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Datasheet for the decision of 5 February 2015

Case Number: T 2108/10 - 3.4.03

Application Number: 01944605.3

Publication Number: 1292973

IPC: H01L21/316, H01L21/3105

Language of the proceedings: EN

Title of invention:
METHOD TO RESTORE HYDROPHOBICITY IN DIELECTRIC FILMS AND MATERIALS

Applicant:
Honeywell International Inc.

Headword:

Relevant legal provisions:
EPC Art. 52(1), 123(2)
EPC 1973 Art. 56, 84

Keyword:
Amendments - added subject-matter (no)
Claims - clarity (yes)
Inventive step - (yes)

Decisions cited:
T 1019/99

Catchword:

This datasheet is not part of the Decision.
It can be changed at any time and without notice.

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Case Number: T 2108/10 - 3.4.03

D E C I S I O N
of Technical Board of Appeal 3.4.03
of 5 February 2015

Appellant: (Applicant)	Honeywell International Inc. 101 Columbia Road Morristown, NJ 07960 (US)
Representative:	Clarke, Lionel Paul Gill Jennings & Every LLP The Broadgate Tower 20 Primrose Street London EC2A 2ES (GB)
Decision under appeal:	**Decision of the Examining Division of the European Patent Office posted on 28 May 2010 refusing European patent application No. 01944605.3 pursuant to Article 97(2) EPC.**

Composition of the Board:

Chairman	G. Eliasson
Members:	S. Ward
	T. Karamanli

Summary of Facts and Submissions

I. The appeal is against the decision of the Examining Division refusing European patent application No. 01 944 605 on the grounds that the claimed subject-matter did not meet the requirements of Articles 123(2), 84, 52(1) and 56 EPC.

II. The following documents cited by the Examining Division are referred to in this decision:

D1: WO 00 02233 A

D2: LIU P ET AL: Enhancing the Oxygen Plasma Resistance of Low-*k* Methylsilsesquioxane by H_2 Plasma Treatment, Japanese Journal of Applied Ahysics, Vol. 38, Part 1, No. 6A, June 1999, pages 3482-3486

Reference is also made to a statutory declaration made by Ms Teresa A Ramos, a co-inventor of the invention disclosed in document D1, which was filed by the appellant with the statement of grounds of appeal.

III. The appellant requested in writing that the decision under appeal be set aside and that a patent be granted in the following version:

Description, pages:	16, 20, 24-26 as published; 1, 2, 2a, 3, 4, 4a, 7, 8, 10a, 11-14 and 21, 23 filed with the letter dated 19 January 2015; and 5, 5a, 6, 8a, 9, 9a, 10, 15 and 17-19, 19a filed with the letter dated 26 January 2015; (page 22 deleted);

Claims, numbers:	1-15 filed with the letter dated 19 January 2015;
Drawings, sheets:	1/2-2/2 as published.

IV. Claim 1 (the sole independent claim) reads as follows:

"1. A method of imparting hydrophobic properties to a damaged silica dielectric film present on a substrate, wherein said dielectric film has been contacted with at least one etchant or ashing reagent in such a way as to substantially damage or remove previously existing hydrophobicity of said dielectric film, the method comprising:

a) contacting the damaged silica dielectric film with a surface modification composition at a concentration and for a time period effective to render the silica dielectric film hydrophobic; and

b) removing unreacted surface modification composition, reaction products and mixtures thereof,

wherein the surface modification composition comprises at least one surface modification agent suitable for removing silanol moieties from the damaged silica dielectric film, said surface modification agent is a compound having a formula selected from the group consisting of: $R_3SiNHSiR_3$, R_xSiCl_y, $R_xSi(OH)_y$, $R_3SiOSiR_3$, $R_xSi(OR)_y$, $M_pSi(OH)_{[4-p]}$, $R_xSi(OCOCH_3)_y$ *and combinations thereof,*

wherein X is an integer ranging from 1 to 3,

y is an integer ranging from 1 to 3 such that y=4-X,

p is an integer ranging from 2 to 3;

each R is independently selected from hydrogen and a hydrophobic organic moiety;

each M is an independently selected hydrophobic organic moiety; and R and M can be the same or different."

