

# PATENT SPECIFICATION (11)

1 397 338

1 397 338

- (21) Application No. 23584/72 (22) Filed 19 May 1972 (19)  
 (31) Convention Application No. 146 252 (32) Filed 24 May 1971 in  
 (33) United States of America (US)  
 (44) Complete Specification published 11 June 1975  
 (51) INT. CL.<sup>3</sup> H01L 21/34  
 (52) Index at acceptance

H1K 217 272 273 277 306 312 413 41Y 422 578 579 581  
 583 611 615 618 61Y 639 63Y 657



- (72) Inventors ALFRED URQUHART MAC RAE,  
 PAUL MILLER,  
 ROBERT ALAN MOLINE  
 and JOHN SIMPSON

## (54) IMPROVEMENTS IN OR RELATING TO IMPURITY REGIONS IN SEMICONDUCTORS

(71) We, WESTERN ELECTRIC COMPANY, INCORPORATED, of 195 Broadway, New York City, New York State, United States of America, a Corporation organized and existing under the laws of the State of New York, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to the formation of regions of impurity in semiconductors.

Several methods have been suggested for fabricating the high conductance layer used for contacting the collector region of transistor structures. In the conventional diffusion technique, the impurities are diffused into the substrate utilizing an oxide mask to form a region of low resistivity in the crystal. After the oxide is removed, the collector is grown epitaxially on the substrate thus locating the low resistivity region between the collector and substrate. Formation of the base and emitter regions follows. It was discovered, however, that during the diffusion, imperfections are created in the oxide mask which are transferred to the substrate surface. These imperfections then manifest themselves as defects in the epitaxial layer resulting in poor device performance.

In order to overcome this problem, it was proposed that the buried, low resistivity layer be produced by simply implanting the impurity ions into the substrate material, and annealing out any resulting damage to the crystal (see for example, U.S. Patent No. 3,457,632). This provides the additional advantage of greater control over the location of the layer than is possible using diffusion techniques. It has been found,

however, that implanting impurities such as As at the high dosage required for buried layers produces damage to the semiconductor crystal lattice which is so severe as to produce an amorphous region. This region shows residual disorder after subsequent annealing.

According to the present invention a method of forming a buried region of impurity, comprises implanting an impurity into a semiconductor substrate by bombarding a surface of the substrate with ions of said impurity, heating the substrate so that ions of the impurity diffuse further into the substrate, and removing from said surface of the substrate material damaged as a result of the bombardment, to form a region of impurity; and growing an epitaxial layer on the surface of the substrate, so burying the region of impurity.

Examples of the present invention will now be described, by way of illustration only, with reference to the accompanying drawings in which:—

Figs. 1A to 1D are cross-sectional views of a silicon substrate at successive stages of manufacture according to one illustrative example of the invention.

Figs. 1A to 1D demonstrate the formation of the buried region in one embodiment of the present invention. It should be emphasized that these Figures are not drawn to scale. In Fig. 1A, a silicon substrate, 10, of p-type conductivity is shown after a region of As impurities, 11, has been implanted. The impurity profile is the normal Gaussian distribution with an average depth of approximately 1000Å. This depth is reached by accelerating the ions to an energy of about 150 keV. The initial depth of the impurities may vary over a wide range. Care must be taken, however, to implant at

a depth which will allow the As atoms to diffuse ahead of the growing oxide film as described below. Thus, the minimum average depth of the implanted region should be approximately 300Å, which requires an ion energy of approximately 50 keV. The exposure of the ion beam was approximately  $10^{16}$  ions/cm<sup>2</sup>. In order to produce an implanted region of sufficiently low resistivity for an ohmic contact, the minimum exposure would be approximately  $10^{14}$  ions/cm<sup>2</sup>. The lateral boundaries of the implanted region were defined by conventional shadow masking techniques.

The high dosage implant described produces damage to the crystal to such an extent as to form an essentially amorphous surface layer in the region of the implant. This layer extends to a depth slightly beyond the range of the implanted impurities (approximately 3000Å).

In order to remove this amorphous region, the substrate is heated to a temperature of approximately 1200°C. in dry oxygen for about 3½ hours. The heating step diffuses the As impurities further into the substrate crystal and out of the amorphous region. The new average depth of the impurities is approximately 1.5 microns. This ultimate depth is immaterial in terms of device applications, and is therefore governed by the extent of the amorphous region and to what extent the crystal will be etched prior to epitaxial growth of the collector layer. This ultimate depth may, therefore, vary anywhere from 1000Å to 20 microns. The temperature may vary between 900 and 1400°C. in order to achieve an adequate rate of diffusion without damaging the silicon substrate.

