MASTER 78-144
CONF-781114--1

Note: This is a draft of a paper being submitted for publication. Contents of this paper should not be quoted nor referred to without permission of the authors.

ELECTRICAL PROPERTY STUDIES OF NEUTRON-TRANSMUTATION-DOPED SILICON

J. W. Cleland, P. H. Fleming, R. D. Westbrook,
R. F. Wood, and R. T. Young

SOLID STATE DIVISION
OAK RIDGE NATIONAL LABORATORY
Operated by
UNION CARBIDE CORPORATION
for the
UNITED STATES DEPARTMENT OF ENERGY
Oak Ridge, Tennessee

September 1978

ELECTRICAL PROPERTY STUDIES OF NEUTRON-TRANSMUTATION-DOPED SILICON*

J. W. Cleland, P. H. Fleming, R. D. Westbrook,
R. F. Wood, and R. T. Young
Solid State Division, Oak Ridge National Laboratory
Oak Ridge, Tennessee 37830

INTRODUCTION

Irradiation of semiconducting materials in a nuclear reactor[1] was initiated about 30 years ago at the Oak Ridge National Laboratory (ORNL). The primary interest at that time was the study of radiation damage effects, but transmutation doping was used to determine isotopic cross sections, introduce a known dopant concentration, and study impurity banding effects. Research on neutron-transmutation-doped (NTD) silicon was resumed at ORNL approximately four years ago. In this paper results of several studies of electrical properties conducted since then will be reviewed and discussed.

NTD silicon offers four clearly identifiable advantages over silicon doped by more traditional techniques. These advantages are (1) areal and spatial uniformity of dopant distribution; (2) precise control of doping level; (3) elimination of dopant segregation at grain boundaries in polycrystalline silicon; and (4) superior control of heavy-atom contaminants. Uniformity of doping has proved to be of importance in a number of device applications, particularly high power rectifiers and thyristors.[2] Precise control of doping levels is important in any application such as avalanche

---

*Research sponsored by the Division of Materials Sciences, U. S. Department of Energy under contract W-7405-eng-26 with the Union Carbide Corporation.

or infrared detectors which require high resistivity material. Transmutation doping of epitaxial layers deposited on low resistivity n-type[3] or p-type[4] silicon substrates has also been demonstrated, and is of interest because conventional chemical vapor deposition and diffusion techniques do not provide well-controlled and uniform dopant concentrations in large area epitaxial layers, especially at low dopant concentrations.

Capture of thermal neutrons converts ^{30}Si to ^{31}P thus resulting in transmutation doping of the material. The anticipated rate of introduction of ^{31}P can be calculated for NTD silicon from the ^{30}Si isotopic abundance, the ^{30}Si thermal neutron absorption cross section, and the thermal neutron flux, n_{th}/cm^2 sec. It has long been recognized that, because of multiple atomic displacements produced by recoiling silicon atoms, a lattice defect concentration many orders of magnitude greater than the anticipated ^{31}P concentration is created. This is the case even for samples irradiated with a low total neutron fluence in a reactor locale with a very large thermal-to-fast (t/f) neutron ratio.[5] Because of this recoil damage, even heavily doped n- and p-type silicon is converted to nearly intrinsic conditions as a consequence of such irradiations.

The annealing conditions required to obtain the anticipated resistivity, carrier concentration, and carrier mobility have been reported[6] for float zone refined (FZ) single crystal silicon of low oxygen content ($\leq 3 \times 10^{16}$ cm^{-3}). Most of the simple recoil-induced defects were removed by annealing up to 400°C. Annealing for 30 minutes at 750°C was sufficient to remove virtually all lattice damage in FZ NTD silicon irradiated up to a total fluence of approximately 10^{21} n cm^{-2} in different reactor locales with t/f ratios of from 1700 (low total fluence) down to 3-10 (high total fluence).

The corresponding annealing requirements for obtaining the anticipated electrical properties in pulled or Czochralski (Cz) grown single crystal NTD silicon that contains a moderate (5 x 10^{17} cm^{-3}) to large (4 x 10^{18} cm^{-3}) oxygen concentration have not been clearly established. Most of the oxygen in Cz silicon after initial crystal growth may be present as electrically inactive interstitial atoms (O_i), but some of it may be present in electrically inactive oxygen clusters, and some as electrically active clusters that act as n-type donors. Commercially available Cz silicon is usually limited to about 50 ohm cm resistivity (10^{14} donors or 3 x 10^{14} acceptors cm^{-3}) unless a special pedestal-type growth technique is employed. Most producers anneal after crystal growth to reduce any donor concentration due to clustered oxygen. The post annealing procedure may vary somewhat among producers, but is normally about 1 hr at 700 to 750°C for ingots up to two inches in diameter and this is followed by quick quenching (2-3 min) to below 200°C to minimize any additional oxygen donor formation.

Heat treatments of Cz silicon after crystal growth and post annealing, which may be required during device processing or to remove lattice damage in NTD Cz silicon, can still form oxygen donors at 400 to 500°C, electrically inactive oxygen clusters at 600 to 900°C, and electrically inactive oxygen precipitates (SiO_2) near 1000°C. Reheating near the melting point can dissociate most of these clusters and precipitates but some re-form during subsequent cooling. Recent experiments[7] have indicated that the apparent interstitial oxygen concentration in Cz silicon, as determined by infrared absorption (IR) techniques, cannot be reduced below about 10 ppm (5×10^{17} cm^{-3}) even by extended annealing in a gettering atmosphere. In fact, because of some remaining clusters and precipitates, the actual oxygen content may be greater by a factor of from 2 to 5 than that indicated by IR techniques.[7]

The annealing requirements to remove lattice defects in Cz NTD silicon were first investigated by Mordkovich *et al.*[8] They used resistivity data to estimate the ^{31}P concentration after irradiation at 50°C with 10^{17} - 10^{19} thermal neutrons cm^{-2}, and after 30 min isochronal annealing in 20°C steps from 100 to 1000°C. Their results for FZ NTD silicon agree almost identically with their calculated values after annealing at 800°C; but the apparent ^{31}P concentration in their Cz NTD silicon after annealing at 1000°C was larger than that predicted by about a factor of 2. This discrepency increased with both initial oxygen content and total neutron fluence. They did not state if their Cz silicon was post annealed. They concluded that highly stable neutron-induced lattice defects are tightly bound to oxygen atoms, but they did not suggest a model for a defect-oxygen complex that could serve as a donor in Cz NTD silicon.

