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METHOD OF IMPROVING THE MINORITY CARRIER LIFETIME IN
A SINGLE CRYSTAL SILICON BODY

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FIG. 1

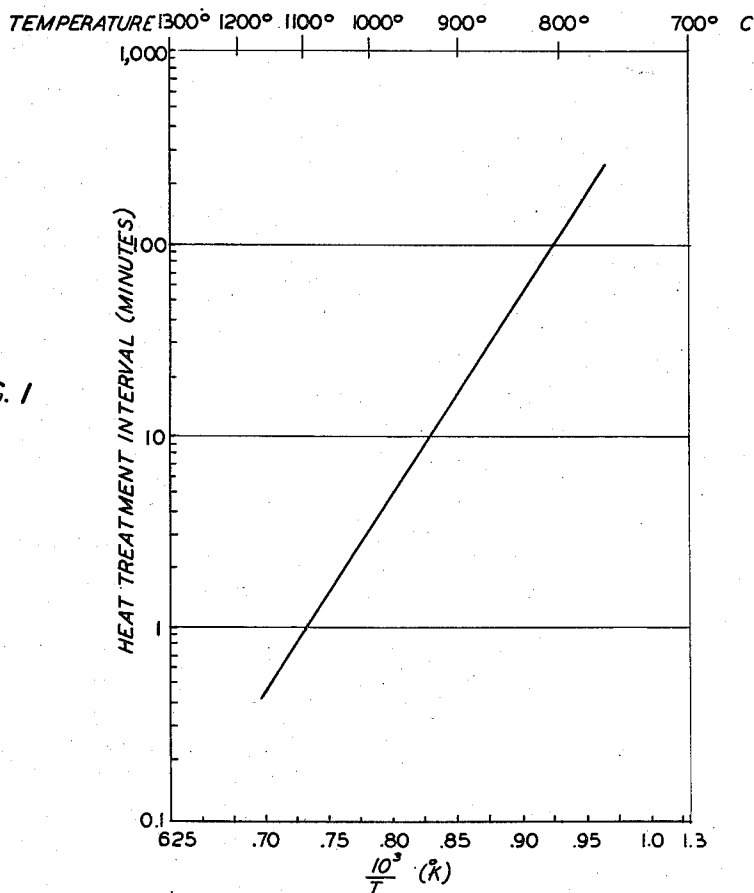
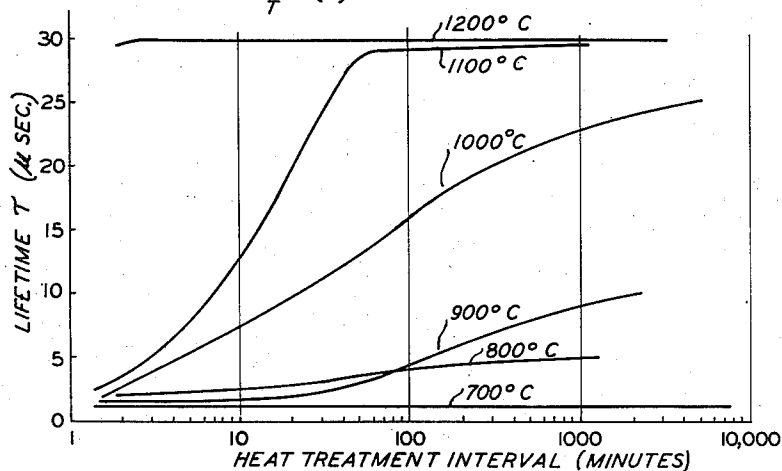


FIG. 2



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METHOD OF IMPROVING THE MINORITY CARRIER LIFETIME IN A SINGLE CRYSTAL SILICON BODY

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8 Claims. (Cl. 252—62.3)

This invention relates to the processing of silicon and more particularly to heat treatments for silicon bodies.

