PROTON-PRODUCED DEFECTS IN n-TYPE SILICON

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SUMMARY

Defect energy levels and concentrations were determined for n-type silicon single crystals with initial resistivities between 10 and 200 ohm-cm after 22.4-MeV proton irradiations. Two defect energy levels were located: one at 0.17 eV below the bottom of the conduction band and one at 0.41 eV below the bottom of the conduction band. The introduction rate of the oxygen-vacancy complex was independent of the oxygen content of the silicon for the samples investigated. Heat treatment of Czochralski-grown silicon at 1000°C for 65 hours had no effect on the introduction rate of the oxygen-vacancy complex.

INTRODUCTION

With the space program came the problem of the effects of space radiation on the semiconductor devices used aboard spacecraft. Since the particle radiation in space is essentially composed of high-energy electrons and protons, defects produced in semiconductors by these particles are of prime interest. Most of the experimental investigations up to now have been conducted with electrons, neutrons, γ-rays, and some heavier ions. Electron damage in silicon has been studied extensively (refs. 1, 2, 3, and 4). However, studies of proton damage in semiconductor materials have been rather limited.

It was the purpose of the investigation reported in this paper to establish defect concentrations and energy levels for defects produced by 22.4-MeV protons in n-type silicon prepared in three different manners. Measurements of the Hall coefficient were made because it is sensitive to lattice defects. The irradiations were performed at room temperature which enhances vacancy motion.

The proton irradiations were performed at the Oak Ridge National Laboratory's 86-inch cyclotron.

SYMBOLS

E energy of electron

E_A energy of acceptor level
$E_C$  energy at bottom of conduction band

$E_F$  Fermi level

$E_i$  energy of $i$th acceptor level

$E_j$  energy of $j$th donor level

$e$  electronic charge

$f$  Fermi-Dirac distribution function

$h$  Planck constant

$k$  Boltzmann constant

$k'$  electron wave vector

$m_l$  longitudinal mass of electron

$m_n$  effective mass of electron

$m_o$  mass of free electron

$m_t$  transverse mass of electron

$N$  concentration of target atoms

$N_A$  concentration of acceptors

$N_{A,d}$  concentration of defects with deep acceptor levels

$N_{A,i}$  $i$th concentration of acceptors

$N_{A,o}$  concentration of ionized acceptors prior to irradiation

$N_C$  effective density of states in conduction band

$N_{D,j}$  $j$th concentration of donors
The Hall coefficient.- For a semiconductor, the Hall coefficient is given by

\[ R_H = \frac{r}{ne} \]  \hspace{1cm} (1)

where \( R_H \) is the Hall coefficient and \( r \) is a numerical factor which depends on the type of scattering, the statistics of the carriers, and the complexities of the band structure. For lattice scattering and classical statistics, \( r = \frac{3\pi}{8} \) (ref. 5). This value of \( r \) is used in this report.

Semiconductor statistics.- A semiconductor is characterized by the existence of allowed energy bands which are separated by forbidden regions of energy. The outermost band of energy normally populated by electrons is called the valence or filled band. The band higher in energy in which conduction can occur by means of electrons is called the conduction band. The two bands of energy are separated by a forbidden energy gap whose width is approximately 1.1 eV in silicon. Electrons can be introduced into the conduction band by means of thermal excitation from donor levels which are introduced by chemical donors existing in the semiconductor. Also, conduction can occur in the valence band by means
of positive-charge carriers called holes. Holes can be introduced into a semiconductor by doping it with chemical acceptors.

Electrons and holes in a semiconductor behave according to Fermi-Dirac statistics. The probability that a given level at energy \( E \) is occupied by an electron is given by the Fermi-Dirac distribution function

\[
f = \frac{1}{(1 + e^{(E-E_F)/kT})} \tag{2}
\]

where \( E_F \), the Fermi level or energy, is the energy at which the probability of a level being filled with an electron is \( 1/2 \). For a nondegenerate semiconductor (that is, the energies of the electrons in the conduction band are well above the Fermi level), the expression for the electron concentration becomes

\[
n = 2\left(\frac{2\pi m_n kT}{\hbar^2}\right)^{3/2} e^{-(E_C-E_F)/kT} = N_CE^{-(E_C-E_F)/kT} \tag{3}
\]

where \( N_C \) is the effective density of states in the conduction band, \( m_n \) is the effective mass of the electron, and \( E_C \) is the energy of the bottom of the conduction band.

