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ELECTRICAL PROPERTY STUDIES OF OXYGEN IN CZOCHRALSKI-GROWN NEUTRON-TRANSMUTATION-DOPED SILICON*

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ABSTRACT

Electrically active oxygen-related donors can be formed in Czochralski (Cz) Si either during crystal growth or during subsequent heat treatment; conventional n- or p-type dopant carrier concentrations are altered if these oxygen donors are present. Neutron transmutation doping (NTD) has been used to introduce a uniform concentration of ^{31}P in Si. However, oxygen donors can also be formed in NTD Cz Si during the process of annealing to remove NTD radiation damage. In the present experiments, the carrier concentration of Cz and NTD Cz Si samples was determined as a function of the initial dopant, oxygen, and ^{31}P concentration before and after isothermal or isochronal annealing. It is shown that low temperature (350-500°C) heat treatment can introduce a significant oxygen donor concentration in Cz Si and in NTD Cz Si that contains radiation-induced lattice defects. Intermediate temperature (550-750°C) heat treatment, which is intended to remove oxygen donors or lattice defects, can introduce other oxygen donors; annealing above 750°C is required to remove any of these oxygen donors. Extended (20 h) high-temperature (1000-1200°C) annealing can remove oxygen donors and lattice defects, but a significant concentration of oxygen donors can still be introduced by subsequent low temperature heat treatment. These results suggest that oxygen-related donor formation in NTD Cz Si at temperatures below 750°C may serve to mask any annealing study of lattice

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defects. It is concluded that annealing for 30 min at 750°C is sufficient to remove radiation damage in NTD Cz Si when the separate effects of oxygen donor formation are included.

INTRODUCTION

Neutron transmutation doping (NTD) has been used to introduce a precisely controlled and very uniform distribution of ^{31}P in Si.[1] In order to remove lattice damage introduced by recoiling atoms in the (n,γ) process and by fast neutron collisions with Si atoms it is necessary to anneal the Si after irradiation before the desired electrical properties of the P can be realized. The lattice damage associated with NTD Si is very complex. This damage consists of simple point defects, interstitial and vacancy complexes, larger defect clusters, and dislocation loops. The relative concentration of these defects depends on the irradiation temperature, the neutron energy spectrum and the neutron fluence. Annealing may result in the removal of some defects but also in the formation of other defect or defect-impurity complexes.

Electrical property studies have been used[2] to establish the annealing requirements necessary to obtain the anticipated carrier concentration and mobility for NTD float zone (FZ) single crystal Si of low ($\leq 3 \times 10^{16}$ cm^{-3}) oxygen content. Most of the simple recoil-induced defects were removed by annealing at 400°C. Annealing for 30 min at 750°C was sufficient to obtain the anticipated carrier concentration and mobility in NTD FZ Si irradiated up to a total fluence of $\geq 10^{20}$ n cm^{-2} in different reactor locales with thermal-to-fast ($t/\bar{f}$) neutron ratios from 1700 (low fluence) to 3 (high fluence). However, the minority carrier lifetime (MCL) was still degraded after annealing at 750°C, irrespective of neutron fluence or t/f ratio.[3] Recovery of the MCL required annealing at 1000°C; the extent of recovery was dependent on the irradiation temperature, neutron fluence, t/f ratio, time of annealing, and rate of cooling after annealing.

Infrared absorption (IR), x-ray diffuse scattering, and transmission electron microscopy (TEM) measurements have also indicated[4] that lattice defect complexes are introduced in NTD FZ Si as a consequence of irradiation or annealing. Dislocation loops of 50-100 Å diameter with a number density of 10^{14} cm^{-3} remained in NTD FZ Si irradiated with a fast ($\geq$ 1 MeV) neutron fluence of 10^{20} n cm^{-2} and annealed at 900°C; it was suggested that these loops may play a role in the trapping of minority carriers.[3]

The characterization of lattice damage introduced by neutron irradiation of Czochralski (Cz)-grown Si is more complex because Cz Si usually contains $\geq 5 \times 10^{17}$ oxygen cm^{-3}, and O or certain defect-O complexes may act as electrically active donors. The initial O concentration in Cz Si is a complex function of crystal growth

conditions; in addition, the O content at the center of a 5 cm diameter ingot is usually larger by a factor of two or more than that near the edge. Oxygen donors are formed during cooldown after crystal growth; commercially available Cz Si ingots are usually post-annealed to reduce that O donor contribution. Capper and Wilkes[5] have described an empirical procedure used by certain Cz Si producers as consisting of post-annealing for 3 h at 650°C in N_2, followed by cooling under natural or forced convection. They examined 5 cm diameter dislocation-free Cz Si ingots and concluded that such annealing was not sufficient for close tolerance specifications, to the extent that reheating of ingot slices was necessary in order to further reduce the O donor concentration.

Kaiser[6] and Fuller[7] have suggested that O donors (possibly associated with vacancies) migrate when Si is heated at 350 to 500°C and that four O combine as SiO_4 to form a single donor. They did not observe any special interaction between O and n-type donor impurities as a consequence of heating doped samples, but they observed that O and p-type acceptor impurities also combined to form a product with donor-like properties. Kaiser[6] reported that the initial rate of O donor formation on heating was proportional to the fourth power of the O concentration and that the maximum donor concentration on extended annealing was proportional to the third power of the O concentration. The rate of donor formation was also a function of the annealing temperature and the time required to attain the maximum donor concentration decreased for material with an increased O concentration. Fuller[7] reported that a maximum donor concentration was observed after annealing for 70 h at 450°C and Kanamori[8] reported that a maximum donor concentration was observed after annealing for 64 h at 475°C. Both authors reported that these maxima were followed by a decrease in donor concentration with continued annealing at these temperatures.

Helmreich and Sirtl[9] have suggested that formation of SiO_4 is not required for thermal donor (TD) generation in Cz Si. They postulated that interaction between interstitial oxygen (O_i) and vacancies will result in the production of TD's if a single O_i becomes a substitutional O_s. They stated that such donors were stabilized against annealing by acceptor impurities. A rapid breakdown of TD complexes in favor of O_i reformation was observed in undoped Cz Si on annealing above 515°C, but some TD's remained in Cz Si that was doped with elements of a strong acceptor character even after annealing above 800°C. Kaiser[6] reported that those donors formed by SiO_4 or by O associated with B or Ga acceptors disappeared with first-order kinetics on annealing above 500°C, but that O-Al donor-like complexes required annealing at 1000°C.

Kanamori,[8] in contrast, has suggested that dislocations or an unknown impurity species X are required in Cz Si to remove a majority

of the O donors at higher annealing temperatures after initial donor formation by extended annealing at 475°C. The ratio of remaining to initial donor concentration was as large as 0.5-0.7 in most of his samples of zero dislocation content n- or p-type Cz Si after initial donor formation at 475°C and reannealing for 20 h at 500°C. His experimental results were not adequate to determine the unknown species X in those samples of low ratio values, but he stated that the annealing behavior in those samples was similar to that reported by Fuller and Logan for Li-doped Cz Si.[10]

Kaiser[6] reported that heating Cz Si for 20 h at 1100°C was sufficient to "stabilize" the O such that no donors were introduced by subsequent annealing at 450°C. Baker[11] stated that heating Cz Si for 20 h at 1000°C was sufficient in that no resistivity change due to donor formation occurred with subsequent annealing at 450°C, even in Cz Si with a large O concentration. de Kock,[12] in contrast, observed that excess O was removed from solid solution by precipitation in Cz Si during high temperature (1000-1200°C) processing, but that some O remained in solution in dislocation-free Cz Si after such heat treatments, even at an O supersaturation ratio of 5. Previous results [6,7,11] have all indicated that a short (30 min) heat treatment at about 1350°C was sufficient to remove all of the O clusters or precipitates and restore most of the O to its normal position in the Cz Si lattice. Of course any subsequent low temperature (350-500°C) heat treatment may then introduce new O donors.[5-12]

Previous investigators[13-15] have reported that O-defect complexes that act as donors are also formed in NTD Cz Si by irradiation or by subsequent annealing to remove lattice damage, and that such donor complexes are stable against annealing up to 850°C,[13] 950°C[14], or 1000°C.[15] More recent experiments[16] indicated that annealing for 30 min at 750°C was sufficient to obtain the anticipated carrier concentration and mobility in either NTD FZ or Cz Si irradiated to introduce $\geq 10^{16}$ ^{31}P cm^{-3}, independent of initial O content or t/f neutron ratio. Any separate effect due to any O-defect complex was not identified in NTD Cz Si at those dopant concentrations.

This paper will discuss the results of annealing experiments using Cz Si samples of different initial dopant and O concentrations prior to irradiation as well as the results of annealing experiments using NTD Cz Si samples. Two reactor locales with different t/f ratios were used.[16] The thermal and fast ($\geq$ 1 MeV) neutron fluxes, as determined by dosimeters, were used to calculate the anticipated ratio of simple (n,γ) recoil events to fast neutron induced events, as previously indicated,[2] and to calculate the anticipated concentration of P introduced by transmutations. We determined the initial O_i content by conventional IR techniques. Carrier concentration and mobility values were obtained for thin 1 cm^2 van der Pauw (vdP) samples. Annealing was carried out in a quartz tube furnace in an

inert atmosphere; the samples were quickly removed and air-cooled on a quartz plate.

EXPERIMENTAL RESULTS

(A) Annealing of Unirradiated Czochralski Silicon

Table 1 lists the initial donor (n) or acceptor (p) concentration, initial interstitial oxygen (O_i) concentration, initial rate of O donor formation on annealing at 450°C, and the maximum carrier concentration observed after extended (120-150 h) annealing at 450°C for samples from ten Cz Si ingots.[17]

Table 1. Ingot Characteristics of Silicon Samples Investigated

Ingot	Initial Donor (n) or Acceptor (p) Concentration (cm^{-3})	Interstitial Oxygen (O_i) Concentration (cm^{-3})	Rate of Donor Formation at 450°C (cm^{-3} hr^{-1})	Carrier Concentration after 120-150 hr at 450°C (cm^{-3})
A-1	5.0×10^{13}-n-	6.1×10^{17}	4.0×10^{13}	2.0×10^{15}-n-
A-3	2.0×10^{13}-n-	7.5×10^{17}	1.1×10^{14}	5.5×10^{15}-n-
A-4	1.0×10^{14}-n-	2.0×10^{18}	3.4×10^{14}	1.6×10^{16}-n-
B-1	2.5×10^{14}-n-	2.4×10^{18}	1.6×10^{15}	2.0×10^{16}-n-
M-85	9.0×10^{13}-n-	8.9×10^{17}	4.0×10^{14}	8.5×10^{15}-n-
M-86	9.5×10^{13}-n-	8.5×10^{17}	4.3×10^{14}	1.3×10^{16}-n-
M-65	3.1×10^{14}-n-	1.8×10^{18}	4.0×10^{14}	9.9×10^{15}-n-
M-73	3.5×10^{14}-n-	1.3×10^{18}	2.7×10^{14}	5.0×10^{15}-n-
W-1	1.0×10^{14}-p-	10^{18}	2.0×10^{14}	3.6×10^{15}-n-
10_B	5.6×10^{16}-p-	8.0×10^{17}	2.0×10^{15}	5.0×10^{16}-p-

Figure 1 is a graph of carrier concentration vs time of annealing at 450°C for samples from some of the ingots listed in Table 1. It is stated above that the initial O concentration in Cz Si is a complex function of different crystal growth conditions and that the O content may vary by a factor of two or more acoss a 5 cm diameter ingot slice. In the present experiments, the IR or vdP samples were not always taken from the same slice or slice locale. There was considerable variation in the initial rate of donor formation, and in the donor concentration after extended annealing for different samples from the same ingot or ingot slice, but the data of Table 1, plotted in Fig. 1, indicate that both the initial rate of donor formation and the donor concentration after extended annealing were dependent on the initial O_i concentration. Note that the apparent donor concentration after extended annealing at 450°C was almost always $\leq$ 1% of the initial O_i concentration.

