ANNEALING CHARACTERISTICS OF AMORPHOUS SILICON ALLOY SOLAR CELLS IRRADIATED WITH 1.00 MeV PROTONS*

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ABSTRACT

a-Si:H and a-Si$_x$,Ge$_{(1-x)}$:H solar cells were irradiated with 1.00 MeV proton fluences in the range of 1.00E14 to 1.25E15 cm^{-2}. Annealing of the short-circuit current density was studied at 0, 22, 50, 100 and 150 °C. Annealing times ranged from an hour to several days. The measurements confirmed that annealing occurs at 0 °C and the initial characteristics of the cells are restored by annealing at 200 °C. The rate of annealing does not appear to follow a simple nth order reaction rate model. Calculations of the short-circuit current density using quantum efficiency measurements and the standard AM1.5 global spectrum compare favorably with measured values. It is proposed that the degradation in J_{sc} with irradiation is due to carrier recombination through the fraction of D^0 states bounded by the quasi-Fermi energies. The time dependence of the rate of annealing of J_{sc} does appear to be consistent with the interpretation that there is a thermally-activated dispersive transport mechanism which leads to the passivation of the irradiation-induced defects.

INTRODUCTION

This work continues our study of 1.00 MeV proton irradiation of plasma enhanced chemical vapor deposited hydrogenated amorphous silicon (a-Si:H) and hydrogenated amorphous silicon-germanium (a-Si$_x$,Ge$_{(1-x)}$:H) solar cells (1-3). The radiation resistance was evaluated using current-voltage (I-V) and quantum efficiency (QE) measurements. Earlier work shows that a-Si:H and a-Si$_x$,Ge$_{(1-x)}$:H solar cells irradiated with 1.00 MeV protons degrade mainly due to the decrease in the short-circuit current (I$_{sc}$) and the fill factor (FF) (1-4). The most recent work shows that a-Si:H solar cells have better radiation resistance than a-Si$_x$,Ge$_{(1-x)}$:H cells (3). However, earlier investigations suggest a-Si:H cells have poorer radiation resistance when compared to a-Si$_x$,Ge$_{(1-x)}$:H cells (4). The irradiated a-Si:H and a-Si$_x$,Ge$_{(1-x)}$:H solar cells regained their original I-V characteristics after a one hour anneal at 200 °C (1,2); some of the cells had improved I-V characteristics as compared with the pre-irradiated values (1). On the other hand,

annealing a-Si:H cells for one hour at 200 °C restored the QE to only 80 % of the pre-irradiated values, while others showed complete recovery; QE was measured without a D.C. light bias (2).

Subsequent measurements under a D.C. light bias corresponding to the AM1.5 global spectrum showed that QE was restored to pre-irradiated values for all cells (3). QE of a-Si$_x$,Ge$_{(1-x)}$:H cells was measured only under D.C. light bias, and showed complete recovery when annealed at 200 °C for one hour (3). It was found that QE depends on the light bias; I_{sc} must be significantly larger than the dark current in order for QE to be independent of light bias (2,3).

The fact that QE and I-V characteristics of both a-Si:H and a-Si$_x$,Ge$_{(1-x)}$:H cells were restored to pre-irradiated values following a one hour anneal at 200 °C is an indication that 1.00 MeV protons do not produce intermixing of doped and intrinsic layers. The nature of the defects is not clear, although, earlier work suggests the defects are introduced in the intrinsic layer (5). The improved radiation resistance of a-Si alloy cells, as compared to crystalline silicon (x-Si), appears to be due to the fact that the active material is fabricated from thin films. The range of 1.00 MeV protons in a-Si alloy and x-Si materials is of the order of 10 microns. Since a-Si alloy cells are about 0.5 microns thick, the energy deposited in the active layers is considerably smaller than the energy deposited in x-Si cells. Stopping power calculations show the thinner the active layer of a cell, the lower the energy deposited in the cell by 1.00 MeV protons, and the fewer the number of defects produced by nuclear displacements (5); the authors propose that nuclear displacements produce defects which are optically and electrically active.

The purpose of this work is to investigate the annealing behavior of a-Si:H and a-Si$_x$,Ge$_{(1-x)}$:H solar cells irradiated with 1.00 MeV proton fluences in the 1.00E14 to 1.25E15 cm^{-2} range.


