RADIATION DAMAGE ANNEALING KINETICS IN LITHIUM-DIFFUSED SILICON SOLAR CELLS

ANNUAL REPORT

JULY 1971

Contract No. 952936

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TECHNICAL CONTENT STATEMENT

This report contains information prepared by M. S. Dresselhaus of the Center for Materials Science and Engineering, Massachusetts Institute of Technology under JPS subcontract. Its content is not necessarily endorsed by the Jet Propulsion Laboratory, California Institute of Technology, or the National Aeronautics and Space Administration.

NEW TECHNOLOGY

No reportable items of new technology have been identified.

ABSTRACT AND SUMMARY

A model for the annealing kinetics of radiation damage in lithium-diffused silicon solar cells has been developed using a phenomenological approach, whereby the carrier recombination rate is found through use of the Shockley-Read-Hall theory for carrier lifetime. The annealing process is handled through a time-dependent recombination center density according to the kinetic equations of Fang. Even though it appears to be an oversimplification to use a single level form of the Shockley-Read-Hall theory and first order kinetics in the Fang theory, we have assumed these forms as a first approximation. With these simplifications, it is feasible to develop a computer program to predict device performance from specified cell characteristics in lithium-diffused silicon solar cells. Because of the oversimplification of the model and the scarcity of lifetime data on well-characterized lithium-diffused silicon solar cells, there is some doubt with regard to the reliability of the predictions of device performance on the basis of this modeling. Elaborations of this model will be necessary to obtain more reliable results.

Rapid progress has been achieved in our spectral response studies of lithium-diffused silicon solar cells and their relations to cell performance. With the relocation of this work at the M.I.T. Lincoln Accelerator Facility, it will be possible to make measurements of both spectral response and the I-V characteristics on the same samples and to have a simulated electron radiation and solar illumination environment. Installation of the apparatus should be completed by the end of the summer.

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INTRODUCTION

Our main efforts this year have been directed toward developing a kinetic model for the production and annealing of radiation damage in lithium-diffused silicon solar cells. As a first approach, it appeared attractive to handle the kinetics problem from first principles. Because of the incompleteness of available defect data for well-characterized lithium-diffused silicon in a well-characterized radiation environment, such an approach does not seem not fruitful at the present time. It is, however, quite feasible to develop a more phenomenological approach in terms of effective defect levels, whereby, (1) the carrier generation is handled by the dynamics of the creation of electron-hole pairs by the incident light, (2) the electron-hole recombination is described by the Shockley-Read-Hall theory, using for simplicity a single effective recombination level, or a generalization of this, if necessary, (3) the annealing process is described by a kinetic rate equation for the recombination center density, and (4) the carrier concentrations are found from the continuity equations and from Poisson's equation. One advantage of this phenomenological approach is the relative simplicity of the formulation of the problem. To obtain specific solutions, the parameters of the Shockley-Hall-Read theory must be evaluated from available lifetime data. The utility of the effort is strongly coupled to the quantity and quality of these lifetime data.

In the course of our work in surveying the literature on lifetime measurements, we became aware of the fact that very little effort has been devoted to making simultaneous measurements in lithium-diffused silicon devices of (1) material parameters such as minority carrier lifetime and spectral response, and device performance through I-V curves, so as to correlate closely the relation between the material parameters and specific features of the device performance. Furthermore, very few systematic measurements have been done in a simulated space radiation environment or in a simulated solar illumination environment. We describe in this report a program of spectral response studies on lithium-diffused silicon solar cells and their relation to cell performance. Using the facilities of the M.I.T. Lincoln Laboratory Accelerator, it is convenient to make spectral response and I-V measurements in a simulated radiation environment, and simultaneously, in a simulated solar illumination environment. These measurements, all performed on the same cells, should provide new insight into the operation of lithium-diffused silicon solar cells and should suggest new means for improving their performance for use in space missions.

TECHNICAL DISCUSSION

Kinetic Modeling

The major objective of our efforts this year in the Lithium Diffused Silicon Solar Cell Program of J.P.L. has been to develop a kinetic model for the production and annealing of radiation damage in lithium diffused silicon solar cells. During the course of this investigation, we have considered the problems from several points of view and these are reviewed here.

