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**Datasheet for the decision
of 28 November 2006**

Case Number: T 0566/05 - 3.4.03

Application Number: 98304002.3

Publication Number: 0880168

IPC: H01L 21/321

Language of the proceedings: EN

Title of invention:

System and method of selectively cleaning copper substrate surfaces, in-situ, to remove copper oxides

Applicant:

SHARP KABUSHIKI KAISHA, et al

Opponent:

-

Headword:

Hhfac/SHARP

Relevant legal provisions:

EPC Art. 56

Keyword:

"Inventive step (no)"

Decisions cited:

-

Catchword:

-



Case Number: T 0566/05 - 3.4.03

D E C I S I O N
of the Technical Board of Appeal 3.4.03
of 28 November 2006

Appellant: SHARP KABUSHIKI KAISHA
22-22, Nagaike-cho
Abeno-ku
Osaka-shi, Osaka 545-8522 (JP)

Representative: West, Alan Harry
R.G.C. Jenkins & Co.
26 Caxton Street
London SW1H 0RJ (GB)

Decision under appeal: Decision of the Examining Division of the
European Patent Office posted 3 November 2004
refusing European application No. 98304002.3
pursuant to Article 97(1) EPC.

Composition of the Board:

Chair: R. G. O'Connell
Members: G. Eliasson
T. Bokor

Summary of Facts and Submissions

I. This is an appeal against the decision of the examining division refusing European patent application No. 98 304 002.3 for lack of an inventive step.

II. The following documents, among others, were cited in the decision under appeal:

D1: 1996 VMIC Conference Proceedings, pages 245 to 250;
D3: EP 0 507 074 A.

III. At oral proceedings before the board, the appellant applicant requested that the decision under appeal be set aside and that a patent be granted in the following version:

Main request or alternatively first to third auxiliary requests, all filed with the statement of grounds of appeal dated 11 March 2005, or

fourth or fifth auxiliary requests filed with letter dated 30 October 2006.

IV. Claim 1 of the main request has the following wording:

"1. A method for *in situ* cleaning CuO from a copper surface, in an integrated circuit (IC) having a dielectric interlevel with a dielectric surface and a plurality of metal levels underlying the dielectric interlevel, the copper surface being accessed through a via from the dielectric surface, the method comprising the steps of:

- (a) surrounding the integrated circuit with a gaseous atmosphere;
- (b) controlling the atmosphere to be substantially free of oxygen, whereby the formation of metal oxides on the first metal level surface is minimized;
- (c) introducing a β -diketone vapor into the atmosphere; and
- (d) volatilizing the metal oxide from the first metal level surface using the β -diketone vapor introduced in step (c), whereby the first metal level surface is selectively cleaned."

V. Claim 1 of the first auxiliary request differs from that of the main request in that the following passage is added at the end:

"characterised in that one of the plurality of metal levels is a metal barrier layer."

VI. Claim 1 of the second auxiliary request differs from that of the main request in that "in-situ" in the first line has been moved to the following passage added at the end:

"characterised in that the method is for in-situ cleaning."

VII. Claim 1 of the third auxiliary request differs from that of the main request in that the first paragraph reads as follows:

"A method for forming an integrated circuit (IC) having a dielectric interlevel with a dielectric surface and a plurality of metal levels underlying the dielectric interlevel, the copper surface being accessed through a via from the dielectric surface, the method including an in-situ cleaning process comprising:"

VIII. Claim 1 of the fourth auxiliary request differs from that of the main request in that "in-situ" in the first line has been omitted, and that step (c) reads as follows (board's emphasis):

"(c) introducing a β -diketone vapor into the atmosphere **at a pressure below 11.5 kPa and a temperature of approximately 20°C;**"

IX. Claim 1 of the fifth auxiliary request differs from that of the fourth auxiliary request in that step (c) reads as follows:

"(c)introducing **hexafluoroacetylacetonate (sic) (Hhfac)** vapor into the atmosphere at a pressure below 11.5 kPa and a temperature of approximately 20°C;"

X. The arguments of the appellant applicant can be summarized as follows:

(a) Since document D1 disclosed many different methods of removing oxides, the skilled person would not have any incentives to pick out the Hhfac treatment alone for the purpose of removing CuO. Instead, the treatment in diluted HF (DHF) would appear more useful as this was found to be

"effective to remove Cu contaminants from the dielectric surface and to remove CuO and CuF₂ from the Cu surface". Also, the method of document D1 was not to be regarded as *in situ*.

