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(54) Title: METHODS OF TREATING A SILICON CARBIDE SUBSTRATE FOR IMPROVED EPITAXIAL DEPOSITION AND RESULTING STRUCTURES AND DEVICES

(57) Abstract: A method is disclosed for treating a silicon carbide substrate for improved epitaxial deposition thereon and for use as a precursor in the manufacture of devices such as light emitting diodes. The method includes the steps of implanting dopant atoms of a first conductivity type into the first surface of a conductive silicon carbide wafer having the same conductivity type as the implanting ions at one or more predetermined dopant concentrations and implant energies to form a dopant profile, annealing the implanted wafer, and growing an epitaxial layer on the implanted first surface of the wafer.



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**METHODS OF TREATING A SILICON CARBIDE SUBSTRATE FOR IMPROVED
EPITAXIAL DEPOSITION AND RESULTING STRUCTURES AND DEVICES**

Background

5 To date, the most successful materials for producing light emitting devices or
"LEDs" (including light emitting diodes, laser diodes, photodetectors and the like)
capable of operation in the UV, blue and green portions of the electromagnetic
spectrum have been the group III-nitride compound semiconductor materials, and in
particular gallium nitride-based compound semiconductors. However, gallium
10 nitride presents a particular set of technical problems in manufacturing working
devices. The primary problem is the lack of bulk single crystals of gallium nitride
which in turn means that gallium nitride or other group III-nitride devices must be
formed as epitaxial layers on other materials. Sapphire (*i.e.*, aluminum oxide or
 Al_2O_3) has been commonly used as a substrate for group III-nitride devices. Sapphire
15 offers a reasonable crystal lattice match to Group III nitrides, thermal stability, and
transparency, all of which are generally useful in producing a light emitting diode.
Sapphire offers the disadvantage, however, of being an electrical insulator. This
means that the electric current that is passed through an LED to generate the
emission cannot be directed through the sapphire substrate. Thus, other types of
20 connections to the LED must be made, such as placing both the cathode and anode of
the device on the same side of the LED chip in a so-called "horizontal" configuration.
In general, it is preferable for an LED to be fabricated on a conductive substrate so
that ohmic contacts can be placed at opposite ends of the device. Such devices,
called "vertical" devices, are preferred for a number of reasons, including their easier
25 manufacture as compared to horizontal devices.

 In contrast to sapphire, silicon carbide can be conductively doped, and
therefore can be effectively used to manufacture a vertical group III-nitride LED. In
addition, silicon carbide has a relatively small lattice mismatch with gallium nitride,
which means that high-quality group III-nitride material can be grown on it. Silicon
30 carbide also has a high coefficient of thermal conductivity, which is important for heat
dissipation in high-current devices such as laser diodes.

 Examples of silicon carbide-based group III-nitride LEDs are shown in U.S.
Patents 5,523,589; 6,120,600; and 6,187,606 each of which is assigned to Cree, Inc.,

the assignee of the present invention, and each of which is incorporated herein by reference. Such devices typically comprise a silicon carbide substrate, a buffer layer or region formed on the substrate, and a plurality of group III-nitride layers forming a p-n junction active region.

5 In particular, U.S. Patent No. 6,187,606 represents an important advance over the state of the art as it previously existed. The invention described in the '606 patent provided a plurality of discrete crystal portions, or "dots," of GaN or InGaN on the substrate in an amount sufficient to minimize or eliminate the heterobarrier between the substrate and the buffer layer. A highly conductive path between the substrate and
10 the active region could thereby be established.

 An important parameter for LEDs is the forward voltage (V_f) drop between the anode and the cathode of the device during forward bias operation. In particular, it is desirable for the forward voltage (V_f) of a device to be as low as possible to reduce power consumption and increase the overall efficiency of the device. Despite the
15 advance of the '606 patent, there remains a measurable voltage drop at the interface between a conventional silicon carbide substrate and the conductive buffer layer. It is desirable to reduce this voltage drop in order to reduce the overall V_f of the resulting device.

