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D E C I S I O N
of 6 August 1998

Case Number: T 0927/93 - 3.4.1

Application Number: 87117894.3

Publication Number: 0298155

IPC: H01L 21/285

Language of the proceedings: EN

Title of invention:
Method of forming refractory metal film

Applicant:
Kabushiki Kaisha Toshiba

Opponent:
-

Headword:
-

Relevant legal provisions:
EPC Art. 52(1), 56

Keyword:
"Inventive step (yes)"

Decisions cited:
-

Catchword:
-

Case Number: T 0927/93 - 3.4.1

D E C I S I O N
of the Technical Board of Appeal 3.4.1
of 6 August 1998

Appellant:

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Decision under appeal:

Decision of the Examining Division of the European Patent Office posted 17 June 1993 refusing European patent application No. 87 117 894.3 pursuant to Article 97(1) EPC.

Composition of the Board:

Chairman: G. Davies
Members: G. Assi
R. K. Shukla

Summary of Facts and Submissions

I. The appellant (applicant) lodged an appeal, received on 17 August 1993, against the decision of the Examining Division, dispatched on 17 June 1993, concerning the refusal of the European application No. 87 117 894.3 (EP-A-0 298 155). The fee for appeal was paid on 17 August 1993. The statement setting out the grounds of appeal was received on 14 October 1993.

According to the decision under appeal, the application, in particular Claims 1 to 9, did not meet the requirements of Articles 52(1) and 56 EC., having regard to the following documents:

(D1) Journal of the Electrochemical Society, volume 133, no. 9, 1986, Manchester, NH, USA, R.A. Levy et al., "Selective LPCVD Tungsten for Contact Barrier Applications", pages 1905 to 1912,

(Do) EP-A-0 143 652,

(D3) EP-A-0 090 319.

During the examination procedure, the Examining Division also considered the following further document:

(D4) Patent Abstracts of Japan, volume 7, no. 136(E-181), 14 June 1983, & JP-A-58 051 510 (Fujitsu K.K.), 26 March 1983.

II. During the appeal proceedings, the Board considered the following further documents for the assessment of inventive step:

(D5) Proceedings of the Second International IEEE VLSI Multilevel Interconnection Conference, 25 to 26 June 1985, Santa Clara, CA, USA, W.A. Metz et al., "LPCVD Tungsten Metallization for Multilevel Interconnect Processes", pages 357 to 362,

(D6) EP-A-0 134 571,

(D7) DE-A-3 134 702.

Documents D1 to D7 were cited in the European search report.

III. The appellant submitted the following requests:

(i) reversal of the decision under appeal,

(ii) grant of a patent on the basis of the following documents:

Claims: No. 1 to 9 as filed with the letter of 2 July 1998,

Description: Pages 1 to 3, 5 to 11, 13 as originally filed,
Pages 4, 4a as filed with the letter of 2 July 1998,
Page 12 as filed with the letter of 14 April 1993,

Drawings: Sheets 1/5-5/5 as filed with the letter of 7 December 1987,

(iii) oral proceedings in the event that the above-mentioned requests should not be granted.

IV. The wording of Claim 1 on file reads as follows:

"1. A method of selectively forming a refractory metal film on a predetermined region on or over a semiconductor substrate in a reactive vessel by a reduction reaction, comprising the steps of:

(a) forming the predetermined region on or over the substrate; and

(b) introducing into the reactive vessel, at least one gas selected from a group of gases of halides of refractory metals selected from tungsten, titanium and tantalum in a quantity Q1, at least one gas selected among a group of gases of SiH_4, Si_2H_6, SiH_2Cl_2, SiH_2F_2, $Si_2H_4Cl_2$, $Si_2H_2Cl_4$, $Si_2H_4F_2$ and $Si_2H_2F_4$ in a quantity Q2 and a hydrogen gas, wherein the ratio $R = Q2/Q1$ is less than or equal to 1.5 when the substrate temperature T is between 350 and 600°C, and the ratio $R = Q2/Q1$ is less than or equal to 3 when the substrate temperature T is between 250°C and 350°C, and the total pressure of the gases is $1.3 \leq p \leq 665$ Pa ($0.01 \leq p \leq 5$ Torr)."

Claims 2 and 3 depend on Claim 1.

