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Role of Electro-Optics in Photovoltaic Energy Conversion

Satyendra K. Deb
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INTRODUCTION

This issue is a proceedings of the symposium on the "Role of Electro-Optics in Photovoltaic Energy Conversion" which was sponsored by the Society of Photo-Optical Instrumentation Engineers and was held at San Diego, California on July 31-August 1, 1980. The symposium was organized by Doctors S. K. Deb and L. L. Kazmerski of the Solar Energy Research Institute, Golden, Colorado. The purpose of this symposium was to present some key developments in a broad range of photovoltaic materials and to emphasize the role of electro-optic techniques in fabricating and characterizing photovoltaic devices.

The first session of the symposium was devoted to photovoltaic solar cells based on silicon. The results on polycrystalline Si were reviewed, and it was shown that grain boundaries play a dominant role in determining the photovoltaic properties. It was argued that in order to make solar cells having efficiencies greater than 10%, grain sizes greater than several hundred microns are necessary. Studies on defects and grain boundaries showed that standard cell processing steps can lead to residual microscopic stresses, defect-defect and impurity-defect interactions causing changes in the diffusion length and cell performance. A surface photovoltage technique was described which could measure the minority carrier diffusion length on a number of materials grown by low cost processes. Opto-electronic properties of various forms of Si were reported which provided valuable information on the quality of materials. The experimental and theoretical investigations of the quality factor for n^+ p Si-solar cells were discussed. A new model was proposed which involved tunneling of n^+ conduction electrons to deeper impurity levels and recombination of these electrons with holes that are thermally excited into the junction from the p-side. The effect of an interfacial oxide layer on an amorphous Si:F:H alloy based M-I-S type device having efficiencies of 6.3% was presented. It was concluded that a-Si:F:H possesses a low density of surface states which was consistent with the variation of V_{oc} and work function of the Schottky metal contact.

The status of photovoltaic solar cells based on nonsilicon compound semiconductors was extensively reviewed in the second session of the symposium. One of the highlights of this session was the disclosure, for the first time, by the Boeing Corporation of the achievement of a 9.4% efficiency in a thin film solar cell consisting of $CuInSe_2/CdS$. Some interesting results on the compositional analysis of $Cu_2S/Zn_xCd_{1-x}S$ heterojunction by Auger electron and atomic absorption spectroscopy, which showed Zn enrichment at the interface, were presented. The growth kinetics of Cu_2S film formed by sulfurization of thin films of Cu was discussed. An ultra high speed electro-optical approach for the measurement of electrical and optical properties of amorphous semiconducting thin films was presented. The basic principle of the electrochemical photovoltaic solar cell and some recent results on the stabilization of semiconductors against photo-induced corrosion were described.

The optical technology is most intensely applied in the development of concentrator type solar cells and the third session was devoted to various means of concentrating solar radiation. The types of concentrator systems that were discussed consisted of the following: (i) luminescent concentrators based on organic and inorganic phosphors; and (ii) high efficiency tandem structure based on monolithic stacks of muiltibandgap semiconductors. An interesting paper on the design and fabrication of a GaAs photovoltaic dense array for concentrator applications was presented. A unique high concentrator test facility for solar cell characterization under a variety of illumination conditions was described.

The final session of the symposium was devoted to electro-optic techniques for characterization of solar cells. Application of complementary surface analysis techniques such as AES, SIMS, XPS to solar cell materials and device problems was reviewed. Laser scanning, which is a powerful tool for isolating defects and mapping spatial variations in the photoresponse of solar cells was presented. The operating principle of a millimeter wave Fabry-Perot interferometer and an ellipsometer which can be conveniently used for the measurement of electrical conductivity and dielectric properties of thin films particularly on conducting substrates was described. Results of a series of measurements using remote sensing methods to study the propogation characteristics of solar radiations through the atmosphere were reported.

