Stable, High Efficiency Amorphous Silicon Solar Cells with Low Hydrogen Content

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C. M. Fortmann, S. S. Hegedus
*Institute of Energy Conversion
Newark, Delaware*

NREL technical monitor: B. von Roedern

National Renewable Energy Laboratory
1617 Cole Boulevard
Golden, Colorado 80401-3393
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PREFACE

This report covers phase I of a three phase project directed towards the demonstration of amorphous silicon solar cells with high stabilized conversion efficiency. The objectives of this work were designed to direct a broad research program spanning material issues (more stable amorphous silicon and better amorphous silicon-germanium alloys) and devices issues (more stable amorphous silicon base solar cells) towards the goal of high stabilized solar cell efficiency. For the historical reasons (the original statement of work) and for greater clarity the work presented here is grouped according to material. Since this is the initial phase of research, the work presented here is weighted towards the fundamental. During this phase of the work IEC has produced and analyzed both amorphous silicon germanium and amorphous silicon films and solar cells with reduced hydrogen content in order to make progress towards high stabilized efficiency multijunction solar cells. Single junction solar cells were numerically modeled in order to identify the best solar cell designs and to determine the relative contributions of interface and bulk properties on solar cell performance. A thermodynamic model of defect formation was developed which when used in conjuncture with a study of high temperature degraded state of a given solar cell can be used to predict the stabilized efficiency of that solar cell. Some of the analysis and measurements of amorphous silicon and silicon-germanium films has been done in collaboration with C. Wronski at Pennsylvania State University, J. D. Cohen at the University of Oregon, P.M. Fauchet at the University of Rochester and the group at the University of Neuchatel. Some of the theoretical work presented in this report was aided by data provided by T. McMahon at National Renewable Energy Laboratory, D. Redfield and R.H. Bube at Stanford University, and E. Schiff at the University of Syracuse.

SUMMARY

A. Objectives

The objectives of the research described in this report were to develop amorphous silicon solar cells with high stabilized efficiencies. In the process of obtaining this goal, it is our intermediate objective to resolve several key material and device issues. These key issues are: 1. whether a reduction in hydrogen content in amorphous silicon intrinsic layers can lead to higher stabilized solar cell efficiencies; 2. how the performance of solar cells made with narrow band gap a-SiGe:H can be enhanced; 3. how the particular materials and device parameters determine stabilized performance of a-Si:H solar cells; and 4. how particular materials and device parameters may enhance performance of a-SiGe:H based solar cells.

B. Discussion

Measurements and analysis were made on amorphous silicon films deposited by photo-CVD under conditions intended to reduce the hydrogen content of the films to determine whether low hydrogen materials offer a means to improved stability directly or permit the design of solar cells with greater stabilized efficiency. Although the deposition of low hydrogen materials proved to be a difficult task, those samples that did not flake appeared to have improved stability as measured by the change in Q.E. at 450 nm.

Due to low hydrogen film's adherence problems to non-conductive substrates an increased reliance on device measurement to obtain material parameters was required. Solar cell device analysis techniques including short wavelength quantum efficiency and primary photo-current were reviewed.

The glow discharge reactor has become fully operational and films are being deposited as a function of hydrogen dilution and substrate temperature in an attempt to develop a reliable means by which to obtain films with low hydrogen content. Also, we expect to use the glow discharge reactor for the fabrication of complex multi-junction solar cells.

In collaboration with the University of Neuchatel low level i-layer doping was used to improve the stabilized red light efficiency of relatively thick amorphous silicon solar cells. Also the collaboration studied the effects of high intensity rapid degradation as a means to obtain the parameters needed to model solar cells for improved end-of-life performance.

In an effort to identify the means to improve the performance of amorphous silicon-germanium solar cells we first sought to better understand the material and the range of parameters that

amorphous silicon-germanium materials could have. Collaborations with the University of Oregon, Penn State University and the University of Rochester examined the alloy materials prepared by photo-CVD. Other measurements and analyses on amorphous silicon germanium films and solar cells continue. A front loaded amorphous silicon germanium solar cell with an efficiency of 6% was made.

The current voltage behavior of some of the amorphous silicon germanium solar cells was analyzed to extract the lumped equivalent circuit parameters needed to represent the devices in a multi-junction configuration for the purpose of modeling designed to enhance the performance of multi-junction solar cells. Only fixed series resistance and shunt conductance terms were needed to represent the current voltage characteristics for this purpose.

Preliminary measurements of the stability of a-SiGe:H solar cells were made. Also, preliminary measurements were made on the effect of test temperature on the efficiency of a-SiGe:H solar cells.

Effort to determine the maximum density of states in amorphous materials as a function temperature and illumination levels continued. Once the maximum density of states is determined for a given materials and condition, solar cell designs aimed at mitigating the deleterious effects of these defects can be developed. Also we expect to use the maximum density of states (for a given illumination intensity and temperature) to compare various materials. Work is continuing on the thermodynamic description of the Staebler-Wronski effect. The description of the high temperature steady behavior has been extended to the normal operating conditions of a solar cell.

We expect to use the parameters determined during this phase of work together with detailed numerical (using the Penn State AMPS model) to design better amorphous silicon germanium solar cells.

C. Conclusions

Thus far the low hydrogen materials prepared to date do not offer greatly improved stability as compared to standard amorphous silicon materials. It is however clear that low hydrogen materials do not have less stability than the standard materials. Low hydrogen amorphous silicon could be useful for some i-layer applications. For example, the triple stacked solar cell could substitute a thinner more degradation resistant lower band gap low hydrogen i-layer in the middle solar cell. The silicon germanium alloys do not appear to be markedly less stable than amorphous silicon.

Several methods of obtaining material parameters from device measurement were reviewed. The measurement of the short wavelength quantum efficiency is confirmed to be sensitive to the density of light induced dangling bonds in the i-layer. However, the primary photo current of p-i-n solar cells is found to be insensitive to bulk dangling bond defects as it does not scale with i-layer thickness.

Solar cells with improved stabilized red light conversion efficiency were prepared by low level i-layer doping to reduce the field distortions caused by the light induced charged dangling bonds. Solar cells with this low level doping scheme will be used in multijunction solar cells for improved stabilized performance during the latter phases of research. The success of the low level i-layer doping experiments have other implications as well. For example, the i-layer Fermi level position in the near interface regions is not solely determining the defect structure as predicted by some theories as light exposure is shown to create further field distortions.

The utility of rapid high intensity degradation was also examined and questioned as high intensity degradation was found to produce defects which unlike defects induced by typical sunlight the high intensity created defects rapidly self anneal in the dark at room temperature.

The self annealing of quickly produced defects is just one example of evidence supporting the thermodynamic equilibrium description of the Staebler-Wronski effect developed during this phase of research. Other supporting evidence is the ability to predict both the illuminated and dark dangling bond concentration as a function of temperature and illumination level. Perhaps the most important prediction of this description is that the dangling bond concentrations will stabilize at a level determined by the temperature and illumination level. The thermodynamic description predicts that at low illumination levels the stabilized defect concentrations will be far less than the number of weak bonds, in contrast a number of other popular defect module predict that defects will form until all weak bonds are consumed.

We found in collaboration with the University of Oregon that the deep level defect concentrations in photo-CVD SiGe materials is not higher than that in degraded silicon. We have also shown that the effects of light induced dangling bonds in amorphous silicon solar cells can be reduced by intentional low level doping of the i-layer as mentioned above. Therefore, a new approach to improved alloy solar cell performance is suggested. That is, the use of low level doping of amorphous silicon-germanium i-layers to intentionally distort the electric field for improved collection efficiency. We have found in collaboration with Penn State University that the $\mu\tau$ of silicon

germanium materials can be nearly as large as that of device quality amorphous silicon. A question remains as to the cause of less than expected solar performance. The performance of these various solar cells is weighed in regard to the improved stabilized efficiency of triple stacked solar cells.

LIST OF CONTRIBUTORS

Wayne A. Buchanan	Photo-CVD Reactor Design Material Preparation, Device Fabrication
TW Fraser Russell	Chemical Reaction Engineering Analysis of Photo-CVD
Sarah Buchanan	Device Measurements
Ronald Dozier	Instrumentation and Measurements
Alissa Eggert	Depositions
Doug Darrell	Instrumentation
Diego Fischer	Device and Materials Analysis
Richard Zielinski	Reactor Analysis and Depositions

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SECTION 1.0

INTRODUCTION

Theoretical studies of multi-junction a-Si:H solar cells project efficiencies greater than 20%. First, this project seeks to determine how material limitations and the current state-of-the-art device design result in demonstrated stabilized efficiencies of less than 10%. Secondly, we will use this understanding of these limitations to find a means to improve the stabilized efficiency of the amorphous silicon solar cells. Clearly multi-junction solar cells offer the greatest potential for increased solar cell performance with acceptable long term stability. However, a number of problems will need be remedied before the multijunction solar cell can achieve its full potential. The research presented here is directed towards the identification and rectification of these problems.

For example, our research indicates that multijunction solar cell stability is apparently controlled by the stability of the middle solar cell which, with present technology, must be made relatively thick to absorb a sufficient quantity of the solar spectrum. It has been reported by a number of groups that the stability of amorphous silicon solar cells decreases with increasing i-layer thickness. Therefore a portion of our research was directed towards finding ways to prepare more stable amorphous silicon solar cells which have relatively thick i-layers. Unique to the multijunction application of these thick i-layer cells is the relaxation of the need for high short wavelength quantum efficiency, since the front cell converts this portion of the solar spectrum. This work explores a number of ways of exploiting the spectral requirements of the middle solar cell to prepare devices with high stabilized efficiency over the spectral range that is important for its intended application.

Problems with the red scavenging solar cell (the third of a triple stack) have also been identified. Due to the need to efficiently convert the near infrared portion of the solar spectrum this solar cell must employ a low band gap alloy. Reports show that researchers have been finding ways to improve the performance of these low band gap alloy solar cells but the performance is still below expectation. The performance of these solar cells is poor enough to limit that of the annealed multijunction solar cell. The alloy solar cell would also limit the stabilized efficiency of multijunction solar cell if more stable second cells were incorporated.

This report covers Phase I research on the development of amorphous silicon based solar cells that have a stabilized efficiency greater than 12%. To establish a basis on which to achieve the goal of 12% stabilized efficiency, it was necessary for some effort to go into the identification of the best

materials as well as the design of single junction solar cells that, in the future phases of this effort, would become component cells of multi-junction solar cells.

