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D E C I S I O N
of 30 September 2004

Case Number: T 0874/02 - 3.4.3

Application Number: 98107039.4

Publication Number: 0874391

IPC: H01L 21/316

Language of the proceedings: EN

Title of invention:
Process for depositing a Halogen-doped SiO2 layer

Applicant:
APPLIED MATERIALS, INC.

Opponent:
-

Headword:
Fluorine-doped silicon oxide layer/APPLIED MATERIALS

Relevant legal provisions:
EPC Art. 56, 52(2)(c)

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

Decisions cited:
T 1173/97

Catchword:
-

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Case Number: T 0874/02 - 3.4.3

D E C I S I O N
of the Technical Board of Appeal 3.4.3
of 30 September 2004

Appellant: APPLIED MATERIALS, INC.
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Decision under appeal: Decision of the Examining Division of the European Patent Office posted 10. April 2002 refusing European application No. 98107039.4 pursuant to Article 97(1) EPC.

Composition of the Board:

Chairman: R. K. Shukla
Members: G. L. Eliasson
P. Mühlens

Summary of Facts and Submissions

I. European patent application No. 98 107 039.4 was refused in a decision of the examining division dated 10 April 2002. The ground for the refusal was that the application did not meet the requirements of novelty and inventive step having regard to the prior art documents

D1: US-A-5 429 995;

D2: US-A-5 261 961: and

D3: Patent Abstracts of Japan, vol. 097, no. 4, 30 April 1997 & JP-A-08 335 579, 17 December 1996.

II. Independent claims 1, 16 and 17 which formed the basis for the decision under appeal have the following wording:

"1. A process for depositing a halogen-doped silicon oxide layer on a substrate in a substrate processing chamber, said process comprising the steps of:

introducing a process gas comprising a silicon source, an oxygen source, a halogen source and a nitrogen source into said chamber;

forming a plasma from said process gas to deposit said halogen-doped silicon oxide layer on said substrate; and

stopping the halogen source gas flow into the chamber before stopping the silicon, oxygen and

nitrogen source gas flows to deposit the halogen-doped silicon oxide layer on the substrate."

"16. A substrate processing apparatus comprising:

a processing chamber;

a gas delivery system configured to deliver a process gas to said processing chamber;

a plasma generation system configured to form a plasma from said process gas;

a controller configured to control said gas delivery system and said plasma generation system; and

a memory, coupled to said controller, comprising a computer-readable medium having a computer-readable program embodied therein for directing operation of said substrate processing apparatus, said computer-readable program including a set of computer instructions for carrying out the method of any of the preceding claims."

"17. A computer-readable medium having a computer-readable program embodied therein for directing operation of a substrate processing apparatus comprising

a processing chamber;

a gas delivery system configured to deliver a process gas to said processing chamber;

a plasma generation system configured to form a plasma from said process gas;

a controller configured to control said gas delivery system and said plasma generation system;

said computer-readable medium program including a set of computer instructions for carrying out the method of any of the claims 1 to 15."

III. In the decision under appeal, the examining division reasoned essentially as follows:

(a) The method according to claim 1 differs from that of document D1 in that the fluorine gas source is stopped before the silicon source in order to avoid the absorption of moisture, whereas in the method of document D1, the gas sources are stopped simultaneously, followed by the step of depositing a halogen-free oxide layer on the halogen-doped layer to protect the film from moisture.

The claimed step of stopping the halogen source gas flow before the other gas sources are stopped is considered to be a straightforward alternative for forming an undoped silicon oxide layer on the halogen-doped oxide layer.

(b) The device of independent claim 16 is not new having regard to document D2, since the set of computer instructions disclosed in document D2 are considered *suitable for* carrying out the method of any of claims 1 to 15.

(c) Under the heading "further remarks", the examining division held that independent claim 17 which was directed to a computer program was not allowable under Article 52(2)(c) EPC, and that its subject matter was not new having regard to document D2.

IV. The appellant (applicant) lodged an appeal on 12 June 2002, paying the appeal fee the same day. A statement of the grounds of appeal was filed on 6 August 2002.

V. In its communication, the Board informed the appellant that since an essential feature of the invention was not clearly defined in claim 1, the claim apparently lacked an inventive step with respect to document D1. In response, the appellant filed amended application documents with the letter dated 16 September 2004.

