



INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

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(21) International Application Number: PCT/US83/01257 (22) International Filing Date: 15 August 1983 (15.08.83) (31) Priority Application Number: 434,677 (32) Priority Date: 15 October 1982 (15.10.82) (33) Priority Country: US (71) Applicant: MOTOROLA, INC. [US/US]; 1303 E. Algonquin Road, Schaumburg, IL 60196 (US). (72) Inventor: WU, Schyi-Yi ; 1340 W. Medina, Mesa, AZ 85202 (US). (74) Agents: GILLMAN, James, W. et al.; Motorola, Inc., Patent Department - Suite 200F, 4350 E. Camelback Road, Phoenix, AZ 85018 (US).		(81) Designated States: DE (European patent), FR (European patent), GB (European patent), JP, NL (European patent). Published <i>With international search report.</i>																														
(54) Title: A METHOD OF FORMING A SHALLOW AND HIGH CONDUCTIVITY BORON DOPED LAYER IN SILICON (57) Abstract Implanting, with low energy (e.g. 75 Kev and below), a dose of boron difluoride (BF₂) into an area on a silicon substrate which is post-damaged or pre-damaged by a silicon implant so that annealing, or activation, can be accomplished at temperatures in the range of 550°C to 900°C. <table border="1"> <caption>Approximate data points from the graph</caption> <thead> <tr> <th>Anneal Temperature (°C)</th> <th>Curve A (log Ω/□)</th> <th>Curve B (log Ω/□)</th> <th>Curve C (log Ω/□)</th> <th>Curve D (log Ω/□)</th> <th>Curve E (log Ω/□)</th> </tr> </thead> <tbody> <tr> <td>600</td> <td>3.2</td> <td>3.0</td> <td>2.8</td> <td>2.5</td> <td>2.2</td> </tr> <tr> <td>700</td> <td>3.5</td> <td>3.2</td> <td>3.0</td> <td>2.8</td> <td>2.5</td> </tr> <tr> <td>800</td> <td>3.0</td> <td>2.8</td> <td>2.5</td> <td>2.2</td> <td>2.0</td> </tr> <tr> <td>900</td> <td>2.5</td> <td>2.2</td> <td>2.0</td> <td>1.8</td> <td>1.5</td> </tr> </tbody> </table>			Anneal Temperature (°C)	Curve A (log Ω/□)	Curve B (log Ω/□)	Curve C (log Ω/□)	Curve D (log Ω/□)	Curve E (log Ω/□)	600	3.2	3.0	2.8	2.5	2.2	700	3.5	3.2	3.0	2.8	2.5	800	3.0	2.8	2.5	2.2	2.0	900	2.5	2.2	2.0	1.8	1.5
Anneal Temperature (°C)	Curve A (log Ω/□)	Curve B (log Ω/□)	Curve C (log Ω/□)	Curve D (log Ω/□)	Curve E (log Ω/□)																											
600	3.2	3.0	2.8	2.5	2.2																											
700	3.5	3.2	3.0	2.8	2.5																											
800	3.0	2.8	2.5	2.2	2.0																											
900	2.5	2.2	2.0	1.8	1.5																											

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A METHOD OF FORMING A SHALLOW AND HIGH
CONDUCTIVITY BORON DOPED LAYER IN SILICON

BACKGROUND OF THE INVENTION

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The trend toward smaller geometry devices in the fabrication of very large scale or very high speed integrated circuits necessitates the use of shallower junctions. For example, in MOS transistors a reduction in
10 source and drain junction depth by a factor of 8 is required to shrink the gate length by a factor of 2 at a given gate oxide thickness and a given substrate doping level.

In the formation of doped layers, which are utilized
15 to form junctions, a common method utilized is to implant a dose of the dopant material into the substrate and then anneal the substrate to activate the doped layer. Implanting is performed by stripping electrons from molecules of the doping material to form ions and
20 accelerating the ions at the substrate by way of a high energy ion beam. As the ions strike the substrate, atoms of the substrate material are moved out of the crystal lattice, or formation. Generally, it is desirable to disturb the position of enough of the substrate atoms in
25 the region to be doped so that an amorphous layer is formed.

