Electrical and Optical Properties of Heat-Treated Silicon

W. KAISER
Signal Corps Engineering Laboratories, Fort Monmouth, New Jersey
(Received December 5, 1956)

Single crystals of silicon exhibit optical scattering between 1 and 3 μ after a heat treatment at 1000°C. The Tyndall effect was observed in such samples by using an infrared image tube. The number of donor states, produced in silicon during a 450°C heat treatment, increased rapidly with increasing oxygen concentration of the sample. These effects were found in silicon crystals which were pulled from quartz crucibles; they could not be detected in samples prepared by the floating-zone technique in vacuum.

INTRODUCTION

RECENT investigations have shown that silicon crystals pulled from a quartz crucible contain oxygen as an impurity.[1,2] The concentration can be as high as 10^{18} cm^{-3}. The silicon-oxygen molecular vibration in these specimens gives rise to an infrared absorption band at 9 μ. The absorption at 9 μ is proportional to the oxygen concentration after taking into account a small lattice band of 0.8 cm^{-1} in the 9-μ range. Thus infrared investigations are a sensitive tool for determining the local oxygen content in a silicon sample.

Fuller, Ditzenberger, Hannay, and Buehler[3] have reported the formation of over 2×10^{16} donors per cm^3 after silicon crystals were heat-treated between 350° and 500°C. The donor states can be annihilated by a subsequent heat treatment above 800°C. Heating the silicon specimen for twenty hours at 1100°C "stabilizes" the sample, and no further donor states can be produced.

New observations were made on the electrical and optical properties of silicon after a heat treatment at 1000° and 450°C. There is strong evidence that the presence of oxygen as an impurity is connected with a number of these heat-treatment effects.

EXPERIMENTAL

The measurements were made with a Perkin-Elmer double-pass spectrometer with a Dewar attachment for low-temperature investigations. Special devices for scanning the samples in the infrared were employed in a number of experiments. The slit width used is indicated in Figs. 5 and 6. The silicon samples were heat-treated in a quartz tube using helium as an inert gas atmosphere unless stated otherwise. The electrical and optical measurements in Part B were made on silicon rods of about 3×3 mm in cross section cut from the more homogeneous center of the pulled crystal. All the crystals investigated were rotated during the pulling process. It should be emphasized that all the effects reported upon are bulk effects on silicon single crystals with carrier concentrations less than 10^{15} cm^{-3}.

A. Heat Treatment at 1000°C

Silicon samples cut from crucible-pulled ingots exhibit a number of interesting effects after a heat treatment at 1000°C (±5%). The observations may be summarized as follows:

1. In all the samples investigated, the absorption band at 9 μ decreased and broadened slightly after prolonged heat treatment.[4] The time dependence of this annealing effect varied greatly from sample to sample. An example is shown in Fig. 1, where the decrease of the band maximum at room temperature and at 90°K is plotted against annealing time. The smallest absorption coefficient observed after heat treatment of 50 hours was 1.5 cm^{-1}. The decrease in absorption is homogeneous throughout the sample.

2. Essentially the same decrease in the absorption at 9 μ was observed in vacuum of 2×10^{-5} mm Hg pressure as well as at one atmosphere of argon, helium, and even oxygen. This indicates that the optical effect described in Sec. A.1 is independent of the ambient gas.

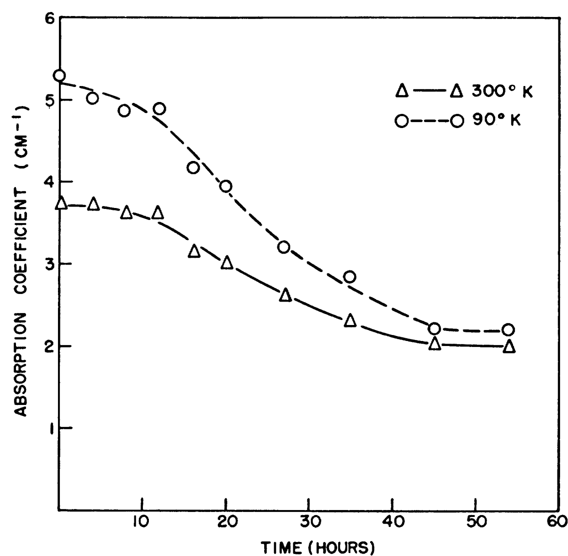


FIG. 1. Decrease of the absorption maximum in the 9-μ range measured at 300°K and 90°K. The sample was heat-treated at 1000°C in a vacuum of 2×10^{-5} mm Hg pressure.

