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FUNDAMENTAL STUDIES OF GRAIN BOUNDARY PASSIVATION IN POLYCRYSTALLINE SILICON WITH APPLICATION TO IMPROVED PHOTOVOLTAIC DEVICES

A Final Research Report Covering Work Completed
from February-December 1979

C. H. Seager and D. S. Ginley

Prepared by Sandia Laboratories, Albuquerque, New Mexico 87185
and Livermore, California 94550 for the United States Department of
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February 1980

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Preface

This report is an account of the work performed under U. S. Department of Energy Contract DE-AC04-DP00789 from February 1, 1979 to December 31, 1979. Principal investigators are C. H. Seager and D. S. Ginley; the program manager is G. A. Samara.

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ABSTRACT

Several aspects of the electrical properties of silicon grain boundaries have been studied. The temperature dependence of the zero-bias conductance and capacitance of single boundaries has been measured and shown to be in good agreement with a simple double depletion layer/thermal emission (DDL/TE) model developed to predict the transport properties of such structures. In addition, it has been shown that deconvolution of the I-V properties of some boundaries via a deconvolution scheme suggested by Pike and Seager yields effective one-electron densities of trapping states which are in good agreement with estimates obtained by low temperature electron emission measurements. Experiments have also been performed which indicate that diffusion of atomic hydrogen into silicon grain boundaries greatly reduces this density of trapping states. In properly prepared, large grained polycrystalline samples all measurable traces of grain boundary potential barriers can be removed to substantial penetration depths after several hours exposure to a hydrogen plasma at elevated temperatures. Initial experiments on prototype polysilicon solar cells have shown that this passivation process can improve AM1 efficiencies. In order to more fully understand and develop this process for improving practical multigrained cells, several device research efforts with other DOE/SERI funded contractors have been initiated.

I. INTRODUCTION

Silicon solar cells offer the potential for inexpensive, maintenance free electrical power production. For that potential to be realized, the cost of cells must be reduced and their efficiency increased. Single crystal silicon solar cells are reasonably efficient, but they are expensive to fabricate. By comparison, polycrystalline silicon (polysilicon) solar cells are economically feasible to produce but suffer from considerably reduced efficiencies.¹

The degradation of efficiency in polysilicon solar cells is thought to result primarily from two grain-boundary-induced effects. The first undesirable effect arises from the attractive potential that grain boundary regions possess for photogenerated minority carriers and, more importantly, the high density of recombination centers these carriers find themselves exposed to once they are trapped at the boundary "cores." A second, probably equally important, effect is the apparent shunting action of grain boundaries which intersect p-n junctions; this lowers device fill factors and open-circuit voltages.²

Although "bent bond" situations must exist at a typical silicon grain boundary, it is thought, from measurements on twinned germanium and silicon crystals, that these are essentially electrically inactive.³ Rather, it is the broken or "dangling" bonds which act as primary recombination centers.³ While

significant theoretical and experimental progress has been made recently in understanding the fundamental nature of grain boundaries in polycrystalline materials, it appears that the electronic effects of these broken bonds must be eliminated before photovoltaic devices meeting the necessary economic and efficiency constraints can be produced.

As an outgrowth of our current research program to understand grain boundaries, we have developed a technique which allows us to modify the potential wells at grain boundaries by the introduction of atomic hydrogen. In so doing, we believe that we are eliminating broken bond states from the forbidden gap. Preliminary experiments have shown that grain boundary potential barrier heights in large grain bulk polysilicon can be both raised and lowered reversibly.⁴ Although these changes can be affected under mild conditions, they are quite stable from room temperature to roughly 300°C.

This passivation of grain boundaries and consequent increase in sample conductance implies that these methods are substantially reducing the number of in-gap electronic states at the boundaries. Given this fact one might well hope to effect substantial improvements in devices made from this material. Indeed, preliminary experiments in our laboratory have shown that such treatments, when applied to polycrystalline silicon solar cells, increase carrier lifetimes and improve junction characteristics, resulting in substantial increases in photovoltaic conversion efficiency.

This present report summarizes the progress we have made in understanding and modifying silicon grain boundaries over the

period 1979-80. The second section deals primarily with the measurements performed on single grain boundaries and the attempts to reconcile this data with a simple one-electron theory of the electronic structure of such boundaries. Included also is a summary of prior work in this field. The third section of this report details our efforts at understanding and improving the grain boundary hydrogenation process. Finally, the last section covers our progress in understanding the effects of hydrogenation on real polysilicon device structures. Although little in-house work was carried out during this period, substantial cooperative efforts were begun with other DOE contractors.

At the end of each section, we have indicated the directions which we feel the research should proceed in 1980. We feel that the coming year will be a crucial one in assessing the ability of grain boundary passivation to contribute to our nation's future solar energy program.

II. Fundamental Grain Boundary Studies

In order to understand the effect grain boundaries have on polycrystalline photovoltaic devices it would appear necessary to develop a model which correctly describes the electronic structure of such structures. In this section we will first briefly describe prior efforts directed at this goal; the grain boundary studies completed during this reporting period will then be reviewed in some detail. Our approach will be to keep the discussion brief with frequent references to the attached publications for more mathematical elaboration.

A. Prior Work

A search of the literature on the subject of the electrical properties of grain boundaries in Group IV semiconductors reveals that this field has been lacking a continuous strong interest from the physics community.

Early rather sparse, but well done work on the properties of germanium bicrystals has not been brought to full fruition. Later, more device oriented research on thin-film polysilicon has been strongly motivated but has not produced the useful data base that comes from focusing on the properties of one grain boundary at a time. As we shall point out during the course of this discussion, learning anything definitive about grain boundaries from the study of these films of fine grained material is a formidable, if not hopeless, task.

The earliest work in this area appears to be that of Taylor, Odell, and Fan⁵ (1952) on n-type Ge bicrystals. These authors measured several properties of the resistive region around these boundaries and formulated an approach which still serves as a basic beginning to the problem. They correctly recognized that the considerable impedance to current flow offered by these boundaries was caused by a transfer of charge (electrons in this case) from the grains to the grain boundary (G. B.) plane leaving a depletion regime of positively charged donors and a substantial (several tenths of an electron volt) upward bending of the energy bands near the G. B. plane. The cause of the charge transfer was postulated to be the existence of trapping levels in the forbidden gap brought about by the mismatch disorder in the intergrain region. By suggesting that the current over such double depletion layer structures was dominated by the thermal emission of majority carriers, Taylor, et al. also provided another important contribution to this subject. This suggestion arose from their calculation that the width of the depletion layer was substantial enough to essentially rule out tunnelling effects. A third and equally important contribution of this work came from their observation that single Ge grain boundaries could sustain voltages in excess of 100 volts. They recognized that this property could only result if the grain boundary contained a substantial number of unfilled traps at low bias.

Taylor, et al's work was followed by the publication of two back-to-back papers by Mueller⁶ in 1960. Mueller's experimental system was also n-type Ge, and in general, most of his observations were quite consistent with Taylor, et al's.⁵ Both sets of authors found that their grain boundary resistances were activated with an energy which was independent of grain dopant level. Both investigators appeared to recognize that this was caused by a high density of trapping states. As we shall discuss later this is a natural consequence of a more detailed treatment of the problem, this phenomena being called the "saturation regime". A curious feature of these two sets of data is that while this activation energy, E_A , is independent of N_d , Mueller's experimental value⁶ is ~ 0.7 eV while Taylor, et al.⁵ claim to find $E_A = 0.52$ eV. This is a remarkable discrepancy which is, at present, inexplicable.

The most significant aspect of Mueller's paper is his elaboration of the general form of the equations for barrier equilibrium. By writing down the equations for the influx and efflux of majority carriers Mueller laid the ground work for a general solution of the barrier problem in which any given density of grain boundary states could be specified. With this formalism he was able to show in a definitive manner how a large density of trapping states could cause the barrier height to be effectively pinned at near zero-bias values despite the application of very large voltages. With the exception of a 1963 paper by

Matakura⁷ detailing some rather general observations on the behavior of several Si and Ge bicrystals these three works appear to constitute the entire literature in this particular area until quite recently.

With the 1971 paper of Kamins⁸ the work in this area resumed; however, both the motivation and the material under study were quite different from previous efforts. Kamins and several authors of more recent papers⁹⁻¹³ were concerned with describing the doping dependence of their films of chemically vapor deposited silicon. These films were characteristically less than $10\mu\text{m}$ thick and were grown by chemical vapor deposition methods; grain sizes ranged from $\sim 1\mu\text{m}$ to less than $500\text{ \AA}$. Clearly the properties of even the grains themselves, not merely the grain boundary regions, were at least in a direct sense, experimentally inaccessible with standard transport techniques. The principal "anomaly" to be explained was the rather drastic decrease in the film conductance below a certain critical doping density N_c ; above N_c , the dependence of conductance on doping density was similar to single crystal silicon. Kamins⁸ and several other authors¹¹⁻¹³ correctly recognized that this phenomena could be most simply interpreted as the onset of substantial grain boundary barrier formation as the dopant level is reduced. Hall effect measurements were made and interpreted to be consistent with this picture, although at least one work⁹ favored grain boundary dopant segregation as the dominant effect.

As a whole, however, the general conclusions of the majority of these authors have been supported by recent work on silicon bicrystals.

There are many difficulties in culling any detailed information about the properties of silicon grain boundaries from the literature on CVD silicon films. Seager and Castner¹⁴ (S+C) pointed out some of these in a recent paper; it is relevant to review some of their arguments at this point.

The first major problem in comparing thin film data with theories of grain boundary electronic behavior is the determination of the active dopant density level in the grains. This quantity does not really lend itself to measurement via standard analytical chemistry methods. The alternative procedure used by some authors is to monitor the resistance of an epitaxial film deposited at the same time. This is a relatively simple approach but one fraught with many possible pitfalls. As many authors have correctly pointed out the theory of the Hall effect in inhomogeneous materials suggests that under certain conditions the Hall constant of a film can reflect that of the grain material.¹⁵⁻¹⁷ The major problem in applying this theory appears to be in ascertaining whether the simple constraints used in these transport calculations are met in the actual film of interest. Among the conditions likely to be present in real films that have not been investigated in the simple¹⁵⁻¹⁷ (resistor network) Hall effect calculations are: 1. A distribution of different

grain sizes; 2. Anisotropy of grain dimensions; and 3. A spread in the actual widths (depletion region size) of the resistive regions at the grain boundary. Considering all these provisos, Hall effect determinations of grain carrier concentrations should be approached with a considerable degree of caution.

The second difficulty in interpreting thin film transport data is the commonly used assumption^{8,12,13} that the temperature or voltage dependence of the film conductance is reflective of one grain/grain boundary subunit. As Seager and Castner¹⁴ have shown, there exists a whole spectrum of grain boundary impedances (except perhaps at very low doping levels). The current path through a three dimensional array of these varying impedances is complex and not easily determinable. Furthermore, this path can be shown by the methods of percolation theory¹⁸ to change substantially with variations in the applied bias or temperature. Thus, measurements made as a function of these variables truly represent a complicated average of the individual regions of the thin film. This is not to say that useful information about a particular thin, fine-grained film cannot be obtained by measuring several of the common transport coefficients; however, using this data to verify a particular model for grain boundary electronic structure is a difficult task at best.

These were some of the considerations that led Seager and Castner¹⁴ to concentrate on single grain boundary measurements in 1978. By measuring the temperature dependence of the zero-bias

conductance of one class of silicon grain boundaries they were able to test some aspects of the double depletion layer/thermal emission (DDL/TE) model and make estimates of the largest grain boundary state densities existing in their polysilicon. The highest impedance grain boundaries were chosen for experimental convenience.

