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On the Cause of the Flat-Spot Phenomenon Observed in Silicon Solar Cells at Low Temperatures and Low Intensities

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ABSTRACT

A model is presented that explains the "flat-spot" (FS) power loss phenomenon observed in silicon solar cells operating under deep space (low temperature, low intensity) conditions. Evidence is presented suggesting that the effect is due to localized metallurgical interactions between the silicon substrate and the contact metallization. These reactions are shown to result in localized regions in which the PN junction is destroyed and replaced with a metal-semiconductor-like interface. The effects of thermal treatment, crystallographic orientation, junction depth, and metallization are presented along with a method of preventing the effect through the suppression of vacancy formation at the free surface of the contact metallization. Preliminary data indicating the effectiveness of a TiN diffusion barrier in preventing the effect are also given.

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INTRODUCTION

It has been known for some time that silicon solar cells operating under deep space conditions (low intensity, low temperature) are susceptible to a power loss phenomenon known variously as the "flat-spot" (FS) or "broken knee" effect.[1,2] The effect is observed as a power-reducing distortion in the current-voltage (I-V) characteristic in the vicinity of the maximum power point that appears and intensifies as the temperature is lowered (figure 1). Cells that show the effect in general give no evidence of being defective when examined at room temperature. The effect can usually be identified by the presence of two abrupt breaks in the I-V characteristic as seen in the figure. One or both of these break points can be obscured, however, by the coexistence of other defects, such as high contact resistance or low shunt resistance. The purpose of this paper is to describe the results of an effort to determine the mechanisms active in the FS effect with the ultimate goal of eliminating or controlling them. After first presenting a general model that appears to be consistent with the observed data we describe a series of experiments which provided an elucidation of some of the details of the phenomenon. This is followed by a discussion of our attempts to find a means of preventing the effect.

Drs. Peter Iles and Frank Ho of Applied Solar Energy Corporation and Professor M. A. Nicolet of the California Institute of Technology provided many of the devices used in this study.

EXPERIMENTAL

It should be mentioned initially that the FS effect is equally observable in both the illuminated and the dark forward characteristic. This is illustrated in figure 2 where the illuminated and the dark characteristics of the same cell are shown. For the sake of experimental convenience we have chosen to use the dark I-V display in these investigations. The voltage and current scales used in the figures to follow correspond to the ranges expected in the illuminated characteristic under Jupiter-like deep space illumination intensities, i.e., $5 mW/cm^2$, corresponding to a satellite-sun separation of about five astronomical units.

The cells used in these investigations came from a variety of sources. The majority of them were, however, standard commercial space type, 2 and 10 ohm cm, TiPdAg contacted cells. The cells with other contacting systems were experimental cells, most of which were made specially for this study. Low temperatures were achieved through immersion in a liquid nitrogen bath. When it was necessary to remove the metallization from a cell, a long soak in concentrated HF followed by a hot aqua regia soak proved to be sufficient. When it was desired to etch the cell without destroying the contacts a 50 percent NaOH solution at 70°C was used.

GENERAL MODEL

A proposed mechanism which appears to fit the observed facts is illustrated schematically in figure 3 (insert). It is suggested that the FS effect is due to a resistive metal-semiconductor-like (MSL) interface in parallel with the PN junction. Devices containing a combination of these two structures have been described by Zettler and Cowley in their Schottky barrier passivation study.[3] The resultant characteristic of such a combination can be determined by summing the normal cell I-V characteristic with that of the MSL interface. As will be seen, the I-V characteristic of a cell exhibiting FS behavior can take on a variety of forms. These variations can be explained as due to differances in the series resistance associated with the MSL interface. Figure 4, for example, shows a typical low temperature I-V curve for a metal-semiconductor diode and its variation with inceasing series resistance. If the series resistance associated with the MSL interface is sufficiently large, as it is in figure 3, addition of the two curves yields the double break characteristic. As the resistance is lowered, however, the second break point occurs further out in the forward characteristic, requiring an increasingly higher forward bias to observe it. In the limit where the resistance is negligible, the device output is controlled completely by the MSL characteristic which is similar to the PN characteristic but which begins to conduct at about one-half of the applied voltage.

DETAILED MECHANISM

Degree of Localization

We have been able to determine that the FS effect is caused by events occurring in localized regions under the front grid metallization. This was accomplished by means of a set of emitter etching and sectioning experiments.

In these experiments the emitters of a group of cells exhibiting the FS effect were chemically removed everywhere except under the metallization pattern. A comparison of the I-V characteristics of such a cell before and after emitter etching is shown in figure 5. It can be seen that while the PN junction characteristic shifted to the right reflecting its decrease in area, the MSL component did not change. It can be concluded, therefore, that the regions responsible for the FS effect lie under the front surface metallization.

The etched cells were then sectioned to determine whether or not the FS-causing regions were homogenously distributed under the metallization. The first sectioning of the cell of figure 5 indicated that the defective region was associated with only one of the grid fingers. When the defective finger was sectioned, further lcalization was indicated, as shown in figure 6. The cause of the FS effect, therefore, was determined to be highly localized and associated with the front grid metallization.