EXPERIMENTAL

Two sets of solar cells were employed in this study, a-Si:H and a-Si$_x$,Ge$_{(1-x)}$:H. The solar cells were fabricated in a Plasma Enhanced Vapor Deposition (PECVD) system. The structure of each solar cell is surface/grid/ITO/p$^+$/i/n$^+$/stainless steel substrate with an active cell area of 1.0 cm^2; ITO serves as the top electrical contact and anti-reflection coating. The a-Si:H solar cells are identified as cells C2, C3, C5, D5, N3, N5, and N6; N5 and N6 have no electrical grid, instead electrical connection was made using silver paint. The a-Si$_x$,Ge$_{(1-x)}$:H cells are identified as cells A1, A2, A3, B4, B5, and B6. The i-layer thicknesses of the a-Si:H and a-Si$_x$,Ge$_{(1-x)}$:H cells are estimated to be between 350-400 and 280-320 nm, respectively. The Ge composition in the a-Si$_x$,Ge$_{(1-x)}$:H cell is estimated to be about 20-30%.

Prior to irradiation each cell was annealed in a 1E-6 Torr vacuum for three hours at 200 °C; the I-V characteristics of the cells were measured at an ambient temperature of about 22 °C both in the dark and under illumination. The illumination source was an ELH lamp with a heat-absorbing filter. The illumination intensity was set to produce an I_{sc} of 20.0 mA in a calibrated crystal silicon

solar cell which corresponded to the I_{sc} produced by an AM1.5 global simulator. The calibration procedure was utilized prior to each measurement. The solar cell efficiencies are about 10% under AM1.5 global illumination. Because of the spectral mismatch between the AM1.5 global spectrum and the ELH lamp used in this investigation, the cell efficiencies will not be discussed; only changes in I_{sc}, FF and open-circuit voltage (V_{oc}) will be discussed. The samples were irradiated with a uniform 1.00 MeV proton beam of 1.0 cm^2 area in a vacuum measuring less than 1E-6 Torr; the beam current was about 50 nanoamperes and the fluences ranged from 1.00E14 to 1.25E15 cm^{-2}. The irradiations took place in the dark and at an ambient temperature of about 22 °C; thermal annealing due to the power deposited by the beam in the samples has been shown to be negligible. The samples were stored at 0 °C following irradiation in order to minimize annealing effects (1). The I-V measurements were repeated under the same conditions as before irradiation.

The I-V measurements of the a-Si:H solar cells N3, N5 and N6 were inadvertently measured under a lower illumination than AM1.5 global. A calibration error resulted in a J_{sc} of 7.16 mA/cm^2 in-
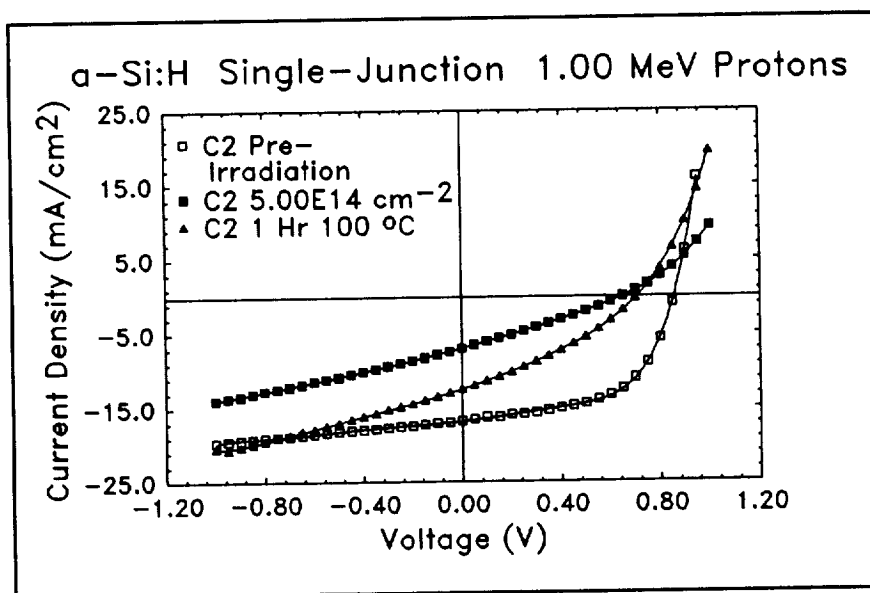