During this segment of research our efforts were also directed towards properly identifying and characterizing state-of-the-art a-SiGe:H materials. These efforts sought to obtain a consistent set of inputs for the modeling efforts from the characterization, analysis and measurement of films and devices. Due to the widespread disagreement between reported values for such basic quantities as the density of dangling bonds in a-SiGe:H, it is not possible to assume that reported values are applicable to our materials or, that the defects detected by a given measurement actually affects solar cell performance. In this phase of research we sought to establish a data base of materials characteristics with our own measurements and with measurements made in collaboration with other laboratories.

Our long range goal of stabilized high efficiencies required that two levels of computer modeling be developed in parallel with the materials effort. One level of modeling relates material parameters to single junction solar cell performance (developed in collaboration with D. Fischer who is studying at IEC for one year as part of his Ph.D. thesis work at the University of Neuchatel, Switzerland). The other level relates single junction solar cell parameters to multi-junction solar cell performance using SPICE routines.

Like no other material currently used for photovoltaic energy conversion, amorphous silicon offers a wide range of controllable and repeatable material parameters, on layers ranging from 25Å to over a micron in thickness. This makes possible an almost infinite number of device configurations. For this reason amorphous silicon in addition to being a major photovoltaic contender in its own right, has also become a test vehicle for a number of advanced concepts including the p-i-n solar cell and band gap grading. The present objectives are to develop the most stable materials, understand the underlying nature of the Staebler-Wronski effect in a-Si:H, and also understand the transport phenomena in the Si-Ge alloy system in order to provide the later phases of this project with the materials and design parameters necessary to develop solar cells with greater stabilized efficiency.

It is an integral part of our research program's objectives to examine low hydrogen materials. The examination of low hydrogen materials interlocks with the other objectives as these materials offer three possible ways to enhance the performance and stability of multijunction amorphous silicon based solar cells. First low hydrogen materials may be more stable than standard amorphous materials (thus far we know that high hydrogen materials are certainly less stable than standard materials).

Secondly, we know that hydrogen content and bonding configuration affect the band gap of amorphous materials and that band gap differences can be exploited by multijunction solar cell design to increase the performance. Finally we know that reduced hydrogen content in the silicon-germanium alloys improves the electronic transport.

Reduced hydrogen content may also improve the stability of amorphous silicon materials (this topic is currently being explored at IEC under EPRI funding). Even if low hydrogen amorphous silicon materials do not have increased stability, they still offer a means by which the solar cell could be made more stable. Reducing the hydrogen content (or perhaps just the dihydride content) of an amorphous silicon film results in a smaller band gap which permits the use of a thinner i-layer in the solar cell, thus enhancing its stability. Ultimately these elements of research will be used to make stable amorphous silicon-based solar cells with greater efficiencies.

Of interest to the NREL program is the potential to use the predictions of the modeling of dangling bond to assist in the modeling of solar cells with high stabilized efficiency. To eliminate as much experimental ambiguity as possible, we began our modeling with the high temperature steady-state Staebler-Wronski effect. Working in association with C. Wronski at Penn State University, J.D. Cohen at the University of Oregon and with data reported by T. McMahon at NREL, E. Schiff at University of Syracuse and D. Redfield at Stanford University, a new model based on classical thermodynamics was developed (several of the manuscripts detailing this work are included as an appendix). The sought after prediction of relative material stability results from the extrapolation of the high temperature steady state to solar cell operating conditions (temperature and illumination level). This extrapolation predicts that material grown at higher temperature (typically lower hydrogen contents) will have stabilized defect densities lower than those grown at lower substrate temperatures.

SECTION 2.0

TASK 1 - STABILIZED a-Si:H MATERIALS AND DEVICES

2.1 TESTS FOR MATERIAL STABILITY

Film adhesion problems were encountered with glass substrates during the deposition of low hydrogen materials by photo-CVD. Since the preparation and testing of low hydrogen materials is integral to our research project, other substrates were found. SnO_2 coated glass substrates did not have the adherence problem found on the glass substrates, so we attempted to find alternate tests that could be used in conjunction with these conducting substrates. Therefore, the primary analysis was shifted away from film based measurements to device based measurements.

Previously, we have published a number of manuscripts on the use of device analysis for material and stability characterization (1). During Phase I several of these techniques were reviewed. The use of the primary photocurrent technique to predict device stability was found to be flawed. Solar cells of similar thickness made from two different materials (7 and 11% hydrogen), although producing markedly different stabilities in their efficiencies and fill factors, showed nearly identical response under primary photocurrent analysis. That is, the primary photocurrents at every stage of the degradation did not depend on i-layer hydrogen content. Also, unlike efficiency or fill factor, the primary photocurrent is not a function of i-layer thickness. These considerations were discussed in detail in a paper presented at the 1991 Spring Materials Research Society Meeting held in Anaheim, CA (2).

The change in the short wavelength quantum efficiency (SWQE) was also reviewed. Unlike primary photoconductivity, SWQE appears to track with the relative solar cell conversion efficiency. More recently, the SWQE has been examined by numerical techniques. The preliminary results of the numerical modeling agree with the previous results of the analytical investigation with the change in SWQE scaling with the bulk recombination which, in turn, is proportional (to first order) with the defect density as shown in Figure 1.

In the course of numerical modeling, it was easy to determine the influence of the p/i interface on the stability of the p-i-n solar cell. By examining the change in SWQE as a function of the bulk density of states and the i-layer thickness, it is apparent that, unlike bulk recombination losses, interface losses are more weakly dependent on the dangling bond density as shown in Figure 2.

Figure 1. The effect of i-layer thickness and dangling bond densities on the short wavelength quantum efficiency @ 450 nm.

Figure 2. The effect of i-layer thickness, dangling bond densities, and interfacial recombination rate, on the short wavelength quantum efficiency @ 450 nm.

2.2 STABILITY OF SCHOTTKY BARRIER DEVICES

The conductive SnO_2 glass substrates precluded photoconductivity measurement, however it was possible to use SnO_2 as a back contact when a Schottky barrier was formed at the front surface. In a collaborative effort with C.R. Wronski at Penn State University, Schottky barrier devices were made by putting Ni on our materials. These devices were measured as a function of deposition conditions. The deposition conditions used for the film preparation are shown in Table 1. Samples which were co-deposited with those sent to Penn State were also sent to Charles Evans East for a determination of hydrogen content. The results of this study are shown in Table 2. The stability of Schottky barrier devices by light attenuated photo-CVD appears to be better than average as judged by the change in SWQE. The hydrogen content as measured by SIMS at Charles Evans East for these materials is somewhat scattered. In one case the hydrogen content of the light attenuated material is only 1 to 2%, while in several other cases the value is close to that of our standard material (~7%). While there appears to be some differences in the deposition conditions of the films that measured at higher hydrogen content as indicated in Table 2, it is not clear whether the hydrogen content of the films is sensitive to substrate cleaning and reactor pressures or the SIMS measurement was in error. During the next phase of research higher substrate temperatures will be used in an attempt to reduce the hydrogen content.

The relative stability of the Schottky barrier devices can also be inferred from the change in SWQE (Table 3). Based on the measurements of the Penn State group, it appears that both 3492 and #3497 appear to have better stability than the standard materials typically measured at Penn State (standard materials provided by manufacturers) even though our reference device (#3491) appears to also exhibit similarly good stability. The apparent stability of the our reference material could result from the short wavelength quantum efficiency sensitivity to sample thickness, as this standard sample turned out to be thinner than expected. The i-layer of #3492 employed light attenuation, low pressure, and He dilution to reduce the possibility of gas phase polymerization (suspected of increasing the hydrogen content). Mercury annealing was used to attempt a reduction in hydrogen content in #3497.

2.3 GROWTH OF LOW HYDROGEN AMORPHOUS SILICON BY PHOTO-CVD

In Phase I, we attempted to grow films with deposition conditions that would reduce the hydrogen content of the a-Si:H. These experiments employed the photo-CVD reactor and used techniques which do not require high substrate temperatures in order to reduce the possibility of solar cell processing problems. One photo-CVD process used light attenuation and helium dilution.

Table 1

Growth conditions of low hydrogen photo-CVD films

--Gas Flow Rate--
(sccm)

Sample #	Comments	Cycle time (min.)	# of cycles	T _{dep} (°C)	Press. (torr)	SiH ₄	He	H
3482	72% light attenuated	-	-	-	-	-	-	-
3491	standard	335	1	205	5	2.0	8.0	0
3492	72% light attenuated	375	1	230	1	2.8	2.0	0
3493	standard	-	-	-	-	-	-	-
∞ 3494	72% light attenuated	-	-	-	-	-	-	-
3496*	1 min growth 2 min anneal	3	78	205	5	2.0	8.0	0
3497	1 min growth 5 min anneal	6	51	205	5	2.0	8.0	0
3505	2 min growth 0.5 min H etch	2.5	20	230	2	2.2	0	20
PB55	Solarex glow discharge	-	-	-	-	-	-	-

* pressure increased to 3 torr during run

Table 2

Thickness and SIMS analysis of low hydrogen photo-CVD films

Sample	d	Concentration ($\times 10^{21} \text{cm}^{-3}$)		
		H	O	C
3482	-	3.0	0.03	0.015 (more O and C at back)
3491	0.60	2.5	0.03	0.005
3492	0.37	1.0	0.009	0.007
3493	-	2.6	0.017	0.005
3494	-	2.2	0.02	0.005
3496	0.55	3.0	0.02	0.005
3497	0.37	3.0	0.05	0.010
3505	0.20	2-3	0.2-0.3	0.05
PB55	-	4.0	0.009	0.010

Table 3

SWQE stability measurements of low hydrogen photo-CVD films

Sample #	QE @ 450 nm	
	Annealed	Degraded (64 hrs. @ AM1.5)
3482	-	-
3491	0.34	0.30
3492	0.46	0.39
3493	-	-
3494	-	-
3496	0.55	0.38
3497	0.40	0.35
3505	-	-
PB55	-	-

This was to reduce the probability of gas phase polymerization which could be one of the major sources of film hydrogen. In another photo-CVD growth process the surface was periodically (approximately every 20 angstroms) exposed to energetic Hg atoms in an attempt to scrub hydrogen atoms from the surface, thereby reducing the film hydrogen content.

Unfortunately, the films grown by these techniques tend to peel and flake from most substrates. These films peeled from both glass and single crystal silicon substrates, thus making standard photoconductivity and IR analysis impossible. Table 2 shows the results of the SIMS study of photo-CVD materials deposited under these conditions.

Several of the results are encouraging. The photo-CVD materials appear to have hydrogen contents lower than the industrial standard provided to us from Solarex. Also, the impurity contents are comparable to the industrial standard. However, our attempts to lower the hydrogen content by light attenuation and Hg annealing seem to have failed with the possible exception of sample #3492 for which the SIMS measurement indicates a low hydrogen content (this value is consistent with a concentration of ~2-3%). This sample also showed relatively good stability. However, sample #3494 grown under similar conditions to #3492 had a larger hydrogen concentration. There are several possible explanations for this including a rise in chamber pressure during the deposition of #3494. Also, the accuracy of the SIMS technique could be questioned. More samples will be grown to answer these questions. We have also increased efforts to drastically reduce hydrogen content by using high deposition temperatures.

