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**CHAMBRES DE RECOURS
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DES BREVETS**

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File Number: T 610/89 - 3.4.1

Application No.: 82 201 230.8

Publication No.: 0 072 603

Title of invention: Process for producing a semiconductor device having an insulating layer of silicon dioxide covered by a film of silicon oxynitride

Classification: H01L21/27

DECISION
of 18 September 1991

Proprietor of the patent: FUJITSU LIMITED

Opponent: Siemens Aktiengesellschaft, Berlin und München

Headword: Semiconductor/FUJITSU

EPC Article 56

Keyword: "Inventive step - (NO)"
"Interpretation of the prior art in view of common general knowledge at the filing date"

Headnote

Case Number : T 610/89 - 3.4.1

DECISION
of the Technical Board of Appeal 3.4.1
of 18 September 1991

Appellant : (Proprietor of the patent)	FUJITSU LIMITED 1015, Kamikodanaka Nakahara-ku Kawasaki-shi Kanagawa 211 (JP)
Representative :	Rackham, Stephen N. GILL JENNINGS & EVERY 53-64 Chancery Lane London WC2A 1HN (GB)
Respondent : (Opponent)	Siemensgesellschaft, Berlin und München Postfach 22 16 34 W - 8000 München 22 (DE)
Representative :	Rabold, Rudolf (authorised employee) Siemens Aktiengesellschaft
Decision under appeal :	**Decision of Opposition Division of the European Patent Office dated 21 July 1989 revoking European patent No. 0 072 603 pursuant to Article 102(1) EPC.**

Composition of the Board :

Chairman : G.D. Paterson
Members : R.K. Shukla
Y. Van Henden

Summary of Facts and Submissions

I. The present appeal lies from a decision of the Opposition Division revoking European patent No. 0 072 603 based on a divisional European patent application No. 82 201 230.8 divided from an earlier parent European patent application No. 79 301 114.9.

II. The Opposition Division revoked the patent on the ground that the subject-matter of each of the independent claims of the main and four auxiliary requests filed by the Patentee did not involve an inventive step having regard to the following prior art documents:

D2 - IBM Technical Disclosure Bulletin, vol. 19, No. 3, August 1976, p. 905;
D4 - IBM Technical Disclosure Bulletin, vol. 17, No. 8, January 1975, p. 2330; and
D8 - US-A-3 385 729.

III. In his Statement of Grounds of Appeal, the Appellant (Patentee) requested that the decision under appeal be set aside and the patent be maintained on the basis of the main request submitted at the oral proceedings held before the Opposition Division on 4 July 1989, that is, the patent be maintained as granted.

Alternatively, the Appellant requested that the patent be maintained on the basis of one of four auxiliary requests submitted in those proceedings.

IV. Main Request

The only independent claim 1 of the set of claims in accordance with the main request reads as follows:

"A process for producing a semiconductor device having an insulating film comprising a film of silicon dioxide covered by a film of silicon oxynitride comprising the steps of forming an exposed film of silicon dioxide over a silicon substrate and then nitriding the exposed surface of the silicon dioxide by heating in a nitriding atmosphere characterised in that the nitriding atmosphere contains ionised nitrogen atoms in a plasma state and the heating temperature of the silicon dioxide film is in the range from 800 to 1300°C."

Claim 1 of the first auxiliary request is identical with claim 1 according to the main request.

Claim 1 of Appellant's second auxiliary request differs from the subject-matter of claim 1 of the main request only in that it specifies that the insulating film "has a thickness of 3 to 18 nm".

Claim 1 according to third auxiliary request is identical with claim 1 of the second auxiliary request except that it specifies that the process is for producing "a dielectric member of a capacitor" for a semiconductor device.

Appellant's fourth auxiliary request is in fact based on three sets of claims so that the fourth auxiliary request amounts to three requests which are designated below as 4(a), 4(b) and 4(c).

Claim 1 of the auxiliary request 4(a) differs from claim 1 in accordance with the main request in that it includes a process step of depositing a metal layer directly on the silicon oxynitride layer.

