EFFECT OF DOPANTS ON ANNEALING PERFORMANCE OF SILICON SOLAR CELLS*

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SUMMARY

Silicon solar cells doped with boron or gallium and ranging in resistivity from 0.1 to 20 ohm-cm were irradiated with 1 MeV electrons to fluences up to $1x10^{15}$ e/cm^2. The cells were then thermally annealed over the range 60-450°C in order to study their recovery characteristics. Spectral response, minority carrier diffusion length and light I-V data were obtained and used to develop a preliminary model to explain the various annealing stages observed.

INTRODUCTION

There has been renewed interest in thermal annealing of solar cells as a technique for extending satellite operating lifetime and as a means of increasing the feasibility of certain advanced mission concepts. Low thrust propulsion systems are being considered for transferring large solar panels from low earth to geosynchronous orbit. One of the primary obstacles to be overcome is the severe degradation that would be experienced by the solar panels due to exposure to the radiation environment encountered during transfer.

Once in geosynchronous orbit, the panels would still be exposed to sufficient radiation such that their electrical performance would be significantly degraded over a period of years. This problem is presently addressed by oversizing panels, a solution which increases cost and mass, to accommodate the reduction in power during mission lifetime. It is doubtful that this solution can be tolerated for concepts such as SPS which are designed to produce and deliver power. Therefore the idea of recovering radiation induced power losses in solar panels by thermal annealing becomes an attractive possibility for solving this problem.

The purpose of this study was to establish the optimum annealing parameters of time and temperature for producing cell output recovery. A variety of cells representing all space solar cell suppliers as well as advanced experimental samples were investigated. Included in this survey were devices made from gallium doped and boron doped silicon. The cells ranged in resistivity from 0.1 to 20 ohm-cm and in thickness from 50 to 250 μm.

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EXPERIMENTAL METHOD

Approximately 80 n on p-type silicon solar cells were investigated in twenty-one separate annealing experiments. The preliminary phase used 2 ohm-cm, 250 μm thick violet cells manufactured by OCLI. In subsequent tests, cells from Spectrolab, Inc. and Solarex Corp. were included, as well as advanced experimental gallium doped solar cells received from WPAFB. Spectral response, minority carrier diffusion length (L_n) using the method of reference 1, and I-V data, taken under AMO conditions at 28°C, were initially recorded.

The samples were then irradiated with 1 MeV electrons, in vacuum, using the JPL Dynamitron. Fluences employed were generally $1x10^{14}$ or $1x10^{15} e/cm^2$. A complete description of the facility and experimental technique is given in reference 2. After irradiation, spectral response and L_n data were taken on a sampling basis, while I-V curves under AMO at 28°C were obtained for all cells.

Thermal annealing was done in dry nitrogen with the cells mounted on a quartz boat within the constant temperature zone of a diffusion furnace. Typical annealing times were 30 minutes, although in some experiments cells were annealed for up to 64 hrs at a given temperature. Initial annealing was begun at 200°C in most cases and after retesting the samples, heating was increased in 50°C increments up to a final temperature of 450°C. For annealing temperatures below 200°C the cells were mounted to a temperature controlled heater block in vacuum and I-V data was obtained using the solar simulator that is part of the JPL Dynamitron test facility as described in reference 2. I-V data was obtained after each annealing step, and when appropriate it was supported with spectral response and L_n measurements. Unirradiated control cells were included in the annealing tests to guarantee that factors such as antireflection coating transmission changes or contact punchthrough were not influencing the data taken.

RESULTS AND DISCUSSION

The experiments reveal a complicated recovery pattern for both gallium and boron doped silicon solar cells. There are marked differences between the two dopants at annealing temperatures of 60°C. Extremely low resistivity (0.1-0.2 Ω-cm) gallium and boron doped silicon cells display a unique form of recovery as compared to higher base resistivity devices. Based on our investigations of isochronal and isothermal behavior of these samples, it appears that significant recovery of radiation induced degradation does not take place until exposure to a temperature of at least 350°C for a period greater than 30 minutes.

The data presented here is in terms of short circuit current, although open circuit voltage and maximum power were also monitored. Unfortunately, many of the cells made with titanium-palladium-silver contacts showed evidence of shunting due to contact punchthrough at annealing temperatures of 400°C, which compromised all but the short circuit current data. Fortunately, the spectral response and minority carrier diffusion length measurements were not influenced by this problem. Cells which had chromium-gold-silver or tantalum-palladium-silver contact systems did not show any signs of shunting even after 30 minutes at 450°C.

