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D E C I S I O N
of 7 March 2002

Case Number: T 1081/98 - 3.4.3

Application Number: 91109506.5

Publication Number: 0461592

IPC: H01L 39/24

Language of the proceedings: EN

Title of invention:
Thin film Josephson device

Patentee:
MITSUBISHI CHEMICAL CORPORATION

Opponent:
Siemens AG

Headword:
-

Relevant legal provisions:
EPC Art. 56

Keyword:
"Inventive step - no"

Decisions cited:
-

Catchword:
-

Case Number: T 1081/98 - 3.4.3

D E C I S I O N
of the Technical Board of Appeal 3.4.3
of 7 March 2002

Appellant: (Opponent)
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Representative: -

Respondent: (Proprietor of the patent)
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Decision under appeal: **Decision of the Opposition Division of the European Patent Office posted 16 September 1998 rejecting the opposition filed against European patent No. 0 461 592 pursuant to Article 102(2) EPC.**

Composition of the Board:

Chairman: R. K. Shukla
Members: E. Wolff
M. J. Vogel

Summary of Facts and Submissions

I. This is an appeal from a decision of the opposition division, dated 16 September 1998, rejecting the opposition against European patent no. 0 461 592 pursuant to Article 102(2) EPC.

Claim 1 of the patent as granted reads as follows:

"1. A Josephson device comprising a substrate and an oxide superconductor film formed thereon, wherein said oxide superconductor film comprises atomic monolayers each composed of at least one kind of element of the oxide superconductor, which are deposited in a predetermined and periodic order substantially in a direction perpendicular to the substrate so that the lattice structure of the oxide superconductor is substantially maintained, and at an intermediate portion of the oxide superconductor film, at least a part of the atoms of the oxide superconductor is substituted by other element in the lattice structure of the oxide superconductor to form a non-superconductor interlayer, and the periodicity of the lattice structure of the oxide superconductor film is substantially maintained across the interface between the oxide superconductor and said non-superconductor interlayer."

II. The appellant (opponent) filed a notice of appeal on 16 November 1998, and paid the appeal fee on the same day. The statement setting out the grounds of appeal was filed on 13 January 1999.

The appellant requested that the decision under appeal be set aside and that the patent with the granted claims 1 to 9 be revoked.

The appellant relied on the following documents:

D1: Solid State Communications, vol. 71, No. 7, 1989, pp. 569-572

D2: Applied Physics Letters, vol. 55, No. 19, 6 November 1989, pp.2032-2034

D3: JP 2-125672 A, 14 May 1990 and corresponding Abstract of "Patent Abstracts of Japan" (E-959), August 3 1990, vol. 14, No. 359

D4: EP-A-0 366 949

D5: 2nd Workshop on High-temperature Superconducting Electron Devices, June 7-9 1989, Shikabe, Hokkaido (JP), pp. 285-292

D6: JP 2-59403 A, 28 February 1990 and corresponding Abstracts of Derwent and JAPIO

D7: Applied Physics Letters, vol. 54, No. 18, 1 May 1989, pp. 1802-1804

D8: Applied Physics Letters, vol. 56, No. 16, 16 April 1990, pp. 1576-1578

D9: Applied Physics Letters, vol. 53, No. 4, 25 July 1988, pp. 337-339

D10: Laser Magazin, Textbook 6, 1989, pp. 25-30.

D11: Second workshop on High-Temperature superconducting Electron Devices, June 7-9, 1989, Extended Abstracts; Title page
pages 1 and 3 - Organisations and Foreword,
pages 9 to 17 - Contents,
pages 423 to 425 - Prospects of Possible Applications of High T_c Josephson Junctions.

Documents D1 to D8 were cited during the opposition proceedings, whereas documents D9 to D11 were cited by the appellant during the appeal proceedings.

III. The respondent requests that the appeal be dismissed.

The respondent submitted the following document during the appeal proceedings:

D12: Ullmann's Encyclopaedia of Industrial Chemistry, 5th ed., vol. A23, p. 551

IV. The appellant's argument in support of his request can be summarized as follows:

Concerning the admissibility of documents D9 to D11, documents D9 and D10 were introduced in response to the arguments made by the opposition division in rejecting the opposition. While these documents admittedly do not have any greater relevance than other documents already cited, they demonstrate the general knowledge of the skilled person and thereby aid the interpretation of the prior art and the claimed invention.