[1] Kaiser, Keck, and Lange, Phys. Rev. **101**, 1264 (1956).
[2] H. J. Hrostowski and R. H. Kaiser, Bull. Am. Phys. Soc. Ser. II, **1**, 295 (1956).
[3] Fuller, Ditzenberger, Hannay, and Buehler, Phys. Rev. **96**, 833 (1954) and Acta Metallurgica **3**, 97 (1955).
[4] In agreement with investigations by Lederhandler, Debye, and Statz (private communication).

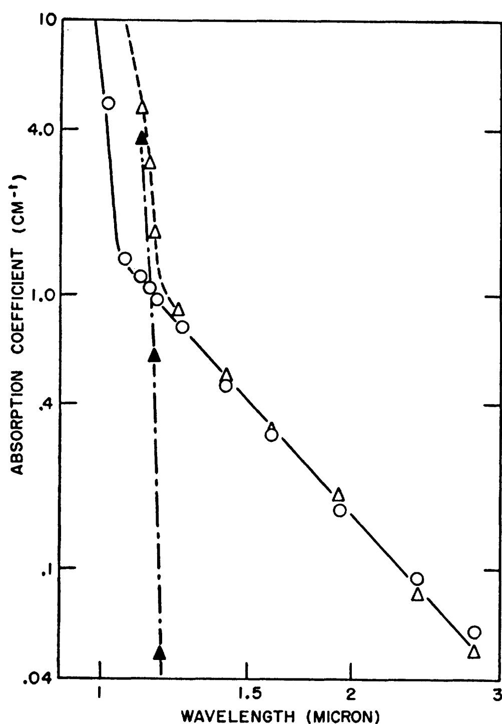


FIG. 2. The absorption edge of silicon at 300°K before (▲) and after (△) a heat treatment at 1000°C for 45 hours; the absorption coefficient of the same heat treated sample measured at 90°K (○).

3. After prolonged heat treatment (10 hours or longer), a distinct tail of the fundamental absorption edge at 1.2 μ appears, which increases with time of heat treatment. In Fig. 2, the absorption coefficient, after a heat treatment of 45 hours, is plotted against wavelength on a log-log scale. The straight line with a slope of 3.4 indicates that α is proportional to $\lambda^{-3.4}$. At 90°K, the absorption edge shifts to shorter wavelength[5] and a larger portion of the temperature-independent tail can be measured. For comparison, the sharp edge of the fundamental absorption of the same sample, previous to the forty-five hour heat treatment, is also plotted in Fig. 2. The wavelength dependence of the tail differed only slightly from sample to sample; the magnitude, however, showed variations within the same sample and between samples after a certain time of heat treatment in vacuum. In sample areas where the 9-μ absorption had shown a greater decrease, the scattering intensity was found to be larger. Samples with strong fluctuations in the absorption at 9 μ along the pulling axis exhibited similar fluctuations in the absorption coefficient at 1.2 μ.

There was no indication of a tail in the absorption edge in samples prepared in the floating-zone equipment, even after heating the specimen in vacuum for 70 hours.

4. Samples with an additional absorption between 1 and 3 μ exhibit optical scattering known as the Tyndall Effect. This can be demonstrated by the experiment outlined in Fig. 3. A rectangular silicon sample is polished on four sides and infrared radiation ($\lambda > 1.1\ \mu$) penetrates the specimen through a diaphragm D_1. At the same time, the light path through the sample can be seen with an infrared image tube through diaphragm D_2. Using a polarizer in position A only, it was proven that the scattered light is polarized with the electrical vector E perpendicular to the plane of Fig. 3. With a polarizer in position B only, radiation could be observed through diaphragm D_2, whenever the incident light had an E component perpendicular to the plane of Fig. 3. Two photographs, taken through the infrared image tube, are shown in Fig. 4. In Fig. 4(a) the light penetrates the sample perpendicular to the pulling direction of the sample, while in Fig. 4(b), the incident light beam traverses the sample parallel to the pulling axis. In Fig. 4(a), the scattered intensity is uniform over the total width of the sample, but in Fig. 4(b) fluctuations of scattered intensity can be seen. The bright stripes follow the growth rings of the crystal and can be explained by fluctuations of the oxygen concentration in the sample.

