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D E C I S I O N
of 26 July 2005

Case Number: T 0941/02 - 3.2.7

Application Number: 98204068.5

Publication Number: 0915178

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Language of the proceedings: EN

Title of invention:
Sputtering target of highly purified titanium

Applicant:
Kabushiki Kaisha Toshiba

Opponent:
-

Headword:
-

Relevant legal provisions:
EPC Art. 54, 76(1), 123(2)

Keyword:
"Claims - extending beyond content of the parent application as originally filed (no, after amendment)"
"Claims - extending beyond content of the application as originally filed (no)"
"Novelty - (Main- and auxiliary request - no)"

Decisions cited:
-

Catchword:
-

Case Number: T 0941/02 - 3.2.7

D E C I S I O N
of the Technical Board of Appeal 3.2.7
of 26 July 2005

Appellant: Kabushiki Kaisha Toshiba
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Decision under appeal: **Decision of the Examining Division of the European Patent Office posted 4 April 2002 refusing European application No. 98204068.5 pursuant to Article 97(1) EPC.**

Composition of the Board:

Chairman: P. O'Reilly
Members: H. Hahn
C. Holtz

Summary of Facts and Submissions

I. The applicant lodged an appeal against the decision of the Examining Division to refuse the European patent application No. 98 204 068.5.

The Examining Division held that claim 1 of the main request filed with fax of 4 February 2002 and claim 1 of the auxiliary request as filed during the oral proceedings on 14 February 2002 although meeting the requirements of Articles 123(2) and 76(1) EPC lacked novelty with respect to the implicit composition of the sputtering target according to document D7.

II. With a communication dated 19 May 2005 and annexed to the summons to oral proceedings the Board presented its preliminary opinion with respect to the claims 1 to 10 as filed together with the grounds of appeal on 6 August 2002. Use claim 10 of this single request was considered to contravene Article 76(1) EPC and additionally not to meet the requirements of Rule 35(12) EPC. The subject-matter of product claim 1 was considered to lack novelty with respect to the disclosure of document D7 and in any case appeared to lack inventive step over the disclosure of D7 and the common general knowledge of the skilled person. To support its arguments the Board introduced documents D9a, D9b and D10 into the proceedings in order to prove the common general knowledge.

III. In response to the communication the appellant filed with its letter of 24 June 2005 a new main request, comprising claims 1 to 10, and an auxiliary request, comprising claims 1 to 9, together with further arguments and the post-published document D11 (= EP-B-0 496 637) in order to support novelty and inventive step of the subject-matter claimed.

IV. Oral proceedings before the Board of Appeal were held on 26 July 2005.

The appellant requested that the decision under appeal be set aside and a patent be granted either on the basis of the claims 1 to 10 according to the main request or on the basis of the claims 1 to 9 according to the auxiliary request, both as submitted with letter of 24 June 2005.

During the oral proceedings the appellant submitted a report of Mr. T. Ishigami concerning experimental test results of a Ti-material stated to be made in accordance with EP-A-0 284 338. The appellant stated that this report has been made in 1994.

V. Independent claims 1, 5, 9 and 10 of the main request read as follows:

"1. A sputtering target of highly purified titanium with an Al content of not more than 10 ppm, each of Na and K contents of not more than 0.1 ppm, each of Fe, Ni, and Cr contents of not more than 10 ppm, each of U and Th contents of not more than 0.001 ppm and an oxygen content of not more than 250 ppm."

"5. A titanium based wiring network formed by a sputtering target according to any of claims 1 to 4."

"9. A semiconductor package comprising titanium based wiring network according to any of claims 5 to 8 as at least a part of a wiring network, a semiconductor chip having a predetermined circuit, a lead electrically connecting the circuit of the semiconductor chip, and a sealing agent hermetically sealing at least the semiconductor chip."