Conduction in and the operation of many semiconductor devices rely at least in part upon the flow of minority charge carriers in the semiconductor. Minority charge carriers, electrons in p conductivity type material and holes in n conductivity type material, disappear from the semiconductor after some interval and are no longer available for conduction. The average interval over which minority carriers persist in semiconductive material has been termed the minority carrier lifetime or, more conveniently, the lifetime of the material. Substantial lifetimes are required for certain device applications, particularly where the minority charge carriers are required to flow across substantial widths of material or it is desired to conductivity modulate the material.

Silicon having lifetimes of from essentially zero to about 1600 microseconds can be produced by present crystal growing techniques. However, it has been observed that these lifetimes deteriorate rapidly when the silicon is subjected to temperatures in excess of about 400° C., unless special precautions are taken. One such precaution which has been applied to silicon which is heated to about 1150° C. is to restrict the thickness of the heated silicon body to less than five mils as proposed by M. B. Prince in his application Serial No. 503,299, filed April 22, 1955, now Patent 2,790,940, issued April 30, 1957, entitled "Silicon Rectifier and Method of Manufacture." Material so treated maintained a final lifetime of a few microseconds instead of the imperceptible lifetimes attained theretofore in material heated to those temperatures. Considerably greater lifetime has been obtained from silicon subjected to high temperatures in accordance with my application Serial No. 559,258, filed herewith, now Patent 2,808,315, granted October 1, 1957, wherein it is taught that slow cooling, cooling at rates of about 20° C. per minute or less as opposed to the normal cooling rates such as those in air at greater than several hundred degrees per minute, and/or annealing in the range from 400° C. to 900° C. prevents lifetime deterioration or recovers some of the lost lifetime.

The primary object of this invention is to increase the ultimate minority carrier lifetime in silicon bodies as they are employed in signal translating devices.

One subsidiary object is to avoid or reduce the deterioration of minority carrier lifetime in silicon incidental to its processing at elevated temperatures.

Another subsidiary object is to recover the minority carrier lifetime in silicon which was lost during heat treatments involving steps which are detrimental to lifetime such as rapid cooling or very high temperatures.

This invention involves two major aspects which both rely upon the heating of silicon in the presence of the metals nickel, copper, or cobalt or combinations of those metals to produce a silicon body having a final minority carrier lifetime within its bulk which is greater than that which might be observed in the absence of such a heat treatment.

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One aspect resides in coating the entire exposed surface of a silicon body, which requires heat treatment at temperatures in excess of 400° C., with a metallic layer prior to subjecting the body to any temperatures in that range. The metal coating has been observed to inhibit the introduction of recombination centers, the deterioration of minority carrier lifetime being attributed to the introduction of those centers, in silicon, even after long heat treatments and rapid cooling cycles.

Another aspect comprises the recovery of lost minority carrier lifetime by a mechanism which functions in the manner of a gettering process to withdraw recombination centers from silicon. In this process the silicon is heated in the presence of the metals which may be in the system, as a coating, a vapor in the surrounding atmosphere, or a support medium, at temperatures above about 750° C. for effective intervals which are inversely related to the heat treating temperature. Thus, some recovery of degraded minority carrier lifetime has been observed by heat treating a silicon sample at 780° C. for about three hours while a corresponding recovery is obtained at a heat treating temperature of 1150° C. in less than a minute.

In accordance with the above objects and summary of the invention, a feature of this invention resides in heating a single crystal silicon body in the presence of one or more of the elements nickel, copper, and cobalt, whereby the ultimate minority carrier lifetime in the body is substantially greater than would be realized in the absence of those elements.

Another feature resides in completely coating the exposed surface portions of a single crystal silicon body with one or more of the metals nickel, copper, and cobalt prior to any heat treatment of the nature which ordinarily would cause a deterioration of the minority carrier lifetime in the silicon to inhibit or avoid such deterioration.

A further feature resides in heat treating silicon at temperatures in excess of about 750° C. in the presence of nickel to recover lifetime which has been lost incidental to previous heat treatments.