While it was stated in their work that these particular boundaries should be representative of the largest intergrain mismatch angles, this conjecture should probably be viewed with some skepticism considering the present state of our understanding of the microscopic structure of these boundaries (see, in particular the discussion in Section II.C. regarding preliminary bicrystal data). The two crucial equations given by Seager and Castner were the expression for the zero bias conductance;

$$G_0 = AT^2 e^{-\phi_{BO}/kT} \quad (1)$$

where ϕ_{BO} is the zero bias barrier height, and the equation determining the charge neutrality condition that fixes the size of ϕ_{BO} . This is:

$$\left(\frac{8\epsilon\epsilon_0 N_d \phi_{BO}}{e^2} \right)^{1/2} = \int_0^{E_C} N_T(E) (f(E, E_F) - f(E, E_{FB})) dE \quad (2)$$

The latter expression is obtained by viewing the barrier as a planar array of one electron trapping states. The left-hand side is the positive charge (per unit area) in the depletion region

and the right-hand side a simple Fermi statistics expression for the number of excess electrons residing in the trapping states [with density $N_T(E)$]. The quantity E_{FB} is the chemical potential of the (roughly) highest filled grain boundary trap state before any charge has transferred from the donors in the depletion region. Equation 1 is essentially the same expression used by Taylor, et al.⁵ and Mueller.⁶ Equation 2 represents an attempt to approximate the barrier situation in simple, one electron terms. The successes and failures of this approach will be discussed later in this report.

The experimental values of ϕ_{BO} deduced by Seager and Castner (S + C) are shown in Figure 1 plotted versus dopant density. Note that if ϕ_{BO} can be expressed to first order as a temperature independent value plus a linear term:

$$\phi_{BO} = \phi_{BO}(T = 0) + aT \quad (3)$$

then it is roughly the $T = 0$ value of the ϕ_{BO} which appears as the slope of $\ln(G_0)$ on an Arrhenius plot. We say "roughly" because, as we shall point out later, a careful examination of the problem shows that the activation energy of G_0 contains an additional non-negligible term. S + C also solved Eq. (2) for various forms of $N_T(E)$; these curves are also plotted in Fig. 1. A universal feature of these curves is the leveling out or "saturation" of the barrier height at low dopant levels. This limit arises because at small N_d only a small transfer of charge from the grains to the grain boundary traps causes sufficient band bending to bring the Fermi level in the G.B. region up to that of the grains. Thus, the highest filled trap states are at

or near the neutral Fermi level, E_{FB} , and the barrier height in this region is:

$$\phi_{BO} = E_{FG} - E_{FB} \quad (4)$$

where E_{FG} is the bulk, grain Fermi energy. If we suppose that E_{FB} is approximately temperature independent we then have the prediction that the temperature dependence of ϕ_{BO} should be essentially that of E_{FG} . As we shall discuss later, this prediction is one which should be experimentally verifiable.

The result of comparing the data with the curves generated by substituting various forms of $N_T(E)$ into Equation 2 can be summarized as follows:

1. The saturation behavior predicted by theory¹⁴ is seen and the deduced value of E_{FB} is around 0.60 ev (measured from the top of the valence band). Actually, as we shall discuss later S + C's data was probably influenced by surface effects; a closer examination of their data at the highest temperatures and other more recent results indicates that $E_{FB} \approx 0.53$ ev.
2. The general trend of the data is for ϕ_{BO} to decrease at higher dopant densities. Because of experimental error a precise determination of the shape of $N_T(E)$ is difficult; the indications were that the trapping density decreased substantially at ~0.2 ev above E_{FB} , and that the total spatial density of states above E_{FB} was $\approx 6 - 10 \times 10^{11} \text{ cm}^{-2}$.

Seager and Castner¹⁴ realized the obvious limitations of using ϕ_{BO} versus N_d data to deduce the effective one-electron trap-state density. The ideal experimental situation of having one set of specifically oriented grain boundaries doped to various donor or acceptor densities is difficult to realize in practice. As an alternative approach to deducing $N_T(E)$, S + C suggested that proper theoretical analysis of the current-voltage (I-V) plots measured on specific boundaries might be useful.

In a 1979 study¹⁹ Pike and Seager (P + S) followed up on this suggestion and gave a prescription for an I-V deconvolution scheme to accomplish this objective. The essence of P + S's approach was to solve the form of Equation 2 appropriate at finite bias. In addition, they wrote down a general form of the emission expression relating barrier current to the applied bias and the barrier height (now a function of bias). Further details are contained in the attached reference. By co-solving these equations, Pike and Seager were able to present a straightforward algebraic approach to deducing $N_T(E)$ from barrier I-V data. They also presented I-V curves generated using reasonable forms for $N_T(E)$ and showed that these contained features seen in Taylor, et al's⁵ data on Ge bicrystals. This is the state in which the subject of silicon grain boundary research found itself at the beginning of 1979. A detailed data base on single silicon grain boundaries was lacking in order to test the extent to which the DDL/TE model provided an accurate prediction of transport

properties. Establishing this data base was one of the primary objectives of our '79-80 research effort.

B. FY '79 Research Progress

There were several goals that we had in mind at the beginning of this research period.

a. We intended to provide a full examination of the extent to which the simple DDL/TE approach works in silicon. In particular, the validity of the one-electron approximation was of considerable interest; if the density of trapped grain boundary electrons was high enough, or if there were particularly restrictive geometrical arrangements of charge, this approach could fail to provide a quantitatively correct picture of these boundaries. Examples of how this could happen are already known in systems uncomfortably close to the grain boundary situation. For example, Read²⁰ and others²¹ have pointed out that the occupation of traps at the core of dislocations is known to be large enough that Fermi statistics are not obeyed. This is because the mean spacing of occupied sites is small enough to cause the energy of any trapped electron to have a first order dependence on the occupation fraction. Under these circumstances, Read²⁰ has shown that it is not possible to represent the occupation of such levels with any sort of one-electron trap-state density. Since it is highly likely that some grain boundary structures are effective combinations of certain types of total or partial dislocations, we might anticipate a problem with this approach.

b. We hoped to answer the question of the degree to which the grain boundary trap states arise from intrinsic defects. That is, how important are the effects of segregated impurities such as oxygen, nitrogen, or the dopant species itself. As a preliminary approach to this question, we intended to compare the grain boundary transport properties in melt-doped polysilicon with the NTD doped material.

c. We had also hoped to study the dependence of the potential barrier height and other properties on the orientation of the grains and the interface plane making up the boundary. These studies are presently just beginning, and no definite results are available as yet.

1. Zero Bias Studies of the Conductance and High Frequency Capacitance.

Several factors convinced us that insufficient data existed to properly verify the DDL/TE prediction of Arrhenius behavior of G_0 in the case of silicon. The first was the aforementioned difficulty of using the existing thin film data to verify single boundary properties. Secondly, Seager and Castner's data¹⁴ on single barriers appeared to be Arrhenius, but the range of temperature covered was rather small.

We also felt that the mere existence of an activated conductance was not sufficient to rigorously test the model, even at zero bias. It would be desirable, for instance, to see if the width of the grain boundary depletion region was

correctly related to the height deduced from G_0 measurements. This would indicate that other distortions of the conduction and valence bands such as might occur in the highly strained "core" of the boundary did not affect the transport of carriers over the barrier. This could come about, for instance, if these band distortions were spatially localized enough to permit tunneling.

Taylor, et al.⁵ pointed out that the grain boundary capacitance could be used to measure this width and that:

$$C_0 = \frac{\epsilon \epsilon_0}{\lambda_0} = \frac{e^2 \epsilon \epsilon_0 N_d}{8 \phi_{BO}}^{1/2} \quad (\text{f/m}^2), \quad (5)$$

where λ_0 is the sum of the depletion widths on both sides of the grain boundary and C_0 is the zero bias capacitance (per m^2) measured at high frequency. By high, we mean measurement conditions such that no extra majority carriers could enter the boundary and become trapped in response to the ac excitation bias. We will dwell further on the subject of barrier capacitance later in this section.

In order to implement conductance and capacitance measurements over a wide range of temperature substantial efforts at both sample preparation and instrumentation were needed. To insure that contact effects did not intrude at the sample doping levels used ($10^{15} - 10^{16} \text{ cm}^{-3}$ of phosphorous) four terminal measurements appeared desirable. However, the capacitive phase angles seen on even large (high resistance)

silicon boundaries were rarely more than $\sim 1^\circ$ at 300 K. Commercial instruments for making accurate, 4 terminal capacitance measurements under these conditions just do not exist, so that considerable time and effort had to be spent in developing our own circuits to provide the data that we wanted. Our final configuration utilized low-phase shift operational amplifiers for measurement of the phase and magnitude of the excitation voltage with driven shield cables running to the sample to maximize input impedance at audio frequencies. A current-to-voltage operational amplifier circuit was used to measure the ac excitation current and a PAR 5204 dual phase lock-in amplifier was employed as the final voltage/phase measuring device. The phase accuracy of this circuit was of the order of 10^{-4} radians even with contact resistances as large as $\sim 1/10$ the sample (barrier) impedance.

Because we had no facilities for growing large area silicon bicrystals, all of our electrical samples had to be cut from the largest grain poly that we had on hand. This was single pass, float-zone material obtained from Monsanto, neutron transmutation doped at ORNL,²² having typical grain sizes on the order of $\sim 0.2 - 1.0$ mm. In order to be able to measure grain boundary capacitance accurately enough to verify the DDL/TE model it is necessary to choose highly resistive barriers. This consideration results from the

small capacitive phase angles discussed previously. A second reason for choosing large barriers is the expectation that at the doping levels available the largest barriers would be in the saturation regime, that is, $\phi_{BO} = E_{FG} - E_{FB}$. If this condition were fulfilled, we would expect to see a barrier height (at $T = 0$) of ~ 0.6 eV from S + C's work and we would expect to first order that the temperature dependence of ϕ_{BO} would follow that of E_{FG} . This follows from the realization that the temperature dependence of the grain boundary chemical potential, E_{FB} , is likely to be small.²³

In order to prepare 4 terminal samples for this study, several steps were followed. Bars of Monsanto poly were prepared having dimensions ~ 1 mm x 1 mm x 1 cm. With this cross sectional area and attention to the orientation of the boule, a reasonable fraction of the grain boundary planes totally bisected the sample along their long axes. The sample bars were then provided with current contacts of titanium-gold sputtered on in an RF sputtering system. By passing current through these bars and dragging a potential probe down their long axis, the impedance of each boundary could be determined. We then isolated our attention on barriers that had the largest impedances ($\sim 10^4 \Omega$ for 1 mm^2 area at 300 K) and etched these boundaries lightly with Sirtl etch for visual examination. This allowed us to determine if the boundary in question was a single plane

crossing the entire bar. If the boundary in question met these criteria, a second contacting operation was carried out which provided two small Ti/Au contacts on either side of the G. B. plane. Small gold wires were then soldered (using indium) to these contacts and the sample was mounted to a sapphire plate with GE7031 varnish for insertion in a cryogenic dewar.

Early along in our investigations we found that the temperature dependence of the barrier conductance did not always appear linear on an Arrhenius plot for some samples. It was noticed that the resistance at low temperatures was very sensitive to surface preparation, whereas the barrier capacitance was not. Figure 2 illustrates this dependence for one sample which was successively etched (with Sirtl etch) and remeasured. The large changes seen in the barrier conductance were accompanied by an essentially constant capacitance value. We reasoned that this behavior resulted from a conductive surface layer induced by the sample preparation conditions²⁴; most likely saw damage from the initial cutting process was the culprit. It was empirically determined that etching off $\sim 40\mu\text{m}$ from the surfaces of our samples removed all traces of this phenomenon and this etch was incorporated into our sample preparation procedure.