Liaw and Varker[9] used resistivity, Hall coefficient, and IR measurements to investigate both FZ and Cz (not post annealed) NTD silicon that had been subjected first to a single irradiation calculated to introduce about 3.5×10^{14} ^{31}P cm^{-3}, and then to 30 min isochronal or extended isothermal annealing from about 450 to 950°C. They obtained fairly reasonable agreement with their calculated value for the ^{31}P concentration in FZ NTD silicon after annealing for 1-2 hrs at 680°C. They stated that excess donors were generated in their Cz NTD silicon to such an extent that annealing for 1 hr at 950°C was required to remove them, and thus obtain reasonable agreement with their calculated value for the ^{31}P concentration. They also do not suggest a model for a defect-oxygen complex that serves as a donor in Cz NTD silicon, and requires annealing at 950°C.

Previous investigators[10-12] have shown that lithium can be introduced into silicon during crystal growth or by subsequent diffusion. Lithium, which is highly mobile in silicon at ambient temperatures, can serve as an electrically active donor unless precipitated and it can interact with other impurities, defects already present and defects introduced by irradiation to form additional donors.[13-15] Because of this and for other reasons, the properties of lithium in NTD silicon have been of particular interest to us at ORNL, and some of our recent results in this area will be discussed.

IRRADIATION FACILITIES AND EXPERIMENTAL PROCEDURES

Figure 1 is a drawing of a new thermal neutron facility (D_2O tank) recently installed in the pool of the 2 MW Bulk Shielding Reactor (BSR) at ORNL. This facility will accommodate ingots or wafers up to 6-in. in diameter in several locales, and samples can be raised, lowered, and rotated as required to maximize the radial and axial dopant uniformity. Some of the sample tubes terminate 6 ft above the tank to permit sample exchange under water without any requirement for reduced reactor power or shutdown. Any of the tubes except those against the BSR core can be equipped with an "S" shaped extension for dry irradiations, and any empty tubes, including those against the BSR core, can be plugged with graphite, magnesium, or D_2O-filled cylinders to increase the thermal neutron fluence and t/f neutron ratio in the other facilities. Preliminary results indicate a thermal neutron flux of $\sim 10^{13}$ and 10^{12} cm^{-2} sec^{-1} for the 4-in. diameter core holes and 6-in. diameter tank holes closest to the BSR core, respectively. The corresponding fast ($\geq$ 1 MeV) neutron flux has been estimated from nickel wire dosimeter techniques as 1.3 x 10^{12} and 10^{10} cm^{-2} sec^{-1} for the above holes, respectively.

Samples from single crystal silicon ingots were characterized by conventional van der Pauw and IR techniques to determine the ingot type, resistivity, initial apparent carrier concentration, and initial apparent oxygen content as indicated in Table I. Isothermal annealing experiments were carried out in a quartz tube furnace in a helium, argon, or nitrogen atmosphere to study the introduction and dissociation of donors due to clustered oxygen in Cz silicon samples prior to irradiation. Ingot sections or slices of FZ and Cz silicon were irradiated in the D_2O tank where the temperature did not exceed 50°C to introduce $\sim 10^{12}$ to 10^{16} ^{31}P cm^{-3} in estimated t/f ratios of 100 and 10. Other ingot sections were irradiated in various locales in the Oak Ridge Reactor (ORR), the High Flux Isotopes Reactor (HFIR) at ORNL, and the National Bureau of Standards Reactor (NBSR) to introduce up to 10^{18} ^{31}P cm^{-3} in a t/f ratio of 3-10. Isochronal (30 min) annealing at 750 to 1000°C was used to remove the radiation-induced defects in both FZ and Cz NTD silicon samples, and additional annealing experiments were carried out to study the introduction and dissociation of donors due to oxygen or of defect-donor complexes in selected Cz NTD silicon samples.

Isotopic ^{10}B (19.8% normal abundance) has a very large (~ 3,840 x 10^{-24} cm^2) thermal neutron absorption cross section and fissions to introduce ^4He and ^7Li. Since the properties of lithium in NTD silicon have been of interest, a special Cz ^{10}B doped single crystal silicon ingot (No. 7 - Table I) was obtained,[16] and samples were subjected to a variety of irradiation and annealing experiments to study the behavior of lithium in this material. Yet another experiment was carried out in which samples of high purity FZ silicon were irradiated, annealed to remove lattice damage, and diffused with lithium from an oil bath suspension to investigate any potential lithium-phosphorus interactions.

EXPERIMENTAL RESULTS

(A) Annealing of Float Zone NTD Silicon

It was stated above that annealing for 30 minutes at 750°C is sufficient to obtain the anticipated electrical activity in FZ NTD silicon irradiated to introduce up to 6 x 10^{16} ^{31}P cm^{-3} irrespective of the t/f neutron ratio. These measurements have very recently been extended to FZ NTD silicon irradiated in a core position of the HFIR with a t/f ratio of no more than 3-10 to introduce up to 3.5 x 10^{17} ^{31}P cm^{-3}, and identical annealing results were obtained. Previous investigators and we agree that one can predict a phosphorus concentration in FZ NTD silicon from the isotopic abundance, cross section, and thermal neutron fluence data and obtain that value after annealing for 1-2 hours at 700 to 800°C.

Recovery of the minority carrier lifetime (MCL) in FZ NTD silicon requires a higher annealing temperature than that required to obtain the anticipated carrier concentration and mobility, and the recovery is also dependent on the time at temperature, furnace atmosphere, and rate of cooling.[17] Studies of the MCL in FZ NTD silicon at ORNL have led to annealing conditions, not yet optimized, that restore lifetimes in the milliseconds in lightly irradiated material. The annealing cycle is one hour at 1000°C in a gettering atmosphere, cooling at 20°C hr^{-1} to 650°C to permit vacancy stabilization, and then rapid cooling to room temperature to minimize oxygen clustering. The process has been used to increase the MCL in commercial NTD silicon and to restore the MCL in samples whose lifetimes were thermally degraded intentionally.

Figure 2 is a graph of the MCL as a function of epithermal neutron fluence for various samples of FZ NTD silicon which were irradiated in a number of different reactor locales to an epithermal neutron fluence as indicated, and after the partial but standard annealing schedule just outlined. The annealing schedule was later extended first to 7 hrs at 1000°C with some improvement in the MCL, and then to 1 hr at 1100°C with little additional improvement. Note that the recovery of the MCL is not dependent on the total fluence or t/f ratio in a manner which might have been anticipated. All of the samples had an identical annealing sequence, but the neutron fluence for sample No. 12 was ten times that for sample No. 8 and thirty times that for No. 6. The fact that the amount of recovery of the MCL in these samples was nearly identical would seem to indicate that the presence of fast neutron induced lattice damage may actually enhance the rate of lifetime recovery in FZ NTD silicon. There is also an evident difference between the neutron energy spectrum of the BSR and the NBSR reactors that was not indicated by any dosimeter data that was available to us.