A most attractive approach to the kinetics problem is a first principles approach, suggested at the Third Annual Conference on the Effect of Lithium on Silicon Solar Cells, held in Pasadena, 1970.[1] According to this approach, it is necessary to identify the concentration of each of the damage centers that are produced upon irradiation by a specific specie, according to the fluence, temperature, and energy of the irradiation. To deal with the kinetics, the annealing rate of each of these defects must also be known. Finally, it is necessary to correlate each of these defects with its effect on the device performance in terms of such parameters as minority carrier lifetime and carrier removal rates. In the identification of the particular defects that are produced upon irradiation, much of the pertinent data, particularly the early data, gives an inadequate characterization of the environmental conditions under which the data were taken. Thus, there is considerable difficulty in correlating related measurements by two groups of workers. We have spoken to various people in our own program about this difficulty, and efforts are being made to provide better characterization of data that are presented.

Although progress has been made in identifying some of the annealing mechanisms, the amount of information available on the annealing processes is inadequate for kinetic modeling from a first principles point of view. Finally, we do not yet know the role played by many of these radiation defects in the degradation of the device performance. When we considered this method of attack in detail during the fall and winter of 1970, the scarcity of available data made this approach look rather bleak. Nevertheless, because of the intimate connection between these defects and any of the approaches that can be used for kinetic modeling, we have kept one of our graduate students, James Tsang, working almost exclusively on the problem of defect production and annealing. We were happy to observe at the Fourth Annual Conference on the Effects of Lithium on Silicon Solar Cells (Pasadena, 1971), that considerable progress had been made in the last year in identifying the various mechanisms that are important in the production and annealing of radiation damage in lithium-diffused silicon solar cells.

It is perhaps worth pointing out that it will be no easy matter to assemble enough meaningful data to make a first principles approach feasible. The basic reason for this difficulty is that the shallow donor and acceptor defects, which are well understood in silicon, play a minor perturbation to the host crystal lattice. On the other hand, the deep levels, which do, in fact, represent a more major perturbation to the lattice, are very important in the device performance. As a matter of fact, just trace concentrations of deep defect level impurities (such as gold) often dominate the minority carrier lifetime in silicon.[2] Furthermore, the theory for deep impurity levels in silicon is not well established at the present time.

Because of these difficulties with the attack from first principles, we turned to a more phenomenological approach. According to this treatment, we will not insist that we understand the mechanisms of radiation defect production and annealing in any detail. We will implicitly assume that there are just a few varieties of radiation defects which are important in the device performance and **that these defects are described phenomenologically** in terms of an effective energy level, an effective cross-section for the capture of minority carriers, an effective annealing rate etc. We assume the solar cell to be of simple one-dimensional geometry, with the z-direction chosen normal to the p-n junction. In this geometry, the continuity equations for electrons (n) and holes (p) are simply written as

$$\frac{\delta n(z,t)}{\delta t} = G(z,t) - R_n(z,t) - \frac{\delta J_p(z,t)}{\delta z} , \quad (1)$$

$$\frac{\delta p(z,t)}{\delta t} = G(z,t) - R_p(z,t) - \frac{\delta J_n(z,t)}{\delta z} . \quad (2)$$

In writing these equations, we assume that electrons and holes are generated in equal numbers as each photon is absorbed by an electron in a valence state to produce an excited electron in the conduction band and leaving behind a hole in the valence band; this process is represented by the function $G(z,t)$, depending primarily upon distance, since the incident light is exponentially attenuated in the silicon, with the light penetration falling off rapidly as the **energy** is increased above the indirect band gap. Not all the carriers that are generated by the light are collected at the electrodes. Some of these are lost in electron-hole recombination processes, represented by the recombination rate $R(z,t)$. To complete our continuity equation, we must take into account the carrier flow through gradients in the current density. Particle currents flow through action of an electric field and particle diffusion

$$J_n = -n\mu_n E - D_n \frac{\delta n(z,t)}{\delta z}, \quad (3)$$

$$J_p = p\mu_p E - D_p \frac{\delta p(z,t)}{\delta z}, \quad (4)$$

where the drift due to the driving electric field is determined by the mobility μ of the carriers and the diffusion currents are determined by the diffusion coefficients D for the carriers. The unbalanced charge gives rise to electric field gradients, which by Poisson's equation is represented as