The document D11 is introduced merely to show that document D5 is addressed to persons skilled in the art of electronic devices of the kind of which Josephson junction devices are the main representative.

Prior to considering the relevance of the cited prior art, it is necessary to clarify what is meant, in claim 1, by the term "atomic monolayers".

Ceramic superconductors of the kind to which the invention relates have a Perovskite crystal structure in which each unit cell of the crystal consists of a sequence of layers. Each layer will generally consist of more than one atomic species. For example, in addition to other layers, each unit cell of the Perovskite structure contains several layers of CuO. It therefore appears proper to take "atomic monolayers" to mean layers with a thickness of atomic dimensions, rather than layers of a single atomic species.

Taking atomic monolayers to be the layers which in sequence make up the unit cell of the Perovskite crystal structure, the invention as claimed in claim 1 can be seen to be anticipated by the disclosure in document D1.

Document D1 describes the growth of epitaxial multi layers of $YBa_2Cu_3O_7$ and $PrBa_2Cu_3O_7$ as a possible basis for superconducting electronic devices, with particular reference to SIS or SNS tunnel junctions in SQUIDs and like devices. According to document D1, such devices are formed by placing a non-superconducting layer of $PrBa_2Cu_3O_7$ between a superconducting strip line and a superconducting ground plane formed from $YBa_2Cu_3O_7$.

Document D1 specifically discloses that the interface between the superconductor and the non-superconducting material should be very sharp. It further states that "the epitaxy is maintained throughout the layer system." It follows that the periodicity of the atomic layers must have been preserved, otherwise, as a result of crystallographic misorientations, epitaxy would not have been maintained and a lower crystal quality would have been obtained than is indicated by the measurement results quoted in document D1.

Should the Board not accept that document D1 destroys the novelty of the invention as claimed in claim 1, then in order to consider whether the invention involves an inventive step it is necessary to take into account document D4 or D5, each of which describes formation of superconducting films by layer-by-layer deposition. Document D4 refers to periodically laminated layers (e.g. column 11, lines 9 to 10) while document D5 concerns a layer-by-layer deposition technique in which site-selective substitution of atoms in a layered structure is used to provide tailored variation of the properties of superconducting films (abstract). Since the most common electronic devices using superconductivity are Josephson junction devices, the skilled person would immediately recognise that the techniques provided by document D4 or D5 would be applicable when forming the structure disclosed in document D1, and would allow the precise tailoring of that structure.

V. The respondent's arguments can be summarized as follows:

Documents D9, D10 and D11 do not appear *prima facie* to be highly relevant. The Board is requested to exercise its discretion under Article 114(2) EPC in disregarding these belatedly submitted documents. Also rejected should be any arguments that these documents represent the common general knowledge of the skilled person at the priority date of the application, because these documents cannot be taken to be equivalent to standard textbooks.

Concerning the meaning of the term "atomic monolayer", it is clear that in building the structure layer-by-layer, the individual layers do not need to consist of a single element. On the other hand, a layer 100 nm thick, say, is clearly not an atomic monolayer. The term atomic monolayer is thus intended to refer to a layer of atomic dimensions which however does not in general consist of merely a single atomic species.

As regards the invention as claimed, it is not disputed that all but the last five lines of claim 1 of the granted patent as published are known. The difference to the prior art is set out in those last five lines which require that the periodicity of the lattice structure is maintained across the interface between superconductor and non-superconductor.

Maintaining epitaxy throughout does not imply that periodicity is also maintained throughout. For example, the definition of "epitaxy" in document D12 lacks any mention of periodicity, epitaxy being defined as "the growth of a crystal on another crystal along essentially the same crystal axis..." (page 551, section 5 "Epitaxy", first paragraph). In the process described in document D1, the change from Y-based material to Pr-based material may interrupt the periodicity of the layer sequence though epitaxy is maintained.

