.2 Both the method of the application in suit (see page 4, lines 16 to 20) and the method of document D2 (page 2, lines 50 to 52) have as object to provide a method of treating samples which, by a post-etch plasma treatment, is capable of imparting a high corrosion preventing performance to the aluminium-containing wiring materials.

As already set forth in the decision under appeal, starting from the particular method of document D2, wherein a second plasma with a mixture of oxygen and a fluorinated gas such as CHF_3 is used, an object of the present invention is to be seen in finding an

alternative to this known plasma gas mixture.

5.2.1 Document D18 (see page 3, lines 16 to 28; page 5, lines 15 to 24), which is concerned with a cleaning process wherein a plasma atmosphere with compounds built on the basis of fluorinated ethers comprising hydrogen and oxygen atoms is used, is not relevant because, as convincingly argued by the appellant, the mentioned fluorinated compounds, e.g. CF_2CHFO, comprise a substantial proportion of fluorine radicals and, together with document D2, would not lead to a plasma having "chiefly" oxygen and hydrogen radicals.

5.2.2 The method of document D5 acknowledged in the application in suit (see page 3, line 26 to page 4, line 6) is for removing the organic resist on a silicon substrate; it uses a treatment in a plasma of an oxygen gas obtained by adding a compound containing at least carbon or hydrogen to the oxygen, e.g., by adding methanol (CH_3OH) to the oxygen, this resulting in improved results.

However, as convincingly argued by the appellant with reference to a translation of document D5 which he has filed, this known method is not concerned with the treatment of aluminium-containing wiring and, although concerned with stripping the resist, is silent about corrosion prevention, so that the skilled person had no incentive to combine document D5 with document D2. This is also the case when considering the simultaneous stripping and corrosion prevention of present dependent claim 2, because there is no indication that this mixture of document D5 is effective against corrosion. Moreover, it is not directly derivable that methanol of

document D5 could be a substitute for CHF_3 of document D2.

5.2.3 Another method is known from document D17, whereby corrosion-free etching of aluminium in a reactive-ion etch system is effected by injecting water vapour or ethanol (i.e. C_2H_5OH) in an inert gas plasma. However, this method is indicated as being a method of etching, and not a method of post-etch treatment. Therefore, starting from document D2, a combination with document D17 does not lead in an obvious way to the method of present claim 1.

5.3 A further method (Method III) is known from document D2 (see page 4, lines 9 to 11; claim 7; see also page 5, lines 7 to 10) which uses a mixture of a nitrogen-containing gas (e.g. N_2, N_2O, NO_2) and oxygen gas for plasma corrosion prevention treatment after metal patterning to remove residual chlorine, and which can also be considered an adequate starting point for the present invention.

Indeed, it is known from D4 for the same purpose of plasma corrosion inhibition, for instance after metal patterning, to remove residual chlorine by exposing the product to a plasma with a forming gas (hydrogen/nitrogen). However, this "forming gas (hydrogen/nitrogen)" is derivable as being a mixture of hydrogen and nitrogen, and not a gas consisting of either hydrogen or nitrogen, and, moreover, proceeding from the information in this short document, there can be seen no incentive for keeping the oxygen component of the plasma mixture of Method III of document D2 while substituting hydrogen for at least some of the

nitrogen.

5.4 It is to be noted in respect of document D2 and of the two above-mentioned alternatives it comprises, i.e. Methods I and II with a mixture of a fluorinated gas with oxygen gas, on the one hand, and Method III with a mixture of a nitrogen-containing gas and oxygen gas, on the other hand, that it has already been considered to be known, for instance from the same document D2 (see page 2, lines 25 to 28 and 39 and 40), to plasma-process substrates in hydrogen gas which reacts with the residual chlorine after a plasma etching step for preventing corrosion.

However, starting from document D2, there is no information which can be derived as being an incentive for using hydrogen as a substitute for, or in combination with, the gas components of other gas mixtures mentioned therein.

5.5 Moreover, it is also to be noted that it is generally known, for instance from document D2 (see page 4, lines 50 to 56), that resists are stripped by plasma etching in an oxygen gas. However, even in the case of simultaneous stripping and corrosion prevention of Method II of document D2, a fluorine component is added and, even when considering the expression "other fluorinated gases, such as CHF_3, C_2F_6, SF_6, NF_3 or $CBrF_3$," the appellant could convince the Board that it is only in one isolated example of a substitute for CF_4 that a component (CHF_3) comprising hydrogen is added. The other prior art documents give no direct incentive for providing a mixture of chiefly oxygen radicals and hydrogen radicals for at least the step of corrosion

prevention.

Therefore, although a combination of chiefly oxygen and hydrogen radicals could be *prima facie* considered to be obvious, the skilled person had no direct teaching in this sense and it is only as a result of hindsight, i.e. by knowing the present invention, that he would arrive at the matter of present claim 1, and this is not allowable when assessing inventive step.

Moreover, the appellant could credibly show, for instance with respect to Figure 4 of the application and the corresponding text concerning a comparison of results in the particular case of simultaneous stripping and prevention treatment, that the method is effective and is advantageous in comparison with the prior art.

5.6 Incidentally, it is to be noted that document D1 has been cited several times in the decision under appeal. However, the cited information mainly related to two documents referred to in document D1, which is a review article. The appellant has credibly shown that the information in the first referred document is not as relevant as the information derivable from document D1.

The appellant has moreover provided a translation of part of the second referred document and shown that the contained information was not exactly that reported in document D1. Therefore, the appellant could convince the Board that, thus, the information contained in document D1 was not valid for use in the assessment of inventive step.

5.7 Therefore, the subject-matter of present claim 1 involves an inventive step in the sense of Article 56 EPC.

Consequently, present claim 1 is patentable in the sense of Article 52(1) EPC and, since the dependent claims 2 to 6 concern particular embodiments of the method of claim 1, they are also patentable, so that a patent can be granted on this basis (Article 97(2) EPC).

Order

For these reasons it is decided that:

1. The decision under appeal is set aside.

2. The case is remitted to the first instance with the order to grant a patent on the basis of the following documents submitted during oral proceedings of 9 September 1999:

   Claims: Nos. 1 to 6;

   Description: Pages 1 to 4, 4a, 5 to 16;

   Drawings: Sheets 1/2 to 2/2 (Figures 1 to 6).

The Registrar: The Chairman:

D. Spigarelli M. Chomentowski