The density-of-states effective mass for n-type silicon is

\[
m_n = 6^{2/3}(m_l m_t^{2})^{1/3} = 1.08m_0 \quad \text{(ref. 6)}
\]

where \( m_l \) is the mass of the free electron, \( m_l \) is the longitudinal mass, and \( m_t \) is the transverse mass of the surfaces of constant energy in \( \vec{k} \)-space which happen to be ellipsoids of revolution. The factor 6 appears because there are six such ellipsoids.

**Radiation-Damage Theory**

**Production of displacements.** When a high-energy proton passes through a semiconductor material, most of the energy lost by the proton is through ionization. However, a small amount of energy is lost through elastic and inelastic interactions of the proton with the nuclei in the crystal. The proton can impart a certain amount of its kinetic energy to the nucleus of any atom with which it interacts. If the amount of energy is sufficient, the atom will be displaced from its normal lattice position. The atom that is displaced by the interaction can interact with other atoms of the crystal to produce other displacements if it has received enough energy during the interaction with the proton. The total number of displacements produced per unit path length per particle is

\[
\frac{dN_d}{d\phi} = N\sigma_d \tilde{\eta} \quad \text{(ref. 7)}
\]

where \( N \) is the concentration of target atoms, \( \sigma_d \) is the total displacement cross section, and \( \tilde{\eta} \) is the average number of displacements resulting from a primary event.

**Ionization.** In a semiconductor, ionization results in the production of electron-hole pairs. However, this is a nonequilibrium condition and the electrons and holes recombine
according to a time constant which varies from a few to hundreds of microseconds at room temperature depending on the impurity concentration. As the electrons and holes recombine, the excess energy is given up to the lattice and, hence, appears as heat. If the rate of ionization were high, the temperature of the silicon could be correspondingly high, and thereby the annealing of the defects that are produced by the irradiation would be enhanced. However, in the experiment described in this report, the beam current from the cyclotron was kept low enough so that annealing due to heating was not significant.

Defect complexes in silicon.—At room temperature, defects which result in changes in the electrical properties of silicon are, in general, not radiation-produced interstitial-vacancy pairs but are defect complexes which are usually formed when vacancies are trapped by impurity atoms (ref. 4). Such defect complexes give rise to electronic energy levels in the forbidden gap of silicon. Watkins (ref. 4) has identified many defect complexes by means of electron-paramagnetic-resonance investigations of radiation-produced defects in silicon. The defect complexes of interest here are those formed in n-type silicon. These complexes include the silicon A-center and E-center.

The silicon A-center is formed by interstitial oxygen trapping a vacancy to become substitutional oxygen. This center gives rise to an acceptor level 0.17 eV below the bottom of the conduction band. Watkins and Corbett (ref. 8) found that the A-center production rate due to 1.5-MeV electrons was reduced by a factor of 2.5 when Czochralski-grown (pulled from a quartz crucible) silicon was heat treated at 1000° C for 100 hours prior to electron irradiation. The heat treatment produces clusters of high oxygen content in the silicon (ref. 9).

The silicon E-center is formed by a vacancy trapped next to a substitutional phosphorus impurity atom (ref. 4). This center was located by Watkins in n-type, vacuum floating-zone silicon in which the oxygen concentration was on the order of $10^{16}$ cm$^{-3}$. The E-center gives rise to a defect energy level approximately 0.40 eV below the bottom of the conduction band.