Figure 1. AM1.5 global J-V characteristics of a-Si:H solar cell C2 irradiated with a 1.00 MeV proton fluence of 5.00E14 cm^{-2} and annealed for one hour at 100 °C.
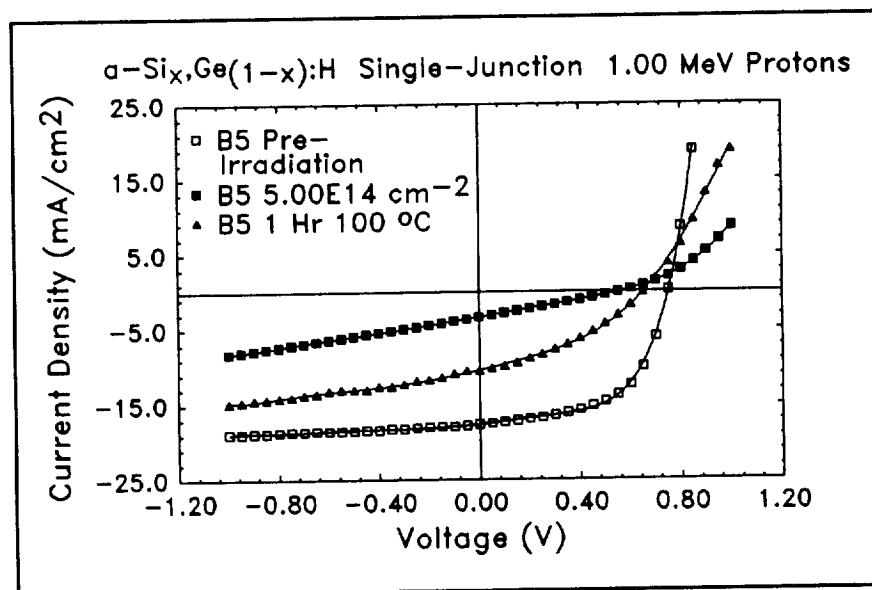
Figure 2. AM1.5 global J-V characteristics of a-Si$_x$,Ge$_{(1-x)}$:H solar cell irradiated with 1.00 MeV proton to a fluence of 5.00E14 cm^{-2} and annealed one hour at 100 °C.

stead of 17.0 mA/-cm^2. Since the cells had already been annealed, it was not possible to repeat the I-V characteristics. J_{sc} for the cells was corrected using a multiplicative factor of 2.37, the ratio of J_{sc} under AM1.5 global illumination to J_{sc} under the erroneous low level illumination. Supporting measurements were made to insure that the correction did not influence the shape of the I-V curves.
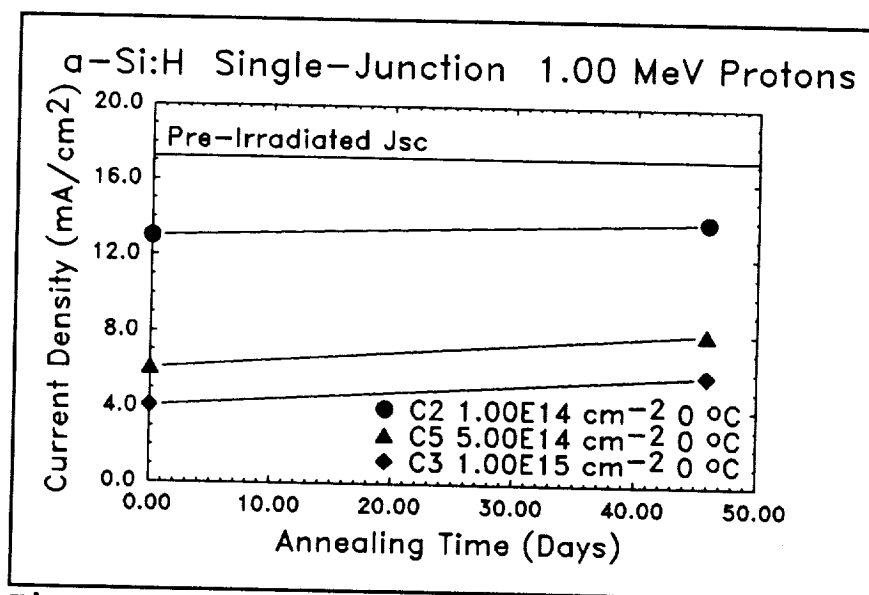
Figure 3. Jsc 0 °C annealing of a-Si:H solar cells irradiated with 1.00 MeV proton to fluences of 1.00E14, 5.00E14 and 1.00E15 cm^{-2}.