We will now review some of the important findings of our zero bias studies. It should first be pointed out that,

because of several factors, our measurements were limited to samples with only two levels of phosphorous doping, 0.20 and $1.3 \times 10^{16} \text{ cm}^{-3}$. It is just in this dopant range where S + C's data¹⁴ (Fig. 1) indicates that we should begin to see G.B. barriers which are "saturated," i.e., have maximum height. Because of the dopant density dependence of the barrier capacitance (Eq. 5), this is also the dopant range where the capacitive phase angles are the largest and, hence, the most measurable.

At this point it is worth making the reader aware that the dopant densities quoted in this report are 30 to 40% higher than the nominal (data supplied by Oak Ridge National Laboratories) dopant densities quoted by us in references 25 and 26. After noting certain discrepancies between our data and the theoretical model we fabricated small boundary-free rectangular specimens of NTD doped polysilicon and determined the above phosphorous concentrations by in-house resistivity measurements. We believe that these determinations are accurate to $\sim \pm 5\%$.

The temperature dependence of the conductance of two "large" barriers are seen in Figures 2 and 3. The activation energy (roughly equal to the zero temperature barrier height) is identical in both cases and is of the order of 0.62 eV. This value was characteristic of virtually all the high impedance barriers of either dopant density during this study. It is, however, somewhat larger than the 0.55 eV

slope reported by S + C. Having become aware of the surface layer problem we went back and reexamined S + C's data to see if this was the cause of this discrepancy. It appears that their $\ln G_0$ versus $1/T$ plots were, in fact, slightly curved and that their slopes at the highest measurement temperatures were consistent with our ~ 0.62 eV number. The data obtained on our small bicrystals leave little doubt that G_0 is truly Arrhenius-like; usually this behavior is seen over at least 5 - 6 decades. We would have liked to verify this behavior at lower temperatures but, as we shall discuss later, the time constant for carriers entering and leaving the G.B. trapping states becomes of the order of seconds below 200 K making measurements on a truly "equilibrium" barrier difficult. This effect manifests itself in several ways, the most obvious being drifting, irreproducible values of G_0 below 200 K as the barrier becomes sensitive to small random noise pulses present in the measuring system.

An example of the barrier height deduced from the high frequency capacitance is shown in Fig. 3. Again, this data is typical of all the high impedance barriers examined. In order to compare these members with theory, we will make an argument that is somewhat different from that presented in references 25 and 26. In these publications we neglected the non-linear temperature dependence of the Fermi

energy, and this can introduce substantial errors into the theoretical estimate of ϕ_{BO} . The simplest and most correct way to deduce ϕ_{BO} is to go to equation (12) of reference 19 and note that the activation energy of G_O has 4 separate terms. If barrier height saturation is assumed, the two differential terms exactly cancel and $E_A = \phi_{BO} + E_C - E_{FG}$. Thus, we can obtain our theoretical estimate of ϕ_{BO} by subtracting the Fermi energy (referred to E_C) from E_A (0.62 ev in this case). This procedure yields the solid line labeled theory in Figure 3.

We see that this prediction is reasonably close to the value deduced from the measured capacitance data. Considering the opportunities for systematic errors in optically estimating the barrier area of these small samples, the experiments are satisfyingly close to the DDL/TE model.

The implication of this agreement is that the major barrier to current flow across barriers of this type is determined by the depletion layer. Additional upward distortions of the bands caused by local strain at the core of the boundaries are, if present, apparently thin enough for majority carriers to tunnel through. A second question that arises in interpreting these results is whether they imply that the grain boundary negative charge is truly uniform in space. We believe that the answer to this question is no. It is probable that because of the finite deBroglie wavelength of the electrons incident upon the barrier that

they "see" an "average" barrier height even if large fluctuations occur in the local electrostatic potential over distances of the order of 50 - 200 Å. So, as we shall mention later it is important to realize that these dc transport measurements probably reflect an average of the local barrier potentials.

2. The Bias Dependence of Grain Boundary Current and Capacitance.

A natural extension of the zero-bias measurements is a study of the bias dependence of grain boundary properties. By applying a bias to a double depletion layer structure, the number of electrons trapped at the intergrain interface can be increased. This fact was realized by Taylor, et al.⁵ and Mueller⁶ and elaborated on by Pike and Seager¹⁹ (P + S). P + S showed how a one electron density of states, $N_T(E)$, could be deduced from "deconvoluting" the I-V data measured on a single grain boundary. Learning whether, in fact, a one electron approach provides a reasonable approximation to the physical situation in real silicon grain boundaries was one of the goals of this phase of our program.

Once the techniques for determining the zero bias characteristics of our specimens had been developed, extending these measurements to finite biases was straightforward. A typical example of I-V data on a high impedance boundary is shown in Figure 4. This data displays the three characteristics predicted from the P + S model calculations.

- a. An ohmic regime at biases less than kT/e .
- b. A sub-ohmic regime which extends to a bias of ~ 1 volt. According to the P + S interpretation this corresponds to filling a trap state population which is large enough to make ϕ_B only weakly dependent on bias. (Clearly, if $N_T(E)$ was infinite at one energy the Fermi level in the barrier and, hence, the barrier height would always be pinned.)
- c. A super-ohmic regime which starts at roughly 1 volt for this sample. Here the barrier height starts to become increasingly dependent upon trapped charge density.

Figure 4 also shows the high frequency (small ac bias) capacitance measured on the same sample. A simple extension of Eq. 3 can be used to deduce the barrier height from this quantity. Conversely, the P + S deconvolution scheme can be used to deduce the barrier height at any bias from the dc current¹⁹ and the expected capacitance can be calculated. This is shown as the line labeled "theory" in Figure 4. The agreement with the measured capacitance is excellent except at low bias; this discrepancy is undoubtedly due to the fairly large (0.1 volts rms) ac excitation bias of the commercial bridge used in the measurement. This type of agreement gave us some encouragement to go ahead with the tedious data reduction procedures necessary to deduce the "effective" density of states $\bar{N}_T(E)$. It should be noted

that while the P + S scheme does not yield $N_T(E)$ directly it's outcome, $\bar{N}_T(E)$, is just the former quantity averaged over a few kT in energy.¹⁹

The values of $\bar{N}_T(E)$ deduced from the I-V data of Fig. 4 are shown in Fig. 5. This type of data is representative of several samples measured although the shape and magnitude of the $\bar{N}_T(E)$ curves were somewhat variable. Several comments are in order about these data.

- a. The data points shown in Figure 4 are somewhat different from Figure 3 of the reference 25. The major difference arises from the previously noted correction to the dopant density number. In addition, the data in Figure 4 was deduced using a computerized curve fitting routine to accurately deduce the slope of the current-voltage curves--formerly this was done by hand.
- b. The total number of available trapping states above the zero bias Fermi level is in reasonable accord with the estimates of Seager and Castner¹⁴ based on the doping dependence of large impedance barriers.
- c. Most of the samples measured yielded values of $N_T(E)$ which changed with temperature (due to the temperature "smearing") roughly as predicted. The problem in making this statement more quantitative is that the analysis of the data is complicated enough that establishing

error bars on the final values of $N_T(E)$ is non-trivial. However, a few samples showed shape changes of $\bar{N}_T(E)$ with temperature which seemed outside of reasonable experimental error. At this stage in our program we are uncertain as to whether to attribute these variations to inapplicability of the DDL/TE model or merely to variations in the homogeneity of the boundary plane which did not show up in low power optical examinations of the grain boundary-sample surface intersection lines. We will comment more on these variations later.

d. An additional variation of the deduced $\bar{N}_T(E)$ from expectations was a universally observed divergence of $N_T(E)$ (towards 0) observed for biases less than 0.1 volts. Although extreme accuracy is required in this region to pin down the trap state density it seemed to us that deviations due to imprecision in the I or V determination should have caused random deviations of $\bar{N}_T(E)$; such was not the case.

To summarize our general feelings about the I-V studies we say that they are encouraging, but not totally convincing. For more details see the attached publication by Seager and Pike.²⁵ A second type of measurement did, however, provide more justification for believing some aspects of the DDL/TE model; these studies will be discussed below.

3. Measurements of Direct Thermal Emission From Grain Boundary Trapping States.

As we have previously mentioned, the largest grain boundary barriers in our polysilicon have an "equilibration time," τ , which is of the order of seconds or longer below ~ 200 K. This fact was made painfully clear to us after repeated attempts to measure capacitance and conductance in this temperature region. To make the equilibration time concept clearer, we can express the rate of change of trapped charge, Q , by:

$$\frac{\partial Q}{\partial t} = \frac{Q - Q_{eq}}{\tau} \quad (6)$$

where Q is the charge state (per unit area) at some time t . Q is assumed to be not at its equilibrium value, Q_{eq} , because of some external perturbation; such a perturbation could result from the application of an external bias, incident light, etc. In the course of our studies, we concluded that τ has a strong dependence on Q and this dependence actually lets us estimate an effective state density from measurements of the decay of barriers "prepared" in non-equilibrium states.

The simplest way to "prepare" such a state is to place a barrier under a large bias at low temperature. If we can believe the results of our I-V deconvolution studies, a typical large barrier in silicon doped to $\sim 10^{16} \text{ cm}^{-3}$ (n-type) can hold two to three times more charge than is trapped in equilibrium at zero bias. Since the zero bias barrier height varies as the square of Q , this suggests that "unrelaxed" barriers of 1.5 - 3.0 eV could be prepared

by high bias application (10 V or more). The band diagram of such a nonequilibrium structure would look like that depicted in Fig. 6A.

Such barriers were, in fact, prepared during the course of our studies²⁶ and the slow decay of Q was monitored by measuring the high frequency value of the small signal capacitance using:

$$Q = \frac{\epsilon \epsilon_0 N_d}{C_{HF}} \quad (7)$$

The rate of decay of such charge at various temperatures is plotted for one sample (as a function of Q) in Fig. 6B. A simplified analysis of this problem is contained in an attached publication.²⁶ Briefly, it is shown that these curves of $\partial Q / \partial t$ versus Q are consistent with the DDL/TE model provided the value of the effective one-electron density of states is $\sim 8.5 \times 10^{16} \text{ m}^{-2} \text{ eV}^{-1}$. (Note again that this number differs from that quoted in reference 26 due to the re-determination of the phosphorous concentration.) Because these particular data were taken on the same sample used in Figs. 4 and 5, obtaining this value of $N_T(E)$ is rather gratifying. Other samples characterized using this capacitance decay technique yielded similarly good agreement with the values of $N_T(E)$ determined from I-V data.

We will spend some time in the next section of the report discussing the implications of these experiments. We will

also show some experimental data that are presently unexplainable within the context of the simple DDL/TE assumptions.

4. Discussion, Unanswered Questions, and Future Work.

a. Discussion

It is first worthwhile to summarize what the previously discussed experimental studies do and do not prove about the electronic structure and of transport across silicon grain boundaries.

The general features of the DDL/TE model are most certainly correct, at least for the class of grain boundaries (high impedance) so far studied. The high impedances seen at these boundaries are due to a transfer of majority carriers to the grain boundary, and the impedance of such structures varies in the way that implies phonon-assisted emission of carriers over an electrostatic barrier. The width and height of this barrier are consistent with a simple one-dimensional solution of Poisson's equation. This implies that regardless of the uniformity and/or substructure of the electrostatic barrier, the carriers attempting to cross this barrier (and to within a reasonable approximation) those attempting to leave the intergrain traps see an average barrier height well described by this one-dimensional solution.

The variation of this "average" barrier height (inferred from I-V measurements) with the amount of negative charge can be used to define an "effective" one-electron density

of states that is reasonably good at describing some barrier properties. For instance, $N_T(E)$ deduced from 300 K I-V curves agrees²⁶ with that deduced from measurements of the thermal release of carriers from G.B. traps at ~ 190 K.