5. Vacuum fusion analysis[6] gave no indication within experimental error of a change in oxygen concentration of a sample after heat treatment at 1000°C. A slice of a silicon single crystal, cut perpendicular to the growth direction, was found to have an absorption maximum at 9 μ of 5.2 cm^{-1}. After a forty-nine hour heat treatment of one-half of the slice, the absorption decreased to 1.9 cm^{-1}. Both halves were then checked for oxygen concentration by vacuum fusion analysis and it was found that the untreated half had 15 ppm (parts per million), while the treated half showed 14 ppm, indicating that the oxygen concentration was unchanged within the experimental error (2 ppm).

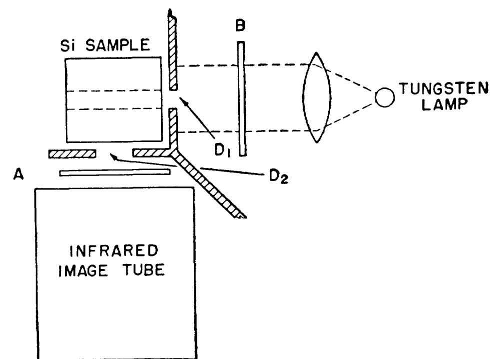


FIG. 3. Schematic arrangement used to investigate the Tyndall Effect in silicon.

[5] H. Y. Fan and M. Becker, *Proceedings of the Reading Conference* (Butterworths Scientific Publications, London, 1951). G. G. MacFarlane and V. Roberts, Phys. Rev. **98**, 1865 (1955). W. C. Dash and R. Newman, Phys. Rev. **99**, 1151 (1955).

[6] The vacuum fusion analysis was made by the National Research Corporation, Cambridge, Massachusetts.

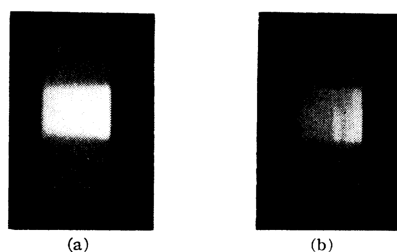


FIG. 4. Photographs taken through an infrared image tube showing the Tyndall Effect in silicon heat treated at 1000°C. The incident light beam is (a) perpendicular, (b) parallel to the pulling direction of the sample. (Magnification 3×.)

6. Heat treatment at 1350°C for ninety hours did not change the absorption at 9 μ in the body of the specimen and did not give rise to an additional absorption between 1 and 3 μ. The situation was quite different in samples where a preceding heat treatment at 1000°C had decreased the absorption band at 9 μ. In this case a heat treatment at 1350°C lasting for only thirty minutes restored the absorption maximum at 9 μ to a large extent.[7]

7. The concentration of free carriers changed by less than 10^{15} cm^{-3} during the heat treatment. Free carriers in silicon give rise to absorption which is proportional to the carrier concentration.[8] Increasing carrier concentration would have shown up in the absorption measurements as an increasing background, yet during heat-treatment studies at 1000°C absorption caused by free carriers was never detected. From this it can be estimated that the concentration of free carriers was definitely less than 10^{15} cm^{-3} at any time. This is in agreement with resistivity measurements on a number of heat-treated samples.