- (b) The references in document D1 on page 247 to removal of CuO by Hhfac (1,1,1,5,5,5-hexafluoroacetylacetone) appeared to be erroneous, since it was stated in this document that CuO was removed in the previous step of DHF treatment. It would therefore appear that the references to CuO in connection with the Hhfac treatment should instead refer to Cu₂O, as the DHF treatment did not succeed in removing the latter oxide.

- (c) As document D1 seemed to suggest at page 247, lines 39 to 40, that Hhfac had no better cleaning effect on CuO than a simple inert Ar ambient atmosphere, the skilled person would have even less reason in view of the disclosure of this document to consider the use of Hhfac for removing CuO.

Reasons for the Decision

- 1. The appeal is admissible.

- 2. *Inventive step - Main request*
 - 2.1 The present application relates to a method of cleaning CuO from a copper surface in the context of fabricating an integrated circuit. The integrated circuit comprises a copper wiring layer covered by a dielectric surface

where the copper surface to be cleaned is exposed through a via from the dielectric surface. As described in conjunction with Figures 1 and 2 of the application, the process of etching the via through the dielectric surface 12 creates contaminants 28 on the exposed copper surface which have to be removed before a further metal layer can be deposited in contact with the copper surface in the via. The contaminants 28 are removed using oxygen plasma etching, a method commonly referred to as "ashing" (see Figure 2; column 6, lines 29 to 45). As explained in the application, since the ashing involves the use of oxygen, copper oxides 32 are formed on the exposed copper surface 29.

In order to remove the oxides caused by the ashing operation, the copper surface is treated with a β -diketone vapour, such as Hhfac (1,1,1,5,5,5-hexafluoroacetylacetone), before further metal layers are deposited in contact with the copper surface (see flow diagram in Figure 8).

The claimed method thus corresponds to the final cleaning step prior to deposition of a further metal layer on the via structure.

- 2.2 Document D1 discloses cleaning of CHF_3 plasma-etched $\text{SiO}_2/\text{SiN}/\text{Cu}$ via structures of a structure having a copper layer underlying a SiO_2/SiN dielectric layer. After etching a via hole in the dielectric layer, contaminants are removed using Dilute HF (DHF) solution (see "Experimental Procedure"). It was found that DHF treatment was effective to remove most contaminants but in particular Cu_2O and carbon contamination remained. A further treatment with oxygen plasma (ashing) was found

suitable for removing the carbon contaminants remaining from the DHF treatment (see page 247 "Cu surface cleaning by Hhfac chemical vapor", first paragraph). A final treatment with Hhfac vapour reduced the remaining Cu-oxides to metallic Cu on the exposed Cu surface (see page 247, last paragraph, page 248 "Conclusions"; Figure 6). It is also shown in Figure 6 that an inert Ar ambient removed some of the oxides but not as effectively as the Hhfac treatment.

- 2.3 The appellant argued that the method of document D1 disclosed different methods of cleaning a copper surface, and therefore, the skilled person would have problems recognising which method would be useful for removing specifically CuO (see item X(a) above).

As discussed above, the claimed method relates to the final cleaning step of removing copper oxides from a copper surface exposed in a via opening in a dielectric layer preparing for a further metallization layer to be deposited on the structure. Hence the board does not agree with the appellant that the skilled person would have difficulty recognising that the relevant steps of the method described in document D1 relate to the step of exposing the device to Hhfac chemical vapour, as this method step aims at removing residual oxides from the exposed copper surface to obtain a clean, metallic copper surface. The other cleaning steps disclosed in document D1 (DHF, oxygen plasma) correspond to the prior cleaning steps discussed in the present application in conjunction with Figure 2. Only the final Hhfac treatment is able to produce a metallic copper surface which is described as an essential requirement for fabricating reliable multilevel copper

interconnections (D1, abstract; page 247, penultimate sentence, page 248, last sentence of the first paragraph).

- 2.4 The appellant further argued that document D1 disclosed that the DHF treatment was described as being successful in removing CuO, and therefore, there would be no CuO left on the copper surface when the Hhfac treatment was carried out. Consequently, the references to removal of CuO by Hhfac in document D1 were probably mistakes and should instead refer to removal of Cu₂O, an oxide which the DHF treatment could not remove (see item X(b) above).