It is important to note that this rough agreement does not prove that the occupation of grain boundary traps is truly a one-electron problem. It is possible that the state density of Figure 5, for instance, may not arise totally from the differences of chemical energy of various trapping states. There may be a set of quite spatially restrictive sites in the measured boundaries which necessarily entail perturbations of one site energy caused by nearby site occupation that are quite large. We feel that under restrictive enough measurement conditions (small temperature ranges, for example) the behavior of such situations might well resemble one-electron theory to within our measurement capabilities. Certainly, as we have said, we have found apparently homogeneous samples which yield I-V deconvolutions which do not match the simple theoretical predictions.

In summary, it is worth keeping in mind that while a diagram such as Figure 5, probably accurately represents the variation of what we might call the "transport effective" barrier height the actual energy position of

the trap levels could perhaps be influenced to a considerable extent by electron-electron interactions. It should be noted that the one-dimensional Poisson solution of the barrier problem does in fact take into account the interaction energy of a one-dimensional "smeared" sheet of uniform charge. However, this energy can be shown to be totally negligible at the charge densities measured experimentally. On the other hand, forcing our trapped electrons to lie on closely spaced edge dislocation (broken bond) sites introduces substantial (several kT) electrostatic interaction energies and rapidly removes the one-electron character of the situation.

iii. As regards the specifics of the energy location of traps at silicon grain boundaries, our data plus that of Seager and Castner¹⁴ appears to indicate that the chemical potential of the grain boundary regions (the proviso, again is that only high impedance barriers have been examined) lies ~ 0.53 eV above the top of the valence band. The maximum number of available trap states is $\sim 10^{12}$ cm⁻². Again one should use the discussion of section "ii" to infer that "available" could mean "available because that is how many traps there are whose chemical levels lie in the energy gap," or "available because occupation up to this spatial density pushes the remaining trap levels up into the conduction band because of inter-electron repulsion effects."

Concluding this section, we present Figure 7 which updates the work of Seager and Castner by providing a more accurate estimate of the maximum, $T = 0$, barrier heights found in our NTD doped, float zone polysilicon. Included in this graph are thin-film data that we shall discuss in more detail.

iv. Initial examination of melt-doped, float zone polysilicon suggests that the trap levels, densities and grain boundary transport properties are virtually identical to material doped via the transmutation process. A full report of this work will be published in the near future; Figure 8 shows a typical result of characterizing a boundary present in a melt-doped bicrystal. Here we have plotted the zero-bias conductance of a typical high-impedance boundary on an Arrhenius plot. These data should be compared with Figure 2 for equivalent NTD results. Not only is the conductance behavior virtually identical to boundaries in NTD material but the observed capacitance parallels that seen in Figure 3. From these data and those taken on numerous other samples we have concluded that the method of doping plays little role in the grain boundary formation and transport properties. This statement must, of course, be restricted to n-type, phosphorous doped, silicon; it is possible that dopant related defects play important roles in silicon having other substitutional impurities. It is also possible that the trapping levels

characteristic of the grain boundaries in our samples are impurity related. Oxygen, for instance, might play a role in this area. However, at the present we feel no need to invoke extrinsic trapping states. Prior studies suggest that it is in fact intrinsic lattice defects which are the likely source of the states observed. A simple, if naive, calculation of the number of dangling bond states resulting from imagining that the grain boundary is made up of rows of undissociated edge dislocations yields state densities which are more than large enough to account for trap-state densities deduced from our transport measurements.³ In addition, various prior work has indicated that dangling bond states in silicon have acceptor-like character²¹ (in n-type material) with energy levels near midgap.

Thus, it appears to be reasonable to assume that the states we are observing are indeed from silicon atoms which find themselves in non-four fold coordinated environments. More definitive proof of this assumption will have to await experiments which are sensitive to the local character of these trapping states. Electron spin resonance measurements or infrared absorption experiments on polysilicon are both possible techniques for exploring these issues.

Before leaving our discussion about the nature of the grain boundary trapping states, it is worth mentioning the fact that trap-state densities in thin CVD films of

silicon appear to be noticeably higher^{12,13} than the maximum values found in our studies. This is apparent from examination of Figure 7, where the thin-film data of Baccarani, et al.¹³ is shown. Although Baccarani, et al. arrived at their $T = 0$ barrier height numbers by measuring the impedance of their films and not single boundaries, reference to arguments put forth earlier about percolative current flow should convince the reader that the highest individual barrier heights should be, if anything, larger than the numbers deduced from thin-film measurements. We must therefore take this discrepancy seriously and address the possible reasons for higher trap-state densities. Other than severe errors in estimates of the dopant concentration (factors of 5-10?) it appears to us that the most likely explanation is that the intrinsic grain boundary defect state densities are larger because of the non-equilibrium nature of the thin-film CVD growth process. The alternative suggestion - that the states are impurity related appeared to be less attractive after our passivation experiments^{4,27} showed that the major effects of hydrogen were the same for grain boundaries in both bulk polysilicon and thin films of this material. More work in this area is clearly in order.

b. Unanswered Questions

Perhaps the severest test of our understanding of this problem has arisen from attempts to interpret measurements

of the low-frequency capacitance. Remember that all the capacitance measurements discussed so far have been made at excitation frequencies ω such that $\omega\tau \gg 1$, where τ is defined by Equation 6. When we extend our measurements to lower frequencies we have found large departures from initial considerations of the predictions of the DDL/TE model. Before describing these deviations it would first be useful to outline our preliminary attempts at calculating the capacitance of double depletion layer structures.

The general idea of this description is to write down the energy functional for the barrier, W_{tot} , and then use the equation:

$$C = \frac{1}{V} \frac{\partial W_{\text{tot}}}{\partial V} \quad (6)$$

Now W can be divided into chemical and electrostatic parts as follows:

$$W_{\text{tot}} = W_{\text{el}}^{\text{l}} + W_{\text{el}}^{\text{r}} + W_{\text{ch}} \quad (7)$$

where W_{el}^{l} and W_{el}^{r} are the total electrostatic energies of the left and right sides of the barrier, respectively, and W_{ch} is the chemical energy of both sides of the barrier.

We have evaluated this expression in the limits of equilibrium charge transfer to the barrier ($\omega \rightarrow 0$) and no charge transfer ($\omega \rightarrow \infty$); as we have previously discussed the high frequency calculation is in good agreement with

the experiments. In this limit charge is never exchanged with the traps and we have a two plate capacitor problem - the theoretical expression in this situation just reflects the total width of the barrier and is thus insensitive to its exact internal structure. However, as $\omega \rightarrow 0$ there is no simple intuitive "width" that one can assign to the barrier and the expressions for C become complicated and sensitive to the details of the exact barrier potential distribution.

The low-frequency capacitance data that we have taken so far are not in agreement with Equations 6 and 7. Figure 9 shows an example of this; numerous other samples have displayed similar behavior. We see that the high-frequency (1 MHz) data fits the theory well, and the one-dimensional DDL/TE calculation predicts a peak in C_{LF} like that seen qualitatively in the data; however, the magnitude of the measured C_{LF} is higher than our initial theoretical estimate by roughly a factor of ten. This type of discrepancy is rather stunning, to say the least. One explanation for this is that it indicates a complex substructure of the barrier, one which greatly enhances its electrostatic energy over the simple onedimensional model calculations. For instance, arranging the negative charge on lines should enhance the local electrostatic fields near the center of the barrier and increase the total barrier energy. A second explanation is that

there are more terms in the double depletion layer capacitance than those in Equations 6 and 7. Both possibilities are presently under study. (At the release date of this report further theoretical studies have shown that these large capacitances are fully compatible with the simple DDL/TE model.)

c. Future Work

The previous two sections have outlined many of the uncertainties that shadow our present understanding of the grain boundary problem. The ability of the DDL/TE theory to predict the average, static properties of the barrier is quite satisfying. However, probes like the low-frequency capacitance that are sensitive to the total energy of the barrier yield rather unexpected results that will require careful theoretical analysis to determine whether more complex assumptions are needed to successfully fit these data. Only after this is accomplished does it seem proper to attempt to diversify our base of transport measurements. It is possible that we may need to investigate arrangements of negative charge other than the uniform case inherent in the one-dimensional model. Preliminary examination of the possibilities in this area indicates that the mathematics becomes quite complex and difficult to handle on an analytical basis.

A separate but related effort will also be made to consolidate our general base of grain boundary knowledge

derived from measurements which are well predicted by theory. For instance, a detailed dependence of zero bias barrier heights on grain mismatch angles would appear to have the potential for giving us clues about the detailed structure of grain boundaries. Preliminary work on a 30° bicrystal grown by W. Phillips at RCA has already shown that even with this large mismatch angle, ϕ_p , is far from its maximum value. In addition we have found that the angle that the boundary plane makes to each grain plays a large role in fixing the magnitude of the barrier height. In lieu of having a large variety of these bicrystals, we are initiating a program based on measuring the zero-bias transport properties of each boundary on bars of Monsanto polysilicon and correlating these with x-ray determined intergranular orientations. Initial structural analysis is being provided by C. Campana at the University of New Mexico.

Another area of experimental studies that would seem desirable is a study of p-type silicon grain boundaries in comparable detail to the work done on n-type material. In addition to verifying the position of the chemical potential for high-trap-state-density boundaries, we would like to obtain an estimate of the number of donor-like states in the lower half of the forbidden energy gap. At present we have two types of p-doped polysilicon on hand that could conceivably be adequate sample material for these

investigations. These are Wacker, "Silso" and Honeywell silicon-on-ceramic poly produced by a dip process.

III. Studies of Grain Boundary Passivation

A. Background

Practical considerations of polycrystalline silicon solar cell performance have shown that grain boundaries have more effect than just raising the impedance of the base material. Certainly these effects alone could degrade device efficiencies under certain conditions but the effects of grain boundaries on the minority carrier population play a much more important role. It is straightforward to calculate that a fine-grained polysilicon film having $\sim 10 \mu\text{m}$ grain size and of the order of 10^{12} trapping states per square centimeter of grain boundary area possesses $\sim 3 \times 10^{15}$ potential recombination sites per cm^3 . Because these states lie near the center of the forbidden gap, they would be expected to have a high recombination cross section. Actually the fact that they are arranged in roughly planar fashion enhances their deleterious effects by creating uniform regions of fields (the G.B. depletion regions) highly attractive to minority carriers. The real life seriousness of this problem is easily appreciated when the AM1 efficiencies (typically $< 3\%$) of typical fine grain polysilicon cells are quoted in the literature.² Of course, it has been recognized that part of this loss of efficiency arises from the difficulty of making a good p/n or Schottky diode in polysilicon. Reverse leakage is generally high and the forward characteristics are generally very "soft" leading AM1 to fill factors well below 0.5. Again, however, it is appreciated that these

effects are due to the electrical activity of the grain boundary regions, i.e. the trap states. It has been noted that p/n junctions made in damaged material (ion implanted, for instance) suffer from excessive generation-recombination currents.²⁸

The key to solving these problems then is to either eliminate grain boundaries or to eliminate the electrical activity of grain boundaries. The former objective has been the goal of several efforts,¹ and at present does not appear to be an economically feasible one because of the restrictions it places on the substrate upon which the polysilicon is prepared. The latter goal - "passivation" of grain boundaries - is the subject of this section of our report.

When we began our program to passivate silicon grain boundaries we found little guidance from searches of the literature on crystalline silicon, or for that matter, from the literature on any of the common crystalline semiconductors. However, the recent progress in the studies of amorphous silicon did provide us with some rather direct clues about the types of chemical agents that might be effective.

