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## RADIATION DAMAGE ANNEALING KINETICS

M. S. Dresselhaus  
Department of Electrical Engineering,  
Center for Materials Science and Engineering,  
Massachusetts Institute of Technology, Cambridge, Mass.

### I. INTRODUCTION

Our primary task is to understand how the presence of lithium assists in the recovery process of irradiated silicon solar cells. Although lithium is more effective in accelerating the recovery rate from neutron and proton bombardment, lithium has also proved useful in the recovery process from electron irradiation. Since neutron irradiation is not especially important for typical NASA space missions involving solar cells, and, furthermore, since it is relatively easy to provide protection against proton damage, our efforts have been mainly directed toward the study of recovery from electron irradiation.

### II. BACKGROUND

To see how to tackle the problem let us start at the beginning and consider the solar cell as a p-n junction where for our case, the base region is the n-region, as is illustrated in Fig. 1. Light incident on this base region produces electron-hole pairs, with the holes capable of surmounting the potential barrier at the p-n junction and reaching the collecting electrode. We are accustomed to thinking of typical carrier diffusion lengths in crucible-grown quartz as  $L \sim 1.2 \times 10^{-4}$  m so that collection can result from electron-hole pairs formed far from the junction. It is this long diffusion length that encourages us to think that the kinetics in bulk silicon might be the crucial factor in determining solar cell behavior. We shall now show why, on one hand, the consideration of bulk effects might by themselves lead to erroneous conclusions and, on the other hand, why it is

nevertheless important to consider the kinetics of bulk silicon.

Any kinetics modeling based on a first-principles approach requires the observation of: (1) the defects that are formed during irradiation, (2) how these defects are annealed out in the recovery process, and (3) how these defects affect the diffusion length, minority carrier lifetime, carrier removal rate, etc. In dealing with this problem, we must classify the defects into various categories, and since each category tends to have a rather different cross section for minority carrier removal, different concentration ranges could significantly affect the minority carrier diffusion length.

In the first category we have the shallow donor and acceptor levels. These defects do not represent a major perturbation to the periodic potential characteristic of the host silicon lattice and consequently offer just a small cross-section for minority carrier removal. Typical concentrations of such defects have little effect on the minority carrier transport problem. On the other hand, the deep defect levels represent appreciable perturbations to the periodic potential and offer large cross-sections for a number of carrier removal processes. For such defects (e.g., gold), a concentration as low as  $\sim 10^{19}/\text{m}^3$  (which is merely a trace concentration) can appreciably affect the minority carrier diffusion length (Ref. 1). Some deep defect levels act like traps and are important in minority carrier removal processes associated with transient phenomena. But in the steady state, once a trap is filled, it will remain filled.

On the other hand, a single recombination center can continuously remove minority carriers by combining them with majority carriers in either a radiative or a non-radiative recombination process. If the process is radiative, it is, in principle, observable by radiation recombination measurements; on the other hand, non-radiative processes are very difficult to study experimentally.

The types of defects most prevalent in the base region before irradiation are: (1) the shallow donor defects which are present in concentrations as large as  $10^{21}/\text{m}^3$ , and (2) deep impurity defects which are present in trace concentrations. Before irradiation, it is these trace quantities of deep impurity recombination centers which control the minority carrier diffusion length. The types of defects introduced by irradiation with electrons in the energy range of  $\sim 1$  MeV are predominantly in the deep defect level classification, since the radiation-induced defects (such as the vacancy) represent a major perturbation to the periodic lattice of the host crystal. For fluences typical of the space environment of a synchronous orbit mission of 5-yr duration, the radiation-induced deep defect concentrations will generally exceed the native deep-defect concentrations. Upon annealing, the radiation-induced defects tend to form complexes which are also associated with deep level states but generally represent less of a perturbation to the periodic potential of the host crystal. In both the irradiation and recovery processes, majority carriers are removed when they become bound to the various defect centers. This carrier removal results in a degradation of the junction.

To consider the kinetics problem from first principles, we must identify the primary radiation-induced defects and determine their effect on the minority carrier lifetime. We must then identify the centers that result upon annealing of the primary centers and determine the effect of these new centers on the minority carrier lifetime. In this connection it would be desirable to carry out measurements of both the minority carrier lifetime and the energy level spectrum of the defects. Such joint measurements should be made on samples that are well-characterized with regard to both material parameters and radiation environment.

### III. EXPERIMENTAL TECHNIQUES

A number of experimental techniques are available for the study of defect levels. The infrared absorption technique is one of the most useful techniques for establishing the energy levels associated with defects. We must remember here that there are many different species of defects present in the base region of an irradiated solar cell. Furthermore, each defect can be found in any one of a number of energy states as shown in Fig. 2. This figure shows the energy levels of the divacancy, one of the common defects occurring in irradiated float-zone silicon (Ref. 2). If the photon energy of the infrared radiation is just sufficient to excite electrons from the singly charged (-1) occupied level, 0.4 eV below the Fermi level, to the conduction band, there is an absorption of power from the incident beam. An experiment closely related to the infrared absorption is the photoconductivity experiment whereby we look at the current of the photoexcited electrons rather than at the power absorbed from the incident beam. These experi-

ments are not actually equivalent insofar as the final state in the photoconductivity experiment must be a band state, while a bound state is an acceptable final state in the infrared absorption process. At any rate, both types of experiments have, in fact, been carried out under our program and some results of the photoconductivity studies by Corelli are shown in Fig. 3. In interpreting such curves, the maxima in the photocurrent are identified with the resonant absorption from or to a defect level. These measurements by themselves do not identify the nature of the defect centers; to make such identifications it is necessary to study concentration dependences, temperature dependences, effects of stress or possibly magnetic fields. To study the effect of these centers on solar cell characteristics, measurements of the minority carrier lifetimes should be made on the same samples and correlated with the optical data.