DISCUSSION OF THE HEAT TREATMENT AT 1000°C

From the scattering phenomena described in Secs. A.3 and A.4 it can be concluded that centers having a dielectric constant which differs from that of the silicon matrix are formed during the heat treatment at 1000°C. There are several facts which suggest that oxygen as an impurity can form scattering particles in silicon: (a) After treatment in vacuum the scattering effect could be observed only in silicon crystals pulled from a quartz crucible. (b) The scattering intensity followed roughly the fluctuations of the oxygen concentration in the specimen. (c) When one considers the scattering centers as being a precipitate of an impurity, then oxygen is the only impurity known to be present in these samples (with carrier concentration of 10^{13} to 10^{15} cm^{-3}) in a concentration of the order of 10^{17} cm^{-3}.*

[7] The increase in absorption at 9 μ during a subsequent heat treatment at 1350°C was first reported by S. Lederhandler.

[8] H. B. Briggs, Phys. Rev. **77**, 727 (1950); H. Y. Fan and M. Becker, Phys. Rev. **78**, 178 (1950); W. G. Spitzer and H. Y. Fan, Bull. Am. Phys. Soc. Ser II, **1**, 126 (1956).

* Oxygen is not the only source which can give rise to scattering in silicon. Small scattering due to other impurities was detected in certain samples.

A possible picture, quite consistent with the experimental findings presented in this paper, is as follows: during the heat treatment at 1000°C, the oxygen atoms in the silicon lattice group together into clusters of high oxygen concentration. Since SiO_2 is the equilibrium phase of the silicon oxides at 1000°C,[9] it can be expected that oxygen in silicon will have the tendency to form a network of SiO_4 tetrahedra.[10] The clusters have an index of refraction n smaller than that of the silicon matrix ($n_0=3.6$). When it is assumed that there are dense SiO_2 particles with $n=1.5$, then the number and size of these scattering centers can be estimated from the experimental values (Fig. 2). For spherical particles with diameters smaller than the wavelength, the absorption coefficient due to Rayleigh scattering[11] is known to be

$$\alpha=24\pi^3 N_p V^2\left(\frac{n^2-n_0^2}{n^2+2n_0^2}\right)^2\left(\frac{n_0^4}{\lambda^4}\right), \tag{1}$$

where N_p is the number of scattering centers per cm^3, V is the volume of the particles, and λ is the wavelength in air. The agreement between the slope of 3.4 in Fig. 3 and the value of 4 according to Eq. (1) is satisfactory, considering the assumption made above. With N_0 the total number of oxygen atoms per cm^3 present in the specimen, the volume is determined as

$$V=\frac{N_0}{N_p}\left(\frac{M}{2\rho A}\right), \tag{2}$$

where M is the molecular weight of SiO_2 ($M=60$ g), ρ is the density ($\rho=2.3$ g cm^{-3}), and A is Avogadro's number.

$$N_p=\frac{24\pi^3}{\alpha}\left(\frac{N_0 M}{2\rho A}\right)^2\left(\frac{n^2-n_0^2}{n^2+2n_0^2}\right)^2\frac{n_0^4}{\lambda^4}. \tag{3}$$

With the experimental values of $\alpha=1.0$ cm^{-1} at $\lambda=1.15\ \mu$ (see Fig. 2) and $N_0=10^{18}$ cm^{-3}, the number of scattering centers is calculated to be 5×10^{10} cm^{-3}. The number of oxygen atoms per cluster is $N_0/N_p=2\times10^7$. The diameter of these centers is determined as $d=0.1\ \mu$. This value is quite feasible for the average effective diameter of the particles and can explain the absorption caused by Rayleigh scattering (Fig. 2) as well as the Tyndall effect (Fig. 4).

From the cluster formation it can be estimated that during the heat treatment oxygen diffuses for distances of only 10^{-4} to 10^{-3} cm. Therefore, the oxygen concentration of the sample will remain essentially constant

[9] H. N. Potter, Trans. Am. Electrochem. Soc. **12**, 191 (1907); G. Grube and H. Speidel, Z. Elektrochem. **63**, 339 (1949); H. V. Wartenberg, Z. Elektrochem. **63**, 343 (1949); H. Schaefer and R. Hoernle, Z. anorg. u. allgem. Chem. **263**, 261 (1950); G. Hass, J. Am. Ceram. Soc. **33**, 353 (1950); L. Brewer and R. K. Edwards, J. Phys. Chem. **58**, 351 (1954).