The above and other objects and features of this invention will be more fully appreciated from the following detailed description when read with reference to the accompanying drawing, in which:

Fig. 1 is a semilogarithmic plot of temperature of heat treatment against a heat treating interval at that temperature, illustrating the threshold level for the effective recovery of some lost minority carrier lifetime in accordance with this invention; and

Fig. 2 is a semilogarithmic plot of minority carrier lifetime against maximum heat treatment temperature, depicting the lifetime which can be obtained for various heat treating intervals in accordance with the lifetime recovery process of this invention.

The development of single crystal silicon having minority carrier lifetimes of the order of or greater than tens of microseconds has revealed that the lifetime of electrons or holes in silicon, after it has been subjected to elevated temperatures, is markedly degraded. For example, it has been observed that silicon, heated to about 400° C. or more, and rapidly cooled from above that minimum, as by quenching in oil or rapid withdrawal from a furnace into air, will exhibit a degraded lifetime which may, for example, be about eight microseconds when quenched from 450° C., although the initial lifetime of the material was greater than 50 microseconds. Quenching of this nature from temperatures in excess of about 650° C. will degrade this material to a minority carrier lifetime of less than one microsecond. Similarly, even a slowly cooled material which has been heated in excess of about 650° C. exhibits some lifetime deterioration so that for a cooling rate of 20° C. per minute from a temperature of 1100° C. the final lifetime of the material may be as low as one microsecond. Only a

fraction of the initial lifetime of silicon, which has been heated to high temperatures, is recovered by a subsequent annealing at some appropriate temperature in the range of from about 700° C. to 800° C. Above about 1200° C. or 1250° C. even with cooling rates as low as one-half degree centigrade per minute the lifetime of material would degrade from an initial 50 microseconds to less than one microsecond.

The production of silicon translating devices often involves the creation of suitable contacts to silicon bodies and the introduction of appropriate impurities to adjust the electrical characteristics of portions of the bodies by processes which require high temperature heat treatments of the solid material in the ranges wherein the above-described lifetime deterioration occurs.

In accordance with this invention the onset of lifetime deterioration in silicon occurs at considerably higher temperatures than in the above processes, the degree of degradation of lifetime is reduced, relatively high levels of lifetime are maintained even at heat treating temperatures of 1350° C., and when it is employed as a lifetime recovery process a higher level of minority carrier lifetime results.

The lifetime values depicted in the drawing were obtained from silicon bodies in which the lifetime had been degraded to about one microsecond by a high temperature treatment such as those which might be used in diffusing conductivity type determining substances in the bodies. The samples used in this series were single crystal rods having 70-mil square cross sections and about 750 mils long. P-N junctions produced during the crystal pulling process were located at about the center of these rods, along their lengths, and were defined on one side by 20 ohm-centimeters p-type material which was derived from high purity silicon containing no additives and on the other side by 0.1 ohm-centimeter n-type material formed by the addition of arsenic to the melt from which the crystal was pulled.

The original lifetime of electrons in the p-type material adjacent the junctions in these bars was about 85 microseconds. This lifetime was degraded to about one microsecond by heat treating the rods at 1100° C. for two hours and cooling them at a rate of about 6° C. per minute to 400° C. Prior to this heat treatment the surfaces of the rods were polished abrasively and then etched in sodium hydroxide or a mixture hereafter referred to as CP8, which comprises 25 parts of nitric acid (1.42 specific gravity) and 15 parts of 48 percent hydrofluoric acid. The etched surfaces were rinsed in deionized water. Subsequent to the heat treatment the surfaces were re-etched, for example again in CP8, rinsed in deionized water, etched in sodium hydroxide, and again rinsed in deionized water. These surfaces were then coated with nickel.