During the diffusion, as shown in Fig. 1B, a layer of silicon dioxide, 12, is grown at the surface of the crystal. The diffusion is conducted for a sufficient length of time so that the oxide layer grows to a depth which is a substantial portion of the depth of the initial amorphous region thus consuming most of the amorphous region. In the embodiment described, the oxide layer consumes approximately 2000Å of silicon.

With the limitation on initial depth previously described, the As impurities should diffuse ahead of the growing oxide layer. Diffusion is, in fact, aided as the oxide is formed in accordance with the "snow-plow effect." That is, the oxide layer acts as a moving boundary that limits the diffusion of impurities to the direction away from the surface and, hence, the impurities tend to "snow-plow" in front of the oxide.

As illustrated in Fig. 1C, the oxide is then removed from the surface. This can be done by any of a variety of means, for example, by applying a solution of hydrofluoric acid. After the oxide is stripped, the

impurities are left in material which contains some residual disorder resulting from the initial amorphous region, which disorder is in this example, about 1000Å deep. In addition, it has been found that dislocation loops extend beyond the original amorphous region. Therefore, it is desirable, subsequent to stripping the oxide, to temperature and length of time diffusion. This further damage. Since the surface of the crystal is usually etched anyway before epitaxial growth in order to clean the surface, this process presents no additional steps.

An additional 5000Å of crystal is, therefore, removed prior to epitaxial growth by means of a conventional vapor etch employing HF. The etch is performed in situ in the epitaxial chamber so that the etched surface will be free of surface contaminants.

It should be clear that the ultimate thickness of the oxide layer depends upon the temperature and length of time diffusion. The portion of the damaged region which will be consumed can therefore vary. The important criterion is whether the bulk of the impurities will diffuse out of the damaged region during the heating step. Any damage which has not been consumed by the resultant oxide can then be removed by etching.

As an alternative to etching the crystal just prior to epitaxial growth, it is possible to grow an oxide of sufficient thickness so as to consume the entire region of damaged material. This cannot be done reasonably in a dry oxygen ambient alone due to the slow growth rate of the oxide. A sufficiently thick oxide can be grown, however, by a combination of dry and steam oxidation. For example, the substrate can be heated in dry oxygen at a temperature of about 1200°C. for about one hour to grow a 2000Å thick oxide layer. A steam oxidation can then be done at the same temperature for another hour to grow another 8000Å of oxide. Initially heating in dry oxygen insures that the impurities will diffuse far enough into the crystal so that they will not be consumed by the oxide during the subsequent rapid steam oxidation. The oxide can then be removed by a vapor etch in the epitaxial chamber as, for example, by using HF vapor. The advantage of this alternative procedure is the retention of a greater number of impurities in the substrate which would otherwise be lost in the etching step. It should be pointed out that it is feasible to employ a steam oxidation alone if the ions are implanted deep enough in the crystal to diffuse ahead of the oxide. The minimum depth required can be determined by routine experimentation by those skilled in the art.

The region of As impurities is then "buried" by growing an epitaxial layer, 13, 130

on the surface of the substrate using conventional techniques as illustrated in Fig. 1D. The epitaxial layer comprises n-type semiconductor material which will be utilized as the collector region in the final transistor structure. The formation of the base and emitter regions then follows according to well-known techniques.

While the invention has been described in terms of an As implantation, it should be clear that other impurities such as P, Sb, and B may be used to form the buried region. The minimum exposure necessary for producing a sufficiently low resistivity region utilizing P and Sb is, again, approximately  $10^{14}$  ions/cm<sup>2</sup>, while the minimum exposure for B is of the order of  $10^{15}$  ions/cm<sup>2</sup>. The other parameters of the process are easily determined by those skilled in the art.

#### WHAT WE CLAIM IS:—

1. A method of forming a buried region of impurity, comprising: implanting an impurity into a semiconductor substrate by bombarding a surface of the substrate with ions of said impurity, heating the substrate so that ions of the impurity diffuse further into the substrate, and removing from said surface of the substrate material damaged as a result of the bombardment, to form a region of impurity; and growing an epitaxial layer on the surface of the substrate, so burying the region of impurity.

2. A method according to claim 1, wherein at least some of the material damaged as a result of the bombardment is treated to form a compound, the compound then being removed.

3. A method according to claim 2, wherein the substrate comprises silicon, and wherein the compound formed is an oxide of silicon.

4. A method according to claim 3, wherein the formation of the oxide includes heating the substrate in oxygen and/or steam such that the impurity ions diffuse while said damaged material is oxidized, the depth of implantation of said impurity and the oxidation rate being such that the diffusion proceeds ahead of the oxidation.