Once the dopant material is implanted in the substrate, the substrate is heated (annealed) to a temperature sufficient to reform the material into a
30 crystalline structure with the ions of the doping material occupying the crystal lattice at regular intervals. Each ion of the doping material which is properly positioned in the crystal lattice is referred to as activated. When all of the atoms of the original substrate material are
35 reformed into a crystal lattice and all, or substantially all, of the ions of the doping material are properly



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positioned in the lattice the doped layer is completely activated. Generally, the amount of activation depends upon the temperature utilized in the annealing process and the length of time the substrate is annealed. The amount
5 of activation is measured by measuring the sheet resistivity of the implanted layer; maximum or nearly maximum activation is signaled by a decrease and then leveling of resistivity as a function of annealing temperature or annealing time at a given temperature. If
10 the doped layer in the substrate is not rendered completely amorphous by the ion implantation, that is some of the atoms of the substrate are still in a partial crystal lattice, the lattice must be broken down and reformed during the annealing process and, in such case, higher
15 temperatures are required for adequate activation. However, because of the smaller geometry devices and the need to reduce processing costs, it is desirable to reduce the annealing temperatures as much as possible.

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SUMMARY OF THE INVENTION

The present invention pertains to a method of forming a relatively high conductivity boron doped layer less than approximately 0.3 microns thick in a silicon substrate by
25 implanting in the substrate, with an energy less than approximately 75 Kev, a dose of boron difluoride in the range of approximately $6 \times 10^{14}/\text{cm}^2$ to $5 \times 10^{15}/\text{cm}^2$, post-damaging or pre-damaging the implanted area of the substrate with an implant such that the damage is approxi-
30 mately equivalent to the damage produced by a $1 \times 10^{15}/\text{cm}^2$ dose of silicon implanted at an energy of approximately 100 Kev; and annealing the substrate at a temperature in the range of approximately 675°C to 990°C. When the implanted area is post-damaged, i.e. after the boron difluoride
35 implant, the range of annealing temperatures can be extended to as low as 550°C.



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It is an object of the present invention to provide a new and improved method of forming a relatively high conductivity, shallow boron doped layer in a silicon substrate.

5 It is a further object of the present invention to provide a new and improved method of forming a relatively high conductivity, shallow boron doped layer requiring relatively low annealing, or activation, temperatures.

10 It is a further object of the present invention to provide a new and improved method of forming a relatively high conductivity, shallow boron doped layer wherein boron difluoride is used for doping at a relatively low energy.

15 These and other objects of this invention will become apparent to those skilled in the art upon consideration of the accompanying specification, claims and drawing.

BRIEF DESCRIPTION OF THE DRAWINGS

FIGURE 1 is a graph of the sheet resistance of the doped layer versus the annealing temperature for five different methods of producing the doped layer using 40 Kev implant energy; and

FIGURE 2 is a graph similar to FIG. 1 using 28 Kev implant energy.

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DESCRIPTION OF THE PREFERRED EMBODIMENTS

In the novel methods embodying the present invention, boron difluoride (BF_2) in the form of singly ionized boron difluoride molecules (BF_2^+) is used as the dopant to produce a relatively high conductivity boron doped layer less than approximately 0.3 microns thick in a silicon substrate. A boron difluoride implant is used to produce P-type shallow layers in a silicon substrate for two reasons. One, by using boron difluoride the shallow boron implant distribution, which depends on the mass ratio of



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boron to boron difluoride ($11/49 = 0.224$), can be produced at a reasonably high accelerator voltage with a stable ion beam. Two, higher throughput and greater savings in capital investment can be realized due to the higher beam current achievable with boron difluoride compared to boron, i.e. greater than 5:1.

