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RADIATION DAMAGE ANNEALING MECHANISMS AND POSSIBLE LOW TEMPERATURE ANNEALING IN SILICON SOLAR CELLS

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ABSTRACT

The defect responsible for reverse annealing in 2 ohm-cm n^+/p silicon solar cells has been identified. This defect, with energy level at $E_V + 0.30$ eV, has been tentatively identified as a boron-oxygen-vacancy complex. Our calculations also suggest that its removal could result in significant annealing for 2 ohm-cm and lower resistivity cells at temperatures as low as 200° C. Those results were obtained by use of an expression derived from the Shockley-Read-Hall recombination theory which relates measured diffusion length ratios to relative defect concentrations and electron capture cross sections. The relative defect concentrations and one of the required capture cross sections are obtained from Deep Level Transient Spectroscopy. Four additional capture cross sections are obtained using our diffusion length data and data from temperature-dependent lifetime studies. These calculated results are in reasonable agreement with experimental data. However, since identification of the atomic constitution of the defect at $E_V + 0.30$ eV is speculative, additional effort is required to effect a firm identification of the sub-microscopic constituents of this harmful defect.

INTRODUCTION

One barrier to extending mission times in space is the radiation damage suffered by the silicon solar cell power supply. Overcoming this barrier by complete elimination of radiation damage to the cell remains an elusive research goal. A more pragmatic approach is to thermally anneal the radiation damage. Significant recovery of the performance of radiation-damaged silicon solar cells can be effected by annealing at temperatures of about 400° C and above (1). Exact temperatures required and the amount of recovery accomplished depend upon radiation dose level and the silicon type, dopant, and resistivity. However, considerably lower temperatures would be required to avoid irreversible damage to array components while achieving the in-situ annealing required to extend mission lifetimes in space. One approach for achieving lower annealing temperatures lies in identification and removal of the major defect(s) whose effect on cell performance necessitates use of the higher annealing temperatures. The primary objective of the present work is to identify this defect(s). An additional barrier to low temperature annealing is the reverse annealing phenomena usually observed in silicon solar cells.

The phenomenon of reverse annealing has been observed in bulk silicon (2) and in silicon solar cells (1,3). Since, during reverse anneal, cell performance degrades at temperatures well below 400° C, it constitutes a detriment toward the achievement of annealing at low temperatures. Thus, to achieve low temperature annealing, identification and elimination of the defect or defects responsible for both the reversal and the high-temperature annealing is necessary. In this paper we report efforts to identify the defect whose presence necessitates high annealing temperatures and the defect responsible for the reverse annealing phenomena in silicon solar cells. In the present case, we combine information from Deep Level Transient Spectroscopy (DLTS) (4) with diffusion length measurements and the Shockley-Read-Hall (SRH) recombination theory (5,6) to identify the responsible defects.

EXPERIMENTAL

Irradiations and isochronal annealing were performed on n^+p silicon solar cells with 0.1 and 2 ohm-cm boron-doped base resistivities. Starting material for the 2 ohm-cm cell was Czochralski grown while the starting material for the 0.1 ohm-cm cell was vacuum float zone refined single crystal silicon. The cells were irradiated by 1 MeV electrons to a fluence of 10^{15} cm^{-2}. After irradiation, the cells were isochronally annealed in 50° C steps, the cells being held at each fixed temperature point for 20 minutes. Minority carrier diffusion lengths and AMO I-V measurements were obtained at room temperature before and after irradiation and after each step in the isochronal anneal. Diffusion lengths were measured by an X-ray excitation technique (7), while the AMO I-V measurements were obtained using a xenon-arc solar simulator.

RESULTS

Figure 1 shows the percent change in short-circuit current during the isochronal anneal for both the 0.1 and 2 ohm-cm cells. The reverse annealing phenomena occurs at temperatures between about 200° to 350° C for the 2 ohm-cm cell. These data are similar to those reported by others (1).