The symposium served a very useful purpose in presenting the current status of several important areas of photovoltaic solar cell technology. I would like to express my sincere thanks to the authors and session chairmen for making it a success.

Satyendra K. Deb
Solar Energy Research Institute

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SESSION 1

PHOTOVOLTAIC SOLAR CELLS BASED ON SILICON

Session Chairman
Alfred P. DeFonzo
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Polycrystalline silicon solar cells

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Abstract

The potential of polycrystalline silicon for large scale terrestrial photovoltaic device application is well recognized. It shares with single-crystal silicon numerous desirable physical and chemical properties, while also showing great promise of reduced cost by circumventing many of the complex and energy intensive steps associated with growth of single crystals. These facts have prompted many scientists to investigate various forms and shapes of polycrystalline silicon. The results involving SIS, MIS and p/n junction devices will be reviewed. Results will also be presented to show how grain boundaries play a dominant role in determining the electrical and photovoltaic properties of polycrystalline silicon.

Introduction

There is considerable interest in polycrystalline silicon because of its applications as solar cells[1] (an electro optic device), high value load resistors in static RAM's, isolated layers in poly I^2L, and distributed RC structure in monolitic filters[2]. Solar cells have been made by thermal diffusion (p/n and n/p), as well as by fabrication of various MIS and SIS structures. For 1 mm grain size polysilicon maximum efficiencies between 10-11 percent have been reported. For smaller grain material the efficiencies are much lower. Though small and large grain materials appear to behave differently, on a first approximation both can be treated in the same manner. The difference between the two types is in the magnitude of the grain boundary area, which obviously is a function of grain size. Grain boundaries act as traps for carriers and as a result a portion of the volume around the surface of the grain can be depleted of mobile charge carriers i.e. the grains may be conducting inside but are surrounded by a high resistivity space charge region which is usually $\leq 1\mu m$, depending on the doping concentration. Thus for certain grain sizes and doping concentrations the space charge region could engulf the whole grain. The intergrain boundary barrier heights and resistivities are a function of doping density. The barrier is about 0.55eV at low doping and approaches 0 eV at higher doping densities.[3] Though the intergrain boundary barriers act as highly resistive paths, they can be made more conducting with appropriate illumination. Reducing or eliminating barriers, however, does not always lead to reduction of recombination of photogenerated carriers at the grain boundaries.

Transport properties of polycrystalline silicon: resistivity, carrier concentration and mobility

The resistivity, mobility and free-carrier concentration of polycrystalline silicon do not vary with doping concentration in the same manner as has been observed for single crystal silicon. The impurity concentration and free carrier concentrations are in general not identical in small grain polycrystalline silicon at low doping densities.[4,5] In contrast with these results, we have recently shown that for polysilicon having grain size about 1mm, the measured free carrier concentration is associated with the bulk of the grain and is not affected by the presence or absence of the intergrain boundary barrier.[6] However, the mobility is affected by intergrain boundary barriers and the measured value corresponds to an effective mobility. We demonstrated (Fig. 1) that light reduces or even eliminates the barriers and the variation of Hall mobility with temperature (with the barriers removed) was very similar to that of size crystals. Thus from such measurements, one could obtain both effective and microscopic mobilities.

The variation of mobility and carrier concentration as a function of doping is shown in Fig. 2 for small grain polysilicon ($<25\mu m$). A theory was presented by Seto[5] to account for the observed results for grains ≤ 1000Å. However, the same theory cannot account for the results for 25μm grain. To explain the results, it is necessary to assume that the grain can be completely depleted. This is true for grains ≤ 1000Å but not for 25μm grains. We found that the results need not be explained on the basis of a depletion approximation. A modified version of Bube's theory of Hall effect measurements in homogeneous materials can account for the results.[7]