Claim 1 according to the auxiliary request 4(b) is distinguished from claim 1 of the auxiliary request 4(a) in that it requires that the insulating film "has a thickness of 3 to 18 nm".

Claim 1 of Appellant's auxiliary request 4(c) is identical with claim 1 of the auxiliary request 4(b) with the exception that the process is stated to be for producing "a dielectric member of a capacitor" for a semiconductor device.

V. In its communication accompanying the summons to oral proceedings requested by the Appellant, the Board referred to the following documents.

D3 - FR-A-2 313 770
D1* - J. Electrochemical Society: Solid State Science and Technology, vol. 127, No. 9, September 1980, pp. 2053 to 2057.

Document D1* which was published after the filing date of the patent in suit is not comprised in the state of the art according to Article 54 EPC, and was cited by the Patentee during the examination proceedings as evidence to show that the process as claimed and described in the parent European patent application No. 79 301 114.9 produced a silicon oxynitride film.

VI. Oral proceedings took place on 18 September 1991. The Respondent was duly summoned, but notified the Board by telephone in advance that he would not attend.

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

The invention as defined in the main claim resides in the surprising discovery that it is possible to form a dense uniform film suitable as a gate insulation film by plasma nitridation of a silicon oxide layer. The main citation D8 relied upon by the Opponent, on the other hand, addresses a totally different problem, that is, formation of thick "dual dielectric" insulator for isolating integrated circuits from the bulk substrate so that the skilled person would attach no relevance to the teaching of this citation when confronted with the task of forming a relatively thin gate insulation film.

Moreover, since the process disclosed in D8 results in the formation of needle-like protrusions on the upper surface of the film, the skilled person would be led away from using this process for forming a thin dielectric film of a capacitor or a gate insulation film which is required to be uniform so as to ensure a correspondingly uniform electric field distribution within the film.

A further serious limitation of the process according to D8 was that it employed process conditions which, as indicated by prior art document D5 (J. Electrochemical Society: Solid-state Science and Technology, vol. 123, No. 7, July 1976, pp. 1177 to 1120), would lead to nitridation at the silicon dioxide/silicon interface rather than at the outer surface of the silicon dioxide film.

Document D2 is also concerned with the production of a thick insulating layer of silicon nitride or silicon oxynitride on a silicon substrate, and the insulating layer is porous. In this document plasma nitridation is used only for the conversion of a porous silicon layer into a silicon nitride or silicon oxynitride layer and the citation nowhere describes forming an exposed silicon dioxide layer and then nitriding it by using a plasma containing ionised nitrogen atoms. It was therefore not obvious to a person skilled in the art to substitute the plasma nitridation according to document D2 in the process of D8.

With respect to the main claim of the third auxiliary request, the insulating layer formed by the claimed process has a high dielectric constant and a dense homogeneous structure. The process according to D8 on the other hand produced needle-like inhomogeneities in the insulating layer thereby making the process entirely unsuitable for producing a dielectric layer of a capacitor.

Concerning the auxiliary requests 4(a), 4(b) and 4(c), in document D4 there is no disclosure that the corrosive reactions which otherwise occur between a metal contact and the underlying insulating layer is avoided by the nitridisation of a silicon oxide layer, so that even when the teaching of this document is taken into consideration, the claimed process is not rendered obvious.

VIII. The arguments of the Respondent can be summarised as follows:

The process for nitridation of a silicon dioxide layer is described in general terms in document D8 and is independent of the thickness of the layer, so that it is also suitable for producing a thin dual dielectric film. Document D2 teaches nitridation to produce a silicon oxynitride film using active nitrogen produced by a plasma discharge. It was therefore obvious to the skilled person to employ a plasma discharge in the process according to D8 with a view to supplying active nitrogen.

The use of a silicon oxide-silicon oxynitride dual insulating film as a dielectric layer of a semiconductor device is known from document D8, and in document D4 such an insulating film is used as a gate insulation so that there is no inventive step involved in these applications of the silicon oxide-silicon oxynitride insulating film.

The Respondent therefore requested that the appeal be dismissed.

IX. At the conclusion of the oral proceedings, the Board announced its decision to dismiss the appeal.

Reasons for the Decision

1. Inventive step

The only issue to be examined in the present appeal is the question of inventive step.