[10] In an initial state possibly interwoven with the silicon matrix.

[11] Only scattering need be regarded, since silicon and the silicon oxides do not absorb in the wavelength range considered here.

which is in agreement with the vacuum fusion analyses (A.5). It also explains the fact that the heat treatment results are independent of the gaseous ambient (A.2).

It is to be expected that the small silicon-oxide clusters contribute to the absorption at 9 μ. For a constant oxygen concentration in the sample, the absorbing power is different for oxygen which is highly dispersed in the silicon lattice[1] and for clusters of high local oxygen concentration. In the latter case, one is dealing with absorbing particles of complex index of refraction, $m=n-in\kappa$ imbedded in a dielectric medium n_0. Mie[12] has given a general treatment of the optical properties of spherical absorbing particles within a dielectric n_0. With the data obtained so far, it is possible to estimate the absorption coefficient at 9 μ as follows.

The absorption coefficient of N_p particles, each of volume V, is given by

$$\alpha=\frac{6\pi n_0}{\lambda}N_pV\,\mathrm{Im}\left(u\frac{m^2-vn_0^2}{m^2+2wn_0^2}\right), \tag{4}$$

where Im denotes the imaginary part of the bracket. u, v, and w are complicated functions of $\gamma=\pi dn_0/\lambda$; they approach unity for $\gamma\rightarrow 0$. In the present case there is $\gamma<0.2$, since $d=0.1\ \mu$, as calculated above. It can be proven that here α is in error by less than 10%, if $u=v=w=1$ is applied. For this calculation, the reasonable assumption of $n=1$ is made, and $n\kappa=2$ is determined from absorption measurements on thin SiO_2 films.[1] Equation (4) can now be rewritten as

$$\alpha=\frac{36\pi}{\lambda}N_pV\frac{n_0^3nn\kappa}{(n^2+n^2\kappa^2)^2+4n_0(n_0^2+n^2-n^2\kappa^2)}. \tag{5}$$

The product VN_p is determined by Eq. (2), and α is calculated as 0.4 cm^{-1}. This absorption coefficient at 9 μ is quite consistent with the experimental results. As discussed in Sec. A.1, the absorption can decrease to about 1.5 cm^{-1} after a heat treatment of fifty hours. At present the residual absorption band at 9 μ cannot be analyzed completely because it is composed of the "background absorption" of 0.8 cm^{-1}, the absorption corresponding to the silicon oxide clusters, and that of the oxygen atoms which might still be in solid solution. To separate the last two components, more extensive investigations of heat treatment at different temperatures are necessary.

The results up to this point may be viewed as follows: During the pulling process, oxygen enters the crystal via the melt. Most of the oxygen might be frozen in, remaining in a dispersed form, as was discussed earlier.[1] A partial grouping of oxygen will occur at nucleation centers during the normal cooling process of the crystal. Heat treatment at around 1000°C forms dielectric particles[13] within the silicon sample. The precipitation[14] of an impurity depends very largely upon nucleation centers in the crystal. Dislocations play a significant role in this respect.[15] It is not surprising, therefore, that variations in the heat treatment effects were observed among different samples. Subsequent heat treatment at higher temperatures (1350°C) seems to reverse the clustering of the oxygen atoms, probably because of the larger solubility of oxygen in the silicon lattice at this temperature.

B. Heat Treatment at 450°C

It was found that in many silicon crystals the oxygen concentration varied greatly along the pulling axis. This fact was utilized to demonstrate the close relationship of the local oxygen concentration in the sample to the formation of donor states during a heat treatment at 450°C.