Description

20 Methods according to embodiments of the present invention include the steps of providing a SiC wafer having a predetermined conductivity type and first and second surfaces; implanting dopant atoms of the predetermined conductivity type into the first surface of the SiC wafer at one or more predetermined dopant concentrations and implant energies to form a dopant profile; annealing the implanted wafer; and
25 growing an epitaxial layer on the implanted first surface of the substrate. Other methods according to embodiments of the present invention include the steps of providing a SiC wafer having a predetermined conductivity type and first and second surfaces; forming a capping layer on the first surface of the wafer; implanting dopant atoms of the predetermined conductivity type into the capping layer and the first
30 surface of the SiC wafer at one or more predetermined dopant concentrations and implant energies to form a dopant profile; annealing the implanted wafer; removing

the capping layer; and growing an epitaxial layer on the implanted first surface of the substrate.

Structures according to embodiments the present invention include a silicon carbide substrate having a predetermined conductivity type and having first and second surfaces with a first implantation profile of implanted dopants of the predetermined conductivity type adjacent the first surface and an epitaxial layer grown on the first surface.

Devices according to embodiments of the present invention include a light emitting device comprising a silicon carbide substrate having a predetermined conductivity type and first and second surfaces, a conductive buffer layer on the first surface of the substrate, and an active region on the conductive buffer, wherein the first surface of the substrate has a first implantation profile of implanted dopants of the predetermined conductivity type adjacent the first surface.

Referring to FIG. 1 which shows a simplified schematic of a silicon carbide-based LED according to the present invention, device 10 comprises a conductive silicon carbide substrate 12 having a first conductivity type and having a first surface 12A and a second surface 12B. Device 10 further includes a conductive buffer region 14 formed on surface 12A of substrate 12 and an active region 18 formed on the conductive buffer 14. Active region 18 preferably includes a p-n junction and most preferably comprises a single heterostructure, double heterostructure, single quantum well, multiple quantum well or the like. A first ohmic contact 22 is formed on the surface of the active region. A second ohmic contact 24 is formed on the surface of the substrate 24. In a preferred embodiment, substrate 12 comprises n-type 4H-silicon carbide. Accordingly, in a preferred embodiment ohmic contact 22 comprises the anode of the device 10 while ohmic contact 24 comprises the cathode of the device 10. Ohmic contact 24 may be formed according to the methods described in U.S. Patent Application Serial No. 09/787,189 filed March 15, 2001, which is incorporated herein by reference. Substrate 12 includes a first implanted region 20 adjacent to surface 12A and comprising implanted dopant atoms of the first conductivity type. The presence of implanted region 20 causes a reduction in the voltage drop observable at the interface between substrate 12 and buffer region 14, which results in a reduction in the overall forward operating voltage (V_f) of the device 10. The

implanted region has a peak concentration of implanted dopant atoms of between about $1\text{E}19$ and $5\text{E}21\text{ cm}^{-3}$ and is between about 10 and 5000 Å thick. Preferably, the implanted region has a peak concentration of implanted dopant atoms of about $1\text{E}21\text{ cm}^{-3}$ and is about 500 Å thick.

5 FIG. 2 illustrates a method of fabrication of structures according to the present invention. A silicon carbide substrate 12 is provided having a first conductivity type and having first surface 12A and second surface 12B. The fabrication of doped silicon carbide substrates such as substrate 12 is well known in the art. For example, U.S. Patent RE34,861 discloses a process for growing boules of silicon carbide via
10 controlled seeded sublimation. The resulting silicon carbide crystal may exhibit one of a number of polytypes, such as 4H, 6H, 15R or others. N-type dopants such as nitrogen and/or phosphorus or p-type dopants such as aluminum and/or boron may be incorporated into the crystal during growth to impart a net n-type or p-type conductivity, respectively. The crystal boules are then sliced into wafers which are
15 chemically and mechanically treated (polished) to provide a suitable substrate for the growth of epitaxial layers and the fabrication of electronic devices thereon.