1.1 Main Request

1.1.1 Closest prior art

In the Board's opinion, the prior art coming closest to the claimed invention is disclosed in document D8 relating to a process for producing a dual dielectric for isolation of integrated circuits, comprising a film of silicon nitride on a silicon dioxide film. According to a preferred version of the process (see column 2, lines 9 to 15; column 4, lines 10 to 14, 42 to 67) pure anhydrous ammonia is flowed past a heated surface of silicon dioxide maintained at a temperature between 900 and 1300°C for a period from 30 minutes to 2 hours or more whereby extensive thermal dissociation of ammonia gas provides active nitrogen which reacts with silicon dioxide. This thermal nitridation of silicon dioxide is stated to produce a film of silicon nitride on the silicon dioxide film.

1.1.2 Interpretation of the Disclosure in Document D8

In the preferred version of the process described in D8 nitridation is carried out using pure anhydrous ammonia gas, and the other relevant process conditions, namely, temperature and period of nitridation, are essentially the same as those used in thermal nitridisation processes described respectively in the parent EP application No. 79 301 114.9 (see, for example, page 15, lines 22 to 24; Examples 2 and 7) and D1* (see, page 2053, "Experimental Procedure"; page 2056, left-hand column, last paragraph; pages 2056, 2057, "Discussion"), the latter two resulting in the formation of a graded silicon oxynitride film on silicon dioxide. Thus, notwithstanding the fact that in document D8 formation of a silicon nitride film, and not a silicon oxynitride film, is reported, the Board holds that the process described in document D8 employing pure anhydrous ammonia must be presumed to lead to the formation of a graded silicon oxynitride film in the outer surface region of silicon dioxide as in the above identified parent application, and consequently, the contested patent.

The Appellant has submitted that since in the process employed in document D8 a small amount of water vapour may be added to ammonia, nitridation tends to occur at the inner silicon dioxide/silicon interface as in the case of a thermal nitridation process described in document D5, rather than at the exposed surface of silicon dioxide. The Board accepts that this might well be true when ammonia gas contains a small amount of water vapour. However, as pointed out above, the preferred example in fact employs pure anhydrous ammonia so that the Appellant's submission is not relevant.

1.1.3 The process as defined in claim 1 is therefore distinguished from the above process only in that the nitriding atmosphere contains ionised nitrogen atoms in a plasma state instead of neutral active nitrogen atoms produced by thermal dissociation of anhydrous ammonia.

Referring to the description in column 4, lines 36 to 43 of the patent specification, the plasma nitridation of silicon dioxide has the advantage that the process can be carried out at relatively low temperatures and the nitridation time is reduced compared to that when non-plasma gases are used. The objective technical problem to which the claimed invention provides a solution can, therefore, be seen in providing a nitridation process for producing a dual dielectric structure comprising silicon oxynitride on silicon dioxide, the process requiring relatively low heating temperatures and less nitridation time.

1.1.4 Notwithstanding the fact that D1* was published after the priority date of the patent in suit so that its teaching was not available to the skilled person at that date, in the Board's view the skilled person, when confronted with the task of producing a silicon oxynitride film as in the present invention, would regard the process in D8 to be relevant to this end. In this connection, in one of the processes described in document D2, thermal treatment of a silicon dioxide layer in a temperature range of 800 to 1300°C in an atmosphere of pure ammonia results in the formation of a silicon oxynitride layer (see paragraph 4, last two lines in combination with paragraph 2). Similarly, in document D5 it is disclosed that on thermal nitridation of silicon dioxide in ammonia gas, it is quite possible that a stoichiometric silicon nitride film is not formed but rather a mixed compound of silicon, nitrogen, oxygen, and possibly, hydrogen (see page 1118, right-hand column, first paragraph, last four lines). Moreover, from the disclosure in document D3 concerning thermal nitridation of silicon dioxide, it emerges that although the film produced by nitridation has been referred to as a silicon nitride film, it may include oxygen and hydrogen (page 2, lines 24 to 27). In the Board's view, therefore, at the priority date of the patent in suit, it was commonly known in the art that thermal nitridation of silicon dioxide using ammonia was likely to produce a non-stiochiometric silicon nitride film containing oxygen, and in the art such films were loosely referred to as silicon nitride films for the sake of simplicity. At the priority date of the patent in suit, the skilled person would, therefore, have expected the process in document D8 to produce a non-stoichiometric silicon nitride film containing oxygen, that is, a silicon oxynitride film.