Although a small tendency toward reverse annealing appears in the 0.1 ohm-cm data at 200° C, the effect is essentially absent, within experimental error, in the low resistivity cells studied here. Figure 2 shows the behavior of the diffusion length ratio L_T^{-2}/L_{IRR}^{-2} for the same two cells during isochronal anneal. The subscript T denotes a measurement made after isochronal anneal at temperature T while the subscript IRR denotes the room temperature measurement made immediately after irradiation. For reasons which are clafified in the next section, these diffusion length ratios are related to measured defect concentrations and capture cross sections. Thus, to further analyze these data, both defect concentrations and capture cross sections are required. The relative defect concentrations shown in Fig. 3 are obtained from the DLTS results of Ref. 4, normalized to the present fluence of $10^{15}/cm^2$.

THEORY AND CALCULATIONS

Working Equation

To obtain an equation relating the diffusion length data to defect parameters such as carrier capture cross sections and relative defect concentrations, we use the Shockley-Read-Hall (SRH) theory of recombination (5,6). Our starting point is the SRH expression for τ_i the carrier lifetimes due to the i^{th} single level defect. For low injection conditions we have;

$$\frac{1}{\tau_i} = \frac{N_i}{\frac{1}{v_p\sigma_{pi}}\left(\frac{n_o + n_1}{n_o + p_o}\right) + \frac{1}{v_n\sigma_{ni}}\left(\frac{p_o + p_1}{n_o + p_o}\right)} \tag{1}$$

Where N_i is the concentration of the i^{th} defect, n_o and p_o are equilibrium electron and hole concentrations, v_n and v_p are thermal velocities for electrons and holes, σ_{pi} and σ_{ni} are hole and electron capture cross sections for the i^{th} defect and n_i and p_i are calculated from the relations:

$$n_1 = N_c \exp\left(\frac{E_i - E_c}{kT}\right) \tag{2a}$$

$$p_1 = N_v \exp\left(\frac{E_v - E_i}{kT}\right) \tag{2b}$$

N_c and N_v are the density of states for the conduction and valence bands k is the Boltzmann constant and E_i is the energy level of the i^{th} defect. The thermal velocities are obtained from the relations:

$$v_p = \left(\frac{3kT}{m_h}\right)^{1/2} \tag{3a}$$

$$v_n = \left(\frac{3kT}{m_e}\right)^{1/2} \tag{3b}$$

where m_h and m_e are hole and electron effective masses, respectively.

For P type silicon p_o is measured and n_o calculated from the relation:

$$n_o p_o = n_I^2 \tag{4}$$

where n_I is the intrinsic carrier concentration.

Using Eqs. (2), (3), and (4), we find for the defects in Fig. 3 that:

$$\frac{p_o + p_1}{n_o + p_o} \approx 1$$

$$\frac{n_o + n_1}{n_o + p_o} \ll 1$$

and

$$v_n \approx v_p \approx 2\times10^7 \text{ cm/sec}$$

Hence Eq. (1) simplifies to

$$\frac{1}{\tau_i} \approx N_i\sigma_{ni}v_n = N_{max}R_i\sigma_{ni}v_n \tag{5}$$

where R_i is the relative concentration of the i^{th} defect with

$$R_i = \frac{N_i}{N_{max}} \tag{6}$$

N_{max} being the maximum defect concentration measured by DLTS during the isochronal anneal. For example in Fig. 3, N_{max} is obtained from the peak amplitude of the $E_v + 0.38$ eV defect (4)

Since

$$\frac{L_T^{-2}}{L_{IRR}^{-2}} \propto \frac{\frac{1}{\tau}_T}{\frac{1}{\tau}_{IRR}} = \frac{\left(\sum_i \frac{1}{\tau_i}\right)_T}{\left(\sum_i \frac{1}{\tau_i}\right)_{IRR}} \tag{7}$$

We obtain the required relation

$$\frac{L_T^{-2}}{L_{IRR}^{-2}} \approx \frac{\left(\sum_i R_i\sigma_{ni}\right)_T}{\left(\sum_i R_i\sigma_{ni}\right)_{IRR}} \tag{8}$$

Capture Cross Sections

The capture cross sections obtained from DLTS (4), are listed in Table I. Since the electron capture cross section, σ_n, for only one defect (E_c - 0.2' eV) is available from DLTS, we cannot calculate diffusion length ratios from Eq. (8) using only this DLTS result. We have therefore obtained the necessary additional σ_n values by other methods.