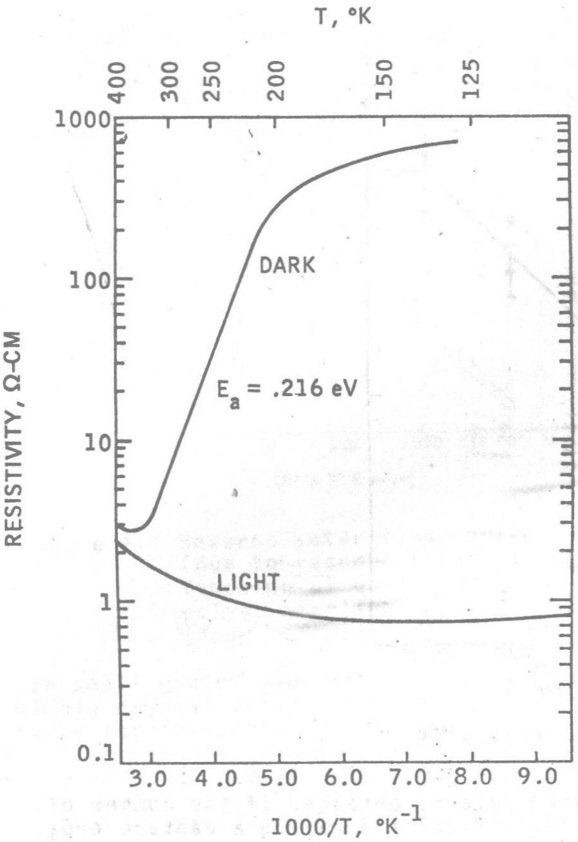

Figure 1. Temperature dependence of the resistivity of polysilicon in the dark and under illumination. (From ref. 6)

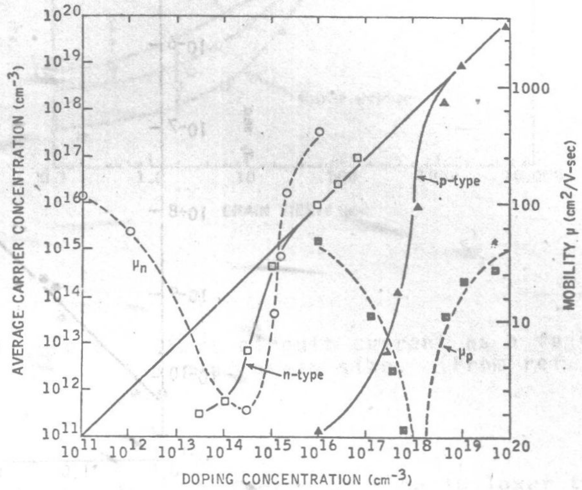

Figure 2. Average free-carrier concentration and mobility as a function of doping density is polycrystalline silicon. (From ref. 1)

Lifetimes

Even though the eliminations or reductions of intergrain boundary barriers is possible by choosing suitable doping levels, there still remains the problem of grain boundary recombination and its effect on carrier lifetime. For polysilicon solar cells, the variation of lifetime with grain size is the most dominant effect. Once the relation between the two is established, the reverse saturation current, the short circuit photocurrents, the open circuit photovoltage, the fill factor and the efficiency can all be calculated by making use of the well established theories for single crystal material. The minority carrier lifetime used in single crystal calculations is replaced by an effective lifetime, which combined the bulk lifetimes and the lifetime encountered at the grain boundary.[1]

Assuming cubic geometry, it can be shown that the effective lifetime is dominated by the grain boundary lifetime so that

$$\tau_{eff} = \tau_s = 5\times10^{-6} d.\text{sec} \quad (1)$$

Fig. 3 shows the experimental and theoretical plots of equation (1). The effective diffusion length is given by

