Effects of Chemical Impurities on the Radiation Damage Constant of Silicon Solar Cells

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The modified damage constant, \( K_L = \left(1/L_i^2 - 1/L_0^2\right) \Phi^{-1} \), is obtained from the drop rate of the photo-current at 1.0 \( \mu \)m monochromatic light irradiation, where the minority carrier diffusion length in the bulk region before \( \gamma \)-irradiation, \( L_0 \), is estimated by fitting the observed spectral response curve to those calculated with the diffusion length as parameter. The values \( L_i \) and \( \Phi \) represent the minority carrier diffusion length after \( \gamma \)-irradiation, and the total flux of incident \( \gamma \)-ray photons, respectively. When N/P-type cells are contaminated with Cu, the values of \( K_L \) by about one order of magnitude compared with non-doped cells, while those of the P/N-type cell contaminated with either Cu or Ni are only slightly smaller than when not doped. The \( K_L \) values of the pulled (C-Z) bulk P/N-type cell are about 1/2 those of the floating zone (F-Z) bulk cell. The curves of \( K_L \) of the non-doped F-Z and C-Z bulk P/N-type cell vs. total dosage begin to decrease from a point below \( 10^{14} \) photons/cm\(^2\) total dose. Also, the damage constant, \( K = (\tau_i^{-1} - \tau_0^{-1}) \Phi^{-1} \), of n-type floating zone (F-Z) and pulled (C-Z) bulk P/N-type cells and of p-type C-Z bulk N/P-type cells, both \( \gamma \)-irradiated, is seen to increase with dopant concentration in the bulk region.

KEYWORDS: radiation effects, gamma radiation, photon beams, radiation dose, silicon solar cell, impurities, carriers, diffusion length, spectral response, floating zone bulk cell, pulled bulk cell, copper

I. INTRODUCTION

Many reports have been published concerning radiation damage in silicon. The aim of these papers is to find a better method of treating the bulk crystal for producing material with which to construct large radiation-resistant equipment\(^{(1)}\)\(^{-(3)}\). Particular reference has been made by several authors to the effects of dopants and their concentrations and the content of O on \( \gamma \)-irradiated silicon\(^{(4)}\)\(^{-(8)}\). The results of their reports, agree with each other only in the case of the floating zone (F-Z) n-type silicon crystal, in regard to which it is concluded that the dominant recombination center at room temperature is the E-center (P-vacancy complex center). Nakano et al.\(^{(6)}\) have pointed out that the predominant recombination center in \( \gamma \)-irradiated F-Z and pulled (C-Z) n-type silicon is the E-center, and they also anticipate that the predominant recombination center in p-type silicon may be the B-vacancy complex (J'-center). On the other hand, Hirata et al.\(^{(7)}\)\(^{(8)}\) have reported that the predominant recombination center in \( \gamma \)-irradiated crystals other than the F-Z n-type crystal is the A-center. From the experimental results under low temperature \( \gamma \)-irradiation, Cheng & Lori\(^{(9)}\) have found that one type of defect exists in p-type silicon at room temperature, which anneals at about 350°K, and this stage is due to the annealing of some vacancy-dopant complexes. Detailed studies of the defects in p-type silicon, irradiated at room temperature, are reported by Nakashima & Inuishi\(^{(10)}\). In all p-type silicon, the most effective recombination center at about 150°K is the A-center, which lies 0.17 eV below the conduction band, and that at around room temperature it is a center that has an energy level 0.3 eV above the valence band. This center is considered contain an acceptor impurity such as B or Ga.

To develop a silicon crystal with larger radiation-resistance, the doping effects of impurities have so far been examined only in the n-type single crystal\(^{(11)}\) and the P/N-type cell\(^{(12)}\). The decrease of minority carrier lifetime by \( \gamma \)-irradiation in Cu- or Fe-doped F-Z n-type silicon crystals is much smaller than that in nondoped crystals.