With respect to the defects at E_v + 0.38 eV and E_v + 0.23 eV, temperature dependent lifetime studies in 1.5 ohm-cm p-type silicon yield values for the ratio σ_n/σ_p from which σ_n is calculated (8). From Ref. 8, for the E_v + 0.38 eV defect $\sigma_n/\sigma_p \approx 150$ and for the defect at E_v + 0.23 eV, $\sigma_n/\sigma_p \approx 1300$ from which the σ_n values for these defects shown in Table II are calculated. For the remaining defects, values for σ_n were computed by fitting Eq. (8) to the diffusion length data of Fig. 2 at 250° and 300° C using R_i values from Fig. 3. In this way, the electron capture cross sections for the defects at E_v + 0.30 eV and E_v + 0.26 eV were obtained. Thus, the required cross sections for all but the defect at E_v + 0.20 eV are obtained for use in Eq. (8). Since we cannot evaluate σ_n for this latter defect, it is assumed that this defect can be ignored in subsequent calculations.

Calculations

Diffusion length ratios calculated from Eq. (8) using the cross sections of Table II and the data of Fig. 3 are shown in Fig. 4 for the 2 ohm-cm cell. The solid curve in Fig. 4 is the curve drawn through the measured diffusion length ratios shown in Fig. 2. The measured and calculated values are in reasonable agreement. The assumption that E_v + 0.2 eV center could be ignored appears warranted. Omitting the defect at E_v + 0.30 eV and repeating the calculations, we find that the reverse annealing disappears from the calculated results as shown in Fig. 5. We note that of the five defects considered in these calculations, only this latter defect eliminates the reverse annealing phenomena when omitted from the calculations. Hence, we conclude that the defect at E_v + 0.30 eV is responsible for the reverse annealing observed in the present 2 ohm-cm cells. These calculations also suggest that removal of the defect at E_v + 0.3 eV could result in significant cell recovery or annealing at 200° C (Fig. 5).

In addition to the 2 ohm-cm cell, Ref. 4 reports the relative defect concentration for a 0.3 ohm-cm cell shown in Fig. 6. These data were used to calculate diffusion length ratios using the capture cross sections of Table II and Eq. (8). We are unable to obtain a capture cross section for the defect at E_v + 0.48 eV, hence it is omitted from the calculation. The calculated results for the low resistivity cell are shown in Fig. 7. These results predict the absence of reverse annealing in this low resistivity cell and are in qualitative agreement with our data for the 0.1 ohm-cm cell. The omission of the center at E_v + 0.48 eV seems warranted. Repeating the calculation by omitting the defect at E_v + 0.30 eV yields the dotted line of Fig. 7. These results suggest that removal of the defect at E_v + 0.30 eV could also result in significant cell recovery or annealing at 200° C. In this respect it is significant to note that cells of this low resistivity presently require annealing temperatures higher than 400° C to effect such recovery.

DISCUSSION

The preceding indicates that the defect at E_v + 0.30 eV is responsible for the observed reverse annealing in the 2 ohm-cm cell. The calculations also suggest that the same defect is responsible for the required high annealing temperatures and that its removal could result in significant performance annealing at 200° C. In making this suggestion, it is implied that with removal of the responsible defect, another will not take its place. The present work is incomplete in the sense that detailed consideration has not been given to this possibility. Before a scheme can be devised to eliminate the E_v + 0.3 eV defect, we must identify its atomic composition. It is therefore important to speculate on the nature of this defect. It is reported that the E_v + 0.30 eV defect always appears when the E_c - 0.27 eV defect disappears (4). The two defects are related in the sense that the E_c - 0.27 eV defect can be called the parent to the defect at E_v + 0.30 eV. Hence, the atomic constitution of both defects is of importance.