The annealing behavior of cells made from gallium and boron doped silicon is shown in figures 1 through 3. The data is given in terms of the unannealed fraction of short circuit current, I_0-I_t/I_0-I_ϕ, versus annealing temperature, where I_0 is the current prior to irradiation, I_t is the current being annealed at temperature t, and I_ϕ is the current after irradiation. Positive annealing is defined as a reduction in the unannealed fraction, while negative or reverse annealing is an increase in the unannealed fraction. Figure 1 shows the effect of 30 minute heat treatments over the range 200 to 450°C for 0.10-0.20 ohm-cm gallium and boron doped cells, while figures 2 and 3 provide data for 2 ohm-cm and 10 ohm-cm gallium and boron doped cells over the range 60 to 450°C. Additional data was obtained for 20 ohm-cm gallium doped cells, but it is not given since it matched precisely the information derived from 10 ohm-cm gallium doped cells. These plots represent a number of individual experiments involving in most cases, at least three cells of each type. Due to the significance of the measurements made at 60°C, these data are included, although it represents 16 hrs at temperature while the other points are for 30 minutes at temperature.

Onset of Annealing

The lowest temperature for which there is substantial data is 60°C. We observed positive annealing in all boron doped samples tested regardless of base resistivity. This has been reported previously (ref. 3). However, with gallium doped silicon solar cells the type of annealing (positive or negative) was related to base resistivity, with 2 ohm-cm cells losing additional output, 10 ohm-cm cells remaining the same, while 20 ohm-cm devices showed a slight increase in output. Both back surface field and conventionally processed samples performed similarly. Additional experiments comparing 2 ohm-cm gallium and boron doped silicon solar cells confirmed the original results with respect to the type of annealing produced at 60°C. In the latter experiments the samples were held at 60°C for 64 hrs after they had been irradiated with $1x10^{15}$ 1 MeV electrons/cm^2. Table 1 summarizes the information taken from all experiments.

Intermediate Annealing Stage

The original annealing experiments began at 200°C for an arbitrarily selected time of 15 minutes. Significant reverse annealing was observed in 2 ohm-cm boron doped cells regardless of manufacturer or thickness (50-250 μm). The output of the samples was now lower than after the irradiation. Spectral response and minority carrier diffusion length measurements confirmed our electrical data. Other experiments using 10 ohm-cm samples did not show evidence of reverse annealing under these conditions. Cell output remained the same as after the irradiation. Further, more detailed investigations revealed that the onset of reverse annealing in 2 ohm-cm boron doped silicon took place somewhere between 120 and 140°C and was extremely rapid (less than one minute). In another test, samples of 10 ohm-cm boron doped silicon were irradiated to $1x10^{14}$ e/cm^2 and then heated for 16 hrs at 200°C. Although in absolute terms the amount of reverse annealing observed was small (1.4 mA average), relative to the amount of initial loss in current from the irradiation (3.2 mA average), it was very significant (>40 percent). Thus it appears that heating cells that had been irradiated to 200°C led to an additional loss in output, a situation not unlike photon induced degradation in irradiated float zone silicon solar cells (ref. 4).

The data given in figure 3 appears to be in conflict with our observations concerning reverse annealing in 10 ohm-cm silicon, but it should be noted that these samples received a 60°C soak for 16 hrs, which according to our model, discussed in a later section, would modify the cell's behavior at 200°C. Further discussion of reverse annealing in 10 ohm-cm samples will be found in the section entitled "Additional Observations".

There is no additional significant change in cell output for 2 and 10 ohm-cm boron doped samples until a temperature of 350°C is reached. Our work indicates that the next annealing stage is located very close to 350°C in point of fact. In one annealing experiment the cells were inadvertently heated to only 340°C for 30 minutes, and they did not show any signs of recovery. The gallium cells by comparison show a gradual recovery of output over this temperature range as can be seen in figures 2 and 3.

The behavior of the low resistivity samples is in sharp contrast (fig. 1). The amount of reverse annealing appears to increase with temperature, peaking at 300°C for gallium and 350°C for boron doped silicon cells. The fact that neither group was originally heated at 60°C is regrettable in light of our proposed model.