The work of Spear and collaborators has demonstrated²⁹ that a-Si prepared by a low-temperature glow discharge in silane is a semiconductor which is "dopable" over many orders of magnitude in resistivity in almost the same fashion as crystalline silicon. On the other hand, investigators studying a-Si prepared by sputtering or vacuum evaporation, found that the conductance of

their samples was remarkably insensitive to the addition of impurities from groups III and IV of the periodic table.³⁰ The nature of this "discrepancy" has been recently clarified by studies which show that Spear's material appears to contain large amounts of hydrogen.³⁰ Other investigators have subsequently shown that the role of at least some of this hydrogen is to remove the large trap state densities characteristic of the amorphous state.³⁰ This "unpins" the Fermi level and permits conventional doping methods to succeed. These traps are thought to arise from the "dangling" or unsatisfied bonds resulting from frozen-in atomic configurations that do not allow local tetrahedral bonding.³⁰ In many ways we might expect these same unfavorable configurations to exist at a grain boundary in polycrystalline silicon. Hydrogen thus appeared as a prime candidate for altering the electrical nature of these trapping states. The fact that hydrogen has a high mobility in many solids suggested attempts at permeation of already prepared polysilicon.

These considerations led to our first grain boundary passivation experiments. Small slices of large grained polysilicon were exposed to atomic hydrogen produced by a tesla coil-induced plasma discharge. At sample temperatures of around 400°C we observed very definite decreases in the impedance of individual grain boundary barriers.²⁷ Coincidentally several investigators at IBM performed similar experiments on thin CVD films of p-type polysilicon.³¹ The results of their experiments were quite

similar to ours: substantial decreases in the (g.b. barrier limited) conductance of their films were observed. Both our work and theirs was motivated by the same observations - i.e., the known role of hydrogen in a-Si.

The experiments that we have performed in the last year and a half to optimize and understand this process have proceeded in many different directions. Because of the rather discontinuous nature of our progress in this area, recounting all our efforts in a historical fashion does not seem to be the most efficient way to inform the reader. Instead, we shall present our recent thinking in this area in a (hopefully) logical step-by-step fashion. Before doing so, however, a description of the present apparatus for carrying out this process will be provided.

B. Apparatus Used for Passivation

Figure 10 is a simplified schematic diagram of the apparatus presently used to hydrogenate grain boundaries. This arrangement gives us the capability of exploring the effects of other gases on polysilicon. It is an outwardly simple design but some of its specific features were dictated by our experience with earlier systems.

The sample sits on a tantalum platform which is connected to a vacuum flange by a stainless steel tube containing a Pt/Pt-Rh thermocouple. The portion of the vacuum system immediately surrounding the sample area consists of a quartz tube with a stainless steel surrounding band connected to a plasma-exciting

tesla coil. The discharge produced by this arrangement is confined to an area approximately two inches long centered on the tantalum boat. Ultra-high purity hydrogen gas is introduced on one end of this tube and removed at the other end with a turbomolecular pump. A quadrupole mass analyzer mounted downstream from the sample facilitates analysis of the composition of the treatment atmosphere. Elevated sample temperatures are achieved by moving a horizontal tube furnace around the center section of the tube. The temperature of this furnace is monitored with a thermocouple and automatically controlled to within $\sim 10^{\circ}\text{C}$ with a standard SCR-based controller. Actual sample heating is, of course, by radiation and the substantial length of the furnace hot zone (~ 8 inches) insures an isothermal environment. The temperature seen by the external furnace thermocouple is generally within 5° of that measured by the thermocouple imbedded in the tantalum sample boat.

C. Optimization of the Passivation Process

In all of the studies performed to date we have taken the viewpoint that the primary measure of the effectiveness of the passivation process should be the number of grain boundary trapping states that the process removes in a given region of the polysilicon. In order to justify this assumption, correlations with minority carrier recombination and p/n junction quality must be made. However, as we shall see this is somewhat of a "chicken and egg" problem since measurements of the effectiveness

of passivation on real devices require a passivation process which has been optimized enough to remove the trap states at a substantial fraction of all the boundaries in the device. We feel that this fact justifies the approach that we will outline below.

As a background for this discussion we will point out to the reader that all our measurements to optimize the hydrogenation process were made by dragging a potential probe (at 300 K) across the surface of a ~ 1 mm cross section bar of large grain polysilicon. By selecting the long axis of the bar properly we could insure that the majority of the grain boundaries traversed the entire cross section of the specimen. The applied current was thus forced to cross the grain boundary planes one at a time. The potential difference existing across the intersection of a particular boundary plane with the sample surface reflects a rather complex average of the properties of the boundary at different depths from this surface. This complexity arises because varying conductances per unit area are present at different depths due to the finite penetration of the passivating agent. These inhomogeneities lead to substantially non-uniform current densities. Before addressing the interpretation of this rather formidably complicated data, it is useful to consult the DDL/TE model for help in clarifying and simplifying this situation.

Figure 11 shows the dependence predicted by this model of the barrier height at $T = 0$ (left scale) and the room temperature barrier conductance per unit area (right scale) as a function of

state density. A uniform (in energy) trap-state density has been chosen and the grain dopant level is $\sim 1.4 \times 10^{15} \text{ cm}^{-3}$, a value near to the doping level in the samples used in this phase of our studies. The right-hand portion of the curve shows the flattening associated with the "saturation" phenomena. That is, all barriers with high enough state densities have similar, large, barrier heights. We have shown this curve extending to $\sim 7 \times 10^{16} \text{ m}^{-2} \text{ eV}^{-1}$ because this trap-state density is roughly the largest that we have observed in our polysilicon.

Presumably, real grain boundaries exist in our polysilicon that have trap-state densities that cover a large range of N_T below $N_{T_{\text{max}}}$. We say presumably because at least at room temperature our ability to verify this assumption is limited. This limitation arises because at practical current densities grain boundary conductances per unit area larger than $\sim 3 \text{ } \Omega^{-1} \text{ cm}^{-2}$ produce voltage drops too small to be seen with the spatial resolution of our voltage probe. An entire range of grain boundaries is thus "unobservable" at 300 K.

It is useful to define another category for barriers which have impedances up to $\sim$ a decade higher than the "unobservable" limit. We will call these "soft" barriers. The distinction between these barriers and those we shall call "hard" comes from the behavior of current flow near these boundaries. Below some impedance level (the "hard/soft" dividing line of Figure 11) it will be easier for current to flow across a given area of

grain boundary than to avoid this area by flowing laterally through the grain material to any nearby lower impedance area of the boundary if one is present. This is because for boundaries in this "soft" range, the grain boundary resistance is less than the spreading resistance of the silicon along this avoidance path. By imagining the possible current flows in a cube of silicon having one of its sides adjoining a grain boundary, these ideas can be translated into the definite numerical estimates of Figure 11. It can also be seen that the hard/soft and soft/unobservable divisions depend on the resistivity of the grains.

We will now argue that it is likely that in a passivated grain boundary the region of soft barriers is quite narrow in depth. If we imagine that the saturation concentration of monatomic hydrogen is of the order of 10^{18} m^{-2} in the G.B. plane and that diffusion proceeds by bulk or grain boundary paths, we would expect the hydrogen concentration in this plane to roughly resemble Figure 12. Here we have assumed bulk (1D solution of Fick's law) diffusion but the curve would be similar for grain boundary permeation. The major assumptions here are that the plasma is always able to saturate the surface (diffusion limited process) and that the diffusion distance, $\sqrt{Dt}$, is substantially less than the sample thickness. The real world details of this distribution undoubtedly differ from Figure 12, but the basic conclusions to be drawn from this model should not change drastically. We now translate our energy density of traps to a

spatial one by imagining the traps to be spread over an energy of the order of 1 eV and further postulate that one trap state is removed from the grain boundary for every hydrogen atom that is present. We then can calculate the hydrogen concentrations N_{H2} and N_{H1} required to reduce a large barrier (one with an initial trap density, $N_{T_{\max}}$) to a soft and unobservable barrier, respectively. These two concentrations are noted on Figure 12, and it is readily seen that the distance over which this transition takes place is small - on the order of $\sqrt{Dt}/10$ in this case. In principal of course, there exists a concentration N_{H0} (in this case = $N_{T_{\max}}$) where the trap concentration is reduced to zero; above the depth where $N_H = N_{H0}$ there are no potential barriers remaining. This depth can be seen to be almost the same as the two lines in Figure 10. It is worth noting that while this picture suggests that there is a very rapid transition from no barriers to hard barriers as we probe down from the polysilicon surface, the region of noticeable change in barrier heights extends quite a long way in from the hard/soft transition point. This is because even a 1% alteration in N_T produces a quite noticeable change in G_0 due to the exponential dependence of G_0 on ϕ_B . Thus, it is possible to have measurable changes in barrier impedance without removing an appreciable fraction of the trapping states in the material. There is one other result of this model that is worth noting; since all the observable barriers have state densities between N_{T1} and $N_{T_{\max}}$

the penetration depth, defined to lie between the two lines of Figure 12, will be similar for all boundaries which we can see at 300 K. Of course this statement assumes that the permeation profile is also similar for a variety of boundaries.

The third step in this rather oversimplified model is to ask how we can experimentally discern this penetration depth from measurements of the surface voltage profile of a sample bisected by a partially passivated grain boundary. A simple model suggested by the existence of a fairly rapid transition from soft to hard barriers is shown schematically in the upper half of Figure 13. Here we are attempting to simulate a grain boundary which is approximately normal to the surface of a bar of polysilicon of thickness t_2 . Passivation is presumed to proceed from only the top surface - experimentally this is a readily achievable restriction. Simulation of the existence of hard barriers below the penetration depth, t_1 , is achieved by equating this region with infinite impedance so that all the current in the bar flows in the region above the penetration depth.

Practically, this model can be simulated with a strip of conductive paper (of thickness t_2) having a slot of depth $t_2 - t_1$ cut in it. The width in the x direction is chosen to be sufficient to cause the current density to become uniform at either current injection contact. A profile of V versus x observed for such a piece of paper having $t_1/t_2 = 0.2$ is shown in the lower

half of Figure 13. The current crowding produced by the slot produces a noticeable curvature of V over a region of x roughly equal to the thickness t_2 . Because the current density right over the slot should be about t_2/t_1 times the uniform ($x = 0$) value you might suspect that the ratio of the apparent impedance $S \equiv \partial V / \partial x$ at the slot to that far away would be roughly t_2/t_1 as well. This is verified in Figure 14 where $f \equiv S_B/S_G$ is plotted for various values, t_1/t_2 . It should thus be possible to ascertain the penetration depth (as we have defined it) of hydrogen in polysilicon by looking for surface voltage profiles at grain boundaries like those of Figure 13 and measuring the ratio of the apparent resistivity at the boundary to that in the portion of the material (bulk) that contains no nearby boundaries.

We have verified that when sufficient penetration is achieved to reduce S_B to a measurable value the predictions of this simple model appear to be reasonably well satisfied in our polysilicon. Not only are the proper shapes observed in the voltage profiles of well-isolated boundaries but the predictions of penetration depth appear to be verified by etching experiments. Figure 15 shows an example of two drag traces measured in the course of such an experiment. The upper trace is that of the treated (but unetched) sample; arrows indicate the positions of two optically discernable grain boundaries. The measured values of f indicate a penetration distance of ~ 0.15 mm. A second trace on the same

sample etched down to just below this inferred depth shows the onset of hard boundaries where $S_B \rightarrow \infty$. Actually the conductive paper analogy does not really tell us what to expect when the entire depth of the grain boundary plane is "hard" but simplistic arguments can be made to suggest that S_B should always be very large in this regime.

We have used this definition of the penetration depth to optimize the hydrogenation process with respect to the experimental parameters at our disposal.³² Our initial efforts have been confined to one-step treatments - it is entirely possible that more complex treatment schedules could be devised that would lead to more efficient reduction of grain boundary traps. Future work will address this issue. The parameters that were varied in the course of this study included the geometric configuration of the discharge-produced plasma and its pressure and the temperature and surface preparation of the polysilicon. Extensive studies of this last parameter have not yet been carried out but initial indications are that a thorough etching of the surface (using the Sirtl etch) leads to much more efficient hydrogenation than treatment of an as-cut sample. It may be that any disruption of the grain boundary diffusion channel (damage induced, for instance) slows down or blocks efficient flow of hydrogen. The other parameter that is easier to discuss on qualitative, rather than quantitative terms, is the plasma geometry. By using the recombination luminescence given off by

the discharge it is possible to visually monitor the plasma current density near the sample. By altering the shape of the tantalum sample boat and the position of the externally placed stainless steel excitation band we were able to intensify the visible discharge at the sample surface. This high-intensity plasma produced noticeably better penetration depths. Presumably, we are maximizing the surface atomic hydrogen concentration with this configuration.