2.4 FILMS GROWN BY GLOW DISCHARGE

During this phase of our research our glow discharge reactor became fully operationable. To confirm the material quality of the glow discharge reactor, several solar cells were prepared. Even though doped and buffer layer recipes were not optimized, a solar cell of 8% efficiency was prepared after only three attempts. No further solar cell work was conducted in the glow discharge reactor during this phase of research.

During this phase of the research, work was also begun on low hydrogen materials prepared by the glow discharge reactor where, in addition to growth temperature, the hydrogen content was modified by hydrogen dilution. Since the parameter space for glow discharge deposition is rather large, the onset of microcrystalline growth was used to establish the condition of "high" hydrogen surface flux during growth.

Compared to the photo-CVD deposition system, the chemistry of glow discharge deposition is less well understood. While the deposition and etching species in the glow discharge system are related to the composition and structure of the growing film as they are in photo-CVD, it is not possible to rely on a mathematical model to predict the fluxes of these species. In glow discharge deposition we are presently limited to experimental data from which relative fluxes can be inferred. For example, from our photo-CVD work we know that the onset of microcrystalline growth begins when the hydrogen radical flux is comparable to the silicon radical flux. Therefore, one of the deposition conditions that was of particular importance was the growth conditions for microcrystalline films since this can be used to establish that a significant hydrogen radical flux rate is present during deposition.

Films were deposited in the glow discharge reactor as a function of hydrogen dilution. The range of deposition parameters was chosen to be large enough to include the deposition of amorphous and microcrystalline films. This work is of interest to our EPRI funded project and an unfunded collaboration with Mobil Solar Co. as well. The absorption coefficient versus wavelength for a number of films is shown in Figure 3. It is interesting to note that some of the doped microcrystalline films absorb light as strongly as amorphous films (a fact that may reduce the utility of microcrystalline films in multi-junction tunnel junctions). Shown in Figure 4 is an X-ray diffraction scan of a microcrystalline film where the sharp peak indicates a crystalline structure. Materials with smaller band gap and lower hydrogen content are expected to be prepared in the coming months as we move to higher substrate temperatures.

At present there is insufficient evidence to suggest that any of the materials grown to date offers a significantly improved stability or prospect of improved stabilized performance when incorporated into conventional solar cell designs (band gap differences could however permit the design of new solar cells which have greater stabilized efficiency). Attempts to grow and test lower hydrogen materials will continue in the next year (with a portion of the effort being carried out under our EPRI funding).

During the latter part of this phase of research, extensive work to computer control the glow discharge reactor was initiated. The computer control should enable us to prepare complex multi-junction solar cells. We expect computer control to be ready during Phase II of this research project.

Figure 3. The absorption coefficient versus wavelengths for a number of films grown by RF glow discharge.

4020/4021

Figure 4. The X-ray scan of a microcrystalline film grown by RF glow discharge.

2.5 THERMODYNAMIC DESCRIPTION OF THE STAEBLER-WRONSKI EFFECT

The thermodynamic description of the Staebler-Wronski effect continues to be developed. Although a negative change in entropy results from the application of thermodynamic equilibrium, it would be unreasonable to attribute such entropic changes to electronic transitions alone since the magnitude is closer to values involved with phase change. Since the thermodynamic description does not a-priori attribute the energetic changes to electronic levels either, it is also reasonable to assume that some of the free energy changes of dangling bond formation are related to lattice relaxations. In this view the loss in energy and the loss in entropy are those of the lattice moving towards a more ordered 'crystalline-like state'.

We are working with J. D. Cohen at the University of Oregon to elucidate the partition between lattice relaxation and electronic transition energies. We plan to present the results of this work at the Spring 1992 Materials Research Society Meeting in San Francisco, CA.

One practical result of this work is the establishment of a theoretical framework which supports the observation that solar cell efficiencies tend to stabilize during field testing. This behavior is expected if one assumes that the equilibrium behavior observed at high temperatures can also be applied to these solar cells at their operating temperatures and illumination level. That is unlike other Staebler-Wronski descriptions the thermodynamic description predicts that a saturation of the dangling bond defects concentrations occur at levels below the total weak bond densities. The saturation level is expected to be a function of the illumination intensity and the operating temperature. The expected saturated defect concentration is important for the comparison of various materials and to obtain parameters for modeling designed to improve the stabilized solar efficiency.

In terms of the thermodynamic description the saturated defect concentration are determined by the extrapolation of the high temperature steady-state behavior to the illumination levels (100 mW/cm²) and temperature (20 to 40°C) expected in an operating of a solar cell. Figure 5 shows the dangling bond density as a function of temperature for non-illuminated films (4). Figure 6 shows the steady-state dangling bond density of films under illumination. By extrapolating to lower temperatures we can see that at the intensity levels found in an operating solar cell, the materials shown in Figure 5 would be expected to have an equilibrium defect density of $\sim 1 \times 10^{17} \text{ cm}^{-3}$. While the data shown in Figures 5 and 6 is from the literature, we have undertaken our own study to confirm these reports. In a collaborative study carried out at Penn State University (4), the defect density was determined by the temperature and intensity dependence of the

Figure 5. The dangling bond density as a function of $1/T$ for a number of different non-illuminated films as reported in reference 3.

Figure 6. The dangling bond density as a function of light intensity as a function of $1/T$ for illuminated samples as reported in reference 3.

steady-state degraded photo conductivity (note photo conductivity is sensitive to the positively charged dangling bond density). Essentially similar results to the literature were found as shown in Figure 7. The degradation of films at high temperature as they approach the steady-state condition is shown in Figure 8.

We believe that it is likely that the thermodynamic description will permit us to establish the maximum number of dangling bonds that would result from a given light flux. These values would then be used as inputs to our modeling efforts aimed at improved stabilized efficiency.

2.6 COMPARISON OF FAST AND SLOW DEGRADATION

Accelerated light soaking has been investigated by a number of groups. In order to determine if we could use accelerated degradation, a collaboration with the University of Neuchatel was undertaken to compare fast (accelerated) light soaking at high light intensities (50 suns) and the more standard (slow) degradation that occurs at illumination levels closer to those that an operating solar cell would encounter.

The collaboration also examined the effect of the reversal of the degradation in the dark initially noted by the University of Neuchatel. The literature has also reported but does not explain the reduction of defect concentrations under low current injection in the dark. The collaborative effort (to be reported in detail at the Spring 1992 MRS meeting) shows that the reduction of defect concentrations only occurs as a result of fast degradation.

It is important to note that the fill factor is a poor measure of defect densities in general since the exact form of mathematical expression is not known and the relationship is generally determined numerically. However, the fill factor (or efficiency) can be used to establish the rate of change of defect densities if precautions are taken. To establish the rate of change of defects concentrations it is only necessary to assume that the relationship between the defect density and the fill factor is one-to-one and monotonic. Because of the complex relationship between dangling bonds and fill factor one must always take the precaution of choosing a constant value of the fill factor at which to measure the rates of change (with this precaution it becomes unnecessary to know the relationship between dangling bond concentrations and fill factor).

$$d(\text{fill factor})/dt = (d(\text{fill factor})/dN_{DB}) * (dN_{DB}/dt) \quad (1)$$

If one compares solar cells of approximately the same configuration (i-layer thickness, deposition conditions, etc.) where care is taken to compare solar cells of the same fill

Figure 7. The steady-state photoconductivity as a function of $1/T$.

Figure 8. The photoconductivity as a function of light exposure time at various temperatures.

factor (or efficiency), the first derivative on the right hand side of equation 1 is constant and, therefore, the changes that occur in fill factor are approximately proportional to the rate of change of defect densities. Figure 9 shows the fill factor as a function of time for two samples (grown in the same system at the time with essentially identical i-layer thicknesses). The fill factor is clearly changing (improving) in the dark at room temperature after the illumination has ceased. One sample was light soaked for 2000 hours at approximately one sun illumination. This cell showed a negligible fill factor relaxation rate (improvement). In contrast a cell which was brought quickly to the same degraded state by high intensity laser light showed a marked increase in relaxation rate as the fill factor markedly improved in the dark after the illumination was turned off. Since both samples were degraded to approximately the same fill factor (the first term on the right hand side of equation 1 is the same for the two cases) we are justified in assuming the rates of recovery are directly proportional to the differences in the rates at which dangling bond defects are eliminated by relaxation in the two samples.

Because of the difference between quickly degraded and slowly degraded fill factor relaxation rates (and hence the defect density relaxation rate), it is not possible to view fast and standard degradation as equivalent. Since the behavior of Neuchatel and IEC samples is similar, this is probably representative of amorphous materials. If an extrapolation is made to other accelerated degradation techniques, a dark reduction of defect densities would be expected. This could explain most relaxation phenomena including the reduction of defect densities due to high density current injection (5,6).

We are presently examining the concept that, unlike standard degradation, the accelerated degradation does not allow sufficient time for the lattice relaxation as suggested by the thermodynamic description. A failure of the lattice to fully relax would permit a larger than equilibrium concentration of defects to be formed, since, the formation of defects is driven by energetics involving lattice relaxation.

cell C060891

Figure 9. Fill factor vs. dark exposure time after high and low intensity light-soaking.

SECTION 3.0

TASK 2 - a-SiGe:H MATERIALS AND DEVICES

As in Task 1 our efforts during this phase of the project focused on materials and characterization on which future devices will be based.

3.1 HOT ELECTRON TRANSPORT

In collaboration with P.M. Fauchet at the University of Rochester, the picosecond carrier dynamics of the alloys prepared by photo-CVD have been investigated. In these experiments a high intensity laser is used to produce a large density of free carriers. The decay of this energetic carrier density is probed by a second beam which is attenuated by free carrier absorption.

It was also found that the electron thermalization time in a-SiGe:H is approximately the same lifetime as in a-Si:H. It is of considerable interest that the electron could be collected or recombine prior to thermalization in thin alloy solar cells. While these results are as yet somewhat controversial they do warrant some consideration. The possibility that the recombination lifetime in these materials is even shorter than the time it takes for a carrier to thermalize within its band may offer a new insight into amorphous silicon-germanium solar cell performance. Our detailed modeling of a-SiGe:H solar cells will attempt to take these considerations into account.