Final Recovery Stage

With the exception of the 0.1 ohm-cm sample, all cells showed a significant amount of positive annealing at 350°C, and at 450°C had recovered from 75 to 90 percent of the radiation induced degradation in output. The absolute amount of recovery appears to be related to base resistivity for both dopants, with the higher resistivity cells displaying the greatest recovery.

Since the purpose of this work is to define practical parameters for producing recovery from the effects of radiation, we feel that a minimum temperature of 350°C is required. New investigations are necessary in order to determine if longer exposures at temperatures such as 350°C can duplicate the effects of shorter times at more elevated temperatures. Table 2 shows the correlation between L_n and electrical output for a typical annealing experiment. Figure 4 shows the spectral response variation over this same run.

Additional Observations

A series of experiments was performed to observe the effect of increasing the annealing time at a particular temperature. It was found that over fifty percent of the original degradation caused by 1×10^{14} e/cm^2 could be eliminated by heating the cells for approximately one hour at 350°C. In some cases there were only relatively small improvements in output after 30 minutes, but one hour seemed to maximize recovery at that temperature. Since many cells showed evidence of contact punchthrough at ∿400°C, we were reluctant to try the same test above 400°C.

The behavior of boron doped two ohm-cm back surface field devices was similar to that seen for conventional cells. The ten ohm-cm boron doped field cells appeared to display a greater amount of output recovery at a given temperature than did 10 ohm-cm conventional samples. Hopefully more data of higher resistivity boron doped field cells will be available in the near future.

The absolute magnitude of the strong reverse annealing described in two ohm-cm boron doped cells irradiated and then heated to 200°C for 30 minutes does not seem to be a function of fluence, which offers additional support for our proposed model. The average additional degradation in current measured for a population of 12 cells was 7.0 mA when irradiated to 1×10^{14} e/cm^2. Another group of 14 cells irradiated to 1×10^{15} e/cm^2 degraded by an average of 7.7 mA after being heated to 200°C for 30 minutes.

Proposed Model

Our observations can be explained in a qualitative manner by postulating a pair of competing mechanisms to account for the low temperature reverse annealing seen in most boron and gallium doped silicon solar cells. Still another mechanism dominates at higher temperatures (350°C and greater) to complete this model. It is assumed that one of the mechanisms, defined as B, allows migrators to couple with radiation induced recombination sites thus increasing or enhancing their capture cross sections. This would tend to reduce minority carrier diffusion length. The new recombination complex is postulated to be thermally stable up to temperatures of ∿350°C.

In competition with this mechanism is another mechanism, defined as G, which provides migrators that seek out the very same recombination sites, and if the recombination site has not been already enhanced, the G-type migrator couples with it in such a manner as to reduce or neutralize its capture cross section. This would result in an increase in minority carrier diffusion length. As with the B-type complex, the G-type complex is thermally stable up to temperatures of ∿350°C. Once a recombination site has become G or B-type, it is no longer susceptible to further coupling with either migrator.

We assume that the B-type migrator is associated with the dopant itself while the G-type migrator is some other species contained within the crystal. The concentration of both migrators is postulated to be relatively small with respect to the concentration of radiation induced defects, and depending on the temperature at which B-type migrators are triggered, the relative concentrations of B and G-type migrators is fairly similar.

Examining the data reported for boron doped samples it can be argued that the positive annealing that takes place at 60°C is due to G-type migrators. However, when a temperature sufficient to trigger B-type occurs, they now dominate, which is what has been seen, namely an abrupt additional loss in diffusion length at a temperature of $\sim$120-140°C. The magnitude of reverse annealing is greater for 2 ohm-cm as compared to 10 ohm-cm cells, which is explained by arguing that B-type migrators are related to dopant concentration. The fact that heating 10 ohm-cm cells at 60°C prior to heat treatment at 200°C mitigates reverse or negative annealing is explained by arguing that type-G migrators have had sufficient time to occupy nearby recombination sites, thus preventing type-B, which does not exist in very high concentrations, from becoming fully activated. The saturation in reverse annealing over the range of 250 to 350°C is also explained by arguing that both types of migrators have now occupied as many recombination sites as they can reach. The idea that the concentration of type-B migrators is less than the number of recombination sites available also might account for the relative constant loss of 7-8 mA observed in 2 ohm-cm cells exposed to fluences of $1x10^{14}$ and $1x10^{15}$ e/cm^2.

