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2,808,315

PROCESSING OF SILICON

Filed Jan. 16, 1956

2 Sheets-Sheet 1

FIG. 1

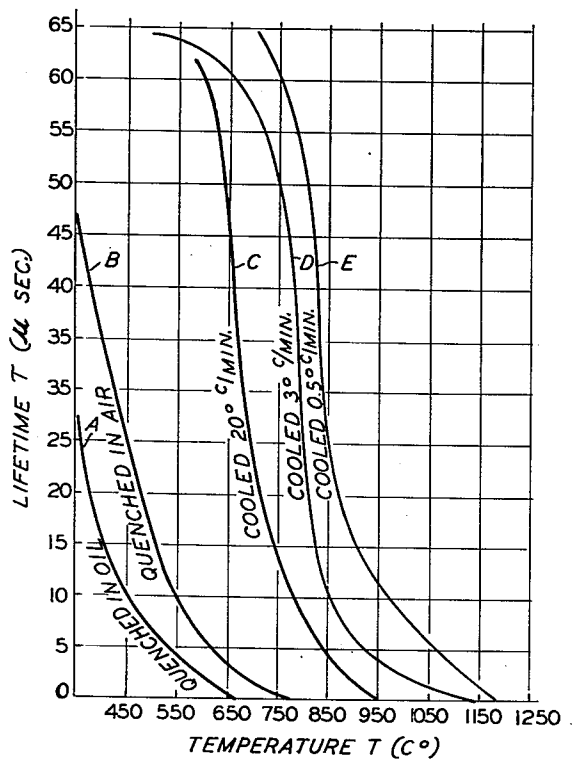
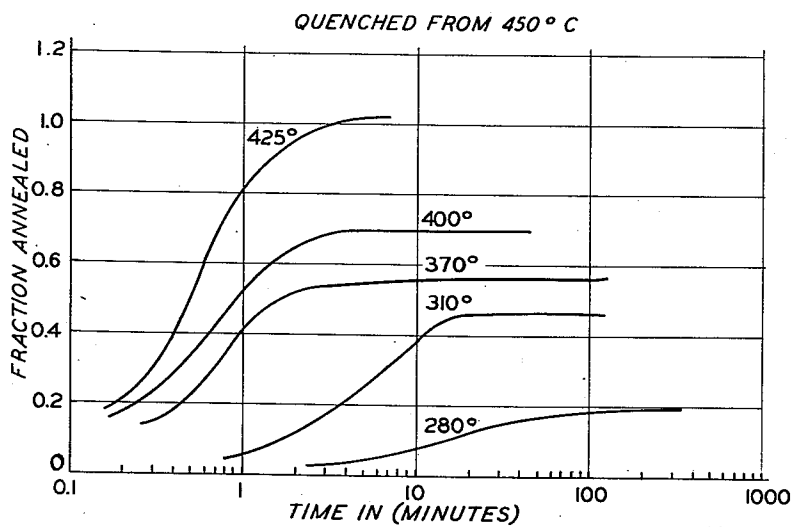


