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**D E C I S I O N**  
**of 29 February 2000**

**Case Number:** T 0471/96 - 3.4.3

**Application Number:** 88303404.3

**Publication Number:** 0287383

**IPC:** H01L 39/24

**Language of the proceedings:** EN

**Title of invention:**

Superconducting ceramic film and a method of manufacturing the same

**Patentee:**

SEMICONDUCTOR ENERGY LABORATORY CO., LTD.

**Opponent:**

Siemens AG

**Headword:**

-

**Relevant legal provisions:**

EPC Art. 123(2), 83, 84, 54(3), 56

**Keyword:**

"Amendments by way of a generalisation (allowed) - clear basis in the application as filed"

"Novelty - (yes) - ion-implantation damage - interpreted in the generally accepted sense of the expression"

"Inventive step (yes) - no reasonable expectation of success in transferring a measure known in the art to "newly" discovered high-Tc ceramic superconductors"

**Decisions cited:**

-

**Catchword:**

-



Case Number: T 0471/96 - 3.4.3

**D E C I S I O N**  
of the Technical Board of Appeal 3.4.3  
of 29 February 2000

**Appellant:** Siemens AG  
(Opponent) Postfach 22 16 34  
D-80506 München (DE)

**Representative:** -

**Respondent:** SEMICONDUCTOR ENERGY LABORATORY CO., LTD.  
(Proprietor of the patent) 398 Hase  
Atsugi-shi  
Kanagawa-ken, 243 (JP)

**Representative:** Milhench, Howard Leslie  
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**Decision under appeal:** Interlocutory decision of the Opposition Division  
of the European Patent Office posted 7 May 1996  
concerning maintenance of European patent  
No. 0 287 383 in amended form.

**Composition of the Board:**

**Chairman:** R. K. Shukla  
**Members:** M. Chomentowski  
P. H. Mühlens

## Summary of Facts and Submissions

I. European patent No. 0 287 383 designating the Contracting states DE, FR and GB was granted in respect of European patent application No. 88 303 404.3 filed on 15 April 1988 and claiming a JP priority of 15 April 1987.

II. The appellant filed an opposition against the granting of the European patent on the ground pursuant to Article 100(a) EPC that its subject-matter was not patentable having regard to inter alia the documents

D3: "Properties of Superconducting Weak Links Prepared by Ion Implantation and by Electron Beam Lithography", E. P. Harris et al, IEEE Transactions on Magnetics, vol. MAG-13, No. 1, January 1977, pages 724 to 730,

and

D9: "International Conference on Applications of Ion Beams to Metals", Sandia, New Mexico (USA), 1973, Paper 1.2 of O. Meyer et al, "Ion Implantation in Superconducting Thin Films", edit. Plenum Press, New York, 1974, pages 15 to 26.

A further ground of opposition under Article 100(b) was raised during the oral proceedings before the opposition division.

III. The European patent was maintained in amended form by the interlocutory decision of 7 May 1996 of the Opposition Division. The only independent claims of the set of 19 claims of the patent as maintained by the

Opposition Division, i.e. claims 1 and 10, read as follows:

Claim 1

"A device comprising a high-Tc superconductive copper oxide ceramic film (2) formed on a substrate (1) and in which at least one region (11) of the film (2) is doped with an impurity which is partially oxidated in the film and provides the impurity doped region with an electrical resistivity: temperature characteristic different from that of the non-doped film so that the impurity doped region (11) can exhibit a finite resistivity at a temperature at which the non-doped superconductive ceramic film (2) has zero resistance."

Claim 10

"A method of manufacturing a device comprising a high-Tc superconductive copper oxide ceramic film (2) formed on a substrate (1) and wherein at least one region (11) of the film has an electrical resistivity: temperature characteristic different from that of another region (10) of the film such that the first mentioned region (11) can exhibit a finite resistivity at a temperature at which the other region (10) has zero resistance, the method comprising forming the superconductive copper oxide ceramic film (2) on the substrate (1), defining said at least one region (11) of the film, and introducing an impurity dopant which is partially oxidated in the film into said at least one region (11) and not into said other region (10) whereby to achieve the required electrical resistivity: temperature characteristic."