The defect at E_v + 0.30 eV has been tentatively identified as a boron-oxygen-vacancy complex (4). The E_c - 0.27 eV defect increases in concentration with increasing boron concentration and has been identified as a boron interstitial-oxygen interstitial complex (4). An alternate identification asserts that the E_c - 0.27 eV defect is composed of a boron interstitial-boron substitutional pair (9). Both a firmer identification of the E_v + 0.30 eV defect and additional research directed at choosing between competing identifications for the E_c - 0.27 eV parent defect are required. Such identifications would be an invaluable guide to processing efforts aimed at decreasing the concentration of these radiation induced defects.

SUMMARY AND CONCLUSION

We have used the Shockley-Read-Hall recombination theory to obtain an expression relating measured diffusion length ratios to defect concentrations and electron capture cross sections in p-type silicon. Because only one of the many required cross sections was available from DLTS data, we utilized temperature dependent lifetime studies and the measured diffusion length data to determine four additional electron capture cross sections. Calculations using these cross sections and reported relative defect concentrations show reasonable agreement between calculated and measured diffusion length ratios. Our calculated results indicate that a defect at E_v + 0.30 eV is responsible for th reverse annealing observed in 2 ohm-cm n^+/p silicon solar cells. It was also determined by calculation that removal of this same defect could result in significant annealing at temperatures as

low as 200° C for 2 ohm-cm and lower resistivity cells. Hence, we identify the defect, whose energy level is at $E_v + 0.30$ eV, as the major defect whose effect on cell performance necessitates use of annealing temperatures around 400° C. Since a firm identification of its atomic constituents has not been made, additional identification efforts are required in order to guide processing efforts directed at removal of the harmful defect.

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TABLE I. - CAPTURE CROSS SECTIONS FROM DLTS

Defect energy level, eV	Capture cross sections, cm^2	
	σ_p	σ_n
$E_v + 0.38$	2×10^{-16}	--------
$E_c - 0.27$	--------	2×10^{-13}
$E_v + 0.23$	3×10^{-16}	--------
$E_v + 0.30$	2×10^{-16}	--------
$E_v + 0.26$	--------	--------
$E_v + 0.2$	--------	--------

TABLE II. - ELECTRON CAPTURE CROSS SECTIONS

Energy level of defect, eV	Electron capture cross section, cm^2	Method for obtaining section
$E_c - 0.27$	2×10^{-13}	DLTS
$E_v + 0.38$	3×10^{-14}	$\sigma_n/\sigma_p \approx 150$*
$E_v + 0.23$	3.9×10^{-13}	$\sigma_n/\sigma_p \approx 1300$*
$E_v + 0.30$	3.6×10^{-13}	Fit of $1/L^2$ ratio to DLTS (250° C)
$E_v + 0.26$	9.5×10^{-14}	Fit of $1/L^2$ ratio to DLTS (300° C)

*Computed from σ_n/σ_p ratios for 1.5 ohm-cm p-type (FZ) from Srour, Curtis, Othmer, Chiu, and Deokar: Report HDL-TR-171-4.

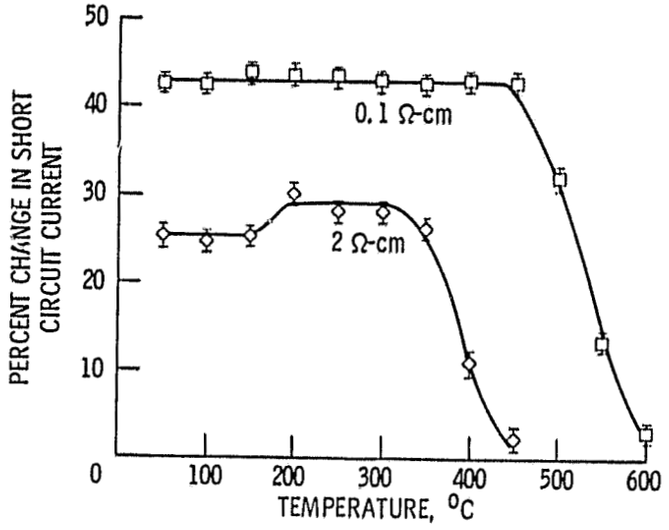

Figure 1. - Isochronal anneal of n^+p silicon solar cells after 1 MeV electron. Irradiation: $\varphi = 10^{15}/cm^2$. (Time at temperature, 20 min.)