RESULTS

Figure 1 shows the effect of 1.00 MeV protons with a fluence of 5.00E14 cm^{-2} on the I-V characteristic of a-Si:H cell C2. Since the cells have area of 1.0 cm^2, the ordinate corresponds to the current density and the graphs represent the J-V characteristics. The solid lines used to fit the data were calculated using a seventh order regression. Pre-irradiated short-circuit current density (J_{sc}), V_{oc} and FF degraded following irradiation from 16.7 mA/cm^2, 0.86 V, and 0.56 to 6.94 mA/cm^2, 0.62 V, and 0.29, respectively. A one-hour anneal at 100 °C resulted in J_{sc}, V_{oc} and FF being restored to 12.4 mA/cm^2, 0.72
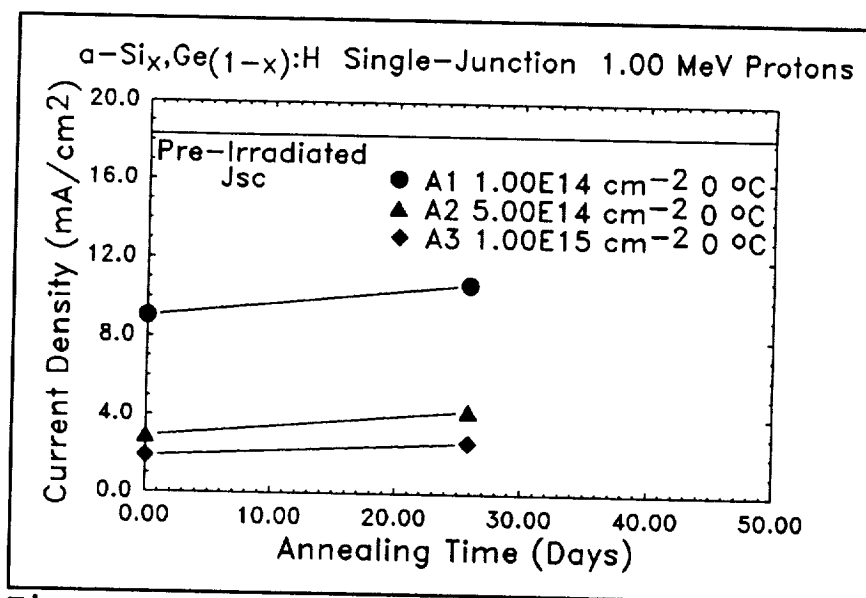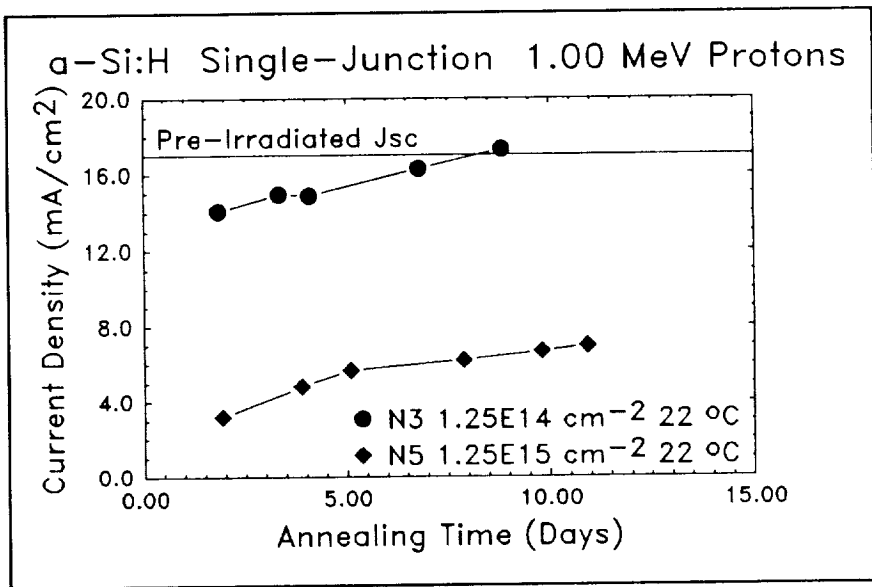
Figure 4. Jsc annealing at 0 °C of a-Si$_x$,Ge$_{(1-x)}$:H solar cells irradiated with 1.00E14, 5.00E14 and 1.00E15 cm^{-2} 1.00 MeV Protons.
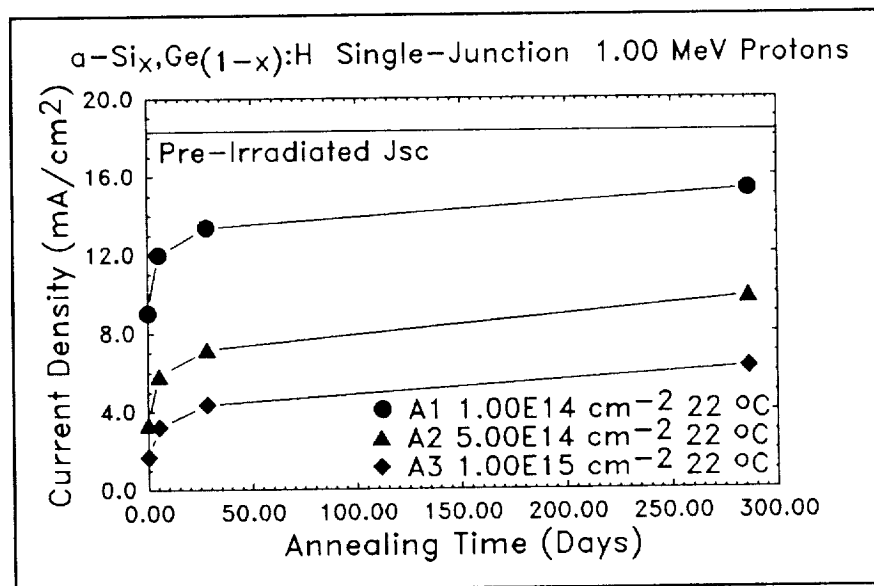
V, and 0.32, respectively.