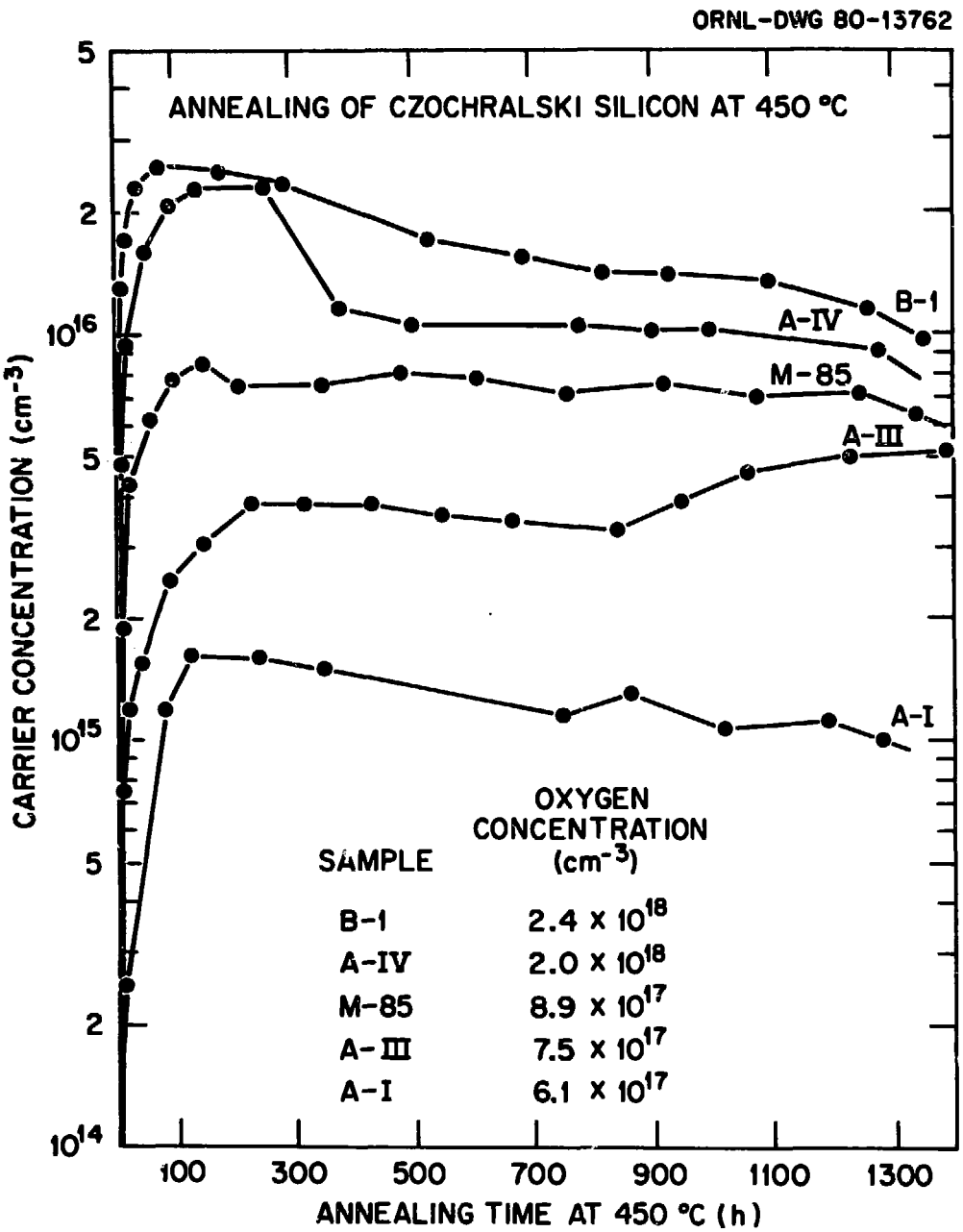
ORNL-DWG 80-13762
ANNEALING OF CZOCHRALSKI SILICON AT 450 °C
CARRIER CONCENTRATION (cm⁻³)
ANNEALING TIME AT 450 °C (h)
B-1
A-IV
M-85
A-III
A-I
SAMPLE
OXYGEN CONCENTRATION (cm⁻³)
B-1 2.4 x 10¹⁸
A-IV 2.0 x 10¹⁸
M-85 8.9 x 10¹⁷
A-III 7.5 x 10¹⁷
A-I 6.1 x 10¹⁷

Fig. 1

Ingot B-1 was not post annealed after growth and the initial donor concentration in samples from that ingot was changed to a low apparent accceptor concentration by 30 min annealing at 750°C and rapid cooling. Ingots M-65 and M-73 were doped with P or B, respectively, and no additional O-dopant interaction was evident as a consequence of extended annealing in these samples at these low dopant concentrations. Ingot ^{10}B was doped with a stable isotope of B enriched to 94.5% abundance. The initial O_i concentration was somewhat less than that for the other ingots but the initial rate of donor formation was somewhat larger. Extended annealing reduced the apparent p-type acceptor concentration due to O-donor formation and the total change in concentration was larger than that observed in the high purity n-type A-1 and A-3 samples that contained more O_i initially. These data may indicate an enhanced O-acceptor interaction that forms additional donors in p-type Cz Si on low temperature (350-500°C) heat treatment, as has also been reported by others.[6,7,9]

Fuller[7] and Kanamori[8] reported a maximum O-donor concentration after annealing Cz Si at 450 or 475°C for about 70 h. The data shown in Fig. 1 indicates that the time required to reach a maximum carrier concentration was not a very sensitive function of the initial O_i concentration and the carrier concentration decreased on extended (150-1300 h) annealing for some of the samples investigated. Samples B-1 and A-IV of Fig. 1 were reannealed for 30 min at 750°C in order to remove most of the O donors and were then reannealed at 450°C. Both the initial rate of O-donor formation and the maximum carrier concentration attained were reduced by about a factor of two by this treatment; the carrier concentration again decreased on extended annealing. Other samples were selected from the center or near the edge of ingot slices, and from different sections of the various ingots. No effect of radial or axial position was observed upon extended annealing at 450°C, other than that attributed to the initial O_i concentration. The data shown in Fig. 1 and that obtained on the other samples do indicate that several competing processes may occur under extended annealing conditions, but that the initial O_i concentration is the primary factor governing O-donor formation in Cz Si via low-temperature annealing.

Previous investigators[6,7,9] have indicated that O donors are introduced in Cz Si by annealing at 350-500°C, but not at higher temperatures. We selected additional samples representative of Cz Si of high, medium, and low initial O_i content from among the ingots listed in Table 1. Figure 2 is a graph of carrier concentration vs extended annealing time at 550°C, followed by 450°C. These data indicate that significant O-donor formation occurs on annealing at 550°C in these samples, irrespective of initial O_i content. The carrier concentration did not decrease on extended annealing at 550°C and no evidence was obtained for additional O-donor formation at 450°C after a near saturation concentration of O donors was

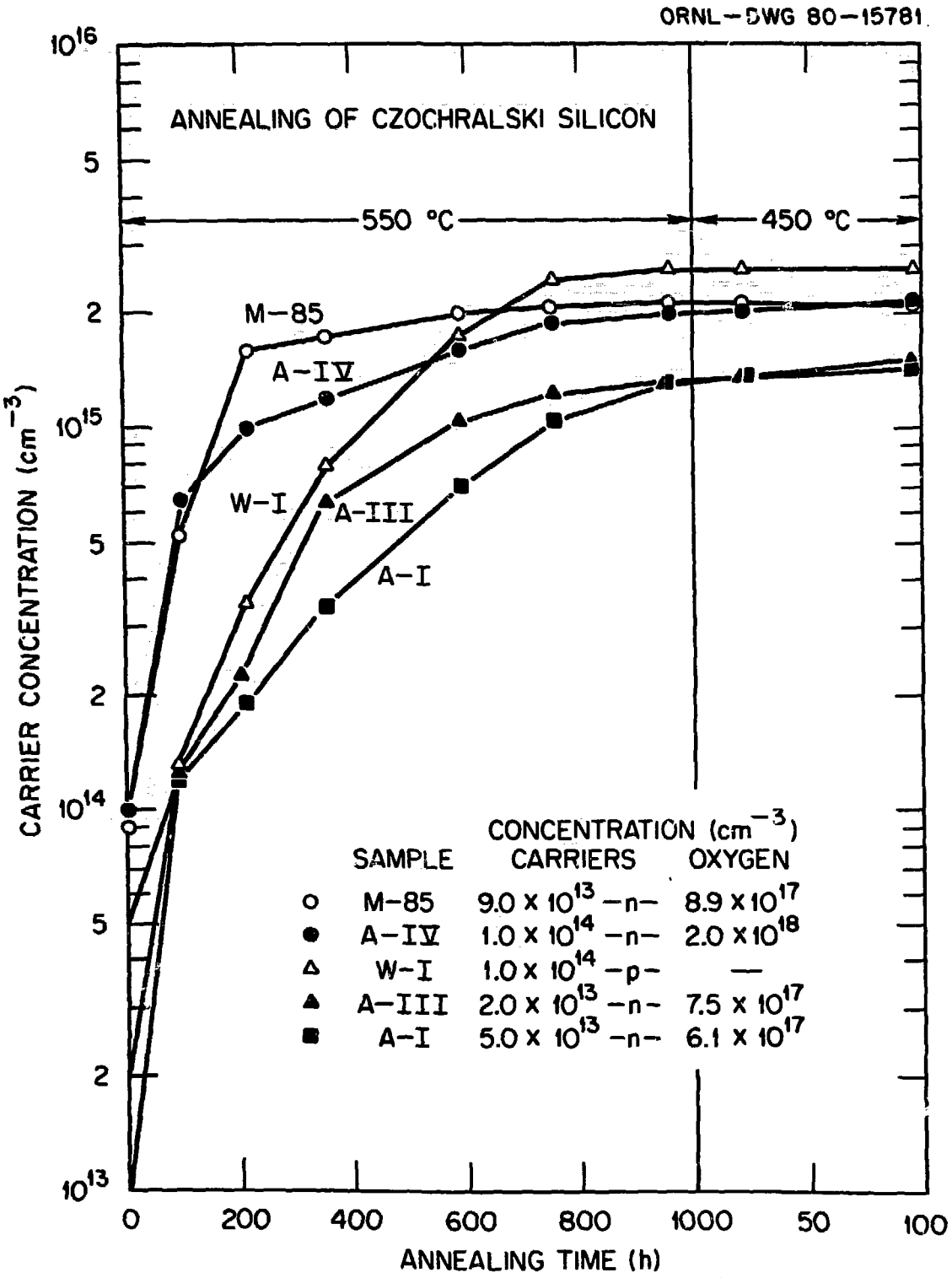
ORNL-DWG 80-15781
ANNEALING OF CZOCHRALSKI SILICON
550 °C
450 °C
M-85
A-IV
W-I
A-III
A-I
CARRIER CONCENTRATION (cm^{-3})
ANNEALING TIME (h)
CONCENTRATION (cm^{-3})
SAMPLE
CARRIERS
OXYGEN
M-85 9.0 x 10^{13} -n- 8.9 x 10^{17}
A-IV 1.0 x 10^{14} -n- 2.0 x 10^{18}
W-I 1.0 x 10^{14} -p- —
A-III 2.0 x 10^{13} -n- 7.5 x 10^{17}
A-I 5.0 x 10^{13} -n- 6.1 x 10^{17}