$$\frac{\delta E(z,t)}{\delta z} = \frac{4\pi e}{\varepsilon} [p(z,t) + N_D^+ - N_A^-] \quad (5)$$

where e is the charge on the electron, N_D^+ is the number of ionized donors and N_A^- the number of ionized acceptors and ε is the static dielectric constant. In the absence of light, the difference in the electron and hole concentrations in typical silicon p-n devices is due to the doping levels in the n and p regions, and the electric field is confined to the junction region. In the lithium-diffused devices, however, the lithium produces a non-uniform donor concentration in the n-type region near the junction and consequently electric fields are also present in part of the base region of the solar cell device. In writing Eq. (5) we consider the carrier concentrations n(z,t) and p(z,t) to include both the diffused carriers that are introduced in the fabrication of the solar cell as well as the carriers that are produced in the operation of the device.

If we are primarily concerned with steady state operation, then we can neglect the effect of electron and hole traps, since these will presumably be rapidly filled and will remain filled during the operation of the device.

Under steady-state conditions, we need then be primarily concerned with recombination centers, and these we propose to describe in the simplest possible terms using the phenomenological Shockley-Read-Hall theory.[3] The simplest form of this theory introduces a single effective defect level, **assumes** that the number of recombination centers is small relative to the excess carrier density, so that there are equal numbers of excess holes and electrons, and **assumes that the recombination rates are equal for** electrons and holes. The recombination rate depends on the lifetime of this defect level which is given by the expression

$$\tau = \tau_{p_o} \left(\frac{n_o+n_1+\Delta n}{n_o+p_o+\Delta n}\right) + \tau_{n_o} \left(\frac{p_o+p_1+\Delta n}{n_o+p_o+\Delta n}\right) \tag{6}$$

where the lifetimes in heavily p-type and n-type material are given by:

$$\tau_{p_o} = \frac{1}{N_R v_{th}(T)\sigma_p(T)} \tag{7}$$

and

$$\tau_{n_o} = \frac{1}{N_R v_{th}(T)\sigma_n(T)}. \tag{8}$$

In these expressions,

N_R = recombination center density

v_{th} = thermal velocity

$\sigma_{p,n}$ = cross sections for recombination of holes or electrons

n_o, p_o = thermal equilibrium carrier concentration

$\Delta n = \Delta p$ = concentration of excess carriers

T = temperature

$n_1 = N_c\, e^{(E_R-E_C)/kT}$

$p_1 = N_v\, e^{(E_V-E_R)/kT}$.

N_c and N_v are the result of integrals over the density of states for the conduction and valence bands, respectively:

$$N_c = 2\left(\frac{2\pi m_e^* kT}{h^2}\right)^{3/2} \tag{9}$$

$$N_v = 2\left(\frac{2\pi m_h^* kT}{h^2}\right)^{3/2}, \tag{10}$$

where m_e^* and m_h^* are the effective masses of the conduction and valence bands respectively. In order to interpret lifetime vs. temperature data, an explicit temperature dependence of the cross sections and of the thermal velocity v_{th} must be assumed. The temperature dependence of σ is complicated but has been treated theoretically.[4] Although there exist divergent opinions on the temperature dependence of σ, there is general agreement that the temperature dependence of v_{th} goes as $T^{1/2}$. Most interpretations of lifetime data consider $\sigma(T) \sim T^{1/2}$ so that σ_{p_o} and σ_{n_o} are temperature independent. If temperature dependences for v_{th} and $\sigma(T)$ are introduced, then it is possible to fit the experimental lifetime measurements as a function of temperature and thereby to deduce the energy of the defect level E_R.