There are, however, some more fundamental difficulties with these data: in order to observe these defects optically, it was necessary to irradiate the samples with fluences which create defect densities far in excess of the lithium concentration. These fluences are larger than are of practical interest for space missions. Since the benefits of lithium donors are realized primarily when the lithium concentration exceeds the damage center concentration (Ref. 3), these experiments are only of limited utility for our kinetic modeling program. Furthermore, this difficulty would not be resolved by increasing the lithium concentration, since the lithium concentrations used in this work were already as high as might be of interest to possible solar cell applications. In order for optical techniques to be useful to us, the sensitivity of the technique must be increased by perhaps two orders of magnitude. To accomplish this, a modulation technique could be exploited to advantage.

To study defect centers in bulk material some rather elegant recombination luminescence studies have been carried out by the University of Illinois group. In recombination luminescence, one measures the spectrum of the radiation emitted when, for example, an electron associated with a particular defect level combines with trapped hole or with hole in the valence band. An example of such a spectrum is shown in Fig. 4. Because recombination luminescence in silicon is not an efficient process, these experiments have also been plagued with the same difficulties as the optical experiments insofar as it has been necessary to employ high irradiation fluences in order to observe recombination luminescence signals. Recently, increased sensitivity has been achieved in silicon through use of a laser source to achieve the initial excitation (Ref. 4). Perhaps such techniques could also be employed in the luminescence recombination work in our program. In the luminescence studies made under our program, considerable success has been achieved in the identification of the nature of the observed defects. For example, the structure at 0.97 eV is identified with the divacancy 0.19 eV below the conduction band and the structure at 0.79 eV is identified with a two-oxygen defect complex. To make such studies valuable to a kinetic modeling effort, it will be necessary to correlate the luminescence studies with minority carrier lifetime measurements in order to understand the role of such defects in the solar cell degradation upon irradiation and subsequent recovery.

The difficulty with the bulk measurements made under conditions of intense irradiation can also be understood in terms of Fig. 5, where the dependence of the minority carrier diffusion length  $L$  is plotted as a function of fluence for 1-MeV electron irradiation on standard n/p solar cells, made from crucible grown silicon (Ref. 5). While  $L$  is  $\sim 1.20 \times 10^{-4}$  m for the pre-irradiated cells, we see a rapid decrease in  $L$  with increasing fluence so that for a fluence  $\sim 10^{20}/\text{m}^2$  the diffusion length is already below  $10^{-5}$  m. This figure tells us that if we are considering fluences in excess of  $\sim 10^{20}/\text{m}^2$ , the solar cell current generation in the base region will become less important compared with the behavior in the vicinity of the junction. Since the impurity concentrations and defect densities tend to be rather different near the junction as compared with the bulk behavior, the kind of data on bulk silicon that is of primary interest for kinetic modeling is that for low fluence levels corresponding to typical space environments. On the other hand, we should not conclude from this figure that measurements on bulk silicon are irrelevant. We shall soon see why it is important to consider both the data on the devices and data on the bulk material.

Another powerful technique that has been applied to the study of radiation-induced defects and their subsequent annealing in the presence of lithium is the electron spin resonance (ESR) technique. This technique is applicable to the study of defects in a singly charged state; for these states, the ESR technique provides a microscopic and detailed probe. With this technique, it has been possible to identify resonances associated with the oxygen-vacancy, the divacancy, the phosphorus-vacancy, the lithium-oxygen, as well as many other centers. The interpretation of these experiments indicates that for oxygen-lean silicon, the presence of lithium favors the formation of lithium-vacancy complexes rather than phosphorus-vacancy complexes and that in the annealing process, lithium can help to neutralize phosphorus in the phosphorus-vacancy complexes that happen to be present (Ref. 6). For the oxygen-rich silicon, the presence of lithium tends to favor formation of LiOV centers rather than the OV center itself. The fluences necessary for observation of ESR signals are still rather large (like  $10^{20}$  to  $10^{21}$  electrons/ $\text{m}^2$ ) but somewhat smaller than are required for the optical measurements.

We have, however, encountered several difficulties in utilizing some of the ESR data: (1) The measurements employ 30-MeV rather than 1-MeV electrons, the lower energy matching more closely other work in the program as well as the environmental conditions in space. Since the production and annealing rates for a given defect are strongly energy dependent, it would be desirable to have ESR data on similar samples as a function of electron irradiation energy. (2) The lithium concentration tends to be higher than the range of interest for solar cell applications and yet the lithium concentration is often less than the density of irradiation defects. Thus, the parameters do not really fall into the desired range for solar cell modeling. (3) Not all centers can be studied by the ESR method because they have the wrong charge state or are unoccupied.

From the point of view of cell modeling, our most useful data have come from less microscopic and perhaps less elegant techniques, but nevertheless capable of yielding information on the defect production and annealing in the parameter range of interest to solar cells and the type of space environment where the cells will be utilized. Such techniques are the bulk Hall and resistivity measurements, minority carrier lifetimes in bulk silicon and in solar cell devices, and capacitance measurements. We will have more to say about relating such data to the kinetic modeling later. From the temperature dependence of the Hall effect and from analysis of the temperature dependence of the minority carrier lifetime data, it is also possible to deduce defect levels. Such techniques have been widely exploited for this purpose in our program by the RCA, TRW, and Gulf-Atomic groups. If we now consider all the defect levels that have been reported in the literature to date we get the typical representation shown in Fig. 6. This diagram shows that a large number of defects have been identified and that a given defect can exist in various energy states. Not only is the number of defect levels overwhelmingly large, but the quantity of reliable and necessary information on each level is discouragingly small. From this situation, we must conclude that it is not feasible at this time to construct a first-principles kinetic model for the annealing of electron radiation damage in lithium-diffused silicon solar cells.