 In a preferred embodiment, substrate 12 comprises n-type 4H or 6H-silicon carbide doped with nitrogen donor atoms at a net dopant concentration of about $5\text{E}17$ to $3\text{E}18\text{ cm}^{-2}$. Subsequent to wafering and polishing, dopant atoms 30 of a
20 predetermined conductivity type are implanted into surface 12A of substrate 12 at one or more predetermined dopant concentrations and implant energies to form a dopant profile in implanted region 20 of substrate 12. Preferably, dopant atoms 30 have the same conductivity type as substrate 12. That is, if substrate 12 is n-type, then dopants 30 comprise a dopant such as nitrogen and/or phosphorus that imparts n-type
25 conductivity in silicon carbide. Alternatively, if substrate 12 is p-type, then dopants 30 comprise a dopant such as boron or aluminum that imparts p-type conductivity in silicon carbide.

 Dopants 30 are implanted into substrate 12 through surface 12A according to a predetermined implant dose and energy level. Implantation may be performed in one
30 step at a single dose and energy level or in a plurality of steps at multiple doses and/or multiple energy levels. In a preferred embodiment, implantation is performed via a plurality of implant doses and energy levels in order to impart a relatively flat

implantation profile to a predetermined depth within substrate 12. For example, in one embodiment, a 6H-silicon carbide substrate is implanted with phosphorus atoms at a first dose of $2\text{E}15\text{ cm}^{-2}$ and an energy of 25 keV and a second dose of $3.6\text{E}15\text{ cm}^{-2}$ at an energy of 50 keV.

5 A schematic of a desired depth profile that could be formed according to this embodiment is shown the graph of FIG. 4. The graph of FIG. 4 shows the profile of implanted atoms in atoms/cm^3 (y-axis) as a function of depth in angstroms from the first surface 12A of substrate 12 (x-axis). As shown in FIG. 4, the implant profile increases to a maximum of about $1\text{E}21\text{ cm}^{-3}$ at a depth of about 300 Å. From there,
10 the profile stays relatively flat to a depth of about 800 Å, and then begins to drop off to background levels. Accordingly, implanted region 20 may be said to extend from surface 12A into substrate 12 for a depth of about 800-1000 Å.

Following the implantation, the substrate is annealed in a standard tube anneal in Argon at a temperature of 1300° for 90 minutes to activate the implanted dopants.
15 A range of temperatures is also effective for annealing, with 1300° being exemplary rather than limiting.

A conductive buffer 14 may then formed on surface 12A of substrate 12.

One drawback of this embodiment is that the dopant profile tends to reach its maximum at some depth within the substrate, determined by the implant doses and
20 energies. That is, the implant concentration at the surface is less than the maximum concentration within the substrate. Implanted dopant concentrations must be kept at less than about $5\text{E}21\text{ cm}^{-3}$ or else the implanted atoms will cause unwanted and irreparable damage to the crystal lattice of substrate 12.

In order to provide the maximum improvement in voltage drop, it is desirable
25 to have the implant concentration at the surface at the surface of the substrate at as high a level as possible, *i.e.*, the implant concentration at the surface should be around $1\text{E}21\text{ cm}^{-3}$. However, in order to achieve such a surface concentration according to the embodiment of FIG. 2, it would be necessary to implant the dopant atoms at a dose and energy level that would produce dopant concentrations within the substrate
30 that would damage the substrate as described above.

Accordingly, in another embodiment of the invention illustrated in FIG. 3, a capping layer 32 is deposited on surface 12A of substrate 12 prior to dopant

implantation. Preferably, capping layer 32 comprises a silicon nitride layer or a silicon dioxide layer deposited using Plasma-Enhanced Chemical Vapor Deposition (PECVD) or grown as a thermal oxide, both of which are well known processes capable for depositing oxide layers of precise thickness and composition. Capping
5 layer 32 may also comprise any other suitable material that may be controllably deposited in thin layers, is susceptible to ion implantation and can be removed without damaging the underlying surface. Other possible materials for capping layer 32 include a metal layer or an epitaxial semiconductor layer.