Fig. 2

introduced at 550°C. Other samples of Cz Si of high, medium, and low initial O_i content were selected for extended annealing at five different temperatures. Figure 3 is a graph of the resulting carrier concentrations vs time. These data indicate that significant concentrations of O donors were introduced on extended annealing at either 550 or 650°C, and that some O-donor formation still occurs at 750°C (possibly even 850°C). Note that the apparent rate of donor formation increases with an increase in anneal-temperature from 550 to 750°C in these samples.

Kaiser[6] and Fuller[7] have indicated that annealing above 500°C is sufficient to remove O donors in Cz Si unless they are associated with impurities of a strong acceptor character and Kanamori[8] has indicated that annealing above 550°C is required for total O donor removal unless dislocations or an unknown impurity are present. Accordingly, samples from five of the ingots listed in Table 1 were heat treated at 450°C to introduce a large O-donor concentration and were then reannealed at 550°C as shown in Fig. 4. The maximum O-donor concentration was initially reduced by more than 90% in each sample, after about 25 to 50 h at 550°C; however, formation of other O donors then occurred on extended annealing at 550°C. Note that the saturation concentration of O donors after extended annealing is comparable to that shown for the samples in Fig. 3, which did not contain O donors initially. Similar data was obtained for other samples, after an initial heat treatment at 450°C to introduce a large O-donor concentration, followed by extended reannealing at 650°C. The results were almost identical to those shown in Figs. 3 and 4, as regards the saturation concentration of O donors, but the time required for removal of the initial O donors and for formation of the new O donors decreased for the samples reannealed at 650°C.

Since more than 90% of the O donors introduced at 450°C were removed by annealing at higher temperatures, before new O donors were formed, it was decided to examine the higher temperature stability of O donors that were initially introduced in Cz Si by extended annealing at 550°C or higher. Figure 5 shows the carrier concentration vs annealing time for samples of high, medium, and low initial O_i concentration, after 300 h at 550°C, and after reannealing for 20 h at 100°C temperature intervals from 650 to 1150°C. There is little, if any, evidence for removal of O donors formed at 550°C below a reannealing temperature of 750°C; extended (20 h) reannealing above 850°C is required to remove most of the O donors. Very similar results to those shown in Fig. 5 were obtained for O donors that were formed in similar samples after extended annealing at 650°C. These data indicate that (1) a significant concentration of O donors can be formed in Cz Si on annealing at 550°C or higher; (2) the maximum O-donor concentration is almost independent of the initial O_i concentration; and that extended high temperature annealing is required to remove these O donors.

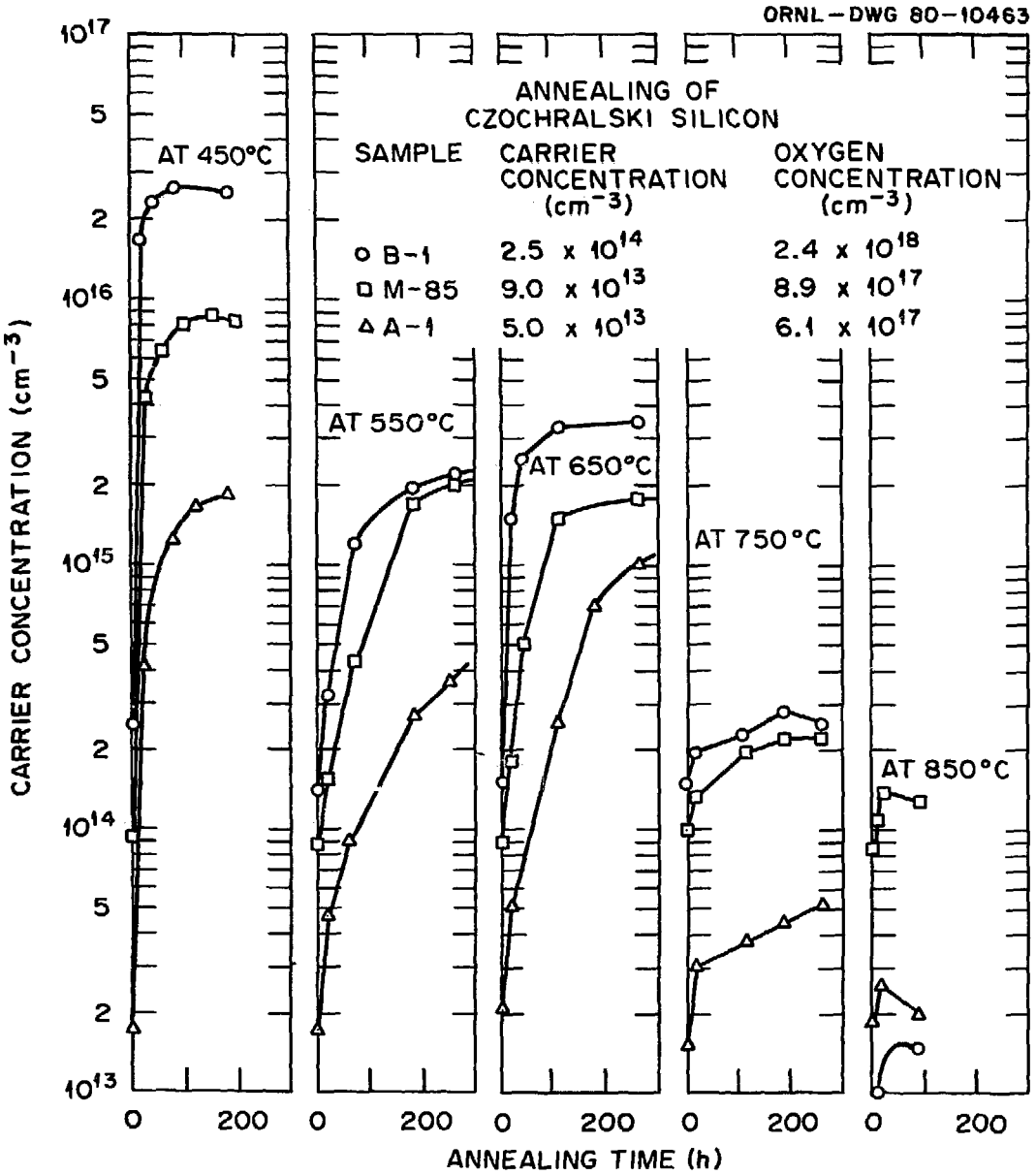
ORNL-DWG 80-10463
ANNEALING OF
CZOCHRALSKI SILICON
SAMPLE
CARRIER CONCENTRATION (cm⁻³)
OXYGEN CONCENTRATION (cm⁻³)
○ B-1
2.5 x 10¹⁴
2.4 x 10¹⁸
□ M-85
9.0 x 10¹³
8.9 x 10¹⁷
△ A-1
5.0 x 10¹³
6.1 x 10¹⁷
AT 450°C
AT 550°C
AT 650°C
AT 750°C
AT 850°C
CARRIER CONCENTRATION (cm⁻³)
ANNEALING TIME (h)

Fig. 3

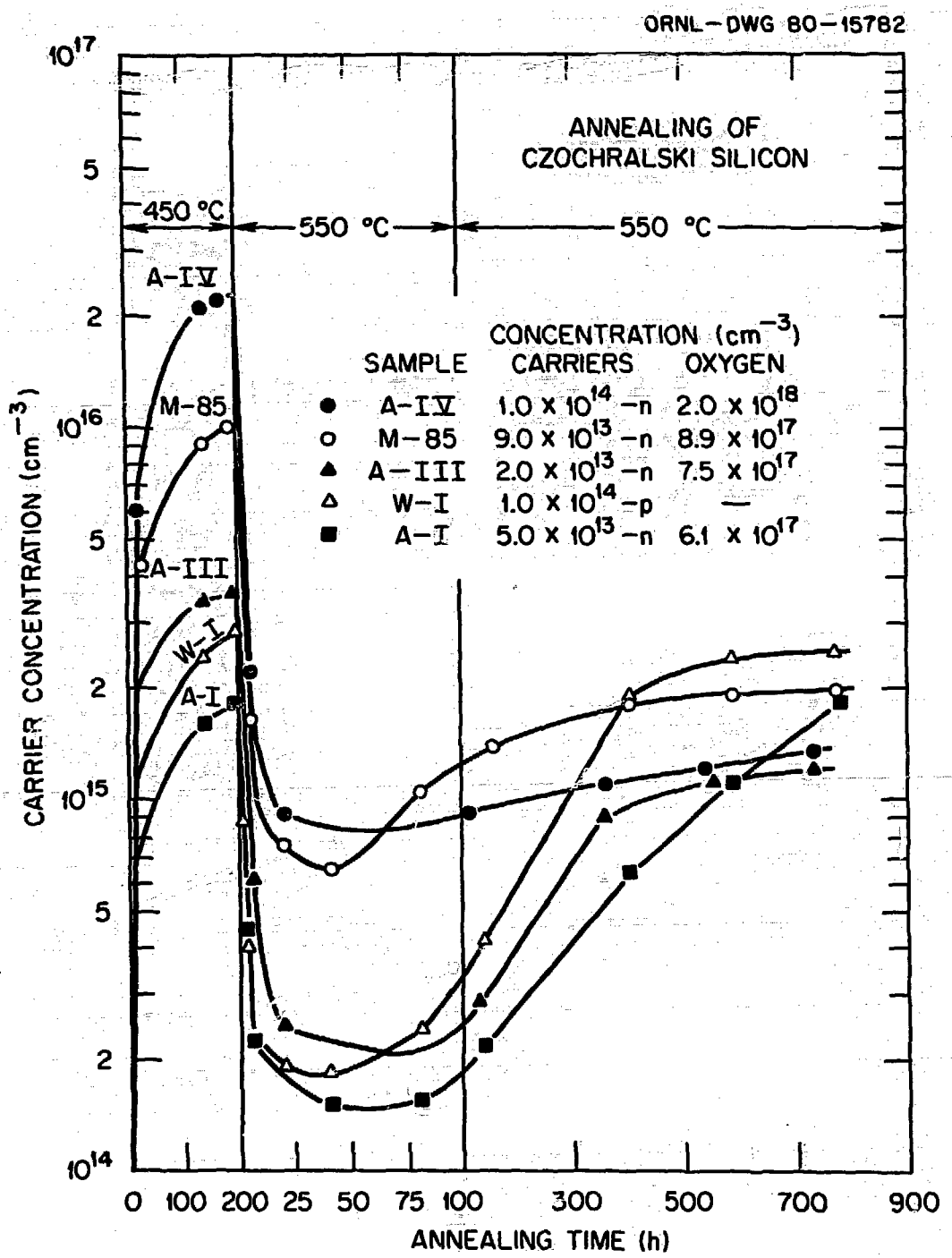
ORNL-DWG 80-15782
ANNEALING OF
CZOCHRALSKI SILICON
450 °C
550 °C
550 °C
CONCENTRATION (cm⁻³)
SAMPLE CARRIERS OXYGEN
A-IV 1.0 x 10¹⁴ -n 2.0 x 10¹⁸
M-85 9.0 x 10¹³ -n 8.9 x 10¹⁷
A-III 2.0 x 10¹³ -n 7.5 x 10¹⁷
W-I 1.0 x 10¹⁴ -p —
A-I 5.0 x 10¹³ -n 6.1 x 10¹⁷
A-IV
M-85
A-III
W-I
A-I
CARRIER CONCENTRATION (cm⁻³)
ANNEALING TIME (h)