"10. Use of a sputtering target according to any of claims 1 to 4 for manufacturing a titanium film on a polycrystal silicon substrate by the steps of exhausting a film-forming chamber including the substrate and the target to a pressure of 1,33 x 10^{-3} Pa (1 x 10^{-5} Torr), subsequently introducing an Ar gas into the film-forming chamber up to a pressure of 6,67 x 10^{-1} Pa (5 x 10^{-3} Torr), and sputtering the sputtering target on the substrate at a film-forming speed of 2 µm/hour by the DC magnetron sputtering method."

VI. The auxiliary request differs from the main request in that the use claim 10 has been deleted.

VII. The following documents are relevant for the present decision:

D7 = Takashi Ishigami et al, "High Purity Ti Sputter Target for VLSIs", Toshiba Review No. 161, autumn 1987, pages 38 to 41

D9a = ASM Handbook, Vol. 2, Properties and Selection: Nonferrous Alloys and Special-Purpose Materials, 9th edition, 1979, ASM International, pages 709 to 713 and 814 to 816

D9b = ASM Handbook, Vol. 2, Properties and Selection: Nonferrous Alloys and Special-Purpose Materials, 10th edition, **1990**, ASM International, pages 1093 to 1097 and 1169

D10 = Sondermetalle, R. Kieffer, G. Jangg, P. Ettmayer, Springer-Verlag 1971, pages 71 to 83

D11 = EP-B-0 496 637

VIII. The appellant argued essentially as follows:

Document D7 does not explicitly disclose a sputter target having an Al content of not more than 10 ppm Al. The preparation method in accordance with figure 3 of D7 does not necessarily result in a sputter target having an Al content of less than 10 ppm. This is due to the fact that not every fused salt electrolytic Ti has a low Al content and therefore does not necessarily result in a low Al content after a purification with an EB-melting step as proven e.g. by the Report of Mr. Ishigami (revealing Al contents of 25.0 to 135 ppm Al) and embodiment 5 of the present application revealing a reduction of from 18 to 12.2 ppm Al (see pages 22 to 23, embodiment 5; and Table 3). Consequently, an Al content of less than 10 ppm Al is not deducible from document D7.
Similarly, the iodide Ti according to figure 5 of D7 does not necessarily have an Al content of less than 10 ppm Al as stated in the submission of 24 June 2005 (see page 16, analysis of iodide Ti). This is proven by comparative example 1 of the present application which corresponds to iodide Ti having an Al content of 25 ppm (see Table 1). Document D9a specifies the chemical

composition for electrolytic and iodide Ti (see D9a, page 815, left column, Table) and mentions an Fe content of 20 ppm for iodide Ti which is not in agreement with the value according to the comparative example 1 (see Table 1). Document D9b is post-published and therefore does not represent a state of the art. Furthermore, the zone-refined Ti-material according to Table 2 of D9b (see page 1096) is silent with respect to its starting material and has an Al content of 6 ppm together with an oxygen content of 570 ppm which does not correspond to that of a fused salt electrolytic Ti. Oxygen has a big influence on the resistivity of the Ti as can also be derived from D7 (see page 38, right hand column, lines 4 to 6). The influence of the Al content on the junction leakage has been proven by document D11 (see embodiment 1 and column 7, lines 5 to 10).

Therefore neither the explicit nor the implicit disclosure of D7 destroys the novelty of the sputtering target as claimed in claim 1. Novelty of the further independent claims 5, 9 and 10 is based on the novelty of claim 1.

Reasons for the Decision

1. *Admissibility of amendments (Articles 76(1) and 123(2) EPC)*

1.1 Claim 1 of the main request is based on claims 1 to 6 of the application as originally filed, claims 5 and 9 are based on claims 10 and 14 of the application as originally filed, and claim 10 is based on the process features of claim 1 (from which the specific resistance value has been deleted) and on page 20, line 28 to page 21, line 4 of the application as originally filed, respectively.

The claims 1, 5 and 9 to 10 of the main request thus meet the requirements of Article 123(2) EPC.

1.2 The present application is a divisional application of the earlier (parent) application 91 301 234.0 of which the description and drawings are identical with those of the present application.