V. The Examining Division argued essentially as follows with respect to the main request then on file:

Claims 17, 19, 26, 27, and 30 did not comply with the provisions of Article 123(2) EPC.

The application did not meet the requirements of Article 84 EPC, because claim 1 of the main request attempted to define the invention by a result to be achieved. In particular, claim 1 attempted to define a method to impart hydrophobicity of a silica film by applying a surface modification composition comprising an agent suitable to remove silanol moieties. However, no agents or chemicals to achieve this goal were specified.

In the independent device claims, an attempt was made to define devices by referring to their methods of manufacture rather than by defining them by device features. If these method steps indeed imparted different properties on the final device/product, these properties would need to be specified as distinguishable device features and not as method steps.

The subject-matter of claim 1 also did not involve an inventive step (Article 56 EPC) in view of the combination of Documents D1 and D2.

Document D2 (the closest prior art) disclosed a method of pretreating a silica dielectric film in order to avoid damage to the film during subsequent processing. The pretreatment (H_2 plasma treatment) reduced the formation of silanol (Si-OH) groups during the ashing process step, the silanol groups being responsible for

moisture absorption and increase in dielectric constant.

The subject-matter of claim 1 differed from the method disclosed in D2 in that the silica dielectric film was treated with a surface modification composition after having been damaged by the ashing step.

Document D2 showed that hydrophobicity was desirable, that the ashing process damaged the film by changing the surface groups of the film to silanol groups which are hydrophilic, and that the disclosed pretreatment did not completely inhibit damage to the films. Hence, the objective technical problem was how to further improve the hydrophobicity of the damaged silica dielectric film.

Dl disclosed a method for increasing hydrophobicity of silica dielectric films comprising contacting a silica film with a surface modification composition which comprises an agent suitable for removing silanol moieties from the silica film (silylation of silanol moieties). Moreover, Dl disclosed the surface modification compositions as claimed in claim 1 [of the auxiliary request, now in claim 1 of the main request]. Dl further taught removing unreacted surface modification composition from the film.

The skilled person, when searching for a method to improve hydrophobicity of a silica dielectric film, would inevitably consult Dl which disclosed such a method. As a consequence, the skilled person would take the teaching of Dl to increase the hydrophobicity and combine it with the teaching of D2.

The objections against the main request under Articles 123(2) and 56 EPC, as well as the objections against the subject-matter of the independent product claims of the main request under Article 84 EPC, also applied *mutatis mutandis* to the auxiliary request on which the contested decision was based.

VI. The appellant's arguments may be briefly summarised as follows:

The claims objected to by the Examining Division under Article 123(2) EPC had been deleted in their entirety.

In relation to Article 84 EPC, claim 1 was now almost identical to claim 1 of the first auxiliary request before the Examining Division, against which no clarity objection had been raised.

The skilled person would not arrive at something falling within the scope of claim 1 by combining the teaching of Dl with the disclosure in D2.

The problems described in Dl and the problems described in the present Application were different. This was an important distinction, and "has not been given proper consideration by the Examining Division."

The claimed invention provides a solution to the problem of imparting hydrophobic properties to a damaged silica dielectric film present on a substrate, wherein said dielectric film has been contacted with at least one etchant or ashing reagent in such a way as to substantially damage or remove previously existing hydrophobicity of said dielectric film. There is nothing in the art that would lead one to believe that the materials of Dl could be used to repair damage from

such etchants or ashing reagents as taught by the Applicant.

Dl had nothing to do with a silica dielectric film which had been damaged, but concerned the production of a nanoporous silica dielectric film, and the subsequent treatment of the undamaged nanoporous silica dielectric film by contacting it with a surface modification agent. This was the end of the process disclosed in Dl and was the starting point of the present method.