Moreover, in the process of document D1 a crystal is grown by a DC sputtering technique in which the target heads are of stoichiometric composition. In this technique, the crystal is not deposited in atomic layers. Instead the material is deposited from an essentially stoichiometric gas cloud.

Similarly, document D2 uses stoichiometric targets to fabricate Josephson devices, although in this case a laser deposition technique is used. As in the case of document D1, the deposition technique is not layer-by-layer since it leads to an atomic cloud being formed from which the material is deposited. Document D2, like document D1, describes the quality of the grown material having been assessed by RBS which provides no information about the periodicity of the layers across the interface.

Document D4, which the opposition division considered the nearest prior art, admittedly uses layer-by-layer deposition of atomic layers. However, it is clear from the disclosure in document D4 that not only is periodicity not taken into consideration by the authors concerned but cannot be maintained because of the inclusion in the structure of the metal layer 10. Document D4 therefore leads away from the claimed invention.

Document D5 makes no mention of Josephson junction device structures. The paper merely discloses that superconducting layers of different properties can be created by substitution of certain atoms in some of the monolayers. In contrast, the invention as claimed relates to a three layer Josephson device.

Document D5 also describes replacement of a single layer by three layers, thereby altering the periodicity from a five layer structure to a seven layer structure.

Documents D6 to D9 are concerned only with the layer-by-layer technique of deposition, but not in the context of manufacturing three-layer Josephson junction devices of the kind to which the claimed invention relates.

The disclosure in document D3 is similar to the disclosure in document D1 in that the crystal structure of the non-superconducting material in a Josephson junction is identical to that of the adjacent superconducting layers, without referring in any way to the periodicity of the lattice structure across the superconductor/non-superconductor interfaces or the need to maintain that periodicity.

In addition to the other differences, the processes described in documents D1 and D2 also involve higher temperatures than those employed by the invention.

VI. Oral proceedings were held on 7 March 2002 in the presence of both parties to the appeal.

Reasons for the Decision

1. The appeal is admissible.

2. Admissibility of documents D9 to D11

The Board reached its decision to revoke the patent without needing to take into account the contents of

Documents D9 to D11. These documents are therefore not admitted into the proceedings.

3. *Novelty*

3.1 The invention as claimed relates to Josephson junction devices based on oxide superconducting films, in which at least some of the atoms of the oxide superconductor are substituted by other elements to form the non-superconducting interlayer without disrupting the periodicity of the lattice structure across the superconductor/non-superconductor interface.

3.2 Document D1 discloses superconducting electronic devices based on epitaxial multi layers of $YBa_2Cu_3O_7$ and $PrBa_2Cu_3O_7$, with particular reference to SIS or SNS tunnel junctions in SQUIDs, that is, devices based on the Josephson effect. In the words of claim 1 of the patent in suit, document D1 discloses Josephson devices comprising a substrate ($SrTiO_3$ as referred to for example in the Abstract and in Figure 3) with a superconductor film formed thereon (e.g. the Abstract, and page 570 left-hand column "Experimental", and Figure 3) wherein the superconducting film comprises atomic monolayers deposited in a predetermined and periodic order substantially in a direction perpendicular to the substrate (page 570 left-hand column, "Results and Discussion" lines 14 to 17 "the films grew epitaxially with the crystallographic c-axis parallel to the substrate normal"), and at an intermediate portion of the oxide superconductor film at least a part of the atoms (Y) of the oxide superconductor is substituted by an other element (Pr) in the lattice structure of the superconductor to form a non-superconductor layer.

3.3 The appellant submitted that the invention as claimed should be considered to lack novelty in view of the disclosure document D1 because the characteristics of the superconducting material described there, together with the explicit statement that epitaxy is maintained throughout the deposition process, lead to the conclusion that the periodicity of the atomic layers is, in fact, maintained across the boundary between the superconducting and non-superconducting materials.

Since only the Perovskite unit cell with three CuO-planes is superconducting, any departure from the sequence of layers would have the negative effects of introducing a non-superconducting layer next to the $PrBa_2Cu_3O_7$ layer, thereby reducing the sharpness of the interface. It would also lead to crystallographic misorientations in the epitaxial growth of both the non-superconducting layer and the subsequent superconducting layer.