This argument overlooks the fact that in the cleaning method described in document D1, the sample is subjected to an ashing treatment between the DHF and Hhfac treatments. Such an ashing treatment, as acknowledged in the application, is known to cause the formation of oxides on the exposed copper surface, among others CuO. The claimed method for removing CuO has the aim of removing the oxides resulting from such an ashing treatment (see the application, column 6, lines 42 to 47).

Moreover, it was known in the art that Hhfac could remove both CuO and Cu₂O (see D3, page 7, lines 37 to 38). Therefore, regardless of which mixture of CuO and Cu₂O there might be left on the copper surface after the ashing treatment, the Hhfac treatment would be able to remove both oxides. It is also confirmed in document D1 that all oxides were removed, leaving a metallic copper surface suitable for forming "reliable

multilevel Cu interconnections" (D1, page 247, last four lines; page 248, "Conclusions").

2.5 As observed by the appellant applicant, document D1 discloses that subjecting the copper surface to an Ar ambient also removes some CuO (see item X(c) above). As shown in Figure 6, however, the cleaning effect of Ar ambient is much smaller than that of the Hhfac treatment. It is also pointed out in document D1 that only the Hhfac treatment produces the desired metallic copper surface. Therefore, faced with the stringent requirements imposed on the fabrication of integrated circuits, the skilled person would not consider "Ar ambient" to be a serious candidate for removing residual copper oxides.

2.6 In other words, the method of document D1 for removing residual copper oxides, among others CuO, from a copper surface exposed in a via opening in a dielectric layer comprises the step of surrounding the device to be cleaned with a vapour of Hhfac, whereby the metal oxides from the copper surface are volatized (page 247, "Cu surface cleaning by Hhfac chemical vapor"). As the treatment takes place in a vacuum chamber (plasma chamber) where the Hhfac vapour is at 1 torr (D1, "Experimental Procedure"), it is implicit from the disclosure of document D1 that the atmosphere is substantially free of oxygen during the Hhfac treatment. The Hhfac treatment takes place at elevated temperatures (150°C) thereby allowing the metal oxides to be volatized from the exposed copper surface.

2.7 The method of claim 1 of the main request differs from that of document D1 in that

- (A) the copper surface is in an integrated circuit, whereas in document D1, a device is used to mimic an integrated circuit having a plurality of metal wiring layers; and
- (B) the method is an *in situ* method of cleaning.

2.8 As regards feature (A), the method disclosed in document D1 was developed with the aim of using it in the production of integrated circuits (see page 245, last two lines). Therefore, it would be obvious to apply the method of document D1 to integrated circuits having copper wiring layers.

2.9 As to feature (B), the *in situ* cleaning, the appellant contested the view of the examining division that the method of document D1 was an *in situ* cleaning method and argued that the term *in situ* should be construed as "in the place where IC formation takes place" (statement of grounds, page 3, first paragraph to page 4, first paragraph).

The board notes that the Hhfac treatment in the method of document D1 takes place in the plasma chamber where the previous oxygen plasma treatment ("ashing") took place (D1, page 247, first paragraph of "Cu surface cleaning..."), and therefore, the cleaning process is carried out in the "same place" where the previous process step took place. It is furthermore evident to the skilled person that a copper surface which has been cleaned with such great effort as described in document D1 should not be exposed to air or any other oxidizing environment before the subsequent metal layer has been deposited. It is also noted that in document D1, the samples were transferred under high vacuum from the

plasma chamber, where the ashing treatment and the Hhfac treatment took place, to the XPS chamber, where the samples were analyzed (page 246, last paragraph of the section "Experimental Procedure", page 247, last paragraph). Therefore, the board cannot see any inventive merit in seeking to integrate the step of Hhfac treatment in the same chamber where the subsequent deposition of the further metal layer will take place.

2.10 Hence, in the board's judgement, the subject matter of claim 1 of the main request does not involve an inventive step within the meaning of Article 56 EPC.

3. *Inventive step - First Auxiliary Request*

3.1 The subject matter of claim 1 of the first auxiliary request differs from the method of document D1 in addition to the above-mentioned features (A) and (B) in that

(C) one of the plurality of metal levels is a metal barrier layer, whereas in document D1 a single copper layer underlies the dielectric interlevel.