Lifetime recovery can be obtained when any of a number of techniques is employed to maintain nickel in the presence of the silicon while it is heat treated. Thus, a nickel vapor ambient, a nickel supporting surface, or a nickel coating are all effective. While a number of different types of nickel coatings can be employed, including suspensions of finely divided nickel, the most advantageous results are realized where the nickel covers the surface as a continuous plating which may be applied by conventional electrolytic processes or, in the case of the specific example depicted, by the following plating technique involving the immersion of the clean silicon rods in a plating bath at 90° C. for about five minutes to deposit a nickel coating thereon about five mils thick. This plating technique offers the advantage that it requires no external electromotive force and no contact to the silicon; hence, a uniform coating is deposited over the entire surface of the silicon rods.

The bath comprises 30 grams of nickel chloride ($\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$), 10 grams of sodium hypophosphite

($\text{NaH}_2\text{PO}_2 \cdot \text{H}_2\text{O}$), 65 grams of ammonium citrate ($[\text{NH}_4]_3\text{HC}_6\text{H}_5\text{O}_7$), and 50 grams of ammonium chloride NH_4Cl , to which is added sufficient water to produce a liter of solution which is then filtered and diluted with ammonium hydroxide (NH_4OH) until the solution turns from green to blue. This solution has a pH of from eight to ten.

The nickel plated samples were heat treated in a temperature series at 100-degree steps over the range from 700° C. to 1200° C. by mounting them in a quartz boat which was inserted in a quartz tube within a furnace maintained at the heat treating temperature. In order to avoid contamination of the silicon, all elements in its vicinity during heat treatment were cleaned in hot nitric acid and heated to 1300° C. for several hours. Dry nitrogen was circulated through the furnace and over the silicon at the rate of about three liters per minute. The samples were cooled rather rapidly after heat treatment, for example, at somewhat greater than 50° C. per minute to room temperature. It is to be noted that the cooling rate does not appear to be significant with respect to the lifetime of the resultant samples provided they are not cooled at rates in excess of several hundred degrees per minute as is the case when they are withdrawn from the furnace into a room atmosphere. The heat treated nickel plate is then removed as by etching in CP8 or aqua regia. It is desirable to remove sufficient material to insure that the rectifying junction is not short circuited by a metallic layer. Since nickel alloys with silicon above about 960° C., it is desirable to remove several mils of the surface from those samples which have been heat treated at temperatures exceeding 960° C. to remove the nickel-silicon alloy which is formed.

Lifetime measurements were made on the high resistivity material adjacent the n-p junctions employing the "junction recovery" technique described by B. Lax and S. Neustadter in their paper, published in *Journal of Applied Physics*, volume 25, page 148, 1954.

From the curves of Fig. 2 it can be seen that there is an effective threshold of lifetime recovery for this process for any given temperature of heat treatment which is a function of the time of heat treatment. Choosing a recovery of two microseconds of minority carrier lifetime as the threshold of effective recovery, the curve of Fig. 1, showing the logarithm of heat treating interval against

$$\frac{10^3}{T}$$

where T is the temperature in degrees Kelvin, can be plotted. This curve confirms the experimental results obtained independently of those discussed above wherein at a heat treating temperature of about 780° C. it is necessary that a heat treating interval of about three hours be employed to realize an effective level of lifetime recovery. This interval declines sharply to about eleven minutes at 900° C. and less than a minute at 1100° C. The threshold of lifetime recovery for the results of Fig. 1 can be defined by the equation

$$t = 5 \cdot 10^{-8} e^{\frac{2.4 \cdot 10^4}{T}}$$

where t is the heat treating interval in minutes and T is temperature in degrees Kelvin. This threshold may vary somewhat from this exact equation for different samples and/or different nickel heat treating environments. However, when generally expressed as

$$t = K_1 e^{\frac{K_2}{T}}$$

where K_1 and K_2 are constants for the particular material and treating conditions, the equation represents the lower limits of heat treating time and temperature for the recovery of a given threshold level of lifetime. In all instances an inverse relation results wherein at the lower

temperatures, about 800° C., intervals of the order of hours are required for appreciable lifetime recovery.

