DECISION
of 26 June 2003

Case Number: T 0409/01 - 3.4.3
Application Number: 94118479.8
Publication Number: 0661732
IPC: H01L 21/316
Language of the proceedings: EN

Title of invention:
A method of forming silicon oxy-nitride films by plasma-enhanced chemical vapor deposition

Applicant:
APPLIED MATERIALS, Inc.

Opponent:
-

Headword:
-

Relevant legal provisions:
EPC Art. 56

Keyword:
"Inventive step (yes, after amendments)"

Decisions cited:
-

Catchword:
-
Case Number: T 0409/01 - 3.4.3

DECISION
of the Technical Board of Appeal 3.4.3
of 26 June 2003

Appellant: APPLIED MATERIALS, INC.
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Decision under appeal: Decision of the Examining Division of the European Patent Office posted 4 December 2000 refusing European patent application No. 94118479.8 pursuant to Article 97(1) EPC.

Composition of the Board:

Chairman: R. K. Shukla
Members: M. Chomentowski
          J. P. B. Seitz
Summary of Facts and Submissions

I. The European patent application No. 94 118 479.8 (Publication No. 0 661 732) was refused by a decision of the examining division dated 4 December 2000 on the ground that its subject-matter did not involve an inventive step having regard to prior art documents


and


II. Claim 1 of the first auxiliary request forming the basis of the decision of the examining division reads as follows:

"1. A method for depositing silicon oxynitride on a substrate (38) in a plasma enhanced chemical vapor deposition chamber (12) fitted with a substrate support electrode (18) and a parallel gas manifold electrode (16), said gas manifold electrode (16) having a face plate (44) adjacent the plasma region between the electrodes (18, 16) and having a plurality of tapered openings (40), said tapered openings having a diameter at gas inlet smaller than the diameter at gas outlet, said silicon oxynitride being formed from a precursor gas mixture consisting essentially of silane, nitrous oxide and nitrogen,

characterized by
maintaining the deposition temperature at less than 250°C and the deposition pressure between 0.666 hPa and 4,666 hPa while maintaining the deposition rate at over 200 nm/min."

Claims 2 to 4 of the first auxiliary request were dependent claims.

Since the appellant's only request concerns the text of claim 1 based on this first auxiliary request, it is not necessary to refer to the text of the main request or of the second auxiliary request forming the basis of the decision under appeal.

III. The reasoning of the examining division for the finding of lack of inventive step in claim 1 of the first auxiliary request can be summarized as follows:

It is well known in the art to deposit oxynitride using plasma enhanced chemical vapor deposition (PECVD) from a precursor gas mixture consisting essentially of silane (SiH₄), nitrous oxide (N₂O) and nitrogen (N₂), these gases being selected to avoid the use of ammonia which results in substantial, unwanted hydrogen incorporation into the formed oxynitride film. Such a method is explicitly discussed in document D1. It is clear that the growth is successful at low temperatures such as 200°C; however, it is quite clear from Figure 3 of this document that the growth rate is very low (about 18 nm/min at 200°C and 10.5 nm/min at 350°C), such that the method is barely feasible for use in a device fabrication technology.
Starting from document D1, the objective problem to be solved by the invention is to increase the growth rate of the silicon oxynitride (SiON) to a level wherein the reaction is rendered feasible. The skilled person faced with the problem will therefore search the prior art to see if any methods are known whereby PECVD growth rates might be increased, and as a result will find document D4 published about one year later than document D1.

Document D4 discusses exactly the problem outlined above for the formation of PECVD silicon oxynitride via silane based chemistry avoiding ammonia. It is clear from the document that the low prior art growth rates arise due to poor dissociation of the nitrogen source gas used. This problem is solved according to document D4 by the use of a manifold electrode with tapered openings exactly as in claim 1. This greatly increases the dissociation rate of the nitrogen and hence results in greatly increased growth rates for the oxynitride. The skilled person will automatically consider using this gas manifold electrode in the method of document D1 and thus arrive at the subject-matter of claim 1, the high growth rate being an automatic result of the use of the gas manifold electrode.