The results of varying the other two experimental variables are shown in Figure 16. Here we have plotted penetration depth as a function of sample temperature (part A) and plasma pressure (part B). The dependence on temperature is rather weak and suggests a weakly activated hydrogen diffusion coefficient. The motional energy for hydrogen diffusion in Si at high temperatures is ~ 0.5 eV,³³ which is quite low for atomic diffusion. Grain boundary diffusion would in general be expected to be a weaker function of temperature than bulk permeation and thus the results in Figure 16 may not be totally unexpected.

The pressure dependence of the data in part B of Figure 16 indicate that the higher the hydrogen concentration, the better. This is an intuitively satisfying result. The difficulty in raising plasma pressures much above ~ 2 Torr is the observed tendency of the plasma to collapse spatially. This phenomena probably results from an increasingly smaller mean-free path at higher densities. Eventually, the discharge region shrinks

to a size incompatible with uniform coverage of our samples.

There are of course other parameters that could conceivably affect the efficiency of hydrogenation. For example, adding a dc bias to attract protons to the silicon surface could be efficacious. We intend to explore this possibility and others in the near future.

D. Passivation of Thin Film Polysilicon

Because it is clear that future, economically viable polysilicon solar cells will probably be fabricated from thin films of CVD silicon, we felt that it was desirable to investigate the effects of the hydrogen passivation process on this type of polysilicon. The intent, at this time, was to perform some rather preliminary studies with the goal of carrying out more complete investigations at a later date. Figure 17 shows some of the results of these rather preliminary thin-film hydrogenation experiments. The materials studied were CVD deposited, in situ doped (with phosphorous) polysilicon films. The conductance of these films was almost totally dominated by grain boundary resistance; however, any quantitative correlation of this conductance with the theories discussed in Section II was made difficult by the uncertainty in the dopant level. This uncertainty arose for the reasons discussed in Section II. The results of exposing these films to atomic hydrogen were quite dramatic with conductance changes of factors of $\sim 10^4$ seen for the most weakly doped samples. We were very encouraged by these results because they

indicate that the ongoing studies of both the physics and hydrogenation of barriers in bulk polysilicon appear to have some relevance to thin, deposited films of this material.

E. Studies of the Physics of the Passivation Process

1. Experiments Designed to Clarify The Mechanism of Hydrogen Permeation.

In order to facilitate our understanding of the grain boundary hydrogenation process we would like to know what determines the rate of hydrogen penetration into the grain boundary trapping sites. Although grain boundary diffusion is an attractive candidate for this mechanism, the experiments performed to date have not permitted us to rule out bulk permeation. Indeed there is evidence that there are substantial amounts of hydrogen in the grains of our samples after typical treatments.

This evidence comes from outgassing samples of single and polycrystalline silicon into a small high-vacuum chamber connected to a quadrupole mass analyzer. For convenience in discriminating between gases evolved from the sample and environmental contaminants desorbed from the boat and vacuum system walls, the passivation treatment was done with a mixture of hydrogen and deuterium. The evolved amount of mass three molecules was then monitored as the sample was heated

from ~300 K to ~900 K. We had previously determined that a deuterium plasma alone was capable of causing substantial grain boundary passivation. The results of heating a single crystal and polycrystalline silicon (25 μm grain size) bar of identical size is seen in Figure 18. The fine structure of both of these curves is not very reproducible but the general shape and magnitude are. Given this fact it is clear that the difference in behavior between poly and single crystal is minimal at best. We have thus concluded that the amount of hydrogen/deuterium present in the bulk of our polycrystalline material after hydrogenation considerably (by at least a factor of five) exceeds that in the grain boundaries. Of course, this result does not prove that experiments of this type cannot give us any information about the amount or evolution kinetics of the absorbed grain boundary hydrogen. It is possible that the hydrogen that has diffused into the bulk is located near to the surface. Experiments involving etching of treated samples could resolve this issue; these measurements are presently being carried out.

A second attempt to decide which hydrogen permeation path plays the dominant role has been based on the sensitivity of the penetration depth to surface preparation conditions. An example of how surface etching of an as-sawed sample enhances passivation is shown in Figure 19. Here the center, etched section is seen to have much more effectively passivated

boundaries than the remainder of the polysilicon bar. We have tried to use this effect to distinguish between bulk and grain boundary permeation. Sample bars have been prepared with etched and unetched sections. Some of the unetched sections were quite narrow ($\sim .2$ to $.4$ mm) and were centered on the intersections of the grain boundary with the sample surface. Since the unetched regions apparently act as masks through which hydrogen penetrates very slowly we hoped to ascertain whether the penetration of certain boundaries was a function of how close by an etched region of the surface was or, alternatively, if this penetration was independent of the width of this unetched "covering strip." The latter result would indicate that lateral, in-grain diffusion of hydrogen (along the length of the bar) was not important in reducing the grain boundary barrier height. At present we have not seen any dependence of this penetration on the width of this covering strip. However, to unequivocally prove that bulk diffusion is not important, better masking techniques for etching around these narrow strips will have to be developed; these experiments promise to be informative and we are attempting to improve the techniques involved.

A third type of measurement that could be useful in establishing which diffusion path is important is a careful measurement of the penetration depth as a function of treatment time. To distinguish grain boundary from bulk diffusion it

may be necessary to have numerous identical samples to remove the scatter associated with different trap-state densities (and possibly different diffusion paths) found on randomly picked grain boundaries. This scatter is evident in the plots in Figure 16. These considerations imply that samples cut from bicrystals would form the ideal set of specimens for this study. Recently, we have received several bicrystal wafers from W. Phillips at RCA and these will be used, at least partly, for this purpose.

A final class of experiments that relates to the movement (and bonding) of hydrogen in polysilicon involves measurements of the stability of the passivation treatment. Our preliminary results in this area have indicated that samples held in vacuum at 300°C appear to stay passivated for periods of at least 50 hours.²⁷ We also know that an extremely short exposure (minutes) to 600°C returns grain boundaries to their virgin state. However, between these two extremes very little is known. Carefully annealed and measured samples could no doubt tell us a great deal about the kinetics of debonding and outgassing of trapped hydrogen. Such experiments are planned for our next research period.

2. Probes of the Local Nature of Virgin and Hydrogenated Grain Boundary Trapping States.

Up to the present the details of the defect states responsible for trapping are largely unknown. One of the factors that makes this a difficult problem is the small

volume density of these traps. Even in a 25 μm grain size material the volume density of these states is probably less than 10^{14} cm^{-3} . This severely limits the types of physical measurements we can make on polysilicon. We will discuss two rather promising techniques that we have applied to this problem. Since both studies are far from completion only brief outlines of these efforts will be given. Work on both is continuing at present.

In principal, electron spin resonance measurements are capable of measuring $\sim 10^{11}$ spins. This sensitivity suggests applying the method to the grain boundary problem. We have begun to pursue this approach in cooperation with K.L. Brower and P. M. Richards of this laboratory. Preliminary measurements on blocks of fine grained (25 μm) polysilicon have been somewhat inconclusive. Some effects, apparently due to surface damage, have been identified and more careful sample preparation is indicated. Since the advent of our "optimized" plasma process we have a reasonable chance of fully hydrogenating the substantial thickness of our ESR specimens; we have thus resumed our efforts in this area. In addition, we have recently become aware that ESR resonance of dangling bonds on edge dislocations in silicon is greatly enhanced by illumination with sub-band-gap light.³⁴ We plan to look for this effect in our material. A second microscopic probe that we have recently applied to studying

the local bonding configurations in hydrogenated polysilicon is Fourier-Transform-Infrared Spectroscopy. FT-IR with its sensitivity to both quantity and structure and with advanced signal averaging capabilities is well suited to this type of investigation.

Samples of fine grain (25 μm) neutron transmutation doped polysilicon have been examined by transmission FT-IR. Peaks in the spectral region of the Si-H modes (1985-2150 cm^{-1}) were monitored. In virgin untreated samples no peaks are observed in the region of interest. However, plasma treatment at 350°C in .5 Torr H_2 , produces a peak at 2019 cm^{-1} , as is illustrated in Figure 20. Experiments on single crystal samples yield no similar peak. The intensity of this peak increases with increasing plasma treatment time and decreases upon vacuum anneal. This peak is in the range normally associated with Si-H stretching modes. A peak at 2102 cm^{-1} has very similar characteristics as well. When treated at 350°C in 2 Torr H_2 , this peak increases much more than that at 2019 cm^{-1} . This absorption may be associated with an Si- H_2 stretch or Si-H surface modes. Experiments are under way to evaluate and explain the observed spectral changes. The bending and wagging spectral regions at 850-1500 cm^{-1} and 500-600 cm^{-1} will be examined as well.

F. Future Work

The optimization of the hydrogenation process has now permitted us to pursue experiments involving the passivation of fairly thick samples. These experiments, of course, include studies of the effect of hydrogenation on device characteristics but discussion of these is deferred to Section IV of this report. The remaining types of measurements that will be carried out are briefly listed below.

1. Future experiments to elucidate the permeation mechanism.

These include:

- a. Studies of penetration distance as a function of time.
 - b. Further determinations of the importance of sample surface preparation.
 - c. More "etch masking" studies of the permeation paths.
 - d. Outgassing studies on treated and etched polysilicon.
 - e. More experiments probing the stability of passivated grain boundaries.
2. Extension of our studies of the local atomic environments of grain boundary defect states. These will primarily involve ESR and FT-IR experiments.
 3. Investigation of the effects of other possible passivation agents. Among the prime candidates for this are fluorine (by plasma processes) and lithium (injected by ion injection techniques from solution).
 4. Future studies of the passivation of thin, CVD films of polysilicon.

IV. Solar Cell Passivation Studies

The fact that the hydrogen passivation process can significantly alter the electrical properties of individual grain boundaries is not sufficient to guarantee that solar cells can be improved by hydrogenation. Although electrical measurements on grain boundaries substantiate that the density of trap states can be significantly decreased, they do not prove that grain boundary recombination is concomitantly reduced. To investigate this issue as well as the effects of passivation process on p-n junction characteristics, polysilicon device structures must be fabricated and examined. Therefore, a number of programs have been initiated in an attempt to assess the effectiveness of the hydrogen passivation process on solar cell parameters.

One of these efforts involves the in-house fabrication of solar cells, the others entail cooperation with other research groups. These programs were initiated not only to answer the questions concerning recombination centers and junction quality, but to establish the effectiveness of the passivation process on different types of polysilicon and on solar cells of varying configurations. The cooperative projects offer a major advantage: we can draw on the expertise in fabrication already existing at other facilities without undergoing a lengthy device development process ourselves. We have initiated five cooperative efforts. These include work with Colorado State University, Honeywell, RCA, Florida State University and Los Alamos Scientific Laboratories.

The scope of these efforts, progress to date and future plans will be reviewed in the succeeding sections. Finally, we will discuss our own preliminary work on solar cells.

The general methodology followed for all the cooperative efforts is quite similar. The as received materials are characterized electrically and optically. The initial electrical characterizations are done to probe the nature of the grain boundaries. To accomplish this, slices are cut and contacted for drag traces and also for four probe I-V and C-V measurements, if applicable. The samples are optically characterized to identify the spacing and orientation of grain boundaries. At this point a series of experiments are conducted both to establish that the material can be passivated and to optimize the conditions for that type of polysilicon. This includes studies of the penetration of the hydrogen through diffused layers.

