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D E C I S I O N
of 19 April 2005

Case Number: T 0585/03 - 3.4.3

Application Number: 97917461.2

Publication Number: 0836748

IPC: H01L 23/532

Language of the proceedings: EN

Title of invention:

Insulating film for use in semiconductor device

Applicant:

KABUSHIKI KAISHA TOSHIBA

Opponent:

-

Headword:

Insulating film/TOSHIBA

Relevant legal provisions:

EPC Art. 56

Keyword:

"Inventive step (no) "

Decisions cited:

-

Catchword:

-



Case Number: T 0585/03 - 3.4.3

D E C I S I O N
of the Technical Board of Appeal 3.4.3
of 19 April 2005

Appellant: KABUSHIKI KAISHA TOSHIBA
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Decision under appeal: Decision of the Examining Division of the
European Patent Office posted 8 November 2002
refusing European application No. 97917461.2
pursuant to Article 97(1) EPC.

Composition of the Board:

Chairman: V. L. P. Frank
Members: G. L. Eliasson
T. Bokor

Summary of Facts and Submissions

I. European patent application No. 97 917 461.2 was refused in a decision of the examining division dated 8 November 2002 on the ground that the claims according to a main request and first to fourth auxiliary requests did not meet the requirements of novelty and inventive step having regard to, *inter alia*, the prior art documents

D1: EP-A-0 277 766; and

D2: US-A-4 692 344.

II. The appellant (applicant) lodged an appeal on 2 January 2003, paying the appeal fee the same day. A statement of the grounds of appeal was filed on 12 March 2003. Annexed to the statement of the grounds of appeal were the same requests which formed the basis of the decision under appeal.

III. At the oral proceedings held on 19 April 2005, the appellant requested that the decision under appeal be set aside and a patent be granted on the basis of the main request or first to fourth auxiliary requests as filed with the statement of grounds of the appeal.

IV. Independent claims 1, 14, and 15 according to the main request read as follows:

"1. A semiconductor device having an insulating film that is formed by means of CVD using material gases containing a gas having Si-H combination, characterized in that the amount of Si-H

combination in the insulating film is $0.6 \times 10^{21} \text{ cm}^{-3}$ or less and the concentration of nitrogen in the insulating film is $3 \times 10^{21} \text{ cm}^{-3}$ or more."

"14. A method of forming an insulating film as defined in any of Claims 1-6 by means of CVD using material gases containing a gas having Si-H combination wherein the flow rate of the gas having Si-H combination is regulated so that the amount of Si-H combination in the insulating film becomes $0.6 \times 10^{21} \text{ cm}^{-3}$ or less."

"15. A method of forming an insulating film as defined in any of Claims 1-6 by means of CVD using material gases containing a gas having Si-H combination, wherein the flow rate of a gas other than the gas having Si-H combination is regulated so that the amount of Si-H combination in the insulating film becomes $0.6 \times 10^{21} \text{ cm}^{-3}$ or less."

V. The independent claims 1, 14, 15 according to auxiliary request 1 have the same wording as claims 1, 14, and 15, respectively, according to the main request.

VI. Claim 1 according to auxiliary request 2 reads as follows:

"1. A method of forming an insulating film by means of CVD using material gases selected from containing a gas having Si-H combination, wherein the flow rate of the gas having Si-H combination or the flow rate of a gas other than the gas having Si-H combination is regulated such that the amount of Si-H combination in the insulating film becomes

0.6 x 10²¹ cm⁻³ or less, and wherein the concentration of nitrogen in the insulating film is 3 x 10²¹ cm⁻³ or more."

VII. Claim 1 according to auxiliary request 3 reads as follows:

"1. A semiconductor device having an insulating film that is formed by means of CVD using material gases selected from the group consisting of SiH₄, SiHCl₃, SiH₂Cl₂, SiH₃Cl, O₂, NO, NO₂, N₂O, CO, CO₂+H₂, H₂O, NH₃, N₂H₄, N₂ and H₂, and containing a gas having Si-H combination, characterized in that the amount of Si-H combination in the insulating film is 0.6 x 10²¹ cm⁻³ or less and the concentration of nitrogen in the insulating film is 3 x 10²¹ cm⁻³ or more."