It is known by those skilled in the art that the critical dose for the formation of an amorphous layer in a silicon substrate is below $1 \times 10^{15}/\text{cm}^2$ for a 150 Kev boron difluoride implant. This critical dose is the implant dose above which an amorphous layer is formed. It is also known by those skilled in the art that the $1 \times 10^{15}/\text{cm}^2$ dose of boron difluoride implanted at 150 Kev can be activated to the maximum level at temperatures greater than or equal to 650°C , resulting in a doped layer greater than 0.3 microns thick. For small geometry devices, however, such as submicron MOS transistors, boron doped layers shallower than 0.3 microns are required. To produce the shallower layers lower energy implants and/or lower activation temperatures are needed. To achieve a final implant depth of less than 0.3 microns the implant energy, using boron difluoride as the dopant, must be limited to less than about 75 Kev. Since the critical dose of dopant required for the formation of an amorphous layer is normally reduced as the implant energy is reduced, one skilled in the art would expect that a lower energy boron difluoride implant could also be activated to the maximum level with a temperature greater than or equal to 650°C .

Unexpectedly, it was found through experimentation that $1 \times 10^{15}/\text{cm}^2$ doses of boron difluoride implanted at 28 Kev and 40 Kev were not activated to the maximum level at less than or equal to 800°C . Curve A of FIG. 1 illustrates the sheet resistance versus the anneal temperature for a $2 \times 10^{15}/\text{cm}^2$ dose of boron difluoride implanted at 40 Kev. Curve A of FIG. 2 illustrates the sheet resistance versus the anneal temperature for a $1 \times 10^{15}/\text{cm}^2$ dose of



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boron difluoride implanted at 28 Kev. For each implant the sheet resistivity is about 290 ohms per cm^2 at 800°C annealing temperature. This value is greater than those obtained for the 900°C anneal indicating activation is not maximized at 800°C.

Since increased activation reduces the sheet resistance, from these graphs it can be seen that decreasing the implant energy from 150 Kev to 28 Kev or 40 Kev decreased the amount of activation at a specific annealing temperature. One skilled in the art would then expect that too much damage is created at the reduced implant energy levels to achieve the maximum activation. Thus, if additional damage, greater than that created by the boron difluoride implant alone, were produced by additional processing of the substrate, the activation would be adversely effected. This assumption was confirmed by implanting a $1 \times 10^{15}/\text{cm}^2$ dose of boron difluoride at 28 Kev into a silicon layer, which was pre-damaged by a $1 \times 10^{15}/\text{cm}^2$ dose of silicon implanted at 100 Kev, and annealing at 800°C and 900°C as indicated by curve B of FIG. 2. A comparison of curves B and A of FIG. 2 quickly illustrates that the additional damage caused by the pre-damaged implant reduced the amount of activation, e.g. 350 ohms per cm^2 versus 290 ohms per cm^2 for the 800°C, 10 minute anneal. Unexpectedly a $2 \times 10^{15}/\text{cm}^2$ dose of boron difluoride implanted at a 40 Kev energy into a substrate pre-damaged by a $1 \times 10^{15}/\text{cm}^2$ dose of silicon implanted at 100 Kev (curve B of FIG. 1) gave better activation than the boron difluoride implanted into an undamaged substrate (curve A of FIG. 1). However, maximum activation was not achieved. In both of the pre-damaged experiments (curves B of FIGS. 1 and 2) the silicon implant was performed at room temperature.

In a second procedure a pre-damaged layer was created in a silicon substrate by implanting a $1 \times 10^{15}/\text{cm}^2$ dose of



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silicon at an energy of 100 Kev and at the temperature of liquid nitrogen. A $2 \times 10^{15}/\text{cm}^2$ dose of boron difluoride was then implanted at 40 Kev at room temperature and samples were annealed at 600°C, 700°C, 800°C and 900°C. The results of this procedure are depicted by curve C of FIG. 1. From a comparison of curve C with curves A and B of FIG. 1 it can be seen that the activation was further improved, particularly for anneals at 700°C and 800°C. In this procedure the activation was improved by more damage since the silicon implant at liquid nitrogen temperature causes more damage than the silicon implant at room temperature (curve B of FIG. 1).