FIG. 2



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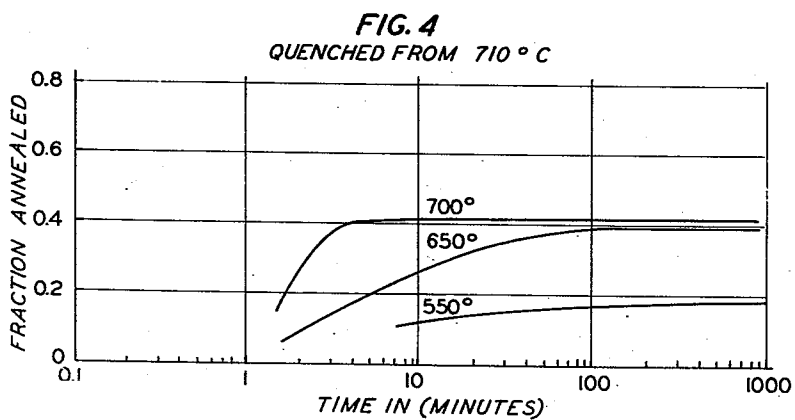
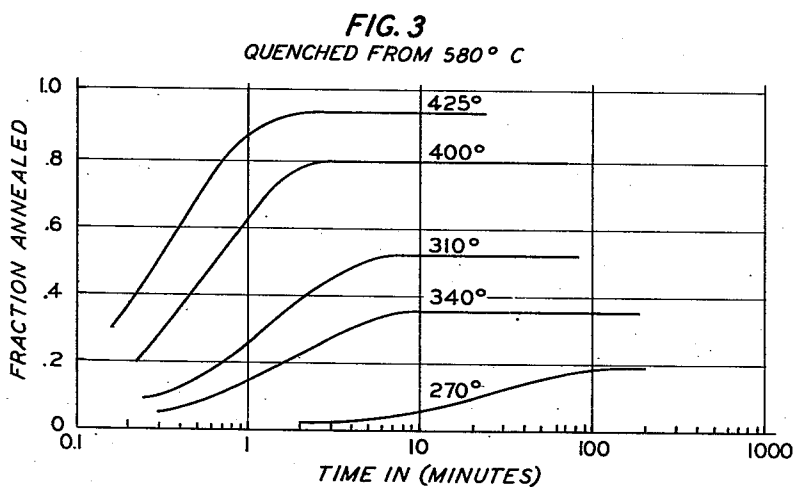
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2 Sheets-Sheet 2



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1

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PROCESSING OF SILICON

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6 Claims. (Cl. 23-223.5)

This invention relates to the processing of silicon and more particularly to heat treatments for silicon bodies, its principal object being to realize high minority charge carrier lifetime in silicon.

It has been observed that minority charge carriers introduced into silicon disappear rather rapidly. The average interval over which such carriers persist has been identified as the minority charge carrier lifetime or, more conveniently, the lifetime of the material. In particular, it is common to observe single crystal bodies of silicon which have been produced by the drawing of a single crystal seed from a molten bath while progressively freezing material on the seed having lifetimes in the bulk material ranging from a few microseconds to about 1600 microseconds with the usual product having a lifetime of the order of magnitude of tens of microseconds.

When subjected to further processing, as in the alloying of contacts to body elements derived from drawn single crystal silicon masses or in the diffusion of substances into such elements to alter the electrical characteristics of certain regions therein, it has been necessary to heat the silicon to temperatures in excess of 400° C. and often to temperatures as high as 1350° C. The lifetime of material which has been subjected to such heat treatments has been observed to deteriorate markedly. It has been suggested in M. B. Prince application Serial No. 503,299, filed April 22, 1955, and entitled "Silicon Rectifier and Method of Manufacture," that this lifetime deterioration, incidental to diffusion and alloying processes, can be avoided to some extent by applying these treatments only to thin silicon bodies, bodies which generally are less than ten mils in thickness and advantageously are less than five mils thick.

One aspect of this invention resides in annealing single crystal silicon which has been subjected to temperatures in excess of 400° C. to avoid the degradation of lifetime heretofore observed when the silicon has been treated at high temperatures. Annealing may be accomplished either by extremely slow cooling of the silicon from elevated temperatures, either from the initial heat treatment or in a subsequent heat treatment, or by a high temperature soak followed by a relatively slow cooling process to about 400° C.

One feature of this invention involves cooling a single crystal silicon body which has been heat treated to temperatures in excess of about 500° C. at the rate of about 20° C. per minute or less, for example, at about 0.5° C. per minute, to a temperature of about 400° C.

Another feature of the invention resides in maintaining a single crystal silicon body at a temperature of about 500° C. for at least several minutes and thereafter cooling it to 400° C. at a rate of less than about 20° C. per minute.

A further feature, particularly applicable to single crystal silicon bodies subjected to heat treatments of 1250° C. or greater, resides in cooling the body from that high temperature at a rate of about 20° C. per minute or less, maintaining the body at from 700° C. to 900° C. for an interval of at least ten minutes to anneal it, and cooling

2

the body from the anneal to about 400° C. at a rate of 20° C. per minute or less.

