Fig. 1

Fig. 2

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This invention relates to semi-conducting pn type crystals, particularly of germanium or silicon, which are used in rectifiers and transistors, and to methods of making such crystals.

As is well known, different types of conductivity can be produced in semi-conducting crystals by means of suitable heat treatment and/or by the addition of extremely small quantities of the type of additives that effect conductivity. Semi-conductors whose conductivity depends on an excess of electrons are termed n semiconductors while those having a deficiency of electrons (or excess of holes) are termed p semiconductors. Semiconducting crystals having 2 or more layers of different types of conductivity are termed pn crystals and are used for making rectifiers or transistors. Such crystals are also referred to as junction type crystals. The pn crystals have the advantage over corresponding arrangements using point contacts in that they may be used with higher current intensities. The operation of such pn crystals depends on the existence and distribution of so-called impurities which may be found in the crystal due either to incomplete purification or by adding additives or impurities. By the addition of relatively large amounts of impurities on both sides of the pn crystal, certain valuable characteristics, such as good forward conductivity, are achieved. When low voltages are applied in the blocking or reverse direction to crystals of high impurity contents, the currents in the reverse direction are extremely small. However, as the voltage is increased in said blocking direction there is obtained a further increase of current because the field intensity inside the pn crystal is sharply increased.

The intensity of this field is determined by the distribution of the impurities in the transition zone between the areas of the different conductivity types. If this zone is made wide enough, it is possible to achieve high cut-off voltages in the blocking direction while employing material of good conductivity on both sides of the transition zone. However, there is a limit to the width of this zone since if it is too wide, recombination of the current carriers in this zone will occur. Thus for example, the transition zone may be made of the order of some tenth of a millimeter thick, thus reducing the intensity of the field in the transition zone and causing a substantial increase of the resistance or dielectric strength in the blocking direction.

From the foregoing it will be seen that it is only possible to achieve a limited increase of the blocking voltage by conventional arrangements. Furthermore experiments have indicated that the theoretically possible increase of the blocking voltage cannot be achieved by simply enlarging the transition zone because other influences which were not appreciated heretofore make it impossible to reach the theoretically possible blocking value.

Studies have shown that the surface or the layers directly underneath the surface of the crystal have a strong effect upon the blocking ability. These surface influen-

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ces are an important reason why the blocking current increases more rapidly than expected with increasing voltages.

An object of the present invention is the provision of a method of producing pn crystals, and the provision of such crystals, in which these surface influences are avoided or diminished and in which the blocking voltage is increased towards the theoretically possible limit.

According to the present invention pn crystals are built up in such a way that the gradation of impurities in, or adjacent the transition zone is substantially flatter on the surface of the crystal than in the inside thereof. In other words the density of impurities decreases from the center of the transition zone towards the ends of the crystal. This results in a substantial reduction of the field intensity on the surface of the crystal thus enabling such crystals to be used for substantially higher voltages than would be possible without such a distribution.

One method of obtaining the desired widening of the transition zone at the surface layers thereof is by the use of a suitable heat treatment. By the phrase "widening of the transition zone" we refer to spreading the impurities which are closely packed or densest at the transition zone over a wider area at the surface of the crystal so that the impurity density becomes less. Another way of stating the same thing is that the density curve of the impurities is flattened at the surface layers of the transition zone. This will become clearer as described hereinafter. The desired degree of flattening of this curve determines the temperature and the duration of the heat treatment. It is known that the diffusion velocity of the impurities in the surface layers of semi-conducting crystals is much greater than in the inside. The impurities will spread more rapidly in the surface layers when heat is applied. Heating of the crystal is performed in such a way that chiefly only the surface layers are heated. Thus the crystal may be intensely heated for a short time from the outside and then quickly cooled before the heat can spread into the inside of the crystal. Another method of heating the surface of the crystal without similarly heating the interior thereof consists of using skin effect of high frequency heating.