IV. The reasoning in the decision of the Opposition Division was in substance as follows:

Late filed document,

D10: Nature, vol. 325, 19 February 1987, M. Strongin et al, " Superconductivity at high temperatures in doped oxides", pages 664 to 665,

cited by the opponent, is of no particular relevance as compared to the acknowledged prior art and is accordingly not admitted into the proceedings. All the remaining prior art documents relate to the technical field of classical superconductive materials. Some of these documents disclose ion implantation in said classical superconductive materials for modifying physical characteristics thereof, for instance reducing or increasing the critical temperature  $T_c$  under which temperature the material starts to exhibit characteristics of superconductivity.

Claim 1 on the other hand concerns a device including a superconductive thin film consisting of a high  $T_c$  copper oxide ceramic material with regions thereof being modified by doped oxidizable impurity dopants which are partially oxidated, and thereby have a lower  $T_c$  compared to the  $T_c$  of the non-doped regions.

There is no prior art document which can be considered as the closest prior art because the materials therein are different from the materials of the claimed device.

The technical problem addressed by the invention is the provision of superconductive patterns made of high  $T_c$  copper oxide films applicable to Josephson devices and

resistors. The problem itself would be obvious, since there was a need in the art for practical applications of the new superconductors. However, at the priority date of the patent in suit, i.e. in April 1987, which was recently after the discovery by Bednorz and Müller of the bulk high Tc copper oxide superconductors (October 1986), there had been very little development in the formation of thin films using the new material or in the technical application thereof, this fact being confirmed by the lack of documents at that time in respect of the formation of thin films of high-Tc copper oxide ceramic superconductors.

Since it was not obvious to the person skilled in the art to select an oxidisable dopant and since the effect of such dopant was not predictable, the solution proposed in claim 1 involves an inventive step.

The objection by the opponent regarding the sufficiency of disclosure of the invention is not well founded, since the application for the patent in suit describes in sufficient detail one way of carrying out the invention.

- V. The opponent lodged an appeal against this decision on 17 May 1996 paying the appeal fee the same day. The statement of the grounds of appeal was filed on 24 July 1996. Document D10 and further documents D11: US-A-4 470 1 90 and D12: EP-A-0 286 891 were cited by the opponent during the appeal proceedings.
  
- VI. During the oral proceedings of 29 February 2000, which had been requested auxiliarily by both parties, the respondent filed a new main request and two auxiliary requests, the main request being as follows:

**Main Request**

**Claims:** 1 to 18 filed during the oral proceedings of 29 February 2000;

**Description:** column 1, (lines 1 to 26), column 2 (lines 49 to 55 ) of the patent as granted;  
pages 2, 3, 4 and 4a filed during the oral proceedings of 29 February 2000;  
columns 3 to 7 of the patent as granted;

**Drawings:** Sheets 1/2 to 2/2 of the patent as granted.

Independent claims 1 and 10 of the main request read as follows:

"1. A device comprising a high-Tc superconductive copper oxide ceramic film (2) formed on a substrate (1) and in which at least one region (11 ) of the film (2) contains partially oxidated, ion implanted, impurity dopant which provides the impurity doped region with an electrical resistivity: temperature characteristic different from that of the non-doped film so that the impurity doped region (11 ) can exhibit a finite resistivity at a temperature at which the non-doped superconductive ceramic film (2) has zero resistance, there being no ion implantation damage to the crystalline structure of the film in the impurity doped region."

"10. A method of manufacturing a device comprising a high-Tc superconductive copper oxide ceramic film (2) formed on a substrate (1 ) and wherein at least one



region (11) of the film has an electrical resistivity: temperature characteristic different from that of another region (10) of the film such that the first mentioned region (11 ) can exhibit a finite resistivity at a temperature at which the other region (10) has zero resistance, the method comprising forming the superconductive copper oxide ceramic film (2) on the substrate (1), defining said at least one region (11 ) of the film, and introducing an oxidizable impurity dopant into said at least one region (11 ) and not into said other region (10), the doping being effected by ion implantation and being followed by thermal annealing of the film (2) in an oxidizing atmosphere to cause the dopant to be partially oxidated in the film and to make good any ion implantation damage to the crystalline structure of the film in the impurity doped region, whereby to achieve the required electrical resistivity: temperature characteristic."