In practicing this invention as a means of recovering lifetime, one should work in the region above and to the left of the curve shown in Fig. 1 when the sample has been plated with nickel. This region of operation appears to be generally consistent for a reasonable level of lifetime recovery in material having a wide range of original lifetimes. Thus, similar results have been observed for material ranging from about seven microseconds to about 90 microseconds of original lifetime, both as to the threshold of recovery and the absolute level of lifetime subsequent to a lifetime recovery treatment. The process, therefore, offers a means of lifetime enhancement for certain low lifetime material.

It has been observed in processing several groups of samples, each group being derived from a common single crystal, that the lifetime of the samples near the surface, those samples with lower lifetimes, could be enhanced to the same level as those samples from the interior for any given heat treatment. For example, a sample having an original lifetime of seven microseconds, when degraded to about one microsecond by the above heat treatment and nickel plated and heat treated in accordance with the lifetime recovery process at a temperature of 900° C., exhibited an increased lifetime to about ten microseconds corresponding to that of material from the same crystal subject to the same treatment which had a higher original lifetime. This effect has been observed consistently throughout the range of heat treatments employed.

Fig. 2 shows a family of curves of resultant lifetime in nickel plated samples heat treated for various lengths of time. Each curve is labelled with its heat treating temperature. They show that the level of lifetime recovery for nickel plated samples increases with increases in temperature up to 1200° C. In all instances the increase asymptotically approaches a maximum value for the given temperature as the heat treating interval is increased. As has been illustrated with respect to the threshold level of lifetime improvement, those heat treatments at higher temperatures approach the maximum recovery level for those temperatures more rapidly than do the low temperature heat treatments. In the example, the maximum lifetime recovered by the recovery treatment at 900° C. was about ten microseconds and this value was approached only after about 2500 minutes. At an 1100° C. recovery treatment a lifetime of about 28 microseconds appears to be the maximum and is attained in about four minutes of heat treatment. No upper temperature limit for lifetime recovery has been observed. A recovery to about 30 microseconds is realized at 1200° C. At higher temperatures the maximum recovery declines so that lifetimes of ten to twenty microseconds result at 1350° C.

When applied to silicon which has not been previously heat treated, nickel has been found to be an extremely effective lifetime preservative. Essentially all of the original lifetime is sustained in 85-microsecond material which is nickel coated and heated to 1000° C. Silicon samples have been packaged in high purity nickel powder and heat treated to just below 960° C., the silicon-nickel eutectic temperature, with no deterioration of lifetime. Similar effects have been observed with electroplated nickel coatings over the entire surface of the silicon body or surfaces wherein the nickel has been applied without an external electromotive force, as described above.

The lifetime of silicon material which has not been subjected to heat treatments prior to being heated in the presence of nickel has been observed to be in the range of 80 to 90 microseconds when heat treated at 900° C. for extended intervals, at least tens of hours. This preservation process appears to offer a characteristic lifetime in the final product for a given heat treatment temperature. Thus, while the samples mentioned above were initially of a lifetime in the 80 to 90 microseconds range, similar samples, derived from the same crystal but having

an initial lifetime of seven to eight microseconds, were also observed to exhibit 80 to 90 microseconds of lifetime after being nickel plated and heat treated for 19 hours at 900° C. Reasonable levels of lifetime can be sustained at higher temperatures of heat treatment. Samples heat treated at 1350° C., when nickel plated before heat treatment, exhibited a lifetime of from 10 to 20 microseconds.

As in the case of the lifetime recovery process, it has been observed that the lifetime preservation appears to have little dependence on the heat treating ambient for the silicon inasmuch as equivalent results have been obtained in vacuum and in gas atmosphere of hydrogen, nitrogen, and helium. The surface treatments such as etching in various solutions and mechanical lapping, had no effect on the bulk lifetime of the material. Further, neither the size of the specimen nor the length of the heat treatment at elevated temperatures were significant in lifetime preservation except that it was necessary that a thermal equilibrium be reached throughout the specimen when heat treated at temperatures above 900° C. Such an equilibrium could be attained within a few minutes of the introduction of the sample into the furnace.