Fig. 4

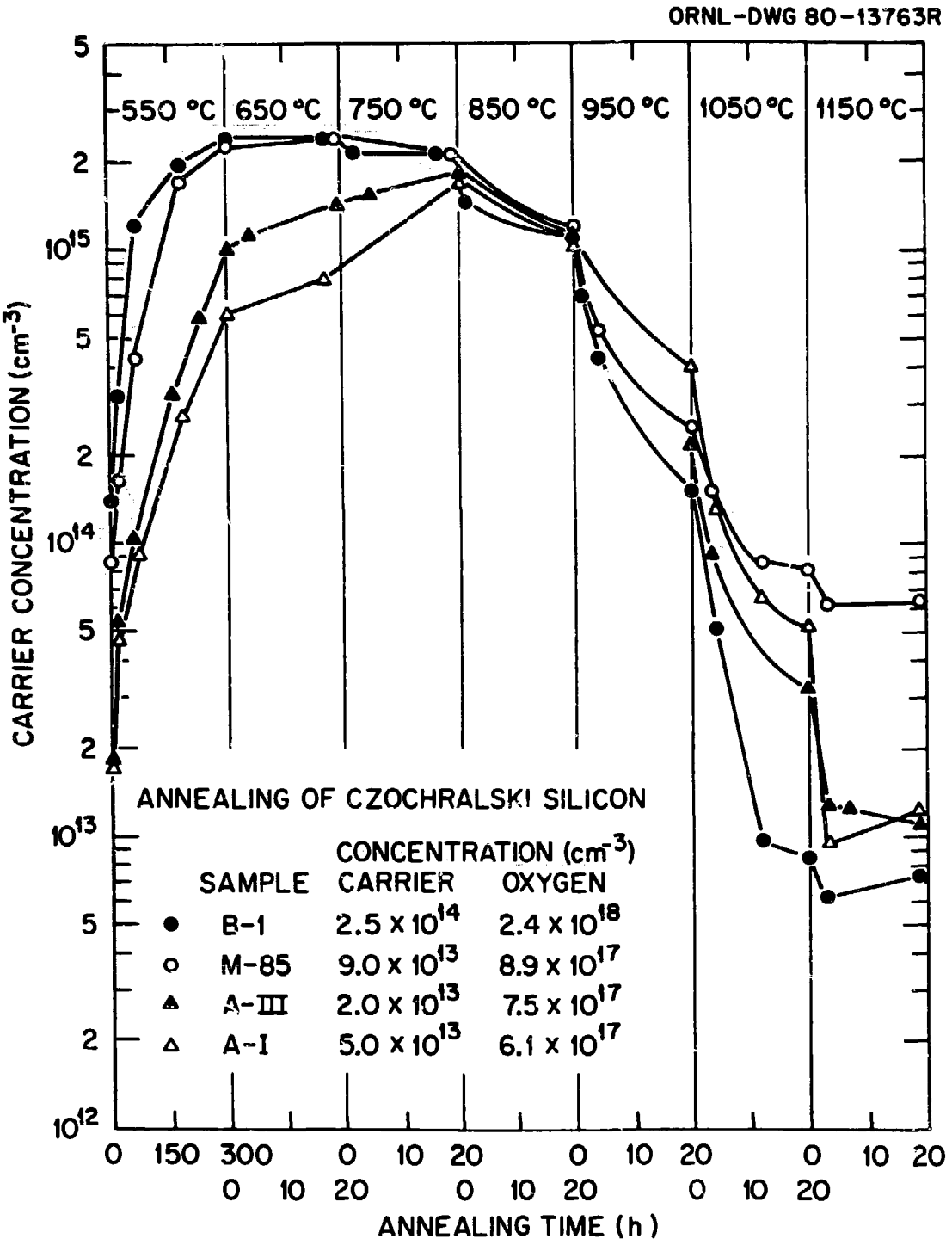
ORNL-DWG 80-13763R
550 °C
650 °C
750 °C
850 °C
950 °C
1050 °C
1150 °C
CARRIER CONCENTRATION (cm⁻³)
ANNEALING OF CZOCHRALSKI SILICON
CONCENTRATION (cm⁻³)
SAMPLE
CARRIER
OXYGEN
B-1
2.5 x 10¹⁴
2.4 x 10¹⁸
M-85
9.0 x 10¹³
8.9 x 10¹⁷
A-III
2.0 x 10¹³
7.5 x 10¹⁷
A-I
5.0 x 10¹³
6.1 x 10¹⁷
ANNEALING TIME (h)

Fig. 5

Previous investigators[6,11] have reported that heat treatment for 20 h at 1000°C or higher is sufficient to eliminate any subsequent low temperature O-donor formation in Cz Si of large initial O_i concentration, although de Kock[12] observed that some O_i remained in dislocation-free Cz Si after high temperature heat treatment. In the present experiments, samples from the ingots listed in Table 1 were annealed for 20 h at 1000, 1100, or 1200°C and air cooled. The carrier concentration after that heat treatment was almost identical to the initial value for each sample so that no evidence of any defect or impurity introduction or removal due to this heat treatment was observed. Table 2 lists the initial (n) or acceptor (p) concentration for each sample and the carrier concentration after extended (120-150 h) annealing at 450°C, for each set of samples after each initial heat treatment. Figure 6 indicates the increase in carrier concentration at 450°C for representative samples from the ingots of high (B-1), medium (M-85), and low (A-1) initial O_i content. All of the results listed in Table 2 and shown in Fig. 6 were such as to indicate a significant increase in O-donor concentration on annealing at 450°C after high temperature heat treatment (with the sole exception of the sample from ingot M-85 after heat treatment at 1000°C only). The samples were reannealed a second time for 20 h at 1000, 1100, or 1200°C, and again no evidence of any defect or impurity introduction or removal was observed other than removal of the O donors formed at 450°C. The results of extended annealing at 450°C on these samples were almost identical to those shown in Fig. 6. All of these data indicate that prior heat treatment for 20 or 40 h at 1000 to 1200°C is not sufficient to stabilize some of the O_i in Cz Si against subsequent O-donor formation by extended low temperature heat treatment.

(B) Irradiation Conditions

Table 3 lists the thermal and fast ($\geq$ 1 MeV) neutron fluence, t/f ratio, and the anticipated concentration of ^{31}P introduced in Si per hour of irradiation in the D-4 and D-6 locales of the D_2O tank in the Bulk Shielding Reactor (BSR) at the Oak Ridge National Laboratory (ORNL). These data were used to estimate the apparent concentration of (n,γ) recoil and of fast neutron-induced events as previously indicated[2] for NTD FZ Si. If there is a correspondence between the rate of lattice defect introduction by neutron irradiation in FZ and Cz Si, as would be anticipated, the data of Table 3 can be used to estimate that the total lattice defect concentration remaining in NTD Cz Si after ambient temperature irradiation is about 10^{16} cm^{-3} or 10^{14} cm^{-3} per h of irradiation in the D-4 and D-6 locales, respectively.

Table 2. Carrier Concentration of Cz Si Samples Before and After Heat Treatment.

Ingot	Initial Donor (n) or Acceptor (p) Concentration (cm^{-3})	Carrier Concentration after 20 h at 1000°C and 120-150 h at 450°C (cm^{-3})	Carrier Concentration after 20 h at 1100°C and 120-150 h at 450°C (cm^{-3})	Carrier Concentration after 20 h at 1200°C and 120-150 h at 450°C (cm^{-3})
A-1	5.0×10^{13}-n-	4.4×10^{14}-n-	9.0×10^{14}-n-	9.2×10^{14}-n-
A-3	2.0×10^{13}-n-	7.2×10^{15}-n-	6.6×10^{15}-n-	7.0×10^{15}-n-
A-4	1.0×10^{14}-n-	1.5×10^{16}-n-	1.5×10^{16}-n-	1.7×10^{16}-n-
B-1	2.5×10^{14}-n-	1.5×10^{16}-n-	1.4×10^{16}-n-	9.5×10^{15}-n-
M-85	9.0×10^{13}-n-	8.3×10^{13}-n-	5.6×10^{14}-n-	7.1×10^{15}-n-
M-86	9.5×10^{13}-n-	1.3×10^{16}-n-	1.2×10^{16}-n-	1.3×10^{16}-n-
M-65	3.1×10^{14}-n-	5.9×10^{15}-n-	1.0×10^{16}-n-	8.9×10^{15}-n-
M-73	3.5×10^{14}-p-	3.9×10^{15}-n-	4.9×10^{15}-n-	7.9×10^{15}-n-
10_B	5.6×10^{16}-p-	5.0×10^{16}-p-	5.1×10^{16}-p-	5.1×10^{16}-p-