Independent claims 14 and 15 according to auxiliary request 3 have the same wording as claims 14 and 15, respectively, according to the main request.

VIII. Claim 1 according to auxiliary request 4 reads as follows:

"1. A method of forming an insulating film by means of CVD using material gases selected from the group consisting of SiH₄, SiHCl₃, SiH₂Cl₂, SiH₃Cl, O₂, NO, NO₂, N₂O, CO, CO₂+H₂, H₂O, NH₃, N₂H₄, N₂ and H₂, and containing a gas having Si-H combination, wherein the flow rate of the gas having Si-H combination or the flow rate of the gas other than having Si-H combination is regulated so that the amount of Si H combination in the insulating film is

0.6 x 10²¹ cm⁻³ or less, and wherein the concentration of nitrogen in the insulating film is 3 x 10²¹ cm⁻³ or more."

IX. The arguments presented by the appellant in support of his requests can be summarized as follows:

- (a) As shown in Figure 18 of the present application, the claimed upper limit of 0.6 x 10²¹ cm⁻³ for the concentration of Si-H bonds in the deposited film has the technical effect that there are virtually no electron traps in the film which are caused by the presence of Si-H bonds in the film. In other words, the present invention resides in the recognition that it is not necessary to push the concentration of Si-H bonds below 0.6 x 10²¹ cm⁻³ in order to eliminate the deleterious effects of Si-H bonds. Thus, the technical problem solved by the present invention relates to providing a dielectric film produced with a low-temperature CVD process which does not have any electron traps caused by Si-H bonds (cf. application, page 5, lines 11 to 24).
- (b) Although document D1 in Example 4 discloses a film having "less than 1.0 x 10²¹ cm⁻³" Si H bonds, this film is described as having similar properties as that of Example 1 which has 1.8 x 10²¹ cm⁻³ Si-H bonds (cf. column 7, lines 47 to 51; column 6, lines 52 to 55). Since the film described in Example 4 had to be deposited at a lower deposition rate as that of Example 1, the skilled person would learn from document D1 that it is not necessary to reduce the concentration of Si-H

bonds below $1.8 \times 10^{21} \text{ cm}^{-3}$ in order to obtain a high-quality dielectric film. As shown in Figure 18 of the application in suit, however, the film according to Example 1 of document D1 having a concentration of $1.8 \times 10^{21} \text{ cm}^{-3}$ Si-H bonds has a considerably higher amount of electron traps than a film according to the present invention. Therefore, document D1 teaches away from the present invention.

- (c) Document D2 only states that the films are "substantially free from Si-H bonds" without stating any upper limit for the concentration of Si-H bonds. As shown in Figure 19 of the present application, it is a delicate task to determine the concentration of Si-H bonds from IR measurements (cf. page 25, line 23 to page 26, line 1). Therefore, the claimed upper limit of $0.6 \times 10^{21} \text{ cm}^{-3}$ Si-H bonds is not derivable from document D2.

Furthermore, document D2 only teaches to vary the flow rate of SiH_4 gas in order to minimize the Si-H bond concentration (cf. Table I). In contrast, Figure 24 of the present application shows that the flow rate of a gas not having Si-H bonds might as well be varied for the same purpose.