The gallium doped cell behavior at 60°C can be explained by arguing that B-type migrators are triggered at a lower temperature, and do not enhance the capture cross section of radiation induced recombination centers as greatly as do B-type migrators in boron doped silicon. However, the B-type are still related to the dopant concentration, thereby accounting for the reverse annealing in 2 ohm-cm cells and the slight positive annealing in 20 ohm-cm gallium doped cells at 60°C. With higher temperatures the G-type migrators dominate and saturate, explaining the slow positive annealing observed in both 2 and 10 ohm-cm gallium doped samples.

At 350°C, a new dominant mechanism is triggered which breaks up the B and G-type complexes and also begins eliminating the radiation induced recombination centers. This explained the similarity in behavior of 2 and 10 ohm-cm gallium and boron doped samples over the annealing range of 350 to 450°C.

This model must also account for the behavior of the very low resistivity cells doped with boron and gallium in order to be worthy of further consideration. The boron doped sample showed a very high etch pit count (10^6 per cm^2) indicating a high dislocation density. The gallium doped samples exhibited striations caused by the method used to incorporate the dopant. It is proposed that the dislocations and striations acted to pin or impede the triggering of type-B migrators until sufficient additional thermal energy allowed them to be released. It is significant that the peak reverse annealing observed for low resistivity samples showed the same trend as for other samples, namely gallium doped at lower temperatures. In addition, the difference in triggering temperatures between the two dopants was $\sim$50°C, very close to the difference observed in higher resistivity cells.

CONCLUSIONS

The model we have proposed to account for our experimental findings is extremely unsophisticated. It is hoped that future work will yield sufficient information to allow the identification of the B and G-type migrators. This effort has yielded a great deal of practical information concerning annealing which will assist us in establishing techniques for providing on panel heating in order to reduce or eliminate radiation damage to solar cells. A great deal of work remains to determine whether there is any relationship between fluence and annealing which could be useful in an engineering sense, e.g. are there advantages to annealing after lower fluences. Of even greater importance is the need for detailed information on the annealing characteristics of proton irradiated solar cells. The greatest challenge still has yet to be addressed, that is designing a solar panel which can still function effectively after being thermally annealed.

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CHANGE IN IRRADIATED ($\phi = 1x10^{15}$ e/cm^2) ELECTRICAL PARAMETERS AFTER 60°C HEATING

Cell Type	Sample Size	Time (hrs)	ΔI_{sc} (mA)	ΔV_{oc} (mV)	ΔP_{max} (mW)
2 Ω-cm Ga	6	16	(3.5)	(3.0)	(1.7)
2 Ω-cm Ga	6	64	(3.4)	(3.2)	(1.5)
10 Ω-cm Ga	6	16	0.1	0.5	-
20 Ω-cm Ga	6	16	0.5	0.6	0.7
2 Ω-cm B	2	16	2.0	3.3	1.2
2 Ω-cm B	2	64	1.1	3.4	0.7
10 Ω-cm B	2	16	2.7	3.0	1.3

( ) - loss

TABLE 1

CORRELATION BETWEEN CELL OUTPUT AND DIFFUSION LENGTH

Condition	Isc (mA)	Voc (mV)	P_{max} (mW)	L_n (μm)
Pre-irradiation	148.2	594	69.3	96.8
$\phi = 1 \times 10^{14}$	137.7	571	60.6	61.9
200°C 15 min.	131.3	560	57.9	42.3
200°C 45 min.	130.5	560	57.5	-
250°C 15 min.	130.2	561	57.4	-
300°C 15 min.	129.8	562	57.6	-
350°C 15 min.	135.1	573	60.9	61.0
350°C 45 min.	144.0	589	66.5	83.2
6 samples 2 ohm-cm boron doped, 250 μm thick				