(B) Annealing of Unirradiated Czochralski Silicon

Figure 3 is a graph of the interstitial oxygen concentration determined by IR spectroscopy, vs the time of annealing at different temperatures for samples from ingot 1 of Table I (not post annealed).[16] This data, taken on a coarse time grid, indicates that ∿ 100 hrs at 450°C were required to introduce ∿ 2.3 x 10^{16} donors cm^{-3} due to clustered oxygen, with no significant decrease in the O_i content. Annealing for ∿ 100 hr at 750°C, in contrast, had little if any apparent effect on the donor concentration, although a major fraction of the O_i was clustered. This data would seem to suggest that annealing for 1-2 hrs at 700-800°C, which is required to remove lattice damage in FZ NTD silicon, would not be expected to significantly alter the O_i concentration or the donor concentration due to clustered oxygen in Cz NTD silicon. However, we shall see in the next paragraph that the situation is not that simple.

Figure 4 is a graph of the donor concentration vs the time of annealing at 450°C for samples of Cz silicon from ingot 1 (not post annealed) and ingots 2, 5, and 6 (post annealed) of Table I, and this data indicates that formation of donors by oxygen should not be ignored in any isochronal or isothermal annealing studies of Cz NTD silicon that includes temperatures around 400 to 500°C, irrespective of any post annealing. Annealing for 1 hr at 450°C was sufficient to introduce ∿ 1.6 x 10^{15} donors cm^{-3} in the sample from ingot 1 (not post annealed) and ∿ 1-4 x 10^{14} donors cm^{-3} in the samples from ingots 2, 5, and 6 (post annealed). The sample from ingot 6, initially p-type, was converted to n-type after annealing for 1 hour. Another sample from ingot 1 (not post annealed) had an apparent p-type acceptor concentration of 3.4 x 10^{13} cm^{-3} after a post anneal of 1 hour at 750°C, and an apparent n-type donor concentration of 2.3 x 10^{14} cm^{-3} after 1 hour at 450°C. All of the samples used to obtain the data of Fig. 3 were reannealed for 1 hour at 900°C, and the apparent donor concentration was reduced to approximately the initial concentration listed in Table I. The subsequent rate of formation of donors as a consequence of additional annealing at 450°C was redetermined, and the final donor concentration after extended annealing was within about 10% of that indicated for all of the samples in Fig. 3.

The most significant point from these results can be summed up as follows. Previous investigators[8,9] examined Cz NTD silicon that was irradiated to introduce only 3 x 10^{14} to 2 x 10^{15} phosphorus cm^{-3} and they used both isochronal and isothermal annealing between 100 and 1000°C. They did not clearly differentiate between donors as introduced by phosphorus and those introduced by oxygen, and they concluded that some type of defect-oxygen donor complex was produced by irradiation and/or annealing that is stable up to 1000°C[8] or requires extended annealing at 950°C.[9] The present data indicates that annealing for 1 hour near 400-500°C is sufficient to introduce $\sim 10^{15}$ donors cm^{-3} in unirradiated commercial Cz silicon, irrespective of any post annealing up to at least 900°C. Clearly, the separate effect of these oxygen-induced donors must be considered in any subsequent annealing experiments that involve Cz NTD silicon.

(C) Comparison of Annealing Results for FZ and Cz NTD Samples

Figure 5 shows a graph of the calculated phosphorus concentration vs the thermal neutron fluence (solid line) and the experimental points are the measured phosphorus concentration for various samples after irradiation and annealing for 30 minutes at 750°C. This data indicates that the calculated and measured ^{31}P concentration were equal within about 5% for all concentrations in excess of about 10^{16} ^{31}P cm^{-3} for both FZ and Cz NTD silicon. The fact that the apparent donor concentration was larger in the Cz NTD silicon at lower total ^{31}P concentrations may be due to the presence of oxygen donors or defect-oxygen complexes, and will be discussed separately.

Subsequent annealing for 30 minutes at 1000°C had little if any effect on the apparent donor concentration in any of the FZ or Cz NTD silicon samples shown in Fig. 5 that contained $\geq 10^{16}$ phosphorus cm^{-3}. The Cz NTD silicon samples that had an apparent donor concentration of $\sim 5 \times 10^{15}$, 10^{16}, and 3×10^{16} cm^{-3} after irradiation and annealing at 750 and 950°C were reannealed for 100 hours at 450°C, and the apparent donor concentration increased by 1.42, 1.69, and 1.26×10^{16} cm^{-3} respectively in the three samples. The fact that one can introduce an almost equivalent concentration of donors by oxygen clustering at 450°C in Cz NTD silicon after extended irradiation, and after annealing at 750 and 950°C to remove lattice defects, shows that it is not necessary to invoke the formation of a special defect-oxygen complex that requires higher temperature annealing. Of course, such a complex may be present but its effects masked at these high donor concentrations.

(D) Comparison of Annealing Results for FZ and Cz NTD Samples after a Low (10^{16} - 10^{18} cm^{-2}) Neutron Fluence

Previous experiments[6] have indicated that most of the simple (n,γ) recoil type defects can be removed in FZ NTD silicon by annealing up to ∿ 400°C, but the data of Figs. 4 and 5 indicate that oxygen donor formation may mask any attempt to determine the annealing of radiation-induced defects in Cz NTD silicon around 400°C. Since it has already been demonstrated[6] that annealing for 1/2 hr at 750°C is sufficient to remove the radiation-induced lattice defects in FZ NTD silicon, it was decided to irradiate companion FZ and Cz samples, anneal them for 1/2 hr at 750°C, and then continue the annealing experiments at 750 and 950°C. Since the anticipated phosphorus concentration was obtained for the FZ NTD samples after the first anneal, and since extended annealing at 750 and 950°C had no apparent additional effect, that data was used to estimate the actual ^{31}P concentration in the companion Cz NTD samples.

Figure 6 is a graph of the measured donor concentration vs the time of annealing first at 750 and then at 950°C for samples from ingot 1 of Table I after irradiation, and after an initial anneal of 1/2 hr at 750°C. The anticipated ^{31}P concentrations obtained from the FZ NTD samples are as shown. This data indicates that the measured donor concentration for the Cz NTD samples was larger than anticipated at the outset, particularly for the low dose irradiations, and may have been even larger than indicated if the probable effect of a reduction in initial donor concentration due to post annealing is included. Note that the apparent donor concentration was increased by ∿ 1-3 x 10^{15} cm^{-3} in each of the six Cz NTD samples as a consequence of annealing for 14 hrs at

750°C, even though the initial lattice defect concentration was in the ratio of ~ 1 to 6,000 for these samples. It is evident that some type of donor formation due to oxygen, or to defect-oxygen complexes, can occur in Cz NTD silicon as a consequence of extended annealing at 750°C after a low total dose irradiation. Some of this enhanced donor concentration remains after additional annealing at 950°C, but the present data does not indicate any obvious correlation between the number of defects present and the potential number of defect-oxygen complexes, unless that number depends almost entirely upon the initial oxygen concentration. Almost identical data to that in Fig. 6 was obtained on samples from ingot 4 of Table I, which contained less oxygen and had been post annealed. Here the apparent donor concentration was increased by ~ 3-6 x 10^{14} cm^{-3} as a consequence of extended annealing at 750°C, irrespective of the number of defects present.