**METHOD OF DATA ANALYSIS**

When silicon is irradiated with particles of sufficient energy to displace a lattice atom, damage results in the form of lattice defects. As was previously pointed out, these defects are usually defect complexes rather than isolated vacancies and interstitials. The principal contributing factor to the formation of defect complexes is that vacancies are mobile even at 78° K and associate with various impurities in the crystal. The two defect complexes of interest in n-type silicon are the oxygen-vacancy complex (A-center) and the phosphorus-vacancy complex (E-center).
Radiation-produced defects introduce energy levels into the forbidden energy gap of a semiconductor. These levels can be located through the temperature dependence of the majority carrier concentration of the silicon. The condition of electrical neutrality after irradiation is represented by the following expression (ref. 10):

\[
n - p = \sum_{j} \frac{N_{D,j}}{1 + e^{(E_F - E_j)/kT}} - \sum_{i} \frac{N_{A,i}}{1 + e^{(E_i - E_F)/kT}}
\]

where \( n \) is the electron concentration in the conduction band, \( p \) is the hole concentration in the valence band, \( N_{D,j} \) is the \( j \)th concentration of donors either chemically introduced or produced by radiation, \( N_{A,i} \) is the \( i \)th concentration of acceptors, \( E_j \) is the energy of the \( j \)th donor level, and \( E_i \) is the energy of the \( i \)th acceptor level.

Because the n-type silicon used in the experiment had electron concentrations greatly exceeding hole concentrations, \( p \) may be neglected with respect to \( n \). Since all previously observed donor levels due to radiation-produced defects lie in the lower half of the forbidden energy gap and since at room temperature or lower temperatures \( e^{(E_F - E_j)/kT} \) would be very large, these donor-level concentrations may be neglected. The donor levels existing prior to irradiation lie near the bottom of the conduction band and acceptor levels existing prior to irradiation lie near the top of the valence band. For the resistivities used, the Fermi level is near one acceptor level and well above any other acceptor level (in terms of \( kT \)); therefore, the expression for \( n \) becomes

\[
n = N_{D,0} - N_{A,0} - N_{A,d} - \frac{N_A}{1 + e^{(E_A - E_F)/kT}}
\]

where \( E_F \) affects only the fraction of \( N_A \) filled with electrons and \( N_{A,d} \) represents the concentrations of acceptors with energy levels much deeper (>4\( kT \)) in the forbidden energy gap than \( E_A \). The terms \( N_{D,0} \) and \( N_{A,0} \) represent the concentration of ionized donors and acceptors existing prior to irradiation. It was pointed out previously that the free-electron concentration is given by \( n = N_C e^{-(E_C - E_F)/kT} \). Therefore,

\[
n = n_0 - N_{A,d} - \frac{N_A}{1 + \frac{N_C}{n} e^{(E_A - E_C)/kT}}
\]

where \( n_0 = N_{D,0} - N_{A,0} \) is the free-electron concentration prior to irradiation. This process results in a quadratic expression for \( n \), the solution of which is given by

\[
n = \frac{-B + \sqrt{B^2 + 4K}}{2}
\]
where

\[ B = \frac{N_C}{e^{(E_C - E_A)/kT}} - \left( n_0 - N_{A,d} \right) + N_A \]

\[ K = \frac{(n_0 - N_{A,d})N_C}{e^{(E_C - E_A)/kT}} \]

It is possible to determine \( N_A \) and \( E_A \) from a least-squares fit of the theoretical expression to the experimental values of free-carrier concentration as a function of the reciprocal of the absolute temperature.