The results of optical and electrical measurements on a silicon sample before and after heat treatment are presented in Fig. 5. In Fig. 5(a) the absorption coefficient at 9 μ was measured along the length of a silicon crystal. There is an increase of oxygen content from the top to the bottom of the ingot. The starting material consisted of silicon needles (Du Pont) which contained little or no oxygen. During pulling (in vacuum), the melt obviously picked up increasing amounts of oxygen through contact with the quartz crucible. Prior to heat treatment, the p-type sample showed a more or less uniform decrease in resistivity from top to bottom with a small maximum at a position 26 mm from the top. After heat treatment at 440°C for thirty minutes, strong changes in the resistivity profile[16] of the sample appeared [Fig. 5(b)], which indicate the formation of donors. The similarity between the fluctuations in the oxygen concentration[17] [Fig. 5(a)] and the resistivity profile after the heat treatment [Fig. 5(b)] is quite striking. There is a definite increase in donor formation at points of higher oxygen concentration. The optical pattern [Fig. 5(a)] does not change during the short heat treatment at 450°C. This might not be surprising, since the electrical data indicate changes of the order of 10^{13} cm^{-3} whereas the absorption of several cm^{-1} at 9 μ corresponds to an oxygen concentration of the order of 10^{17} cm^{-3}.

[12] G. Mie, Ann. Physik **25**, 377 (1908). The absorption is given by a series. For $\gamma<0.2$ and the values for n and $n\kappa$ used in this calculation, only the first term has to be considered; the higher terms contribute less than 1%.

[13] Since the dielectric constant will be smaller in these areas than in the surrounding silicon, the electric field will be accordingly higher. This fact might have consequences in the high fields of a p-n junction in the breakdown region, as pointed out by L. Apker (private communication).

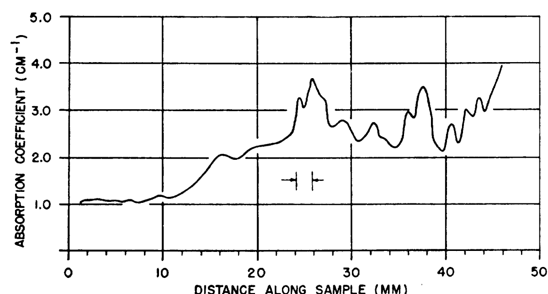
[14] Preliminary measurements indicate that heat-treated samples show larger and more uniform etch pits than untreated specimens. Precipitation can enhance the etching process.

[15] Pearson, Read, and Feldmann, Bull. Am. Phys. Soc. Ser. II, 1, 295 (1956).

[16] A micromanipulator was used for the electrical measurements in Fig. 5(b). Each point represents an average over 1 mm length in the untreated and $\frac{1}{2}$ mm length in the treated sample. Up to 18 mm, the two curves coincide within the experimental accuracy.

[17] The strong changes in oxygen concentration along the length of the ingot are the result of small temperature fluctuations during the pulling process.

A more quantitative correlation between the oxygen concentration in the crystal and the production of donors can be obtained from samples with less pronounced fluctuations in oxygen concentration. In Fig. 6 the absorption coefficient at 9 μ and the resistivity before and after a heat treatment for 105 minutes were measured along the length of an n-type specimen (pulled in argon atmosphere). The decrease in resistivity [Fig. 6(b)], corresponding to the formation of donors during the heat treatment, again follows the absorption pattern [Fig. 6(a)]. Similar measurements were made on a number of different crystals, covering absorption coefficients at 9 μ from 2 cm^{-1} to 7.1 cm^{-1}. During the first two hours of treatment, the formation of donors was found to be approximately proportional to the time of treatment.[18] From the change in resistivity during the treatment, the number of donor states produced per minute, N_D, was calculated.[19] The oxygen concentration [O] is proportional to $\alpha-0.8$, where α is the absorption coefficient at 9 μ. In Fig. 7 the data of 4 n-type samples are summarized.[20] The number of donors produced per minute at specific points of the sample is plotted against the measured value of $\alpha-0.8$. N_D increases rapidly with increasing oxygen content. The empirical line in Fig. 7 has a slope of 4.



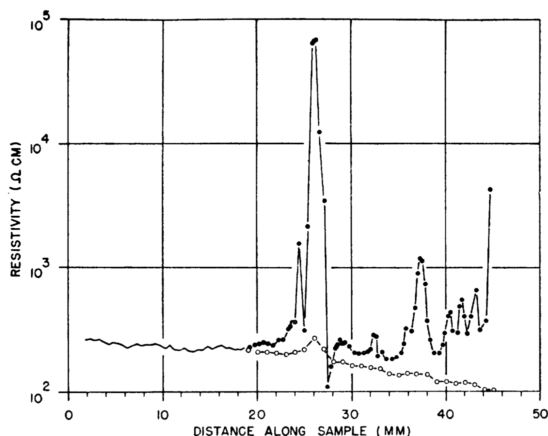


FIG. 5. (a) Absorption coefficient at 9 μ measured along the pulling axis of a silicon crystal; top of the crystal to the left. (b) Resistivity of the same sample (p-type) before (○) and after (●) heat treatment at 450°C for 30 min.