Perhaps the major point to be made from the results of these low total fluence irradiation experiments is that ~ 1-3 x 10^{15} and ~ 3-6 x 10^{14} donors cm^{-3} were introduced into Cz NTD silicon samples of high (ingot 1) or moderate (ingot 4) oxygen content by extended annealing at 750°C after irradiation. Some fraction of that additional donor concentration remained after additional annealing at 950°C, but that fraction was $\leq$ 10% of the number of donors that can be introduced by clustered oxygen in these same samples, irrespective of any defect concentration due to irradiation. There may be some type of special defect-oxygen donor complex in Cz NTD silicon that can only be removed by extended high temperature annealing, but the actual donor content is apparently not neutron fluence dependent, and the total donor contribution is minimal ($\lesssim$ 10%) compared to that which may be introduced by clustered oxygen alone.

(E) Irradiation Experiments on Heavily Doped Silicon

Potential defect-impurity interactions between an NTD epitaxial silicon layer and its substrate may be of importance in a number of applications. The published data on thermal neutron cross sections, half-lifes of radioactive decay, and transmutation end products can be used to select a preferred silicon substrate dopant. The standard n-type silicon dopants are phosphorus, arsenic, and antimony, but antimony has a large cross section and long half-life, and phosphorus has extensive autodoping tendencies during any subsequent device fabrication. The standard p-type dopants are boron, indium, or gallium, but indium is difficult to introduce during initial crystal growth, and isotopic ^{10}B fissions to introduce ^{4}He and ^{7}Li. The above would suggest n-type arsenic or p-type gallium as the preferred substrate dopant impurities.[3,4]

It was also stated that lithium can act as an electrically active donor in silicon, and can interact with other impurities or lattice defects. One can use cross section data to calculate that the rate of introduction of ^{31}P (donor) and the rate of removal of ^{10}B (acceptor) by fission should be about comparable for NTD silicon initially doped with $\sim 5 \times 10^{16}$ ^{10}B or $\sim 2.5 \times 10^{17}$ normal B cm^{-3}. A special Cz silicon single crystal ingot (No. 7 - Table I) that was doped with $\sim 5.5 \times 10^{16}$ ^{10}B cm^{-3} from a stable isotopic source in which ^{10}B was $\sim$ 94.5% abundant was provided for our experiments.[16] The initial oxygen concentration, determined by IR spectroscopy, was somewhat less than that for some of the other Cz ingots in Table I, but isothermal annealing for 100 hr at 450°C decreased the apparent p-type acceptor concentration in a sample from ingot 7 of Table I by about 7.5 x 10^{15} cm^{-3} by addition of donors due to clustering. This value is comparable to that obtained for the other Cz ingots on the basis of their relative oxygen content.

Samples of the ^{10}B-doped Cz silicon were irradiated with FZ control samples, and the results on the impurity concentrations are given in Table II. One must calculate the amount of ^{10}B removed by fission, since the total concentration is reduced by extended irradiation, but some ^{11}B remains. The ^{31}P concentration was determined after annealing the FZ NTD control samples for 1/2 hr at 750°C. The net concentration (line 5) is the anticipated value if the only change is that of addition of ^{31}P donors and removal of ^{10}B acceptors. The calculated concentration of ^{7}Li (line 6) should be identical with the calculated removal of ^{10}B (line 3), and this value was used to estimate the net concentration (line 8) if ^{7}Li is active as a donor. The measured concentration was obtained (line 9) for the Cz NTD ^{10}B silicon after annealing for 1/2 hr at 1000°C to remove lattice damage introduced by (n,γ) recoils, fast neutrons, and fission, since annealing for 1/2 hr at 750°C was not sufficient to stabilize the apparent impurity concentration in every sample.

It is evident that ^{7}Li is present as a donor in the low total dose samples in Table II that remained p-type, and in the 21-day NBSR sample that was converted to n-type. The 84-day NBSR sample required six months for radioactive decay, and a major portion of the ^{7}Li may have precipitated in that time period. An alternative explanation is that the ^{7}Li interacts with boron to form a stable donor, and the remaining boron concentration was insufficient in this sample to retain such a donor activity. Previous experiments have indicated that annealing for 1/2 hr at 750°C was sufficient for both FZ and conventionally doped Cz NTD silicon to remove the lattice damage and obtain the anticipated carrier concentration out to a total ^{31}P concentration of 10^{18} cm^{-3}. The ^{10}B-doped Cz NTD silicon was different in that annealing up to 1000°C was required to stabilize the carrier concentration in the low total dose, 7-day and 21-day NBSR samples, whereas annealing at 750°C was sufficient for several samples from the 84-day NBSR ingot section. Another major difference is that reannealing at 450°C was used to introduce additional donors due to oxygen clustering after irradiation in conventional Cz NTD silicon, but there was little if any indication of oxygen clustering in any of the ^{10}B-doped Cz NTD silicon samples as a consequence of extended annealing at 450°C after irradiation. The higher temperature annealing requirement may be due to more extensive lattice damage as a consequence of fission, and the absence of donor formation at 450°C may be due to some type of interaction between the ^{7}Li and oxygen.

Yet another experiment was carried out in which samples of high purity FZ silicon were irradiated, annealed for 1/2 hr at 750°C to remove lattice damage, and diffused with lithium from an oil bath suspension at 600°C. Figure 7 is a graph of the carrier concentration as a function of time of accelerated annealing at 400°K. This data indicates that there is no evident interaction between the lithium and ^{31}P in NTD silicon, and that the lithium precipitates to a final solubility that may depend on the actual oxygen concentration in FZ NTD silicon.

DISCUSSION

The primary result of these various experiments is that a better understanding of the annealing requirements to remove lattice damage and observe the anticipated ^{31}P concentration in FZ and Cz NTD silicon has been obtained. It has been demonstrated that annealing for 1/2 hour at 750°C is sufficient to obtain the anticipated resistivity, carrier concentration, and carrier mobility in both FZ and Cz NTD silicon irradiated in a low t/f ratio to introduce $\sim 10^{16}$ to 10^{18} ^{31}P cm^{-3}, but the annealing requirements to recover the anticipated MCL are still under investigation. The electrical role of clustered oxygen and of any defect-oxygen complex in Cz NTD silicon was investigated, but any separate effects between these two types of potential donor sources were not clearly identified. It has also been shown that one can produce an NTD epitaxial layer on a heavily doped n- or p-type substrate, but careful choice of substrate dopant is recommended. The use of boron will result in the introduction of ^{7}Li that may migrate and alter the desired dopant concentration in the epitaxial layer. There is no evident interaction between lithium introduced by diffusion and ^{31}P introduced by irradiation, but there may be some type of pairing reaction between ^{7}Li introduced by ^{10}B fission and any remaining boron, since samples that contain an equivalent concentration require a higher annealing temperature than those in which most of the ^{10}B was removed by fission. The ability to add a known concentration of ^{7}Li in silicon by the technique of ^{10}B fission should lead to a better understanding of the interaction between lithium and oxygen in silicon, if FZ ^{10}B-doped samples of low or controlled oxygen content can be made available.