The wording of Claim 4 on file reads as follows:

"4. A method for selectively forming a refractory metal film on a predetermined region on or over a semiconductor substrate in a reactive vessel by a reduction reaction, comprising the steps of:

a) forming the predetermined region on or over the substrate;

b) introducing into the reactive vessel at least one gas selected among a group of gases of halides of refractory metals selected from tungsten, titanium and tantalum at a first predetermined quantity, and a hydrogen gas to selectively deposit the refractory metal on the predetermined region by the reduction reaction; and

c) introducing into the reactive vessel at least one gas selected among the group of gases of halides of the above refractory metals at a second predetermined quantity Q1 which is greater than said first predetermined quantity, at least one gas selected among a group of gases of SiH_4, Si_2H_6, SiH_2Cl_2, SiH_2F_2, $Si_2H_4Cl_2$, $Si_2H_2Cl_4$, $Si_2H_4F_2$ and $Si_2H_2F_4$ in a quantity Q2, and a hydrogen gas, wherein the ratio R=Q2/Q1 is less than or equal to 1.5, when the substrate temperature T is between 350°C and 400°C and the ratio R=Q2/Q1 is less than or equal to 3 when the substrate temperature T is between 250°C and 350°C, and the total pressure of the gases is $1.3 \le p \le 665$ Pa ($0.01 \le p \le 5$ Torr), in order to selectively deposit the refractory metal further on the deposited refractory metal by a reduction reaction."

Claims 5 to 9 depend on Claim 4.

V. The appellant argued as follows:

According to the teaching of document D1, tungsten is deposited by using WF_6, SiF_4 and H_2, wherein SiF_4 is used as a starting material in order to suppress or reduce the reaction of WF_6 with Si in the deposition of tungsten. Document D1 is thus concerned with the erosion of silicon which occurs during the selective deposition of tungsten on a silicon substrate. In contrast thereto, the deposition of tungsten is effected according to the present invention by the reaction of a gas of halides of refractory metals with

silanes including hydrogen atoms. This leads to the formation of good quality refractory metal films at selected locations at a high deposition speed. Moreover, according to the invention as claimed, other types of silane compounds are used in comparison to those used in document D1, resulting in a different deposition mechanism of tungsten, which cannot be deduced in an obvious way from D1.
As to Do, it relates to a process for depositing refractory metal silicides, whereas the present invention is directed to the deposition of pure refractory metals. Moreover, Do addresses a different problem, i.e. of preventing a disconnection of an interconnection layer, so that the document is not relevant to the problem underlying the present invention.

Reasons for the Decision

1. The appeal is admissible.

2. The Board is satisfied that the requirements of Articles 123(2), 84 and 54 EC. are met.

3. *Article 56 EC.*

3.1 The method according to **Claim 1** refers to the selective deposition of a refractory metal film on a semiconductor substrate by a reduction reaction. The gas reactants are:

(i) at least one halide of a refractory metal selected from W, Ti and Ta,

(ii) at least a silane including hydrogen atoms, selected from SiH_4, Si_2H_6, SiH_2Cl_2, SiH_2F_2, $Si_2H_4Cl_2$, $Si_2H_2Cl_4$, $Si_2H_4F_2$ and $Si_2H_2F_4$,

(iii) hydrogen gas (H_2).

Claim 1 furthermore mentions deposition parameters like ratio R between the quantity of silane Q2 and the quantity of halide Q1, substrate temperature T and total gas pressure p.

The method according to **Claim 4** includes all the features of Claim 1 and the further deposition step (b). Moreover, for the case $R \leq 1.5$, according to Claim 4, step (c), the temperature lies in a range $350°C < T < 400°C$, whereas according to Claim 1 the range is $350°C < T < 600°C$.

3.2 The present invention aims at providing a method of selectively forming good quality refractory metal films on a semiconductor substrate at a high deposition speed (see the original application, page 4, lines 7 to 14). This object is achieved by the method according to Claim 1.

3.3 It is useful to subdivide the cited documents into the following groups according to the composition of the metal films produced by the methods described in the documents:

(j) D1, Do, D5 and D7 relating to the deposition of a **refractory metal** (tungsten), and

(jj) Do, D3, D4 and D6 concerning the deposition of **silicides** of a refractory metal.

D1 discloses a selective low pressure chemical vapour deposition of **tungsten** on a silicon substrate exposed through a layer of SiO_2 (see page 1905, Experimental, first three sentences).

