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Bezeichnung der Erfindung: Process for producing a semiconductor device having
Title of invention: an insulating layer of silicon dioxide covered by a
Titre de l'invention : film of silicon oxynitride

Klassifikation / Classification / Classement : H01L 21/318

ENTSCHEIDUNG / DECISION

vom / of / du 13 September 1990

Anmelder / Applicant / Demandeur :

Patentinhaber / Proprietor of the patent /
Titulaire du brevet : Fujitsu Limited

Einsprechender / Opponent / Opposant : Siemens AG

Stichwort / Headword / Référence :

EPÜ / EPC / CBE Art. 56 EPC

Schlagwort / Keyword / Mot clé : "Inventive step - main and first to fourth auxiliary requests: no; fifth auxiliary request: yes"

Leitsatz / Headnote / Sommaire

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Case Number : T 329/89 - 3.4.1

D E C I S I O N
of the Technical Board of Appeal 3.4.1
of 13 September 1990

Appellant : (Proprietor of the patent)
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Respondent : (Opponent)
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Representative :

Decision under appeal : **Decision of Opposition Division of the European Patent Office dated** 25 January 1989 and posted on 16 March 1989, **revoking European patent No.** 0 006 706 **pursuant to Article 102(1) EPC.**

Composition of the Board :

Chairman : K. Lederer
Members : J. Roscoe
L. Mancini

Summary of Facts and Submissions

I. European patent No. 0 006 706 was granted on the basis of European patent application No. 79 301 114.9.

II. The Respondent filed a notice of opposition against the patent, requesting that it be revoked in its entirety because of lack of inventive step in view, inter alia, of the following documents:

DE-A-1 644 012 (D2);
IBM Technical Disclosure Bulletin, Vol. 19, No. 3, August 1976, page 905 (D4);
IBM Technical Disclosure Bulletin, Vol. 17, No. 8, January 1975, page 2330 (D5); and
US-A-3 385 729 (D10).

III. The Opposition Division revoked the patent.

IV. The Appellant (patentee) lodged an appeal against the decision.

V. Oral proceedings were held before the Board, at the end of which the Appellant requested that the decision under appeal be set aside and, according to his main request, that the patent be maintained in amended form on the basis of a set of Claims 1 to 7 of the main request as filed during the oral proceedings.

Claim 1, the only independent claim of the set of claims in accordance with Appellant's main request, reads as follows:

"1. A process for producing a semiconductor device, having an insulating film having a film of silicon dioxide covered by a film of silicon oxynitride, comprising the steps of

forming an exposed film of silicon dioxide and heating said silicon dioxide film in a nitriding atmosphere, characterised in that the silicon dioxide film has a thickness between 3 and 70 nm and the silicon oxynitride insulating film is formed by heating at 900 to 1300°C in a nitriding atmosphere that consists of 100% ammonia, optionally together with inert gas."

Alternatively, the Appellant requests that the patent be maintained as amended in accordance with either of five successive auxiliary requests.

Claim 1 of Appellant's first auxiliary request is distinguished from Claim 1 of his main request only by the addition, at the end of the latter claim, of the words "and in that the silicon oxynitride is formed to a thickness of 3 to 18 nm".

Claim 1 of Appellant's second auxiliary request corresponds to Claim 1 of his main request, the word "semiconductor" being however replaced by "MIS".

Claim 1 of Appellant's third auxiliary request corresponds to Claim 1 of his first auxiliary request, the word "semiconductor" being however replaced by "MIS".

Claim 1 of Appellant's fourth auxiliary request reads as follows:

"1. A process for producing an MIS semiconductor device comprising the steps of:

(a) forming, on a substrate, an exposed film of silicon dioxide comprising, portions thereof corresponding to the MIS structure and having a thickness of 3 to 70 nm and the

remaining portions thereof having a larger thickness than that of the above-mentioned portions,
(b) converting at least a portion of the silicon dioxide film to a dense and uniform silicon oxynitride insulation film having a thickness of 3 to 19 nm by heating the silicon dioxide film at a temperature of 900°C to 1300°C in a nitriding atmosphere consisting of 100% ammonia and optionally an inert gas;
(c) forming a gate metal on the silicon oxynitride insulating film; and
(d) patterning the gate metal to form the gate for the MIS structure".