ACKNOWLEDGMENTS

The authors wish to thank L. E. Katz of the Bell Telephone Laboratories, Allentown, PA, for providing both the heavily oxygen-doped and ^{10}B-doped ingots.

Table I

Ingot Number	Ingot Type	Dopant	Growth Technique	Post Anneal	Resistivity (ohm cm)	Carrier Concentration (cm^{-3})	Oxygen Content (cm^{-3})
1	-	-	Cz	No	50	2.5×10^{14}	2.4×10^{18}
2	n	P	Cz	Yes	30	3.0×10^{14}	1.3×10^{18}
3	n	P	Cz	Yes	194	1.8×10^{13}	1.7×10^{18}
4	n	P	Cz	Yes	41	8.3×10^{13}	8.5×10^{17}
5	n	P	Cz	Yes	149	2.5×10^{13}	7.5×10^{17}
6	p	B	Cz	Yes	50	3.5×10^{14}	1.3×10^{18}
7	p	^{10}B	Cz	No	0.42	5.5×10^{16}	8.0×10^{17}
8	n	P	FZ	No	1000^{+}	$1\text{-}5\times10^{12}$	$\leq3.0\times10^{16}$

Table II

Reactor	BSR	BSR	NBSR	NBSR	NBSR
Irradiation (days)	20	40	7	21	84
Calc. ^{10}B Removed	0.34	0.52	1.05	2.57	4.74
Total B Remaining	5.16	4.98	4.45	2.93	0.76
Measured ^{31}P Added	-0.34	-0.52	-1.21	-3.66	14.00
Net Concentration	4.82	4.46	3.24	-0.73	-13.24
Calculated ^{7}Li Added	-0.34	-0.52	-1.05	-2.57	-4.74
Net Concentration	4.48	3.94	2.19	-3.30	-17.98
Measured Concentration	4.18	3.14	1.57	-2.35	-14.40

All data are in units of 10^{16} cm^{-3}

Minus sign indicates n-type donor concentration

REFERENCES

1. J. W. Cleland, K. Lark-Horovitz, and J. C. Pigg, Phys. Rev. 78, 814 (1950).
2. *Third International Symposium on Silicon Materials Science and Technology: Semiconductor Silicon/1977:* PV 77-2: Electrochemical Society, 1977: IEEE Trans. Electron Devices, Vol. ED-23, No. 8, 1976: (Special Issue on High Power Semiconductor Devices).
3. S. Prussin and J. W. Cleland, J. Electrochem. Soc. 125, No. 2, 350 (1978).
4. C. W. Pearce, Western Electric Co., Allentown, PA: private communication.
5. R. F. Wood, R. D. Westbrook, R. T. Young and J. W. Cleland, p. 109 in *Proceedings of the Solar Cell High Efficiency and Radiation Damage Conference,* NASA Conference Publication 2020.
6. R. T. Young, J. W. Cleland, R. F. Wood and M. M. Abraham, J. Appl. Phys. 49, 4752 (1978).
7. L. E. Katz and D. W. Hill, J. Electrochem. Soc. 125, No. 7, 1151 (1978): G. A. Rozgonyi and C. W. Pearce, Appl. Phys. Letters 32 (11), 1 June 1978.
8. V. N. Mordkovich, S. P. Solov'ev, E. M. Temper and V. A. Kharchenko, Sov. Phys. Semicond. 8, No. 1, July, 1974.
9. H. M. Liaw and C. J. Varker, Semiconductor Silicon/1977: PV 77-2: Electrochemical Society, 1977, p. 116.
10. E. M. Pell, *Solid State Physics in Electronics and Communication* (Academic Press, Inc., New York, 1960), Vol. 1, p. 261.

11. C. S. Fuller, J. Phys. Chem. Solids 19, 18 (1961).

12. J. W. Cleland, F. J. James and R. D. Westbrook, IEEE Trans. Nucl. Sci. NS-19, No. 6, 224 (1972).

13. V. S. Vavilov, I. V. Smirnova, and V. A. Chapnin, Sov. Phys. Solid State 4, 830 (1962).

14. G. J. Bruckner, Phys. Rev. 183, 712 (1969).

15. L. C. Kimerling, P. J. Drevinsky, and C. S. Chen, *Defects in Semiconductors* (Reading, Enlland, 1972), Conf. Series No. 16, p. 182.

16. We are indebted to L. E. Katz, Bell Telephone Laboratories, Allentown, PA, for the careful preparation of Ingots 1 and 7.

17. R. D. Westbrook and J. W. Cleland, Extended Abstracts, J. Electrochem. Soc. 125 (No. 3) 144 C (1978).

TABLE CAPTIONS

Table I. Ingot characteristics of silicon samples studied

Table II. Transmutation reactions in isotopic ^{10}boron-doped silicon

FIGURE CAPTIONS

Fig. 1. Thermal neutron facility (D_2O tank) of the Bulk Shielding Reactor.

Fig. 2. Minority carrier lifetime vs epithermal neutron fluence for selected FZ NTD silicon samples after irradiation and partial annealing.

Fig. 3. Interstitial oxygen concentration vs time of annealing at indicated temperatures for samples from ingot 1 of Table I and the donor or acceptor concentration after annealing.

Fig. 4. Carrier concentration vs time of annealing for samples from ingots 1, 2, 5, and 6 of Table I.

Fig. 5. Calculated and measured phosphorus concentration vs thermal neutron fluence for selected samples of FZ and Cz NTD silicon after irradiation and annealing.

Fig. 6. Carrier concentration vs time of annealing at 750 and 950°C for Cz NTD silicon samples. The anticipated ^{31}P concentration obtained from companion FZ NTD silicon samples are also indicated.

Fig. 7. Carrier concentration vs time of annealing after lithium diffusion in FZ NTD silicon samples and a FZ silicon control sample.