Independent claims 1, 5, 9 and 10 of the main request have their corresponding counterparts in the parent application (see published application EP-A-0 442 752; claims 1, 2 and 9 and page 6, lines 53 to 57; claim 13; claims 17 and 19 in combination with claim 13; and page 10, lines 36 to 38, respectively).

Consequently, claims 1, 5, 9 and 10 of the main request also meet the requirements of Article 76(1) EPC.

1.3 Claims 1, 5 and 9 of the auxiliary request are identical with the claims of the main request and therefore likewise meet the requirements of Articles 76(1) and 123(2) EPC.

2. *Novelty (Article 54 EPC) of claim 1*

2.1 Document D7 discloses a high purity Ti sputter target for VLSI's which contains less than 3 ppm N, less than 20 ppm H, 80 ppm O (oxygen), less than 1.0 ppb of U and Th, less than 100 ppb of Na and K, less than 5 ppm of Fe, Ni and Cr and less than 10 ppm Cu (see page 39,

Table 1). The high purity sputter target is produced from electrolytic Ti raw material which has been electron beam melted, forged and machined into the desired shape at room temperature to prevent the absorption of oxygen and others (see page 39, left column, paragraph 2.1, and Figure 3).

2.1.1 Said high-purity Ti sputter target represents a 4N-Ti, i.e. it contains 99.99% Ti and a total impurity content of only 100 ppm but the Al impurity content thereof is not specified.

Besides the impurities specified in point 2.1 above the 4N-Ti-target conclusively contains some other inevitable impurity elements such as C or Si which, similarly to Al, are also not specified in D7.

Taking account of the - implicit - chemical composition based on the chemical analysis of said Ti material according to Table 1 it is evident that the Al content cannot be above 10 ppm.

This conclusion of the Board is based on the fact that the vapour pressure of Al is higher than that of Fe, Ni or Cr so that it can be expected that the EB-melting treatment results in a reduction of these elements in the order of about the same magnitude. Particularly when considering the statement in the application that "**The EB-melting is** a method for the separation of impurities using a difference of vapor pressure and **highly efficient in removing particularly Al, Na and K each having a high vapor pressure**" (see application, page 10, second full paragraph, last sentence).

2.1.2 The conclusion of point 2.1.1 above is supported by document D9b which in its chapter "Preparation and Characterization of Pure Metals" reveals a zone refined Ti having an Al-content of 6 ppm, a Cr content of 4.1 ppm, an Fe content of 1.5 ppm, a Ni content of < 0.02 ppm, Na and K both < 0.01 ppm and which gives the content values of some further impurities (see page 1096, Table 2). The values of Fe, Cr, Ni, Na and K of the zone-refined Ti according to Table 2 of D9b are in good agreement with the values of the EB-melted 4N-Ti material according to document D7.

"Zone refining" as mentioned in D9b is another more common designation for the purification method of "EB-melting" which designation is used in the present application. "EB-melting" thus represents "zone refining" wherein an electron beam is used for heating the metal and the moving molten zone therein (see D9b, page 1093, middle column, fourth paragraph to right hand column, lines 2 to 5 from the bottom); an induction coil could be used alternatively as the heat source (see D9b, page 1093, middle column to page 1094, left hand column, "Zone Refining"; see also D10, pages 81 to 82; and figure 45). Zone refining is stated to be "probably the most widely used of all preparation methods" for pure metals and in the form of the floating (molten) zone technique is used for Ti (see D9b, page 1093, middle column, fourth paragraph; and page 1094, left hand column, first paragraph).

2.1.3 Document D9b has a publication date of 1990 as compared to the claimed date of 15 February 1990 for the application in suit priority. Although document D9b is considered to be post-published by the Board, it represents a standard text book and the content thereof is considered to reflect the state of the art before the priority date since the submissions for such a standard text book are prepared well before its publishing date. In this context the Board remarks that the content of said chapter "Preparation and Characterization of Pure Metals" in D9b beginning at page 1093 up to the end of the Resistance-Ratio Test at page 1096 is essentially identical with the same chapter of the earlier edition which is document D9a and which comprises also said Table 2 but without the chemical analysis of said zone-refined Ti (compare D9a, pages 709 to 713).