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Such properties of radiation-resistance are attributed to the following mechanism: in Cu- or Fe-doped crystals, Cu- or Fe-vacancy complex centers are formed and the capture cross section of these complex centers for holes is smaller than that of the E-center in non-contaminated crystals. The radiation-resistant properties of the Li-doped P/N-type cell is due to spontaneous annealing of the Li-vacancy complex defects at room temperature. The Li-dopant is useful only in the P/N-type cell, since it acts as a donor impurity. The short-circuit current of the silicon solar cell can be represented with the minority carrier diffusion length in the bulk region of the cell. Hence, the radiation-damage properties of the solar cell can be considered to derive from the degradation of the minority carrier diffusion length in the bulk region of the cell.

The aim of the present study is to examine the effects of Cu or Ni, and O on the radiation damage of P/N- and N/P-type cells, and to find a more radiation-resistant Cu-doped N/P-type cell.

II. EXPERIMENTAL PROCEDURE

1. Sample Preparation and Measurement

Boron-doped p-type and P-doped n-type crystals, grown by pulled or floating zone method, were chosen for bulk material. Copper- and Ni-doping of the bulk crystal was carried out by impurity diffusion techniques in N₂ gas flow under a temperature range from 500° to 850°C. As impurity sources, cupric nitrate (Cu(NO₃)₂·3H₂O) for Cu and nickel chloride (NiCl₂·6H₂O) for Ni were used. The p-n junction were formed by the diffusion of B into n-type and P into p-type bulk crystals, which had been contaminated with Cu or Ni. The samples were polished to a level that had an angle of 3° with respect to the original surface and defined by an etchant, and then the junction depth of the cell was measured by microscopic observation. The junction depth of the Cu-doped N/P-type cell was found to be about 30% larger than those of non-contaminated cells.

A radiant efficiency of 7 to 10% under sunlight were obtained for the solar cells, and they are not coated with antireflecting film such as SiO. The maximum output power of the most heavily Cu-doped N/P-type cell before γ-irradiation was about 67% of those non-doped. The samples examined are summarized in Table 1; the number of samples in each group was from 3 to 7.

The spectral response of photocurrents was measured at room temperature under excitation with monochromatic light with a Hitachi EP-3 spectrometer, and the incident photon numbers were calculated by measuring the light energy with a Charles Reader PR-3 thermocouple. Gamma-irradiation from a 60Co source with a dose rate of about 7×10¹⁴ photons/cm².hr was performed at room temperature. The relative efficiency of the cells after irradiation to 2×10¹⁷ γ-ray

<table>
<thead>
<tr>
<th>Sample</th>
<th>Type</th>
<th>(X_j(\mu m))</th>
<th>Bulk resistivity ((\Omega\cdot cm))</th>
<th>Crystal growth method</th>
<th>Oxygen concentration (cm⁻³)</th>
<th>Chemical impurity</th>
</tr>
</thead>
<tbody>
<tr>
<td>NC-1</td>
<td>P/N</td>
<td>2.0</td>
<td>0.1~1.0</td>
<td>pulled</td>
<td>(5\times10^{17})</td>
<td>Cu-doped 750°C×180 min</td>
</tr>
<tr>
<td>NC-2</td>
<td>P/N</td>
<td>2.0</td>
<td>5</td>
<td>pulled</td>
<td>(5\times10^{17})</td>
<td>Ni-doped 700°C×180 min</td>
</tr>
<tr>
<td>NC-3</td>
<td>P/N</td>
<td>2.0</td>
<td>8~12</td>
<td>pulled</td>
<td>(5\times10^{17})</td>
<td>Cu-doped 750°C×50 min</td>
</tr>
<tr>
<td>NF-1</td>
<td>P/N</td>
<td>2.0</td>
<td>0.1~1.0</td>
<td>F:Z</td>
<td>(\leq10^{16})</td>
<td>Cu-doped 600°C×30 min</td>
</tr>
<tr>
<td>NF-2</td>
<td>P/N</td>
<td>2.0</td>
<td>8~12</td>
<td>F:Z</td>
<td>(\leq10^{16})</td>
<td></td>
</tr>
<tr>
<td>PC-1</td>
<td>N/P</td>
<td>2.3</td>
<td>2~5</td>
<td>pulled</td>
<td>(5\times10^{17})</td>
<td></td>
</tr>
<tr>
<td>PC-2</td>
<td>N/P</td>
<td>1.5</td>
<td>5~10</td>
<td>pulled</td>
<td>(5\times10^{17})</td>
<td></td>
</tr>
<tr>
<td>PC-3</td>
<td>N/P</td>
<td>2.0</td>
<td>15~20</td>
<td>pulled</td>
<td>(5\times10^{17})</td>
<td></td>
</tr>
<tr>
<td>PC-70</td>
<td>N/P</td>
<td>7.0</td>
<td>5~10</td>
<td>pulled</td>
<td>(5\times10^{17})</td>
<td></td>
</tr>
<tr>
<td>N(Cu)-1</td>
<td>P/N</td>
<td>2.0</td>
<td>0.1~1.0</td>
<td>pulled</td>
<td>(5\times10^{17})</td>
<td></td>
</tr>
<tr>
<td>N(Ni)-2</td>
<td>P/N</td>
<td>2.0</td>
<td>0.1~1.0</td>
<td>pulled</td>
<td>(5\times10^{17})</td>
<td></td>
</tr>
<tr>
<td>P(Cu)-1</td>
<td>N/P</td>
<td>2.0</td>
<td>5~10</td>
<td>pulled</td>
<td>(5\times10^{17})</td>
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<td>P(Cu)-2</td>
<td>N/P</td>
<td>2.0</td>
<td>5~10</td>
<td>pulled</td>
<td>(5\times10^{17})</td>
<td></td>
</tr>
</tbody>
</table>
photons/cm² was estimated by measuring the short-circuit current at room temperature under illumination with a 5000lx W lamp.