#### IV. KINETICS MODELING

We have, therefore, looked toward a phenomenological approach whereby a parametric model is developed to predict lifetime damage constants and carrier removal rates relevant to the operation of the solar cell. In dealing with the kinetics problem, we divide it into two parts: (1) a determination of the minority carrier lifetime as a function of the material and environmental parameters, and (2) the deduction of solar cell performance from the minority carrier lifetime, and from doping profiles in the n- and p-material and of the diffused lithium in the solar cell. The second part of the problem has been dealt with by the Exotech and Gulf-Atomic groups. For this reason, we have mainly concerned ourselves with the determination of minority carrier lifetimes. (We have recently learned that the Gulf-Atomic group has also been successful in modeling minority carrier lifetimes under a variety of material and environmental parameters).

Almost all lifetime data is analyzed in terms of the Shockley-Read-Hall theory for recombination processes. According to this theory, the lifetime for a single level defect is given by the expression,

$$\tau = \tau_{p_0} \left( \frac{n_0 + n_1 + \Delta n}{n_0 + p_0 + \Delta n} \right) + \tau_{n_0} \left( \frac{p_0 + p_1 + \Delta n}{n_0 + p_0 + \Delta n} \right)$$

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

$$\tau_{p_0} = \frac{1}{N_R v_{th} (\tau) \sigma_p (\bar{n})}$$

and

$$\tau_{n0} = \frac{1}{N_R v_{th}(T) \sigma_n(T)}$$

In these expressions

$$\begin{aligned} N_R &= \text{recombination center density} \\ v_{th} &= \text{thermal velocity} \\ \sigma_{p,n} &= \text{cross sections for recombination of} \\ &\quad \text{holes or electrons} \\ n_0, p_0 &= \text{thermal equilibrium carrier} \\ &\quad \text{concentration} \\ \Delta n = \Delta p &= \text{concentration of excess} \\ &\quad \text{carriers} \\ T &= \text{temperature} \\ n_1 &= N_c e^{[(E_R - E_C)/kT]} \\ p_1 &= N_v e^{[(E_V - E_R)/kT]} \end{aligned}$$

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

$$\begin{aligned} N_c &= \int \rho_c(E) e^{[-(E - E_C)/kT] dE} \\ N_v &= \int \rho_v(E) e^{[-(E_V - E)/kT] dE} \end{aligned}$$

In order to interpret lifetime versus temperature data, an explicit temperature dependence of the cross sections and of the thermal velocity  $v_{th}$  must be assumed. The temperature dependence of  $\sigma$  is complicated but has been treated theoretically (Ref. 8). Although there exist divergent opinions on the temperature dependence of  $\sigma$ , 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  $\sigma_{p0}$  and  $\sigma_{n0}$  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  $E_R$ .

We are at present trying to understand how to use the Shockley-Hall-Read theory to find this effective defect level in an unambiguous way. It is our hope that the minority carrier lifetime is controlled by one or two dominant defects, e.g., the divacancy in oxygen-lean silicon and 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. In this context, it would be most desirable to make measurements on the same samples by different techniques.

The application of the Shockley-Read-Hall approach to the minority carrier lifetime problem is itself beset with complications. To illustrate these complications, Fig. 7 displays the various energy levels identified with radiation defects produced by 1-MeV electrons in n-type silicon. In all cases, the levels were obtained from Shockley-Read-Hall analysis of the temperature dependence of lifetime data. 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. Because of the collaborative aspect of the JPL program, we have a unique opportunity to correlate lifetime measurements in a more significant way. 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 Fig. 7, the upper energy level is relatively less sensitive than is the lower level to these two classes of differences.

As a first stab at the annealing problem, we have decided to use the Shockley-Read-Hall approach and to consider 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 (Ref. 9).

Although we have given some thought to radiation annealing in the presence of lithium, we are still developing techniques for handling the kinetics problem for non-lithium-diffused irradiated silicon. We are trying to understand such questions as the presence of multiple competing defects and defects with more than one important recombination level. The introduction of lithium donors suggests a need for such a generalization to multi-level Shockley-Read-Hall models.

Because of the complexity of the annealing process itself, it will be necessary to develop some physical insight into the problem in order to know what type of approximations can be made. The first problematical fact about lithium is its rather low solubility in silicon:  $\sim 10^{20}/m^3$ . Yet, it is customary for us to unconcernedly characterize our materials with Li concentrations as high as  $10^{23}/m^3$ . Electron microscopy studies such as those shown in Fig. 8 show a precipitation of lithium metal in oxygen-lean silicon having nominally a  $10^{23}/m^3$  lithium concentration. Substantive evidence for such precipitation comes from the identification of body-centered cubic electron diffraction patterns with the lattice constant of metallic lithium. We have not yet understood how this property can be incorporated into the kinetic model.

A second property that must be considered is the fact that the lithium profile in a solar cell

exhibits a linear concentration gradient across the junction, as well as concentration gradients far into the base region, as is seen in Fig. 9. Since the minority carrier diffusion lengths for irradiated material become comparable to a few junction widths, this lithium gradient is important in analysis of lifetime data. The presence of lithium gradients introduces electric fields. Since the minority carrier drift to the collecting electrodes is assisted by these electric fields, the interpretation of the minority carrier lifetime measurement in solar cell devices becomes more complicated. The effective minority carrier diffusion lengths now become an average over the lithium concentration profile and thus we cannot now write simply  $L = \sqrt{D\tau}$ .

One promising technique for studying the minority carrier diffusion lengths in just such a situation is the spectral response curve. For incident light with photon energies in excess of the indirect gap, absorption will occur. As the photon energy is increased above the band gap, the absorption will increase and the effective length for the penetration of the light will decrease, as can be seen in Fig. 10, showing the frequency dependence of the optical absorption coefficient in silicon. The presence of impurities and radiation defects has no important effect on such a curve, which is characteristic of the valence and conduction band states. Therefore, we can use the wavelength of the light to control the dimensions of the active region of the solar cell, i. e., minority carrier generation will proceed only up to the penetration depth of the light.