Indeed, in the method of document D1, the pressure is 0.4785 hPa (0.36 torr) and thus lower, and, in the method of document D4, the pressure is 5.985 to 6.65 hPa (4.5 to 5.0 torr) and thus higher than those, between 0.666 hPa and 4.666 hPa, in claim 1. Moreover, to arrive at the claimed method, pressure, temperature and deposition rate of the methods of documents D1 and D4 must be varied.
However, the indication in document D4 that the apparatus has a wide pressure regime and that this, amongst other variables, provides a wide range of processing capabilities, is an indication that the pressure can be varied whilst still using the claimed manifold electrode.

Moreover, concerning the applicant's argument that the variation in all three parameters is not straightforward, it was considered that the pressure range claimed is simply filling the gap between the pressures known from both documents. This variation, as well as the variation of the other parameters, which can be selected because of the requirements of the device to be fabricated, does not result in any unexpected effect.

Therefore, the subject-matter of claim 1 of the first auxiliary request lacks an inventive step.

IV. The applicant lodged an appeal against this decision on 26 January 2001 paying the appeal fee on the same day. A statement setting out the grounds for the appeal was filed on 4 April 2001.

V. In an official communication issued on 20 February 2003, the Board expressed its provisional opinion that the appellant's main request did not comply with the requirements of clarity and inventive step and suggested amendments to claim 1 of the first auxiliary request which could meet the above requirements of the EPC.

VI. With letter dated 17 April 2003, the appellant agreed to the amendments suggested by the Board.
VII. The appellant requested that the decision under appeal be set aside and a patent be granted on the basis of the following documents:

**Description:**

Pages 1, 2, 8 and 9 as filed;

Pages 3, 3a, 4 to 7, 10 and 11 filed with the letter dated 11 May 1999;

Pages 12 and 13 annexed to the communication of the Board of 20 February 2003 and agreed to by the appellant by the letter dated 17 April 2003;

**Claims:**

No. 1 annexed to the communication of the Board of 20 February 2003 and agreed to by the appellant by letter dated 17 April 2003;

Nos. 2 to 4 of the first auxiliary request filed with the letter dated 5 October 2000;

**Drawings:**

Claim 1 of the appellant's request reads as follows:

"1. A method for depositing a film of silicon oxynitride on a substrate (38) in a plasma enhanced chemical vapor deposition chamber (12) fitted with a substrate support electrode (18) and a parallel gas manifold electrode (16), said gas manifold electrode (16) having a face plate (44) adjacent the plasma
region between the electrodes (18, 16) and having a plurality of tapered openings (40), said tapered openings having a diameter at gas inlet smaller than the diameter at gas outlet, said silicon oxynitride being formed from a precursor gas mixture consisting essentially of silane, nitrous oxide and nitrogen, characterized by

maintaining the deposition temperature at less than 250°C and the deposition pressure between 0.666 hPa and 4.666 hPa while maintaining the deposition rate at over 200 nm/min, whereby the deposited film is substantially without voids."

(The amendments with respect to claim 1 of the first auxiliary request forming the basis of the decision have been highlighted by the Board)

Claims 2 to 4 are dependent claims.

VIII. The appellant has submitted in substance the following arguments:

The invention is directed to a method of depositing SiON at low temperatures and high deposition rates using tapered gas manifold openings as in document D4.

However, in document D4, the deposition temperature is indicated as being 300 to 360°C, thus much higher than the maximum temperature of 250°C, in claim 1.

From document D1, it is known that SiON can be deposited at low temperatures, e.g. 200°C or 250°C.
However, in document D1, only very low deposition rates are achieved at low temperature. Moreover, Figure 2 of document D1 shows that at a temperature of deposition of 250°C on a substrate, films do not have uniform thickness across the substrate and thus cannot be considered as useful.

The present claims are for obtaining useful SiON films and require both a low temperature of deposition and high deposition rates using the manifold electrode of document D4. Document D4 having been published after document D1 and the authors of document D4 having anyway chosen a high temperature, they must have thought that both tapered openings for the manifold electrode and high temperatures are required for depositing SiON at high deposition rates. All of their N-containing films were deposited at 300°C to 360°C. Moreover, as set forth above, films deposited in document D1 do not have a uniform thickness.

Therefore, to the skilled person, it was not obvious to combine the documents D4 and D1 and, thus, the subject-matter of claim 1 involves an inventive step.