5. A method according to claim 4, wherein when the oxidation includes heating the substrate in oxygen, the method further comprising etching the substrate in order to remove remaining damaged material.

6. A method according to claim 4 or 5, wherein the substrate is heated between 900°C and 1400°C.

7. A method according to claim 4, wherein the substrate is heated in oxygen for a period of substantially one hour and then in steam for a period of substantially one hour, the temperature of the substrate being maintained at substantially 1200°C.

8. A method according to claim 7, wherein the substrate is maintained at a temperature of substantially 1200°C for a period of substantially three and a half hours.

9. A method according to any preceding claim, wherein the impurity comprises arsenic.

10. A method according to any of claims 1 to 8 wherein the impurity comprises phosphorus or antimony.

11. A method according to claim 9 or 10, wherein the bombardment comprises at least  $10^{14}$  ions/cm<sup>2</sup>.

12. A method according to any one of claims 5 to 8, wherein the impurity comprises boron.

13. A method according to claim 11, wherein the bombardment comprises at least  $10^{15}$  ions/cm<sup>2</sup>.

14. A method according to claim 9, wherein the arsenic ions are accelerated to an energy of at least 50 KeV for bombarding the substrate.

15. A method of forming a buried region of impurity, substantially as herein described with reference to the accompanying drawings.

16. A substrate including a buried region of impurity, having been produced by a method according to any preceding claim.

K. G. JOHNSTON,  
Chartered Patent Agent,  
5 Mornington Road,  
Woodford Green, Essex.  
Agent for the Applicants.



on the surface of the substrate using conventional techniques as illustrated in Fig. 1D. The epitaxial layer comprises n-type semiconductor material which will be utilized as the collector region in the final transistor structure. The formation of the base and emitter regions then follows according to well-known techniques.

While the invention has been described in terms of an As implantation, it should be clear that other impurities such as P, Sb, and B may be used to form the buried region. The minimum exposure necessary for producing a sufficiently low resistivity region utilizing P and Sb is, again, approximately  $10^{14}$  ions/cm<sup>2</sup>, while the minimum exposure for B is of the order of  $10^{15}$  ions/cm<sup>2</sup>. The other parameters of the process are easily determined by those skilled in the art.

#### WHAT WE CLAIM IS:—

1. A method of forming a buried region of impurity, comprising: implanting an impurity into a semiconductor substrate by bombarding a surface of the substrate with ions of said impurity, heating the substrate so that ions of the impurity diffuse further into the substrate, and removing from said surface of the substrate material damaged as a result of the bombardment, to form a region of impurity; and growing an epitaxial layer on the surface of the substrate, so burying the region of impurity.
2. A method according to claim 1, wherein at least some of the material damaged as a result of the bombardment is treated to form a compound, the compound then being removed.
3. A method according to claim 2, wherein the substrate comprises silicon, and wherein the compound formed is an oxide of silicon.
4. A method according to claim 3, wherein the formation of the oxide includes heating the substrate in oxygen and/or steam such that the impurity ions diffuse while said damaged material is oxidized, the depth of implantation of said impurity and the oxidation rate being such that the diffusion proceeds ahead of the oxidation.

5. A method according to claim 4, wherein when the oxidation includes heating the substrate in oxygen, the method further comprising etching the substrate in order to remove remaining damaged material.

6. A method according to claim 4 or 5, wherein the substrate is heated between 900°C and 1400°C.

7. A method according to claim 4, wherein the substrate is heated in oxygen for a period of substantially one hour and then in steam for a period of substantially one hour, the temperature of the substrate being maintained at substantially 1200°C.

8. A method according to claim 7, wherein the substrate is maintained at a temperature of substantially 1200°C for a period of substantially three and a half hours.

9. A method according to any preceding claim, wherein the impurity comprises arsenic.

10. A method according to any of claims 1 to 8 wherein the impurity comprises phosphorus or antimony.

11. A method according to claim 9 or 10, wherein the bombardment comprises at least  $10^{14}$  ions/cm<sup>2</sup>.

12. A method according to any one of claims 5 to 8, wherein the impurity comprises boron.

13. A method according to claim 11, wherein the bombardment comprises at least  $10^{15}$  ions/cm<sup>2</sup>.

14. A method according to claim 9, wherein the arsenic ions are accelerated to an energy of at least 50 KeV for bombarding the substrate.

15. A method of forming a buried region of impurity, substantially as herein described with reference to the accompanying drawings.

16. A substrate including a buried region of impurity, having been produced by a method according to any preceding claim.

K. G. JOHNSTON,  
Chartered Patent Agent,  
5 Mornington Road,  
Woodford Green, Essex.  
Agent for the Applicants.