The appellant requests that the decision under appeal be set aside and a patent be granted on the basis of following documents:

Claims 1 to 14 as filed with the letter dated 16 September 2004;

Description pages 1 to 22 filed with the statement of the grounds of appeal;

Drawings Sheets 1/21 to 21/21 as originally filed

Oral proceedings are requested in case the Board considers dismissing the appeal.

VI. The independent claims 1, 13, and 14 have the following wording (amendments with respect to the corresponding independent claims forming the basis of the decision have been emphasised by the Board):

"1. A process for depositing a halogen-doped silicon oxide layer on a substrate in a substrate processing chamber, said process comprising the steps of:

introducing a process gas comprising a silicon source, an oxygen source, **SiF_4 as** a halogen source and an **additional** nitrogen source into said chamber;

forming a plasma from said process gas to deposit said halogen-doped silicon oxide layer **at a deposition rate of 1.5 - 1.8 µm/min** on said substrate; and

stopping the halogen source gas flow into the chamber **2 - 3 sec** before stopping the silicon, oxygen and nitrogen source gas flows to deposit the halogen-doped silicon oxide layer on the substrate."

"13. A substrate processing apparatus comprising:

a processing chamber;

a gas delivery system configured to deliver a process gas to said processing chamber;

a plasma generation system configured to form a plasma from said process gas;

a controller configured to control said gas delivery system and said plasma generation system; and

a memory, coupled to said controller, comprising a computer-readable medium having a computer-readable program embodied therein which, when carried out, directs the operation of said substrate processing apparatus,

said computer-readable program including:

a first set of computer instructions which, when carried out, control said gas delivery system to introduce a process gas into said substrate processing chamber; and

a second set of computer instructions which, when carried out, control said plasma generation system to form a plasma from said process gas to deposit a silicon oxide layer on a substrate in said chamber;

characterized in that

the first set of computer instructions, when carried out, control said gas delivery system to introduce a process gas comprising a halogen source, a silicon source, a nitrogen source, and an oxygen source into said substrate processing chamber; and in that

said computer-readable program on said computer readable medium includes a set of computer instructions which, when carried out, direct the apparatus to carry out a process of any of the preceding claims."

"14. A computer-readable medium having a computer-readable program embodied therein which, when carried out, directs the operation of a substrate processing apparatus, the apparatus having

a processing chamber;

a gas delivery system configured to deliver a process gas to said processing chamber;

a plasma generation system configured to form a plasma from said process gas;

a controller configured to control said gas delivery system and said plasma generation system;

said computer-readable program including:

a first set of computer instructions which, when carried out, control said gas delivery system to introduce a process gas comprising a halogen source, a silicon source, a nitrogen source, and an oxygen source into said substrate processing chamber; and

a second set of computer instructions which, when carried out, controls said plasma generation system to form a plasma from said process gas to deposit a silicon oxide layer on a substrate in said chamber;

characterized in that

said computer-readable program on said computer readable medium includes a set of computer instructions which, when carried out, directs the apparatus to carry out a process of any of the claims 1 to 12."

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

(a) The step of stopping the supply of the SiF_4 halogen source gas 2 - 3 seconds before finishing the layer in the method of claim 1 has the effect of reducing the concentration of fluorine towards the top of the layer, so that some fluorine remains in the top portion, as shown in Figure 4L of the application. This measure contributes to keeping a low dielectric constant throughout the oxide layer while preventing out-gassing of fluorine.

(b) The skilled person would not consider the claimed measure of stopping the fluorine source 2 to 3 seconds before the other gas sources to be adequate for preventing outgassing of fluorine, since document D1 teaches that a halogen-free cap layer is required for this purpose.

(c) The claimed process has the advantage over that of document D1 in that a single halogen-doped oxide layer can be made thinner than the two-layer structure taught in document D1, since it has a lower dielectric constant. Furthermore, the claimed layer can be formed faster than the known two-layer structure. Finally, the separate nitrogen source allows for better control of the process.