The degradation in the J-V characteristic of a-Si$_x$,Ge$_{(1-x)}$:H cell B5 by a 1.00 MeV proton fluence of 5.00E14 cm^{-2} is shown in figure 2. The pre-irradiated J$_{sc}$, V$_{oc}$ and FF were 17.3 mA/cm^2, 0.73 V and 0.57, respectively. The irradiation degraded the J$_{sc}$, V$_{oc}$ and FF to 3.35 mA/cm^2, 0.57 V and 0.26, respectively. J$_{sc}$, V$_{oc}$ and FF increased to 10.1 mA/cm^2, 0.67 V and 0.37, respectively, following a one-hour anneal at 100 °C.

Figure 5. Jsc 22 °C annealing of a-Si:H solar cells irradiated with 1.00 MeV proton to fluences of 1.25E14 and 1.25E15 cm^{-2}.

Figure 3 shows the annealing of J$_{sc}$ at 0 °C for a-Si:H cells C2, C5 and C3 following 1.00 MeV proton irradiation with fluences of 1.00E14, 5.00E14 and 1.00E15 cm^{-2}, respectively. Figures 1 and 2 show J$_{sc}$ is negative; figures 3 through 8 plot the absolute value of the short-circuit current density as a function of time, J$_{sc}$(t). The first J$_{sc}$ measurements were taken on the first day following irradiation of the samples. Straight line segments are employed to connect the data points in order to make it easier to follow the trend of the data. Figure 3 clearly shows that annealing of J$_{sc}$(t) at 0 °C occurs for the three cells during the 45.9 days following irradiation. The effect of 0 °C annealing on the J$_{sc}$(t) of a-Si$_x$,Ge$_{(1-x)}$:H cells A1, A2 and A3 is show in figure 4. Again, it is clear that during the 25.8 days following irradiation, 0 °C annealing occurs.