Document D2, like D1, was unrelated to the treatment of damaged films, and focused on the preventive benefits of hydrogen plasma on films which had not been contacted with an etching or ashing reagent prior to the hydrogen plasma treatment.

Furthermore, one of ordinary skill in the art would have expected a post-etch silylation treatment to be undesirable, as it would be expected that the silylation agent would add an undesirable build-up on the side walls inside the freshly etched vias and/or trenches by reaction with silanols at the via/trench sidewalls.

Reasons for the Decision

1. The appeal is admissible.

2. *Article 123(2) EPC*

2.1 The subject-matter objected to under Article 123(2) EPC in the contested decision no longer appears in the

claims of the main (and sole) request, and hence this objection has been rendered moot.

Claim 1 is essentially based on claims 1 and 3 as originally filed. Claims 2-15 are based on claims 2 and 4-16 as originally filed. The description has been suitably adapted to the current claims without, in the opinion of the Board, adding subject-matter which extends beyond the content of the application as filed. The Board is therefore satisfied that the requirements of Article 123(2) EPC are met.

3. *Article 84 EPC 1973*

3.1 The objection of the Examining Division under Article 84 EPC 1973 that claim 1 failed to specify the surface modification agents suitable for removing silanol moieties according to the invention has been overcome by the incorporation of the subject-matter of claim 3 as originally filed into claim 1.

3.2 The objections under Article 84 EPC 1973 in the contested decision against the independent product claims have been rendered moot by the deletion of these claims.

3.3 The Board sees no further objections in this respect, and hence is satisfied that present claims 1-15 meet the requirements of Article 84 EPC 1973.

4. *Inventive Step*

4.1 The Board agrees with the Examining Division that document D2 is to be regarded as the closest prior art. The subject-matter of claim 1 differs from document D2 in that the claimed method:

a) is a method of imparting hydrophobic properties to a *damaged* silica dielectric film present on a substrate, wherein said dielectric film *has been contacted* with at least one etchant or ashing reagent in such a way as to substantially damage or remove previously existing hydrophobicity of said dielectric film (emphasis added by the Board);

b) comprises the step of contacting the *damaged* silica dielectric film with a surface modification composition (emphasis added by the Board);

c) employs a surface modification agent being a compound having a formula selected from the group consisting of $R_3SiNHSiR_3$, R_xSiCl_y, $R_xSi(OH)_y$, $R_3SiOSiR_3$, $R_xSi(OR)_y$, $M_pSi(OH)_{[4-p]}$, $R_xSi(OCOCH_3)_y$ and combinations thereof; and

d) comprises a step wherein unreacted surface modification composition, reaction products and mixtures thereof are removed.

4.2 According to established case law, "the correct procedure for formulating the problem is to choose a problem based on the technical effect of exactly those features distinguishing the claim from the prior art that is as specific as possible without containing elements or pointers to the solution" (T 1019/99, point 3.3 of the Reasons). Hence, in the present case, the objective problem cannot be regarded as merely obtaining an improvement in hydrophobic properties in a general silica film, but must reflect the specific technical contribution of the invention as claimed, in that the method results in a film having a reduced

level of damage and loss of hydrophobicity despite having been in contact with an etchant or ashing reagent.

The problem to be solved may therefore be regarded as reducing the damage to a silica dielectric film resulting from the application of aggressive plasmas and/or etching reagents which cause a loss of hydrophobicity and an increased dielectric constant (see e.g. page 4, line 6 to page 5, line 8 of the application).

4.3 This is essentially the same problem addressed by document D2, which deals with reducing the damage suffered by a Methylsilsesquioxane (MSQ) dielectric film caused by oxygen plasma during photoresist stripping (see abstract; page 3482, passage bridging left and right hand columns, and first complete paragraph in the right hand column).

The solution proposed in document D2 involves applying a hydrogen plasma treatment to the MSQ film *prior* to the O_2 plasma ashing. As pointed out by the appellant, this approach is based on *prevention*, as "the H_2 plasma treatment can enhance the resistance of MSQ film to O_2 plasma attack during photoresist stripping" (D2, page 3485, last sentence of the first paragraph).