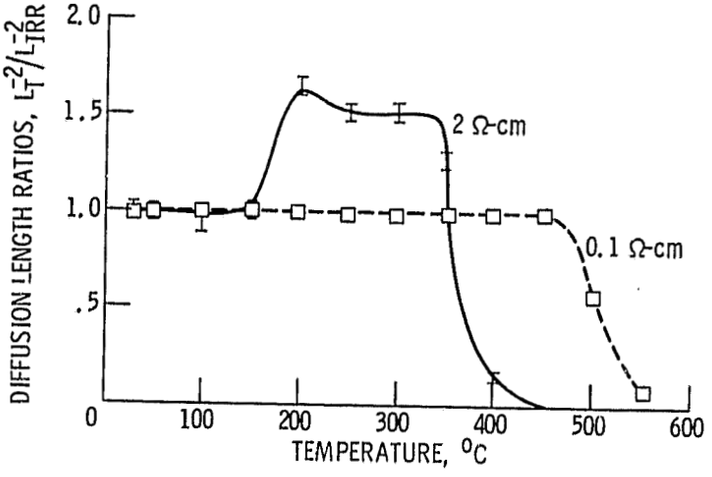

Figure 2. - Measured diffusion length ratios during isochronal anneal.

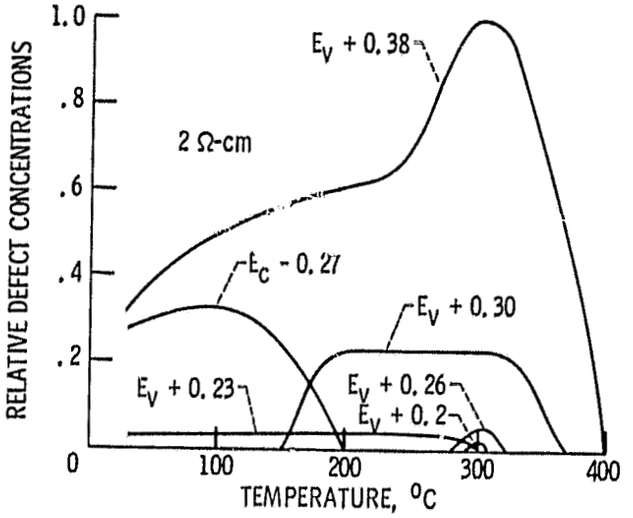

Figure 3. - Relative defect concentrations from DLTS (after Mooney et al.).

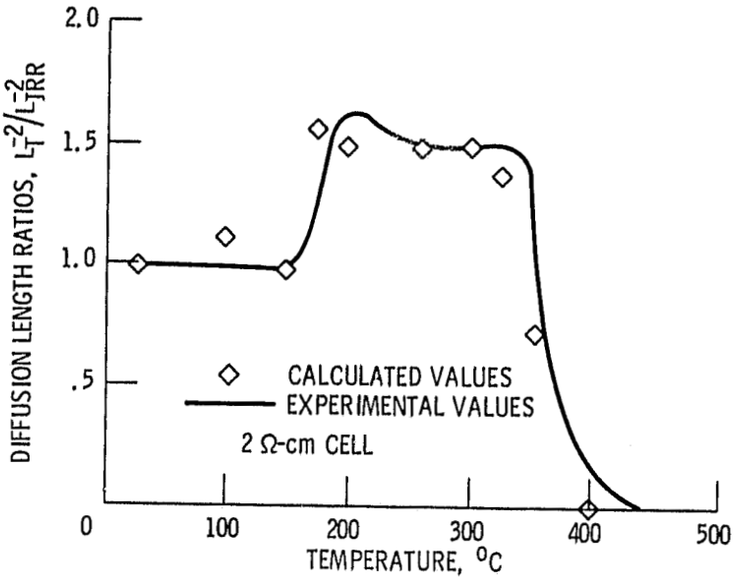

Figure 4. - Comparison of calculated and measured diffusion length ratios.