The set of claims in accordance with Appellant's fifth auxiliary request comprises five claims filed during the oral proceedings as fifth auxiliary request, of which Claim 1, the only independent claim, reads as follows:

"1. A process for producing a semiconductor device, having an insulating film having a film of silicon dioxide covered by a film of silicon oxynitride, comprising the steps of forming an exposed film of silicon dioxide and heating said silicon dioxide film in a nitriding atmosphere, characterised in that the silicon dioxide film has a thickness between 3 and 70 nm and the silicon oxynitride insulating film is formed by heating at 900 to 1300°C in a nitriding atmosphere that consists of 100% ammonia, optionally together with inert gas, and in that the silicon dioxide film is made by the preliminary step of forming a silicon nitride surface film by thermal nitridation of a silicon surface layer of a silicon substrate and converting the exposed surface of the silicon nitride film to silicon dioxide by oxidation."

Each of Appellant's main and auxiliary requests further calls for the description and the drawings of the patent to be adapted to the corresponding claims.

The Respondent (opponent) for his part requests that the appeal be dismissed.

VI. Appellant's arguments in support of his requests can be summarised as follows:

Whilst document D5 indeed disclosed a semiconductor device comprising a thin insulating film made of a layer of silicon dioxide covered by a layer of silicon oxynitride, the composite insulating film was obviously constituted by adjacent layers each formed by successively applied classical controlled vapour deposition techniques. Consequently, internal stresses built up within the thin insulating film, at the interfaces between the individual layers, and the film could not exhibit the flatness, smoothness and uniformity required by thin insulating films to ensure optimal operation of the semiconductor devices in which they are included.

In contrast, the invention afforded a technique for forming thin insulating films made of silicon dioxide covered by silicon oxynitride which exhibited superior insulating properties because of a continuous, gradual transition between the compositions of the silicon dioxide and silicon nitride layers.

The teaching of document D10 was clearly directed to the formation of thick field oxide layers as used for isolating adjacent active device areas on a common semiconductor substrate. There was however no suggestion in D10 to use the same process conditions to form a thin insulating film as needed for instance in MIS devices. In particular, the

process disclosed in D10 was explicitly said to result in the formation of needle-like protrusions on the upper surface of the film, which would have deterred the skilled person from using this process for forming thin insulating films in which such needles would be expected to affect the electrical field distribution in the film and therefore cause the appearance of detrimental hot spots.

In addition, the skilled person at the date of the invention had no clear understanding of what really happened in silicon dioxide films when subjected to heating in a nitriding atmosphere, and certain documents published both earlier and later drew attention to the appearance of nitrogen piling up beneath a silicon dioxide film when subjected to the process conditions set out in the claims (see in particular Philips Journal of Research, Vol. 38, 1983, pages 19 to 36). Accordingly, the skilled person striving to improve the characteristics of thin films would not without hindsight and as a matter of mere routine have investigated the suitability of a process known only to be effective for forming thick films.

Finally, even if it was assumed that the technical effect of achieving a graduated transition from silicon dioxide to silicon nitride was already obtained in the conditions described in D10, this technical effect was not itself disclosed in the document but made available only by the invention. Accordingly, following the principles set out in the decision G 2/88 (OJ EPO 1990, 93) in connection with the discovery of a new property (friction reducing effect) of an oil additive known for its anti-corrosive properties, patent protection should not be denied to an invention based on the discovery of the advantageous effect of the process of document D10 on the fine structure of the resulting insulating films.

Concerning more particularly Appellant's fifth auxiliary request, forming the silicon dioxide film by the preliminary step of thermally nitriding a silicon surface layer of a silicon substrate and then converting the exposed surface of the silicon nitride film thus obtained to silicon dioxide by oxidation results in a particularly dense silicon dioxide film of improved insulating properties because of the excellent structural characteristics of the underlying silicon nitride film. This relatively complicated and rather illogical way of forming a thin film including a terminal layer of silicon oxynitride by first forming silicon nitride and converting it into silicon dioxide before re-converting thus obtained silicon dioxide into silicon oxynitride was not in any way suggested by the prior art.

VII. The Respondent essentially contended that the teaching of document D10 was of general nature and that a skilled person would, without the exercise of inventive ingenuity, have contemplated the use of the process described there also for forming the thin insulating films disclosed in document D5.

The choice of a thickness between 3 and 70 nm or between 3 and 18 nm for the silicon dioxide film on which to perform the nitriding process of document D10 was no more than the outcome of the constant trend in the semiconductor technology towards ever more miniaturised devices, and could not be considered as an inventive selection. In particular, the Appellant neither disclosed nor demonstrated that any specific effect occurred only when the silicon dioxide being nitrided was of the indicated thicknesses, but not, for instance, when it was in the thickness range between 200 and 2000 nm which was both covered by the patent as granted and disclosed in document D10. Quite on the contrary, the later published document

Philips Journal of Research referred to by the Appellant himself shows that under the process conditions set out in the present patent the film structure is independent of the oxide thickness.