The thickness of capping layer 32 and the implantation parameters (dose and
10 energy) are selected such that the maximum implant concentration resulting from the implantation step occurs at or near the surface 12A of the substrate 12 (*i.e.*, at or near the interface between substrate 12 and capping layer 32). The resulting structure is then annealed in a standard tube anneal in argon at a temperature of 1300°C for 90 minutes to activate the implanted dopants. Capping layer 32 is removed using
15 conventional techniques. For example, if capping layer 32 comprises a PECVD oxide layer, it may be removed with a wet chemical etch process. The resulting structure then ideally comprises a substrate 12 having an implanted region 20 wherein the peak concentration of implanted atoms in the implanted region 20 occurs at or near surface 12A of substrate 12.

20 A schematic of the desired depth profile that could be formed according to this embodiment is shown the graph of FIG. 5. The graph of FIG. 5 shows a schematic profile of implanted atoms in atoms/cm³ (y-axis) as a function of depth in angstroms from the first surface 12A of substrate 12. As shown in FIG. 4, the implant profile is approximately 1E21 cm⁻³ at the surface 12A of the substrate 12. From there, the
25 profile stays relatively flat for a depth of about 500 Å, and then begins to drop off to background levels.

In one embodiment, a silicon dioxide layer 32 having a thickness of about 500 Å is formed via PECVD on surface 12A of substrate 12. Nitrogen atoms are implanted into the oxide layer and the substrate 12 in a first dose at an implant energy
30 of 25 keV and a second dose at an implant energy of 50 keV. The first implant may have a dose of about 4E12 cm⁻² to 1E15 cm⁻², while the second implant may have a dose of about 7E12 cm⁻² to 1.8E15 cm⁻².

- A graph of the interfacial voltage (V_f) at the substrate/buffer region interface versus 25keV implant dose is shown in Figure 6. To generate the data shown in Figure 6, sample 4H and 6H silicon carbide wafers having a net concentration of nitrogen dopants of between $3.3\text{E}17$ and $2.1\text{E}18 \text{ cm}^{-3}$ were employed. A 500 Å thick
- 5 PECVD silicon dioxide layer was formed on the surface of the wafers, and the wafers were implanted with various controlled doses of nitrogen at energy levels of 25keV and 50 keV respectively. The implant doses and energy levels for each wafer are shown in Table 1.

Table 1				
Wafer	Type	Dopant	25 keV Dose (cm^{-2})	50 keV Dose (cm^{-2})
A	4H	28N2+	2.5E14	4.38E14
B	4H	28N2+	3.0E14	5.25E14
C	4H	28N2+	3.5E14	6.13E14
D	4H	28N2+	4.0E14	7.0E14
E	6H	28N2+	2.5E14	4.38E14
F	6H	28N2+	3.0E14	5.25E14
G	6H	28N2+	3.5E14	6.13E14

- 10 Conductive buffers were then formed on the implanted substrates. The interfacial voltage (*i.e.*, the voltage drop attributable to the substrate/buffer interface) was measured at three locations on the wafer and an average value was calculated. The average values are plotted against the 25 keV implant dose in Figure 6. As shown in Figure 6, the interfacial voltage of the substrate/buffer interface decreases
- 15 with increasing dosage.

CLAIMS:

1. A method of treating a silicon carbide substrate for improved epitaxial deposition thereon and for use as a precursor in the manufacture of devices such as light emitting diodes, the method comprising:

- 5 implanting dopant atoms of a first conductivity type into the first surface of a conductive silicon carbide wafer having the same conductivity type as the implanting ions at one or more predetermined dopant concentrations and implant energies to form a dopant profile;
- annealing the implanted wafer; and
- 10 growing an epitaxial layer on the implanted first surface of the wafer.