The above and other objects and features of this invention will be more fully understood from the following detailed description when read in conjunction with the accompanying drawings, wherein:

Fig. 1 depicts a plot of minority charge carrier lifetime in silicon against temperature of heat treatment of the silicon for various rates of cooling from the heat treating temperature; and

Figs. 2 through 4 are semilogarithmic plots of the fraction of lifetime recovered against annealing time for various annealing temperatures illustrating the degree of recovery for silicon samples quenched from 450° C., 580° C., and 710° C., respectively.

Interest in silicon transistors and conductivity modulation devices requiring reasonable levels of lifetime in the silicon material has reached a high level with the evolution of silicon processing techniques to the point where large single crystals of silicon can be produced in commercial quantities. In the past, silicon lifetime considerations have been only secondary in the design of practical devices since reasonable lifetimes were unobtainable in polycrystalline material. Accordingly, it is to be emphasized that this invention and the following detailed description are directed to single crystal silicon materials and would be of little applicability to polycrystalline material wherein minority carrier lifetimes would be low under any circumstances due to the trapping and recombination of charge carriers at crystal grain boundaries.

As may be seen from Fig. 1, the lifetime in single crystal silicon is extremely dependent upon the temperatures and cooling rates to which the silicon is subjected. Fig. 1 is a family of curves for a group of rods having a cross section of 0.100 inch by 0.100 inch which were 0.750 inch long and contained a p-n junction having a resistivity adjacent the junction of 30 ohm-centimeters on the p side and 0.3 ohm-centimeter on the n side. These rods were derived from a pulled single crystal silicon body grown along a [100] axis at a rate of two mils per second. The p-type characteristics resulted from a starting material of high purity silicon having a purity in excess of 99.98 percent. The n-type characteristics were obtained by adding 20 milligrams of arsenic to the 50-gram melt after about 20 percent of the melt had been grown on the crystal. These samples were cut parallel to the growth axis as bars having the junction about halfway between the ends. They were cleaned by first etching them in a mixture of about 25 parts of nitric acid (1.42 specific gravity) and about 15 parts of 48 percent hydrofluoric acid. Next they were etched in hot nitric acid and then rinsed in deionized water. A tantalum tray supported them within a fused silica tube in an electric radiation furnace during the various heat treatments reported herein. To insure against contamination of the silicon, the tube and tray were cleaned in hot nitric acid and heated to 1300° C. for several hours. No significant differences in results were noted between heat treating ambients for the silicon such as vacuum or flowing helium, hydrogen, or nitrogen.

The measured lifetimes depicted in Fig. 1 are those which were observed on the high resistivity p side of the n-p junction by the "junction recovery" measuring technique set forth for example in the paper by B. Lax and S. Neustadter, Journal of Applied Physics, Volume 25, page 1148, 1954. The specimens under consideration, as well as translating devices manufactured by processes incorporating this invention, are subjected to a surface cleaning subsequent to heat treating and prior to utilization or measurement. One such surface cleaning involves etching in hydrofluoric acid and rinsing in deionized

water. Curves A and B represent specimens which were cooled from various temperatures by withdrawing the specimens from a furnace at the indicated temperature and, in the case of curve A, quenching by immersion in an oil such as castor oil, octoil, and ethylene glycol, at room temperature, 20° C., within about a second of their withdrawal from the furnace, or, in the case of curve B, by quenching in air. Oil quenching cools the specimen at a rate of about 1000° C. in 0.1 second while air quenching offers a rate of about 1000° C. per minute.

While the specific results reported are for lifetimes of the high resistivity material adjacent a grown n-p junction, it is to be understood that the techniques and results set forth herein are typical of single crystal silicon of both conductivity types. Further, a behavior after the heat treatments of this invention which is similar to that observed for p-n junctions, has been demonstrated in monocrystalline silicon bodies of a single conductivity type by photoconductivity decay type of measurements. These heat treatments have improved the lifetime of material of a wide range of resistivities extending from less than two to more than 300 ohm-centimeters.

Heretofore, diffusion and alloying techniques have usually involved a cooling such as depicted in curve B, namely the withdrawal of the specimen from the furnace with a rather rapid cooling rate. The p-type material from which these results were obtained initially exhibited a bulk lifetime of about 50 microseconds. It will be noted that oil quenching from 650° C. reduces this lifetime to less than one microsecond as does air quenching from 750° C.