Thermal Activation

We have found that FS behavior can be thermally induced. This is illustrated in figure 7 where the low temperature (-196°C) I-V characteristics of a cell not initially exhibiting a FS is shown at various stages during a series of isochronal (20 minute) heat treatments in an inert atmosphere. Although the lack of a quantitative description of FS development precludes determination of an activation energy, the process can be seen to proceed rapidly when the temperature is raised above 450° C. At the completion of thermal processing the cell output can be seen to be controlled almost completely by the MSL characteristic. In some cases even localized heating is sufficient to induce FS behavior. Cells with initially good low temperature characterics, for instance, have been observed to show the effect subsequent to interconnect-bus bar parallel gap welding.

Metal-Silicon Reactions

The observed temperature range for the formation of the FS effect corresponds to the temperature range cited in the literature for low temperature solid state metallurgical reactions that take place in most metal-silicon systems.[4] With a few exceptions these reactions involve the dissolution of silicon into the metal to form either a silicide or a solid solution, depending on the system. Because of local variations in the dissolution rate, the resulting silicon surface has usually been reported to be irregular or pitted. And indeed, when the metallization is removed from a cell that has been heat treated to induce FS behavior, the underlying silicon is invariably observed to be pitted. Conversely, cells not showing FS behavior have never been found to exhibit pitting. It is consistent with the evidence, therefore, to suggest that the cause of the FS effect is the localized reaction of silicon with the adjacent metallization and the attendent formation of highly conductive metal or metal silicide regions that make direct electrical contact between the front contact metallization and the base of the cell.

Most of the investigations described here were performed on cells with TiPdAg contacting. However, in an attempt to find a metallization system that would resist FS formation, cells with a variety of contact materials were subjected to a one hour heat treatment at 500°C. The results were discouraging in that all metalization systems studied (Table I) produced FS behavior. While all systems investigated degraded upon heat treatment, the temperature for onset of the effect was lower for some metals than for others. Aluminum contacts, for example, began to show FS behavior after only 20 minutes at 350° C, 100° below the onset for the TiPdAg System.

DISCUSSION: PREVENTION TECHNIQUES

Crystallographic Orientation Effects

Since the FS effect is thought to be due to a reaction between the silicon surface and the contact metal, it was felt that degradation should proceed less rapidly on (111) oriented silicon than on the more reactive (100) material. To determine the FS suppressing qualities of (111) oriented material, two groups of 10 ohm-cm TiPdAg contacted cells were identically fabricated, the only difference between the two groups being their crystallographic orientation. These cells were then subjected, in pairs, to a series of either isothermal or isochronal heat treatments in an inert atmosphere. Contrary to expectations, however, the results indicated little difference between the (100) group and the (111) group.

Junction Depth Variations

Another approach to reducing the deleterious effects of the metal-silicon reaction is to increase the junction depth. This would increase the distance the reaction would have to proceed before it penetrates the emitter. To investigate the effects of junction depth variation, two groups of 2 ohm-cm TiPdAg contacted cells with junction depths of 0.25 and 0.75 μM were heat treated in an inert atmosphere. A comparison of I-V characteristics after an isochronal heat treatment (30 minutes each at 377°, 415°, 449°, 485°, 537°, and 555° C) is given in figure 8. As expected a shallow junction makes a device much more susceptable to FS formation. While the 0.75 μM junction cell exhibits a moderate FS, the 0.25 μM cell has completely degraded (output entirely controlled by MSL junction). It should be noted that although these deep junction cells are less prone to FS generation, they suffer from a 10 percent power loss due to the presence of the deep junction.

Effect of Ta_2O_5 Overcoating

In the course of these investigations it was found that the commonly used anti-reflection coating material, Ta_2O_5, can have a marked effect on FS formation in cells contacted with the standard TiPdAg metallization system. It was found that a layer of Ta_2O_5 (no dependence on thickness found) deposited over the TiPdAg metallization can prevent metal-silicon interaction during subsequent heat treatment. This effect is illustrated in figure 9. Prior to a 2-hour, 560° C heat treatment the silicon face shown in the figure was entirely covered by contact metallization, the lower half of which was covered with a 650 Å coating of evaporated Ta_2O_5. After heat treatment the Ta_2O_5 and the metallization were removed, revealing the structure shown in the micrograph. As can be seen the silicon surface below the overcoated metal is unaffected by the heat treatment, while the surface under the uncoated metal is severely pitted. The Ta_2O_5 coating on the surface of the metallization apparently prevents the reaction that would normally take place between the silicon and the adjacent titanium metal.

