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D E C I S I O N
of 9 July 1998

Case Number: T 0029/94 - 3.4.1

Application Number: 87311196.7

Publication Number: 0272143

IPC: H01L 21/306

Language of the proceedings: EN

Title of invention:
Bromine and iodine etch process for silicon and silicides

Applicant:
Applied Materials, Inc.

Opponent:
-

Headword:
Bromine etch process/APPLIED MATERIALS

Relevant legal provisions:
EPC Art. 54, 56

Keyword:
"Novelty - yes (after amendments)"
"Inventive step - yes"
"Interpretation of a disclosure in the prior art"

Decisions cited:
-

Catchword:
-

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Case Number: T 0029/94 - 3.4.1

D E C I S I O N
of the Technical Board of Appeal 3.4.1
of 9 July 1998

Appellant: Applied Materials, Inc.
3050 Bowers Avenue
Santa Clara
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Representative: Bayliss, Geoffrey Cyril
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Decision under appeal: Decision of the Examining Division of the European Patent Office posted 22 July 1993 refusing European patent application No. 87 311 196.7 pursuant to Article 97(1) EPC.

Composition of the Board:

Chairman: G. Davies
Members: R. K. Shukla
U. G. O. Himmler

Summary of Facts and Submissions

I. European patent application No. 87 311 196.7 claiming the priority date of 19 December 1986 from a US patent application No. 944 491, relates to an etch process for silicon. This European patent application was refused by a decision of the Examining Division, dated 22 July 1993, on the ground that claim 1 as filed with the letter, dated 25 February 1993, was not novel in accordance with Article 54 EPC over the following prior art document:

D2: US-A- 4 502 915.

The following documents, which were cited during the examination proceedings, are relevant to the present decision:

D1: EP-A- 0246 514
D4: Journal of Electrochemical Society, vol. 132, no. 4, April 1985, pages 938 to 942.

II. The applicant lodged an appeal on 6 September 1993, paying the appeal fee on the same day, and filed a new set of claims with the statement of the grounds of appeal on 1 December 1993. Oral proceedings were requested before the issue of an adverse decision by the Board.

III. In its communications, dated 15 October 1996 and 3 July 1997, the Board raised objections under Article 84 EPC against the subject-matters of claims 1 and 2, and cited the following prior art document referred to in document D2:

D5: US-A-4 490 209.

With a letter, dated 13 February 1997, the appellant filed a copy of a Declaration sworn by Mr. Jerry Y. K. Wong, one of the inventors, as submitted to the U.S. Patent Office in the prosecution of the appellant's corresponding U.S. case. The appellant also filed with a letter dated 12 September 1997, a new set of claims 1 to 11 and amended pages of the description. A new claim 1 containing minor amendments and an amended description were filed with a letter dated 17 June 1998 in response to a communication from the Board, dated 8 June 1998.

IV. The appellant thus requests the grant of a patent on the following text and the drawings:

Description: pages 2 to 4, 14, 15, 18, 19 and 21 as originally filed;
pages 5 to 7 filed with the letter dated 9 September 1992;
pages 10, 12, 13, 16 and 17 filed with the letter dated 25 February 1993;
pages 8, 9, 11, 20, and 22 filed with the letter dated 12 September 1997; and
pages 1 and 23 filed with the letter dated 17 June 1998;

Claims: 6 to 11 filed with the letter dated 12 September 1997; and
1 to 5 filed with the letter dated 17 June 1998;

Drawings: Sheet 1/1 filed with the letter dated 18 January 1988

V. Claim 1 of the above request has the following wording:

"A plasma etch process for anisotropically etching straight walled openings in a silicon body, said openings having rounded bottoms, using a plasma precursor etch gas mixture, characterised in that the plasma precursor gas mixture is composed of HBr as the main etchant, oxygen to provide protection for the sidewalls of the openings and to control selectivity with respect to an oxide etch mask, and a fluorine containing gas to remove residual contaminants from the sidewalls of the openings."

Independent claim 2 has the following wording:

"A plasma etch process for anisotropically etching straight walled openings in silicon body, said openings having rounded bottoms, using a plasma precursor gas mixture, characterised in that the plasma precursor gas mixture is composed of HBr as the main etchant, oxygen to provide protection for the sidewalls of the openings and to control selectivity with respect to an oxide etch mask, and a silicon-fluorine compound to remove residual contaminants from the sidewalls of the openings, and helium as a carrier gas."

Claims 3 to 11 are dependent claims.

VI. The appellant made essentially the following submissions in support of the appeal:

The specific example in document D2 discloses a combination of HCl and HBr, HCl being predominant. The disclosure in column 3 at lines 47 to 51 that "any standard chlorine-containing and /or bromine-containing etchant can be used alone or in combination." is not entirely clear. The Examining Division has concluded that this statement suggests that an etchant of only

HBr is a standard etchant. The applicants believe that until the date of their invention, HBr had not been used as the sole active ingredient in an etchant gas. Moreover, there is no suggestion in document D2 that bromine containing etchant produces high aspect ratio trenches with rounded bottoms. The applicants' discovery that using HBr alone as the etchant gas enables such trenches to be created is a major breakthrough. Mr. Wong's Declaration shows that chlorine-containing etchants could not produce deep, straight walled trenches with rounded bottoms.