Lifetime can be maintained where nickel is present in other than a solid form encompassing all exposed silicon surfaces. This is illustrated by a series of samples which were heat treated in the presence of nickel in the vapor state. Samples heat treated in a nickel plated quartz tube at 850° C. for one hour, with a nitrogen ambient flowing at a rate of two or three liters per minute, after being cooled at a rate of 30° C. per minute to below 450° C. and after having their surfaces etched, exhibited essentially the same lifetime as observed before any heat treatment, namely, about twelve microseconds. The same heat treatment of essentially identical silicon samples in an unplated, high purity quartz tube resulted in a lifetime after heat treatment of less than one-half microsecond. Somewhat equivalent results were obtained by introducing nickel vapor into the heat treating atmosphere. One suitable source of nickel vapor was nickel powder contained in a bulb separate from a second bulb in which the silicon samples were located by a constricted tube.

Copper and cobalt were also found to function effectively in maintaining some degree of minority carrier lifetime greater than that obtainable in the absence of these metals. In particular, a copper plated quartz tube was employed to contain silicon rods while they were heat treated, for one hour in a nitrogen ambient at 850° C. One sample which initially exhibited a lifetime of 11.6 microseconds had a lifetime of 4.4 microseconds after this treatment and another having an initial lifetime of 6.8 microseconds had a final lifetime of 2.8 microseconds.

Copper plated silicon samples also were observed to have lifetimes which were sustained at relatively high levels after heat treatments. One such sample, heat treated at 850° C. for 60 minutes, had its original lifetime of 22 microseconds decline to 15 microseconds. Another, heat treated at 1050° C. for 60 minutes, declined from an original 11.6 microseconds to two microseconds.

Cobalt has been found to be an effective lifetime preservative for silicon in tests of the same nature as those employed for copper. Silicon samples heat treated for 60 minutes at 850° C. in cobalt coated quartz tubes, declined from an original lifetime of about 11 microseconds to about six microseconds. Cobalt plated silicon, when heat treated at 850° C. for 60 minutes, declined from an original lifetime of 13.5 microseconds to 11.6 microseconds. It has been observed, in the case of both cobalt and copper, that their effectiveness as lifetime preservatives declines rather rapidly above about 900° C. and for this reason in many applications nickel, particularly when employed as a plating, is the most advantageous preservative.

While not subscribing to any particular mechanism of operation to explain the lifetime recovery and preserva-

tion observed when silicon is heat treated in the presence of nickel, copper, or cobalt, it at present appears that one or both of the following mechanisms may be occurring. In view of the improved results obtained when the surface coating is continuous, it is quite possible that these coatings are either preventing the introduction of recombination centers in the silicon or acting as a sink to which those centers diffuse, thereby gettering them from the silicon during heat treatment. It is also possible that the metal of these surface coatings diffuses into the silicon body and occupies the recombination centers, thereby flooding them and rendering them inoperative. However, at present the nature of recombination centers observed in heat treated silicon is not known. Accordingly, it is not possible to relate the effects observed in the present process to any particular mechanism.

The results described above, as obtained from the processing of single crystal silicon containing n-p junctions, are typical of what may be expected of the application of this process to silicon bodies, whether they contain rectifying n-p junctions or are of a single conductivity type. The improvement of lifetime occurs for either type of minority carrier and hence the processes are applicable to both n- and p-type silicon. Similarly, these processes are effective as applied to single crystal silicon bodies containing rectifying junctions produced by techniques other than that of growth from a melt. It is to be emphasized, however, that inasmuch as a high rate of carrier recombination and trapping occurs at crystal boundaries in polycrystalline material, any improvement which might be obtained by the use of these processes in such material is masked and, accordingly, the practical application of this invention is restricted to single crystal silicon.