2. A method according to Claim 1 comprising:

- forming a capping layer on the first surface of the conductive silicon carbide wafer from a material that can be controllably deposited in thin layers, can be
- 15 implanted with ions having the same conductivity as the silicon carbide wafer, and can be removed without substantially damaging the underlying surface of the wafer;
- implanting the dopant atoms into and through the capping layer and into the silicon carbide wafer at one or more predetermined dopant concentrations and implant energies to form a dopant profile;
- 20 annealing the implanted wafer;
- removing the capping layer; and
- growing the epitaxial layer on the implanted first surface of the substrate wafer.

25 3. A method according to Claim 1 of forming a light emitting diode further comprising the steps of:

- forming a conductive buffer region on the implanted first surface of the silicon carbide wafer;
- forming an active region on the conductive buffer region;
- 30 forming a first ohmic contact on said active region; and
- forming a second ohmic contact on the second surface of said silicon carbide wafer.

4. The method according to Claim 1, 2, or 3 wherein the step of implanting dopant atoms comprises carrying out a plurality of implanting steps at varying doses and energy levels in order to impart a relatively flat implantation profile to a predetermined depth within the wafer.

5

5. The method according to Claim 4 wherein the implanting step comprises implanting dopant atoms in the implant region to a peak concentration of implanted dopant atoms of between about $1\text{E}19$ and $5\text{E}21\text{ cm}^{-3}$.

10

6. The method according to Claim 4 wherein the implanting step comprises implanting dopant atoms in the implant region to a peak concentration of implanted dopant atoms of about $1\text{E}21\text{ cm}^{-3}$ and to a depth within the silicon carbide wafer of about 500 Angstroms.

15

7. The method according to Claim 4 wherein the implanting step comprises implanting the silicon carbide wafer with phosphorus donor atoms at a first dopant concentration of $2\text{E}15\text{ cm}^{-2}$ and an implant energy of 25 keV and a second dopant concentration of $3.6\text{E}15\text{ cm}^{-2}$ at an implant energy of 50 keV.

20

8. The method according to Claim 1, 2, or 3 wherein the implanted wafer is annealed in Argon at a temperature of 1300°C for 90 minutes.

9. The method according to Claim 1, 2, or 3 comprising implanting dopant atoms selected from the group consisting of nitrogen and phosphorus into an n-type silicon carbide wafer.

25

10. The method according to Claim 1, 2, or 3 comprising implanting dopant atoms selected from the group consisting of boron and aluminum into a p-type silicon carbide wafer.

30

11. The method according to Claim 2 comprising forming the capping layer from the group consisting of silicon nitride, silicon dioxide, and a metal layer.

12. A method according to Claim 11 comprising depositing the capping layer on the silicon carbide wafer using plasma-enhanced chemical vapor deposition.

13. The method according to Claim 2 comprising forming the capping layer
5 from silicon dioxide and to a thickness of about 500 Angstroms.

14. The method according to Claim 13 comprising implanting nitrogen atoms into and through the silicon dioxide layer and into the silicon carbide wafer in a first dose with a dopant concentration of between about $4 \times 10^{12} \text{ cm}^{-2}$ and $1 \times 10^{15} \text{ cm}^{-2}$ at an
10 implant energy of 25 keV and a second dose with a dopant concentration of between about $7 \times 10^{12} \text{ cm}^{-2}$ and $1.8 \times 10^{15} \text{ cm}^{-2}$ at an implant energy of 50 keV.

15. The method according to Claim 2 comprising removing the capping layer with a wet chemical etch process.

15

16. The method according to Claim 3 further comprising the step of fabricating the active layer from the group consisting of single heterostructures, double heterostructures, single quantum wells, multiple quantum wells and combinations thereof.

20

17. A silicon carbide structure suitable for use as a substrate in the manufacture of electronic devices such as light emitting diodes comprising:

a silicon carbide wafer having a first and second surface and having a predetermined conductivity type and an initial carrier concentration;

25 a region of implanted dopant atoms extending from said first surface into said silicon carbide wafer to a predetermined depth, said region having a higher carrier concentration than said initial carrier concentration in the remainder of said wafer; and

an epitaxial layer on said first surface of said silicon carbide wafer.