The document (see page 1906, left-hand column, lines 5 to 21) describes a two-step process as follows:

(k) In the first step, a tungsten film is deposited via silicon reduction of WF_6 (in the presence of Ar) according to the following reaction:

$$2WF_6 + 3Si \rightarrow 2W + 3SiF_4 \quad (1)$$

at a temperature T=290°C and at an operating total pressure p_{total}=3 torr (p_{WF6}=0.005 torr, p_{Ar} accounting for the balance).

(kk) In the second step, tungsten is further deposited via the hydrogen reduction of WF_6 according to the reaction:

$$WF_6 + 3H_2 \rightarrow W + 6HF \qquad (2)$$

at a temperature T=290°C and at an operating total pressure p_{total}=1.4 torr (p_{WF6}=0.01 torr, p_{H2} accounting for the balance).

The document further mentions (see page 1906, left-hand column, lines 26 to 30) a one-step process based on the (hydrogen) reduction of WF_6 but with the addition of SiF_4 to the reactant gases, tungsten being deposited at a temperature T=290°C and at a pressure p_{total}=1.42 torr (p_{WF6}=0.01 torr, p_{SiF4}=0.02 torr, p_{H2} accounting for the balance).

The one-step process using SiF_4 as reactant gas minimizes Si erosion by shifting the chemical equilibrium of the silicon reduction reaction (1) to the left side (see page 1907, right-hand column, last paragraph, page 1908, left-hand paragraph, first paragraph).

Thus, D1 discloses:

(l) a two-step process based on reactants WF_6, Ar (first step) and WF_6, H_2 (second step), and

(ll) a one-step process using WF_6, SiF_4, H_2, whereby the silane SiF_4 inhibits the Si erosion.

The document does not suggest reduction of refractory metal halides with silanes **including hydrogen atoms** as claimed in Claim 1, this reaction selectively depositing refractory metal films on a silicon substrate.

D5 (see the paragraph "Deposition procedure") discloses a low pressure chemical vapour deposition of **tungsten** on a Si substrate. The deposition procedure is carried out by the reduction of WF_6 by silane SiH_4 and H_2 at a temperature $500°C \leq T \leq 600°C$ and at an operating total pressure $0.2\ torr \leq p_{total} \leq 0.5\ torr$.

Since tungsten itself exhibits very poor adhesion to most dielectrics, an intermediate layer of tungsten silicide is used as adhesion layer.

The process according to this document is quite close to the method of Claim 1: the same gas reactants (WF_6, SiH_4, H_2) are used, the pressure interval $0.2\ torr \leq p_{total} \leq 0.5\ torr$ is within the claimed one, i.e. $0.01\ torr \leq p \leq 5\ torr$, and the temperature interval $500°C \leq T < 600°C$ is within the claimed interval $350°C < T < 600°C$. D5 does not give any information concerning the quantities of reactants WF_6 and SiH_4 used, so that the value of R is not known.

D7 (see Claims 1 to 3) also discloses a method of forming a layer of a **high melting point metal** (tungsten) on a Si substrate. It is based on the reduction of WF_6 by H_2 (see reaction (2) in D1) at a temperature $200°C \leq T \leq 400°C$ and at an operating total pressure $0.1\ torr \leq p_{total} \leq 10\ torr$.

In Claim 7 the intervals $270°C \leq T \leq 330°C$ and $0.1\ torr \leq p_{total} \leq 1.0\ torr$ are mentioned.

However, it is also possible to use temperatures in the interval $220°C \leq T \leq 400°C$ and pressures in the interval $0.1\ torr \leq p_{total} \leq 10\ torr$ (see page 10, lines 27 to 31). An example is given on page 9, lines 19 to 30, with $T=300°C$ and $p_{total}=0.5\ torr$.

Do (see page 4, lines 17 to 31) discloses the deposition of a **tungsten** layer by a selective CVD process using WF_6 and H_2 (see reaction (2) in D1) at a temperature 250°C≤T≤500°C and at a pressure 10^{-3} torr≤p_{total}≤760 torr (10^{-4} torr≤p_{WF6}≤0.05 torr).
Refractory metal **silicides** may also be deposited by a selective CVD process using a mixture of refractory metal halide gas and silane gas including hydrogen atoms, e.g. SiH_4, SiH_2Cl_2 (see page 6, lines 27 to 31, Claim 3).