Reasons for the Decision

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

2. *Novelty and Inventive Step - Auxiliary Request 4*

2.1 Document D2 is considered closest prior art and discloses a plasma CVD process of forming silicon nitride using SiH₄ and NH₃ as material gases (cf. abstract; column 2, line 61 to column 3, line 19; Table I). Since the presence of Si-H bonds in the deposited dielectric film is known to have detrimental effects on the dielectric film, the flow rate of SiH₄ is varied in order to obtain a film which is "substantially free from Si-H bonds". This condition is reached when the ratio of Si atoms over N atoms is between 0.56:1 to about 0.73:1 (cf. column 2, lines 5 to 14; column 3, lines 12 to 17; Table I). The term "substantially free from Si-H bonds" means that no Si-H bonds are detected using infrared analysis (cf. column 2, lines 29 to 36). In order to measure the stability of the deposited silicon nitride films, capacitance-voltage (CV) measurements were carried out with the result that the films being "substantially free from Si-H bonds" provided a voltage shift due to charge trapping between 2.5 and 5.0 V, whereas silicon nitride films produced with conventional low temperature methods provided voltage shifts between 10 and 20 V (cf. column 4, lines 18 to 37). In comparison, thermally grown silicon oxide films exhibit "little" or no voltage shifts.

2.2 It is common ground that the subject matter of claim 1 according to auxiliary request 4 only differs from that of document D2 in that the Si-H bond concentration is $0.6 \times 10^{-21} \text{ cm}^{-3}$ or less, whereas document D2 does not disclose the concentration of Si-H bonds. Document D2 merely discloses that the silicon nitride film is "substantially free of Si-H bonds", i.e. below the

limit of what the authors of document D2 could measure without stating this limit of detection (cf. item IX(c) above).

- 2.3 Document D1 discloses a plasma CVD process of forming silicon nitride using SiH_4 as silicon source and NH_3 as nitrogen source (cf. Examples 3 and 4). In order to reduce the concentration of Si-H bonds in the deposited film, a fluorine-containing gas such as SiF_4 is added to the deposition process (cf. column 1, line 44 to column 2, line 1). In the examples disclosed the concentration of Si-H bonds varies from $1.8 \times 10^{21} \text{ cm}^{-3}$ to "less than $1 \times 10^{21} \text{ cm}^{-3}$ " (cf. Examples 1 to 4; column 7, lines 50 and 51).

Thus, document D1 does not disclose that the upper limit of the Si-H bond concentration should be $0.6 \times 10^{21} \text{ cm}^{-3}$. Furthermore, the method of document D1 uses a fluorine-containing gas such as SiF_4 which is not included in the list of possible material gases specified in claim 1 of auxiliary request 4.

- 2.4 For the above reasons claim 1 according to auxiliary request 4 is new having regard to the available prior art.
- 2.5 As shown in Figure 18 of the application in suit, when the concentration of Si-H bonds is $0.6 \times 10^{21} \text{ cm}^{-3}$ or less, the amount of electron traps is the same as in a film produced with a CVD method without material gases having Si-H bonds (cf. page 25, lines 6 to 20). In other words, when the concentration of Si-H bonds falls within the claimed range, the detrimental effect of

Si-H bonds with respect to the number of electron traps is eliminated (cf. item IX(a) above).

Document D2 also raises the issue of reducing the number of electron traps in the deposited film (cf. column 4, lines 17 to 37). It is found from charge-voltage measurements that the films "substantially free of silicon-to-hydrogen bonds" have a smaller amount of electron traps than that of dielectric films produced by conventional low temperature methods but a higher amount of traps than in thermally grown silicon oxides. No comparison with dielectric films produced with CVD process without material gases containing Si-H components is made in document D2.

Therefore, having regard to document D2 the objective technical problem relates to minimizing the formation of electron traps in a silicon nitride or silicon oxynitride film formed with a low-temperature CVD process such that it has comparable properties with films grown using material gases without Si-H components (cf. item IX(a) above; application in suit, page 5, lines 11 to 24).

- 2.6 Since document D2 teaches that Si-H bonds in silicon nitride films are undesirable and that the films should be "substantially free of Si-H bonds", the skilled person seeking to improve the films of document D2 would therefore seek to minimize the Si-H bond concentration further. In practice this means that attempts are made to reduce the Si-H bond concentration below the level which can be detected using the technique available. The Board is unable to see any inventive merit in this activity, in particular since

the technique used in the application in suit (Fourier Transform infrared spectroscopy; cf. page 25, line 21 to page 26, line 1) for measuring the concentration of Si-H bonds appears to be well-known in the art (cf. D1, column 6, lines 52 to 55; D2, column 3, lines 35 to 37).