ORNL-DWG 77-12846

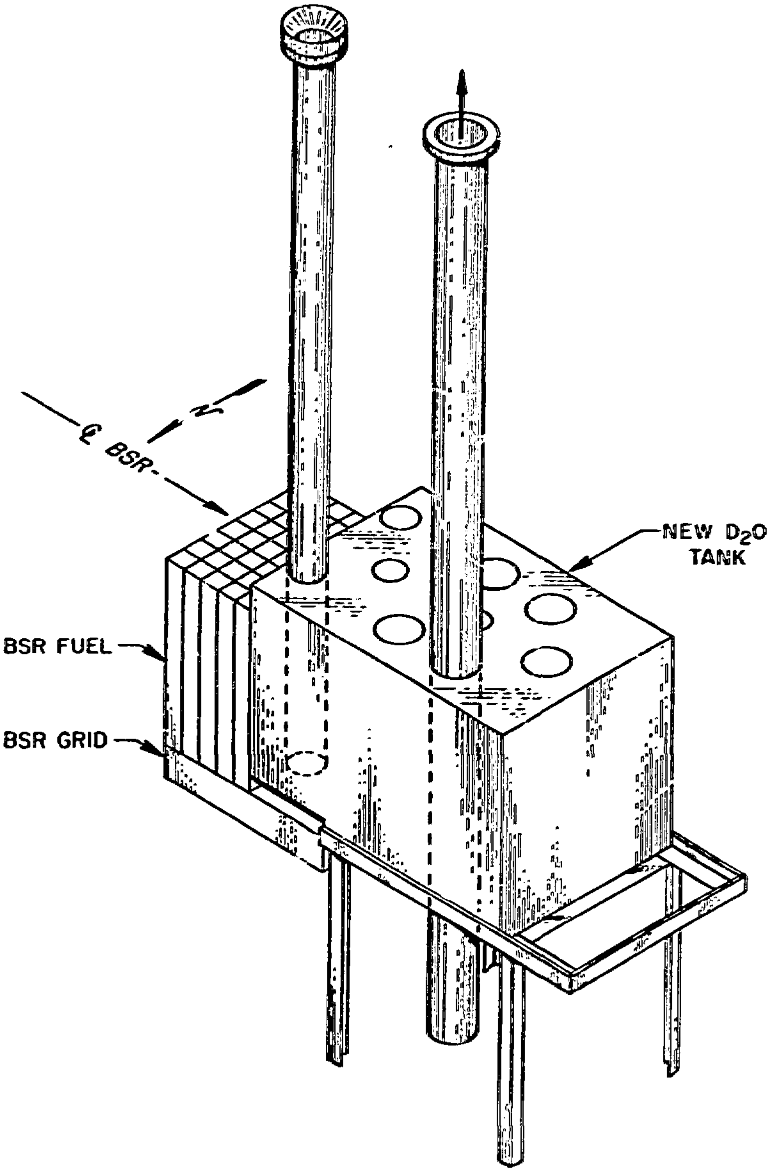

Fig. 1

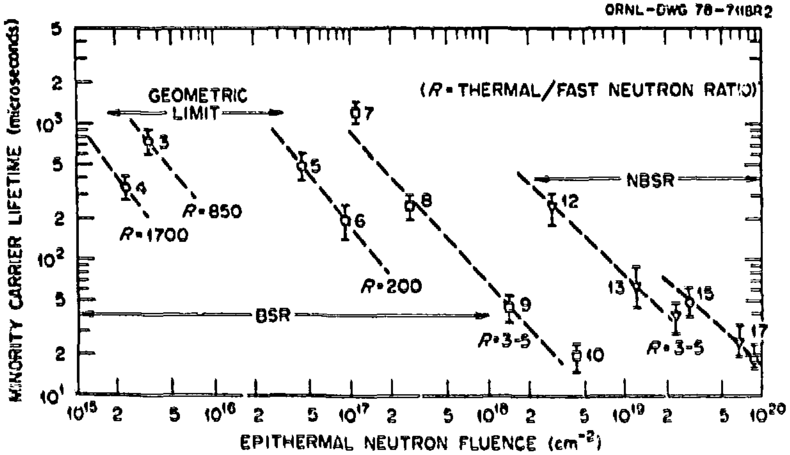
ORNL-DWG 78-7118R2
MINORITY CARRIER LIFETIME (microseconds)
EPITHERMAL NEUTRON FLUENCE (cm^{-2})
(R = THERMAL/FAST NEUTRON RATIO)
GEOMETRIC LIMIT
NBSR
BSR
R=1700
R=850
R=200
R=3-5
R=3-5
3
4
5
6
7
8
9
10
12
13
15
17
5
2
10^3
5
2
10^2
5
2
10^1
10^{15}
2
5
10^{16}
2
5
10^{17}
2
5
10^{18}
2
5
10^{19}
2
5
10^{20}

Fig. 2

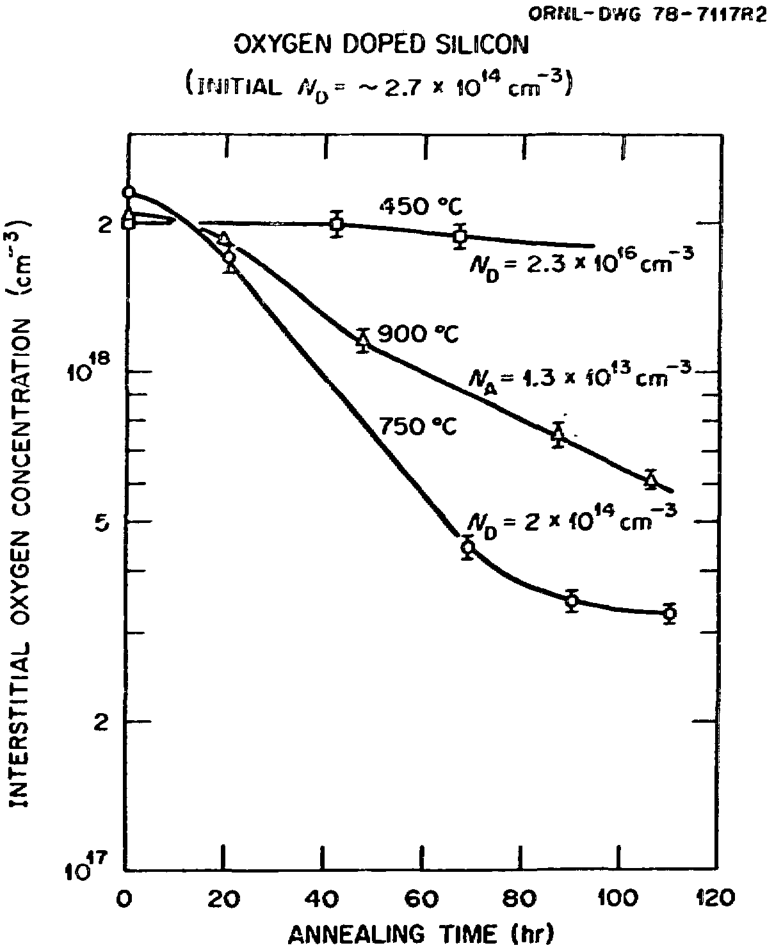
ORNL-DWG 78-7117R2
OXYGEN DOPED SILICON
(INITIAL N_D = ~2.7 × 10^{14} cm^{-3})
450 °C
N_D = 2.3 × 10^{16} cm^{-3}
900 °C
N_A = 1.3 × 10^{13} cm^{-3}
750 °C
N_D = 2 × 10^{14} cm^{-3}
INTERSTITIAL OXYGEN CONCENTRATION (cm^{-3})
10^{17}
2
5
10^{18}
2
0
20
40
60
80
100
120
ANNEALING TIME (hr)