TABLE 2

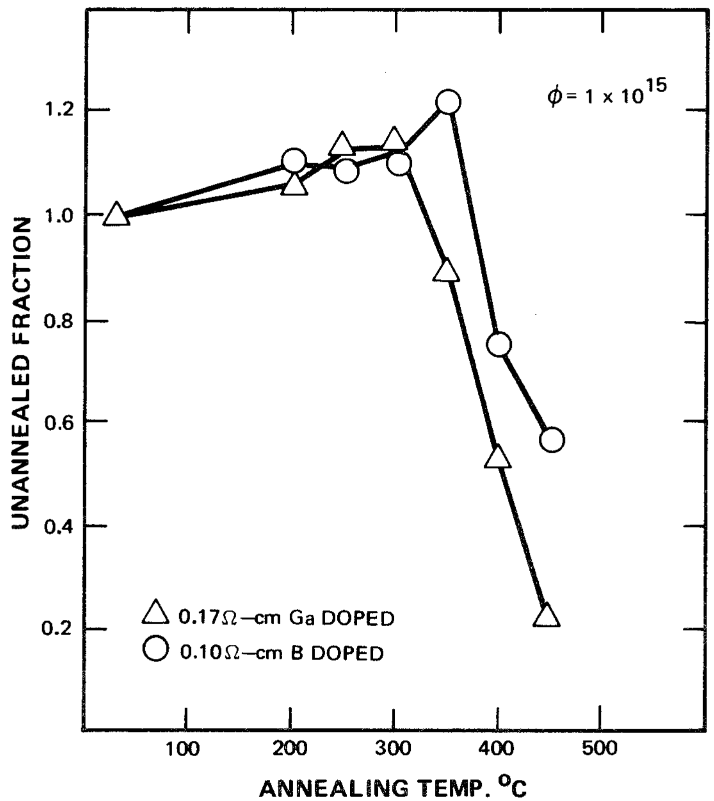

FIGURE 1

I_{SC} RECOVERY IN ELECTRON IRRADIATED
0.1-0.2 Ω-CM SILICON

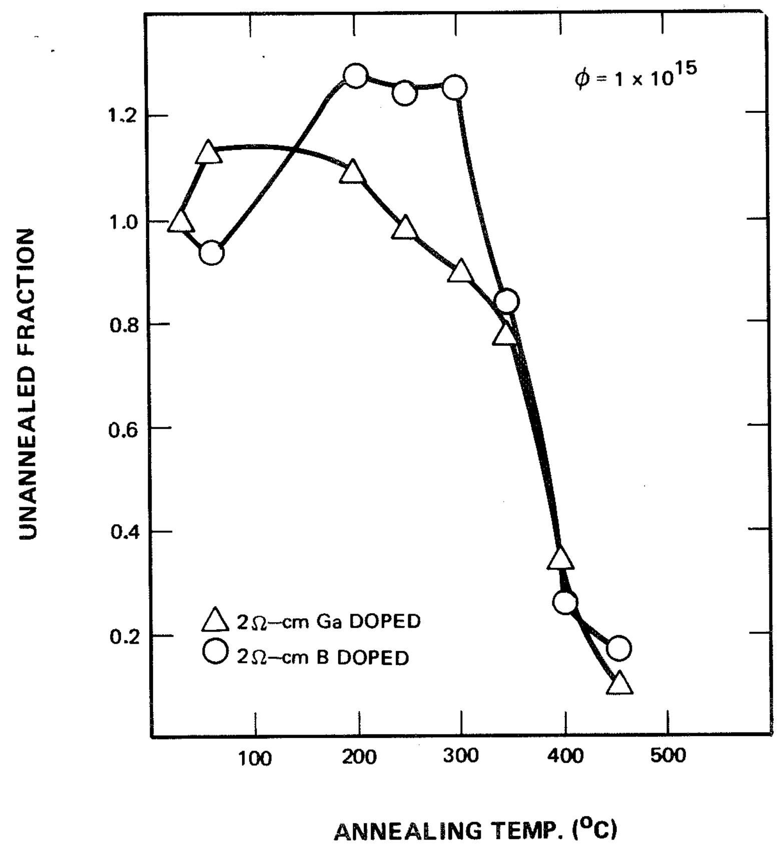

FIGURE 2

I_{SC} RECOVERY IN ELECTRON IRRADIATED
2 Ω-CM SILICON