Curves C, D, and E, on the other hand, represent the cooling of specimens heated over a range of temperatures including substantially higher temperatures at rates of 20° C. per minute, 3° C. per minute, and 0.5° C. per minute, respectively. It is apparent from these curves that as the cooling rate is decreased the lifetime for a particular material is enhanced substantially. Thus, at 750° C. that material which has a lifetime of less than one microsecond for air quenching has about 15 microseconds at a cooling rate of 20° C. per minute, about 50 microseconds at a cooling rate of 3° C. per minute, and about 61 microseconds for a cooling rate of 0.5° C. per minute. In addition, it will be noted that a five microseconds lifetime can be maintained for material subjected to temperatures in excess of 1050° C. if cooled at a rate of 0.5° C. per minute while air cooled material can only be maintained at that lifetime when heated to a maximum of 600° C.

The results shown in Fig. 1 are attributable to the cooling cycles and apparently are independent of such parameters as heat treating ambient, surface treatment, and specimen size. In particular, similar results have been obtained in vacuum ambients or while heat treating in helium, hydrogen, and nitrogen. Further, bulk lifetime characteristics are not altered by the creation of an oxidizing film during the heat treating process.

The above results are typical of those for single crystal silicon. The process of lifetime improvement is reversible so that the degradation of lifetime incidental to the rapid cooling of silicon can be at least partially overcome by an appropriate heat treatment. The maximum cooling rate for effective lifetime maintenance or recovery appears to be about 20° C. per minute down to 400° C. from any temperature below about 1200° C. In all instances higher lifetimes are realized with lower cooling rates. Slow cooling appears to offer no beneficial effects with regard to lifetime below about 400° C. These cooling rates also can be effective to enhance the lifetime in the original crystal by employing suitable means to retard the cooling of the solidified material following crystal growth from the time it reaches 1200° C. to the time it cools to 400° C. Thus, not only is a process of this nature effective upon single crystal silicon which has had

its lifetime degraded by a high temperature treatment, followed by a rapid cooling, but also to enhance the lifetime of silicon as it is grown over that obtainable heretofore.

The underlying reason for the above-mentioned phenomenon has not been definitely established. Such evidence as is available, however, indicates that the thermal treatment of silicon determines the distribution of recombination centers therein. The changes in lifetime are at present believed to be due to interactions between crystal imperfections.

Another successful technique for enhancing minority carrier lifetime in single crystal silicon involves maintaining the silicon at elevated temperatures for an interval sufficient for the equilibrium distribution of recombination centers for that temperature to be reached. Thus, a silicon body which has been cooled by the usual technique of withdrawal from a heat treating furnace, from maximum to room temperature in a few minutes so that its lifetime is low, can have its lifetime enhanced by reheating for a reasonable interval.

The curves of Figs. 2, 3, and 4 illustrate the effects of heat treatments on single crystal silicon bars containing grown n-p junctions. These bars had been subjected to a heating cycle including an oil quench from the maximum temperature of the cycle. Silicon which had an initial lifetime of about 40 microseconds was degraded to about nine microseconds by a quench from 450° C., to about two microseconds by a quench from 580° C., and to less than 0.2 microsecond by a quench from 710° C. Some recovery of lifetime has been noted for even very low temperature anneals, particularly for the quenches from low temperature. However, the maximum recovery is realized by reheating for at least several minutes to a temperature near that from which the silicon was quenched. Since the lifetime of the material is not adversely affected by the rate of cooling below about 400° C., provided that rate does not exceed that of the usual room air cooling, a slow cooling rate is effective in improving lifetime primarily in the range from the maximum annealing temperature down to 400° C.

As illustrated in Figs. 2, 3, and 4, the length of time required to complete the redistribution of recombination centers in silicon for a particular quenching cycle decreases as the annealing temperature approaches the temperature from which the specimen was quenched. The degradation of lifetime is less for low temperature quenches and lifetime recovery is accomplished in a shorter anneal time and is more complete. At an anneal of 425° C. for about two minutes essentially all of the lifetime lost in a quench from 450° C. is recovered. About 0.9 of the initial lifetime is recovered with a 425° C. anneal for about two minutes for silicon quenched at 580° C. However, no recovery is noted even at a 450° C. anneal for a sample quenched from 710° C.