Concerning Appellant's fifth auxiliary request, document D10 calls only for the disclosed process to be performed on a layer of silicon dioxide, without prescribing any specific way of forming such starting layer. Document D2 not only disclosed that thermal nitridation of a silicon surface resulted in an extremely adhesive layer of silicon nitride, which was further said in document D4 to form relatively dense films, but also taught the subsequent oxidation of the obtained silicon nitride film into silicon dioxide. Accordingly, no inventive step could be recognised in the choice of the technique of document D2 to form a layer of silicon dioxide on which to perform the process of document D10.

Reasons for the Decision

1. The appeal is admissible.

2. Appellant's main request

2.1 Novelty

(a) Document D5 discloses a semiconductor device (a MISFET transistor) comprising an insulating film comprising a layer 16; Figure) of thermal silicon dioxide having a thickness between 3 and 70 nm (about 10 nm) covered by a film of silicon oxynitride (18); see last paragraph in connection with the figure. Document D5 does not however specify in which way the oxynitride layer is obtained.

Thus, the process set out in Claim 1 is distinguished from the teaching of document D5 in that it requires the silicon dioxide film to be heated at 900 to 1300°C in a nitriding atmosphere consisting of 100% ammonia, optionally together with inert gas.

(b) Document D10 discloses a process for producing a semiconductor device having an insulating film having a film of silicon dioxide covered by a further insulating film, comprising the steps of forming an exposed film of silicon dioxide and heating said silicon dioxide film at 900 to 1300°C in a nitriding atmosphere that consists of "high purity anhydrous", i.e. 100%, ammonia, optionally together with inert gas; see abstract and column 4, lines 34 to 75.

The insulating film formed over the silicon dioxide film according to the process disclosed in document D10 is said therein to be formed of silicon nitride whilst it is specified in Claim 1 to be constituted by silicon oxynitride. However, the process of Claim 1, being performed under exactly the same operating conditions as that described in D10, would inevitably produce the same effect on the silicon dioxide film to which it is applied. This has not been contested by the Appellant.

Accordingly, the process set out in Claim 1 is distinguished from the process disclosed in document D10 only in that the silicon dioxide film subjected to nitridation has a thickness between 3 and 70 nm, whilst the silicon dioxide film in D10 is grown to a thickness between 200 and 2000 nm (column 3, lines 61 to 63).

(c) The remaining documents on the file do not come closer to the subject-matter of Claim 1.

(d) For these reasons, the subject-matter of Claim 1 is novel in the sense of Article 54 EPC.

2.2 Inventive step

(a) The nearest prior art is, in the Board's view, constituted by document D5 which the Appellant also implicitly considers to be the starting point of his invention.

Document D5 discloses a multilayered gate dielectric structure consisting of a succession of thin insulating films of silicon dioxide, silicon oxynitride and silicon nitride (first paragraph) and stresses its superiority over most conventional structures comprising only silicon nitride over silicon oxide which often exhibit certain instabilities (second paragraph). The document does not reveal how the described insulating structure should be formed. Accordingly, the technical problem to which the subject-matter of Claim 1 achieves a solution is to be seen in providing a process by which a multilayered insulating structure comprising silicon nitride over silicon dioxide, possibly with an intermediate layer of silicon oxynitride, could actually be formed.

(b) Document D10 pertains to the same general technical field as document D5, which is the manufacturing of integrated semiconductor circuits, and it discloses a process for forming an insulating film consisting of so-called "silicon nitride" covering silicon dioxide by heating the latter at 900 to 1300°C in a nitriding

atmosphere consisting of 100% ammonia, optionally together with inert gas (see point 2.1(b) above). This process admittedly is disclosed only in connection with the formation of thick insulating field oxide films as commonly used in the semiconductor devices produced at the filing date of the document (October 1964), when thin gate insulating structures such as that of document D5 could hardly have been envisaged. However, at the date of the invention (June 1978), the skilled person would find in document D10 which, incidentally, does not impose any limitation on the film thicknesses in its claim, no indication or suggestion that the process described would not be just as effective when applied to thinner silicon dioxide layers.