3.2 SOLAR CELL PERFORMANCE

To test our ability to prepare abruptly graded solar cells, a front loaded a-SiGe:H solar cell was prepared using designs previously shown to yield good performance. A 400Å thick a-SiGe:H layer was used in an i-layer which had a total thickness of 1000Å. Abrupt transitions were used between the a-Si:H regions (150Å p/i interface buffer and the back 450Å of the i-layer) and the a-SiGe:H i-layer regions. Even with these abrupt transitions the performance of this solar cell was satisfactory with an efficiency of 6.0% ($V_{oc}=0.605V$, $J_{sc}=16.8 \text{ mA/cm}^2$, fill factor=58.5).

In order to determine where future efforts should be placed, the stability of the thin amorphous silicon-germanium alloy solar cells was checked. The limited stability investigation of the alloy solar cells was to determine if more effort should be placed on the stability of the alloy cells at this time. Ultimately the stability of the multijunction solar cell will be determined by the stabilities of its component cells. Several thin (1000 Å) solar cells were degraded under one sun

illumination. After 100 hours the solar cell efficiency degraded by 10 to 15%. These values are much smaller than the amount that a thick amorphous silicon solar cell would degrade under these conditions. However, due to the small sample size of our study it can not be concluded that the alloy cells degrade faster or slower than amorphous silicon solar cells of the same i-layer thickness. Presently, the stability of the alloy solar cell is not expected to limit the stability of the multijunction solar cell (as new alloy solar cell designs and materials are developed stability tests will be made).

3.3 ALLOY FILM OPTICAL AND ELECTRICAL ANALYSIS

Because numerical modeling can decrease the time needed to prepare efficient red light scavenging a-SiGe:H solar cells, little effort was spent on solar cell fabrication. Instead a number of films were grown for detailed analysis which would then provide independent inputs to our numerical model. A series of a-SiGe:H films ($E_g=1.3$ eV) with varying thicknesses was prepared for analysis at Penn State (in collaboration with C. Wronski). Film thicknesses ranged from 200Å to approximately 1 micron. These films were analyzed at Penn State University. The optical absorption versus wavelength is shown in Figure 10.

It is important to note that the logarithmic intensity dependence of the photoconductivity of the alloy films tends to be significantly higher than that of standard amorphous silicon. For example, the photoconductive gamma ($\sigma=\sigma^0\gamma$) of the alloy can be less than 0.6 (see Figure 11) while that of a-Si is much closer to unity (0.8 to 0.95). As a result of these small gammas, the $\mu\tau$ values will also depend on the light intensity as seen in data of Table 4. For this reason, care must be taken in extrapolating the values of electron transport parameters measured at one light intensity to another when modeling solar cells. Since electron $\mu\tau$ for the alloy materials is intensity dependent, one must first consider the illumination levels (or quasi-Fermi level splitting) the solar cell is to be optimized for.

3.4 STABILITY OF a-SiGe:H FILMS AND DEVICES

In an effort to insure that the alloy based red scavenging solar cell of the triple stacked solar cell does not itself represent a potential source of degradation, several a-SiGe:H solar cells and films were prepared for stability analysis.

The photoconductivity was used to establish the $\mu\tau$. Surprisingly, the $\mu\tau$ of this alloy at low intensities is almost as large as that of high quality amorphous silicon ($\sim 1 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1}$). The sub bandgap absorption was also determined

Figure 10. The optical absorption of an a-SiGe:H film with a band gap of 1.3 eV.

Figure 11. The photoconductivity of an alloy film with band gap of 1.3 eV as a function of intensity (near uniformly absorbed light).

Table 4
Electrical parameters of two alloy films
as a function of light intensity

Sample#	E_g (eV)	d (μm)	G (cm^{-3}/s)	σ_p (ohm-cm) $^{-1}$	$E_c - E_{fn}$ (eV)	$\mu\tau$ ($\text{cm}^2/\text{V-s}$)
3533	1.3	0.32	2.65E19	6.05E-6	0.482	1.42E-6
			2.65E18	2.04E-6	0.511	4.81E-6
			3.07E17	7.23E-7	0.537	1.47E-5
			3.57E16	2.77E-7	0.562	4.84E-5
			5.29E15	1.12E-7	0.585	1.32E-4
3534	1.3	0.60	2.38E19	8.15E-7	0.534	2.14E-7
			2.38E18	1.89E-7	0.572	4.95E-7
			2.76E17	5.31E-8	0.605	1.20E-6
			2.88E16	1.43E-8	0.638	3.10E-6
			3.34E15	4.05e-9	0.671	7.58e-6

from the photoconductivity using dual beam illumination. The sub bandgap absorption of the 1.3 eV band gap alloy tested was particularly low for an alloy material (which is consistent with the large $\mu\tau$). After 100 hours of light soaking with a uniformly absorbed illumination at $\sim 100 \text{ mW}/\text{cm}^2$, the sub bandgap absorption showed very little change. This amount of change in sub bandgap absorption is less than one would expect from a typical device grade amorphous silicon material.

3.5 CHARGE RELEASE ANALYSIS OF ALLOY FILMS

In collaboration with J. D. Cohen at the University of Oregon, a-SiGe:H materials were investigated using charge release techniques. Thus far we have found that the Urbach energy for our alloy with a band gap of 1.3 eV grown by photo-CVD is similar to that of high quality a-Si:H ($\sim 50 \text{ meV}$). The midgap density of states was found to be $\sim 2 \times 10^{16} \text{ cm}^{-3}$ which is amongst the lowest reported for an alloy of such a low band gap. Also an alloy with a band gap of $\sim 1.45 \text{ eV}$ has been measured and found to have a midgap density of states of $\sim 8 \times 10^{15} \text{ cm}^{-3}$. ESR measurements done at the University of Oregon on a sample of our standard 1.3 eV alloy that we had originally grown last year for analysis at the University of Utah (C. Taylor), shows an extremely low neutral dangling bond density (those that can be seen by ESR) for an alloy material (total defect density of $\sim 1 \times 10^{16} \text{ cm}^{-3}$). We expect to fully report these results in a joint paper to be presented at the Spring 1992 Materials Research Society Meeting. While low values are encouraging, we believe the real value of these numbers are as inputs to the detailed models that we will use to guide device design.

As outlined in reference (7), it is possible to use charge release methods to obtain information on hole transport. In this paper we reported that the hole $\mu\tau$ in the alloy films studied is approximately 30% of the electron value. Since we know the electron $\mu\tau$ from conductivity measurements, we conclude that the hole $\mu\tau$ is relatively unaffected by Ge alloying. This confirms our earlier work which arrived at a similar conclusion based on solar cell measurements.

Samples of a-SiGe:H alloys with band gaps between a-Si:H and our standard 1.3 eV band gap alloy were prepared. Many of these samples with intermediate band gaps were thinner than ideal. In some cases useful measurements were made by creating light induced defects to shorten the depletion regions. Results of this study will be reported as they become available.

3.6 NUMERICAL MODELING OF ALLOY SOLAR CELLS

D. Fischer began to numerically model the effect of a mobility gradient on solar cell performance. Select cases were compared to those of the Penn State AMPS model. It should be emphasized that the output of these numerical models is highly sensitive to the input parameters. For the input parameters chosen, both ours and the Penn State model show that a poor mobility material in the front of a graded band gap p-i-n solar cell would result in a high electron concentration in the back of the device (see Figure 12). In principle, this large electron concentration would result in enhanced recombination losses if the electron lifetime was equal to or less than its value in amorphous silicon. We expect to model the electron mobility in a self consistent way. A parallel effort to develop a multi-junction solar cell model based on the parameterization of single junction solar cell behavior is described below.

3.7 MODELS FOR MULTI-JUNCTION SOLAR CELL OPTIMIZATION

The current-voltage behavior of several a-SiGe:H and a-Si:H solar cells with different grading schemes has been measured. The study includes various illumination intensities and spectra. The data was analyzed to obtain lumped diode parameters for use with SPICE software which in turn would use these parameters to determine their performance as part of a multi-junction solar cell.

During this stage of research a number of alloy and standard a-Si:H (#3396) solar cells were measured. The testing included two alloy solar cells, one (#3380) with smooth grading between a-SiGe:H (1.3 eV band gap) and, the other (#3520) with abrupt grading between layers of various band gaps. Descriptions of these grading schemes is detailed elsewhere (1). Testing

Figure 12. The effect of mobility gradient on the carrier density of a uniform band gap p-i-n solar cell.

included J-V measurements at 25°C with the voltage ranging from -0.2 to 1V. Illumination levels included dark, AM 1.5 @ ~ 100 mW/cm² with ELH lamp and red filtered ELH illumination (to approximate illumination levels found in the second p-i-n of a multi-junction solar cell).

The illuminated diode behavior was assumed to have a constant light generated current (J_L). With the addition of a shunt-like term (GV) to improve the fit, the following is obtained:

$$J_m(V) + J_L - GV = J_0 \exp(BV) \quad (2)$$

where $J_m(V)$ is the measured current and J_L was taken as either $J_{sc} = J(V=0)$ or $J(V=-0.2)$. The value of G was varied to obtain the best fit. The temperature dependence was not explicitly investigated, therefore B was equated to q/kT for the temperatures studied (since SPICE inputs require that a value of A be defined).

The results are given in Table 5 and Figure 13 and 14. There are some differences between solar cells on a given substrate. These differences are largely related to the values of G. The best fit value for G is strongly coupled to the choice of J_L . The best fit value of A in the dark is 1.9 to 2.0 while under illumination a good fit is obtained with values ranging from 3.0 to 5.0. Since G and J_0 are also much smaller in the dark, the dark diode does not contribute significantly to the illuminated current in the power quadrant. A, G and J_0 appear to be intensity dependent but not spectrally dependent on the samples studied (spectral dependencies are apparent on other devices). Therefore, values under solar spectrum or red light illumination were approximately the same. It was not necessary to include a series resistance like term to explain the behavior of these cells in the power quadrant.

Next J-V curves were generated by the SPICE software using A, J_0 , G and J_L as inputs. Figures 15 and 16 compare the SPICE diode model to the measured values of #3396 and #3520. Next SPICE modeling will be used to predict the performance of solar cells when they are operated in a tandem.

Table 5
Results of fitting illuminated J(V) data to $J_0 \exp(BV)$

Sample #	i-layer	J_L (mA/cm ²)	G (MS/cm ²)	J_0 (mA/cm ²)	A
3396	a-Si:H	9.0	1.6	3.5E-4	3.2
3380	graded a-SiGe:H	4.0	1.0	7.0E-3	4.4
3394	a-SiGe:H	4.0	0.5	1.6E-1	5.5
3520	graded a-SiGe:H	17.0	1.0	9.0E-2	4.4
		9.0	2.1	1.6E-2	3.6

Figure 13. $J(V)$ corrected for J_L and fixed shunt for an a-Si:H solar cell (#3396) under ELH illumination ($J_{sc} = 9 \text{ mA/cm}^2$).