Annealing has been established to afford essentially complete recovery of lost lifetime in silicon in material quenched from temperatures below about 600° C. when the anneal is for the order of a few minutes, about ten minutes, and is at a temperature approaching that from which quenching occurred. Above about 600° C. lifetime recovery for quenched material is incomplete and the lifetime recovery is imperceptible for samples quenched from temperatures above about 900° C. As shown in Fig. 4, only 0.4 of the original lifetime could be recovered by annealing even at 700° C. The degree of recovery possible by annealing of quenched samples is inversely related to the temperature from which quenching occurred in the range of about 600° C. to about 900° C.

Results similar to those depicted in Fig. 1 for the very low cooling rates have been achieved by employing the heat treating or annealing process discussed above. Samples heated to temperatures of from 1000° C. to 1200° C. for varying lengths of time have exhibited bulk lifetimes of the same magnitude as shown for cooling rates

5

of 0.5° C. per minute and less when cooled at a rate of 20° C. per minute from these temperatures followed by an anneal in the 700° C. to 900° C. range for intervals of from 30 minutes to four hours. Some improvement is obtained even outside this range of annealing temperatures, specifically, in the range from 400° C. to 900° C. The silicon can be cooled to room temperature and reheated or it can be cooled to the annealing temperature and permitted to dwell at that temperature. In either instance a greater improvement in lifetime is realized when the silicon is cooled at a rate of less than about 20° C. per minute from the annealing temperature.

The improvement in the lifetime of the high resistivity material adjacent various silicon n-p grown junctions obtained with annealing heat treatments typical of this invention is represented by the results set forth below. These samples, which were picked at random from a large group, had lifetimes on the high resistivity side of the junction which were markedly degraded by heat treatments which were much less severe from the standpoint of lifetime than those typical of the type heretofore employed in diffusing substances into silicon. The samples were cooled from the heat treatment temperatures at a rate of 20° C. per minute and after their lifetimes were again measured, they were reheated for an annealing cycle from which they were cooled at 20° C. per minute. A bar having a 30 ohm-centimeters n-type region contiguous with an 0.03 ohm-centimeters p-type region exhibited an original lifetime of 28 microseconds which was degraded to two microseconds by a heat treatment at 950° C. for ten minutes and recovered to nine microseconds when annealed at 730° C. for four hours. Another sample having an n-type resistivity of 23 ohm-centimeters adjacent a p-type zone of 0.11 ohm-centimeters had its original lifetime of 20 microseconds degraded to less than 0.5 microsecond by a 1100° C. heat treatment for one-half hour. This sample exhibited a lifetime of four microseconds when heat treated at 750° C. for four hours. Similar results were observed for the electron lifetime in p-type material in a sample having an 0.1 ohm-centimeter n-type zone adjacent a 65 ohm-centimeters p-type zone wherein the lifetime initially was six microseconds and was degraded to less than 0.5 microsecond by a 1150° C. heat treatment for one-half hour. A heat treatment at 760° C. for four hours produced a final lifetime of three microseconds.

Another technique and that which is most beneficial from the standpoint of lifetime in single crystal silicon heated to temperatures in excess of 700° C. is to cool the silicon at 0.5° C. per minute from the maximum to about 700° C. From 700° C. the silicon can be cooled at 20° C. per minute to below about 400° C. Specimens cooled in this manner from a temperature of 1250° C. have exhibited lifetimes of four microseconds.