$$L_{eff} = 3.36\times10^{-4} (\mu d)^{1/2} \text{cm.} \quad (2)$$

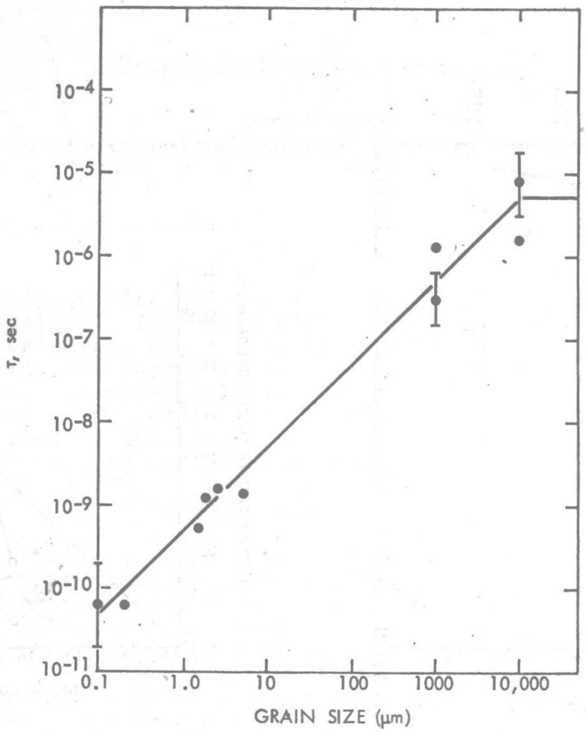

Figure 3. Lifetime versus grain size. (From ref. 12)

The best fit of the above relations to experimented data is obtained if the number of grain boundary recombination sites is taken to be $1.6x10^{13}/cm^2$ and having a capture cross section of $2x10^{-16}cm^2$. This results in a grain boundary recombination velocity of $3x10^4$cm/sec.

p/n Junction, MIS and SIS polycrystalline silicon solar cells

p/n Junction. Polycrystalline p/n junctions in principle behave exactly as a single crystal device; the only difference is that it is less efficient. The efficiency as in all polycrystalline devices (assuming that the grains are perfect) is a function of grain size. The larger the grains the more efficient the device is.

The dark I-V curve is then given by the relation

$$J = J_{od}[\exp(\lambda_d V-1)]+J_{or}[\exp(\lambda_r V-1)] \quad (3)$$

in which

$$\lambda_d = \frac{q}{kT}, \text{ and } \lambda_r = \frac{q}{2kT} \quad (4)$$

J_{od} = reverse saturation current due to diffusion.

J_{or} = reverse saturation current due to recombination.

Both J_{od} and J_{or} are a function of grain size but J_{or} varies much more rapidly with grain size then J_{od}.

Our calculations show that $J_{or} > J_{od}$ for grains $\leq$ 100μm and as a result or small grains one can write

$$J = J_{or}[\exp(\lambda_r V)-1]. \quad (5)$$

The variation of J_{or} as a function of grain size is shown in Fig. 4. The variation in J_{sc} as a function of grain size is shown in Fig. 5. The top curve is for the case where mobility is assumed to be constant, the middle curve for mobility variation with grain size.

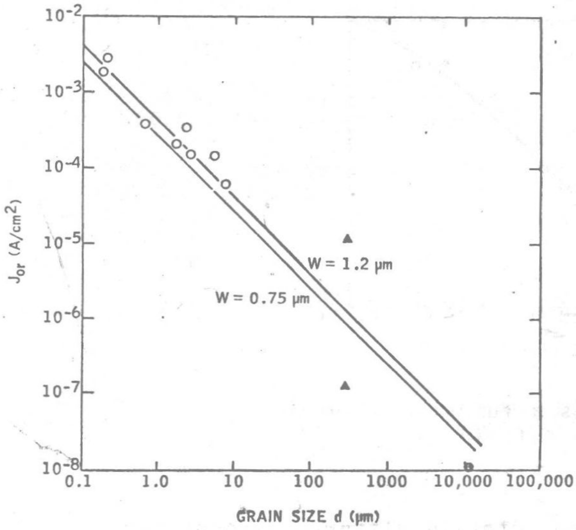

Figure 4. Reverse saturation current J_{or} (due to recombination) as a function of doping density is polycrystalline silicon. (From ref. 1)