Reasons for the Decision

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

2. *Amendments and clarity*

Claim 1 is based on claims 1 and 2 as filed and the features disclosed in column 14, lines 23 to 28 and 44 to 48 of the application as published. Independent claims 13 and 14 according to the main request are based on independent claim 12 as filed and have been amended for clarity. The Board is therefore satisfied that the present claims meet the requirements of Articles 84 and 123(2) EPC.

3. *Prior art*

3.1 Document D1 discloses a method of forming fluorinated silicon oxide using plasma CVD (cf. abstract). In order to reduce the absorption of moisture by the fluorinated oxide film, the film deposition takes place in the presence of nitrogen (cf. column 3, lines 57 to 64).

Several different sets of source gases are disclosed, such as N_2O for N and O, and NF_3 for F (column 7, lines 5 to 15); or SiH_4 for silicon, NH_3 for N, O_2 for O, and ClF_3 for F (cf. column 9, lines 53 to 56). A further reduction of moisture absorption is attained by providing a silicon oxide cap layer free from fluorine on the fluorine-doped oxide layer (column 7, line 61 to column 8, line 2; column 8, lines 20 to 25). Structural details of a plasma CVD apparatus for depositing the fluorine-doped silicon oxide film are disclosed (cf. Figures 1, 10, 12, 14, 17, 18, 20, and 21), but no details are given as to how the process parameters are controlled during deposition.

3.2 Document D2 discloses a substrate processing apparatus for forming a deposited film using plasma CVD on a substrate (cf. abstract). The apparatus comprises a processing chamber 1, a gas delivery system 35 configured to deliver a process gas to the processing chamber 1, and a plasma generation system 4 to form a plasma from the process gas (cf. Figures 1 and 2 with accompanying text). The gas delivery system and the plasma generation system are controlled through a computer program on a computer, which, when carried out, directs the operation of the substrate processing apparatus (cf. Figures 3 and 4 with accompanying test). A first set of computer instructions includes a set of computer instructions which control the gas delivery system to introduce several process gases into the process chamber (cf. column 4, line 59 to column 5, line 21; "Gas Pressure Control" and "Gas Flow Rate Control" in Figure 3). A second set of computer instructions includes a set of computer instructions, which control the plasma generation system to form a

plasma from the process gas to deposit a layer on a substrate in the process chamber 1 (cf. "Plasma Control" in Figure 3; "Plasma Control Interface" 108 in Figure 4; column 5, lines 40 to 42).

Although it is not disputed that the apparatus of document D2 could be used for depositing a fluorine-doped silicon oxide layer, document D2 does not disclose the deposition of such a layer.

4. *Inventive step - Claim 1 (Main Request)*

4.1 With regard to claim 1 defining a method of forming a fluorine-doped silicon oxide layer, document D1 is considered the closest prior art.

The method according to claim 1 differs from that of document D1 in that the SiF_4 gas source is stopped 2 - 3 seconds before stopping the silicon oxygen and nitrogen gas sources, whereas document D1 does not disclose that the halogen gas source is stopped before the other gas sources.

4.2 The distinguishing feature of the claimed method has the effect of reducing "outgassing" of fluorine, i.e. fluorine leaving the fluorine-doped layer when exposed to a heating process, such as annealing, a phenomenon which is partly due to moisture absorbed in the fluorine-doped layer (cf. application as published, column 2, lines 25 to 44). This is illustrated in Figures 4I and 4J of the application in suit where a thermal desorption spectrum of a fluorine-doped silicon oxide layers produced according to the method of claim 1 is compared to the corresponding thermal

desorption spectrum of a fluorine-doped layer produced without the claimed step of stopping the SiF_4 gas source before the other gas sources. In the layer where the SiF_4 gas source was not stopped before the other gas sources, outgassing of fluorine and HF starts to occur in the temperature range of 475°C to 500°C (cf. Figure 4I), whereas for the layer produced according to the claimed method, outgassing of fluorine and HF does not start until about 700°C (cf. application as published, Figure 4J; column 18, lines 17 to 40).

4.3 Figure 4L of the application in suit shows the result of Secondary Ion Mass Spectrometry (SIMS) to determine the fluorine content throughout an oxide layer produced according to the claimed method (cf. Figure 4L; column 18, lines 41 to 49). As shown in Figure 4L, the claimed step of stopping the supply of SiF_4 gas before the supply of the other gases does not affect the distribution of fluorine in the layer significantly, so that the concentration of fluorine is almost constant throughout the layer. Therefore, the dielectric constant is kept uniformly low throughout the layer produced according to the claimed method.