Figure 14. Measured and calculated (SPICE) data for an a-SiGe:H solar cell (#3520). Shown are the input parameters in mA/cm², S/cm², and ohm/cm² respectively.

Figure 15. Measured and calculated (SPICE) $J(V)$ data for an a-Si:H solar cell (#3396).

Figure 16. Measured and calculated (SPICE) $J(V)$ data for an a-Si:H solar cell (#3520).

SECTION 4.0

CONCLUSIONS

Thus far the low hydrogen materials prepared to date do not offer greatly improved stability as compared to standard amorphous silicon materials. A problem with film flaking became apparent as the hydrogen content was reduced. Since, film flaking was less of a problem on conductive substrates, low hydrogen materials could be incorporated into device structures. The use of device structures however required us to reconsider the analysis techniques by which material parameters are obtained from device characteristics.

During Phase I several of these techniques were reviewed. The use of the primary photocurrent technique to predict device stability was found to be flawed. Solar cells of similar thickness made from two different materials (7 and 11% hydrogen), although producing markedly different stabilities in their efficiencies and fill factors, showed nearly identical response under primary photocurrent analysis. That is, the primary photocurrents at every stage of the degradation did not depend on i-layer hydrogen content. Also, unlike efficiency or fill factor, the primary photocurrent is not a function of i-layer thickness. These considerations were discussed in detail in a paper presented at the 1991 Spring Materials Research Society Meeting held in Anaheim, CA (2). Unlike the primary photocurrent the measurement of the short wavelength quantum efficiency is confirmed to be sensitive to the density of light induced dangling bonds in the i-layer.

It is however clear that low hydrogen materials do not have less stability than the standard materials. Low hydrogen amorphous silicon could be useful for some i-layer applications. For example, the triple stacked solar cell could substitute a thinner more degradation resistant lower band gap low hydrogen i-layer in the middle solar cell. The silicon germanium alloys do not appear to be markedly less stable than amorphous silicon.

In collaboration with the University of Neuchatel solar cells with improved stabilized red light conversion efficiency were prepared by low level i-layer doping to reduce the field distortions caused by the light induced charged dangling bonds. Solar cells with this low level doping scheme will be used in multijunction solar cells for improved stabilized performance in the latter phases of research. The success of the low level i-layer doping experiments has other implications as well. For example, the i-layer fermi level position in the near interface regions is not solely determining the defect structure as predicted by some theories because the light exposure is shown to create further field distortions.

Also in collaboration with the University of Neuchatel the utility of rapid high intensity degradation was also examined and questioned. High intensity degradation was found to produce defects which (unlike standard light induced defects created over long times by one sun illumination) rapidly self anneal in the dark at room temperature.

The self annealing of quickly produced defects is just one example of evidence supporting the thermodynamic equilibrium description of the Staebler-Wronski effect (developed during this phase of research). Other supporting evidence is the ability to predict the both the illuminated and dark dangling bond concentration as a function of temperature and illumination level. Perhaps the most important prediction of this description is that the dangling bond concentrations will stabilize at a level determined by the temperature and illumination level. The thermodynamic description predicts that at low illumination levels the stabilized defect concentrations will be far less than the number of weak bonds, in contrast a number of other popular defect module predict that defects will form until all weak bonds are consumed.

We found in collaboration with the University of Oregon that the deep level defect concentrations in photo-CVD materials is not higher then that in degraded silicon. We have also shown that the effects of light induced dangling bonds in amorphous silicon solar cells can be reduced by intentional low level doping of the i-layer as mentioned above. Therefore, a new approach to improved alloy solar cell performance is suggested. That is, the use of low level doping of amorphous silicon-germanium i-layers to intentionally distort the electric field for improved collection efficiency. We have found in collaboration with Penn State University that the $\mu\tau$ of silicon germanium materials can be nearly as large as that of device quality amorphous silicon. A question remains as to the cause of less than expected solar performance. The performance of these various solar cells is weighed in regard to the improved stabilized efficiency of triple stacked solar cells.

The work and collaborations described above spanning film characterization, solar cell modeling and testing provide us with the opportunity to comment on the range of materials that are possible within a given band gap range and also on the utility of specific measurements which are used to identify parameters that relate to solar cell performance. In a number of ways this stage of the alloy work mirrors the EPRI SMART effort to relate hydrogen content to amorphous silicon stability. But, first the measurements must be evaluated and differences reconciled before it will become possible to see the real differences between materials as a function of composition and/or deposition technique. After the better materials are identified, it then becomes possible to select the material most suitable for solar

cell application. Thus far, the photo-CVD alloy materials appear to be substantially better than any reported in the literature having similar band gaps.

The triple stacked solar cell offers a means by which to circumvent material stability problems through device design. As stated above our goal in the Phase I research is to identify the material that will assist us in our pursuit of high stabilized efficiency. In the later phases of this research we will be using these materials in concert with our device design optimization to obtain the best performing solar cells.

In work that was initiated at Neuchatel and continued at IEC through the efforts of D. Fischer, the improvement in the stabilized efficiency of the middle cell through low level doping of the i-layer was studied. In a joint paper to be presented at the Spring 1992 MRS Conference, we will report the success of low level phosphorus doping of the latter portion of the i-layer. Low level phosphorus doping was found to selectively improve the stabilized spectral response of relatively thick p-i-n amorphous silicon solar cells in the portion of the solar spectrum which must be converted in the second cell.

It is important to point out that although we can present a set of consistent measurements that all suggest a low defect density in our alloy materials we are also aware of reports that disagree with our findings. We are only just beginning to understand the origins of these differences. In some cases the various measurement techniques reveal different aspects of the material that may not be observable in solar cells. In other cases, the differences are due to the differences in materials (we previously showed a wide range of parameters for a given alloy band gap which depends on a number of factors, including the hydrogen content). Finally, it is possible that some experimental techniques are flawed. As was done for the primary photocurrent case cited above, techniques and materials will be reviewed as necessary.

SECTION 5.0

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APPENDIX A

"Charge-Defect Equilibrium Description of the
Staebler-Wronski Defect Concentration
and Formation Energy"

CHARGE-DEFECT EQUILIBRIUM DESCRIPTION OF THE STAEBLER-WRONSKI DEFECT CONCENTRATION AND FORMATION ENERGY

C.M. FORTMANN*, R. M. DAWSON** AND C.R. WRONSKI**

*Institute of Energy Conversion, University of Delaware, Newark, Delaware
19716 USA

** Dept. of Electrical Engineering, Pennsylvania State University,
University Park, PA 16802 USA

ABSTRACT

An equilibrium framework for the high temperature behavior of dangling bond defects in amorphous materials is developed. With this framework it is possible to relate the thermal formation of defects directly with those created by high temperature illumination or current injection. It is found that the free energy change associated with dangling bond formation is negative. The negative free energy change means that if one considered only the structural changes, the lowest energy state for the system is with the weak bonds split into neutral and charged dangling bonds!

INTRODUCTION

Most attempts to explain the phenomena by which illumination creates dangling bonds are cast in a kinetic framework. The kinetic framework provides for the rate at which photon absorption creates dangling bonds and the inverse process whereby thermal energy restores the lattice to its annealed state [1,2]. Each of the several kinetic descriptions can provide relationships that describe the time evolution of defect concentrations due to illumination. However, the authors of [1] recognize some difficulty in interpreting the smaller than expected activation energies for the high temperature steady state defect densities due to illumination.

This work will explore an alternate framework wherein the high temperature ($T > 150^\circ\text{C}$) defect concentrations are considered to be the result of a true thermodynamic equilibrium. While equilibrium considerations have been previously presented [3,4,5], it is the intent of this work to develop a quantitative and predictive equilibrium framework for the high temperature steady state defect behavior. Furthermore, even though equilibrium in principle implies a balance of rates, a kinetic approach that does not include temperature dependant rate coefficients can not explain an arbitrary set of reaction conditions both near and far from thermodynamic equilibrium.

Little background exists in the a-Si:H related literature on the use of equilibrium thermodynamics applied to high temperature defect densities. However, equilibrium defect chemistry in other semiconductor systems has been well studied. For example, the interested reader will find the cadmium telluride (CdTe) defect chemistry [6,7] helpful. In CdTe the room temperature resistivity is determined by its annealing history including the annealing temperature and Cd partial pressure. These dependencies were elegantly explained in terms of charged defect equilibria. These investigation can also provide a guide for the development of arguments here. In the CdTe studies the charge density was varied by dopant impurities and the charge density was determined by in-situ resistivity measurement. The temperature, and the partial pressure of Cd present were also determined. This work will attempt to identify and quantify the relations between species responsible for light induced degradation in a-Si:H.

DISCUSSION

The thermodynamic equilibrium framework requires a set of equilibrium relations. To develop such a set of relations knowledge of the Staebler-Wronski defect will need be invoked. From electron spin resonance (ESR) analysis this defect has been identified as a dangling bond (DB). The most intuitively appealing creation mechanism requires that two DB be created upon the rupture of a susceptible silicon bond site or weak bond (WB). The DB can have three possible charge states, neutral (DB^0) when occupied by one electron, negative (DB^-) when occupied by two electrons and positive (DB^+) when occupied by no electrons. The DB density increases due to illumination [1], current injection [8] and temperature [9]. With considerable hindsight a set of equilibrium expressions and the associated mass action relationships can be proposed.

$$WB + e \rightleftharpoons DB^- + DB^0, \Delta G_1 : [DB^0][DB^-]/([WB][e]) = K_1 \quad (1)$$

$$WB + p \rightleftharpoons DB^+ + DB^0, \Delta G_2 : [DB^+][DB^0]/([WB][p]) = K_2 \quad (2)$$

$$DB^0 + e \rightleftharpoons DB^- \quad (3a)$$

$$DB^0 + h \rightleftharpoons DB^+ \quad (3b)$$

$$DB^- + DB^+ \rightleftharpoons 2DB^0, \Delta G_3 : [DB^0]^2/([DB^-][DB^+]) = K_3 \quad (3c)$$

$$e + p + 2WB \rightleftharpoons 2DB^0 + 2D^{\pm}/-, \Delta G_1 + \Delta G_2 : [DB^0]^2[DB^+][DB^-]/([e][p][WB]^2) = K_1 K_2 = K_4 \quad (4)$$

$$[e] \cdot [p] = N_V N_C \exp(-E_g/kT) \quad (5)$$

Equations 1 and 2 represent a means of obtaining DB's in pairs as a result of charge due to illumination, temperature or current injection. Equation 3 allows for the possibility for interaction among charged DB. Equation 4 is the summation of equations 1, and 2. Each K is an equilibrium constant which is related to the corresponding free energy change, ΔG , by $K = \exp(-\Delta G/kT) = \exp(-E/kT) \cdot \exp(\Delta S/k)$ where E is the change in internal energy and ΔS is the change in entropy upon creation of a DB. Equation 5 is the mass action relation for holes and electrons. Now the various unknowns are determined through appeal to experimentation.