VII. The respondent's arguments in support of his main request can be summarised as follows:

The subject-matter of the main request is new with respect to EP-A-0 286 891, wherein, in particular, no annealing for making good any damage is carried out. Among the documents cited, only document D10 provides a teaching about the newly discovered high-Tc superconductive copper oxide ceramic films, all the other prior art documents being concerned with "conventional" superconductive materials generally made of metals or alloys. As can be seen from document D10 and the statutory declaration of Mr A. T. Boothroyd, the knowledge about the high-Tc superconductors was not established at the priority date of the patent in suit and the structures of these new high-Tc superconductors

and of the conventional superconductors were very different from each other. It was therefore not obvious to transpose to the new materials the techniques known for the conventional materials. Moreover, none of the prior art documents discloses annealing of the superconductive film so as to oxidise the ion implanted impurity and to remove the crystal damage caused by the ion implantation. Therefore, the subject-matter of the invention according to the main request cannot be regarded as obvious to a person skilled in the art.

VIII. The appellant requested that the decision under appeal be set aside and that the patent be revoked. The appellant's arguments can be summarised as follows:

The information in the patent in suit concerning the extent to which ion implantation damage has been removed is insufficient. In any case, since the implanted and oxidized ions are still in the structure of the superconductive film after implantation and annealing, the doped regions could still be regarded as containing implantation damage after annealing. Therefore, the main request is not new having regard to the disclosure in EP-A-0 286 891.

The person skilled in the art of high-Tc superconductors discussed in document D10 is the same as the one skilled in the art of documents D3, D9 or D11. Therefore, for the skilled person, it was obvious to transpose to the newly discovered superconductive materials of document D10 the techniques known for the conventional superconductive materials for modifying the transition temperature of the conventional materials by ion implantation.

Therefore, the subject-matter of the main request lacks an inventive step.

## **Reasons for the Decision**

1. The appeal is admissible.

2. *Main request*

2.1 Allowability of amendments

With regard to the requirement of Article 123(2) EPC in respect of the amendments to Claim 1 of the main request, it was contended by the appellant that in the application as filed, partial oxidation was disclosed only in relation to the embodiment of Figures 1(A) to 1(C) described in column 3, lines 15 to 63 wherein the doped impurity is silicon, whereas the amended claim 1 does not specify silicon as the dopant impurity, so that the partial oxidation according to the claim is not restricted to silicon. This generalisation, according to the appellant, has therefore no basis in the application as filed, and the amended claim thus contravenes the requirement of Article 123(2) EPC.

In this connection, as correctly pointed out by the respondent, dependent claim 2 of the application as filed specifies that the impurity contained in the doped region is in an oxidised form without specifying that the impurity is silicon. Moreover, in column 4, lines 24 to 29 of the application as filed, impurities other than silicon are disclosed to be suitable for obtaining a desired drop in the critical temperature. In the Board's view, therefore, partial oxidised state

of an impurity in general as claimed has a clear basis in the application as filed.

Moreover, the amendment in claim 1 specifying that there is no ion implantation damage to the crystalline structure of the film in the impurity doped region has a basis in the application as filed in column 2, lines 39 to 43, wherein in connection with the general description of the invention, it is disclosed that after ion implantation, the superconducting film is subjected to thermal treatment to make good any damage to the crystalline structure.

There were no objections under Article 123(2)EPC or Article 123(3)EPC by the appellant in respect of the other amendments to claims 1 and 10. The Board is also satisfied that the other amendments in relation to claim 1 as filed and granted, respectively, comply with Articles 123(2) and 123(3)EPC.