Fig. 3

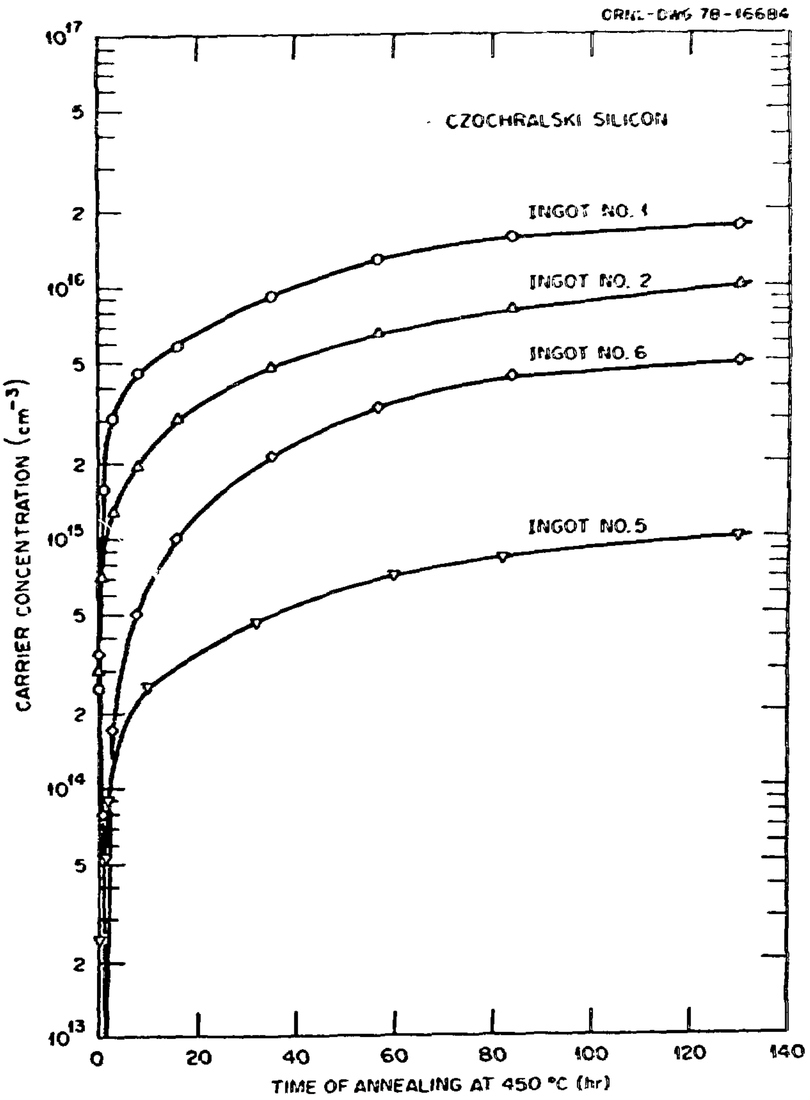
ORNL-DWG 78-16684
CZOCHRALSKI SILICON
INGOT NO. 1
INGOT NO. 2
INGOT NO. 6
INGOT NO. 5
CARRIER CONCENTRATION (cm^{-3})
10^{17}
5
2
10^{16}
5
2
10^{15}
5
2
10^{14}
5
2
10^{13}
0
20
40
60
80
100
120
140
TIME OF ANNEALING AT 450 °C (hr)

Fig. 4

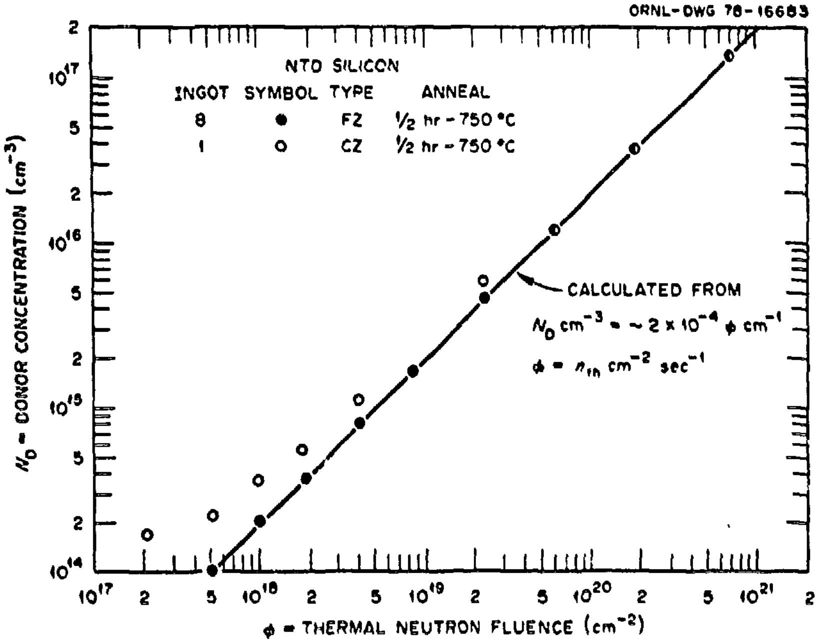
ORNL-DWG 78-16683
NTD SILICON
INGOT SYMBOL TYPE ANNEAL
8 ● FZ ½ hr - 750 °C
1 ○ CZ ½ hr - 750 °C
CALCULATED FROM
N_D cm^{-3} = ~2 × 10^{-4} ϕ cm^{-1}
ϕ = n_{th} cm^{-2} sec^{-1}
N_D = DONOR CONCENTRATION (cm^{-3})
ϕ = THERMAL NEUTRON FLUENCE (cm^{-2})
10^{14}
2
5
10^{15}
2
5
10^{16}
2
5
10^{17}
2
10^{17}
2
5
10^{18}
2
5
10^{19}
2
5
10^{20}
2
5
10^{21}
2