In the spectral response curve itself shown in Fig. 11, we measure the short-circuit current as a function of the wavelength (or photon energy) of the light. In the long wavelength region, where the absorption coefficient is small and the light penetrates far into the base of the cell, the spectral response is dominated by the base region minority carrier lifetime or diffusion length. At shorter wavelengths where the optical penetration depth is somewhat larger than the junction depth, the effect of concentration gradients near the junction become important. At yet shorter wavelengths where the optical penetration depth is confined to the diffused layer, the spectral response will be sensitive to the minority carrier lifetime in the diffused layer and to the front surface recombination velocity. Our main interest in this work is to study the spectral response curves for optical penetration depths traversing the base region of the cell. It should be noted that the spectral response curve rises for photon energies above the indirect band gap even though the optical penetration length decreases; this is because the optical absorption is increasing with increasing photon energy. For sufficiently high photon energies the effect of the decreased penetration depth begins to dominate over the effect of increasing optical absorption.

Spectral response studies have been made in non-lithium solar cells covering a variety of environmental parameters, though very little has so far been done on lithium-diffused solar cells. The spectral response of a solar cell with uniform doping in the base region and in the front diffused layer can be analyzed relatively simply. In addition, exponential carrier concentration gradients

and their resulting electric fields can also be included in the analysis.

The spectral response method is complementary to the short-circuit current determination of the damage constant where one measures some effective diffusion length characteristic of the entire base region of the cell. On the other hand, in the analysis of spectral response measurements it will be necessary to include the effect of: (1) lithium concentration gradients, and (2) the electric field resulting from such gradients. This analysis will involve a fairly complicated computer program. We aim to correlate these spectral response measurements with diffusion length measurements made on the same samples.

A spectral response apparatus has been built and tests are being made on a preliminary batch of cells. Here we measure the wavelength dependence of the collection efficiency,  $Q = I_{sc}/qN_{ph}$  where  $I_{sc}$  is the short-circuit current produced by the incident photon flux  $N_{ph}$  and  $q$  is the electronic charge.

A block diagram of the apparatus is shown in Fig. 12. Here the monochromator is a double-pass Perkin-Elmer prism monochromator with a resolution of better than  $1 \text{ cm} \times 10^{-8}$ , and the light source is a flat filament tungsten lamp. The output of the monochromator is chopped and imaged uniformly over the active area of the cell by a toroidal section mirror. In these measurements, the cell is loaded to short-circuit conditions. In the first mode of operation, the measurements will be made first using only the illumination of the monochromator. In the second mode of operation, spectral response will be probed by the low intensity light from the monochromator while the cell is simultaneously illuminated by the solar simulator (a powerful tungsten source). The simulated sunlight will allow observation of injection level dependence in the recombination mechanisms. In the second mode of operation, high power output will be obtained from the solar cell and, consequently only a small load will be needed to keep the voltage low. The ac signal from the appropriately loaded cell is amplified, synchronously rectified, and recorded.

As a first step in our experimental program, we will develop a reliable technique for spectral response measurements using non-irradiated (i. e., undamaged) standard n/p solar cells.

The next step will involve the extensions of the spectral response measurements to non-irradiated lithium solar cells. In this work, we will determine values of the same set of characteristic parameters for the lithium-doped cells as for the non-lithium-doped cells.

As a third step, we will irradiate both standard cells and the lithium diffused cells with 1-MeV electrons and measure the spectral response at several fluence levels. This procedure is important for the identification of the particular parameters which are being degraded by the irradiation and in ultimately determining the damage constants for minority carrier lifetime degradation. If the kinetic modeling of the lifetime damage mechanism is to be successful, it is imperative that the cell degradation be attributed to the

appropriate degraded parameters. If, for example, the electric field changes in a lithium-doped cell due to radiation damage, then there will be consequent changes in the short-circuit current which of course must not be attributed to changes in lifetime. Such misinterpretation of the cell degradation could lead to a seriously distorted model of the damage mechanism. It is this kind of separation of the radiation damage effects which makes the spectral response method a valuable tool for studying the complexities of the annealing kinetics in lithium-diffused solar cells.

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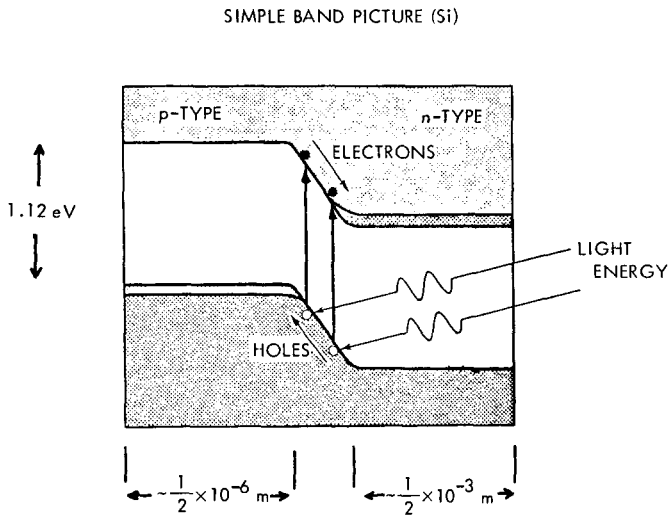