2. Method of Estimation of Damage Constant

To estimate the effect of radiation damage on the collecting efficiency of the cell, the change in the minority carrier lifetime has to be related to the total radiation flux to which the cell has been subjected. The relationship between the minority carrier lifetime \( \tau \) and the total flux \( \Phi \) of incident \( \gamma \)-ray photons, which introduce crystal defects acting as recombination centers, can be expressed by

\[
1/\tau_i - 1/\tau_0 = K \cdot \Phi, \tag{1}
\]

where subscripts 0 and \( i \) denote before and after irradiation, respectively. The change of the minority carrier diffusion coefficient brought about by radiation damage is much smaller than that of the lifetime, so that Eq. (1) can be expressed in terms of carrier diffusion length\(^{11} \): 

\[
\Delta(1/L^2) = 1/L_i^2 - 1/L_0^2 = K_L \cdot \Phi, \tag{2}
\]

where, \( K_L = \Delta(E_0) \cdot \sigma \cdot v \cdot f(E_r - E_F) \cdot D^{-1} \) and \( \Delta(E_0) \) are probability that an incident particle produces a recombination center, \( \sigma \) is cross section for capture of minority carrier, \( v \) thermal velocities of the carrier, \( E_r \) energy level of recombination center, \( E_F \) Fermi level, \( f(E_r - E_F) \) probability that the recombination center is occupied by majority carrier, and \( D \) minority carrier diffusion coefficient. Here \( L \) is the minority carrier diffusion length in the bulk region, while the subscripts 0 and \( i \) denote before and after \( \gamma \)-irradiation, respectively. In general, the minority carrier diffusion length in the bulk region of the cell is derived from electron injection measurements, but in this study we estimated it by measurements of the drop rate of photocurrent by infrared monochromatic light irradiation.

As the minority carrier lifetime and diffusion coefficient in the diffused layer of the cell are much smaller than in the bulk region of the cell, the photocurrent derived under the long wavelength monochromatic light irradiation is mostly due to the bulk region response.