Figure 6. Jsc 22 °C annealing of a-Si$_x$,Ge$_{(1-x)}$:H solar cells irradiated with 1.00 MeV proton to fluences of 1.00E14, 5.00E14 and 1.00E15 cm^{-2}.

Figure 5 shows the annealing of J_{sc} at 22 °C (room temperature) for a-Si:H cells N3 and N5 following 1.00 MeV proton irradiation with fluences of 1.25E14 and 1.25E15 cm^{-2}, respectively. The first J_{sc} measurements were taken 1.83 days after irradiating the samples. Annealing cell N3 at 22 °C for 8.83 days resulted in J_{sc} increasing from 14.1 to 17.3 mA/cm^2. The corresponding data for cell N5, annealed for 10.92 days, ranged from 3.2 to 6.9 mA/cm^2.

The effect of annealing a-Si$_x$,Ge$_{(1-x)}$:H cells A1, A2 and A3 at 22 °C is show in figure 6. Irradiation with 1.00E14, 5.00E14 and 1.00E15 cm^{-2} fluences of 1.00 MeV protons degraded J_{sc} to 9.0, 3.4 and 1.7 mA/cm^2, respectively. Annealing cell A1 at 22 °C for 286 days resulted in J_{sc} increasing to 15.3 mA/cm^2. Annealing cells A2 and A3 resulted in the increase of J_{sc} to 9.8 and 6.3 mA/cm^2, respectively.

Figure 7 shows $J_{sc}(t)$ at various annealing temperatures for a-Si:H cells D5, C2 and C5 following irradiation with a 1.00 MeV proton fluence of 5.00E14 cm^{-2}. The post-irradiated J_{sc} values of cells D5, C2 and C5 were 5.16, 6.94 and 7.55 mA/cm^2, respectively. Cells D5, C2 and C5 were isochronally annealed for three one-hour intervals at 50, 100 and 150 °C, respectively. The measurements show that J_{sc} for cells
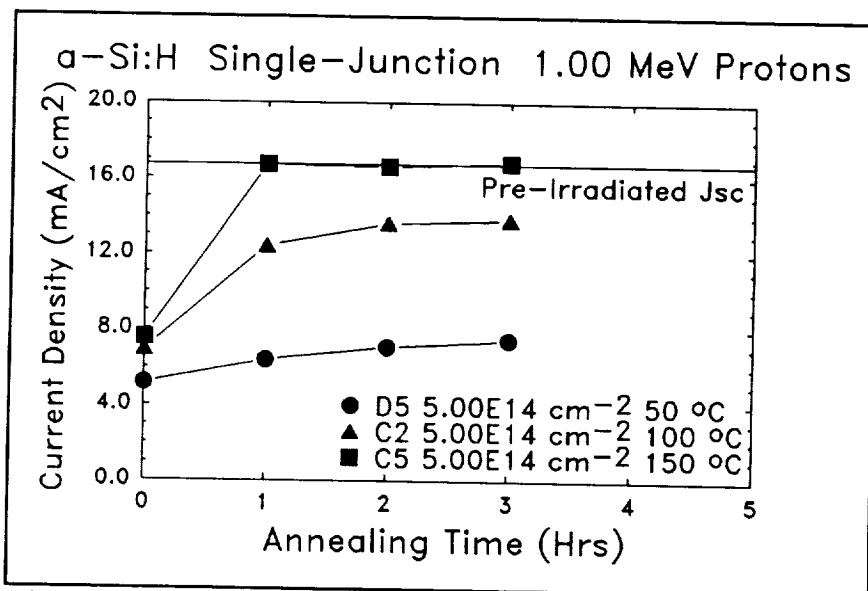
Figure 7. Jsc annealing characteristics of a-Si:H cells at 50, 100 and 150 °C following 5.00E14 cm^{-2} 1.00 MeV proton irradiation.
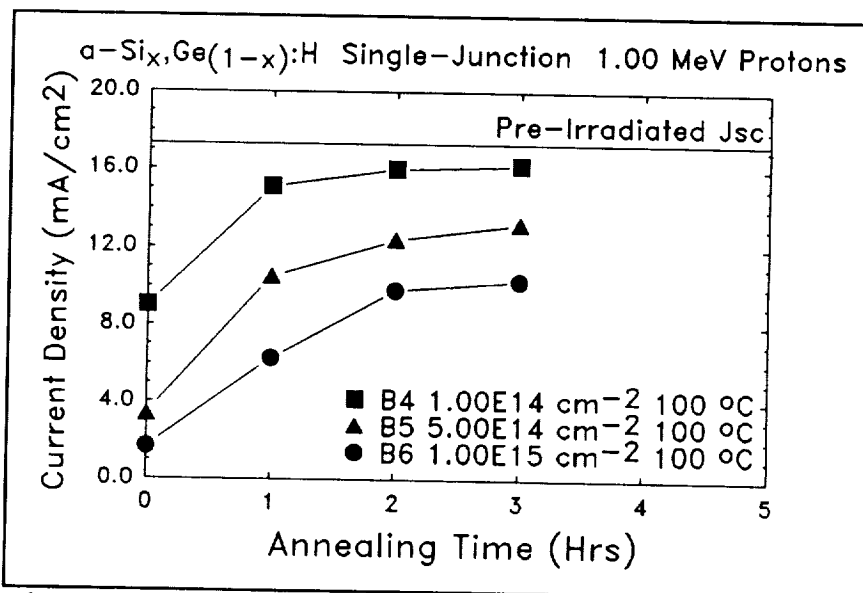
Figure 8. Jsc annealing characteristics of a-Si$_x$,Ge$_{(1-x)}$:H cells 100 °C following 1.00E14, 5.00E14 and 1.00E15 cm^{-2} 1.00 MeV proton irradiation.