Fig. 1. The P/N junction as a photovoltaic device in silicon

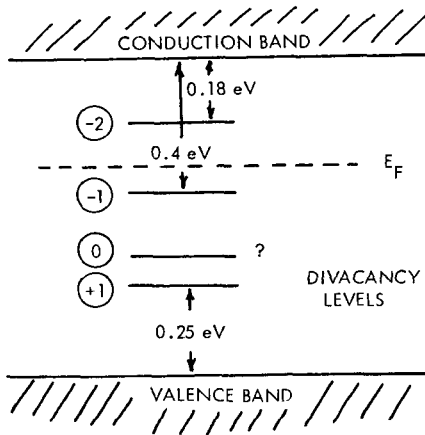


Fig. 2. Energy levels of the divacancy defect in silicon

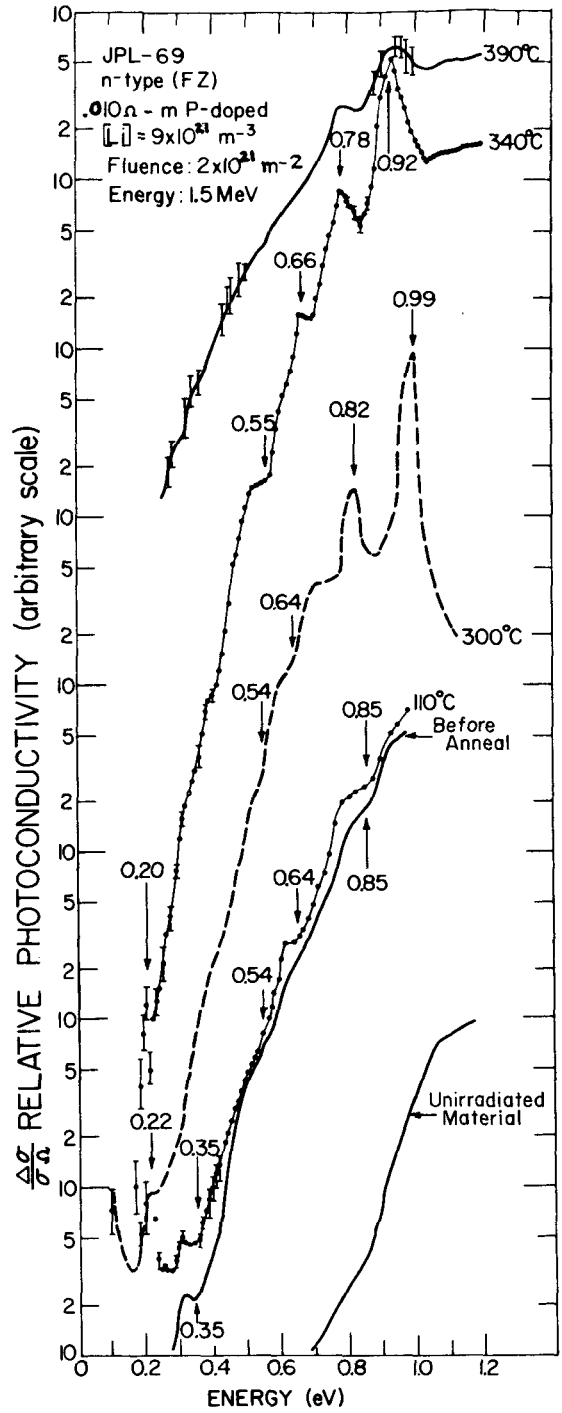


Fig. 3. Relative photoconductivity as a function of photon energy (Ref. 10).

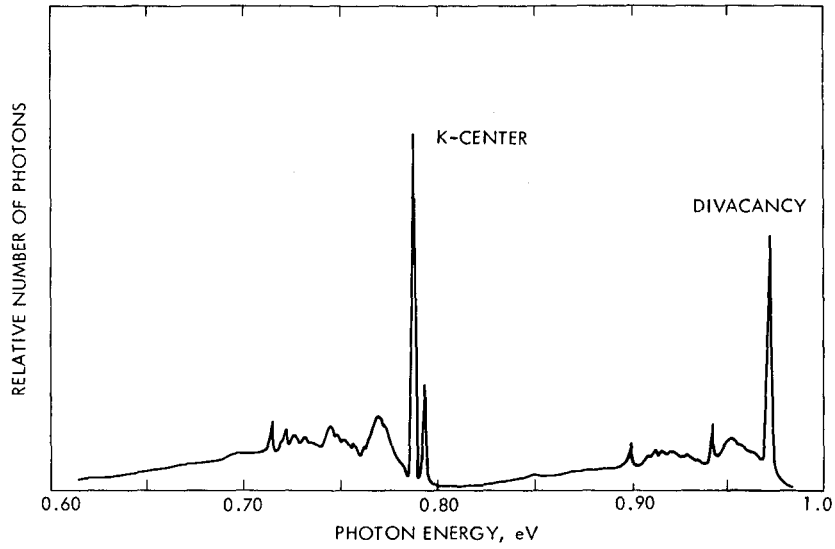


Fig. 4. Luminescence spectrum of n-type pulled silicon, phosphorous doped, irradiated with  $10^{21}$  electrons/ $m^2$  at 2.5 MeV. Here the indirect energy gap is 1.164 eV (Ref. 11)

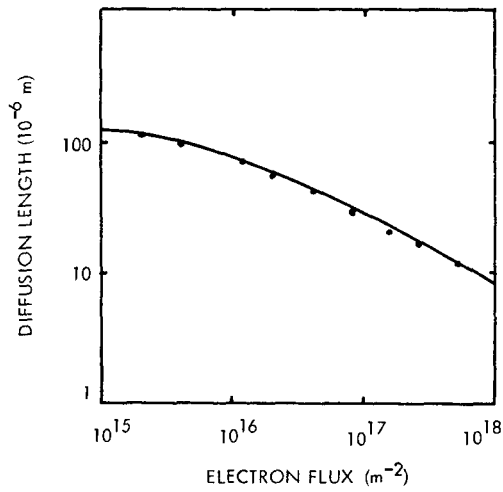


Fig. 5. Minority carrier diffusion length as a function of fluence for 1-MeV electron irradiation on standard N/P solar cells made from crucible-grown silicon (Ref. 5)