If \( N_A \) is sufficiently large, \( E_A \) can be determined in a more straightforward manner. This method is treated in the appendix and results in the following expression:

\[ \ln nT^{-3/2} \approx \ln \frac{2(2\pi mn_k)^{3/2}(n_0 - N_{A,d})}{\hbar^3 N_A} - \frac{(E_C - E_A)}{kT} \] (8)

The slope of the straight portion of a plot of \( \ln nT^{-3/2} \) as a function of \( T^{-1} \) locates \( E_A \) because

\[ \frac{d(\ln nT^{-3/2})}{d(T^{-1})} \approx \frac{(E_C - E_A)}{k} \]

DESCRIPTION OF EXPERIMENTAL PROCEDURES

Three types of silicon were used in this experiment: vacuum floating zone, Czochralski grown, and Czochralski grown which had been heated to 1000° C. All the silicon was phosphorus doped and possessed nominal resistivities of 10 and 100 ohm-cm. The vacuum floating-zone and Czochralski-grown silicon were obtained commercially. The third type of silicon was obtained through heat treatment of Czochralski-grown silicon in a helium-atmosphere furnace at a temperature of 1000° ± 20° C for 65 hours to precipitate some of the oxygen in the silicon (ref. 9). The Czochralski-grown samples of the same resistivity were obtained from the same ingot. Checks of the 9-μm infrared absorption band were made for all the silicon ingots at liquid-nitrogen temperature as an indication of the oxygen content.

Silicon slices (0.038-cm thick) oriented in the [111] direction were cut from silicon ingots by means of a diamond saw. From these slices, samples were cut with an ultrasonic impact grinder. The samples were then mechanically lapped to thicknesses less than 0.025 cm. Next, the silicon samples were etched in a chemical etchant (five parts hydrofluoric acid, five parts acetic acid, and eight parts nitric acid). The tabs of the
samples were then plated with nickel through an electrodeless chemical plating method (ref. 11). The final thicknesses of the samples were measured with a micrometer. The thickness measurements were made at three points along the body of each sample. Finally, leads were soldered to the nickel-plated tabs of the samples (see fig. 1). With a sample of this particular shape, it is possible to obtain ohmic contacts since this sample shape offers the advantages of reduction of contact resistance and minimization of carrier injection.

The proton irradiations were performed at the Oak Ridge National Laboratory's 86-inch cyclotron and were conducted at room temperature. The energy of the protons from the cyclotron had been determined previously to be 22.4 ± 0.1 MeV by the cyclotron personnel. The silicon samples were mounted immediately behind a thin-wall ionization chamber which is used for the determination of the beam current of the protons from the cyclotron. A collimator was placed in the beam pipe in front of the ionization chamber. By exposing photographic film and darkening glass slides with the proton beam, the beam spot at the sample position was determined to be approximately 1/2 inch (1.27 cm) in diameter. The proton-beam current and the integrated proton flux were determined from the output of the ionization chamber which had been calibrated against the output of a Faraday cup by the cyclotron personnel. This calibration is checked periodically by means of activation analysis. The flux rate used for the irradiation was approximately $2 \times 10^9$ protons-cm$^{-2}$-sec$^{-1}$.

The Hall coefficient of the silicon was determined as a function of temperature prior to and subsequent to proton irradiation at Oak Ridge National Laboratory in a liquid-nitrogen cryostat (see figs. 2 and 3). Prior to any measurements, the samples were mounted on a cold finger which could be in contact with or isolated from liquid nitrogen by means of a manually controlled valve which regulated the flow of liquid nitrogen to the cold finger. The temperature of the sample was controlled by the amount of heat emitted by a heater coil wound inside the sample chamber. The sample chamber was filled with helium gas to reduce any temperature gradient across the sample. The temperature of the sample could be maintained to ±0.5°C with this type of temperature-control system.

The Hall voltage and the current through the sample were measured. The current was determined from the voltage across a 1000-ohm resistor. All voltage measurements were made with a precision digital voltmeter; the accuracies of the voltage measurements were better than 0.1 percent. The magnetic field was maintained at 2700 gauss during the Hall coefficient determinations and was measured with a rotating-coil gauss meter. The overall absolute accuracy of the Hall coefficient was 10 percent or better. Most of the uncertainty was in the measurement of sample dimensions.
RESULTS AND ANALYSIS

Each of the six samples listed in table I was temperature cycled (the temperature dependence of the electron concentration was determined) before and after proton irradiation to allow the defect energy levels and the defect concentrations to be determined. Two resistivities of each kind of silicon were included in the experiment.