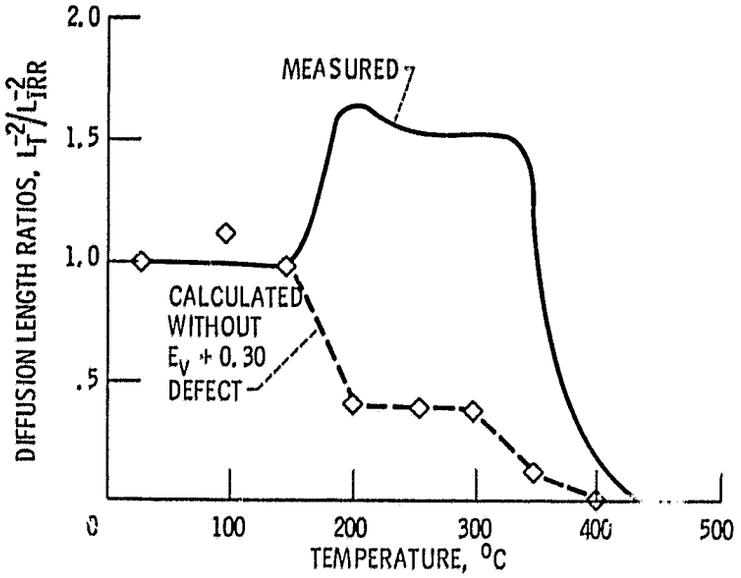

Figure 5. - Calculated and measured diffusion length ratios omitting the $E_V + 0.30$ defect.

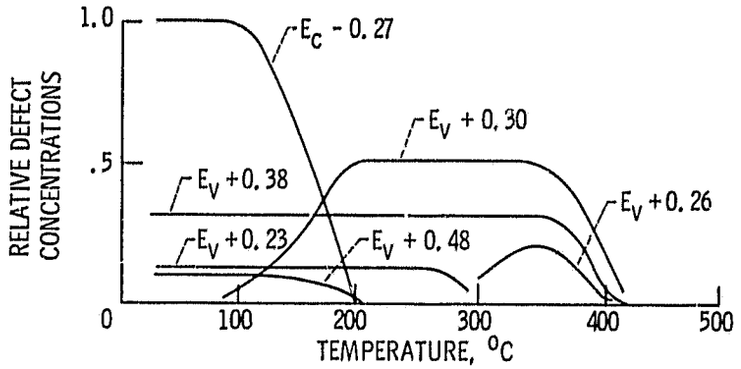

Figure 6. - DLTS data for 0.3 Ω-cm P-Si. Isochronally annealed after 1 MeV electron irradiation (after Mooney et al.).

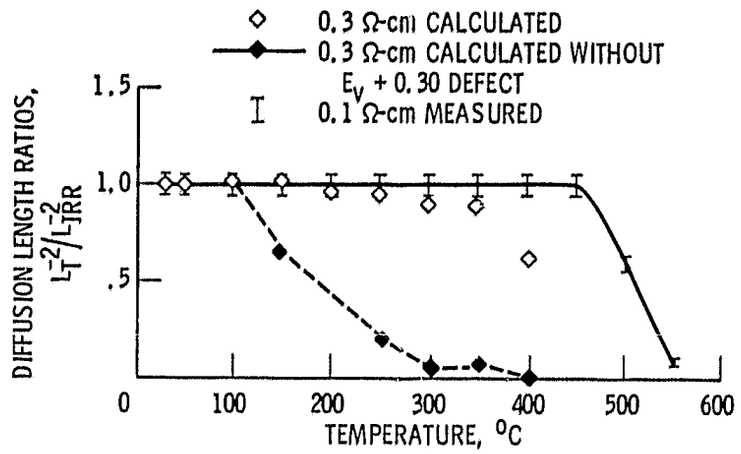

Figure 7. - Calculated and measured diffusion length ratios, low resistivity P-Si.

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15 Supplementary Notes

16 Abstract

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