## 2.2 Sufficiency of disclosure

It was contended by the appellant that the application as filed does not sufficiently disclose the invention in so far as impurities other than silicon are concerned. In particular, there was no teaching regarding thermal annealing of the film to partially oxidise impurities other than silicon, and whereby there is no damage to the crystalline structure of the film in the doped region.

In the Board's opinion, however, the embodiment of the invention comprising silicon as the implanted and oxidised impurity provides sufficient information regarding the doping concentration of silicon and the

annealing temperatures employed in an oxidising atmosphere to cause oxidation of some of the implanted silicon, so that for a skilled person it was merely a question of finding by routine trials appropriate annealing temperatures in an oxidising atmosphere for other impurities to obtain a desired drop in the critical temperature  $T_c$  of the doped regions. In the light of the skilled person's common general knowledge in the art, such trials could not be regarded as putting any undue burden, so that in the Board's view the teaching in relation to silicon was clearly extendable to other impurities.

Therefore, the patent according to the main request satisfies the requirements of Articles 83 and 100(b) EPC that a European patent must disclose the invention in a manner sufficiently clear and complete for it to be carried out by a person skilled in the art.

### 2.3 Clarity

According to the appellant, the expression, "an impurity which is partially oxidated" in claim 1 relating to a device is not clear since it relates to a process step. The Board however agrees with the submission made by the respondent that the expression defines the oxidised state of the impurity after its implantation in the doped region, so that the claim clearly defines the subject-matter for which protection is sought (Article 84 EPC).

### 2.4 Novelty

The objection of lack of novelty was raised by the appellant only with respect to EP-A-0 286 891, i.e

document D12, which designates *inter alia* the Contracting states DE, FR and GB; has the filing date of 25 March 1988, claims the priority date of 13 April 1987 and was published on 19 October 1988, i.e after the filing date of 15 April 1988 of the European patent application for the patent in suit. Thus, the priority date of document D12 is earlier than the priority date of the European patent application for the patent in suit (cf. item I above ). Document D12 is therefore comprised in the state of the art pursuant to Article 54(3) EPC.

Document D12 discloses a device comprising a high-Tc superconductive copper oxide ceramic film formed on a substrate and in which at least one region of the film contains ion implanted impurity dopant which provides the impurity doped region with an electrical resistivity: temperature characteristic different from that of the non-doped film; the impurity doped region can exhibit a finite resistivity at a temperature at which the non-doped superconductive ceramic film has zero resistance.

The following is to be noted with respect to the feature of the claim that the impurity dopant is "partially oxidated":

One of the impurity dopants mentioned for the device of EP-A-0 286 891 (see page 4, lines 31 to 33 and page 6, lines 29 to 31) is arsenic, which is generally known as being an easily oxidizable element. Following implantation, any organic masking material used to define the pattern in the ion implantation mask is removed, as by ashing, i.e. by a generally known treatment which can be effected at high temperature in

an oxidizing atmosphere. Also, according to the patent in suit (see column 4, lines 14 to 24) the thermal treatment for oxidizing some of the impurities is effected at the same time as the firing treatment for removing the resist of the mask. Therefore, in the opinion of the Board, the ashing treatment in document D12 would inevitably lead to partial oxidation of arsenic, so that the partially oxidised state of the doped impurity cannot be considered as a feature distinguishing the device as claimed from the device of document D12.

However, as convincingly argued by the respondent, it is derivable from the whole content of EP-A-0 286 891 (see page 3, lines 32 to 42, page 4, lines 21 to 30; page 6, lines 18 to 22, page 8, lines 12 to 15) that the device disclosed therein relies on damaging specific regions of the superconductive film by ion implantation. Indeed, there is no derivable information in this document that the ashing treatment for removing organic masking material, i.e. the only firing treatment mentioned in the document, is such that it results in the removal of ion implantation damage to the crystalline structure of the film in the impurity doped region, as in claim 1 of the main request.

In this respect, the appellant argued that, since the implanted and oxidized ions are still in the structure of the superconductive film after implantation and annealing, implantation damage is also present in the superconductive film of the main request. However, the Board does not find this argument convincing because, in the relevant technical field, it is the damage caused by the bombardment by the ions, and not distortions or lack of uniformity caused by the

presence of the ions in the implanted structure, which is generally understood under the term "damage".