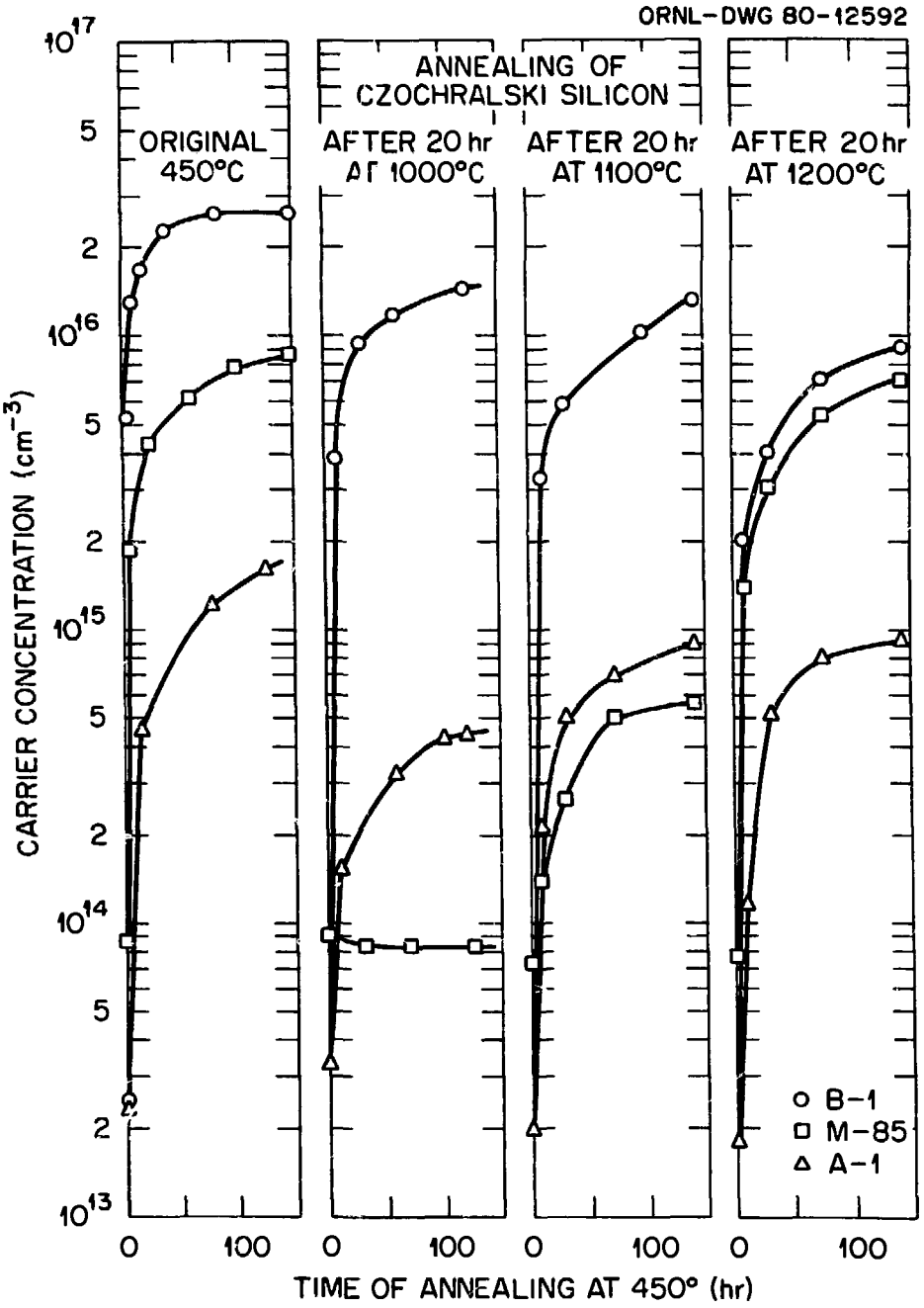
ORNL-DWG 80-12592
ANNEALING OF
CZOCHRALSKI SILICON
ORIGINAL
450°C
AFTER 20 hr
AT 1000°C
AFTER 20 hr
AT 1100°C
AFTER 20 hr
AT 1200°C
CARRIER CONCENTRATION (cm⁻³)
TIME OF ANNEALING AT 450° (hr)
B-1
M-85
A-1

Fig. 6

Table 3. Neutron fluence in the D_2O tank, Bulk Shielding Reactor, ORNL

Reactor Locale	Irradiation Time (h)	Thermal Neutron Fluence (cm^{-2})	Fast Neutron Fluence (cm^{-2})	Thermal/Fast Neutron Ratio (t/f)	Phosphorus Concentration (cm^{-3})
D-4	1	3.2×10^{16}	4.7×10^{15}	7	6.5×10^{12}
D-6	1	2.9×10^{15}	3.6×10^{13}	80	5.8×10^{11}

(C) Isothermal Annealing of NTD Cz Si at 450°C

Samples from ingots B-1, A-3, and A-1 listed in Table 1 were irradiated in the D-6 locale for times of 1 to 100 h and then annealed for $\geq$ 100 h at 450°C. The initial rate of O-donor formation and the O-donor concentration after extended annealing were almost identical to the values obtained on unirradiated samples (as listed in Table 1) for these samples irradiated with a fast neutron fluence of up to 3.6×10^{15} cm^{-3}. Most of the (n,γ) recoils may have annealed at 450°C, but these results indicate that the simultaneous presence of $\leq 10^{16}$ fast neutron-induced defects (D_f) cm^{-3} had little if any apparent effect on the rate of formation or final concentration of O donors as a consequence of extended annealing at 450°C.

Other samples from the same ingots were irradiated in the D-4 locale for times of 1 to 800 h. Figure 7 is a graph of the carrier concentration vs annealing time at 450°C for some of the B-1 samples. These data indicate that the rate of O-donor formation and the final O-donor concentration after extended annealing at 450°C were reduced as a function of increasing D_f concentration. Note that the carrier concentration was much larger than the anticipated ^{31}P concentration in samples B-1 to B-3 in Fig. 7, following irradiation and annealing at 450°C, and that a considerable concentration of O donors was still introduced in sample B-3 despite an estimated 10^{18} D_f cm^{-3}. A small amount of O-donor formation may have occurred in sample B-4 on annealing at 450°C, but the presence of almost 10^{19} D_f cm^{-3} evidently masked any observation of extensive O-donor formation or the presence of 5.4×10^{15} P cm^{-3}. Results very similar to those described above were also obtained on the A-3 and A-1 samples that contained less oxygen.

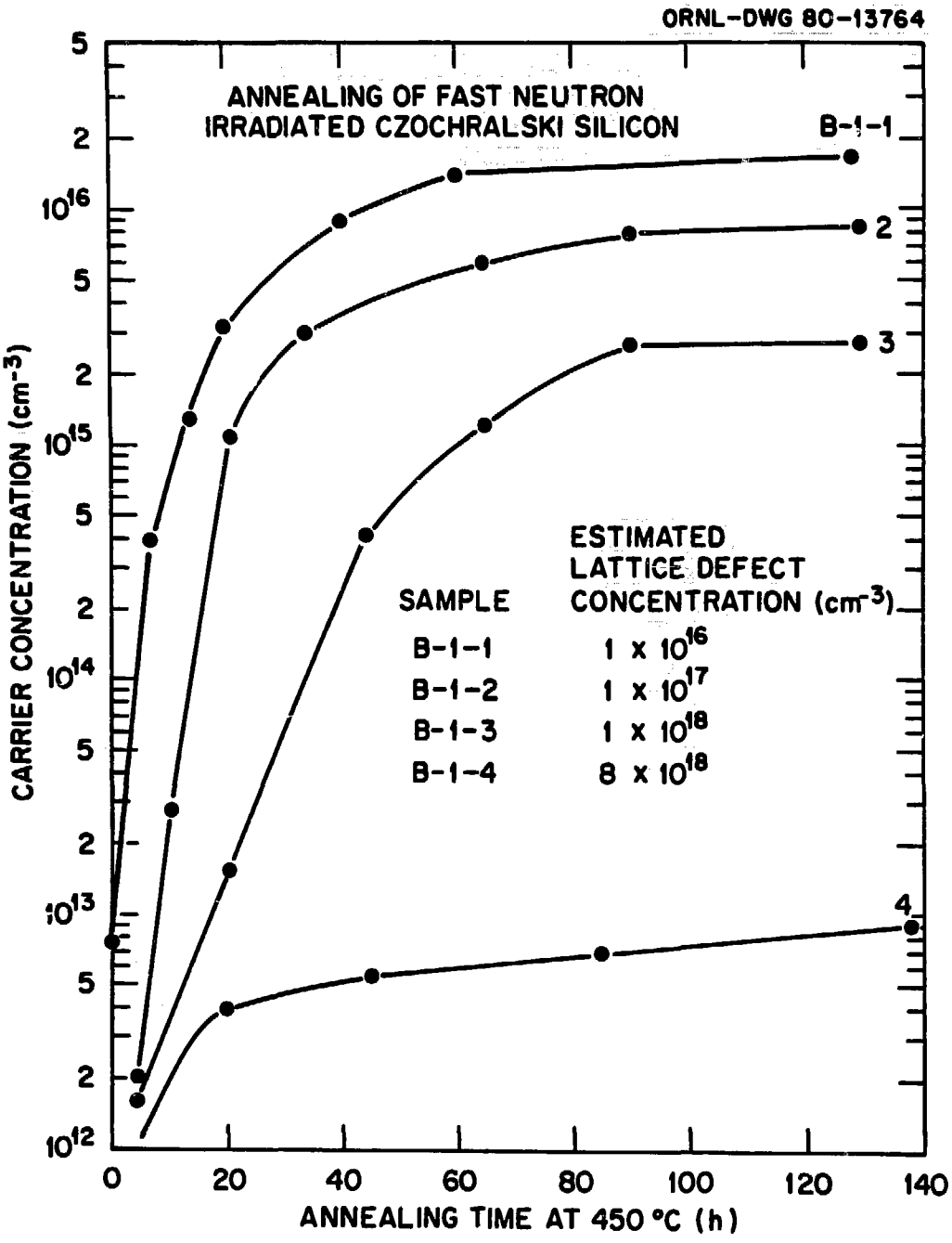
ORNL-DWG 80-13764
ANNEALING OF FAST NEUTRON
IRRADIATED CZOCHRALSKI SILICON
B-1-1
2
3
4
SAMPLE
ESTIMATED
LATTICE DEFECT
CONCENTRATION (cm-3)
B-1-1
1 x 10^16
B-1-2
1 x 10^17
B-1-3
1 x 10^18
B-1-4
8 x 10^18
CARRIER CONCENTRATION (cm-3)
ANNEALING TIME AT 450 °C (h)
0
20
40
60
80
100
120
140

Fig. 7

(D) Isothermal Annealing of Cz and NTD Cz Si at 750°C

Since previous results[2,16] have indicated that 30 min annealing at 750°C is sufficient to remove fast neutron-induced lattice defects in NTD FZ Si, selected samples from some of the ingots listed in Table 1 were given a similar heat treatment before extended annealing at 450°C to form O donors. Other samples were given a similar heat treatment after O-donor formation at 450°C, after neutron irradiation to introduce lattice defects, or after irradiation and O-donor formation at 450°C. Samples from those ingots that were probably post-annealed after growth to remove O donors did not indicate any significant change in carrier concentration after heat treatment for 30 min at 750°C. Samples that contained O donors initially, that contained O donors after extended annealing at 450°C, or contained O donors and D_f, all indicated a residual excess donor concentration $\geq 10^{14}$ cm^{-3} after the 30 min at 750°C heat treatment. There was a small variation in the final carrier concentration in different samples from the same ingot, that may have been due to the initial O_i content, the number of O donors introduced, or the D_f content after irradiation. However, every sample investigated had an additional donor concentration $\geq 10^{14}$ cm^{-3} except for the post-annealed, unirradiated Cz Si samples. The ratio of remaining-to-initial O-donor concentration was ≤ 0.1 in almost every sample, but these data indicate that annealing for 30 min at 750°C is sufficient to remove D_f, but is not sufficient to remove all of the O donors in either Cz or NTD Cz Si that contains such donors initially.