- 2.7 The appellant argued that since document D1 taught that a silicon nitride film having $1.0 \times 10^{21} \text{ cm}^{-3}$ Si-H bonds had "properties similar" to a film having $1.8 \times 10^{21} \text{ cm}^{-3}$ Si-H bonds, the skilled person would infer from document D1 that it would not be worthwhile to reduce the concentration of Si-H bonds beyond $1.8 \times 10^{21} \text{ cm}^{-3}$ and would therefore not consider the claimed range at all (cf. item IX(b) above).

The Board is however not convinced by this argument, since the silicon nitride film with $1.0 \times 10^{21} \text{ cm}^{-3}$ Si-H bonds has a higher breakdown voltage (5 MV/cm), higher resistivity ($4 \times 10^{15} \Omega \cdot \text{cm}$), and lower compressive stress (10^7 dyne/cm^2) than the film with $1.8 \times 10^{21} \text{ cm}^{-3}$ Si-H bonds (4 MV/cm, $5 \times 10^{14} \Omega \text{ cm}$, and $1.8 \times 10^9 \text{ dyne/cm}^2$, respectively) (cf. D1, Examples 1 and 4). Therefore, the skilled person would learn from document D1 that a silicon nitride film having less than $1.0 \times 10^{21} \text{ cm}^{-3}$ Si-H bonds has improved properties compared to one having $1.8 \times 10^{21} \text{ cm}^{-3}$ Si-H bonds, and that it would therefore be likely that these properties would continue to improve as the concentration of Si-N bonds is reduced further below $1.0 \times 10^{21} \text{ cm}^{-3}$.

- 2.8 As shown in Figure 18 of the application in suit, the number of electron traps in the deposited film decreases steadily as the concentration of Si-H bonds in the deposited film is reduced down to $0.6 \times 10^{21} \text{ cm}^{-3}$.

Thus, the skilled person reducing the Si-H bond concentration according to the teachings of documents D1 and D2 would inevitably arrive at a method falling within the scope of claim 1 according to auxiliary request 4.

2.9 Although document D2 only discloses the alternative of varying flow rate of the SiH₄ gas having Si-H combination in order to minimize the concentration of Si-H bonds in the deposited film (cf. item IX(c) above), it is taught that the condition of having substantially no Si-H bonds is achieved when the ratio of Si-atoms over that of N-atoms in the deposited film lies within the range of 0.56:1 and 0.73:1 (cf. column 3, lines 12 to 19; Table I). The skilled person would infer from this that the important parameter is the ratio of Si-atoms over N-atoms and would thus expect that the same reduction in Si-H bonds could be achieved by varying other process parameters, such as the flow rate of the NH₃ gas, instead of varying the flow rate of the SiH₄ gas. Therefore, the Board considers both alternatives as claimed of varying either the flow rate of the gas "having Si-H combination" or the flow rate of the gas "other than having Si-H combination" to be obvious.

2.10 For the above reasons, the subject matter of claim 1 according to auxiliary request 4 does not involve an inventive step within the meaning of Article 56 EPC.

3. Claim 1 according to auxiliary request 4 contains all features of the independent method claims 14 and 15 according to the main request and auxiliary requests 1 and 3 and of claim 1 according to auxiliary request 2. Therefore, the subject matter of these claims does not

involve an inventive step for the same reasons as stated above in respect to auxiliary request 4.

4. The method according to claim 1 of auxiliary request 4 when applied in a method of producing a semiconductor device inevitably results in a semiconductor device having all features of claim 1 according to the main request and auxiliary requests 1 and 3. Since both the prior art documents D1 and D2 relate to the technical field of manufacturing semiconductor devices (cf. D1, abstract; D2, abstract), the subject matter of these claims does not involve an inventive step for the same reasons as stated above.

Order

For these reasons it is decided that:

The appeal is dismissed.

The Registrar:

The Chairman:

P. Cremona

V. L. P. Frank