Figure 4 shows a plot of the carrier concentration as a function of the reciprocal of the temperature before and after irradiation to an integrated flux of $3.4 \times 10^{12}$ protons-cm$^{-2}$ for sample FZ-1. FZ-1 was a sample of vacuum floating-zone silicon with an initial resistivity of 14.7 ohm-cm. The values of $E_A$ and $N_A$ which were obtained from the theoretical fit (eq. (7)) were $E_A = E_C - 0.16$ eV and $N_A = 7.90 \times 10^{13}$ cm$^{-3}$. This defect level appears to be the same one observed by Wertheim (ref. 2) and Hill (ref. 1) in electron-irradiated silicon. Watkins and Corbett have labeled the defect responsible for this energy level an oxygen-vacancy complex, the silicon A-center (ref. 8). The concentration of acceptors with deep levels (levels much lower in the forbidden energy gap than the level associated with the silicon A-center) was determined to be $1.02 \times 10^{14}$ cm$^{-3}$ from the radiation-produced change in the carrier concentration at room temperature.

A defect energy level deeper in the forbidden energy gap was located by irradiation of FZ-1 to a larger integrated flux and then temperature cycling the specimen. In figure 5, the product of carrier concentration times the absolute temperature to the $-3/2$ power is plotted as a function of the reciprocal of the temperature for sample FZ-1 after irradiation to an integrated flux of $1.55 \times 10^{13}$ protons-cm$^{-2}$. From the slope of the plot (eq. (8)), a defect energy level is located at $E_C - 0.41$ eV. This level has also been located in electron-irradiated silicon by Hill (ref. 1). According to Watkins (ref. 4), the defect responsible for this level is the silicon E-center which is a vacancy trapped next to a substitutional phosphorus atom.

Figure 6 shows results obtained with sample FZ-2 which had an initial room-temperature resistivity of 97.2 ohm-cm. The carrier concentration is plotted as a function of the reciprocal of the temperature before and after a proton irradiation of $6.9 \times 10^{11}$ protons-cm$^{-2}$. The theoretical fit to the experimental curve obtained after bombardment gave the following: $E_A = E_C - 0.15$ eV and $N_A = 1.04 \times 10^{13}$ cm$^{-3}$. The concentration of acceptors with deep levels was $1.01 \times 10^{13}$ cm$^{-3}$. The defect level due to the silicon E-center was not located in this sample because the sample was not irradiated heavily enough.

Two samples of Czochralski-grown silicon were also irradiated and then the temperature dependence of the carrier concentration was determined. Figure 7 shows results obtained with sample CZ-2 which had a room-temperature resistivity of
22.4 ohm-cm prior to irradiation. By means of the theoretical fit to the experimental curve obtained after an irradiation to \(3.4 \times 10^{12}\) protons-cm\(^{-2}\) the energy level was determined to be 0.17 eV below the bottom of the conduction band \((E_A = E_C - 0.17\ eV)\) and the concentration of centers giving rise to this energy level was determined to be \(6.21 \times 10^{13}\) cm\(^{-3}\). Here again, the energy level at \(E_C - 0.17\ eV\) is attributed to the silicon A-center. The concentration of acceptors with deep levels was found to be \(3.70 \times 10^{13}\) cm\(^{-3}\). Figure 8 shows curves obtained before and after irradiation for sample CZ-3 which had a resistivity of 117 ohm-cm prior to irradiation. A theoretical fit to the experimental curve obtained after irradiation to \(6.9 \times 10^{11}\) protons-cm\(^{-2}\) yielded the following: \(E_A = E_C - 0.18\ eV\) and \(N_A = 1.15 \times 10^{13}\) cm\(^{-3}\). The concentration of acceptors with deep levels was \(7.24 \times 10^{12}\) cm\(^{-3}\).