(E) Isothermal Annealing of NTD Si at 500 and 600°C

A sample (M-1) of n-type, high purity (2.23×10^{12} cm^{-3}) FZ Si of low ($\leq 3 \times 10^{16}$ cm^{-3}) O_i content was irradiated to introduce an estimated 6×10^{16} lattice defects cm^{-3} and 3.8×10^{13} P cm^{-3}. Figure 8, a graph of carrier concentration vs annealing time at 500°C, indicates that the apparent net donor concentration in sample M-1 was less than the anticipated P concentration after extended annealing at 500°C. Subsequent results (not shown) gave a donor concentration of 3.1×10^{13} cm^{-3} after annealing for 125 h at 600°C and 3.9×10^{13} cm^{-3} after 30 min at 750°C; the last value is in good agreement with the anticipated concentration of P. Equivalent data is shown in Fig. 8 for samples from ingot A-1 of Table 1 that contained 8.5×10^{17} O_i cm^{-3} as unirradiated (A-1-2), or as irradiated to introduce 10^{16} (A-1-3) or 10^{17} (A-1-4) D_f cm^{-3}. These results indicate that the introduction of O donors due to annealing at 500°C was delayed by the presence of D_f. Note that the apparent donor concentration of A-1-4, that contained 10^{17} D_f cm^{-3}, remained at a low 10^{12} cm^{-3} value during an annealing time of about 30 h before any O-donor formation was observed.

Similar experiments were carried out on samples from ingot B-1 of Table 1 that contained 2.4×10^{18} O_i cm^{-3} as unirradiated (B-5),

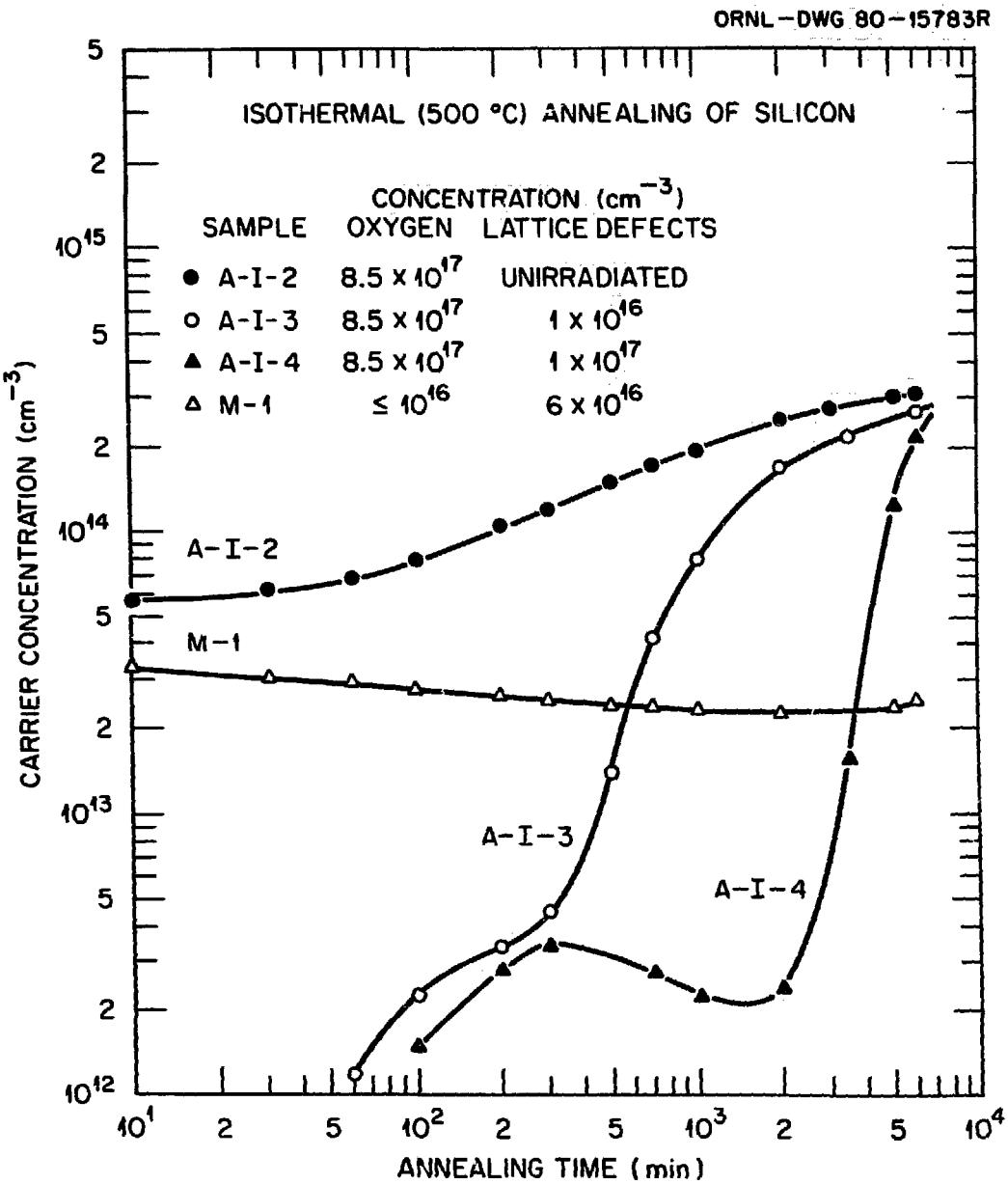
ORNL-DWG 80-15783R
ISOTHERMAL (500 °C) ANNEALING OF SILICON
CONCENTRATION (cm⁻³)
SAMPLE OXYGEN LATTICE DEFECTS
A-I-2 8.5 x 10¹⁷ UNIRRADIATED
A-I-3 8.5 x 10¹⁷ 1 x 10¹⁶
A-I-4 8.5 x 10¹⁷ 1 x 10¹⁷
M-1 ≤ 10¹⁶ 6 x 10¹⁶
A-I-2
M-1
A-I-3
A-I-4
CARRIER CONCENTRATION (cm⁻³)
ANNEALING TIME (min)

Fig. 8

or as irradiated to introduce 10^{16} (B-6) or 10^{17} (B-7) D_f cm^{-3}. Figures 9 and 10 show that O donors were introduced at 500°C and removed at 600°C. The formation of donors is delayed by the presence of D_f (Fig. 9). The apparent donor concentrations after extended annealing at 500°C were about 2.3, 1.8, and 0.9 x 10^{16} cm^{-3} for the three samples that contained very few, 10^{16}, or 10^{17} D_f cm^{-3}. The data of Fig. 10, indicates that 90-95% of the O donors were removed by annealing for about 150 h at 600°C, irrespective of the initial D_f concentration. These results demonstrate that the presence of D_f may impede the formation of O donors in NTD Cz Si by annealing at 500°C, but they do not indicate the presence of any significant concentration of any special type of lattice defect-O donor complex that is stable against annealing at temperatures above 500°C. The relatively small increase in donor concentration as a consequence of continued annealing of 600°C (Fig. 10) is not due to removal of D_f, since it occurred in all samples, but may be due to the formation of some more complex type of oxygen donor at this annealing temperature.

(F) Isothermal Annealing of NTD Si at 750 and 950°C

Previous experiments[2] have demonstrated that annealing for 30 min at 750°C is sufficient to obtain the anticipated carrier concentration and mobility in NTD FZ Si, irrespective of neutron fluence or t/f ratio. In more recent experiments,[16] samples of FZ and Cz Si were irradiated simultaneously and annealed for 30 min at 750°C. The donor concentration measured in the NTD FZ Si samples was always nearly identical to the P concentration, as calculated over a wide range of neutron fluence. The donor concentration as measured in the NTD Cz Si samples, however, was larger than the calculated P concentration, particularly for low fluence irradiations. No change was observed in the donor concentration in any of the NTD FZ Si samples as a consequence of extended annealing at 750°C, but the donor concentration increased in each NTD Cz Si sample by about 10^{15} cm^{-3}, irrespective of an initial D_f concentration that was increased from about 10^{14} to 10^{18} cm^{-3} in different samples. This additional donor concentration in the NTD Cz Si samples was decreased substantially by subsequent annealing at 950°C, but some fraction ($\leq$ 10%) remained even after extended annealing at 950°C.