30

18. A silicon carbide precursor structure according to Claim 17 further comprising:

a capping layer on said first surface of said silicon carbide wafer formed of a material that can be controllably deposited in thin layers, can be implanted with ions having the same conductivity as the silicon carbide wafer, and can be removed without substantially damaging the underlying surface of the wafer; and

- 5 a region of implanted dopant atoms extending completely through said capping layer and through said first surface into said silicon carbide wafer to a predetermined depth, said region having a higher carrier concentration than the initial carrier concentration in the remainder of said wafer.

- 10 19. A light emitting diode incorporating the substrate of Claim 17, and further comprising:

a conductive buffer region on said first surface of said conductive silicon carbide wafer;

an active region on said conductive buffer region;

- 15 a first ohmic contact to said active region; and

a second ohmic contact on the second surface of said silicon carbide wafer.

- 20 20. A silicon carbide structure according to Claim 17, 18, or 19 wherein said silicon carbide wafer comprises n-type 6H-silicon carbide or n-type 4H-silicon carbide.

- 25 21. A silicon carbide structure according to Claim 20 wherein said silicon carbide wafer is doped with nitrogen donor atoms at a concentration of between about $5E17$ and $3E18\text{ cm}^{-2}$.

22. A silicon carbide structure according to Claim 17, 18, or 19 wherein said region of implanted dopant atoms comprises phosphorus in a concentration of between about $1E19$ and $5E21\text{ cm}^{-3}$.

- 30 23. A silicon carbide structure according to Claim 17, 18, or 19 wherein said region of implanted dopant atoms comprises nitrogen in a concentration of between about $1E19$ and $5E21\text{ cm}^{-3}$.

24. A silicon carbide structure according to Claim 23 wherein said region of implanted dopant atoms comprises phosphorus in a concentration of about $1\text{E}21\text{ cm}^{-3}$.

25. A silicon carbide structure according to Claim 17, 18, or 19 wherein said
5 region of implanted dopant atoms extends from said first surface into said silicon carbide wafer to a depth of between about 10 and 5000 Angstroms.

26. A silicon carbide structure according to Claim 25 wherein said region of implanted dopant atoms has a peak concentration of implanted dopant atoms of
10 between about $1\text{E}19$ and $5\text{E}21\text{ cm}^{-3}$.

27. A silicon carbide structure according to Claim 26 wherein said region of implanted dopant atoms has a peak concentration of implanted dopant atoms of about $1\text{E}21\text{ cm}^{-3}$ and extends from said first surface into said silicon carbide wafer to a
15 depth of about 500 Angstroms.

28. A silicon carbide structure according to Claim 17, 18, or 19 wherein the peak concentration of implanted atoms in said implanted region occurs at or near the first surface of said silicon carbide substrate.

20 29. A silicon carbide structure according to Claim 18 wherein said capping layer comprises a material selected from the group consisting of silicon nitride, silicon dioxide, and a metal.

25 30. A silicon carbide structure according to Claim 29 wherein said capping layer has a thickness of about 500 Angstroms.

31. An LED according to Claim 19 wherein said active layer is selected from the group consisting of a single heterostructure, a double heterostructure, a single
30 quantum well, a multiple quantum well, and combinations thereof.

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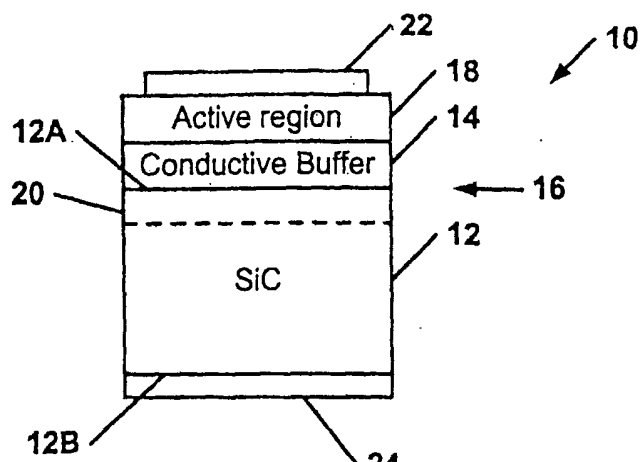