1.1.5 It therefore remains to be considered whether it was obvious for a skilled person to employ reactive nitrogen in ionised state in the process of document D8.

In document D2 various processes are described for direct conversion of a layer of silicon substrate into silicon nitride or silicon oxynitride film. In a thermal nitridation process to form silicon oxynitride, a porous silicon layer is converted to silicon dioxide and then to silicon oxynitride by thermal dissociation of pure ammonia optionally containing nitrogen (see lines 10 to 17 in combination with lines 26 to 27). For the formation of a silicon nitride film, porous silicon layer is directly nitrided. As an alternative to thermal nitridation of porous silicon to form silicon nitride or silicon oxynitride film, use of field enhanced plasma nitridation is suggested, which, as the name implies, employs reactive nitrogen in ionised state (see fifth paragraph).

Thus, although nitridation of silicon, and not silicon dioxide, using ionised nitrogen is disclosed in D2, in the Board's view such a use for nitriding silicon dioxide was obvious to the skilled person since, as already mentioned above, it was known that during the formation of silicon oxynitride, nitridation of silicon dioxide does take place when pure ammonia is thermally dissociated.

Furthermore, it is a well established fact in conventional chemical vapour deposition processes for deposition of silicon nitride or silicon oxynitride films on a substrate that chemical reactions take place at relatively low substrate temperatures and require less time when, instead of thermally assisting a reaction, a plasma is produced in the gas phase. This is because the plasma is known to excite the reactant gas species into a highly reactive state. This fact was not disputed by the Appellant during the oral proceedings.

In view of the above considerations, in the Board's judgement, it was obvious for the skilled person to use ionised nitrogen, instead of thermally dissociated atomic nitrogen, in the process described in D8 with a view to employing relatively low temperature and reducing nitridation time. The subject-matter of claim 1 of the main request therefore does not involve an inventive step in accordance with Article 56 EPC.

2.0 First Auxiliary Request

Since claim 1 according to the first auxiliary request has the same wording as claim 1 of the main request, the first auxiliary request is not allowable.

3.0 Second to Fourth Auxiliary Requests

The subject-matter of claim 1 of the auxiliary request 4(c) contains all the features of claim 1 of the main request and additionally incorporates each of the features by which each of the main claims of the remaining auxiliary requests is distinguished from claim 1 of the main request. The following examination of inventive step in the subject-matter of claim 1 forming the basis of the auxiliary request 4(c) is therefore also applicable to the subject-matter of the independent claims according to the remaining auxiliary requests.

3.1 The process as defined in claim 1 is distinguished from the nitridation process described in Document D8 in that:

(a) ionised nitrogen is used for nitridation;
(b) the process is for producing a dielectric film of a capacitor having
(c) a thickness in the range of 3 to 18 nm; and
(d) a metal layer is deposited on silicon oxynitride. In other words, the dielectric film consists only of silicon dioxide and silicon oxynitride layers.

3.2 The objective problem to which the claimed invention provides a solution can, therefore, be seen as providing a process for forming a dual thin insulating film consisting of a silicon oxynitride layer on a silicon dioxide layer for a capacitor, the process requiring relatively less time and low processing temperatures.

3.3. A MISFET transistor is already known from document D4, having a multilayered gate insulating structure consisting of a succession of thin films of silicon dioxide (about 10 nm thick), silicon oxynitride (about 10 nm thick) and silicon nitride (10 - 30 nm thick; see last paragraph and the figure). A gate electrode is in contact with the silicon nitride film. The process for forming such a gate insulating structure is not described.

3.4 The initial question which is to be considered is whether it was obvious for the skilled person to employ the nitridation process as described in document D8 for forming a thin dielectric film of a MISFET such as known from document D4.