The measured characteristics of the deposited films provide a strong indication that the crystal quality was high, since otherwise the reported critical current densities of $10^6 A/cm^2$ (page 570, left-hand column, "Results and discussion", lines 20 to 23) could not have been achieved, and that the junction was sharp since the presence of the Pr-layer is reported to have had no adverse effects on the superconducting properties of the Y-band layer (page 571, right-hand column, lines 17 to 20). It follows that the periodicity of the atomic layers must have been preserved. Although the deposition method described in document D1 results in a stoichiometric cloud, deposition from this cloud must result in the same layer structure as in the invention as claimed otherwise the deposited material would not be the superconducting crystal structure.

Document D2 corroborates the teaching of document D1 in that it states that it is necessary to select a barrier which is compatible with growth of the second YBCO layer in the correct orthorhombic phase and with the correct stoichiometry. The particular material considered in document D2 is $PrBa_2Cu_3O_{7-x}$(PBCO) which is non-superconducting and provides a very good lattice match to $YBa_2Cu_3O_{7-x}$ (e.g., document D2, page 2032, lefthand column, penultimate line to right-hand column, first line).

3.4 The respondent, on the other hand, contended that although the periodicity of the monatomic layer sequence would not necessarily be broken at the boundary between the superconducting and non-superconducting materials when using the deposition method described in document D1, it is essential that special measures enabling selective substitution of the atoms of the superconductor layer are taken to ensure that the periodicity is maintained across the boundary.

More specifically, the unit cell of the Perovskite structure which forms both the superconducting films and the intermediate non-superconducting film of the Josephson device, can be visualised as consisting of six separate layers. The change from Y-based material to Pr-based material may cause the periodicity of this layer sequence to be interrupted in that, for example, the last layer of the Y-based material could consist of only four layers. According to the definition in document D12, epitaxy is nevertheless maintained.

Other differences between the invention and the cited prior art in document D1 concern the crystal growing process. Document D1 employs a DC sputtering technique in which the target heads are of stoichiometric composition. In this technique, the crystal is not deposited in atomic layers. Instead the material is deposited from an essentially stoichiometric gas cloud. The layers formed are about 100 nm in thickness, much thicker than the layers employed by the invention. Rutherford Backscattering Spectroscopy (RBS) was then used to measure the thickness of the Y-based film and the Pr-based film and to confirm the stoichiometry of the film system. As the resolution of RBS is only around 10 nm, the measurement system employed in document D1 is about an order of magnitude too coarse for establishing whether or not periodicity of the lattice structure is maintained across the interface between the superconducting Y-band material and the non-superconducting Pr-band material.

Maintaining epitaxy throughout does not imply that periodicity is maintained throughout. For example, the definition of "epitaxy" in document D12 lacks any mention of periodicity, epitaxy being defined as "the growth of a crystal on another crystal along essentially the same crystal axis..." (page 551, section 5 "Epitaxy", first paragraph). The process described in document D1 has to be interrupted when targets are changed, which is a further indication that breaks in the periodicity of the layer structure are to be expected at the interfaces between superconducting and non-superconducting materials. That despite such interruptions epitaxy would be maintained is demonstrated, for example, by document D7 which, in Figure 3, shows unit cells which are of different lengths as a result of variations in the numbers of CuO layers, and of differences in the layers located between the CuO layers.

3.5 The Board is not convinced by the appellant's argument that document D1 takes away the novelty of the invention as claimed. The reported material characteristics and maintained epitaxy do not conclusively show that periodicity was maintained across the boundary in the case of the experiments reported in document D1. The Board therefore concludes that, for the reasons submitted by the respondent, it is not unambiguously derivable from document D1 that in the crystal structure resulting from the process described in document D1 periodicity is **necessarily** maintained as required by claim 1.

4. *Inventive step*

4.1 In view of the features which, as set out in paragraph 3.2 above, claim 1 and document D1 have in common, document D1 represents the closest prior art. The only difference between the disclosure in document D1 and the invention is that, as claimed, the invention requires explicitly that the periodicity of the lattice structure is maintained across the boundary between the superconductor and the non-superconducting interlayer.