The desired flattening of the distribution curve of the impurities in the surface of the crystal can also be effected by the addition of an impurity of the type effecting conductivity, to the surface of the crystal at or near the transition zone and by heating the same to cause diffusion of this impurity into or near the zone as will be described hereinafter.

For a better understanding of the present invention, reference is had to the accompanying drawings in which Fig. 1 is a schematic cross sectional view of a bar shaped semi-conducting crystal of the pn type according to the prior art while Fig. 2 is a similar view according to the present invention.

Referring now to Fig. 1, the crystal there shown has 2 areas of different conductivity designated by the letters P and N respectively. The transition zone between the 2 areas is denoted by 1. The density of the lines 2 serves to illustrate the distribution of field intensity along the length or greatest dimension of the crystal. Within the area of the pn transition at 1, the density of the lines of equal potential is a very great one, but rapidly decreases within a short distance in the transition zone, while remaining nearly constant or uniform within the rest of the crystal. The lines 2 likewise serve to indicate the field strength in the crystal.

Fig. 2 shows the distribution of the lines of equal potential according to the present invention. In the center of the crystal, that is in the inside thereof, the distribution of the lines of equal potential is almost equal to that in Fig. 1 whereas at the surface of the crystal the distribu-

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tion curve of the density of the lines of equal potential in the transition zone is much flatter, as may be seen from the greater width of zone 1. This likewise applies to the field intensity inside the crystal in which the intensity is substantially lower at the surfaces of the crystal in Fig. 2 while in the center or interior of the crystal it is closer to that indicated in the transition zone of Fig. 1.

As has been pointed out hereinbefore, one method of producing the flattening of the gradient of the impurity density is by a heat treatment. Assuming for example, that the crystal to be so treated is a grown crystal produced from a melt, the melt for example surrounding the growing crystal may be first "doped" with indium and the pn transition produced by the addition of arsenic. The effective impurity density at both sides shall be for example approximately $10^{16}/cm.^3$. This expresses the number of atoms of the impurity per cubic centimeter. By heating the crystal at which time the crystal surface is kept at 900° C. for about 1 hour, the impurity density is reduced at the edge of the transition zone to approximately $10^{15}/cm.^3$. Since the diffusion coefficients of nearly all impurities are known, the diffusion time can be easily computed. The below formula is given as an example for a prescribed gradient "a" of the impurity density and a gradual increase of the impurity being diffused from O to "N" for the diffusion time:

$$t = \frac{N^2}{4\pi D a^2}$$

(this formula is given for symmetric junctions)

wherein D is the diffusion constant at the temperature employed. For other substances and eventually at other temperatures the period of diffusion must be varied accordingly. For achieving a diffusion on the surface of the pn-crystal only, the crystal must have a great temperature gradient. The diffusion takes a great value only on the hottest part of the crystal on account of the relation

$$D = D_0 \cdot e^{-\frac{\Delta E}{k.T}}$$

wherein D is the diffusion coefficient, E is the activation energy of the diffusion, k is the Boltzmann's constant and T is the absolute temperature. The temperature gradient is produced by a cooled support. The surface layer of the crystal is heated either by radiant heat or by high frequency heating.

With regard to the high frequency heating, frequencies higher than mc./s., especially 10 and 100 mc./s., may be of particular advantage because of the better skin effect.

The flattening of the surface profile with the aid of subsequently diffused impurities differs according to impurity or annealing temperature. A general approximate formula for the diffusion depth x is: $x \approx \sqrt{D.t}$ (D=diffusion constant, t=time). At the diffusion coefficient of 10^{-10} cm.²/sec. diffusion depth of approximately 1μ is obtained at approximately 1 minute diffusion time. The impurity must be of such condition that it reduces the effective impurity difference at the surface, which means that if n-substance is to be weakened the subsequently diffused substance must be of p-type. However, only such quantity of p-substance may be subsequently diffused that the n-substance at the surface will not be converted. When a conversion takes place it is sufficient to subsequently reduce the crystal by etching.