In the case of P/N-type cell, the photocurrent \( I(\lambda) \) at the wavelength \( \lambda \) can be expressed, under the condition of \( W \gg L \), by\(^{12} \):

\[
I(\lambda) = q \cdot \frac{\alpha(\lambda) \cdot L}{1 + \alpha(\lambda) \cdot L} \cdot H \cdot e^{-\alpha(\lambda) x_f}, \tag{3}
\]

where \( W \) is the thickness of the cell, \( \alpha(\lambda) \) absorption coefficient, \( x_f \) junction depth, \( H \) incident photon number, and \( L \) the diffusion length. If the wavelength and the intensity of the illuminated light are constant during successive \( \gamma \)-irradiations of the cell, Eq. (3) can be reduced to

\[
I(\lambda) = A \cdot \frac{\alpha(\lambda) \cdot L}{1 + \alpha(\lambda) \cdot L}, \tag{4}
\]

where \( A \) is a constant. The minority carrier diffusion length of the damaged bulk of the cell is obtained by

\[
L_i = \frac{1}{1 - b \cdot \frac{1}{\alpha(\lambda)}}, \tag{5}
\]

where \( b = \frac{\alpha(\lambda) \cdot L_0}{1 + \alpha(\lambda) \cdot L_0}, \quad a = \frac{I(\lambda(=1.9\mu m))}{I(\lambda(=1.9\mu m))}, \)

the subscripts 0 and \( i \) denoting before and after \( \gamma \)-irradiation, respectively.

The carrier diffusion length before \( \gamma \)-irradiation is obtained from the diffusion coefficient and lifetime. The diffusion length \( L_0 \) in the bulk region before \( \gamma \)-irradiation is estimated by fitting the observed spectral response curve to that calculated with diffusion length as parameter, using the diffusion coefficient obtained by Prince\(^{13} \). The values of \( L_i \) estimated by Eq. (5) using the drop rate of photocurrent coincide precisely with the results derived from the electron injection method\(^{14} \). In that work, \( L_i \) was obtained with the drop rate of photocurrent under 1.0 \( \mu \)m monochromatic light irradiation.

III. EXPERIMENTAL RESULTS AND DISCUSSIONS

1. Effects of Cu and Ni Doping

Gamma-induced change in \( \Delta(1/L^2) \), or \( L_i^{-2} - L_0^{-2} \), of the Cu- and Ni-doped C-Z bulk P/N-type cells and N/P-type cells are plotted in Figs. 1 and 2, respectively.

As seen from Fig. 1, \( L_i^{-2} - L_0^{-2} \) of the damaged Cu- or Ni-doped P/N-type cells is slightly smaller than that of the non-doped up to a dosage of \( 5 \times 10^{16} \) photons/cm², and not markedly dependent on whether doping is by Cu or Ni. The tendency of this Cu- or Ni-doping effect is similar to the results reported by Nakano & Inuishi

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on damaged n-type Cu-contaminated F·Z single crystal\textsuperscript{(11)}, and the explanation was provided by a model in which the Cu-vacancy complex center has a smaller capture cross section for holes than the E-center. In the present experiment, the non-contaminated cell in Fig. 1 has given a curve that begins to deviates from the 45° straight line beyond a certain point. This must be associated with a change in the Fermi level in the n-type bulk region. It is reasonable, since the change in the majority carrier concentration in the non-doped n-type bulk region becomes appreciable when the dose reaches this level. When the number of majority carriers begins to change, $\Delta(1/L^2)$ in Eq. (2) is no longer proportional to the dose. On the other hand, the values of $\Delta(1/L^2)$ of $\gamma$-irradiated N/P-type cells contaminated with Cu decrease with increasing concentration of contamination. In a particular case, $\Delta(1/L^2)$ in $\gamma$-irradiated N/P-type cell contaminated with Cu is smaller by one order of magnitude compared with non-doped cells.

The radiation-resistance of the Cu-contaminated N/P-type cell is explained as follows. Since the same amount of Frenkel defects should be primarily introduced at the same total dosage, the capture cross section for electrons of the Cu-vacancy complex center in the Cu-contaminated p-type bulk is considered to be smaller than that of the complex defect containing a dopant impurity in the non-contaminated p-type bulk of the cell. The smaller radiation-resistance of the Cu- and Ni-contaminated P/N-type cell may be explained by a model in which the capture cross section for holes of the Ni- or Cu-vacancy complex center is comparable with that of the E-center in the n-type bulk. As an another explanation, it may be supposed that the solubility and the diffusion coefficient of interstitial Cu in p-type crystals are larger than those in n-type crystals\textsuperscript{(17)}, and that the rate of introduction of the Cu-vacancy complex center under $\gamma$-irradiation is larger in p-type than in n-type bulk.