Fig. 5

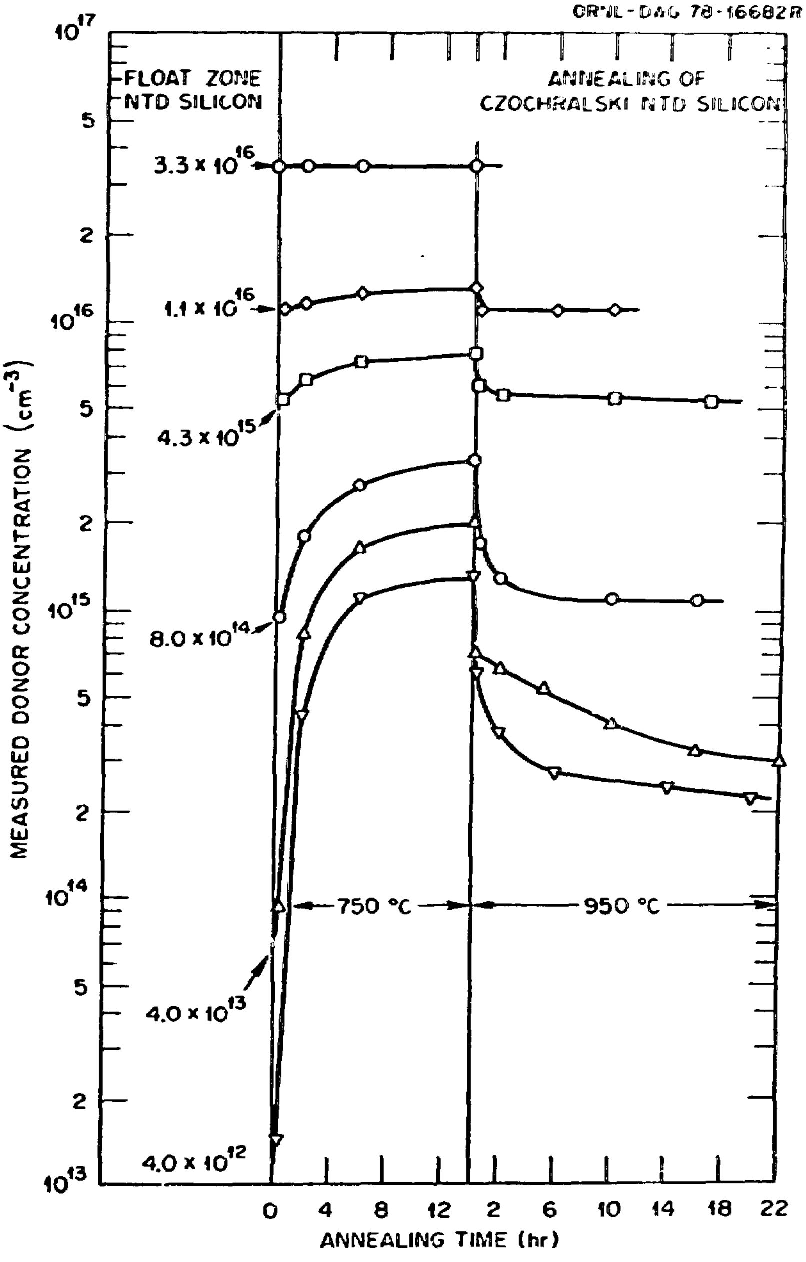
ORNL-DWG 78-16682R
FLOAT ZONE NTD SILICON
ANNEALING OF CZOCHRALSKI NTD SILICON
3.3 x 10^16
1.1 x 10^16
4.3 x 10^15
8.0 x 10^14
4.0 x 10^13
4.0 x 10^12
750 °C
950 °C
10^17
5
2
10^16
5
2
10^15
5
2
10^14
5
2
10^13
MEASURED DONOR CONCENTRATION (cm^-3)
0
4
8
12
2
6
10
14
18
22
ANNEALING TIME (hr)

Fig. 6

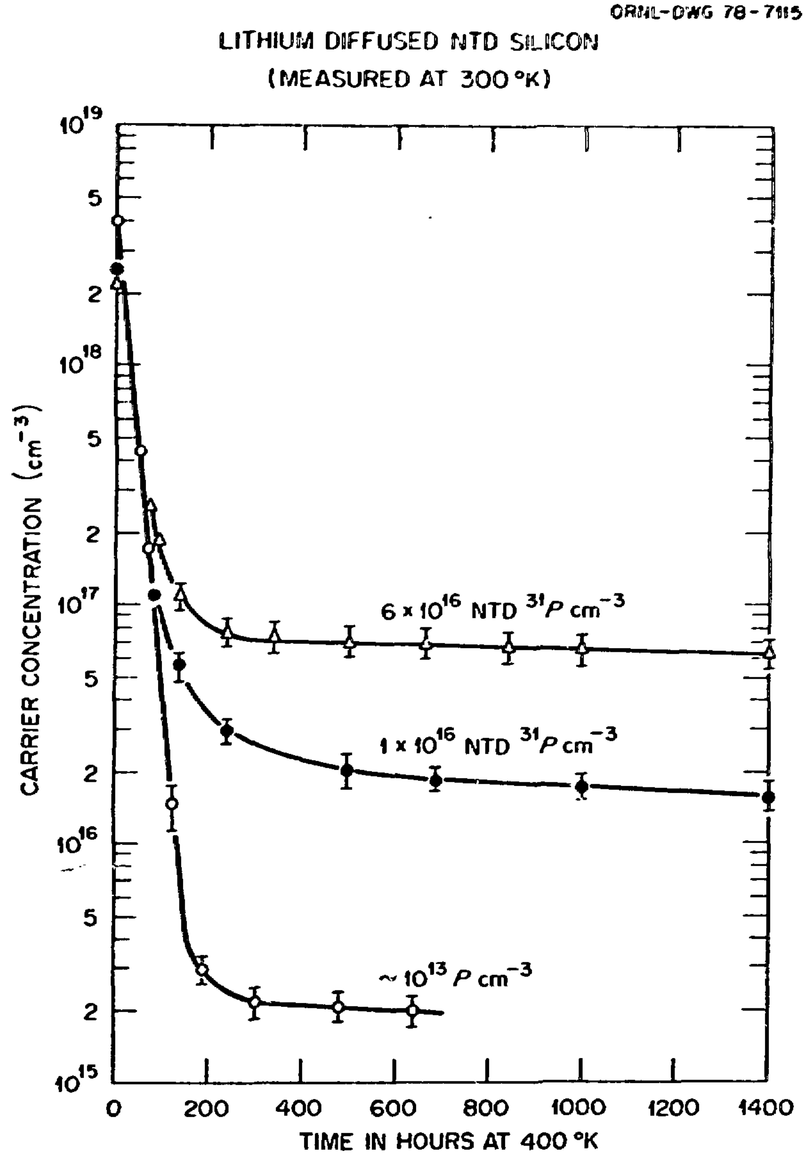
ORNL-DWG 78-7115
LITHIUM DIFFUSED NTD SILICON
(MEASURED AT 300 °K)
CARRIER CONCENTRATION (cm^{-3})
10^{19}
5
2
10^{18}
5
2
10^{17}
5
2
10^{16}
5
2
10^{15}
6×10^{16} NTD ^{31}P cm^{-3}
1×10^{16} NTD ^{31}P cm^{-3}
$\sim 10^{13}$ P cm^{-3}
0
200
400
600
800
1000
1200
1400
TIME IN HOURS AT 400 °K

Fig. 7