In particular, the statements in D10 that the process produces needle-like protrusions of silicon nitride on the surface of the silicon dioxide that form growth nucleating centres during the subsequent vapour deposition of polycrystalline silicon would not, in the Board's view, have deterred the skilled person from envisaging the use of the same process to form thin gate insulating layers of MIS devices. For, on the one hand, growth nucleating centres for polycrystalline silicon may obviously be of interest also in the latter application and, furthermore, needle-like protrusions formed in the upper portion of the insulating film and pointing towards the gate electrode would not be expected to result in a marked degradation of the electrical properties of the film as they might well if they pointed in the opposite direction. On the other hand, document D10 teaches that conversion of the silicon dioxide into silicon nitride to a depth of only 50 -200 nm provides adequate growth nucleation centres (column 2, lines 38

to 42), which implies that such growth nucleation centres would not appear in silicon nitride layers of inferior thicknesses. Accordingly, the problem of the formation of needle-like protrusions would not have been of any serious concern to a skilled person estimating the capacity of the disclosed process to form also thinner insulating layers.

The Board therefore holds that the skilled person would actually have envisaged the use of the process of document D10 to form thin insulating layers as required in the semiconductor device of document D5 and expected it to achieve satisfactory results when used, which he could have confirmed by mere routine tests well within his professional capacity, and that he would thus have arrived at the claimed process without the exercise of any inventive ingenuity.

The Appellant contended that the invention amounted to the discovery of a novel effect, namely that the process disclosed in D10 achieved a gradual transition between the silicon dioxide and silicon nitride layers, which avoided the drawbacks resulting from the presence of interfaces within the conventional insulating films and justified the patentability of the claimed process in conformity with the findings in the decision G 2/88.

It should be noticed in this respect that the decision of the Enlarged Board of Appeal referred to by the Appellant dealt only with the novelty of the use of a known compound for a particular purpose, such use being based on a technical effect not disclosed in the prior art. Novelty however is not in question in the present case and, furthermore, the invoked decision cannot in any way be interpreted as meaning that the

disclosure in a patent of a technical effect which was not described before should necessarily be considered to involve an inventive step. In the present case, the thermochemical reaction by which silicon dioxide is converted to silicon nitride in accordance with document D10 clearly involves diffusion of oxygen and nitrogen in opposite directions through the layer in which conversion takes place, otherwise silicon nitride could not be formed to a depth of 50 to 200 nm as disclosed in D10 (column 2, lines 38 to 42). Such diffusion processes, by their very nature, cannot but produce a certain gradient of composition between the regions in which diffusion has occurred and those in which it has not. The mere confirmation, however, of the occurrence of a technical effect which the skilled person would have expected to be produced by a known process cannot by itself positively contribute to the assessment of inventive step.

(c) For these reasons, the subject-matter of Claim 1 does not involve an inventive step in the sense of Article 56 EPC.

2.3 Accordingly, the patent as amended in accordance with Appellant's main request and the invention to which it relates do not meet the requirements of the Convention as is required under Article 102(3) EPC, and Appellant's main request, therefore, cannot be accepted.

3. Appellant's first to fourth auxiliary requests

3.1 Claim 1 in accordance with Appellant's first auxiliary request is distinguished from Claim 1 of the main request only by the further indication that the silicon oxynitride is formed to a thickness of 3 to 18 nm.

The independent Claims 1 in accordance with Appellant's second and third auxiliary requests are distinguished from the corresponding independent claims of his main and first auxiliary requests only in that they specify that the semiconductor device produced by the process is a MIS device.

The semiconductor device disclosed in document D5 comprises a film of silicon oxynitride formed to a thickness of 10 nm (third paragraph) and it clearly constitutes a MISFET device. Since the only additional features of the independent Claims 1 in accordance with Appellant's first to third auxiliary requests are all disclosed in document D5, which forms the starting point of the reasoning set out above in connection with Claim 1 of the main request, the same reasoning also applies to the assessment of patentability of said auxiliary requests.

Accordingly, the subject-matter of the independent Claims 1 of the Appellant's first to third auxiliary requests does not involve an inventive step either, and these auxiliary requests therefore cannot be accepted.

3.2 Claim 1 in accordance with Appellant's fourth auxiliary request corresponds in substance to the subject-matter of Claim 1 of the third auxiliary request with the following additional limitations:

- the exposed film of silicon dioxide further comprises portions which do not correspond to the MIS structure portions and have a larger thickness than that of the latter portions;

- the gate metal is formed on the silicon oxynitride insulating film; and

- the gate metal is patterned to form the gate for the MIS structure.

These additional steps define standard procedures in the manufacturing of MIS semiconductor devices, as illustrated for instance by the document IEEE Spectrum October 1969, pages 28 to 32 cited in the Board's communication of 1 March 1990 and the Appellant did not put forward any argument in support of their non-obviousness.

For these reasons, the subject-matter of Claim 1 in accordance with Appellant's fourth auxiliary request does not involve an inventive step in the sense of Article 56 EPC and this request, therefore, cannot be allowed.