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D5, C2 and C5 increased from the post-irradiated values to 7.5, 13.8 and 16.8 mA/cm^2, respectively, following the third one-hour anneal.

The annealing of J_{sc} at 100 °C of a-Si$_x$,Ge$_{(1-x)}$:H cells B4, B5 and B6 is shown in figure 8. The post-irradiated values of J_{sc} following 1.00E14, 5.00E14 and 1.00E15 cm^{-2} fluences of 1.00 MeV protons were 9.0, 3.4 and 1.7 mA/cm^2 for cells B4, B5 and B6, respectively. The cells were annealed for three one-hour intervals at 100 °C. Following the anneals, J_{sc} of cells B4, B5 and B6 increased to 16.2, 13.2 and 10.3, respectively.

QE measurements show the same behavior with fluence as we reported earlier (3). The short-circuit current density was calculated using a convolution of the measured QE and a standard AM1.5 global spectrum. A comparison of the calculated short-circuit current density, J_{sc-cal}, with the measured J_{sc} is shown in table I; the error in the comparison is of the order of 10%. These results are characteristic of our analyses for several cells under different conditions including various stages of annealing. We find that convoluting QE with a standard AM0 spectrum, predicts the AM1.5 global power density should be multiplied by 1.28 in order to obtain the AM0 power density for these cells.

Table I. J_{sc} (measured) and J_{sc-cal} (calculated) in mA/cm^2 for a-Si:H cell C3 and a-Si$_x$,Ge$_{(1-x)}$:H cell A3 under AM1.5 global conditions. PRE=pre-irradiated, POST=post-irradiated with 1.00 MeV proton fluence 1.00E15 cm^{-2}, and %DIFF=percentage difference between J_{sc} and J_{sc-cal}.

	a-Si:H		a-Si$_x$,Ge$_{(1-x)}$:H	
	PRE	POST	PRE	POST
J_{sc}	16.7	4.08	18.3	1.89
J_{sc-cal}	15.1	4.26	17.8	2.17
%DIFF	9.6	4.4	2.7	15