3.2 It was well-known in the art at the priority date of the application that copper diffuses easily into the semiconductor substrate and into dielectric layers. In order to prevent the destructive effects of diffusion of copper, metal barrier layers were usually used whenever copper wiring layers were used in integrated circuits (see for example column 1, lines 52 to column 2, line 8 of the present application discussing the prior art). Therefore, it would be obvious to

include such a metal barrier layer whenever copper wiring layers are used in an integrated circuit.

- 3.3 For the above reasons, the subject matter of claim 1 of the first auxiliary request does not involve an inventive step within the meaning of Article 56 EPC.

4. *Inventive step - Second and Third Auxiliary requests*

Claim 1 of the second auxiliary request has the same features (in a different order) as claim 1 of the main request. Claim 1 of the third auxiliary request defines a method for forming an integrated circuit which includes an in-situ cleaning method having all the features of claim 1 of the main request. As the discussion on inventive step regarding the main request was made in the context of a method of forming an integrated circuit, these reasons apply *mutatis mutandis* to claim 1 of the third auxiliary request.

Therefore, the subject matters of claims 1 of the second and third auxiliary requests do not involve an inventive step within the meaning of Article 56.

5. *Inventive step - Fifth Auxiliary request*

- 5.1 Relative to claim 1 of the main request, claim 1 of the fifth auxiliary request further specifies that the β -diketone vapour is hexafluoroacetylacetonate (sic) (Hhfac) vapour introduced into the atmosphere at a pressure below 11.5 kPa and a temperature of approximately 20°C (see claims 4 and 5 as originally filed). The restriction to *in-situ* cleaning has been dropped.

5.2 Figure 7 of the application shows the Hhfac vapour pressure as a function of temperature. The Hhfac vapour pressure at 20°C is about 85 torr which corresponds to 11.3 kPa (see also column 10, lines 11 to 20). In other words, claim 1 specifies the pressure to be less than the vapour pressure for Hhfac at the ambient temperature of 20°C.

5.3 The subject matter of claim 1 of the fifth auxiliary request differs from the method of document D1 in addition to the above-mentioned feature (A) in that

(D) the Hhfac vapour is introduced at a temperature of 20°C and at a pressure less than the vapour pressure of Hhfac at this temperature, whereas document D1 does not specify the conditions for introducing the Hhfac vapour into the reaction chamber.

5.4 As the features (A) (application of the process to integrated circuits) and (D) (conditions for introducing the Hhfac vapour into the reaction chamber) are functionally independent, they can be treated separately in the assessment of inventive step.

5.5 For the same reasons as stated above for the main request, the introduction of feature (A) does not involve an inventive step.

5.6 In the method of document D1, the Hhfac treatment is carried out at a reaction temperature of 150° C at a pressure of 1 torr (=0.13 kPa) (see page 247, "Cu surface cleaning by Hhfac chemical vapor"). No

information is given as to the temperature of the vapour when introduced into the reaction chamber. As is well-known in the art, when a substrate is to be treated in a reaction chamber at elevated temperatures but at very low vapour pressures, the substrate has to be heated by a substrate heater which is usually integral with the substrate holder. Incidentally, the present application discloses that the substrate temperature should be in the range between 100 and 450°C during the Hhfac treatment (column 10, lines 21 to 25).

When the gas pressure in the reaction chamber is very low, as the case is for the method of document D1, the temperature of the vapour when entering the reaction chamber is less important, since the pressure in the chamber would be well below the vapour pressure(s) of the substance(s) introduced into the chamber, and the reaction temperature is controlled by heating the substrate. In this situation, it would be obvious to consider introducing the vapour at room-temperature, as this would not require any heating or cooling of the vessels containing the substance to be introduced in vaporised form. In the present case, the claimed temperature of 20°C lies within the range commonly considered as room-temperature and the pressure of 1 torr disclosed in document D1 is much lower than the vapour pressure of Hhfac at 20°C (about 85 torr).

- 5.7 For the above reasons, in the board's judgement, the subject matter of claim 1 of the fifth auxiliary request does not involve an inventive step within the meaning of Article 56 EPC.

6. *Inventive step - Fourth auxiliary request*

As claim 1 of the fourth auxiliary request subsumes claim 1 of the fifth auxiliary request, the above finding of lack of an inventive step within the meaning of Article 56 EPC applies *a fortiori* to the fourth auxiliary request.

Order

For these reasons it is decided that:

The appeal is dismissed.

Registrar

Chair

S. Sánchez Chiquero

R. G. O'Connell