Therefore, the subject-matter of claim 1 of the main request is new having regard to the disclosure in Document D12. The Board is also satisfied that the subject-matter of the claim is new having regard to the other cited prior art documents.

## 2.5 Inventive step

- 2.5.1 Document D10 is the only cited prior art document within the meaning of Article 54(2) EPC which is concerned with superconductivity at high temperatures in doped oxides. This document provides a historical review of the evolution of the technique of superconductive materials since the discovery of this phenomenon in 1911, and mentions the conventional superconductive materials having superconductivity confined to temperatures less than 23 K and stresses the relatively recent discovery at the end of 1986 of oxide superconductors with Tc values greater than 30 K. The document further mentions the hesitant acceptance of the new phenomenon by the scientific world and speculates over possible developments and future uses of such high Tc superconductive materials.

Thus, in the context of claim 1 of the main request, the relevant disclosure in document D10 can be regarded as that the new materials are copper oxide ceramic materials exhibiting superconductivity at critical temperatures higher than 30 K. Document D10 (see the footnotes 2 to 6) makes reference to recent studies following the discovery of these new high-Tc superconductive materials and confirming it.



However, contrary to claim 1 of the main request, document D10 does not disclose a device comprising a film of such a high-Tc material formed on a substrate and in which at least one region of the film contains partially oxidated, ion implanted, impurity dopant which provides the impurity doped region with an electrical resistivity: temperature characteristic different from that of the non-doped film so that the impurity doped region can exhibit a finite resistivity at a temperature at which the non-doped superconductive ceramic film has zero resistance, there being no ion implantation damage to the crystalline structure of the film in the impurity doped region.

2.5.2 Starting from document D10, an object of the invention of the patent in suit can be seen in providing a device comprising a high-Tc superconductive copper oxide ceramic film containing impurity doped regions with an electrical resistivity: temperature characteristic different from that of the non-doped film and, in particular, the impurity doped regions exhibiting a finite resistivity at a temperature at which the non-doped superconductive ceramic film has zero resistance (cf. also the application as filed, page 2, lines 13 to 16)

2.5.3 Document D11 is concerned with the conventional low Tc superconductors. It was known from this document (see in particular column 1, lines 5 to 6 and 26 to 34; column 3, line 3 to column 4, line 19, in particular column 3, line 63 to column 4, line 2; column 5, line 1 to column 8, line 49; Figures 1 and 2) that by local implantation of doping elements, in particular doping elements forming oxides in the superconducting counter electrode (13) of a superconductive tunnelling

(Josephson) device, the parameters of said counter-electrode and of the device can be trimmed. The material of the counter-electrode is based on Pb, an exemplary material being Pb-Bi (29 wt %).

It is known from document D3 (see page 724, right-hand column, last paragraph, to page 725, left-hand column, first paragraph; Figure 1; see also the abstract and the introduction), that the transition temperature  $T_c$  of superconducting materials can be spatially changed by ion implantation. In particular, the transition temperature of metal thin films of Nb or Mo is considered, whereby  $T_c$  of Nb can be reduced by ion implantation.

Furthermore, it is known from document D9 (see in particular the abstract) to implant ions in superconducting thin films; in particular, thin films of the transition metal superconductors Ti, Zr, V, Nb, Ta, Mo, W, and Re, the A-15 compound  $Nb_3Sn$  and the interstitial compounds NbC and NbN with NaCl structure were implanted with ions which are chemically active or with inert ions for causing radiation damage and/or other effects influencing the superconducting transition temperature  $T_c$ .

- 2.5.4 The question of inventive step thus involves first the consideration whether it was obvious to transfer to the recently discovered high- $T_c$  ceramic superconducting materials the knowledge and techniques which were well established for the conventional superconducting materials. More specifically, whether it was obvious to modify locally the transition temperature in high- $T_c$  ceramic superconducting materials by ion implantation of impurities. The second consideration in the

assessment of inventive step is even if it was considered obvious to apply the ion implantation technique to high-TC ceramic superconducting materials, whether the skilled person would arrive at the claimed subject-matter by using this technique.