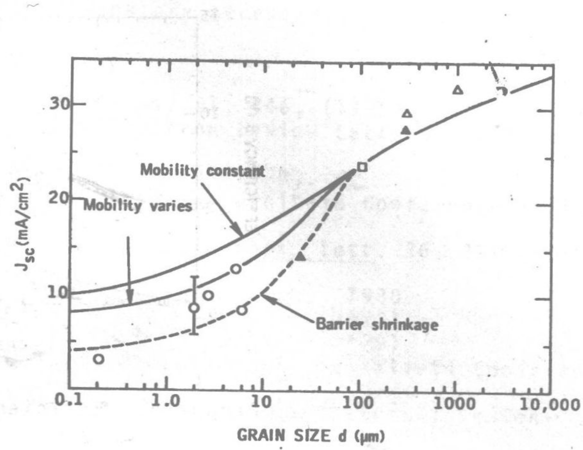

Figure 5. Short circuit current as a function of grain size. (From ref. 1)

For small grains experimental values of mobilities are about a factor of 5 to 10 lower than single crystal values. In the middle curve this fact is taken into account. In the bottom curve barrier shrinkage is assumed. In modeling solar cells, the barrier is usually assumed to be constant, that is, having the same width in light and dark. For materials, which are trap free and have long minority carrier diffusion lengths, this is a valid assumption. However, barrier shrinkage becomes pronounced in materials with traps which have low mobilities and lifetimes. The effect is very similar to the narrowing of the barrier width with increased dopant concentration, and the terms "photon doping" describing the phenomenon well. Because of low mobilities and lifetimes, the barrier shrinkage has a large effect on the short circuit photocurrent, and the device can no longer be considered as a constant current generator.

The variation of open circuit voltage and fill factor with grain size is shown in Figs. 6 and 7. For larger grains the values approach single crystal values. Fig. 8 shows the variation of efficiency as a function of grain size. Excellent agreement is observed between theory and experiment.

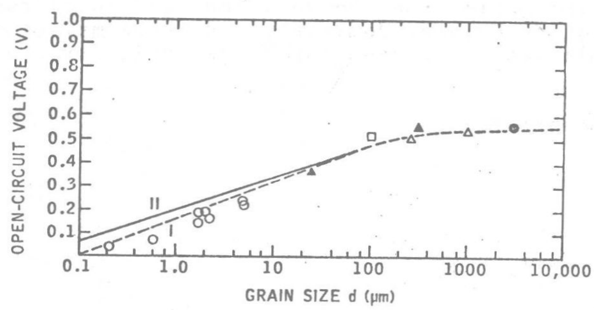

Figure 6. Open circuit voltage as function of grain size. (From ref. 1)

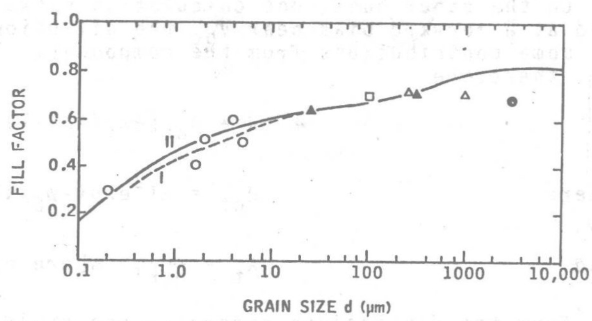

Figure 7. Fill factor as function of grain size. (From ref. 1)