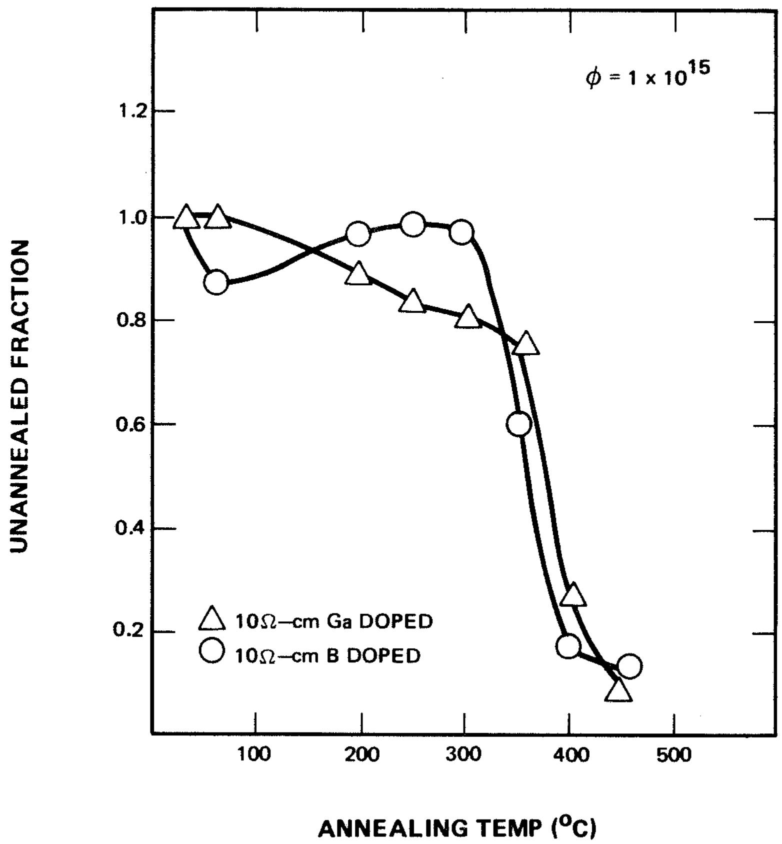

FIGURE 3

I_{SC} RECOVERY IN ELECTRON IRRADIATED 10 Ω-CM SILICON

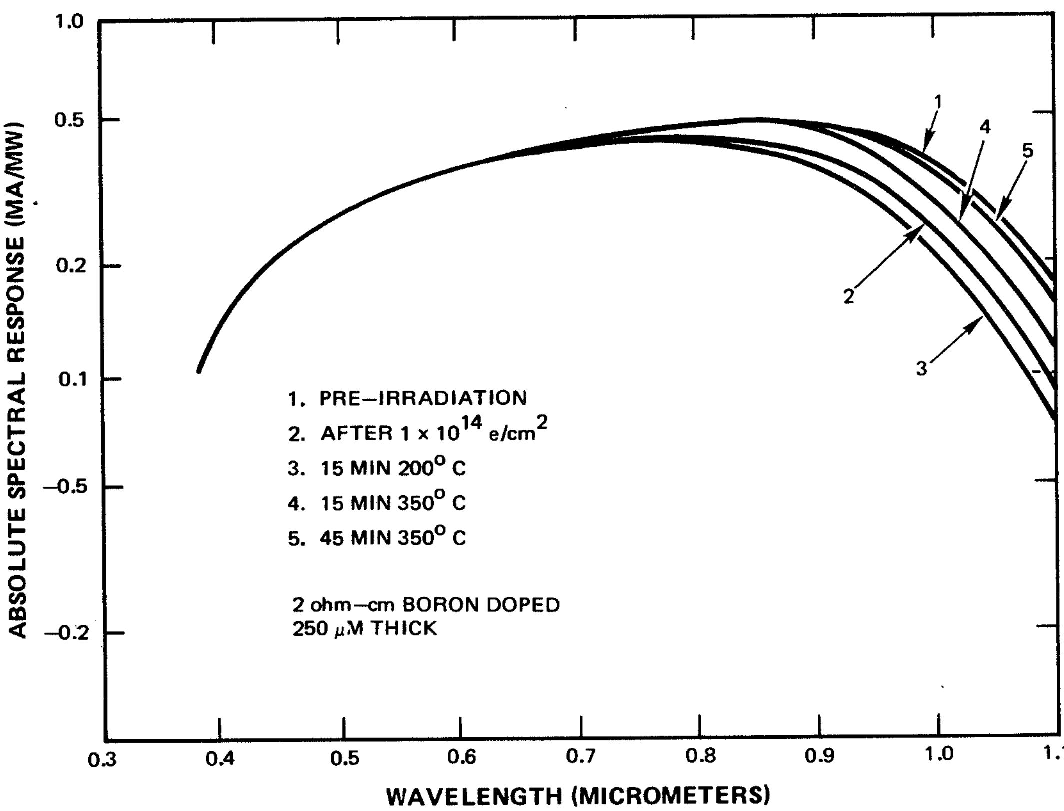

FIGURE 4

SPECTRAL RESPONSE OF IRRADIATED AND ANNEALED
2 Ω-CM BORON DOPED SILICON