This general approach is meaningful, provided that the minority carrier lifetime is controlled by one dominant defect - say the divacancy in oxygen-lean silicon or the oxygen-vacancy complex in oxygen-rich silicon. If this is the case, then we might expect the effective defect level E_R to be correlated with an important defect level that has been identified by more direct measurements on bulk material - e.g. optical, luminescence, ESR, temperature dependence of the Hall effect, etc. Whereas this simple version of the Shockley-Hall-Read theory may be appropriate for the analysis of standard n/p silicon solar cells, it is not at all clear that the more complicated recombination processes that occur in lithium-diffused silicon can be handled by this simple theory. Generalizations of the lifetime calculation, involving several effective defect centers, each with more than one energy level, may be required to handle the recombination problem in lithium-diffused silicon.[5,6]

The annealing problem can be handled within the framework of the Shockley-Read-Hall approach, by considering the recombination center density N_R to be time dependent. The determination of N_R then is governed by a rate equation, such as has been developed by Fang and others.[7]

The application of the Shockley-Read-Hall approach to the minority carrier lifetime problem is itself beset with complications. To illustrate these complications, it is instructive to consider the various energy levels identified with radiation defects produced by 1 MeV electrons in n-type silicon. (see Fig. 1) In all cases, the levels were obtained from Shockley-Read-Hall analysis of the temperature dependence of lifetime data.[8-11] The two most important reasons for the variety of effective levels in this diagram are: (1) differences in material parameters in the n-type silicon and (2) differences in the use of the Shockley-Read-Hall theory. Differences in the material parameters are difficult to handle because it has not been customary to give a complete characterization in the literature of the material and environmental parameters. This lack of information has made it exceedingly difficult to compare the work of different groups. This lack of sample characterization may also be responsible for the tendency on the part of some workers to ignore past work and to report their findings with little or no attempt to correlate their results with previous measurements. Differences in the use of the Shockley-Read-Hall theory arise largely through differences in the assumptions for the temperature dependence of the cross sections. As can be seen in this figure, the upper energy level is relatively less sensitive than is the lower level to these two classes of differences.

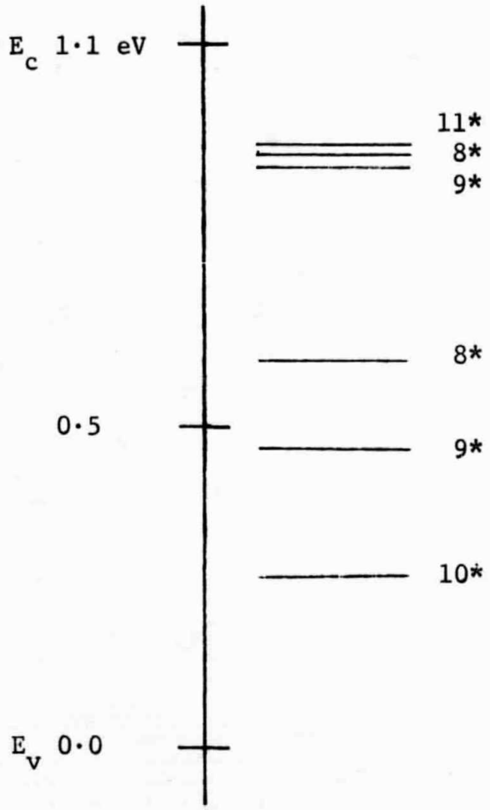

Fig. 1

Defect induced energy levels of h-type P-doped Silicon Irradiated with 1 Mev Electrons.

* see references in text

To obtain explicit solutions to the kinetic modelling problem, it is necessary to develop a computer program. Exploratory work along these lines has been carried out and within the framework of the simple form of the Shockley-Read-Hall theory for the recombination processes, it seems feasible to implement the phenomenological approach with a computer solution. We have, in fact, learned that the group at Gulf Atomic has produced such a computer solution.[12]

SPECTRAL RESPONSE STUDIES OF LITHIUM-DIFFUSED SILICON SOLAR CELLS AND THEIR RELATION TO CELL PERFORMANCE

Although the beneficial radiation hardening effects of lithium in silicon solar cells are well established, the mechanisms by which the lithium inhibits cell degradation are far from being completely understood. Furthermore, while the best lithium cells are approaching the efficiency of standard n on p cells, additional and more systematic design improvements will likely depend on a careful analysis of the lithium cell parameters. This kind of understanding is the objective of our continuing investigation. We discuss below a coordinated set of experimental measurements. These measurements, all performed on the same cells, will allow us to correlate the cell parameters and their behavior during as well as after irradiation with the performance characteristics of the devices in their simulated environment.