Unfortunately due to the complex manner in which dopant atoms interact with the amorphous silicon network [3] it is not possible to vary the charge density by impurities. Therefore we are forced to consider external means of controlling charge density. In this work illumination (of films and p-i-n devices) and current injection (of devices) were used. Some caution must be exercised as the use of external energy sources may or may not negate a thermodynamic equilibrium argument.

This work will attempt to find a consistent set of parameters that satisfy the proposed equilibrium relations both in closed systems (where equilibrium arguments should apply) and in open experiments where charge density is externally imposed by illumination or current injection [8,10]. Two illumination studies will be considered by this work, an ESR study reported in reference [1] and a new in-situ study using photoconductivity [11].

Charge Controlled by Illumination

Under illumination the hole (p) and electron (e) concentrations are a function of DB^+ and DB^- , since:

$$e = F_{I_n} \text{ and } p = F_{I_p} \quad (6)$$

$$\tau_n = 1/(A_1 \cdot DB^+) \text{ and } \tau_p = 1/(A_2 \cdot DB^-) \quad (7)$$

Where F is the photo generation rate of carriers, and A_1, A_2 are the product of the carrier thermal velocity and capture crosssection for the electron and hole respectively by an oppositely charged DB. We have chosen to relate the electron and hole lifetime to the oppositely charged DB since charged and uncharged DB have roughly equivalent densities and the capture crosssection for the oppositely charged DB should be much greater. This assumption is not critical and the developments that follow would also result (with slightly different values) had we chosen to relate both lifetimes to the sum of all charged DB or, for that matter, neutral DB. By substituting equation 7 into 6 and 6 into 4, equation 4 for the illuminated case is recast as:

$$(DB^+)^2 (DB^-)^2 (DB^0)^2 = A_1 A_2 F^2 K_4 \quad (8)$$

The equilibrium assumption requires that both the left-hand and right-hand sides of equation 8 have the same temperature dependence. Therefore the measured temperature dependence of any one of the species of equation 8 is related to the others by:

$$2E^+ + 2E^- + 2E^0 = E_4 \quad (9)$$

Where E^+ , E^- and E^0 are the effect activation energies for the creation of charged DB and neutral DB. E^+ can be determined from the temperature dependence of the photoconductivity. Photoconductivity was measured as a function of time at several different temperature ranging from 150 to 225°C. The photoconductivity was measured in-situ under the same illumination used to degrade the films (~100mW/cm²). The short time photoconductivity at a given temperature reflects that of the annealed state which is not temperature dependent. On the other hand at these same temperatures the steady-state degraded condition does have a temperature dependence (the steady state is achieved in approximately 30 minutes as seen figure 1) with the photoconductivity increasing with increasing temperature (or decreasing 1/T). DB^+ affects the photoconductivity through $[e]$ (equations 6-7) since:

$$\sigma_p = q\mu_e - q\mu_h F I - q\mu F / (A_1 \cdot DB^+) \quad (10)$$

Where equation 10 is an expression for the photoconductivity (σ_p) in terms of D^+ , q is the electronic charge and μ is the electron mobility. Therefore, DB^+ is decreasing with increasing T . The plot of the photoconductivity vs $1/T$ shown in figure 2 indicates the activation energy of the photoconductivity is -0.2 eV and therefore E^+ is --0.2eV.

Since ESR measurement can only detect neutral DB (DB^0), the measurement of light induced ESR signal strength versus $1/T$ described in reference 1 determined E^0 to be -0.13eV. The results thus far can be summarized by using equation 9 as follows:

$$2E^0 = 2(-0.13 \text{ eV}) = E_4 - 2E^- - 2E^+ \quad (11)$$

$$2E^+ = 2(-0.20 \text{ eV}) = E_4 - 2E^0 - 2E^- \quad (12)$$

Thermal Defect Formation

Recently McMahon [8] presented the results of an amorphous silicon ESR study which measured the DB^0 concentration as a function of temperature (see figure 3) in the same high temperature region. This was a closed system measurement since no external energy sources were used. The dangling bond density increased with increasing temperature and with an activation energy

(E_a) of -0.35eV . Substituting equation 5 into equation 4 and rearranging:

$$[\text{DB}^0]^2 [\text{DB}^+] [\text{DB}^-] = \text{DB}_{00} \exp(-E_g/kT) \exp(-E_4/kT) \quad (13)$$

Where DB_{00} is $(\text{WB}^2 N_c N_v \exp(\Delta S_4/k))$. Since temperature dependences of both left and right-hand sides of equation 13 must be equivalent, the apparent activation energy (E_a) for the thermal creation of DB^0 can be written:

$$2E_a = 2(+0.35 \text{ eV}) = E_g + E_4 - E^- - E^+ \quad (14)$$

With E_g equal to 1.7 eV a set of values that satisfy equations 11, 12 and 14 are: $E_4 = -1.74 \text{ eV}$, $E^- = -0.13 \text{ eV}$, $E^+ = -0.54 \text{ eV}$, and, $E^+ = -0.20 \text{ eV}$.

Figure 1.
 i_p of films under
 100mW/cm^2
 illumination
 versus time at
 190°C (top) and
 170°C (bottom).

Charge Controlled by Current Injection

In a manner similar to illumination, charge can also be non-thermally controlled by current injection. Unlike the illumination studies, above, the DB concentration was determined after quenching p-i-n devices to room temperature and n and p are independent of DB^0 , DB^- and DB^+ . The high temperature current injection (CI) studies [8,10] found that the DB density is proportional to $[i]^{0.5}$ where $[i]$ is the injected current density. This result is consistent with equation 4 if we assume that upon cooling the charged DB react via equation 3c to form neutral DB and that at the high injection levels used n and p are proportional to the applied current.

Free Energy Changes

Extrapolation of the data of Figure 3 yields $[\text{DB}^0] = 10^{18} \text{ cm}^{-3}$ at $1/T = 0$. Since at $1/T = 0$, $\text{DB}^0 = \text{DB}^+ = \text{DB}^- = \text{WB}$ it is possible to estimate ΔS_4 using equation 13. With reported values of $[\text{WB}]$ ranging from 10^{17} to 10^{18} cm^{-3} [12] and $N_v - N_c$ ranging from 10^{19} to 10^{21} cm^{-3} , the range of values calculated for ΔS_4 are from -3.8×10^{-4} to $-1.6 \times 10^{-3} \text{ eV-deg}^{-1} \cdot \text{K}^{-1}$. Therefore, defect creation decreases the entropy. The magnitude of the decrease could be accounted for by a loss of a vibration degree of freedom. Thus, the total free energy change associated with defect formation (assuming an intermediate value of ΔS) at $T = 450^\circ\text{K}$ is $\Delta G_4 = E_4 - T\Delta S_4 = -1.74 \text{ eV} - 450^\circ\text{K} \cdot (-9 \times 10^{-4} \text{ eV} \cdot \text{K}^{-1}) = -1.3 \text{ eV}$.

Figure 2.
Steady state σ_p
of the films
of figure 1
versus $1/T$.

Figure 3. The dangling bond density of an a-Si:H film versus temperature. (this plot is from reference [9]).

CONCLUSIONS

For the first time high temperature steady state DB densities are analyzed in a thermodynamic equilibrium framework. The equilibrium framework was extended to cover open systems resulting from illumination and current injection. The most interesting conclusion of this work results from the negative value of ΔG_4 , a result which is a direct consequence of DB reductions with increasing temperature when charge is externally fixed. A negative ΔG_4 means that the creation of dangling bonds proceeds via an exothermic reaction and the lowest energy state for the system is that with the weak bonds split into neutral and charged dangling bonds! It is also interesting to note that unlike the case of point defects in crystals, the creation of dangling bond defects in amorphous silicon decreases the entropy of the system.

In all of the experiments considered here the equilibrium is controlled by the charge density. If charge density is increased, the dangling bond density responds with a corresponding increase. Alternatively we could say that it is the lack of available charge that maintains amorphous silicon in its unstable higher energy annealed state. While this result is discouraging there is considerable evidence (including the loss of entropy upon defect formation) that the weak bond density is related to a specific structure (for example poly-hydride) or impurity which could be reduced.

From the vista provided by this framework it is possible to categorize the factors that influence the stability. Three factors control the equilibrium DB density: the weak bond density (indicated by a non temperature dependent change in DB density), activation energy (indicated by the negative of the high temperature photoconductivity activation energy) and purely kinetic changes (indicated by a change in degradation rate but no change in any equilibrium quantity).

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APPENDIX B

"Analytical Modelling of Thin Amorphous Silicon-Germanium Solar Cells"

ANALYTICAL MODELLING OF THIN AMORPHOUS SILICON-GERMANIUM
SOLAR CELLS

C.M. Fortmann

Institute of Energy Conversion
University of Delaware
Newark, De 19716
302-451-6236

ABSTRACT

The a-SiGe:H material parameters pertinent to the operation of the red scavenging component of a multi-junction solar cell are explored. Analytical modelling of p-i-n graded a-SiGe:H, a-Si:H solar cells is used to probe the relative minority carrier transport. These results are compared to film measurements including photo and dark conductivity as well as to capacitance measurements. The primary result is that the electron lifetime in a-SiGe:H is significantly longer than previously thought. This multifaceted analysis suggests new directions for the attainment of efficient silicon-germanium devices.

INTRODUCTION

Sophisticated numerical models have been applied to a-SiGe:H solar cells¹. While these techniques are extremely powerful, the solutions obtained are not unique. The large parameter space that effects solar cell performance includes grading schemes, alloy band gap, and i-layer thickness. This parameter space is too large for effective experimental exploration as well. It is, therefore, necessary to develop a large base of facts on which detailed numerical modelling and experiment can be based.

In this work we will explore the physical properties of high quality a-SiGe:H materials. From our previous work^{2,3} the a-SiGe:H materials with the best electronic transport are those with low hydrogen content. This work will further characterize the high quality a-SiGe:H materials with band gaps of ~1.3 eV (Ge content ~55%). These parameters can be used as inputs for the more detailed numerical modelling and more importantly they provide the necessary information for the intuitive process of solar optimization.

DISCUSSION

The analytical modelling of the collection efficiency of graded a-Si:H/a-SiGe:H solar cells has been previously described^{2,3}. This modelling is based on the simplification that occurs when photo generated carrier collection can be described in terms of a single carrier.