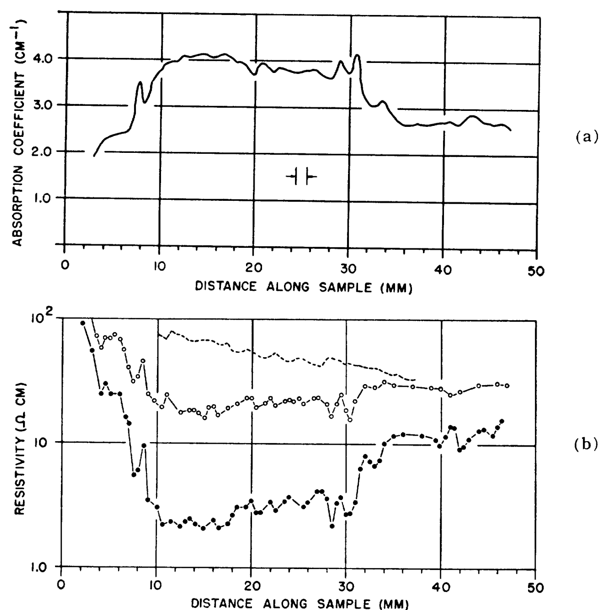


FIG. 6. (a) Absorption coefficient at 9 μ measured along the pulling axis of a silicon crystal; top of the crystal to the left. (b) Resistivity of the same sample (n-type) before (○) and after (●) heat treatment at 450°C for 105 min. Resistivity of a parallel cut before (○) and after (– –) heat treatment at 1000°C for 30 min.

DISCUSSION OF THE HEAT TREATMENT AT 450°C

The strong dependence of N_D on the oxygen concentration can explain a number of experimental findings.

Fuller *et al.*[3] reported first that the skin of a pulled crystal is less affected by a heat treatment at 450°C than its center. Optical measurements during the present study along the cross section of a crystal have shown that the oxygen concentration increases rapidly a short distance below the surface and reaches its maximum value in the center of the crystal. The number of donors produced during the heat treatment is therefore larger in the center of the crystal than in the skin area.

There is a similarity between the absorption pattern [Fig. 6(a)] and the resistivity profile of even the untreated sample [Fig. 6(b)]. This fact suggests that during the normal cooling process in the pulling system, the sample experiences a "heat treatment" long enough to produce donor states of the type discussed above. A sample with the same initial properties as the untreated specimen in Fig. 6(b) (a parallel cut from the same ingot) was heat treated for 30 minutes at 1000°C to annihilate thermally introduced donors.[3] As expected, the resistivity profile is changed quite considerably, and resistivity fluctuations corresponding to

[18] After prolonged heat treatment a different time dependence sets in. (See reference 3.)

[19] The assumption was made that all the impurity states are ionized at room temperature. For mobility data used, see M. B. Prince, Phys. Rev. **93**, 1204 (1954).

[20] At the bottom part of one crystal, deviations from Fig. 7 were found up to a factor of 10.