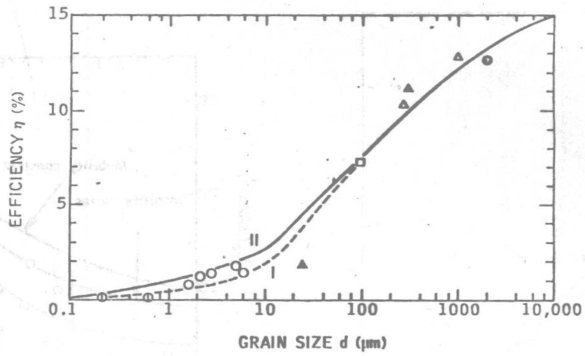

Figure 8. Efficiency as a function of grain size. (From ref. 1)

MIS and SIS Solar Cells

Metal-Insulator-Semiconductor (MIS) and Semiconductor-Insulator-Semiconductor (SIS) structured solar cells have been considered a viable alternative to pn junction solar cells. For MIS solar cells the better known ones are Cr/Insulator/p-Si and Al/Insulator/n-Si solar cells. SIS cells studied so far SnO_2/Insulator/n-Si, ITO/Insulator/n or p-Si cells. For 1mm grain size efficiencies around 10 percent have been reported.

In these devices the thin insulating layer is between 15-20Å. There are different ways of viewing the role of the insulating layer. Some suggest that the layer blocks the majority carrier currents injected into the metal at forward bias from the semiconductor while still being transparent to the photogenerated minority carrier current and thereby increasing the open circuit voltage.[8] We on the other hand attribute the role of the oxide to an increase in the diode constant which also leads to an increase in open circuit voltage.[9,10] The insulating layer, which is usually SiO_2, also reduces the surface recombination velocity by several orders of magnitude.

In general we find it convenient to express the dark I-V characteristics of MIS and SIS cells as the sum of two exponential terms as in equation(3). However, in normal MIS and SIS devices the recombination component is replaced by a thermionic component. In polycrystalline devices with small grains this may no longer hold. The recombination component possibly plays a dominant role. Furthermore, the silicon at the insulator interface usually has an inversion layer. For SnO_2/n-Si, the Fermi level at the interface in Si is only 0.3eV from the valence band.[11] The device behaves like a p/n junction device sliced in the space charge region. However there are no good experimental data available for small grain MIS or SIS devices to verify such a view point.

On the other hand, one calculation shows that for grain sizes above a few hundred microns and at a forward bias near V_{oc} the diffusion component becomes dominant, and there may also be some contributions from the component. The relation to be used for large grain material is, therefore

$$J = J_{ot}[\exp(\lambda_t V-1)]+J_{od}[\exp(\lambda_d V)-1] \quad (6)$$

where

$$J_{ot} = AT^2\exp(-\emptyset_B/kT) \quad (7)$$

and

$$\lambda_t = \frac{q}{\eta_t kT} \text{ where } \eta_t \text{ is usually} \geq 2. \quad (8)$$

From the discussions presented one could conclude that in general, the same curves shown in Fig. 4 to Fig. 8 describes the properties of MIS and SIS polycrystalline silicon devices. The limited experimental data that is presently available do confirm our conclusions.

Conclusions

The grain size of silicon plays a dominant role in determining the electrical and photovoltaic properties of polysilicon. Grain boundaries act as traps and recombination centers. The recombination loss at grain boundaries is the predominant loss mechanism in polycrystalline solar cells. For small grains, the grain boundary recombination affects the lifetime more than any dopant concentration. To make solar cells having efficiency greater than 10 percent, grain sizes greater than several hundred microns are necessary.