It is known to those skilled in the art that a damaging implant subsequent to the main doping implant (post-damage) creates more damage than the pre-damaged implants discussed above. Thus, one skilled in the art would expect: (1) better or at least equal activation if the damaging implant at liquid nitrogen temperature is performed after the boron difluoride implant; and (2) better activation by the post-damage at liquid nitrogen temperature than at room temperature. In a third procedure a substrate having a $2 \times 10^{15}/\text{cm}^2$ dose of boron difluoride implanted at 40 Kev was post-damaged by a $1 \times 10^{15}/\text{cm}^2$ dose of silicon implanted at 100 Kev at liquid nitrogen temperature and annealed at 600°C, 700°C and 800°C. Curve D of FIG. 1 illustrates the results of this procedure. For anneals at 700°C and 800°C better activation was achieved by the post-damage at liquid nitrogen temperature than at room temperature (curve C of FIG. 1). However, the post-damage at liquid nitrogen temperature gave substantially worse activation than the pre-damage at liquid nitrogen temperature for anneals of 600°C.

In a still further procedure, a substrate having a $2 \times 10^{15}/\text{cm}^2$ dose of boron difluoride implanted at 40 Kev was post-damaged by a $1 \times 10^{15}/\text{cm}^2$ dose of silicon implanted at



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100 Kev, both implants at room temperature. This post-damaged substrate was annealed at 550°C, 600°C, 700°C and 800°C, the results being illustrated by curve E of FIG. 1. Unexpectedly, the post-damage at room temperature gave
5 better activation than the post-damage at liquid nitrogen temperature for anneals at 550°C and 600°C. For the anneal at 550°C the room temperature post-damaged sample gave 640 ohms per cm² after a 10 minute anneal and 197 ohms per cm² after a 1 hour anneal. For the anneal at 600°C the
10 sample pre-damaged at liquid nitrogen temperature gave 300 ohms per cm² after a 10 minute anneal and 187 ohms per cm² after a 30 minute anneal.

The as implanted boron profile is essentially preserved for all of the room temperature post-damaged
15 samples for all of the anneals reported here (550°C, 600°C, 700°C and 800°C for 10 minutes, and 550°C for 1 hour). The sheet resistance values indicate that maximum activation was realized by post-damage at room temperature for anneals at 550°C to 800°C, by pre-damage at liquid nitrogen
20 temperature for anneals at 600°C to 800°C, and by post-damage at liquid nitrogen temperature for anneals at 700°C and 800°C. In a final procedure, a substrate having a $2 \times 10^{15}/\text{cm}^2$ dose of boron difluoride implanted at 28 Kev was post-damaged with a $1 \times 10^{15}/\text{cm}^2$ dose of silicon
25 implanted at 100 Kev. These substrates were annealed at 700°C and 800°C for 10 minutes. These post-damaged substrates also gave nearly maximum activation, as illustrated by curve C of FIG. 2.

Thus, a method of forming a relatively high conductivity boron doped layer less than approximately 0.3
30 microns thick in a silicon substrate is disclosed. While all of the damaging implants utilized herein were silicon, it will be understood by those of skill in the art that other types of implant, such as neon and argon might be
35 utilized. Further, any low energy, 75 Kev and below, implants of boron difluoride will provide the desired



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shallow boron doped layers with high electrical activity. Also, while doses of $1 \times 10^{15}/\text{cm}^2$ and $2 \times 10^{15}/\text{cm}^2$ were utilized herein, doses in the range of approximately $6 \times 10^{14}/\text{cm}^2$ to $5 \times 10^{15}/\text{cm}^2$ will provide sufficiently shallow
5 layers. Similarly, although the damaging implant disclosed herein is a $1 \times 10^{15}/\text{cm}^2$ dose of silicon implanted at an energy of approximately 100 Kev, it will be understood that alterations or adjustments in the size of the dose and amount of energy would be well within the purview of those
10 skilled in the art and all such alterations and changes are considered to be within the teachings herein if the damage is approximately equivalent.

While I have shown and described specific embodiments of this invention, further modifications and improvements
15 will occur to those skilled in the art. I desire it to be understood, therefore, that this invention is not limited to the particular forms shown and I intend in the appended claims to cover all modifications which do not depart from the spirit and scope of this invention.