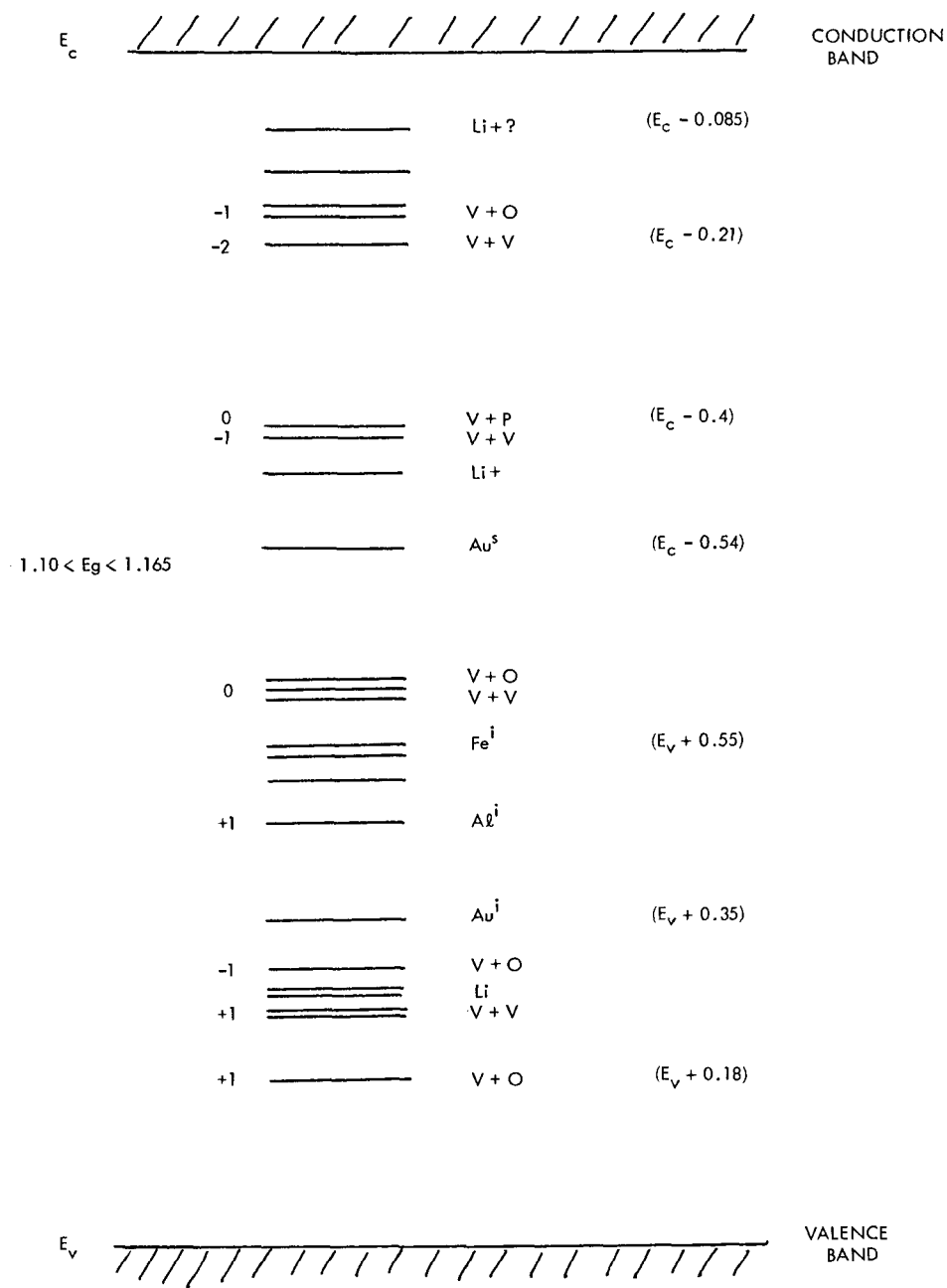


Fig. 6. Energy levels of various defect levels in silicon given in units of electron volts

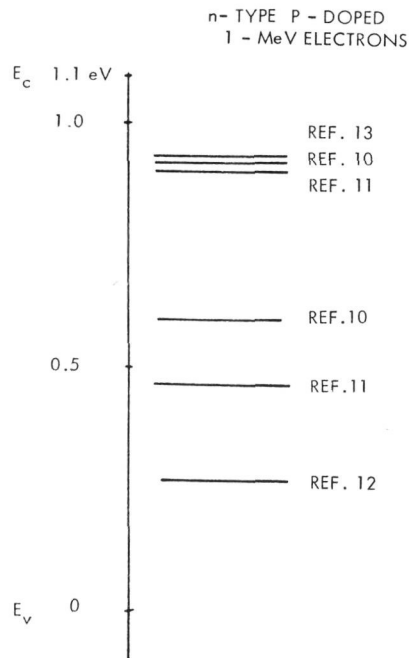


Fig. 7. Energy levels of radiation defects produced by 1-MeV electrons in n-type silicon as obtained from analysis of Shockley-Read-Hall lifetime data

NOT REPRODUCIBLE

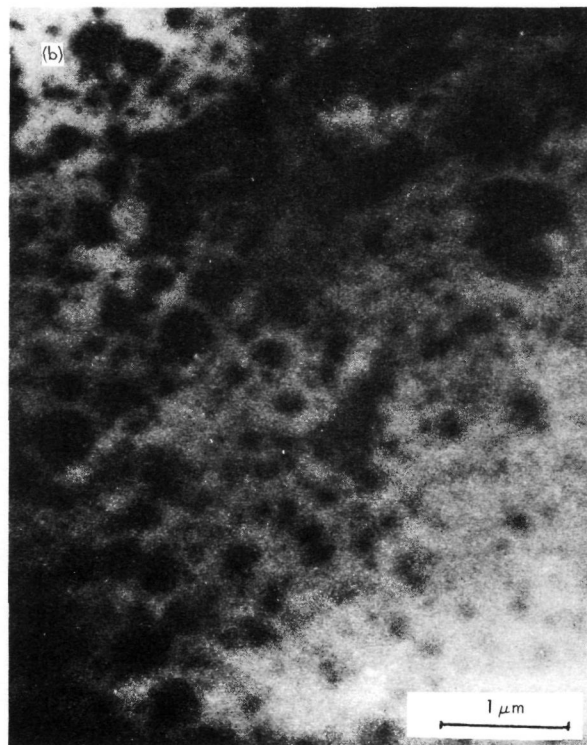
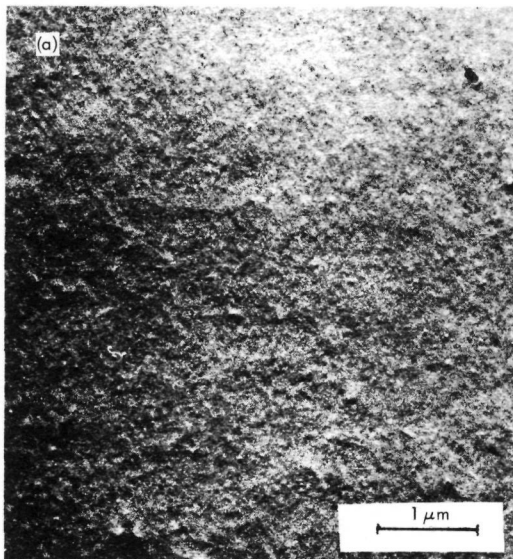