FIGURE 1

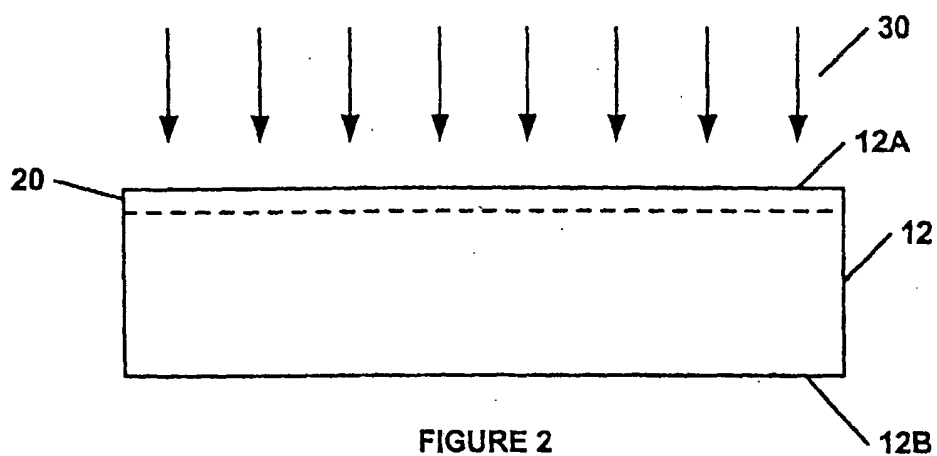


FIGURE 2

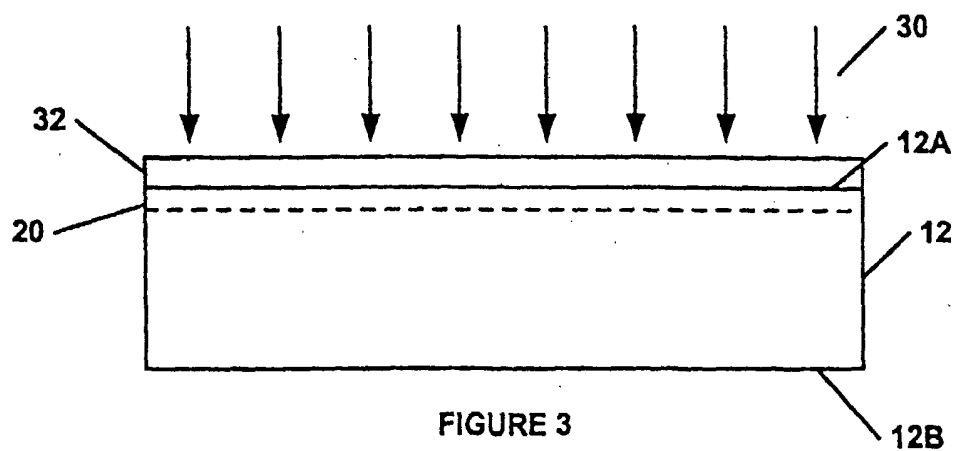


FIGURE 3

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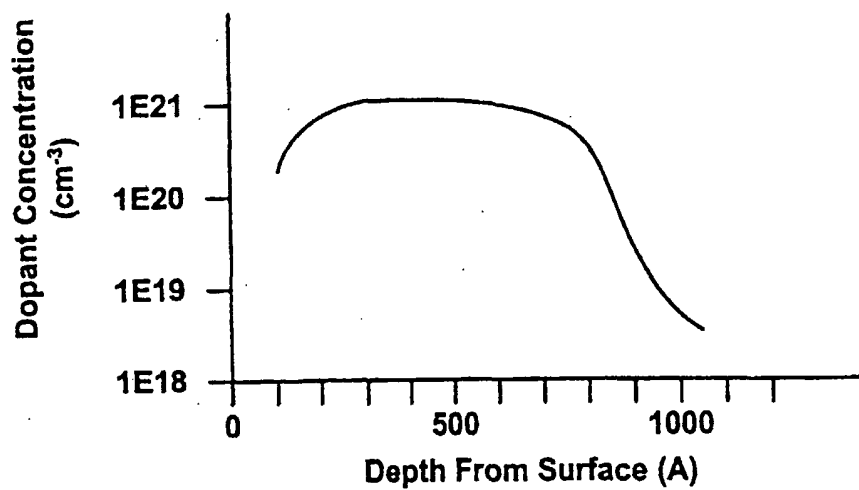