This type of experiment has been continued. Figure 11 is a graph of donor concentration vs time of annealing at 750 and 950°C, for selected samples from the A-111 and B-1 ingots of Table 1, after irradiation in the D-6 locale for 1 to 800 h to introduce 5.8 x 10^{11} to 4.6 x 10^{14} P cm^{-3}. The apparent donor concentration in the A-111 samples was nearly identical to the anticipated P concentration after annealing for 30 min at 750°C. It was stated in Section (A) that ingot B-1 was not post-annealed, and that the initial donor concentration in B-1 samples was changed to an apparent low acceptor

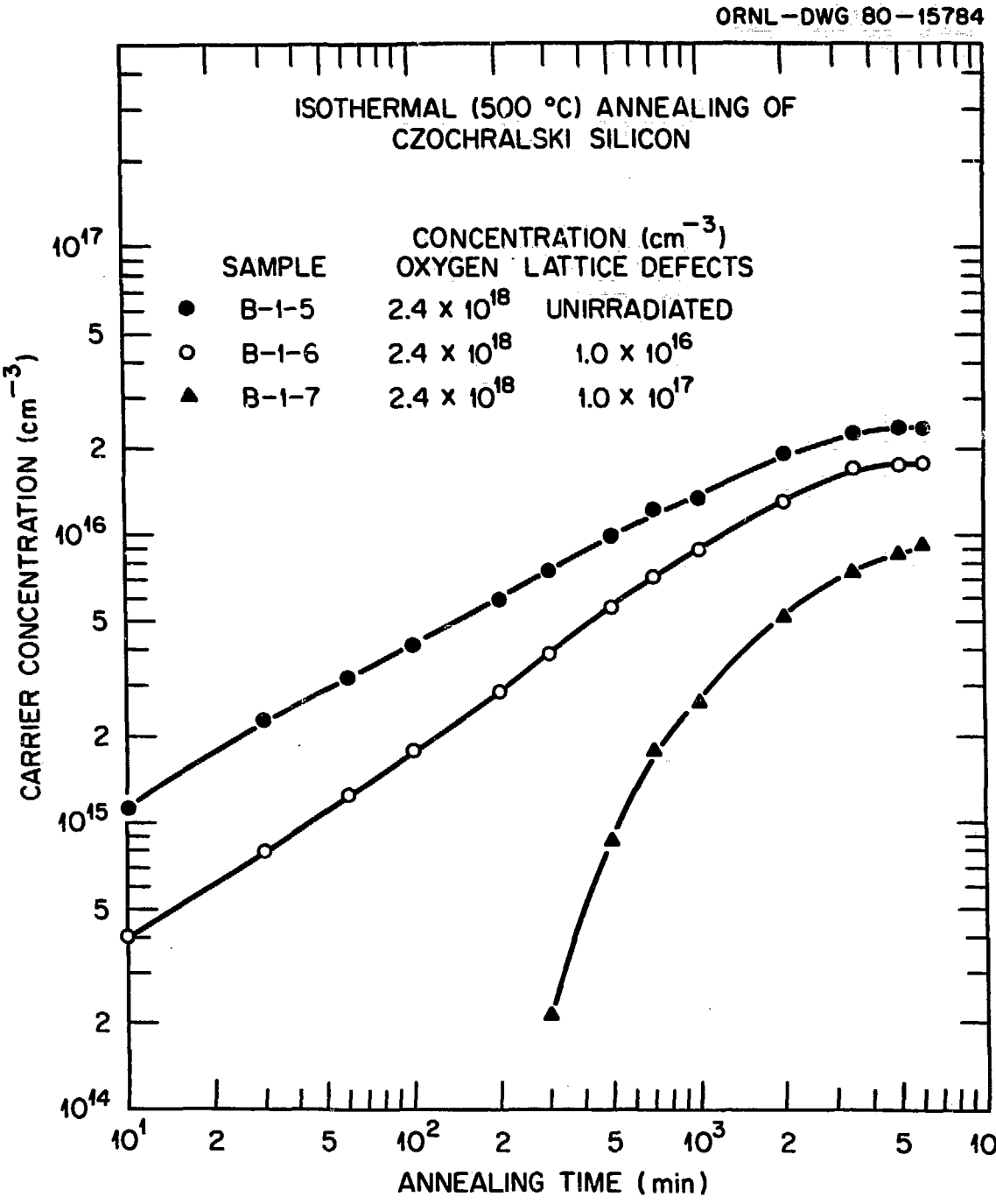
ORNL-DWG 80-15784
ISOTHERMAL (500 °C) ANNEALING OF
CZOCHRALSKI SILICON
CONCENTRATION (cm^{-3})
SAMPLE
OXYGEN
LATTICE DEFECTS
B-1-5
2.4 x 10^{18}
UNIRRADIATED
B-1-6
2.4 x 10^{18}
1.0 x 10^{16}
B-1-7
2.4 x 10^{18}
1.0 x 10^{17}
CARRIER CONCENTRATION (cm^{-3})
ANNEALING TIME (min)

Fig. 9

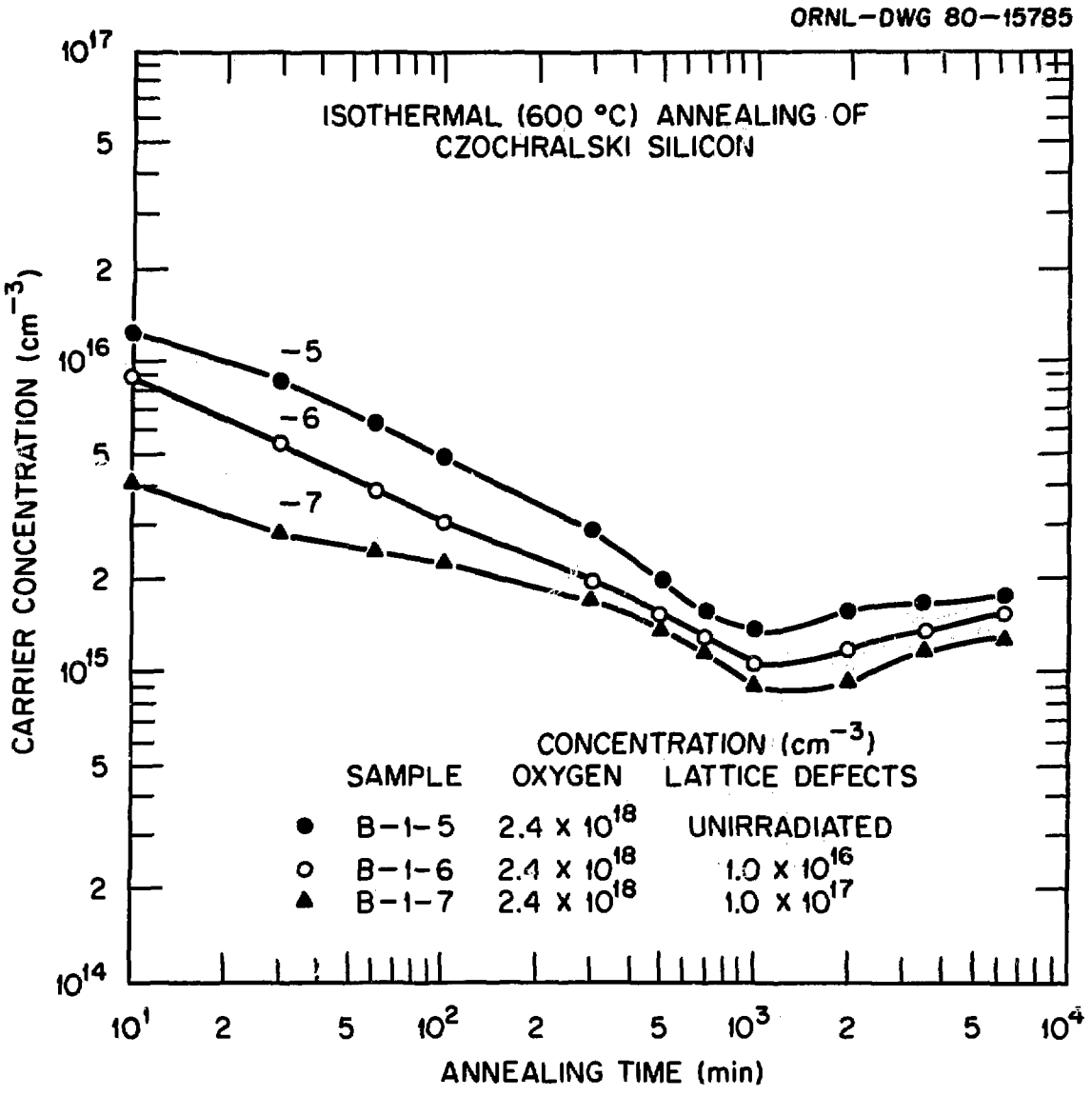
ORNL-DWG 80-15785
ISOTHERMAL (600 °C) ANNEALING OF
CZOCHRALSKI SILICON
CARRIER CONCENTRATION (cm^{-3})
ANNEALING TIME (min)
-5
-6
-7
CONCENTRATION (cm^{-3})
SAMPLE OXYGEN LATTICE DEFECTS
B-1-5 2.4 x 10^{18} UNIRRADIATED
B-1-6 2.4 x 10^{18} 1.0 x 10^{16}
B-1-7 2.4 x 10^{18} 1.0 x 10^{17}

Fig. 10

ORNL-DWG 80-15786

ISOTHERMAL ANNEALING OF NTD CZOCHRALSKI SILICON

SAMPLE	CONCENTRATION (cm^{-3}) OXYGEN	LATTICE DEFECTS
A-III-1	7.5×10^{17}	1.0×10^{14}
A-III-2	7.5×10^{17}	1.0×10^{15}
A-III-3	7.5×10^{17}	1.0×10^{16}
B-1-1	2.4×10^{18}	1.0×10^{14}
B-1-2	2.4×10^{18}	8.0×10^{16}