Reasons for the Decision

1. The appeal is admissible.

2. *Amendments*

According to Claim 1, the plasma precursor gas mixture is composed of HBr as the main etchant, oxygen and a fluorine containing gas. In independent claim 2, fluorine containing gas of the plasma precursor gas mixture is a silicon-fluorine compound and the gas mixture according to claim 1 additionally includes helium as a carrier gas.

According to the application as filed (see, e.g. page 8, lines 1 to 6) one of the objects of the invention is to provide a process for etching silicon that produces trenches having a U-shaped profile with vertical sidewalls and rounded bottom edges. Also, in the application as filed, the first reference to a bromide or brominate etchant gas for etching a silicon or silicide body, according to the invention, is on page 8, last paragraph. It is followed by a disclosure on page 9 that the reactive gas mixture comprises

brominate etching gas hydrogen bromide, which may be doped with fluorinate gas such as silicon tetrafluoride. In the second paragraph on page 9, it is further disclosed that the reactive gas mixture may include a diluent gas (such as helium, argon, nitrogen and hydrogen) to improve the process results. Finally, it is stated that the brominate-based gas mixture may be doped with a preselected flow of oxygen to better control profile and obtain higher selectivity. Thus according to the most general description of the invention, the reactant gas comprises either HBr as the sole constituent or HBr in combination with a diluent gas, a fluorinate gas or oxygen.

In the detailed description of the invention on page 10, lines 4 to 10, 24 and 25 and page 11, line 29 to page 12, line 4 HBr or HI is disclosed as the sole constituent of the reactant gas mixture (see lines 4 to 10, 24, 25). On page 11, lines 8 and 9, it is stated "In addition,(that is, in addition to HBr or HI) fluorinate gases such as SiF_4, SF_6 and NF_3 can be employed as dopants to eliminate the problem of black silicon without cross contamination or other disadvantages to the etch process."

From the above it is evident the invention as filed envisaged as a reactant gas HBr alone or HBr in combination with any of a fluorinate gas, a diluent gas and oxygen.

With regard to the role of oxygen in the plasma etching process, stated in the claim, it is disclosed on page 16, lines 3 to 15, of the application as filed, that oxygen deposits on the oxide mask and enhances the selectivity to the mask. Moreover, according to the cited text, the oxide contributes to the formation of inorganic sidewall deposits and thus contributes to profile control and high aspect ratios.

Moreover, it is disclosed on page 15, line 28 to page 6, line 1, of the application as filed, that the dopant gas SiF_4 makes the reaction more volatile, and helps to control "black silicon" and remove etch products. The condition of "black silicon" is caused by the presence of surface contaminants such as oxides, which act as localised etch masks during plasma etching, and thus give rise to rough, light-scattering dark surface appearance at the bottom of an etched trench (see page 5, line 18 to page 6, line 3 of the application as filed). It also follows from the above cited text, that the formation of black silicon can be controlled by any fluorine containing gas.

In view of the above, claims 1 and 2 as amended comply with the requirement of Article 123(2) EPC.

The description has been amended for consistency with the amended claims, so that the amended description complies with Article 123(2) EPC.

3. *Novelty*

As mentioned above, the present application claims the priority date of 18 December 1986, based on the US patent application No. 94 44 91. From the content of the priority document, it is evident that the European patent application is entitled to this priority date.

Document D1 is a European patent application having a priority date of 16 May 1986 and was published on 25 November 1987, i.e. after the priority date of the present application. Document D1 thus belongs to the state of the art pursuant to Article 54(3) EPC. This document discloses plasma etching of silicon using an

atmosphere of NF_3, a hydrofluorocarbon, such as CF_2Br_2 and an inert diluent gas. There is, however, no disclosure in the document that the plasma gas mixture comprises oxygen, as in the claimed invention.

Document D2 discloses a two-step plasma etching process, wherein the first etching step is non-selective and isotropic and is employed to remove a silicon dioxide layer (5) covering a polycrystalline silicon layer (1) and exposed through an opening (15) in a mask (7), and additionally a portion of the polycrystalline layer. The second etch step is a selective anisotropic etch step as in the present invention, and is disclosed to utilise "the hydrogen chloride, hydrogen bromide, helium etch of the type set forth" in the co-pending application no. 566 128 (i.e. US-A-4 490 209 -D5; see column 1, lines 48 to 51; column 2, lines 14 to 16, and 34 to 36).