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CLAIMS

1. A method of forming a relatively high conductivity boron doped layer less than approximately 0.3
5 microns thick in a silicon substrate comprising the steps of:
- implanting in the substrate with an energy less than approximately 75 Kev a dose of boron difluoride in the range of approximately $6 \times 10^{14}/\text{cm}^2$ to $5 \times 10^{15}/\text{cm}^2$;
10 damaging the implanted area of the substrate with an implant an amount approximately equivalent to the damage produced by a dose of silicon approximately $1 \times 10^{15}/\text{cm}^2$ implanted at an energy of approximately 100 Kev; and
annealing the substrate at a temperature in the
15 range of approximately 675°C to 900°C .
2. A method as claimed in claim 1 wherein the damaging implant is performed at approximately room temperature.
20
3. A method as claimed in claim 1 wherein the damaging implant is performed at approximately liquid nitrogen temperature.
- 25 4. A method as claimed in claim 1 wherein the boron difluoride implant is a dose of approximately $2 \times 10^{15}/\text{cm}^2$ implanted at an energy of approximately 40 Kev.
5. A method as claimed in claim 1 wherein the
30 damaging implant is chosen from the group consisting of silicon, argon and neon.
6. A method as claimed in claim 5 wherein the damaging implant is silicon.



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7. A method as claimed in claim 1 wherein an energy of approximately 40 Kev is used to implant the dose of boron difluoride.

5 8. A method of forming a relatively high conductivity boron doped layer less than approximately 0.3 microns thick in a silicon substrate comprising the steps of:

implanting in the substrate with an energy less than approximately 75 Kev a dose of boron difluoride in the
10 range of approximately $6 \times 10^{14}/\text{cm}^2$ to $5 \times 10^{15}/\text{cm}^2$; and then
damaging the implanted area of the substrate with an implant an amount approximately equivalent to the damage produced by a dose of silicon approximately $1 \times 10^{15}/\text{cm}^2$ implanted at an energy of approximately 100 Kev at
15 approximately room temperature; and then

annealing the substrate at a temperature in the range of approximately 550°C to 900°C .

9. A method of forming a relatively high
20 conductivity boron doped layer less than approximately 0.3 microns thick in a silicon substrate comprising the steps of:

implanting in the substrate with an energy less than approximately 75 Kev a dose of boron difluoride in the
25 range of approximately $6 \times 10^{14}/\text{cm}^2$ to $5 \times 10^{15}/\text{cm}^2$; and then
damaging the implanted area of the substrate with an implant an amount approximately equivalent to the damage produced by a dose of silicon approximately $1 \times 10^{15}/\text{cm}^2$ implanted at an energy of approximately 100 Kev at a
30 temperature of approximately liquid nitrogen; and then

annealing the substrate at a temperature in the range of approximately 675°C to 900°C .

10. A method of forming a relatively high conduc-
35 tivity boron doped layer less than approximately 0.3



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microns thick in a silicon substrate comprising the steps of:

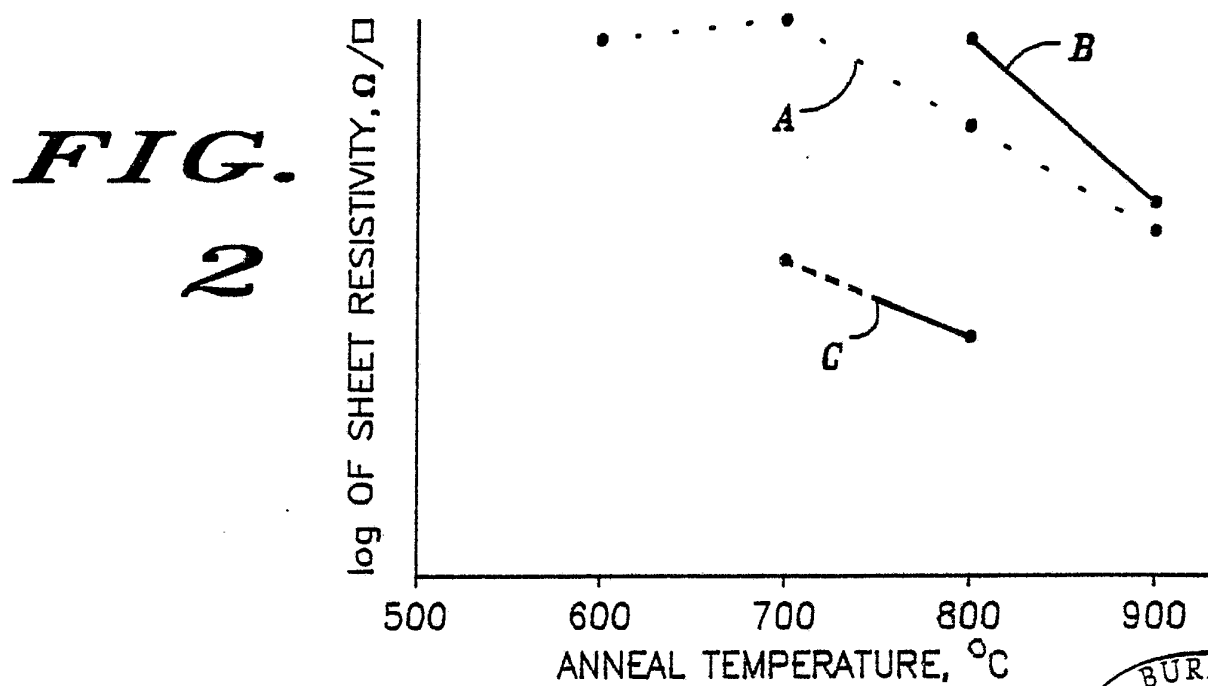
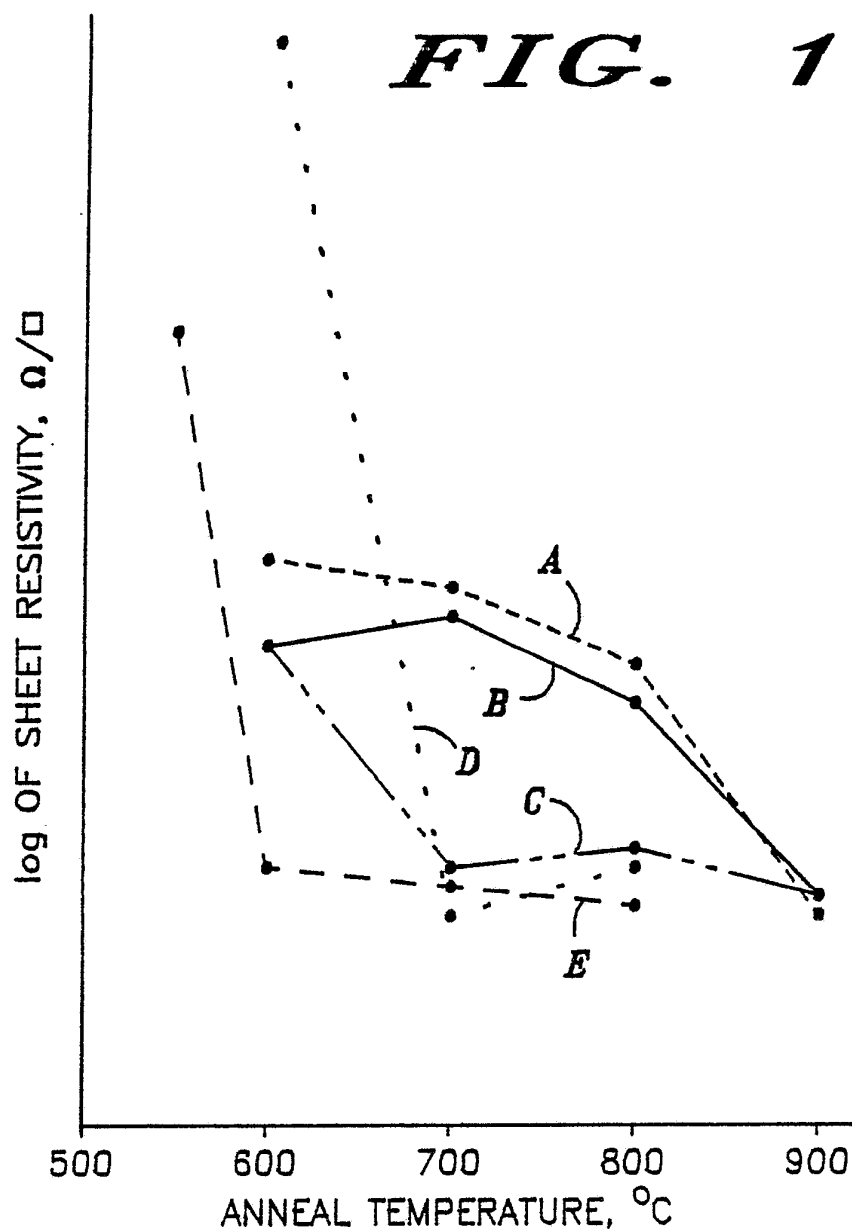
damaging an area in the substrate with an implant an amount approximately equivalent to the damage produced by a dose of silicon approximately $1 \times 10^{15}/\text{cm}^2$ implanted at an energy of approximately 100 Kev at a temperature of approximately liquid nitrogen; and then