Ultimately, of course, the voltage-current characteristics and overall collection efficiency are the important device parameters from the application engineering point of view. Unfortunately, the analysis of these performance characteristics alone cannot provide the necessary understanding of device degradation which is required for design improvement. Likewise, measurements of radiation damage in bulk silicon, while very helpful in understanding the problem of damage mechanisms do not complete the picture of cell operation. Because of the complicated inter-relationship between device performance and a wide variety of parameters, specifying the device fabrication including junction depth, oxygen content, lithium doping concentration and profile, an analysis of more extensive measurements on the solar cells themselves is necessary. In a device with a number of variable fabrication parameters, it is imperative that a number of complementary measurements be made on each cell to determine the effect of these measurements on cell performance.

While there are no straightforward ways to measure directly each of the important parameters affecting a cell's performance, spectral response studies provide a means of partially separating the effects of some of the device parameters. The shape of the spectral response characteristics, that is, the relative collection efficiency as a function of wavelength, is strongly dependent on several cell parameters, the long wavelength response being dominated by the base region lifetime and electric fields, and the short wavelength response being dominated by carrier lifetime and electric fields in the front surface and junction regions and the surface recombination velocity. Differences in spectral response between various standard n/p cells and cells containing a range of lithium concentrations can be interpreted in terms of lifetime variations with depth and with lithium concentration profiles. Changes in these spectral response characteristics with irradiation will allow us to monitor the degradation of the cell not just in terms of the overall efficiency but rather in terms of which of the cell parameters are affected most seriously. For example, serious changes in the short wavelength response might indicate the necessity of developing cells with a different lithium concentration profile in the vicinity of the junction.

The analysis of spectral response data in lithium cells is more complicated than in the case of standard silicon solar cells because of the lithium concentration gradient. Together with other measurements (I-V curves, series resistance) of cell performance, however, these data should provide new insight into the operation of the cells and suggest new means for improving their performance.

To initiate our program on spectral response studies we have performed preliminary measurements on cells using a simplified version of the spectral response apparatus shown in Fig. 2. The differential technique, including analog to digital information processing capabilities, will improve the accuracy of results as well as increase the convenience of the data collecting process. These automation features will be implemented in future spectral response measurements. The monochromator shown in the figure is a Perkin Elmer double pass unit with resolution greater than 1Å.

The output of the monochromator is chopped and imaged over the active areas of (1) a reference cell whose absolute spectral response has previously been measured, and (2) the cell whose response is to be measured. In these measurements, the cells are loaded to short circuit conditions. Since only light from the monochromator is incident upon the cells, only a small amount of power is produced, so that short circuit conditions can be achieved with a large resistor. The a.c. signals from the two cells are fed to appropriate stages of synchronous amplification and detection and then to a divider module. The resultant signal is digitized and compared with the reference cell response using our programmable calculator.

We feel that spectral response measurements will yield valuable information on lithium concentration profiles, surface recombination velocity, electric field distributions near the junction, and provide an indication of the depth dependence of damage centers. By combining this information with cell I-V measurements, which are a direct measure of cell performance, a correlation between the controllable cell parameters (surface preparation, Li gradient, junction depth, etc.) and terminal behavior will result. The experimental apparatus necessary for these measurements is shown in Fig. 3. A current source provides energy for measurements in the dark. A third