The appellant argued that the zone-refined Ti-material according to Table 2 of D9b is silent with respect to its starting material and has an Al content of 6 ppm together with an oxygen content of 570 ppm which does not correspond to that of a fused salt electrolytic Ti. Furthermore, the influence of the Al content on the junction leakage has been proven by document D11 (see embodiment 1 and column 7, lines 5 to 10) and the prior art is silent in this respect. These arguments cannot be accepted for the following reasons.

First of all, it is noted that document D9b (likewise D9a) mentions that amongst the most common starting materials of commercial purity for the described ultra purification preparation methods are those of electrolytic methods. For Ti fused salt baths are used (see page 1093, left hand column, last paragraph to middle column, first paragraph). Thus it is credible to the Board that the Ti material according to Table 2 of document D9b was obtained by zone-refining fused salt electrolytic Ti.

With respect to the higher oxygen content of the zone-refined Ti it is remarked that document D9b is totally silent with respect to the process conditions and it is also not known whether or not said material has been treated and/or stored under an oxygen free atmosphere. Indeed, for the most common non-semiconductor applications of highly purified Ti the oxygen impurity content is normally not particularly relevant.

Finally, any influence of the Al content on the junction leakage is not particularly relevant if the Ti material *per se* is already implicitly known.

2.1.4 The conclusion of point 2.1.1 above is also supported by the examples and comparative examples of the present application.

According to comparative example 2 the crude fused salt electrolytic Ti used for embodiment 2 comprised the following impurities (in ppm) **15 Al**, 5 Fe, 15 Ni, 10 Cr, 150 Na, 210 K, < 0.001 U, < 0.001 Th and 120 O (see page 18, Table 1; page 16, embodiment 2; page 17, last paragraph).

According to embodiment 5 the crude fused salt electrolytic Ti which was obtained from an electrolyte comprising NaCl-NaCl (KCl: 16% by weight, NaCl: 84% by weight) and electrolysed at a temperature of 755°C, a current of 200 A and a voltage of 8.0 V (see page 22, third paragraph in combination with page 11, third paragraph) comprised the following impurities (in ppm)

18 Al which was then EB-melted under conditions of a high vacuum of 1 x 10^{-5} mbar, an EB output of 26-30 KW and a melting speed of 4 kg/h (see page 23, second to third paragraphs). The Al impurity content of the Ti was reduced by the described EB-melting purification from 18 ppm to 12.2 ppm (see page 24, Table 3).

In this context it has to be noted that the specified EB-melting rate of 4 kg/h according said embodiment 5 is about twice the preferred melting rate or speed of 1.75 to 2.3 kg/h (see page 10, last paragraph to page 11, first paragraph). Thus this embodiment 5 apparently was not made at the optimum conditions for obtaining the lowest impurity content.

Therefore, since these - non-optimum - conditions resulted in a reduction of the Al content of 5.8 ppm by the mere EB-melting of the crude fused salt electrolytic Ti it can be conclusively expected that another crude fused salt electrolytic Ti comprising an Al content of 15 ppm will be reduced to a similar extent of about 5.8 ppm and thus should have an Al content of less than 10 ppm.

2.1.5 The Board also notes in this context that the appellant argued that the EB-melting of fused salt electrolytic Ti "**does not necessarily result**" in a purified Ti having an Al content of less than 10 ppm. This argument, however, can neither throw discredit onto the zone-refined Ti material of document D9b nor onto the above assumption with respect to said comparative example 2.