implanting in the damaged area with an energy less than approximately 75 Kev a dose of boron difluoride in the range of approximately $6 \times 10^{14}/\text{cm}^2$ to $5 \times 10^{15}/\text{cm}^2$; and then

annealing the substrate at a temperature in the range of approximately 600°C to 900°C .



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INTERNATIONAL SEARCH REPORT

International Application No PCT/US83/01257

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) ³		
According to International Patent Classification (IPC) or to both National Classification and IPC INL. CL. ³ H01L 21/265, 21/263, U.S. CL. 29/576B, 576T; 148/1.5, 187; 357/2,63,91.		
II. FIELDS SEARCHED		
Minimum Documentation Searched ⁴		
Classification System	Classification Symbols	
U.S.	29/576B, 576T 148/1.5, 187; 357/2, 63, 91	
Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched ⁵		
III. DOCUMENTS CONSIDERED TO BE RELEVANT ¹⁴		
Category *	Citation of Document, ¹⁶ with indication, where appropriate, of the relevant passages ¹⁷	Relevant to Claim No. ¹⁸
X	U.S., A, 3,589,949, 29 June 1971 (NELSON), See column 3, lines 36-55 and line 71 to lines 1-2 of column 4.	1-10
Y	U.S., A, 4,391,651, 05 July 1983,(YODER)	1-10
Y	U.S., A, 4,240,096, 16 December 1980, (HIRAKI et al)	1-10
Y	U.S., A, 4,216,030, 05 August 1980, (GRAUL et al)	1-10
Y	U.S., A, 4,144,100, 13 March 1979, (McIVER et al)	1-10
Y	U.S., A, 4,133,701, 09 January 1979, (GREENSTEIN et al)	1-10
X	B.L. Crowder, "Ion Implantation In Semi- conductors And Other Materials, By Plenum, New York, 1973, pages 215-224, See page 215 and figure 1.	1-10
* Special categories of cited documents: ¹⁵ "A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier document but published on or after the international filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art. "&" document member of the same patent family		
IV. CERTIFICATION		
Date of the Actual Completion of the International Search ²	Date of Mailing of this International Search Report ²	
September 29, 1983	07 OCT 1983	
International Searching Authority ¹	Signature of Authorized Officer ²⁰	
ISA/US	U. Roy <i>U. Roy</i>	

III. DOCUMENTS CONSIDERED TO BE RELEVANT (CONTINUED FROM THE SECOND SHEET)

Category *	Citation of Document, ¹⁶ with indication, where appropriate, of the relevant passages ¹⁷	Relevant to Claim No ¹⁸
A	Journal Of Applied Physics, 50(1), January 1979, BLOOD et al 'Incorporation Of Implanted In and Sb in Si During Amorphous Layer Regrowth' pages 173-182, See Table I	1-10
A	Pysica Status Solidi, 70(a), April 1982, KERKOW et al, "disorder Production in Ion Implanted Si' pages 489-495, See figure 2 and Figure 6	1-10
Y	Journal Of Electrochemical Society: Solid State Science 117, May 1970, Crowder; The Role of Damage in the Annealing Characteristics of Ion Implanted Si', pages 671-674, See Abstract	1-10