The methods of lifetime preservation and recovery disclosed above are applicable to the fabrication of many forms of signal translating devices. In some instances, where it is necessary to have a high resistivity surface in the final device, it will be necessary to employ a starting blank, somewhat oversized, in order to provide for the removal of the high conductivity metal and/or semiconductor surface layer formed thereon incidental to these processes. In other instances this high conductivity surface layer can be used to advantage. In particular, very favorable low, substantially ohmic, base characteristics can be obtained in conjunction with long lifetimes by the utilization of the nickel film produced by the plating, set forth in detail above, as a base contact. These favorable characteristics arise out of the fact that about seven percent by weight of the deposited coating is phosphorus which diffuses into the silicon when heated to temperatures of about 1100° C., thereby reducing the resistivity of n-type silicon material adjacent the nickel coating and making a smooth transition electrically from the coating to the silicon. Conversely, it is possible to use a coating of this nature, coupled with the phosphorus diffusion, to produce a rectifying junction on p-type silicon by virtue of the conversion of the material immediately under the coating to n conductivity type incidental to the phosphorus diffusion.

The above-described arrangements are illustrative of the application of the principles of the invention. Numerous other arrangements may be devised by those skilled in the art without departing from the spirit and scope of the invention.

What is claimed is:

1. The method of improving the minority carrier life-

time in a single crystal silicon body which comprises heating said body to a temperature in excess of 750° C. in contact with nickel for an interval which is inversely related to the temperature and exceeds about three hours at 780° C. and about a minute at 1100° C.

2. The method of improving the minority carrier lifetime in a single crystal silicon body which comprises coating said body with nickel and heating said body to a temperature in excess of 750° C. for an interval which is inversely related to the temperature and exceeds about three hours at 780° C. and about a minute at 1100° C.

3. The method of improving the minority carrier lifetime in a single crystal silicon body which comprises applying a continuous plating of nickel to said body and heating said body to a temperature in excess of 750° C. for an interval which is inversely related to the temperature and exceeds about three hours at 780° C. and about a minute at 1100° C.

4. The method of processing a single crystal silicon body while maintaining its minority carrier lifetime at a substantial level which comprises plating a layer of nickel on the surface of said body and heating said body to a temperature in the range of from 1000° C. to 1350° C.

5. The method of improving the minority carrier lifetime in a single crystal silicon body which comprises heat treating said body to a temperature in excess of about 750° C. in contact with nickel for an interval, t in minutes, which exceeds about 180 minutes at 780° C. and is related to the absolute temperature of heat treatment, T in degrees Kelvin, in accordance with the equation

$$t = K_1 e^{\frac{K_2}{T}}$$

wherein K_1 and K_2 are constants.

6. The method of improving the minority carrier lifetime in a single crystal silicon body which comprises heat treating said body to a temperature in excess of about 750° C. in contact with nickel for an interval, t in minutes, which is related to the absolute temperature, T in degrees Kelvin, of heat treatment in accordance with the equation

$$t = 5 \cdot 10^{-8} e^{\frac{2.4 \cdot 10^4}{T}}$$

7. The method of preserving the minority carrier lifetime of a single crystal silicon body which is heat treated to temperatures in excess of 400° C. for intervals greater than about five minutes which comprises applying to said body a coating including one of the elements selected from the group consisting of nickel, copper, and cobalt, and then heat treating said body at a temperature in excess of 400° C. for an interval greater than about five minutes.

8. The method of preserving the minority carrier lifetime of a single crystal silicon body which is heat treated to temperatures in excess of 400° C. for intervals greater than about five minutes which comprises mounting said body in a heat treating chamber, introducing a vapor of one of the elements selected from the group consisting of nickel, copper, and cobalt, and then heat treating said body at a temperature in excess of 400° C. for an interval greater than about five minutes.

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