At this point, most of the material with p-n junctions is passivated and returned to the supplier for their final device fabrication steps and analysis. In some cases (diffused) devices are contacted in-house in a solar cell configuration and their I-V properties, efficiency and spectral response are determined. We also have the capability to investigate these materials by a variety of other techniques including EBIC, Fourier transform infrared spectroscopy and pulsed x-ray excitation methods.

In the succeeding sections we will present a brief discussion of all of the ongoing cooperative efforts. In each case the

material is described, the results for sample preparation and passivation discussed and our own or the principal investigators observations on the devices made from the passivated material are summarized.

A. Cooperative Efforts

1. Honeywell Corporate Technology Center

Principal Cooperative Investigator - Dr. J. D. Zook.

Material - The materials provided were samples of Honeywell's silicon on ceramic (SOC) both with and without a p-n junction region. Fabrication involves dipping or pulling the ceramic from a melt of silicon. This produces a coating which varies somewhat in thickness and has a reasonably smooth surface. These samples had a base doping level of 2.3×10^{16} atom/cm³ (boron) and were nominally 200-300 μ m thick. Some of the samples had a ~ 0.3 μ m thick n-type surface region diffusion doped with phosphorus. Several of the samples with these p-n junctions contained back contacts of platinum silicide formed through slots in the ceramic support material.

Passivation - The Honeywell samples were significantly different from any materials we had previously tried to passivate, since they were both p-type and melt doped. Thus, effective passivation of the grain boundaries in this material represented a significant extension of the applicability of the hydrogenation process. The largest barriers in this material were noticeably smaller than in previously examined n-type polysilicon; typical impedances for

a ~ 1 nm cross sectional area) were 40-100 Ω . A representative drag trace for the bulk p-type base polysilicon before and after passivation is shown in Figure 21. Using the penetration depth analysis discussed in the last section we found that plasma exposures as mild as 3-4 hours at 0.5 Torr removed visible grain boundary barriers all the way down to the substrate. However, where the n-type surface layer was present hydrogen passivation was much harder to achieve. The penetration depths were measured in this case by etching off the n-layer and then making our usual drag trace. Even after 15 hours of treatment at 2 Torr and 350°C we could only penetrate to depths of 100-150 μm . Studies of the retarding effect of this heavily diffused layer suggest that under equivalent treatment conditions penetration depths are 10-50 times smaller if the diffused layer is present. A complete explanation of the retarding effect of this layer is not known at this time; one possible explanation is that extensive segregation of dopant atoms at the grain boundaries depresses the diffusion of hydrogen.

Solar Cells - We have begun some preliminary in-house investigation of solar cells fabricated from diffusion doped, SOC, samples. Front surface contacts were indium, which was removed before passivation, then reapplied. We are currently investigating the use of tungsten contacts; we expect that these may be able to endure the passivation process without degrading cell performance.

The dark I-V characteristics for a cell before and after passivation (100°C, 500 millitorr H_2 , 19 hrs.) of the configuration

Pt/p-Si/n-Si/In are illustrated in Figure 22. Generally, leakage currents are reduced and the forward characteristics improved (I increases more rapidly with bias). This junction quality improvement suggests that we might expect increased fill factors for illuminated cells. N-layer conductances have been observed to occasionally increase after prolonged hydrogenation. The exact cause of this effect is currently being investigated.

Future Plans - An extensive investigation of various metallizations is under way in order to find a top contact capable of withstanding the passivation process. It is of course necessary that this contact remains not only mechanically intact, but also it does not diffuse substantially into the cell, shunting the p-n junction.

A continued investigation of the I-V properties of Honeywell diffused solar cells will be made both under AM1 illumination and in the dark. Attention will be directed to evaluating AM1 efficiencies and spectral response. Electron beam induced current (EBIC) maps of the cells before and after passivation will also be made to directly evaluate the effect of the passivation process on minority carrier life times.

2. University of Florida (UF)

Principal Cooperative Investigator - Dr. Jerry Fossum

Material - A number of n⁺p Wacker Silso wafers were received; these had a variety of grain dimensions and shapes. The samples were ~250 μm thick and the base doping level was $4 \times 10^{15} \text{ cm}^{-3}$

(boron). The junction was formed (at UF) by diffusion; this junction depth was $\sim 1 \mu\text{m}$. No metallizations were present on the as-received samples.

Passivation - Similar to other Wacker samples we have examined, the University of Florida samples did not initially passivate effectively. In the case of the UF wafers this may be due either to the presence of the n-layer on these particular samples or to any residual polishing damage at the surface. Whatever the cause of this problem, chemically removing 25 microns with Sirtl etch considerably enhances the effective penetration of the passivation process. Because these samples were received rather early in our program, no definitive studies of the penetration of hydrogen through the n^+ layer were carried out. These measurements will be made in the near future and the results will be applied to maximize hydrogen penetration in the next batch of wafers which will be returned for cell fabrication. The first group of wafers were returned to UF after the following plasma exposure: 18 hrs at 400°C and 0.5 Torr hydrogen pressure.

Solar Cells - No work has been done in-house and no results have been forthcoming thus far from UF.

Future Plans - The depth of penetration of the passivation process will be examined in detail as a function temperature and pressure for base UF (Wacker) material and for slices having an n^+ layer. Simple solar cells will be fabricated of the n^+ -p slices and these will be examined using our standard solar cell characterization methods.

3. Colorado State University (CSU)

Principal Cooperative Investigator - Dr. J. DuBow

Material - We have received a number of half wafers of Czochralski grown diffusion doped single and polycrystalline silicon. All the wafers were diffusion doped (p-type) between .1 and 1.5 Ω -cm, and all base contacts of an evaporated copper-aluminum alloy. Some of the wafers had a top ITO coating. There was a considerable variation in grain size across the polycrystalline wafers from 20 μ m to millimeters.

Passivation - Samples were prepared for the passivation process by removing the copper/aluminum with 1 M NaOH and the ITO with 10% HF. The wafers were cut into slices for drag traces and contacted with annealed Al/Ti/Au contacts at both ends. The as-received samples all had rather low impedance barriers (less than 10 Ω for samples 500 μ m thick and 2 mm wide). These impedances only increased marginally with vacuum annealing. Hydrogen plasma treatments for 3-4 hours at 350°C and 2 Torr hydrogen resulted in the removal of all visible signs of grain boundary barriers; see Figure 23. If the ITO layer was directly exposed to the plasma, its bluish appearance changed to a silvery one. This was accomplished by conductance increases of the order of 30%. This is likely due to some in situ reduction of the ITO surface by the hydrogen plasma. However, it appears that in the future these samples may be passivated from the back (after contact removal). Our experiments have shown that if the ITO is in intimate contact

with the support platform, little if any reduction of the film is observed; this is due to the low concentration of atomic hydrogen at the unexposed surface. CSU samples which had no ITO layer passivated well with no surface etching required. A number of these "bare" polycrystalline wafers have been returned to CSU after passivation for device processing and evaluation.

Solar Cells - NO work in progress.

Future Plans - EBIC experiments will be conducted to try and examine the effect of hydrogen on recombination center density in this material. Further experimental planning will depend on the evaluation of devices made from the material returned to CSU.

4. RCA Laboratories

Principal Cooperative Investigators: B. Faughnan and D. Redfield

Material - A single Wacker wafer was received from RCA.

This material had a grain resistivity on the order of $10 \Omega\text{-cm}$ and was $\sim 25 \mu\text{m}$ thick.

Passivation - This wafer was cut into slices for drag traces and contacted with annealed Al/Ti/Au metallizations. Typical barrier impedances were 100Ω with the largest being $\sim 400 \Omega$ (for a 1 mm^2 cross sectional area). Initial treatments revealed that hydrogenation of the virgin material produced only partial passivation of these G.B. barriers. It was found that this problem was due to a thin surface layer which was greatly impeding the passivation process. This layer may be due to damage resulting from the sawing and polishing operations or it may be chemical

in nature. Chemically removing 25 μm from the sample alleviated this problem. Treatments of 15 hrs at 350°C and 2 Torr resulted in hydrogen penetration depths of 150 - 250 μm . Work is currently under way on optimizing the passivation process for this material.

Solar Cells - No work in progress.

Future Plans - We are awaiting the arrival of prototype solar cells from RCA. These will be passivated and examined by EBIC and returned to RCA for laser scanning and AM1 efficiency measurements.

5. Los Alamos Scientific Laboratories (LASL)

Material - Three samples were received which had previously been examined by photoluminescence spectroscopy. All were of ultra-high purity intrinsic Dow-Corning polysilicon and had been cut from the polycrystalline ends of a single crystal boule.

Passivation - The samples were nearly intrinsic and thus had very high bulk resistivities; consequently, because of contact resistance problems, it was difficult to obtain meaningful (noise free) drag trace information. There was, however, a significant increase in the current required to obtain the same potential drop across the samples after passivation indicating a substantial reduction in barrier heights. After hydrogenation, the samples were returned to LASL for repetition of the photoluminescence measurements.

Solar Cells - No work in progress.

Future Plans - Samples other than intrinsic will be investigated. Samples will be annealed and the effect of the incorporation of impurities, O_2 and N_2 on photoluminescence evaluated.

B. In-House Solar Cell Research

Though we do not have the experience or facilities to make state-of-the-art polysilicon solar cells, the information to be gained from solar cells is so significant that we have produced a few prototype cells. These have been made with no thought towards achieving optimum efficiencies but rather simply as an indicator of the effect of the passivation processes on minority carrier lifetime, spectral response and junction characteristics.

Material - The base material used was obtained from J. Cleland at Oak Ridge National Laboratory. It was bulk polysilicon in which doping was implemented via neutron irradiation (NTD-neutron transmutation doped) at the National Bureau of Standards reactor facility. The materials used were exposed to one and seven day irradiations which resulted in doping levels of 2.0×10^{15} and $1.3 \times 10^{16} \text{ cm}^{-3}$ respectively. The materials required 1 - 2 hr anneals at 850°C in vacuum to remove most of the defects caused by transmutation. Solar cells were constructed of material that had either 25 micron or 200 micron average grain size of both doping levels. The diode was formed by either ion implanting boron or by the standard borate glass diffusion technique. The depth of the junction was approximately .2 - .5 micron. The ion implanted samples required a thermal anneal at 1000°C for 1 hour in hydrogen

to remove the majority of the implantation-induced damage.

Contacts to the cells consisted of a Ti/Au or Cr/Au back contact and an Al/Au or Ti/Au front contact. The front contact was removed and reapplied after passivation.

Passivation - The passivation of NTD silicon has been discussed thoroughly in the passivation section. It was the prototype material for evaluating process parameters. It should be emphasized that the results reported in this section were all obtained before the hydrogenation process was optimized in the new system. We estimate, therefore, that the grain boundary barriers in these cells are thus passivated only very near the surface, primarily in the first 10 - 50 microns. Of course, at this stage in the project we had made no detailed study of the effect of the p/n junction on hydrogen penetration depth so that the extent of grain boundary barrier reduction in these cells is uncertain.

Solar Cells - Figure 24 illustrates typical I-V curves for two cells before and after hydrogen treatment. Overall efficiencies are low because the neutron transmutation doped (NTD) polysilicon employed suffers from a very low bulk lifetime. The upper set of curves are for a boron diffused solar cell fabricated from one drag, NTD (phosphorous) doped polysilicon (200 micron grains). The dashed curves represent the light and dark traces for the virgin cell; the solid lines are the curves for the plasma treated cell. The efficiency increase (AM1) of a factor of ~26

is probably due to two distinct factors. One is an increase in the short-circuit current ostensibly due to improved transport of minority carriers across grain boundaries. The other is a substantial improvement in the open-circuit voltage due to an elimination of the shunting action of the grain boundaries which intersect the p/n junction. The lower half of Figure 24 shows three illuminated I-V curves for a boron ion implanted, bulk NTD phosphorous doped polysilicon solar cell. The 1000°C H₂ anneal is an attempt to remove some of the ion implantation defects. Curve 3 again shows that the hydrogen plasma treated cell increases in efficiency as a consequence of improvements in both the short-circuit current and open-circuit voltage in the cell.