Fig. 8. Electron microscopy studies of unirradiated float-zone silicon: (a) no lithium, (b) with  $10^{23}$  lithium atoms/ $m^3$ , and showing lithium precipitation (Ref. 16)

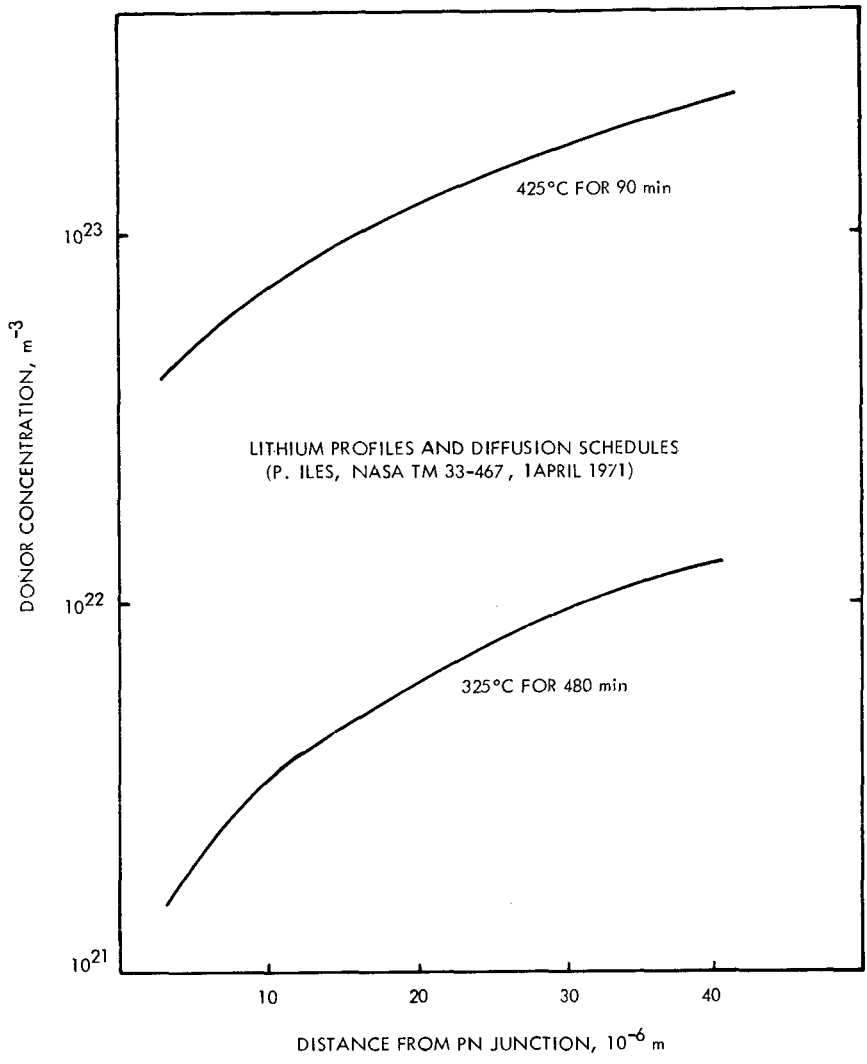


Fig. 9. Lithium profiles and diffusion schedules (Ref. 17)