Finally, two samples of Czochralski-grown silicon which had been heated to \(1000^\circ C\) for 65 hours were irradiated and temperature cycled. Figure 9 shows curves of the carrier concentration as a function of the reciprocal of the temperature for sample CH-2 which had an initial resistivity of 20.2 ohm-cm. The sample was irradiated to an integrated flux of \(3.4 \times 10^{12}\) protons-cm\(^{-2}\). The theoretical fit to the curve obtained after irradiation gave the following values: \(E_A = E_C - 0.18\ eV\) and \(N_A = 6.95 \times 10^{13}\) cm\(^{-3}\). The concentration of acceptors with deep levels was \(3.62 \times 10^{13}\) cm\(^{-3}\). Figure 10 shows experimental curves of the carrier concentration as a function of the reciprocal of the temperature before and after irradiation to \(6.9 \times 10^{11}\) protons-cm\(^{-2}\) for sample CH-3. This sample had a room-temperature resistivity of 182 ohm-cm prior to irradiation. The theoretical fit to the experimental curve obtained after irradiation yielded \(E_A = E_C - 0.18\ eV\) and \(N_A = 1.23 \times 10^{13}\) cm\(^{-3}\). The concentration of acceptors with deep levels was found to be \(7.98 \times 10^{12}\) cm\(^{-3}\).

The concentrations and energy levels of A-centers and concentrations of centers giving rise to deep acceptor levels are listed in Table I, in addition to the sample number and integrated flux. This table serves as a basis for comparison of the three types of silicon used in the experiment. Because FZ-1, CZ-2, and CH-2 had approximately the same resistivity and were irradiated to the same integrated flux, they can be compared. Similarly, FZ-2, CZ-3, and CH-3 can be compared.

A slightly larger concentration of A-centers was produced in FZ-1 than was produced in CZ-2 or CH-2. This result appears to be somewhat out of line with FZ-2, CZ-3, and CH-3 where the concentration of A-centers appears to be slightly larger in CZ-3 and CH-3 than in FZ-2. The concentration of A-centers appears to be surprisingly large in the vacuum floating-zone silicon. It would appear that the introduction rate of A-centers is independent of oxygen concentration, at least for the group of samples investigated here. This observation is somewhat surprising because the oxygen concentration in the vacuum floating-zone silicon was on the order of \(10^{16}\) cm\(^{-3}\) while the oxygen concentration in the Czochralski-grown silicon was greater than \(10^{17}\) cm\(^{-3}\) (verified by
measurements of the 9-µm absorption band). One plausible explanation is that the formation of the silicon A-center is not directly proportional to the oxygen concentration when it is much greater than the chemical impurity concentration which is the case with the silicon used in this investigation. Corbett and his coworkers (ref. 12) have found that the intensity of the 12-µm infrared absorption band, which is due to the silicon A-center, cannot be correlated simply with oxygen content alone.

As can be seen from table I, the heat treatment had little effect on the A-center introduction rate. A check of the 9-µm infrared absorption band, which is due to silicon-oxygen molecular vibrations (ref. 9), revealed that the intensity of this band had been reduced by only a factor of 1.8 as a result of heat treatment. Thus, probably not enough oxygen was precipitated to have an effect on the A-center introduction rate.

A larger concentration of deep centers (that is, centers giving rise to deep acceptor levels) is produced in vacuum floating-zone silicon than in either type of Czochralski-grown silicon. This result would mean that the total concentration of defects was greater in FZ-1 than in CZ-2 and CH-2. Similar behavior has been observed by Chris Gross of the Langley Research Center when vacuum floating-zone and Czochralski-grown silicon were bombarded with cobalt-60 γ-rays and 2.0-MeV electrons. At present, this behavior cannot be explained by existing theory.

In all cases, the concentration of A-centers produced was greater than the concentration of deep centers produced in the two types of Czochralski-grown silicon. However, in vacuum floating-zone silicon, the concentration of deep centers was greater than or equal to the concentration of A-centers.

The results in table I were obtained from theoretical fits to experimental data for one level of integrated flux for each sample. The samples were irradiated to higher levels of integrated flux, but, in general, the theoretical fits were not nearly as good as the theoretical fits that are presented here. It appears that at higher levels of irradiation, the simple mathematical model used here will not completely describe the situation.