**Reasons for the Decision**

1. The appeal is admissible.

2. *Formal requirements*

The present claims are based on the claims of the first auxiliary request before the examining division. Claim 1 now specifies that the method is for depositing
a silicon oxynitride film, this film being substantially without voids, i.e. having substantially no porosity. These amendments are based on the application as filed (see e.g. page 1, first paragraph and page 4, second paragraph to page 5, first paragraph; see also independent claim 12).

Therefore, the application complies with 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 which extends beyond the content of the application as filed.

Moreover, inconsistencies between claim 1, wherein the silicon oxynitride is formed from a precursor gas mixture consisting essentially of silane, nitrous oxide and nitrogen, and the paragraph bridging pages 12 and 13 of the description citing other gas components, have been eliminated by deleting said paragraph.

3. Inventive step

3.1 A method for depositing a silicon oxynitride film on a substrate in a plasma enhanced chemical vapor deposition chamber is known from document D1 (see the abstract; page 1211, left-hand column, second and third paragraphs); it is derivable from the document that the chamber is fitted with a substrate support electrode and that there is a second, parallel electrode having a face plate adjacent the plasma region between the electrodes; the silicon oxynitride is formed from a precursor gas mixture consisting essentially of silane, nitrous oxide and nitrogen; the deposition temperature can be maintained at e.g. 200°C, thus at less than 250°C.
However, contrary to the method of claim 1, the known method is not carried out in a deposition chamber wherein the second, parallel electrode is a parallel gas manifold electrode having a plurality of tapered openings, said tapered openings having a diameter at gas inlet smaller than the diameter at gas outlet.

Moreover, in the method of document D1 (see page 1211, left-hand column, third paragraph), the pressure in the deposition chamber is maintained at 0.4785 hPa (0.36 torr) and is thus lower than the lowest pressure of the range between 0.666 hPa and 4,666 hPa of claim 1.

It is also to be noted that, in the known method (see the bottom figure in Figure 3), at the indicated temperatures, e.g. 200°C and 350°C, and at the indicated deposition pressure, the deposition rates are about 16 and 11 nm/min, respectively, for a film of the same type of material; at 250°C (see Figure 5), for a SiON film, similar values of the deposition rates are shown. These rates are thus not maintained at over 200 nm/min, as in claim 1.

3.2 Thus, a problem of the method known from document D1 is that the deposition rate is too low.

3.3 Another method for depositing silicon oxynitride on a substrate in a plasma enhanced chemical vapor deposition chamber (10) fitted with a substrate support electrode (12) and a parallel gas manifold electrode (11), is known from document D4 (see column 3, lines 21 to 36; column 9, line 47 to column 10, line 36; Figures 1 to 3; Example 4 and the corresponding text);
the gas manifold electrode (11) has a face plate (30) adjacent the plasma region between the electrodes (12, 11) and has a plurality of tapered openings (31) having a diameter at gas inlet smaller than the diameter at gas outlet; the silicon oxynitride is formed from a precursor gas mixture consisting essentially of silane, nitrous oxide and nitrogen.

In this other known method, the deposition rate is maintained at 400 nm/min or 500 nm/min (see Tables 6 and 7, respectively), and is thus in accordance with the rates in claim 1, i.e., above 200 nm/min.

However, in document D4 (see Tables 6 and 7), the pressure for forming SiON films is indicated as being 6.65 hPa (5.0 torr) and thus higher than the highest pressure of the range between 0.666 hPa and 4.666 hPa of claim 1, and the temperature range is from 300 to 360°C, which is higher than the maximum temperature in the method of claim 1, i.e., 250°C.

3.4 The skilled person starting from the method of document D1 and intending to increase the deposition rate of SiON layers would refer to document D4 and learns therefrom that the use of a manifold electrode as disclosed therein (see column 2, lines 27 to 37 and 46 to 54; see also column 5, lines 8 to 18) results in higher deposition rates.

The appellant has argued that, in the method of document D4, the deposition temperature is indicated as being 300 to 360°C and that, therefore, the skilled person would not be incited to use only part of the teaching of document D4, i.e., the manifold electrode
with tapered openings, ignoring the further method parameters, such as the temperature or the pressure.

The following is to be noted with respect to the pressure and temperature:

(A) It has been argued in the decision under appeal that, in view of document D4 (see column 4, lines 53 to 60) indicating that the apparatus therein has "a wide pressure regime" and that this, amongst other variable "provides a wide range of processing capabilities", there is a clear teaching that the pressure can be varied whilst still using the claimed manifold electrode. It was also pointed out that the pressure range claimed simply filled the gap between the known pressures of documents D1 and D4, and that no surprising effect resulted from the selection of this pressure range.