As mentioned already hereinbefore, it has been proved by experiments that the properties of the pn crystal at its surface, particularly in the surroundings of the transition zone between the areas of different conductivity type, are substantially determinative of the load capacity in the blocking direction. According to the invention, therefore, it is further suggested to provide unchangeable conditions on the surface of the pn crystal so that the crystal is embedded in a medium exhibiting a high degree of dielectric strength. This has proved to be particularly

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advantageous when employed with the inventive method of distributing the impurities in the crystal, but is also of great importance with respect to preventing deterioration of the crystal in the blocking direction.

It has already been suggested to protect semiconductors consisting of an intermetallic compound of an element of the third group of the periodic system with an element of the fifth group against corrosion by coating them with a layer of Al_2O_3. In the case of semiconductors such as germanium or silicon, however, there was no need up to date to provide them with a coating as protection against corrosion.

In accordance with the invention the crystal is either embedded in a most finely distributed aluminum oxide, titanium dioxide or a similar substance, or is coated with a layer thereof. It is necessary that the size of granulation of the powder into which the crystal is embedded or with which the crystal is coated, is small as compared with the thickness of the transition zone. The transition zone, as is well known, may range in the size of some hundredth part of a millimetre, but it is also possible that it exhibits thicknesses down to 1μ. From this it will be evident that with such slight thicknesses of the transition zone there have to be employed extremely fine powders for the embedding or surface coating of the crystal respectively. In some cases it will be sufficient to only provide the coating in the surroundings of the transition zone.

With respect to silicon pn crystals, heating in air at a temperature of about 1000° C. has proved to be particularly advantageous for producing the inventive distribution of the impurities. There is thus achieved a sufficient widening of the impurity profile and, at the same time there is formed a coating of silicon dioxide on the body of silicon. With the aid of this coating, conducting bridges are prevented from forming on the surface by means of dust or conversion products of the semiconductor which bridges would substantially deteriorate the blocking properties of the semiconductor.

Likewise germanium pn crystals can be coated advantageously with a coating of silicon dioxide. This can be effected by, for example, evaporating silicon monoxide on the surface, particularly adjacent the transition zone and then changing it into silicon dioxide.

Of course, there may also be employed coatings of other substances with a high dielectric strength, such as organic plastics. Apart from a change of the impurity profile on the surface of the pn crystal, there may also be diminished the difference in the density of the impurities in the surface layer. This means that the entire surface layer from one end of the crystal to the other has a lower density of impurities instead of merely widening the distribution of the densities at the transition zone. In this case, however, care has to be taken that the surface layer around the transition zone will not become too thick, because otherwise the saturation current will be unnecessarily increased in the blocking direction.

The invention can be employed with all types of semiconductor pn crystals in which there exists a solitary or reiterated change of the conductivity character. The invention, however, is in no way limited to the exemplified methods and substances mentioned hereinbefore.

What is claimed is:

1. A junction type semiconductor crystal comprising two layers of semiconductor material of different electrical properties joined together by a junction layer constituting a region of transition between said semiconductor layers, the electrical properties of said layers being determined by the nature of impurities in said layers, and the impurity density being greatest in said junction layer, characterized in that the density of impurities is greatest towards the center of said junction layer and decreases towards the peripheral surface area thereof.

2. The crystal according to claim 1, and characterized in that the surface of said crystal is coated with a layer

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of material of high dielectric strength, the size of the particles constituting said layer being small in comparison to the thickness of said junction layer.

3. A method of altering the distribution of impurities in a transition layer intermediate two layers of different conductivities in a semiconductor crystal, comprising subjecting the surface of the crystal to a temperature of approximately 900° C. for a time sufficient to cause greater diffusion of the impurities at the surface of the crystal than towards the center thereof, and cooling said crystal to maintain such impurity distribution.

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4. The method according to claim 3, wherein the desired temperature on the surface of the crystal is produced by high frequency heating.

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