In document D2, the reactant plasma gas is consistently disclosed to be a mixture of HCl, HBr and He in the second etch step, HCl being the main constituent (see column 2, "Summary of the Invention"; column 3, lines 20 to 29). The only statement in column 3, lines 47 to 50 - "In the case of the step two etch, any standard chlorine-containing and/or bromine-containing etchant can be used alone or in combination.", and the statement in claim 2 - "wherein said selective etchant is taken from the class consisting of chlorine-containing etchants, bromine-containing etchants, chloride-containing etchants, bromide-containing etchants and combinations thereof." are not clear, mainly because it is not clear in the statement in column 3, what is meant by a **standard** bromine-containing etchant. Chlorine-containing and bromide-containing etchants, which are acknowledged as known, are disclosed in column 1, lines 17 to 29 in document D2 and are respectively Cl_2 and a mixture of HCl, HBr

and He. In the absence of any other reference to a standard bromine- or bromide-containing etchant in document D2, the Board agrees with the appellant that the statement in column 3 has to be interpreted in the light of the disclosure in column 1, lines 23 to 27. The skilled reader would, therefore, understand the statement in column 3 to mean that the second etch step may be carried out using a chlorine-containing gas alone or using a chlorine-containing gas in combination with HBr and He, HBr providing additional selectivity (with respect to silicon dioxide).

Document D4 reports the results of reactive ion etching of silicon with magnetron discharge, using a mixture of CHF_3 and SF_6 gases (see page 939, "Experimental").

The anisotropic etching process for silicon, described in document D5, employs a Cl-containing compound, such as HCl, with HBr added thereto, so as to provide nearly perfectly vertical etching of silicon (see, column 2, "SUMMARY OF THE INVENTION").

The remaining prior art documents cited in the European search report are not relevant to the invention as claimed.

In view of the above, claims 1 and 2 are new within the meaning of Article 54 EPC.

4. *Inventive step*

Document D2 can be regarded as the closest prior art. As discussed in paragraph 3 above, in the anisotropic plasma etching of silicon, either a chlorine-containing etchant gas or a gas mixture containing hydrogen chloride, hydrogen bromide, and helium is employed, hydrogen chloride being the major or main constituent

of the gas mixture. In contrast to this closest prior art, in the invention as claimed in claims 1 and 2 of the application in suit, HBr is used as the main etchant, and there is no chlorine-containing gas in the gas mixture.

It follows from the application as filed that one of the objects of the present invention is to provide a process for etching silicon that produces deep narrow silicon trenches having a U-shaped profile that is characterised by vertical sidewalls and rounded bottoms (see, e.g., page 8, lines 1 to 6). Mr. Wong's Declaration (see, paragraph III above) compares results of tests carried out at the Applied Materials Inc. using HCl or Cl_2 with or without additional ingredients, with those of the tests carried out using the etchant gas mixture of the present invention containing only HBr as the main etchant gas. It is clear from the scanning electron microscope photographs (see, in particular, Exhibits V,W,X,Y,Z,A2 and B2) supplied with the Declaration, that the etchant according to the present invention (see Examples 19 to 25) produces high aspect ratio trenches with straight walls and rounded bottoms, whereas chlorine-containing etchants (without any bromine-containing gas) as in Examples 1 to 18 could not produce such trenches (see Exhibits A to U).

The role played by HBr in plasma etching of silicon using a HCl and HBr mixture is discussed in document D5 (see column 2, lines 27 to 32, lines 50 to 64; column 3, lines 23 to 29, lines 50 to 52) referred to in document D2. According to the above-cited texts in document D5, HBr acts as a passivating agent by forming a passivation layer of silicon tetra bromide on the side walls, so that lateral etching is prevented and the etching is mainly in the vertical direction (i.e.

anisotropic). Also, HBr removes free chlorine atoms responsible for lateral etching from the reactant gas mixture containing HCl as the main active constituent reacting with silicon, and thereby reduces or prevents lateral etching.

In the Board's opinion, therefore, the use of HBr in a reactive ion etch process (RIE) as the major constituent so as to produce high aspect ratio, straight-walled trenches with rounded bottoms is not suggested by the most relevant documents D2 and D5. Also, there is no suggestion in these documents to dispense with the use of a chlorine-containing gas, such as HCl, as in the present invention.

For the foregoing reasons, in the Board's judgement, the invention as claimed in independent claims 1 and 2 was not obvious to the skilled person within the meaning of Article 56 EPC.

Order

For these reasons it is decided that:

1. The decision of the Examining Division is set aside.

2. The case is remitted to the department of the first instance with the order to grant a patent with the text and drawings as specified below:

Description: pages 2 to 4, 14, 15, 18, 19 and 21 as originally filed;
pages 5 to 7 filed with the letter dated 9 September 1992; pages 10, 12, 13, 16 and 17 filed with the letter dated 25 February 1993; and
pages 8, 9, 11, 20, and 22 filed with the letter dated 12 September 1997;
pages 1 and 23 filed with the letter dated 17 June 1998;

Claims: 6 to 11 filed with the letter dated 12 September 1997; and
1 to 5 filed with the letter dated 17 June 1998;

Drawings: Sheet 1/1 filed with the letter dated 18 January 1988

The Registrar: The Chairman:

M. Beer G. Davies