The differential approach to the analytical modelling of a p-i-n solar cell requires a situation simple enough to be adequately treated by solvable equations. The literature has considered the "electron and hole limited cases". The limiting carrier language is however misleading because what one really needs is a solvable equation for either carrier. The other carrier with its associated current is automatically determined since in steady state operation the total current is constant throughout the device:

$$J_p(x) + J_n(x) = J_{total} \quad 1$$

where J_p and J_n are respectively the electron and hole currents at position x in the i-layer. The goal of the analytical approach is to find a solution for the continuity equation:

$$d/dx(J) + G_x - R_x = 0 \quad 2$$

where J is the current, G_x is the generation rate as function of position and R_x is the recombination rate. The current for the electron and hole respectively are given by:

$$J_n = D_n(dn_x/dx) + \mu E n_x \quad 3a$$

$$J_p = D_p(dp_x/dx) - \mu E p_x \quad 3b$$

where E is the electric field which is given by, $(V_{bi} - V)/w$ where V_{bi} is the built in potential, V is the applied bias and w is the i-layer thickness. E was assumed

to be constant. The chief difficulty is that in general R_x is a function of both carrier densities leading back to a need for numerical solutions. Yet, if the experiment is limited to strongly absorbed illumination then the recombination in the region nearest the interface through which the illumination is entering is linearly related to that region's minority carrier density with the result that equation 2 can be analytically solved. The photo generated current is given by:

$$J = J_{n,x=0} = J_{p,x=0} = D_n \left(\frac{dn}{dx} \right)_0 = D_p \left(\frac{dp}{dx} \right)_0 \quad 4$$

A further generalization is possible in graded solar cells. When a portion of the i-layer is comprised of a-SiGe:H, only this layer will generate hole-electron pairs under long wavelength illumination (photon energies lying between the band gaps of a-Si:H and a-SiGe:H). Therefore, the minority carrier in the a-SiGe:H layer can be used to describe the collection.

The electron is the minority carrier in solar cells under long wavelength illumination when a-SiGe:H is in the front half of the i-layer (front loaded solar cells). Conversely, the hole is the minority carrier for graded solar cells under long wavelength illumination when the a-SiGe:H layer is near the n-layer or back of the solar cell (back loaded solar cell). Front and back loaded a-Si:H/a-SiGe:H solar cells are shown in Figure 1.

Previously^{2,3} the recombination rate in the i-layer was assumed to be proportional to a constant lifetime. Actually as the electron travel towards the n-layer its lifetime increases, while the hole lifetime increases towards the p-layer. For this reason the analytical model tends to overestimate recombination losses. The overestimation of recombination losses is more severe for the case of an electron generated near the p/i interface transversing an a-Si:H i-layer in the back half of the i-layer. This situation occurs in a front loaded a-SiGe:H or a non-graded a-Si:H solar cell under strongly absorbed illumination. In these cases recombination losses in the back half of the i-layer are minimal because the transit time can become shorter than the recombination time (see comments on picosecond carrier dynamics below) since:

$$t_{\text{transit}} = w / (2 * \mu * E) \quad 5$$

where $w/2$ is half the thickness of the i-layer. The transit time is ~5 ps for an i-layer 0.1 μm thick, with an electron mobility of $10 \text{ cm}^2/\text{V-s}$ and E of 10^5 V/cm .

Note the relatively poor electron mobility in a-SiGe:H and small hole mobilities in both a-Si:H and a-SiGe:H means there will be greater recombination losses for electrons crossing an a-SiGe:H back half of the i-layer as well as for holes crossing the front half of a-Si:H or a-SiGe:H i-layer.

Figure 1. Band diagrams of front loaded (a), back loaded (b) graded alloy solar cells. A schematic of an alloy solar cell with two transparent contacts as used for analysis is shown in (c).

The lifetime of photo generated carriers is generally a function of position in the i-layer⁶. Analytical modelling with constant lifetimes has been directly compared to detailed numerical modelling (with non-constant lifetimes) for the case of strongly absorbed illumination. Both techniques were found to yield good fits to the collection efficiency⁵. In the previous reports the behavior (shown in Figure 2) of actual p-i-n solar cells under strongly absorbed illumination is consistent with a poor electron mobility in a-SiGe:H, good electron lifetime and similar hole $\mu\tau$ products in a-Si:H and a-SiGe:H. We are presently comparing numerical and analytical techniques to improve both.

Figure 2. Voltage bias dependence of the quantum efficiency at 450 nm of graded alloy solar cells illuminated through either the p or n-layer as indicated.

Corroborating evidence from a number of different and independent experiments has been obtained. In a study of film photo and dark conductivity the conclusion of poor electron mobility can also be reached. By taking the ratio of the photo to dark conductivity and multiplying by $\exp(-E_g/kT)$, where E_g is assumed to be given by the activation energy of the dark conductivity the small effect of alloying on the electron lifetime can be seen (Figure 3). Alijishi used similar analysis to suggest that there was more to the electronic transport than an increase in the mid gap density of states⁶.

Figure 3. The effect of alloying on the photo to dark conductivity ratio multiplied by $\exp(-E_g/kT)$.

Thus far using film measurements the poor electron mobility found by the analytical modelling has been confirmed. The effect of alloying on hole transport will require greater effort. Recently a collaborative effort with J. David Cohen at the University of Oregon⁷ examined a-SiGe:H films prepared by our Laboratory. The a-SiGe:H materials were deposited by the same reactor and conditions used in our solar cell studies ($E_g \sim 1.3\text{eV}$). These a-SiGe:H materials were deposited onto single crystal silicon substrates. Semi-transparent palladium contacts were deposited to form Schottky barriers. It is noteworthy that the Schottky diode is a close relative to the p-i-n solar cell.

Measurements of the transient photocapacitance and the photocurrent were determined the relative hole $\mu\tau$ values to be only about a factor of three smaller than that of the electron. Also, the mid-gap density of states in this alloy (again $E_g \sim 1.3\text{eV}$) was found to be $2 \times 10^{16}\text{cm}^{-3}$ (approximately the same as that in degraded a-Si:H).

These values are of great importance to the solar cell analysis described above. The assumption of constant electric fields in the thin solar cells is consistent with the low density of mid-gap states. Also, this low density of states implies the relatively long electron and hole lifetimes found by the solar cell analysis.

A collaborative study of picosecond carrier relaxation in a-SiGe:H materials was undertaken with P.M. Fauchet at the University of Rochester⁸. This experiment used the Free Electron Laser at Stanford University⁹ to produce a large uniform carrier density ($\sim 10^{19}\text{cm}^{-3}$) throughout a thin ($0.1\text{ }\mu\text{m}$ thick) a-SiGe:H layer. Analysis⁸ of decay time of the free carrier absorption (Figure 4) found the relaxation time in a-SiGe:H is $\sim 6\text{ ps}$ compared to $\sim 10\text{ ps}$ in a-Si:H. These results are consistent with the idea that the recombination rate for photo generated carriers is similar in a-Si:H and a-SiGe:H.

By a number of different measurements we have arrived at the same conclusion that a-SiGe:H has a poor electron mobility. The front loaded cell is superior at lessening the impact of poor electron mobility because of the mobility gradient enhancement and the transit time for electrons crossing the back half of the i-layer can be shorter than the recombination time.

Further optimization of the i-layer of the solar cell is possible, however it may require a substantial increase in

cell complexity. Perhaps it is better to view a front loaded alloy solar cell as a p/n device since the alloy region actually behaves as a p-type region where the minority carrier is the electron (under the long wavelength illumination in which this cell is meant to operate).

Figure 4. Time-dependence of the changes in transmission of an a-SiGe:H sample measured at a wavelength of $1.5 \mu\text{m}$ after carrier injection at $0.75 \mu\text{m}$ (open circles). Also shown is the autocorrelation of the $1.5 \mu\text{m}$ pulse (closed circles) as explained in reference 8.

CONCLUSIONS

The carrier transport in a-SiGe:H materials can be summarized as poor electron mobility with relatively good hole mobilities combined with relatively long electron and hole lifetimes. When this result was first presented it was far from universally accepted. While this work has attempted to use a wide range of measurements and analysis techniques to establish the parameters of a-SiGe:H materials, the literature still contains a number of contradictory reports. It is beyond the scope of this work to find the underlying reason for each of these discrepancies however some are due to material quality and/or the analysis technique used.

In previous work^{2,3,10} we showed that the electron mobility in a-SiGe:H materials was a function of hydrogen and germanium contents. The present work is consistent with these earlier findings. The Institute of Energy Conversion is presently seeking new lower hydrogen content alloys through a variety of deposition techniques. Future work will incorporate these improved materials into p-i-n solar cells which use refinements in grading to mitigate the poor electron mobility and take better advantage of the good lifetime. Subsequently, these single junction solar

cells will be incorporated into multi-junction solar cells.

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APPENDIX C

"Charge-Defect Equilibrium Description of Metastable Defect Concentrations"

CHARGE-DEFECT EQUILIBRIUM DESCRIPTION OF METASTABLE DEFECT CONCENTRATIONS

C.M. FORTMANN*, R.M. DAWSON** AND C.R. WRONSKI**

*Institute of Energy Conversion, University of Delaware, Newark, DE 19716 USA

**Dept. of Electrical Engineering, Pennsylvania State Univ., University Park, PA 16802 USA

A thermodynamic equilibrium framework in which charge carriers are in equilibrium with charged and uncharged dangling bonds (DB) is developed. Thermal and light DB creation are related. DB formation is an exothermic reaction with negative entropy and free energy changes. Thus, the lowest energy state is with the weak bonds split into DB!

1. INTRODUCTION

The kinetic framework for metastable defect formation in a-Si:H provides for the rate at which light creates DB and the inverse process whereby thermal energy restores the lattice. The kinetic descriptions predict the time^{1,2} evolution of defect concentrations due to illumination. However, this framework can not interpret the smaller than expected activation energies of the high temperature light induced DB densities.

While thermodynamic considerations have been previously suggested^{3,4,5} the determination of parameters and the successful treatment of experiment are necessary for the greater acceptance of this description. Here a novel approach will be applied to high temperature ($T > 150^\circ\text{C}$) steady state (time independent) DB behavior. Activation energies are used to establish the heat of formation (enthalpy) of DB's. DB densities are used to determine the entropy and thus the free energy change can be determined. Both thermal and light generated defects are considered.

Application of thermodynamic equilibrium to low temperature time dependent behavior will be considered in the conclusion.

2. DISCUSSION

The most intuitively appealing creation mechanism requires that two DB be created upon the rupture of a susceptible site or weak bond (WB). The DB have three possible charge states: neutral ($\text{DB}^\bullet$), negative (DB^-) and positive (DB^+). The DB density increases due to illumination¹, current injection⁶ and temperature^{5,7}. A set of equilibrium expressions and the associated mass action relationships can be proposed.