DISCUSSION

The results show that, qualitatively, J_{sc} of both a-Si:H and a-Si$_x$,Ge$_{(1-x)}$:H solar cells anneal in a similar manner. However, the radiation resistance of a-Si:H cells is better than that of the a-Si$_x$,Ge$_{(1-x)}$:H cells, and quantitatively, the details are different. Both a-Si:H and a-Si$_x$,Ge$_{(1-x)}$:H solar cells exhibit annealing in the temperature range from 0 through 150 °C. The annealing rate of J_{sc} is dependent upon the 1.00 MeV fluence and the annealing temperature. The larger the fluence and the lower the annealing temperature, the smaller the annealing rate of J_{sc}. For the annealing temperature range studied, the rate of annealing in $J_{sc}(t)$ is initially faster, and slows as the annealing time increases; this feature is common to both a-Si:H and a-Si$_x$,Ge$_{(1-x)}$:H cells. Our attempts to characterize the annealing of J_{sc} with nth order reaction rate kinetics have not been successful. We plan on pursuing the annealing kinetics with the aid of a numerical device

model in an effort to understand the defect passivation mechanism.

The similarity of the annealing characteristics of $J_{sc}(t)$ in both a-Si:H and a-Si$_x$,Ge$_{(1-x)}$:H solar cells suggests that hydrogen plays a role in the passivation of D° defects; we do not have any direct evidence to support this conjecture. Additionally, we are unable to confirm the hydrogen glass model proposed by Kakalious and Jackson (10). We quenched our cells from 200 to 45 °C in times as short as 2.0 minutes; no glass-like metastable effects have been observed in light and dark I-V characteristics, nor in measurements of the dark conductivity activation energy. However, the time dependence of the rate of annealing of J_{sc} does appear to be consistent with the interpretation that there is a thermally-activated dispersive transport mechanism which leads to the passivation of the irradiation-induced defects.

The difference between J_{sc} and J_{sc-cal} is about 10%. We believe that this difference is due to the experimental technique employed. The cells were illuminated with an ELH lamp which only approximates the AM1.5 global spectrum; the difference in the spectra will introduce error in the comparison. Other sources of error must also be investigated. Accurate QE measurements are necessary in order to investigate the details of carrier transport. We remain puzzled by our earlier observations that the I-V characteristics of some cells improved following irradiation and annealing at 200 °C (1). While we do not have QE measurements for the cells, the shapes of the I-V curves suggest that the surface recombination velocities at the interfaces between the p^+-i-n^+ layers are altered by irradiation and annealing. QE measurements should enable us to shed light on the role of surface recombination velocities in these cells.

The 1.00 MeV proton fluence has been correlated with irradiation-induced defects and a sub-band-gap density of states function (DOSF); a peak in the DOSF located about 1.35 eV below the conduction-band edge was proposed (6). Recent device modelling work by Schumm and Bauer suggests that the peak is due to the neutral dangling bond (D°); they show that the high level of optical injection under AM1.5 global illumination suppresses the D^- and D^+ peaks in the DOSF, and that the D° state dominates (7). The modelling work of Hack and Shur suggests that the electric field in the intrinsic layer under high injection conditions is somewhat constant (8). If this is the case in our cells, then the density of the D° states will be fairly uniform throughout the intrinsic layer. Taylor and Simmons have shown that only the states between the quasi-Fermi levels are important in carrier recombination (9). We propose that the degradation in J_{sc} with irradiation is due to carrier recombination through the fraction of D° states bounded by the quasi-Fermi energies.

CONCLUSION

We have shown that a-Si:H and a-Si$_x$,Ge$_{(1-x)}$:H solar cells anneal qualitatively in the same fashion after irradiation with 1.00 MeV proton fluences ranging between 1.00E14 and 1.25E15 cm^{-2}. Annealing at temperatures as low as 0 °C was observed for both types of cells

for the first time. The rate of annealing does not appear to follow a simple nth order reaction rate model. Calculations of the short-circuit current density using quantum efficiency measurements and the standard AM1.5 global spectrum compare favorably with measured values. It is proposed that the degradation in J_{sc} with irradiation is due to carrier recombination through the fraction of D^0 states bounded by the quasi-Fermi energies. The time dependence of the rate of annealing of J_{sc} does appear to be consistent with the interpretation that there is a thermally-activated dispersive transport mechanism which leads to the passivation of the irradiation-induced defects.

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