Radiation induced change in $\Delta(1/L^2)$, or $L_{\text{irr}}^{-2} - L_0^{-2}$, is plotted in Fig. 2 also for the larger junction depth (the depth $X_j$ of the junction is 7 $\mu$m). While the cell with $X_j=7 \mu$m can better withstand radiation environment than that with $X_j=1.5 \mu$m, it still compares poorly with Cu-contaminated N/P-type cells. It should thus be noted that the larger radiation-resistance of the Cu-doped N/P-type cell is not due to the deeper depth of the junction, but to the Cu-contamination itself. The radiation-resistant properties of the maximum output power, short-circuit current of the Cu-contaminated N/P-type cells has been published elsewhere by the author\textsuperscript{(18)}.

2. Effects of Oxygen and Dopant

The change of $\Delta(1/L^2)$ in both C·Z and F·Z bulk crystal caused by the $\gamma$-irradiation in the bulk region of P/N-type cells are shown in Fig. 3. The values of $\Delta(1/L^2)$ in the n-type F·Z bulk
of the P/N-type cell are larger than those of C·Z bulk. The recombination center in the n-type F·Z bulk may be the E-center, as has been reported by several authors, but based only on the foregoing results, we cannot conclude that the predominant recombination center in the C·Z bulk of the P/N-type cell is the O-vacancy complex (A-center). The $\Delta(1/L^2)$ curves for the P/N-type cell begin to deviate from the 45° straight lines at a total dosage of about $10^{16}$ photons/cm². This deviation appears quite markedly in the F·Z bulk P/N-type cell, the explanation being the same as in the case of Fig. 1.

The dopant concentration dependence of the damage constant $K$, in the bulk region of the P/N- and N/P-type silicon solar cells, are plotted in Fig. 4.

The damage constant $K$ in the n-type C·Z bulk region increases with impurity concentration, as in the case of the n-type F·Z bulk cell. The predominant recombination center produced by irradiation in both n-type F·Z and C·Z bulk P/N-type cells may be the E-center. That the damage constant $K$, in the p-type bulk of the N/P-type cell increases with the dopant concentration cannot be explained by the introduction of the O-vacancy complex center (A-center). As shown by Nakashima & Inuishi, the dominant recombination center in $\gamma$-irradiated p-type silicon may be complex defects containing a dopant impurity. The energy level of the $E_{v}+0.3\text{eV}$ center, involving acceptor impurity, is comparable in energy level to the J'-center (0.27eV) in the $\gamma$-irradiated p-type F·Z silicon. This $E_{v}+0.3\text{eV}$ defect containing a dopant impurity in $\gamma$-irradiated p-type silicon could also be explained by attribution to the annealing stage at 350°C, which corresponds to the annealing of the vacancy-impurity complex center. The values of $K$ in the n-type F·Z bulk P/N-type cell are smaller than Stein's in F·Z single crystal by a factor of 4. This discrepancy does not necessarily imply incorrectness of the values adopted for the initial bulk material lifetime and dislocation density.

**IV. SUMMARY**

1. The modified damage constant, $1/L_i^2 - 1/L_0^2 = K_i \cdot \Phi$, of Cu- or Ni-doped P/N-type cells is slightly smaller than that of non-doped cells.
2. For N/P-type cells, appropriately doped with Cu, the corresponding value of $K_i \cdot \Phi$ is smaller by one order of magnitude compared with that for non-doped cells. Appropriate Cu-doping enhances the radiation-resistance..
of the N/P-type cells.

(3) The plots of $K_L \cdot \Phi$ against total dose for non-doped P/N-type cells deviates from the 45° straight line at a total dosage of about $10^{16}$ photons/cm².

(4) The damage constant, $1/\tau_1 - 1/\tau_0 = K \cdot \Phi$, of the n-type F·Z and C·Z bulk crystal P/N-type cells and C·Z bulk N/P-type cells is proportional to the dopant concentration in the bulk region of the cells.

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