The lifetime of the minority carriers and the spectral response of some of the ion implanted cells has been probed more directly as is shown in Figure 25. The lower curve and number refer to the virgin sample, the upper set are after hydrogen plasma treatment. The lifetimes were determined by following the short-circuit current decay after a 5 nsec x-ray pulse. The data show a measurable increase in bulk minority carrier lifetime after plasma treatment. This is substantiated by an examination of the spectral response curves for the cell. There is a large increase in the quantum efficiency of the long wavelength tail where the photons are absorbed well below the junction. The indications of this research are encouraging, but the effectiveness of the passivation process can only be evaluated by looking more carefully at state-of-the-art polysilicon cells. It is especially desirable to utilize material

having a minority carrier lifetime in the grains which is significantly longer than 1 μ sec.

Future Plans - To overcome the limitations of our first, rather primitive solar cell experiments, a new set of solar cells is being fabricated. These cells will have a base material of 2 ohm-cm diffusion doped polysilicon having an average grain size of ~250 microns. We anticipate the minority carrier lifetime in the grains will be substantially better in this material than in NTD doped samples. Diodes will be formed by ion implantation with a subsequent laser annealing to remove defects in the heavily doped layer. Metallizations are being developed which will withstand the passivation process, obviating the need to repeatedly recontact samples. The cells will be passivated in the new system under the optimum conditions. Cell characterization methods will include dark and illuminated I-V curves, EBIC response, spectral response and x-ray lifetimes; both before and after treatment.

FIGURE CAPTIONS

Figure 1. The largest grain boundary barrier heights (extrapolated to $T = 0$) as a function of dopant density for NTD silicon. Open circles are data from small-area potential profile experiments, and filled circles are from four-probe bulk resistivity data at ~ 270 K. At $\sim 2.0 \times 10^{15}$ μ/cm^3 these two experiments give identical results; below this dopant concentration, the potential probe data were difficult to obtain due to the sample resistance level, and hence four-probe data are shown. The three curves shown are the results of model calculations described in Sec. III B of Reference II.

Figure 2. The effect of removing the surface layer of an as-sawn polysilicon bar on the zero-bias conductance of a single grain boundary. The zero-bias capacitance per unit area remained essentially constant during this experiment.

Figure 3. Conductance and barrier height versus reciprocal temperature. The zero bias, dc conductance for a Si G.B. is plotted using the logarithmic, left ordinate scale; an activation energy of 0.62 eV is found. From this curve a zero-bias barrier height ϕ_{BO} is calculated and shown as the THEORY line using the linear, right ordinate scale. Experimental values of ϕ_{BO} found from capacitance data are plotted as triangles.

Figure 4. DC current and high-frequency capacitance versus applied voltage for a Si G.B. The dc current through the G.B. is plotted logarithmically using the left ordinate scale. The location of the largest α value is indicated in the upper right corner. Also plotted as circles on this graph is the measured, high-frequency capacitance per unit area using the linear, right ordinate scale. The solid line through those points is the capacitance calculated from the density of G.B. states deduced from the I-V curve. The inset show a simplified version of the G.B. barrier model from Reference 15.

Figure 5. Density of G.B. states versus energy. The density of states in the Si G.B. deduced from the dc I-V data is plotted as a function of energy measured from the valence band. Information about $\bar{N}_T(E)$ is only available at energies above the equilibrium Fermi level.

Figure 6. (A) The electron energy diagram for a grain boundary is an n-type semiconductor which has a large amount of non-equilibrium trapped charge. This gives rise to barrier heights ϕ_B , much larger than the equilibrium value. E_{FB} is the neutral (unjoined) Fermi level; see Reference 2 for details of the double barrier model. (B) Values of the charge decay rate $\partial Q/\partial t$, deduced from capacitance recovery measurements at five temperatures on a single grain boundary in silicon. The equilibrium value of Q is $\approx 6.1 \times 10^{15} \text{ m}^{-2}$ in this temperature range.

Figure 7. The activation energies of the largest grain boundary barriers in both thin film and bulk polysilicon. Open circles are the data of Seto (Reference 12); open squares are from the work of Baccaranni, et al. (Reference 12). The filled circles are the data of Seager and Caster (Reference 14) obtained from $\sim 25 \mu\text{m}$ grain size, NTD doped polysilicon. The dashed curve is our estimate of what the true bulk poly curve should look like based on recent measurements on large grain, Monsanto polysilicon. Part of the discrepancy with Seager and Castner's data arises from the influence of surface effects on their measured barrier conductances.

Figure 8. The zero-bias conductance of a large grain boundary barrier in Monsanto, melt-doped polysilicon. Note the similarity of this data to that presented in Figure 3 for transmutation doped silicon.

Figure 9. The low (1 KHz) and high-frequency (1 MHz) capacitance as a function of bias for a single NTD doped grain boundary. The solid and dashed lines show our initial theoretical estimates of these capacitances calculated using an energy formalism and the DDL/TE model parameters.

Figure 10. A simplified schematic diagram of the current apparatus used to passivate grain boundaries with hydrogen.

Figure 11. The values of the $T = 0$ barrier height (left scale) and 300 K grain boundary conductance (right scale calculated assuming a variable value for an energy independent density of grain boundary trapping states. The assumed n-type dopant concentration is $1.4 \times 10^{15} \text{ cm}^{-3}$.

Figure 12. The hydrogen concentration in the grain boundary plane estimated if penetration is by bulk diffusion with $\sqrt{Dt} = 5 \times 10^{-3} \text{ cm}$. The surface concentration is assumed to be $\sim 10^{18} \text{ m}^{-2}$. Vertical lines show the hydrogen concentrations where a grain boundary initially having $\sim 7 \times 10^{16} \text{ states/m}^2$ would be reduced to a "soft" and an "unobservable" barrier.

Figure 13. A diagram (inset) of the conducting paper experiment used to simulate the current flow around a partially passivated barrier. The slot in the paper simulates the existence of a "hard" barrier of depth $t_2 - t_1$. The graph shows a typical potential profile obtained along the top edge of this conducting paper for $t_1/t_2 = 0.2$. S_B and S_G are the values of $\partial V/\partial x$ measured at the slot and far away from the slot, respectively.

Figure 14. The ratio S_B/S_G plotted as a function of the (passivated) fraction, t_1/t_2 , for the conducting paper experiment.

Figure 15. Drag traces of a passivated (upper) and etched (lower) sample of NTD doped polycrystalline silicon. The existence of hard ($S_B/S_G \gg 1$) boundaries below the penetration depth predicted

by the slopes of $\partial V/\partial x$ measured at the boundaries after passivation is verified when the sample is etched down 220 μm with Sirtl etch.

Figure 16. The hydrogen penetration depth as a function of sample temperature and plasma pressure. The samples used were large grain ($\sim 250 \mu\text{m}$) NTD doped ($N_D \approx 2.0 \times 10^{15} \text{ cm}^{-3}$) polysilicon.

Figure 17. The effect of hydrogen passivation on thin, CVD films of polysilicon grown on oxidized silicon wafers. Plotted is the ratio of film conductance (zero-bias) measured before and after treatment. The exact doping levels (phosphorous) are uncertain, but the abscissa reflects the relative amounts of phosphine added during film growth.

Figure 18. The results of outgassing samples of single and polycrystalline silicon identically plasma treated with a mixture of hydrogen and deuterium. The abscissa shows both time and temperature as the sample was heated in a small chamber accessed by a quadrupole mass spectrometer monitoring the partial pressure of mass 3 species.

Figure 19. The effect of etching an as-sawn polycrystalline sample on the passivation of grain boundaries with atomic hydrogen. The center section of the sample was etched with a Sirtl etch to remove $\sim 25 \mu\text{m}$ of the damaged surface layer before treatment. The lower trace shows the markedly more effective passivation achieved in this etched region.

Figure 20. The infrared spectra of hydrogen incorporated in polycrystalline silicon (after correcting baseline). A. Fresh sample after 800°C vacuum anneal, B. Sample after H-plasma treatment at 400°C, C. Sample after 600°C vacuum anneal, D. Sample after H-plasma treatment at 400°C, E. Sample after 2 additional H-plasma treatments at 400°C.

Figure 21. A typical potential vs. distance (drag trace) plot for a virgin (top) and hydrogen plasma-treated (bottom) p-type, 250 micron thick Honeywell silicon on ceramic (SOC) polysilicon sample. The voltage scales are the same in each case. Hydrogen pressure during treatment was 500 millitorr.

Figure 22. Dark current-voltage traces obtained before and after hydrogen plasma treatment (19 hr., 500 millitorr, 400°C) for an n or p diffused Honeywell silicon on ceramic solar cell with a back Pt and front In contact.

Figure 23. Potential vs. distance plots for a virgin (top) and hydrogen plasma-treated (bottom) .1 - .3 Ω -cm p-type polysilicon sample obtained from Colorado State University. Total voltage drop across the sample is approximately 60 mV in both traces the current before treatment was 2.0 mA and after 2.2 mA. The largest barrier impedance before treatment is 2.25 Ω .

Figure 24. The upper portion of the figure and the light and dark I-V curves for a prototype solar cell of n-type neutron

transmutation doped polysilicon with a boron diffused p-layer before (dashed curves) and after (solid curves) hydrogen plasma treatment (19 hrs, 500 millitorr, 375°C). The efficiencies are AM1. The current is plotted vertically in mA and potential horizontally in volts. The lower portion of the figure is a similar cell with a boron implanted surface layer. The figure illustrates the illuminated I-V curves for the virgin cell, the cell after a 1000°C thermal anneal in molecular hydrogen and after hydrogen plasma treatment (19 hrs, 500 millitorr, 400°C). The efficiencies are AM1.

Figure 25. Spectral response curves (external quantum efficiency vs. wavelength) for an n-type neutron transmutation doped polysilicon sample with a boron implanted junction before and after hydrogen plasma treatment (17 hrs, 500 millitorr, 380°C). The lifetimes are derived from current vs. time data collected after irradiating the cell with a 5 nanosecond x-ray pulse.

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Fig. 1
Seager/
Ginley

Fig. 2
Seager/
Ginley

Fig. 3
Seager/
Ginley

Fig. 4
Seager/
Ginley

Fig. 5
Seager/
Ginley

Fig. 6
Seager/
Ginley

Fig. 7
Seager/
Ginley

Fig. 8
Seager/
Ginley

NTD DOPED SINGLE
GRAIN BOUNDARY
 $N_D = 1.3 \times 10^{16} \text{ cm}^{-3}$
 $\text{AREA} = 1.31 \times 10^{-2} \text{ cm}^2$

Fig. 9
Seager/
Ginley

Fig. 10
Seager/
Ginley

Fig. 11
 Seager/
 Ginley

Fig. 12
 Seager/
 Ginley

Fig. 13
Seager/
Ginley

Fig. 14
Seager/
Ginley

H^+ TREATED NTD POLYSILICON

$$N_D = 2 \times 10^{15} \text{ cm}^{-3}$$

Fig. 15
Seager/
Ginley

Fig. 16 (a)
Seager/
Ginley

Fig. 16(b)
Seager/
Ginley.

Fig. 17
Seager/
Ginley

- SINGLE CRYSTAL SILICON
- POLYSILICON

Fig. 18
Seager
Ginley

Fig. 19
Seager/
Ginley

Fig. 20
Seager/
Ginley

Fig. 21
Seager/
Ginley

Fig. 22
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Fig. 23
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Fig. 24
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Fig. 25
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