References

1. Ghosh, A.K., Fishman, C. and Feng, T., J. Appl. Phys. 51, 446, (1980).
2. Lu, N.C.C., Gerzberg, L. and Meindl, J.D., IEEE Electron Device Letters EDL-1, 38 (1980).
3. Seager, C.H. and Castner, T.G., J. Appl. Phys. 49, 3879 (1978).
4. Young, R.T., Cleland, J.W. and Wood, R.F., 12th IEEE Photovoltaic Conference 1976.
5. Seto, J.Y.W., J. Appl. Phys. 46, 5247 (1975).
6. Maruska, H.P., Ghosh, A.K., Rose, A. and Feng, T., Appl. Phys. Lett. 36, 381 (1980).
7. Details to be published later.
8. Cheek, G. and Merterns, R., SERI Report #1 SERI/TR-311-493, Feb., 1980.
9. Ghosh, A.K., Fishman, C. and Feng, T., J. Appl. Phys. 49, 3490 (1978).
10. Ghosh, A.K., Fishman, C. and Feng, T., J. Appl. Phys. 50, 3454 (1979).
11. Feng, T., Ghosh, A.K. and Fishman, C. 13th IEEE Photovoltaic Specialists Conference Record (IEEE, New York, 1978) p 519.
12. Ghosh, A.K., Feng, T. and Maruska, H.P., 14th IEEE Photovoltaic Specialists Conference Records, (IEEE, New York, 1980) p 1169.

A study of photovoltaic loss-mechanisms due to defects and grain boundaries in polycrystalline silicon

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Abstract

Various photovoltaic loss-mechanisms associated with defects and grain boundaries (g.b.'s) in polycrystalline silicon have been experimentally studied. Analysis was carried out on two types of substrates/cells viz. Wacker Silso and laser crystallized RTR ribbons. Solar cells were fabricated on selected regions of the substrates and their characteristics (V_{OC}, I_{SC}, F.F.) related the substrate structure. Mechanisms related to photovoltaic losses are divided into two categories: electronic and physical. Parameters describing electronic loss mechanisms, such as changes in minority carrier diffusion length, dark current and local photo-current losses were measured and their dependence on density and type of defects was determined. A variety of analytical techniques were used for this study. These include I-V characterization of solar cells, I-V characterization of g.b.'s and light intensity dependences of some material parameters. Loss mechanisms associated with physical effects are defect-defect and impurity-defect interactions. It is shown that physical effects such as impurity segregation and defect annihilation can lead to significant loss/gain in photovoltaic characteristics.

Introduction

Currently there is considerable interest in polycrystalline silicon substrates because of their potential for low-cost solar cells. Although fairly good efficiency solar cells can be fabricated on polycrystalline silicon substrates with present technology, the optical and electronic processes taking place in this material are not well understood. In particular, presence of defects/grain boundaries (g.b.'s) profoundly affects the electrical properties of those materials as compared to equivalently doped monocrystalline silicon. Presence of defects/g.b.'s in a solar cell result in photovoltaic losses. An understanding of the loss mechanisms, which influence the attainable efficiencies of solar cells is important in order to improve substrate quality as well as to determine appropriate processing steps for cell fabrication. This paper describes some investigations that we have carried out to determine cell degradation mechanisms associated with defects/g.b.'s. Objective of this study are two fold: (i) to relate electronic (photovoltaic) effects to the physical characteristics of defects/g.b's and (ii) to determine changes in P.V. losses due to variation in physical characteristics caused by processes required for cell fabrication.

Basics of photovoltaic loss mechanisms

Photovoltaic losses in polycrystalline silicon can be evaluated in terms of electronic and physical characteristics of defects/g.b.'s. Electronic effects are associated with localized states introduced in the forbidden gap by the discontinuities in the periodic lattice potential. Upon fabrication of a solar cell, the electronic effects can influence the cell performance in several ways. Conceptually these are separated into bulk effects and junction effects. Bulk effects of defects/g.b.'s arise because of the significantly increased number of recombination sites available. Minority carriers diffusing to defects/g.b.'s have a high probability of recombination, with the result that the photocurrent arriving at the solar cell junction is reduced. Consequently the effective lifetime of a carrier is significantly lower than in a single crystal sample.

Junction effects are due to "interface states" which alter the barrier height and can lead to significantly higher generation-recombination currents near defects/g.b.'s. Other carrier transport mechanisms such as tunneling can also occur. The over-all effect is to lower the solar cells' open-circuit voltage.