2.1.6 The appellant argued that comparative example 1 specifies the impurities of iodide Ti. The Board cannot accept this argument since it is absolutely clear from the description of embodiment 1 that sponge Ti from the Kroll process was used as the crude Ti material (see page 15, second full paragraph; and page 17, third paragraph). This fact is also clear from the general definition of the expression "crude Ti materials" in the description of the present application according to which the crude Ti materials "are obtained by various manufacturing methods such as the Kroll process, Hunter process, fused salt electrolysis process and the like" (see page 10, first full paragraph).

As a consequence the appellant's further arguments - that the analysis of comparative example 1 due to its Fe content of 65 ppm is not in agreement with the value of the Fe content of 20 ppm for iodide Ti according to the Table in document D9a which specifies the chemical composition for electrolytic and iodide Ti (see D9a, page 815, left column, Table) - also cannot be accepted.

Furthermore, if the appellant's arguments were true then the analysis according to comparative embodiment 1 would also substantially differ from the composition of the iodide Ti material mentioned in document D7 as given in the last submission of the appellant (see letter of 24 June 2005, page 16, Table) for having much higher Al, Fe, Ni, Na, K and O impurity contents. Actually said value of 20 ppm Fe of iodide Ti according to document D9 is exactly the same value as submitted by the appellant for the iodide Ti material of document D7.

2.1.7 The appellant's arguments with respect to the report of Mr. T. Ishigami concerning experimental test results of

Ti-material stated to be made in accordance with EP-A-0 284 338 cannot be accepted for the following reasons.

First of all, the application EP-A-0 284 338 quoted in said report concerns anti-tumour agents of the quinazoline type and is thus erroneous. Most presumably it should read EP-A-0 248 338 which corresponds to document D4 of the present proceedings.

Secondly, according to said report sponge Ti was electrolysed in a molten bath of 16% by weight K_2TiF_6 and 84% by weight NaCl at an electrolytic temperature of 755°C in combination with an electric current of 200 A and a voltage of 8.0 V (see report, paragraph "1. Preparation of Test Samples"). The fused salt electrolytic Ti according to said report thus has been made in accordance with the - preferred - electrolytic conditions as set out in the present application, i.e. sponge Ti as starting material; an electrolyte comprising NaCl-NaCl **or the like**; electrolytic temperature of 730-755°C and a voltage of 6.0-8.0 V (see page 11, third paragraph; compare also embodiment 5).

However, according to the report the resulting Ti material after it has been purified by EB-melting at a pressure of 5 x 10^{-5} mbar and an EB output of 26-30 KW and a melting rate of 2 kg/h (which thus has been made within the preferred limits for the EB-melting step given in the present application, see page 10, second full paragraph to page 11, first paragraph in combination with page 13, third paragraph) discloses much lower impurity contents of Fe, Ni, Cr than for example document D7 for its 4N-Ti material but mentions Al contents of 135, 25.0 and 50 ppm which are much higher than said 12.2 ppm Al of the EB-melted electrolytic Ti according to embodiment 5 of the present application.

These Al content values of this report are even worse than the Al content of 15 ppm of the crude fused salt electrolytic Ti according to comparative embodiment 2 which has not undergone any EB-melting purification step.

The results of this report are thus considered by the Board not to be credible. This report is therefore not taken into account.

2.2 Taking account of all the facts in points 2.1 to 2.1.7 above the Board came to the conclusion that novelty cannot be acknowledged since the application of an EB-melting step onto (fused salt) electrolytic Ti as taught by document D7 results in a purified Ti material having an Al impurity content of "lower than 10 ppm".

Claim 1 of the main request therefore does not meet the requirement of Article 54 EPC. Consequently, there is no need to further examine novelty of the other independent claims.

The main request is thus not allowable.

2.3 Claim 1 of the auxiliary request is identical with that of the main request so that the conclusions of point 2.3 above apply *mutatis mutandis*.

Consequently, the auxiliary request is also not allowable under Article 54 EPC.

3. Under these circumstances the Board has to dismiss the appeal.

Order

For these reasons it is decided that:

1. The appeal is dismissed.

The Registrar: The Chairman:

G. Nachtigall P. O'Reilly