CONCLUSIONS

Three types of phosphorus-doped silicon were irradiated with 22.4-MeV protons. The following conclusions were derived from the experiment:

1. A defect energy level approximately 0.17 eV below the bottom of the conduction band is introduced into n-type silicon by proton irradiation. This level is attributed to an oxygen-vacancy complex (silicon A-center).

2. A defect energy level approximately 0.41 eV below the bottom of the conduction band is produced in n-type silicon by proton irradiation. This defect level is attributed to a phosphorus-vacancy complex (silicon E-center).
3. The introduction rate of the silicon A-center appeared to be independent of the oxygen content of the silicon for the resistivities studied.

4. Heat treatment of Czochralski-grown silicon to 1000°C for 65 hours had little or no effect on the introduction rate of the silicon A-center.

Langley Research Center,
National Aeronautics and Space Administration,
Langley Station, Hampton, Va., June 18, 1968,
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APPENDIX

A METHOD FOR DETERMINING A DEFECT ENERGY LEVEL

An expression for the carrier concentration of n-type silicon can be written as follows:

\[
\begin{align*}
\text{n} &= N_{\text{D},\text{o}} - N_{\text{A},\text{o}} + \sum_j \left[ \frac{N_{\text{D},j}}{1 + e^{(E_F - E_j)/kT}} \right] - \sum_i \left[ \frac{N_{\text{A},i}}{1 + e^{(E_i - E_F)/kT}} \right] \\
\end{align*}
\]

where \( N_{\text{D},\text{o}} \) represents the ionized donor concentration, \( N_{\text{A},\text{o}} \) represents the ionized acceptor concentration either introduced chemically or produced by radiation, \( N_{\text{A},i} \) is \( i \)th concentration of acceptors, \( E_j \) is energy of the \( j \)th donor level, and \( E_i \) is energy of the \( i \)th acceptor level. Because all previously noted donors produced by irradiation lie in the lower half of the forbidden energy gap, and because \( e^{(E_F - E_j)/kT} \) would be very large, their contribution is negligible. If the assumption is made that the acceptor level of interest lies well away from any other acceptor level (in terms of \( kT \)), the expression for \( n \) becomes

\[
\begin{align*}
\text{n} &= N_{\text{D},\text{o}} - N_{\text{A},\text{o}} - N_{\text{A},\text{d}} - \frac{N_{\text{A}}}{1 + e^{(E_A - E_F)/kT}} \\
\end{align*}
\]

where \( E_F \) is assumed to affect only the fraction of \( N_A \) filled with electrons and \( N_{\text{A},\text{d}} \) represents the concentrations of acceptors with energy levels much deeper in the forbidden energy gap than \( E_A \). Since \( n = N_{\text{D},\text{o}} - N_{\text{A},\text{o}} \) is the free-electron concentration prior to irradiation,

\[
\begin{align*}
\text{n} &= n_0 - N_{\text{A},\text{d}} - \frac{N_{\text{A}}}{1 + e^{(E_A - E_F)/kT}} \\
\end{align*}
\]

If \( E_A - E_F > 3kT \), the equation becomes

\[
\begin{align*}
\text{n} &\approx n_0 - N_{\text{A},\text{d}} - N_{\text{A}} e^{-(E_A - E_F)/kT} \\
\end{align*}
\]

Since \( n = N_{\text{C}} e^{-(E_C - E_F)/kT} \),

\[
\begin{align*}
\text{n} &\approx n_0 - N_{\text{A},\text{d}} - \frac{N_{\text{A}} n}{N_{\text{C}}} e^{(E_C - E_A)/kT} \\
\end{align*}
\]
APPENDIX

and

\[ n \left[ 1 + \frac{N_A e^{(E_C - E_A)/kT}}{N_C} \right] \approx n_0 - N_{A,d} \]