4.4 In the contested decision, it was essentially argued that, starting from document D2 and attempting to reduce further the damage to the silica film, a skilled person would (firstly) find it obvious to incorporate the teachings of document D1 to solve the objective problem, and (secondly) would thereby be led to the solution of the present invention. The Board does not find either of these assertions convincing.

4.5 Firstly, as stated above, the objective problem relates to reducing damage caused to a silica dielectric film by ashing or etching during the manufacture of ICs. Document D1 not only fails to disclose any solution to this problem, it does not even acknowledge that this problem exists.

Document D1 discloses surface modification agents, including those mentioned in present claim 1 (see e.g. D1, claim 2). However, they are used for a different purpose, namely for "*converting the starting nanoporous silica film into one that has a stable and low dielectric constant suitable for use in producing integrated circuits...*" (page 9, lines 16-20). There is no mention of ashing, etching or any other IC manufacturing step or the damage to a silica film which may result from such processes.

It cannot therefore be considered convincing that a skilled person would look for a solution to the above-mentioned technical problem in document D1, a document which is in no way concerned with this problem.

4.6 Secondly, even if it occurred to a skilled person to combine the teachings of documents D2 and D1, the most that could be expected is that the surface modification agents of document D1 would be applied in the manner and for the purposes disclosed in document D1, namely as a treatment to be applied to the starting silica layer *before* the integrated circuit processing steps to provide a stable and low dielectric constant. This would not lead to the method of present claim 1.

4.7 Unlike document D2, which proposes the *prevention* of damage to the silica film by means of a hydrogen plasma

pre-treatment applied prior to plasma ashing, and document D1 which is silent on the matter of damage to the silica film, the idea behind the present invention is to employ surface modification compositions for *repairing* or *reversing* damage already caused in a silica dielectric film by previous ashing or etching steps (see description as originally filed, page 8, lines 25-28). Such an approach is not disclosed in the available prior art.

The Board can accept that some of the technical details on which the present invention is based are individually disclosed in documents D2 and D1. The pertinent question, however, is whether a skilled person - lacking any capacity for creative or imaginative thought - would go beyond what is presented in these documents and arrive at the concept of applying surface modification agents *after* etching or ashing to *repair* damage caused by these processes.

Given that there is no hint of such a repair strategy in any of the available prior art citations, the Board's answer to this question is no.

4.8 Finally, although document D1 discloses the removal of any unreacted surface modification composition, the claimed removal of the *reaction products* is not disclosed. In document D1 it appears that the reaction products (the capped silanols) remain in place after the reaction to "result in a film with effective hydrophobicity" (see e.g. page 11, lines 25-29).

Within the context of the claimed method, however, in which the surface modification takes place after the etching/ashing steps, the negative consequences of allowing the silylation products to remain in the

etched vias or trenches have been plausibly set out by the appellant (see e.g. the Statutory Declaration of Ms Teresa A Ramos, points 15 and 16). Hence the removal of the reaction products is considered to be a further significant difference between the claimed subject-matter and the prior art.

4.9 The Board therefore judges that the method of claim 1 involves an inventive step within the meaning of Article 56 EPC 1973. The remaining claims 2-15 are dependent, directly or indirectly, upon claim 1.

Order

For these reasons it is decided that:

1. The decision under appeal is set aside.

2. The case is remitted to the department of first instance with the order to grant a patent in the following version:

Description pages:	16, 20, 24-26 as published; 1, 2, 2a, 3, 4, 4a, 7, 8, 10a, 11-14 and 21, 23 filed with the letter dated 19 January 2015; and 5, 5a, 6, 8a, 9, 9a, 10, 15 and 17-19, 19a filed with the letter dated 26 January 2015; (page 22 deleted);
Claims, numbers:	1-15 filed with the letter dated 19 January 2015;
Drawings, sheets:	1/2-2/2 as published.

The Registrar: The Chairman:

S. Sánchez Chiquero G. Eliasson

Decision electronically authenticated