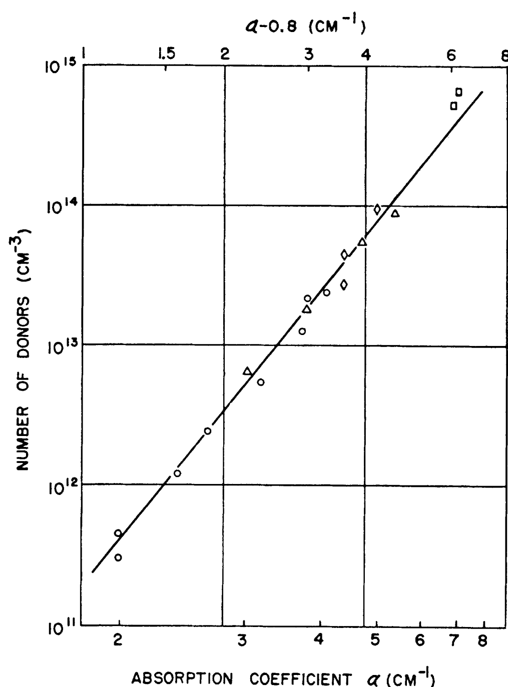


FIG. 7. Number of donor states N_D produced per min during a heat treatment at 450°C as a function of the absorption coefficient α at 9 μ. The different symbols represent data obtained from different crystals.

oxygen fluctuations disappeared (see Fig. 6 around the 30-mm mark). Similar effects were observed in a number of samples. In general it can be said that the resistivity profile of a high resistivity silicon sample can be greatly affected by the formation of donors during the normal cooling of the crystal.

At present, it is not possible to give a final picture of the physical nature of the thermally introduced donors. Nothing is known about the interaction of oxygen with lattice defects and with other impurities. Spin resonance experiments and more data concerning the energy levels of thermally introduced donors[21] will be of great value in solving this problem. In Fig. 7 it was demonstrated that the initial rate of donor production is proportional to the fourth power of the oxygen concentration in the sample. One is therefore tempted to speculate that $[SiO_4]$ complexes are formed during the heat treatment at 450°C, which give rise to singly or multiply charged electrically active donor states. At higher temperatures larger units of silicon-oxide of considerably smaller number may be formed (owing to the higher diffusion constant). It is interesting to note that silicon no longer produces donor states at 450°C after the sample has been previously heated for more than twenty hours at 1100°C. Clustering of oxygen was suggested at this temperature in conjunction with the scattering effects demonstrated in Part A. There seems to be insufficient oxygen remaining in solid solution to produce an appreciable number of donor states.

[21] Morin, Maita, Shulman, and Hannay, Phys. Rev. **96**, 833 (1954). These authors determined from Hall measurements as a function of temperature three energy levels in samples annealed at 475°C.

SUMMARY

During prolonged heat treatment at 1000°C, the absorption band at 9 μ decreases while the oxygen content of the sample remains essentially unchanged. This effect can be explained by the clustering of silicon oxide into particles of smaller dielectric constant than the silicon matrix. Rayleigh scattering was measured close to the fundamental absorption edge of silicon permitting an estimate of the number and diameter of the scattering centers as 5×10^{10} cm^{-3} and 0.1 μ, respectively. The Tyndall Effect was observed in such samples using an infrared image tube, and the scattered light was proven to be highly polarized. Inhomogeneous scattering was attributed to small-scale fluctuations in oxygen concentration associated with the growth-ring pattern of the crystal. Even stronger changes in oxygen content were measured over wider ranges along the pulling axis of silicon single crystals. Heat treatment at 450°C produced donor states in such samples depending upon the oxygen concentration of the specific area in the sample. The number of donor states produced during a heat treatment increased rapidly with the measured oxygen concentration.

ACKNOWLEDGMENTS

The author is greatly indebted to Dr. P. H. Keck for his interest and support of this work and to Dr. H. Kedesdy and Dr. J. Kohn for valuable discussions. He also wishes to thank J. Breslin and E. Unger for their assistance with the experimental measurements. The contribution of silicon crystals from the following research laboratories is greatly appreciated: Bell Telephone, Evans Signal Laboratory, General Electric, Philco, Siemens-Schuckert, and Westinghouse.

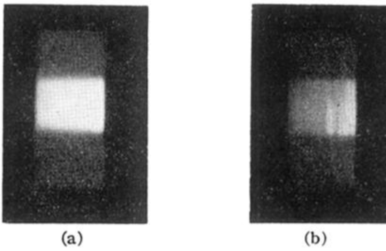


FIG. 4. Photographs taken through an infrared image tube showing the Tyndall Effect in silicon heat treated at 1000°C. The incident light beam is (a) perpendicular, (b) parallel to the pulling direction of the sample. (Magnification 3×.)