$\text{WB} + e \rightleftharpoons \text{DB}^- + \text{DB}^\bullet$, ΔG_1 :

$$[\text{DB}^-][\text{DB}^\bullet]/([\text{WB}][e]) = K_1 \quad (1)$$

$\text{WB} + p \rightleftharpoons \text{DB}^+ + \text{DB}^\bullet$, ΔG_2 :

$$[\text{DB}^+][\text{DB}^\bullet]/([\text{WB}][p]) = K_2 \quad (2)$$

$\text{DB}^\bullet + e \rightleftharpoons \text{DB}^-$ (3a)

$\text{DB}^\bullet + h\nu \rightleftharpoons \text{DB}^+$ (3b)

$\text{DB}^- + \text{DB}^+ \rightleftharpoons 2\text{DB}^\bullet$, ΔG_3 :

$$[\text{DB}^\bullet]^2/([\text{DB}^-][\text{DB}^+]) = K_3 \quad (3c)$$

$e + p + 2\text{WB} \rightleftharpoons 2\text{DB}^\bullet + \text{DB}^+ + \text{DB}^-$, ΔG_4 :

$$[\text{DB}^\bullet]^2[\text{DB}^+][\text{DB}^-]/([e][p][\text{WB}]^2) = K_4 \quad (4)$$

$$[e][p] = N_v N_c \exp(-E_g/kT) \quad (5)$$

Equations 1 and 2 represent the equilibrium between DB pairs, charge and WB. Equation 3 allows for interaction among charged DB. Equation 4 is the summation of equations 1 and

2. Each K is an equilibrium constant which is related to the corresponding free energy change, ΔG , by $K = \exp(-\Delta G/kT) = \exp(-E/kT) \cdot \exp(\Delta S/k)$ where E is the change in enthalpy and ΔS is the change in entropy upon creation of a DB. Equation 5 is the mass action relation for holes and electrons.

Due to the complex manner in which dopant atoms interact with the amorphous silicon network³ it is not possible to vary charge by impurities. Therefore external means including illumination and current injection must be considered. While equilibrium thermodynamics may not apply to every open system, equilibrium has been applied to many open systems including engines⁸ and in this work equilibrium is assumed to apply to illuminated samples.

2.1 Charge Controlled by Illumination

Under illumination the $[p]$ and $[e]$ are a function of DB^+ and DB^- which in the simplest form can be written as:

$$[e] = Fr_n \text{ and } [p] = Fr_p \quad (6)$$

$$\tau_n = 1/(A_1[DB^+]) \text{ and } \tau_p = 1/(A_2[DB^-]) \quad (7)$$

where τ_n and τ_p are the electron and hole lifetimes, A_1 and A_2 are the product of the carrier thermal velocity and capture cross section by an oppositely charged DB and F is the photon flux. Note, it is assumed that τ_n and τ_p are related to the oppositely charged DB. This assumption is considered in more detail below. In the interest of clarity this simple relation between photoconductivity, σ_p , and DB^+ will be used. The results that follow would also be obtained (with slightly different values) had lifetimes been related to both charged DB and neutral DB.

By substituting equation 7 into 6 and 6 into 4, equation 4 becomes:

$$[DB^+]^2[DB^-]^2[DB^0]^2 = [WB]^2(1/A_1A_2)F^2K_4 \quad (8)$$

the equilibrium assumption requires that both

the left-hand and right-hand sides of equation 8 have the same temperature dependence:

Therefore the measured temperature dependence of any one of the species of equation 8 is related to the others by:

$$2E^+ + 2E^- + 2E^0 = E_4 \quad (9)$$

Where E^+ , E^- and E^0 are the effective activation energies for the creation of charged DB and neutral DB. E^+ can be determined from the temperature dependence of the σ_p . σ_p was measured⁹ as a function of temperature (150 to 225°C). The steady-state (achieved in ~ 30 min.) defected condition shows σ_p increasing with increasing temperature. The DB^+ density affects the σ_p through $[e]$ (equations 6-7) since:

$$\sigma_p = q\mu[e] = q\mu Fr_n = q\mu F/(A_1[DB^+]) \quad (10)$$

Where q is the electronic charge and μ is the electron mobility. Therefore, $[DB^+]$ is decreasing with increasing T. Previously we reported⁹ that the activation energy (E^+) is ~ 0.2eV.

Since ESR measurement detects only DB^+ , the measurement of light induced spins versus $1/T$ (ref. 1) determined E^+ to be ~0.13eV. The results thus far are:

$$2E^+ - 2(-0.13 \text{ eV}) = E_4 - 2E^- - 2E^0 \quad (11)$$

$$2E^+ - 2(-0.20 \text{ eV}) = E_4 - 2E^- - 2E^0 \quad (12)$$

2.2 Intensity Dependence of DB Density

The intensity dependence of the steady state DB density is dependent on the measurement. The steady state increase in sub band gap absorption has a $-F^{0.33}$ dependence (from data of figure 1). CPM based measurements (which like σ_p depends on τ_n) have a $-F^{0.5}$ dependence¹⁰. Equation 8 can be used to identify the DB charge states that contribute to the measurement. The activation energy of the DB density determined by either optical absorption or CPM is a function of intensity as predicted by equation 8. Some limiting cases which lead to a well defined

intensity dependence are: if the measurement is influenced by only one DB charge state (e.g., DB^+) then the steady state measurement is proportional to F ; if all DB have similar influence on the measurement then the intensity dependence is $F^{0.33}$; and, if two charge states contribute (e.g., DB^0 and DB^+) then the measurement is proportional to $F^{0.5}$. An electron lifetime that is a function of both DB^0 and DB^+ would explain the CPM intensity dependence (the intensity dependence of σ_p is being investigated). Sub band gap absorption however seems to involve all of the DB charge states equally.

2.3 Thermal Defect Formation

ESR studies^{5,7} measured the DB^+

concentration as a function of temperature. These are closed system measurements with no external energy sources. The $[DB^+]$ increased with increasing temperature with an activation energy (E_a) ranging from 0.32 to 0.35 eV (this work assumes the 0.35 eV value). Substituting equation 5 into equation 4 and rearranging:

$$[DB^+]^2[DB^-][DB^0] = DB_{00} \exp(-E_g/kT) \exp(-E_a/kT) \quad (13)$$

Where DB_{00} is $(WB^2 N_c N_v \exp(\Delta S_a/k))$. Since temperature dependences of both left and right-hand sides of equation 13 must be equivalent, the apparent activation energy (E_a) for the thermal creation of DB^+ is:

$$2E_g = 2(+0.35 \text{ eV}) = E_g + E_a - E^- - E^+ \quad (14)$$

With E_g equal to 1.7 eV a set of values that satisfy equations 11, 12 and 14 are: $E_a = -1.74$ eV, $E^+ = -0.13$ eV, $E^- = -0.54$ eV, and $E^0 = -0.20$ eV. These values are consistent with the reported small correlation energies¹¹.

2.4 Free Energy Changes

Extrapolation of the ESR data^{5,7} yields $[DB^+] \sim 10^{18} \text{ cm}^{-3}$ at $1/T=0$. Since at $1/T=0$, $[DB^+] = [DB^0] = [DB^-] = [WB]$, ΔS_a can be estimated using equation 13. Reported¹² values of $[WB]$ range from 10^{17} to 10^{21} cm^{-3} and $N_v \sim N_c$ range from

10^{19} to 10^{21} cm^{-3} , therefore, ΔS_a ranges from -3.8×10^{-4} to $-1.6 \times 10^{-3} \text{ eV} \cdot \text{K}^{-1}$. DB creation decreases the entropy. The magnitude of the decrease could be accounted for by a loss of a vibrational degree of freedom. The total free energy change (assuming an intermediate ΔS) at $T=450^\circ\text{K}$ is $\Delta G_a = E_a - T\Delta S_a = -1.74 \text{ eV} - 450^\circ\text{K} \cdot (-9 \times 10^{-4} \text{ eV} \cdot \text{K}^{-1}) = -1.3 \text{ eV}$.

Figure 1 N_s (DB) versus $1/T$ for an illuminated sample (generation rate = $6e20$ (bottom), $1.9e21$, $4.9e21$ and $1.8e22 \text{ s}^{-1}\text{cm}^{-3}$) and dark measurements of a variety of samples grown by different techniques.

CONCLUSIONS

High temperature steady state DB densities are shown to result from thermodynamic equilibrium. The enthalpy change due to DB creation was found to be negative. Also the free energy change of DB creation (ΔG_a) is negative. Therefore, DB creation proceeds via an exothermic reaction and the lowest energy state is that with the WB split into neutral and charged DB! Unlike defects in crystals, DB in a-Si:H decrease the entropy.

In Si:H the equilibrium is controlled by charge density. If charge density is increased, the DB density responds with a

corresponding increase. Alternatively we could say that it is the lack of available charge that maintains amorphous silicon in its unstable higher energy annealed state.

In order to extend the theory to time dependent behavior it is necessary to remind ourselves of the interaction of thermodynamic driving forces that underlie change and the kinetic factors that control the rate. When a system is in equilibrium there is no driving force for change and the system is stable. The present theory predicts that there will be a driving force for a change in DB density whenever charge density is increased (for example by illumination) or decreased (e.g., thermal annealing of degraded samples). The DB density necessary to exhaust this driving force will be a function of; the charge density, [WB] and K_4 in accordance with equation 8. Note, it is not necessary to convert all WB to DB to achieve equilibrium (steady state condition).

Since charge density controls the high temperature DB behavior, it is probable charge dominates the kinetic processes (time dependence) as well. Under this assumption, the activation energy of annealing reflects the energy needed to promote a carrier out of the charged DB to its respective band. Under illumination it may be possible to anneal a larger than equilibrium DB density at low temperature as recombination can replace thermal excitation to discharge the DB.

The [WB] appears to be a function of deposition conditions as the intercepts of the $\log(N_s)$ versus $1/T$ plots seen in figure 1 are dependent on deposition conditions. A reduction in [WB] could conceivably result in a material that has a low equilibrium [DB] at the illumination levels encountered in an operating solar cell.

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ABSTRACT

Results and conclusions obtained during a research program of the investigation of amorphous silicon and amorphous silicon based alloy materials and solar cells fabricated by photo-chemical vapor and glow discharge depositions are reported. Investigation of the effects of the hydrogen content in a-Si:H i-layers in amorphous silicon solar cells show that cells with lowered hydrogen content i-layers are more stable. A classical thermodynamic formulation of the Staebler-Wronski effect has been developed for standard solar cell operating temperatures and illuminations. Methods have been developed to extract a lumped equivalent circuit from the current voltage characteristic of a single junction solar cell in order to predict its behavior in a multijunction device.

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