If \( N_A \) is much greater than \( \frac{N_C}{e^{(E_C - E_A)/kT}} \), then

\[ n \approx \frac{(n_0 - N_{A,d}) N_C}{N_A} e^{-(E_C - E_A)/kT} \]

Finally,

\[ n T^{-3/2} \approx \frac{2(2\pi m_n kT)^{3/2}}{h^3} \frac{(n_0 - N_{A,d})}{N_A} e^{-(E_C - E_A)/kT} \]

and

\[ \ln n T^{-3/2} \approx \ln \frac{2(2\pi m_n k)^{3/2}}{h^3 N_A} \frac{(n_0 - N_{A,d})}{N_A} - \frac{(E_C - E_A)}{kT} \]

The slope of the straight portion of a plot of \( \ln n T^{-3/2} \) as a function of \( T^{-1} \) locates \( E_A \) because

\[ \frac{d(\ln n T^{-3/2})}{d(T^{-1})} \approx -\frac{(E_C - E_A)}{k} \]
REFERENCES


<table>
<thead>
<tr>
<th>Sample</th>
<th>Initial resistivity, ohm-cm</th>
<th>Irradiation flux, protons-cm$^{-2}$</th>
<th>Energy level</th>
<th>A-center concentration, cm$^{-3}$</th>
<th>Deep-center concentration, cm$^{-3}$</th>
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<td>a FZ-1</td>
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<td>$1.01 \times 10^{13}$</td>
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<tr>
<td>b CZ-2</td>
<td>22.4</td>
<td>$3.4 \times 10^{12}$</td>
<td>$E_C - 0.17$ eV</td>
<td>$6.21 \times 10^{13}$</td>
<td>$3.70 \times 10^{13}$</td>
</tr>
<tr>
<td>b CZ-3</td>
<td>117.0</td>
<td>$6.9 \times 10^{11}$</td>
<td>$E_C - 0.18$ eV</td>
<td>$1.15 \times 10^{13}$</td>
<td>$7.24 \times 10^{12}$</td>
</tr>
<tr>
<td>c CH-2</td>
<td>20.2</td>
<td>$3.4 \times 10^{12}$</td>
<td>$E_C - 0.18$ eV</td>
<td>$6.95 \times 10^{13}$</td>
<td>$3.62 \times 10^{13}$</td>
</tr>
<tr>
<td>c CH-3</td>
<td>182.0</td>
<td>$6.9 \times 10^{11}$</td>
<td>$E_C - 0.18$ eV</td>
<td>$1.23 \times 10^{13}$</td>
<td>$7.98 \times 10^{12}$</td>
</tr>
</tbody>
</table>

*a* Floating-zone silicon.

*b* Czochralski-grown silicon.

*c* Czochralski-grown and heated silicon.
Figure 1.- Silicon sample.
Figure 2.- Experimental setup for determining the electrical conductivity and the Hall coefficient as a function of temperature.
Figure 3.- Schematic of experimental setup.
Figure 4.- Carrier concentration as a function of the reciprocal of temperature for sample FZ-1 irradiated with 22-MeV protons.
Figure 5.- Carrier concentration multiplied by temperature$^{-3/2}$ as a function of the reciprocal of temperature for sample FZ-1 irradiated with 22-MeV protons to an integrated flux of $1.55 \times 10^{13}$ protons-cm$^{-2}$. 

$\varepsilon_C = 0.41$ eV
Figure 6.- Carrier concentration as a function of the reciprocal of temperature for sample FZ-2 irradiated with 22-MeV protons.
Figure 7.- Carrier concentration as a function of the reciprocal of temperature for sample CZ-2 irradiated with 22-MeV protons.
Figure 8.- Carrier concentration as a function of the reciprocal of temperature for sample CZ-3 irradiated with 22-MeV protons.
Figure 9.- Carrier concentration as a function of the reciprocal of temperature for sample CH-2 irradiated with 22-MeV protons.
Figure 10.- Carrier concentration as a function of the reciprocal of temperature for sample CH-3 irradiated with 22-MeV protons.
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