D3 (see page 2, lines 31 to 34, page 3, lines 27 to 34) discloses the deposition of refractory metal **silicides** by using metal halides $MeCl_x$, hydrogen H_2 and silanes $SiH_{4-n}Cl_n$ (n=1-4) at a temperature 450°C≤T≤900°C and at an operating total pressure 50 Pa (0.375 torr)≤p_{total}≤1000 Pa (7.50 torr). The gas quantities are 1($MeCl_x$) : 10(H_2) : 2($SiH_{4-n}Cl_n$) so that R=2.
On page 4, lines 9 to 31, an example is given, which provides a tantalum silicide layer on a Si substrate with SiO_2 coating, the example being based on a temperature T=850°C, a total pressure p_{total}=133 Pa (0.99 torr) and gas quantities 1($TaCl_5$) : 10(H_2) : 2(SiH_2Cl_2) so that R=2.

D4 (see abstract) describes a method of forming a layer of high melting point metal **silicide** on a Si substrate. The reactant gases are WF_6, SiH_4 and H_2. The abstract does not give any detail concerning the deposition conditions.

D6 (see page 3, line 36, to page 4, line 7) discloses the selective CVD deposition of tantalum **silicide** with the same conditions as in document D3 (see example).

3.4 It is evident from the description of the present application that the selective deposition of the refractory metal on a substrate region is caused by the surface reaction of the refractory metal halide and the silane containing hydrogen (see page 6, lines 27 and 28, page 10, lines 20 and 21). Furthermore, it follows from the description (see page 7, line 30, to page 8, line 19) that a relatively good selectivity of the deposition of the refractory metal is achieved by optimising the flow rates Q1, Q2, respectively of the refractory metal halide and the hydrogen containing silane, the deposition temperature and pressure, as set out in Claim 1 of the application in suit.

In view of the foregoing discussion of the cited prior art, the Board considers D5 as the closest prior art. Although this document describes deposition of tungsten by reduction of a refractory metal halide using silane SiF_4 and hydrogen, it is not concerned with selective deposition of the refractory metal. As a result, there is no discussion of any process parameters, in particular of the quantities Q1 and Q2, with a view to controlling the selectivity of the deposition of the refractory metal.

Document D1 is concerned with selective deposition of tungsten. However, in the process disclosed in D1, hydrogen is employed in the reduction of tungsten halide, and the reactant gases do not include a hydrogen containing silane. Thus, there is no teaching in this document that the selectivity of tungsten deposition can be improved by selecting the quantities Q1 and Q2.

The remaining prior art documents discussed above also do not address the problem of controlling the selectivity of the deposition of the refractory metal, and, as such, are not relevant.

In the decision under appeal, the Examining Division argues (see the decision under appeal, page 6, end of first paragraph), that the skilled person would select the substrate temperature and the gas quantity ratio in accordance with circumstances, as a matter of routine practice, without the exercise of inventive skill. In this connection, in the Board's view, it would indeed be a routine activity for a skilled person to select and also adjust various process parameters in the process disclosed in document D5. However, as mentioned above, there is no teaching in any of the cited prior art documents that a selection of R value in the range specified in Claim 1 of the application in suit would lead to an improved selectivity in the deposition of the refractory metal. Consequently, since there was no expectation of an improved selectivity in the deposition of the refractory metal, the selection of the R value as in the claimed invention cannot be regarded as a routine activity without any inventive merit.

3.5 For the foregoing reasons, the subject-matter of Claim 1 involves an inventive step within the meaning of Article 56 EPC. Thus, the dependent claims, in particular Claim 4 including the subject-matter of Claim 1, also involve an inventive step.

4. The application and the invention to which it relates meet the requirements of the EPC.

Order

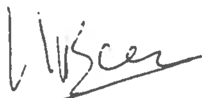
For these reasons it is decided that:

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:

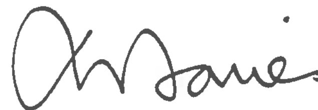
Claims:	No. 1 to 9 as filed with the letter of 2 July 1998,
Description:	Pages 1 to 3, 5 to 11, 13 as originally filed, Pages 4, 4a as filed with the letter of 2 July 1998, Page 12 as filed with the letter of 14 April 1993,
Drawings:	Sheets 1/5 to 5/5 as filed with the letter of 7 December 1987.

The Registrar:



M. Beer

The Chairman:



G. Davies