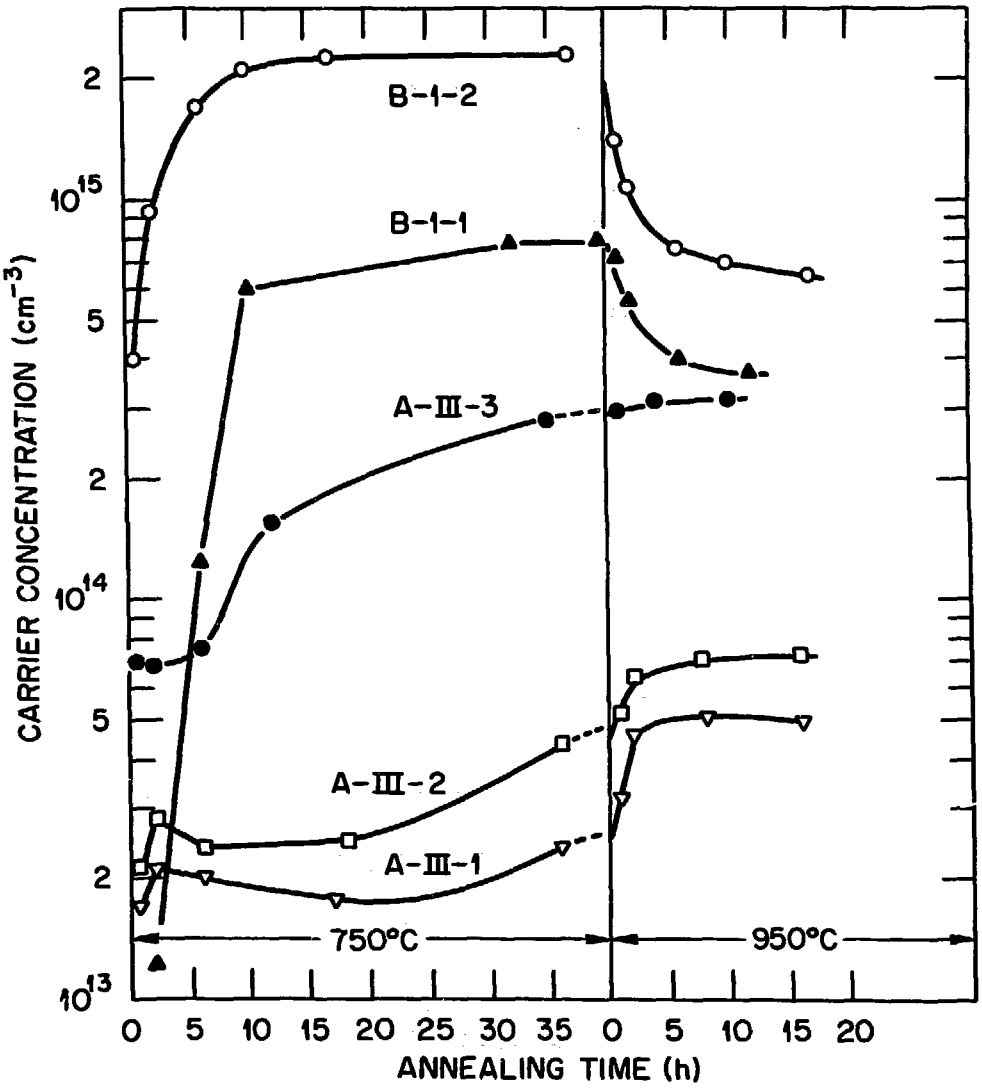

Fig. 11

concentration after annealing for 30 min at 750°C. The apparent donor concentration in the B-1 samples shown in Fig. 11 was much larger after irradiation and annealing for 30 min at 750°C than would be anticipated if the initial O-donor concentration had been removed by the first annealing treatment. The donor concentration increased in both the A-111 and B-1 samples upon extended (30-40 h) annealing at 750°C. Note that the apparent increase was only about 4×10^{12} cm^{-3} for the A-111-1 sample that contained about 10^{14} D_f cm^{-3}; whereas, the corresponding increase was about 5×10^{14} cm^{-3} for the B-1-1 sample that also contained about 10^{14} D_f cm^{-3}. The initial D_f concentration in these samples was presumably identical, and the initial O_i concentration was only different by about a factor of 2, but the apparent increase in donor concentration on extended annealing at 750°C was different by a factor of more than 100. The fact that the increase in donor concentration in the B-1-1 sample was larger than the D_f concentration, by a factor of 5, would also appear to argue against the formation of a special type of lattice defect O complex as a consequence of irradiation or extended annealing at 750°C.

It is evident from the data of Fig. 11 that the apparent donor concentration increased to some extent in the A-111 and B-1 samples as a consequence of extended annealing at 750°C, and that the increase was larger for those samples that contained more D_f initially. However, there is no evident correlation between the initial D_f concentration and the increase in donor concentration on extended annealing. Note also that the apparent donor concentration continued to increase in the A-111 samples, that contained less O_i, as a consequence of annealing at 950°C; whereas, the corresponding data for the B-1 samples indicates a substantial reduction in donor concentration. Some fraction of an excess donor concentration remained, over that anticipated, in every sample investigated, but the excess amount was $1\text{-}3 \times 10^{15}$ cm^{-3} in the B-1 samples and $0.3\text{-}2 \times 10^{14}$ cm^{-3} in the A-111 samples. The fact that the initial increase in donor concentration on extended annealing was not a linear function of the initial D_f concentration, and the fact that donors were introduced at 950°C in the A-111 samples, but removed in the B-1 samples, also suggests that donor addition or removal at the different annealing temperatures was a function of initial O_i content but was not a sensitive function of the D_f concentration.

DISCUSSION

The primary result of these experiments is a better understanding of the electrical properties of O donors in Cz Si and of the annealing requirements to remove such donors and thus obtain the anticipated carrier concentration and mobility in Cz or NTD Cz Si. Commercially available Cz Si is usually post-annealed to remove O donors, but some such donors may remain. Any subsequent heat treatment above about 300°C can form O donors at an initial rate $\geq 10^{15}$ cm^{-3} hr^{-1} in Cz Si that contains $\geq 10^{18}$ O_i cm^{-3}. The maximum O

donor concentration on extended ($\geq$ 100 h) annealing can exceed 1% of the initial O_i concentration. There is no evident interaction between O and donor impurities in n-type Cz Si, but previous investigators[6,7,9] have reported that O and acceptor impurities form some type of donor in p-type Cz Si. They stated that annealing above about 500°C can reduce the O-donor concentration in n-type Cz Si, or in p-type Cz Si doped with B or Ga, but that O-Al donors may have been formed that require annealing above 1000°C.

In the present experiments, it was determined that a small fraction ($\sim$ 1%) of any O donors introduced in Cz Si by heat treatment at 350-500°C remained after subsequent heat treatment to about 1000°C. Most of the O donors formed at 350-500°C were removed by annealing for 20-50 h at 550°C, 5-10 h at 650°C, or 30 min at 750°C, but new O donors were then formed by extended annealing at these temperatures. An O-donor concentration in excess of 10^{15} cm^{-3} was introduced in samples of Cz Si of different initial O_i concentration by annealing for 900 h at 550°C or for 100 h at 650°C; these O donors were stable against higher temperature annealing to at least 850°C.

High temperature (1000-1200°C) heat treatment for 20 h has been reported[6,11] to be sufficient to eliminate any subsequent low temperature (350-500°C) O-donor formation in Cz Si, although de Kock[12] observed that some O_i remained after 1200°C heat treatments. In the present experiments, it was demonstrated that prior heat treatment for 20-40 h at 1000-1200°C was not sufficient to prohibit some O-donor formation in samples of Cz Si of different initial O_i concentration by subsequent low temperature heat treatment.

The initial rate of O-donor formation and the final concentration of O donors introduced in NTD Cz Si by annealing at 450°C was not altered by the simultaneous presence of up to $\leq 10^{16}$ cm^{-3} fast neutron-induced lattice defects (D_f). Both the initial rate and the final concentration were reduced after comparable annealing at 450°C in more heavily irradiated samples, but a donor concentration in excess of 10^{15} cm^{-3} was formed in a NTD Cz Si sample that contained 10^{18} D_f cm^{-3}.

Previous studies[1,2] have indicated that 30 min annealing at 750°C was sufficient to obtain the anticipated carrier concentration and mobility in NTD FZ Si irradiated up to a large ($\geq 10^{20}$ cm^{-2}) neutron fluence. In the present experiments, it was determined that comparable annealing reduced the O-donor concentration in NTD Cz Si, but a residual concentration of $\geq 10^{14}$ cm^{-3} remained irrespective of the D_f concentration. These results indicate that formation of O donors in NTD Cz Si, by heat treatment at 450°C, and any subsequent removal of O donors by 30 min annealing at 750°C, was not altered significantly by the simultaneous presence of lattice defects.—No evidence was obtained for the formation of an O-lattice defect

complex that reputedly acts as a donor and is stable against high temperature (850-1000°C) annealing.[13-15] A residual donor concentration of $\geq 10^{14}$ cm^{-3} was observed in every sample, irrespective of initial O_i and D_f concentration, after annealing, but that was probably due to incomplete removal of all O donors.

The primary result of iochronal annealing studies on NTD FZ or Cz Si samples that contained 10^{16} or 10^{17} D_f cm^{-3} was that the presence of D_f impeded the formation of O donors in Cz Si samples at 500°C, but 90-95% of the O donors were removed on annealing at 600°C, irrespective of D_f concentration. These data may indicate some type of interaction between O and D_f as a consequence of irradiation or partial annealing, but they do not indicate the presence of a special type of O-defect complex that is stable against higher temperature annealing. It was demonstrated that O donors are formed in unirradiated Cz Si by isothermal annealing at 500 or 600°C and that such donors are stable against annealing to about 850°C, at which temperature the introduction and removal of that type of O donor in Cz Si was totally independent of any initial D_f concentration.

Some type of O donor was also formed in NTD Cz Si samples by extended (30-40 h) annealing at 750°C. The apparent increase in donor concentration was a factor of 5 larger than the D_f concentration for samples with a large initial O_i concentration, but the total increase in donor concentration was not a linear function of the initial D_f concentration. The apparent donor concentration continued to increase in samples of low initial O_i content, on extended annealing at 950°C, but decreased in samples of large O_i content under similar annealing conditions. The fact that the initial increase in donor concentration on extended annealing at 750°C was not a linear function of the D_f concentration, together with the fact that donors were added at 950°C in samples of low O_i content, but removed in samples of large O_i content, would also indicate that donor addition or removal was a function of the O_i content but was not a function of the D_f concentration.

SUMMARY

It has been demonstrated that one can introduce O donors in Cz or in NTD Cz Si by low temperature (300-500°C) annealing. The donor concentration on extended annealing is a sensitive function of the O_i content, but is not a function of the lattice defect content up to about 10^{16} D_f cm^{-3}. Some fraction of the O-donor concentration remains in Cz or NTD Cz Si after isochronal or isothermal annealing up to about 1000°C. That fraction is also a sensitive function of the O_i content, but is not a function of the D_f content. The results of isochronal annealing studies are such as to indicate that the presence of D_f impedes the formation of O donors on annealing at 500°C, but 90-95% of the O donors are removed on annealing at 600°C. It was also demonstrated that one can introduce O donors in unirradiated

Cz Si by annealing at 500 or 600°C, and that such donors are stable against annealing to about 850°C. Introduction and removal of that type of O donor is totally independent of any initial D_f concentration. Some type of O donor is also formed in NTD Cz Si by extended (30-40 h) annealing at 750°C, but the increase in donor concentration in different samples is not a linear function of the D_f concentration. All of these results serve to indicate that annealing for 30 min at 750°C is sufficient to remove virtually all of the D_f in NTD FZ or Cz Si and virtually all of the O donors in NTD Cz Si, irrespective of neutron fluence or t/f ratio. Previous observations of an O-defect-induced donor, that required high temperature annealing, may have been due to the presence of O donors prior to irradiation, or to the introduction of additional O donors during annealing.

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30 x 47 picas final size

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17. The authors wish to thank L. E. Katz, Bell Telephone Laboratories, Allentown, PA, and H. M. Hobgood, Westinghouse R and D center, Pittsburgh, PA, for providing the B-1, ^{10}B and W-1 ingots, respectively.

FIGURE CAPTIONS

Fig. 1. Carrier concentration vs annealing time at 450°C for Cz Si samples.

Fig. 2. Carrier concentration vs annealing time at 550 and 450°C for Si samples.

Fig. 3. Carrier concentration vs annealing time at 450 to 850°C for Cz Si samples.

Fig. 4. Carrier concentration vs annealing time at 450 and 550°C for Cz Si samples.

Fig. 5. Carrier concentration vs. annealing time at 550 to 1150°C for Cz Si samples.

Fig. 6. Carrier concentration vs annealing time at 450°C for Cz Si samples after high temperature heat treatment.

Fig. 7. Carrier concentration vs annealing time at 450°C for NTD Cz Si samples.

Fig. 8. Carrier concentration vs annealing time at 500°C for FZ and Cz Si samples.

Fig. 9. Carrier concentration vs annealing time at 500°C for Cz Si samples.

Fig. 10. Carrier concentration vs annealing time at 600°C for Cz Si samples.

Fig. 11. Carrier concentration vs annealing time at 750 and 950°C for NTD Cz Si samples.