4. Appellant's fifth auxiliary request

4.1 The Claims in accordance with Appellant's fifth auxiliary request meet the requirements of Article 123(2) and (3) EPC.

In particular, the range of between 3 and 70 nm set out in Claim 1 for the thickness of the silicon dioxide film results from an admissible limitation of the originally disclosed range of between 3 and 2000 nm (page 17 as originally filed, lines 19 to 22) by introduction as an upper limit of a specific value disclosed originally in a specific example (page 27, Example 6), this value being clearly independent of the remaining operating conditions of the specific example (see decision T 201/83, OJ EPO, 1984, 481).

Claim 1 also comprises all the features of Claim 1 as granted together with additional features which clearly restrict the scope of protection.

The range of between 3 and 18 nm set out in Claim 2 for a thickness of the silicon oxynitride film was disclosed on page 11, lines 16 to 19 of the original application documents.

4.2 Novelty

The subject-matter of Claim 1 in accordance with Appellant's fifth auxiliary request comprises all the features of Claim 1 of his main request and it is therefore novel for the reasons indicated above in relation to Claim 1 of the main request.

4.3 Inventive step

As compared to Claim 1 of the main request, present Claim 1 further specifies that the silicon dioxide film is made by the preliminary step of forming a silicon nitride surface film by thermal nitridation of a silicon surface layer of a silicon substrate and converting the exposed surface of the silicon nitride film to silicon dioxide by oxidation.

This procedure, which improves the adherence and density of the silicon dioxide film as compared to silicon dioxide films directly formed on a silicon surface, could not be derived in an obvious manner from the cited prior art.

In particular, document D2 which was cited by the Respondent relates to the formation of a diffusion mask made of silicon nitride on a silicon substrate. To this effect, a continuous silicon nitride film is formed by thermal nitridation of a silicon substrate and portions thereof corresponding to the desired windows of the diffusion mask are converted to silicon dioxide by oxidation. Subsequently, the thus obtained silicon dioxide

portions are removed by selective etching, leaving the diffusion mask of silicon nitride.

In this process, the whole thickness of the initial silicon nitride layer is converted to silicon dioxide in the window regions, and not only its exposed surface as defined in Claim 1. In addition, the conversion of silicon nitride to silicon dioxide in D2 is not performed as in accordance with the claimed process in order to form an adherent and dense silicon dioxide layer capable of forming the base of a composite insulating film. Quite on the contrary, the silicon dioxide regions resulting from the conversion of silicon nitride in accordance with document D2 are formed only to provide regions affording inferior resistance to specific etching agents than the remaining regions of silicon nitride.

Document D4, which was also cited by the Respondent, discloses a process in which a silicon oxynitride film is formed by first converting silicon to silicon nitride by nitridation, and then oxidising the silicon nitride (fourth paragraph, second sentence). Document D4 however is dedicated to the formation of thick films of silicon nitride or silicon oxynitride on silicon substrates which have been rendered porous by anodisation, and the process disclosed is intended to convert silicon nitride into silicon oxynitride but not to silicon dioxide as set out in Claim 1.

Accordingly, the skilled person contemplating the use of the process disclosed in D10 to form a semiconductor device as disclosed in D5 would not have found in either document D2 or D4 any incentive to apply the process of document D10 to a thin layer of silicon dioxide obtained by nitridation of the silicon substrate and subsequent oxidation of its exposed surface.

For these reasons, the subject-matter of Claim 1 in accordance with Appellant's fifth auxiliary request involves an inventive step in the sense of Article 56 EPC.

4.4 The patent as amended does not yet meet the requirements of the Convention since, in particular, the description fails to be adapted to the claims and to acknowledge the relevant prior art documents D2, D5 and D10 (Rule 27(1)(c) and (d) EPC). In addition, all the examples and drawings of the patent specification as granted relate to processes or semiconductor devices produced by processes which are no longer covered by the present claims, and they are therefore obviously irrelevant or unnecessary. These elements should therefore be deleted (Rule 34(1)(c) EPC).

However, having regard to the extent of the amendments required, the Board, before reaching its final decision, did not insist upon the Appellant filing a complete set of documents for each of his numerous requests, but in these circumstances deemed it appropriate to make use of the power conferred upon it under Article 111(1) EPC to remit the case to the Opposition Division for further prosecution.

Order

For these reasons, it is decided that:

1. The decision under appeal is set aside.

2. Appellant's main and first to fourth auxiliary requests are rejected.

3. The case is remitted to the Opposition Division for further prosecution on the basis of Claims 1 to 5 filed during the oral proceedings as fifth auxiliary request.

The Registrar: The Chairman:

P. Martorana K. Lederer