FIGURE 4

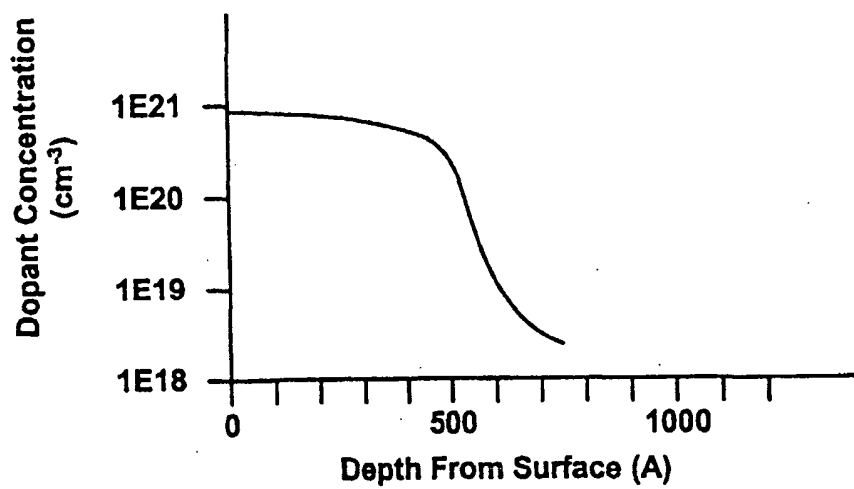


FIGURE 5

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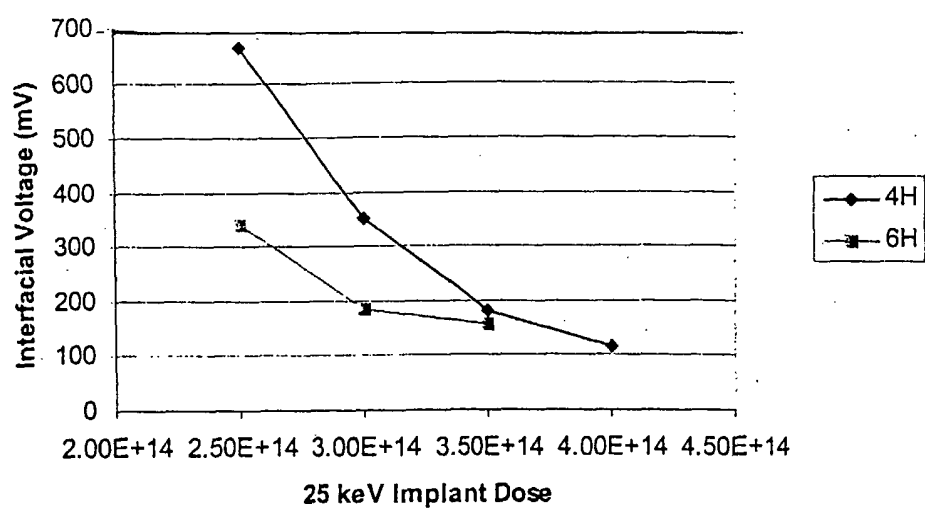


FIGURE 6