4.2 Both document D1 and the invention as claimed relate to Josephson junction devices in which the non-superconducting interlayer is formed by replacing certain atoms in the superconducting layer by other atoms. The problem addressed by the skilled person is to provide an improved Josephson junction device of this type.

4.3 Document D1 is not only the closest prior art but also informs the skilled person about certain aspects of an improved device. Thus, the skilled person is informed that a device of this kind requires high crystal quality throughout because, in the case of $YBa_2Cu_3O_7$, "the superconducting properties depend very sensitively on the structure and stoichiometry of the films" (page 569, left-hand column, last paragraph) and "epitaxy has to be maintained throughout the multilayer system" (page 569, right-hand column, lines 7 to 9). Also, the non-superconducting layer needs to be formed thin enough to correspond to the coherence length which "is known to be extremely short in high T_C superconductors" (page 569, right-hand column lines 26 to 28) and, for that same reason, "the interface between the superconductor and the non-superconducting material" should be "be very sharp" (page 569, right-hand column, last line to page 560, left-hand column line 2).

4.4 Document D5 discloses layer-by-layer deposition of high T_C superconductors and site-selective substitution of atoms in order to alter the superconducting properties of the material. According to document D5, the superconducting properties of the material are varied solely by substitution of atoms during the layer-by-layer deposition process. These substituted atoms are, moreover, incorporated into the crystal structure (e.g. document D5, page 286, Figure 1).

4.5 It is the appellant's submission that in the light of the clear statements in document D1 that high crystal quality is necessary and epitaxy needs to be maintained, the skilled person would immediately recognise that with the method disclosed in document D5 better Josephson devices can be made. Applying the layer-by-layer deposition technique of document D5 to form Josephson junction devices as described in document D1 would necessarily result in a Josephson junction device in which periodicity is maintained across the boundary between superconducting and non-superconducting material. The same layers sequence needs to be maintained throughout the deposition process to ensure the necessary high crystal quality and the sharp boundary is achieved by the substitution of some of the atoms in certain layers.

4.6 The respondent has expressed the view that document D5 relates to the deposition of superconducting layers of different properties, not to the formation of multi layer devices.

4.7 The Board does not consider the respondent's argument persuasive. The skilled person would not consider document D5 to be irrelevant merely because it does not explicitly refer to multi layer device structures. The skilled person would recognise, as submitted by the appellant, that the method of deposition and substitution described in document D5 is applicable to the formation of multi layer devices of the kind described in document D1, where the non-superconducting film is formed by substituting atoms of one species, Pr, for those of another, Y, and would appreciate that being able to tailor the properties of superconducting layers in the manner described there gives improved control over the device structure.

4.8 In document D5, the sequence of targets for laser ablation and thus the sequence of layers is described in terms of corresponding letters such as A-B-C-B-A for the deposition of a standard film (page 286, lines 2 and 3). Under the heading "I-3. Substitution of Ba at Ca site", is discussed the complete substitution of Ca by Ba, resulting in the sequence A-B-D-B-A, and the partial substitution, resulting in the sequence A-B-(C/D/C)-B-A. It is clear from this that replacing the layer C by the layer (C/D/C) merely indicates the change in the target for laser ablation to obtain the **partial** replacement within that layer of one atomic species by another, rather than replacement of one layer by three layers and thereby a break in periodicity. Contrary to the submission by the respondent, document D5 cannot on this count be considered to teach away from the invention.

4.9 The layers deposited by the method according to document D5 are layers the thickness of which is of atomic dimensions, consisting of one or more species of atoms. They are therefore atomic monolayers as understood in connection with the claimed invention.

4.10 Applying the deposition technique of document D5 to manufacturing devices of the kind described in document D1 will inevitably result in devices in which the same sequence of monatomic layers is deposited throughout.

4.11 For the foregoing reasons, in the Board's judgement, the invention as claimed in claim 1 does not involve an inventive step as required by Article 56 EPC.

Order

For these reasons it is decided that:

1. The decision under appeal is set aside.

2. The patent is revoked.

The Registrar: The Chairman:

D. Spigarelli R. K. Shukla