Electronic effects described above depend strongly on the physical characteristics of defects/g.b.'s (which may be altered by yhe processes required for cell fabrication). Physical characteristics of interest include: type of defects, g.b. misfit, impurity segregations at defects/g.b. residual stress etc.[1] Cell processing steps can cause such effects as defect-defect and defect-impurity interactions leading to strong changes in P.V. losses. Knowledge of these effects can be important in designing processing sequences for fabrication of high quality cells.

Overall characteristics of polycrystalline cells may be described in terms of diode equations with due consideration to various carrier transport mechanisms. Accordingly we may write (assuming superposition):

$$I = I_L - I_d \qquad (1)$$

where I is the diode current, I_d and I_L are dark and light generated currents respectively. I_d can be written as (neglecting series resistance effects)

$$I_d \approx I_{01} e^{ev/kT} + I_{02} e^{ev/nkT} + k_1 N_t e^{BV_j} + V/R_{SH} \qquad (2)$$

Various terms in I_d, right hand side of equation 2 are the following components, respectively: injection, space change recombination, tunneling and shunting currents. Expressions for various quantitites in equations 1 and 2 can easily be formed in literature, e.g. see [2].

Experimental measurements

We have studied several aspects of photovoltaic (P.V.) loss mechanisms in cells fabricated on two types of polycrystalline substrates viz. RTR ribbons and Wacker Silso. Arrays of small area solar cells (50 mil diameter mesas) were fabricated on p-type polished substrates by a process described previously [3]. Measurements made on the cells include determination of bulk minority carrier diffusion length (L) and I-V characterization (dark and illuminated). Selected diodes were light scanned with a two-wavelength laser scanner to determine: (a) local variations in L (b) recombination in the vicinity of the depletion region and (c) such as spectral response were also done on selected diodes.

Following these measurements the devices were dislocation etched and densities of defects and g.b.'s determined in each diode. Dependences of cell parameter (V_{OC}, I_{SC}, F.F.) and L on the density of defects/g.b.'s were determined.

Other physical characteristics such as residual stresses and impurity (in particular oxygen) segregation at g.b.'s were also determined. Their implication on P.V. were analysed.

Bulk effects

Bulk losses were determined in terms of minority carrier diffusion length. This parameter determines the short circuit current obtainable from the cell. Figure 1 shows dependence of L on the density of g.b.'s (in this case plotted as number of grains per diode; diode area equals 1.26 mm^2). Data in figure 1 is shown by two symbols. Open circles represent data

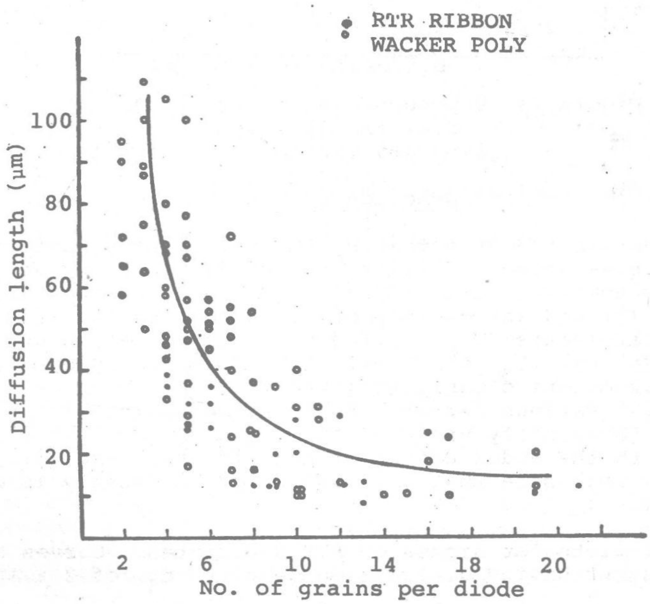

Figure 1. Dependence of minority carrier diffusion length on number of grains per diode.