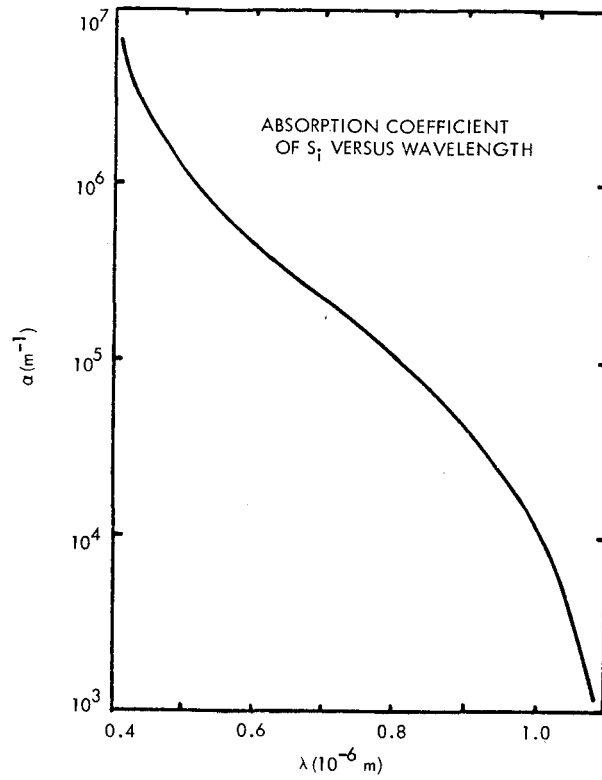


Fig. 10. Optical absorption coefficient of silicon versus wavelength

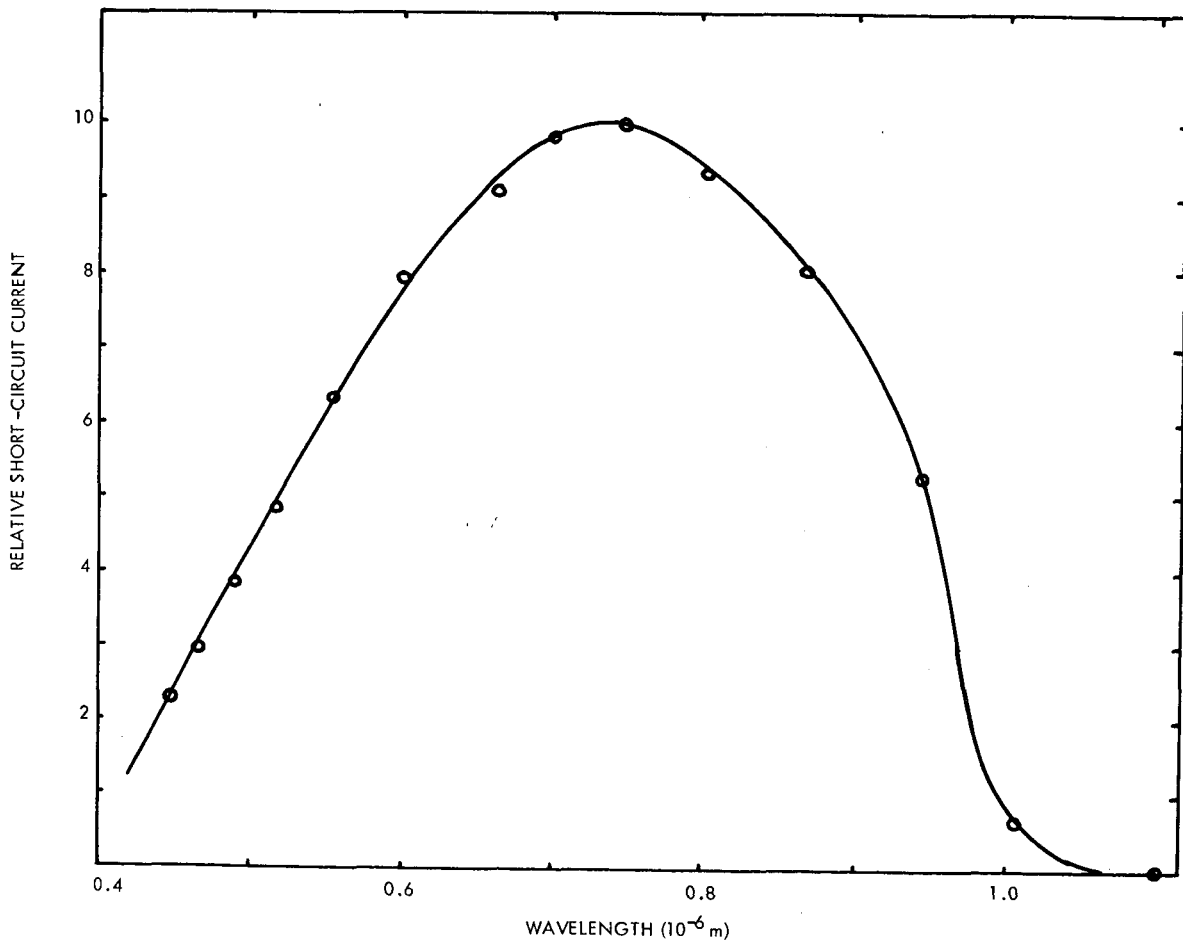


Fig. 11. A spectral response curve for a silicon solar cell exposed to a tungsten light source

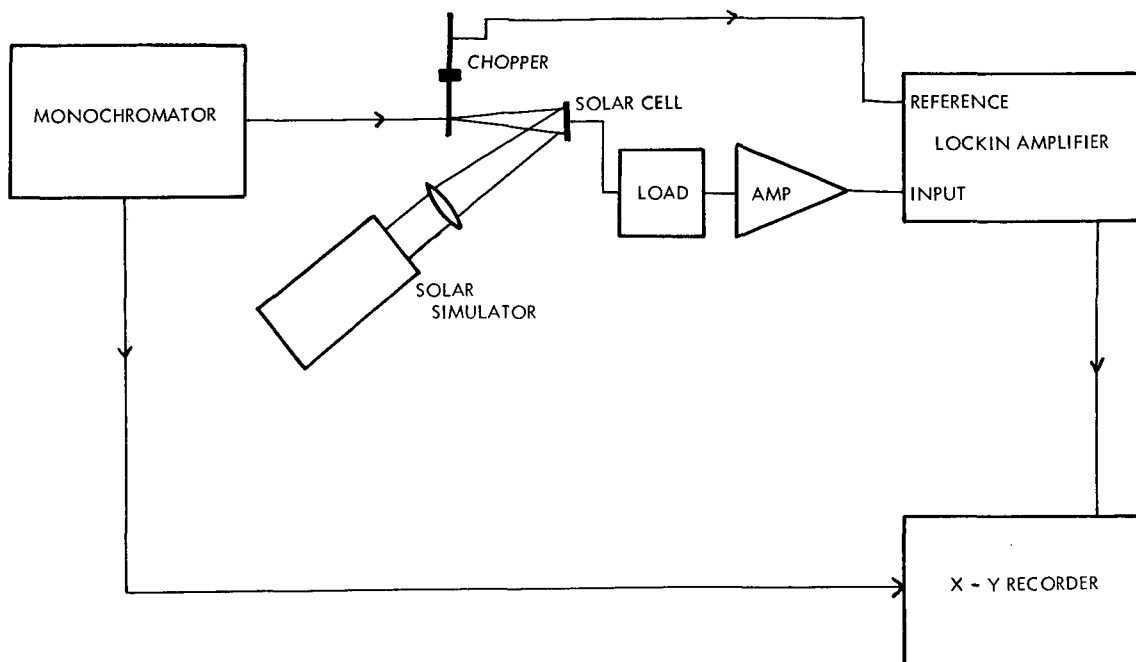


Fig. 12. Block diagram for spectral response measurements