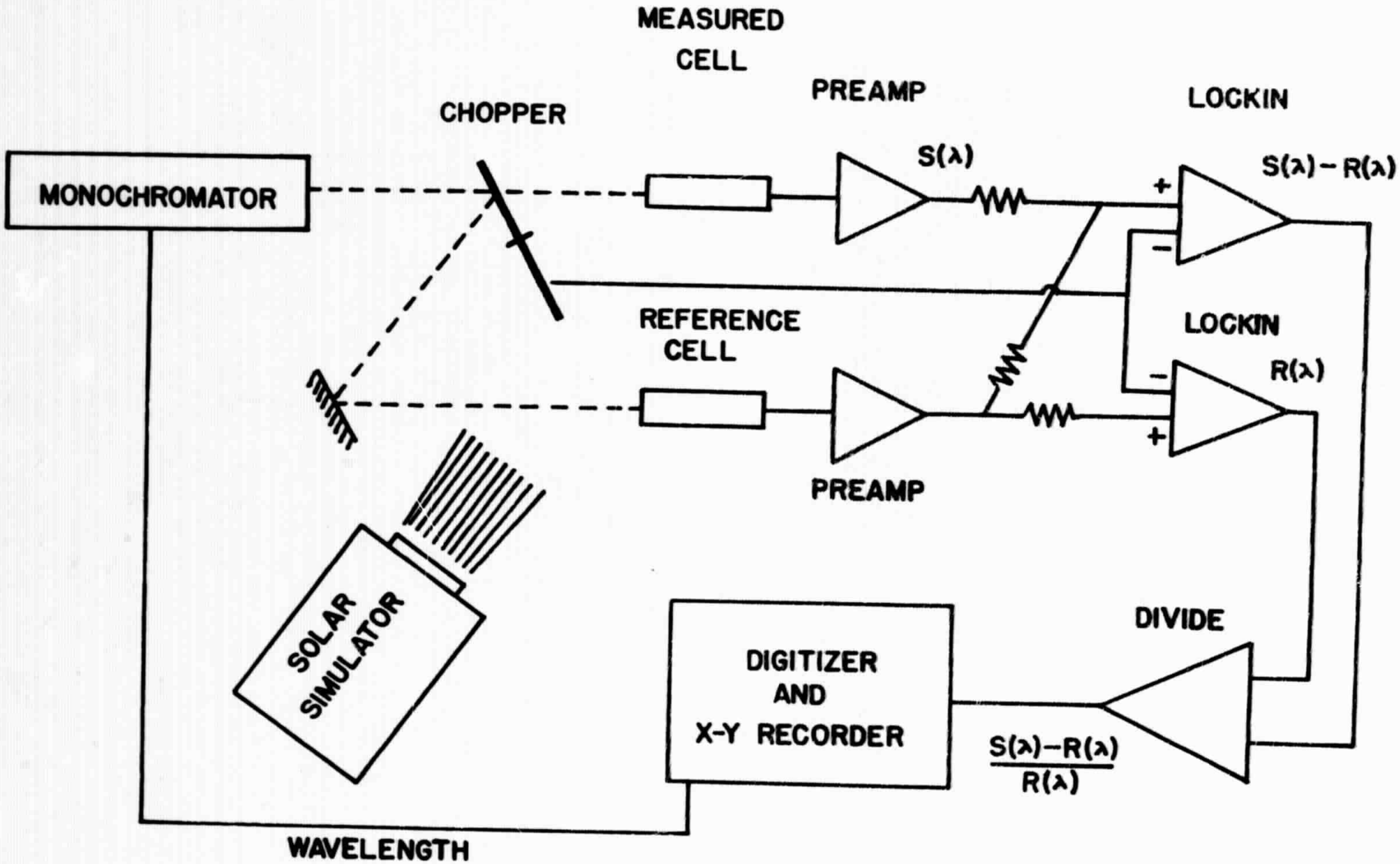

FIG. 2 ABSOLUTE SPECTRAL RESPONSE BY DIFFERENTIAL MEASUREMENT

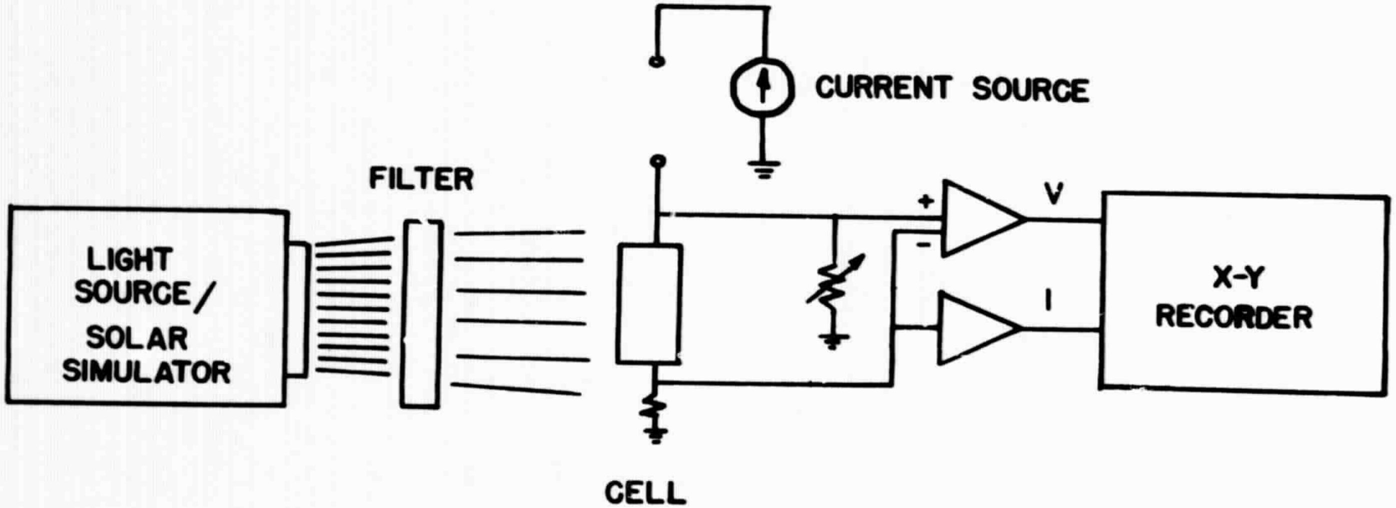

FIG. 3 I-V CURVES AND SERIES RESISTANCE MEASUREMENT

meaningful measurement, series resistance, can also be made with the apparatus of Fig. 3.[13] Analysis of results from these experiments should lead to fabrication procedures necessary to optimize device performance.

To irradiate the cells we are using the facilities of the Lincoln Accelerator Laboratory at the M.I.T. Lincoln Laboratory. Since we desire to perform measurements in situ to provide close simulation of space environment, the entire base of operations has now been shifted to this site. An added advantage of this location is the close collaboration that has been established between our work and that of Dr. A. G. Stanley and the Lincoln Laboratory Satellite Program. The accelerator facility allows solar simulation test measurements, and irradiation to be run simultaneously. Although proton irradiation is available at this facility, we will first study the effect of electron irradiation. The electron energies that will be used are in the range $1 < E < 3$ MeV with fluences appropriate to between one and 20 years of synchronous orbit. Two light simulation sources are available -a 20 kW filtered Xe-arc unit and a tungsten halogen quartz lamp array. We are now putting into operation the 20 kW filtered Xe-arc source. At the higher light intensities of simulated solar environment, it will be necessary to utilize a constant temperature heat reservoir to correct for light source heating effects. We also anticipate using an inductive solar cell load to obtain adequate spectral response signals while insuring that device loading is kept near short circuit load conditions when solar simulation is used. In summary, this accelerator facility provides us with a unique opportunity to make meaningful measurements relating a variety of bulk parameters with device performance.