The process in document D8 is admittedly disclosed only in connection with nitridation of thick field oxide films as commonly used for isolating integrated circuits from the bulk substrate. However, the nitridation reaction with silicon dioxide is described in general terms and the document does not impose any limitation on the thickness of the silicon dioxide film (see column 4, lines 44 to 67 and the claims). The Board therefore concurs with the Respondent that there is no indication in document D8 that the described nitridation would not be equally effective for thinner silicon dioxide layers. The disclosure in column 2, lines 38 to 40 that growth nucleation centres are formed when silicon dioxide is nitrided up to a depth of 50 to 200 nm, on the contrary, suggests that active nitrogen diffuses at least up to a depth of 200 nm so that nitridation of thinner silicon dioxide layers would also be possible.

The nitridation process in D8 is carried out primarily with a view to forming needle-like growth nucleating centres on the surface of the oxide. The needle-like protrusions, as already mentioned above, are formed even when silicon dioxide is nitrided to a depth of only 50 to 200 nm, which implies that such protrusions would not be formed when silicon dioxide is nitrided to smaller depths. In the Board's view, therefore, the formation of needle-like protrusions would not have led the skilled person to conclude that the known nitridation process was unsuitable for forming thin dielectric layers of capacitors or thin gate insulation layers of MIS devices.

The Board therefore concludes that the skilled person would have considered using the process of document D8 for forming thin dielectric films for MISFET devices without the exercise of any inventive ingenuity. Also for the reasons given in paragraphs 1.1.1 to 1.1.5 above, he would have regarded the use of ionised nitrogen as obvious.

3.5 Insofar as the thickness range of 3 to 18 nm for the dielectric film is concerned, the Board agrees with the Respondent that this merely represents a development in conformity with the normal trend towards more miniaturisation in semiconductor devices. Furthermore, no specific effects have been demonstrated by the Appellant when the oxide films being nitrided are sufficiently thin so as to form a dual dielectric film having a thickness in the above specified range. The claimed thickness range is therefore to be regarded as an arbitrary and, therefore, a non-inventive selection.

3.6 As regards the feature (a) above, the dielectric films for capacitors and field effect transistors are required to have essentially the same electrical properties so that, in the Board's opinion, the use of the known dielectric film for a MIS type capacitor was obvious for a skilled person.

3.7 Though in the patent specification (see Example 4 (control)) oxidation of a metal electrode deposited directly on a silicon dioxide is reported, there is no significance attached to the use of a double dielectric film of silicon dioxide and silicon oxynitride as against the known triple dielectric film consisting of silicon dioxide, silicon oxynitride and silicon nitride. In the absence of any evidence to the contrary before the Board, therefore, the choice of a double dielectric film has to be regarded as arbitrary. Moreover, the conventional thin insulating films for semiconductor devices include materials such as silicon dioxide, silicon oxynitride and silicon nitride. Dual thin dielectric films consisting of a silicon nitride layer laminated on a silicon dioxide have also been commonly employed in the art (see document D4, paragraph 4) so that in the Board's view, the choice of a dual film as in the claimed invention was obvious to a skilled person.

3.8 The Appellant has submitted that whereas in the conventional chemical vapour deposited dual silicon dioxide/silicon oxynitride film, such as known from document D4, there exists a sharp interface, such an interface does not exist in a silicon oxynitride film formed by nitridation of silicon dioxide since the nitrogen concentration decreases along the depth of the insulating film. In the Board's view, since progressive nitridation of silicon dioxide described in document D8 necessarily requires diffusion of active nitrogen into the silicon dioxide layer, the skilled person would expect that in the nitridation process in document D8 the degree of nitridation was most likely to decrease with depth in the silicon dioxide layer so that a graded silicon oxynitride was most likely to form.

3.9 For the foregoing reasons, in the Board's judgement, the subject-matter of each of the independent claims of the second to fourth auxiliary requests does not involve an inventive step within the meaning of Article 56 EPC. These requests are therefore also not allowable.

Order

For these reasons, it is decided that:

The appeal is dismissed.

The Registrar The Chairman

M.Beer G.D.Paterson