4.4 As the appellant convincingly argued, the structure produced according to the method of document D1 has the disadvantage that the dielectric constant of the upper, fluorine-free oxide layer is higher than that of the fluorine-doped layer (cf. item VII(c) above). Moreover, the two-layer structure of document D1 takes longer time to grow than the single-layer structure produced with the claimed method, since in the method of document D1, the reaction chamber had to be purged

between the steps of forming the fluorine-doped oxide layer and that of forming the fluorine-free oxide layer.

4.5 Having regard to the closest prior art document D1, the objective technical problem thus relates to providing a fluorine-doped silicon oxide layer which has a uniform, low dielectric constant throughout the layer while maintaining a high resistance against absorption of moisture and outgassing of fluorine.

4.6 The Board accepts the appellant's argument that the skilled person would infer from the teaching of document D1 that in order to ensure sufficient protection from moisture absorption, the surface portion of the oxide film should be completely free from fluorine (cf. item VII(b) above). Therefore, the skilled person seeking to improve the method of document D1 would not consider introducing the claimed step of stopping the fluorine gas source merely two to three seconds before the other gas sources are stopped, since it would not be expected that this measure would be sufficient for eliminating fluorine from the surface portion of the resulting layer. Therefore, the claimed method has the surprising effect of being effective for preventing absorption of moisture in a fluorine-doped silicon oxide layer, while at the same time being able of producing an oxide layer with a uniform, low dielectric constant.

4.7 For the above reasons, the subject matter of claim 1 involves an inventive step within the meaning of Article 56 EPC.

5. *Claim 14 (Main Request)*

5.1 Independent claim 14 is directed to a computer-readable medium having a computer-readable program embodied therein. In the decision under appeal, the examining division made the remark that such a claim relates to subject matter excluded from patentability under Article 52(2)(c) EPC (cf. item III(c) above).

Claim 14 as amended, however, contains the features that the set of computer instructions, when carried out on a substrate processing apparatus as specified, directs the apparatus to carry out a process of any of the claims 1 to 12. Thus, following T 1173/97, the computer program according to independent claim 14 produces a further technical effect going beyond the normal physical interactions between program and computer, and is therefore not excluded from patentability under Article 52(2) and (3) EPC.

5.2 Document D2 is considered the closest prior art, since it discloses a computer readable medium having a computer-readable program embodied therein for directing the operation of a substrate processing apparatus (cf. D2, column 5, lines 23 to 27; Figure 4). Document D2 does not, however, disclose the deposition of fluorine-doped silicon oxide layers, and therefore, the subject matter of claim 14 is new. Furthermore, since independent claim 14 includes a set of computer instructions which, when carried out, directs the apparatus to carry out a process having at least the process steps of claim 1, the subject matter of claim 14 involves an inventive step for the same reasons as for claim 1.

6. *Claim 13 (Main Request)*

6.1 With regard to independent claim 13 defining a substrate processing apparatus, document D2 is considered the closest prior art, since it discloses an substrate processing apparatus for deposition of layers using plasma CVD where the process parameters are controlled by a computer during deposition (cf. Figures 1, 3, and 4 with accompanying description). Document D1, on the other hand, does not disclose any details how the process parameters are controlled during deposition.

6.2 In the decision under appeal, the examining division held that the independent apparatus claim was not new with respect to the apparatus of document D2, since the set of computer instructions in the apparatus of document D2 were considered suitable for carrying out the method of any of the previous method claims (cf. item III(b) above).

6.3 The substrate processing apparatus according to claim 13 as amended contains the computer-readable program according to claim 14 whereby the apparatus is programmed to carry out the process as defined in claim 1. The subject matter of claim 13 is therefore new and involves an inventive step for the same reasons as those for claim 14.

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 the first instance with the order to grant a patent on the basis of the following documents:

   Claims 1 to 14 as filed with the letter dated 16 September 2004;

   Description pages 1 to 22 filed with the statement of the grounds of appeal;

   Drawings Sheets 1/21 to 21/21 as originally filed

The Registrar: The Chairman:

D. Meyfarth R. K. Shukla