Most of the specific examples discussed above have involved the reduction in the loss of lifetime or the regaining of a portion of the lost lifetime of silicon single crystals subject to rapid cooling. The slow cooling principles have been found to be beneficial even to the extent of increasing the lifetime of material as derived from a pulled single crystal. Thus, portions of single crystals of silicon containing p-n junctions formed from material undoped on the originally grown p side and arsenic doped while rotated three-quarters revolution per minute in accordance with the application of N. B. Hannay, Serial No. 432,792 filed May 27, 1954, and entitled "Method of Forming Junctions in Silicon," have been increased in lifetime by appropriate heat treatments, one such crystal exhibiting a resistivity on the p side of 25 ohm-centimeters and on the n side of two ohm-centimeters and an electron lifetime on the p side of 25 microseconds, had its lifetime increased on the p side to 50 microseconds by a ten minute anneal at 500° C. when cooled at a rate of 20° C. per minute to below 400° C. Similar improvements have been realized with grown junctions of other

6

resistivities and lifetimes. Specimens having 30 ohm-centimeters n-type material of five microseconds lifetime near a junction with 0.03 ohm-centimeter p-type were increased to 20 microseconds by a three hour anneal at about 475° C., followed by slow cooling to below 400° C. These results can be obtained during the initial cooling of a single crystal silicon ingot by employing a cooling cycle in the critical range from about 1200° C. to about 400° C. involving slow cooling and/or an anneal at some temperature between 400° C. and 800° C. For example, the cooling of the ingot can be retarded from its usual rate by employing a series of supplemental heaters adjacent its frozen portions.

Summarizing the above results, it has been determined that the lifetime in single crystal silicon bodies can be enhanced or its loss as a result of heat treatments above about 400° C. reduced by appropriate heat treatments. These treatments may be a cooling of the specimen at less than 20° C. per minute and advantageously at about 0.5° C. per minute, from the maximum heat treating temperature to about 400° C., by annealing the specimen between 400° C. and 800° C. followed by slow cooling to below about 400° C., or by a combination of these techniques.

The processes set forth above are merely exemplary and are not to be interpreted as placing the limits thereof upon this invention. Other processing parameters than those set forth in the examples may be employed in practicing this invention without departing from its spirit and scope.

It is to be noted that another method of fabricating silicon bodies having long bulk lifetimes for use in semi-conductive translators is disclosed in my application Serial No. 559,259 filed herewith.

What is claimed is:

1. In the process of manufacturing a single crystal silicon body wherein said body is subjected to an elevated temperature in excess of 400° C. the method of limiting the thermal degradation of minority carrier lifetime comprising cooling said body from said elevated temperature to below 400° C. at a maximum rate of 20° C. per minute.

2. In the process of manufacturing a single crystal silicon body wherein said body is subjected to an elevated temperature above 1150° C. the method of limiting the thermal degradation of minority carrier lifetime comprising the steps of cooling at a maximum rate of 0.5° C. per minute from the elevated temperature to below 400° C.

3. In the process of manufacturing a single crystal silicon body wherein said body is subjected to an elevated temperature in the range of 1000° C. to 1200° C., comprising the steps of cooling at a maximum rate of 20° C. per minute to an annealing temperature in the range of 700° C. to 900° C., maintaining said body at said annealing temperature for a period of from 30 minutes to four hours, and cooling to below 400° C. at a maximum rate of 20° C. per minute.

4. In the process of manufacturing a single crystal silicon body wherein said body is subjected to an elevated temperature in excess of 700° C., the method of limiting the thermal degradation of minority carrier lifetime comprising the steps of cooling at a maximum rate of 0.5° C. per minute from the elevated temperature to a temperature about 700° C., and cooling at a maximum rate of 20° C. per minute to below 400° C.

5. The method of essentially complete recovery of minority charge carrier lifetime which has been lost as a result of quenching a single crystal body of silicon from a temperature in the range of 400° C. to 600° C. which comprises the steps of heating the single crystal to an annealing temperature near that from which said crystal was quenched, maintaining said body at said annealing temperature for a period of several minutes, and

cooling at a maximum rate of 20° C. per minute to below 400° C.

6. The method of partially regaining minority charge carrier lifetime which has been lost as a result of quenching a single crystal body of silicon from a temperature in the range of 400° C. to 900° C. which comprises the steps of heating the single crystal to an annealing temperature near that from which said crystal was quenched,

maintaining said body at said annealing temperature for a period of several minutes, and cooling at a maximum rate of 20° C. per minute to below 400° C.

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