Yet, it is to be noted that, although the passage of document D4 cited stresses the capabilities of the apparatus, this known apparatus however is for depositing also different materials, e.g. silicon nitride, whereby the pressure can be either 5.96 hPa (4.5 torr) or 6.65 hPa (5 torr), i.e., higher than the highest limit (4,666 hPa) of the claimed range. Moreover, for silicon oxy-nitride, only a pressure of 6.65 hPa (5 torr) is indicated. There is thus no clear indication for modifying the pressure for depositing specifically silicon oxy-nitride.

Moreover, it is to be noted that since the claimed pressure range between 0.666 hPa and 4,666 hPa is
not comprised in a range resulting from the overlapping of the pressures 0.4785 hPa (0.36 torr) and 6.65 hPa (5.0 torr) known from the documents D1 and D4, respectively, there is no selection from a known range and it is thus of no importance, whether the choice of parameters outside of the known ranges results in a surprising effect, or not.

(B) It has also been argued in the decision under appeal (cf. lines 4 and 5 of paragraph 2.3 of the reasons) that the temperature range in the method of document D4, i.e., 300 to 360°C, partially overlaps the temperature range indicated for the method of document D1, i.e., 200 to 350°C and that, therefore, the skilled person could be incited to use, in the overlapping temperature range of 300 to 350°C, a manifold electrode according to document D4 in the method of document D1, thereby increasing the deposition rate by a factor which can be determined by comparing deposition rates at the same temperature in both documents. It was further argued that lowering the temperature to the bottom of the range (200 to 350°C) in document D1, together with the choice of the other method parameters, could be the result of routine experiments.

However, as argued by the appellant with reference to Figure 2 of document D1, at a deposition temperature of 250°C, the thickness of deposited films of similar materials may be non uniform across the wafer and thus result in films which are not useful.
Thus, in the opinion of the Board, it was not straightforward to ignore part of the teaching of document D4 and lower from 300 to 360°C the deposition temperature to less than 250°C, as in document D1 while simultaneously lowering the pressure from the value of 6.65 hPa indicated in document D4 to a value higher than that of 0.4785 hPa of document D1.

Therefore, starting from document D1, a combination with document D4 is not considered as leading in an obvious manner to the method of claim 1.

3.5 Alternatively, starting from document D4, which discloses a method with a deposition rate maintained at 400 nm/min or 500 nm/min (see Tables 6 and 7, respectively), a temperature of 300 to 360°C, higher than the maximum temperature in the method of claim 1, i.e., 250°C, and a pressure of 6.65 hPa (5.0 torr) and thus higher than the highest pressure of the range between 0.666 hPa and 4,666 hPa of present claim 1, there can be seen no incentive to combine with the teaching of document D4 the teaching of document D1 in view of the much lower deposition rates disclosed therein.

The other documents are less relevant.

3.6 Therefore, in the Board's judgment, having regard to the state of the art, the subject-matter of claim 1 is not obvious to the person skilled in the art and thus involves an inventive step in the sense of Article 56 EPC.
3.7 Consequently, claim 1 is patentable in the sense of Article 52(1) EPC.

Claims 2 to 4, which concern particular forms of the method of claim 1, are also patentable for the same reasons.

4. Therefore, a patent can be granted on this basis (Article 97(2) EPC).

Oral proceedings, requested auxiliary by the appellant, are thus not necessary.

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 patent application documents:

   Description:

   Pages 1, 2, 8 and 9 as filed;

   Pages 3, 3a, 4 to 7, 10 and 11 filed with the letter dated 11 May 1999;

   Pages 12 and 13 annexed to the communication of the Board of 20 February 2003 and agreed by the appellant by the letter dated 17 April 2003;
Claims:

No. 1 annexed to the communication of the Board of 20 February 2003 and agreed by the appellant by the letter dated 17 April 2003;

Nos. 2 to 4 of the then first auxiliary request filed with the letter dated 5 October 2000;

Drawings:

Sheet 1/1 as filed.

The Registrar:    The Chairman:

M. Beer                  R. K. Shukla