According to the statutory declaration of Mr Boothroyd (see in particular paragraph 2), at the priority date of the patent in suit, most researchers in the field were still debating the results obtained by Bednorz and Müller and endeavouring to replicate them.

The Board finds that the above statement in the Declaration is supported by the general tenor of document D10 (see for instance page 665, right-hand column, the two last paragraphs), which is the only cited prior art document in the sense of Article 54(2) EPC concerning the high-Tc ceramic superconductors, wherein doubts expressed by the technically skilled persons are stressed concerning accurate determination of some crucial parameters of said new materials and the question, whether said new materials exhibit true superconductivity, or not. Moreover, it emerges from document D10 that it was not until December 1986, i.e. only four months before the priority date of the patent in suit that the discovery of superconductivity in Ba-La-Cu-O system by Bednorz and Müller was finely accepted by the scientific world (cf. page 665, left-hand column, third paragraph). Also according to the document, the crystalline structure of the newly discovered high-Tc superconducting ceramic material is a layered perovskite structure and that the states responsible for the superconductivity lie in CuO plane. Thus, there are important differences in composition and in structure between the high-Tc ceramic copper

oxide ceramic materials and the metals or alloys of NaCl crystal structure of the conventional superconductors known, for instance, from document D9 (see the abstract). In this respect, it is to be noted that there is no indication in document D10 about the effect of oxidized implanted ions on the superconductivity in impurity regions wherein there is no implantation damage to the crystalline structure of the material. Consequently, the Board concurs with the submission by the respondent that the effect of doping impurities and oxidising them on the resistivity: temperature characteristic, i.e on the critical temperature could not be predicted. Consequently, contrary to the respondent's argument, starting from document D10, the application of the ion implantation method of tailoring properties known for the "conventional" superconductive materials, for instance, from document D11, was not a measure which a person skilled in the art would have tried in a high-Tc ceramic with a perovskite structure with a reasonable expectation of success.

The appellant's arguments based on document D11 as a starting point and the replacement of the conventional superconducting material by the high-Tc ceramic copper oxide materials known from document D10 are not considered as leading to another finding for the above reasons because the counter-electrode of the devices known from document D11 is a Pb containing material such as Pb-Bi (29 wt. %), having different crystalline structure from that of high-Tc material.

Moreover, as was correctly emphasised by the respondent, the known method of trimming superconducting properties by ion implantation relies

on producing damage to the crystalline structure of the material, which is contrary to the teaching of the patent in suit, wherein the superconducting properties are locally changed by the partially oxidised state of the implanted impurities and by removing the damage to the crystalline structure due to the implantation.

Thus, an application of the known prior art method of locally trimming the superconducting properties to the high-Tc copper oxide materials would not lead to the device as claimed in the patent in suit.

- 2.5.5 Therefore, in the Board's judgement, the subject-matter of claim 1 of the main request was not obvious to a person skilled in the art and thus involves an inventive step in the sense of Article 56 EPC.

Consequently, claim 1 is patentable according to Article 52(1) EPC.

- 2.6 Since claim 10 of the main request expresses the same invention, albeit, in terms of a method, it is also patentable for the above reasons (Article 52(1) EPC).

3. Therefore, the European patent can be maintained in the amended form according to the respondent's main request (Article 102(3) EPC).

## Order

### For these reasons it is decided that:

1. The decision under appeal is set aside.
2. The case is remitted to the first instance with the order to maintain the patent with the following documents:

**Claims:** 1 to 18 of the main request filed during the oral proceedings of 29 February 2000

**Description:** column 1, (lines 1 to 26), column 2 (lines 49 to 55) of the patent as granted;  
pages 2, 3, 4 and 4a filed during the oral proceedings of 29 February 2000;  
column 3 to 7 of the patent as granted;

**Drawings:** Sheets 1/2 to 2/2 of the patent as granted.

The Registrar

The Chairman

D. Spigarelli

R. Shukla