Conclusions

Our work on the kinetic modeling of radiation damage in lithium-diffused silicon solar cells has proceeded to the point where a computer program is required to obtain explicit results. On the basis of our studies to date, we anticipate that a rather sophisticated form of the Shockley-Read-Hall theory will be necessary for handling the recombination processes. Furthermore, the scarcity of lifetime data on well-characterized lithium-diffused silicon solar cells will limit the utility of the computer modeling for predicting the performance characteristics of cells with arbitrary specifications. In summary, we do not feel that we can add much to the modeling work of the Gulf Atomic Group;[12] furthermore, we do not share their confidence in the reliability of this modeling, because of the vast simplifications that are made.

We feel that our spectral response studies of lithium-diffused silicon solar cells and their relation to cell performance provide a unique tool for understanding and improving device performance. This program is particularly attractive because it provides for simultaneous measurement of several properties on the same solar cells. Furthermore, these measurements are all to be carried out directly in a simulated electron irradiation and solar illumination environment. We are convinced that this is a fruitful area for research at this time.

Future Plans

In the next half year, we expect to devote out full energies to the spectral response measurements as related to the solar cell device performance. We are now setting up the spectral response apparatus and the solar simulator in a more quantitative fashion at the M.I.T. Lincoln Laboratory Accelerator Facility, and we expect the setup to be working by the end of the summer. Detailed measurements and analysis of data are planned for the fall and winter.

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