In order to understand the mechanisms operating here it is helpful to look closely at the details of the titanium-silicon reaction. According to the literature this reaction is unilateral, i.e., silicon diffuses into the titanium with little or no diffusion of titanium into the silicon.[2] It has also been established that when two solids inter diffuse via a vacancy interchange mechanism, any imbalance in the diffusion rates is compensated for by a flow of vacancies in a direction opposite to that of the faster diffusing species.[7] In the present case, therefore, the unilateral flow of silicon atoms into the titanium lattice requires an equal and opposite flow of vacancies through the metal toward the silicon. The large volume of vacancies needed to support the unilateral silicon diffusion must be generated either at a free surface or in a region of high lattice disorder. The most likely source here is the free surface of the contact metallization. Vacancies generated at this surface would diffuse through the metal toward the silicon as required to support the diffusion of silicon into the metallization. It is suggested that the effect of the Ta_2O_5 overcoating on the metal surface is to disturb the vacancy generating ability of this surface and thus to affect the rate of silicon diffusion into the metal. The suppression of pitting by the Ta_2O_5 overcoating is therefore explained by its ability to retard vacancy formation at the metal surface.

If the above reasoning is correct, the passivating qualities of the Ta_2O_5 should be effective for all metallization systems in which silicon is the primary diffuser. These would include systems where metals such as Al[8], Au[8], Hg[9], V[10], or W[11] are deposited in contact with the silicon. On the other hand one would not expect any effect in the case of Mg or Ni contacts where the metal atoms are the diffusing species.[10,12] Some effect would be expected in the intermediate cases of Pt and Pd where the metal and the substrate interdiffuse at roughly equal rates.[10,12]

It should be mentioned at this point that there is one area where the Ta_2O_5 overcoating is not effective in suppressing pitting, i.e., at the edges of the metallization. This is illustrated in figure 10 where pitting can be seen at the edges of a contact finger after heat treatment even though the cell was overcoated with Ta_2O_5. (Special care was taken here to insure that all metal surfaces, both normal and perpendicular to the silicon surface were coated.) The cause of this behavior is believed to be the presence of localized lattice disorder along the edges of the metallization which permits vacancy generation in these regions in spite of the presence of a Ta_2O_5 layer. To illustrate the vacancy generating ability of a disordered metal surface, let us consider the following experiment. Prior to the application of a Ta_2O_5 overcoating to a group cells their contacts were mechanically abraded in localized regions. After heat treatment (560° C, 2 hr) examination of the underlying silicon surface revealed that pitting had occurred where the metal surface had been abraded. The regions where there had been no abrasion were free of pitting. Furthermore, the pits in the abraded regions were arranged in linear arrays parallel to the scratch patterns that had been present on the abraded metal surface. The conclusion is, therefore, that the damaged regions are apparently capable of supplying a vacancy flux sufficient to support silicon dissolution even though the metal surface had been overcoated with Ta_2O_5.

If we consider now the mechanical stresses generated in cell contacts due to the difference in thermal expansion between the cell and the contacts we see there is reason to believe that the edge regions of the contacts are indeed likely to be regions of lattice disorder. Zeyfang,[13] for example, has calculated the magnitude and distribution of the stresses developed in a thin plate of finite dimensions bonded to a semi-infinite substrate with a different thermal expansion coefficient. According to these calculations, the stresses induced in the plate as the temperature is varied are highly nonuniform. They are, in fact, found to be concentrated almost entirely at the edges of the plate. Depending on the circumstances these stresses could exceed the yield point of the plate and the resulting plastic flow would result in a concentration of lattice disorder in these regions. It is suggested, therefore, that thermal excursions subsequent to the deposition of the contact metallization are in general sufficient to cause lattice disorder near the edges of the contact metallization. These regions would then act as vacancy sources and support localized disolution of the underlying silicon even though a Ta_2O_5 overcoating may have been applied. It would follow that this type of pitting should be able to be prevented by eliminating large temperature excursions after metal deposition.

Diffusion Barriers

While Ta_2O_5 overcoating shows some promise in the prevention of the FS effect, the most straightforward approach would be to impose a diffusion barrier between the metal and the silicon. Two such systems have been advocated in the literature but neither has been applied specifically to the present problem. The first is the use of an amorphous metal-silicon alloy barrier.[14] While it has been shown that diffusion proceeds extremely slowly in these materials, they have the disadvantage that they are limited to temperatures below their recrystallization temperatures which, for the alloys investigated, are in the range $500° < T < 550°$ C.[14] Also suggested as barrier materials are the metal nitrides, and in particular, TiN.[15] This compound has reportedly prevented silicon-metal interdiffusion to temperatures approaching 600° C. In an attempt to apply this approach to the problem at hand we have generated some encouraging preliminary data. A group of cells with a 1000 Å TiN interlayer deposited between the silicon and the TiPdAg metallization were subjected to a series of 20-minute isochronal heat treatments at 25° intervals from 350° to 600° C. In contrast to previous experience with barrier-free cells, a number of the TiN barrier cells maintained good characteristics throughout the testing, finishing with only a slight indication of FS behavior. It should be noted that before this run we had never observed a cell that was able to withstand a 550° C heat treatment without severe degradation. The TiN interlayer thus appears to be effective in attenuating to a great extent the FS-causing metal-silicon interactions. The implicit assumption here of course is that the TiN barrier cells that failed in this run did so because of a lack of integrity (pin holes or such) in the as deposited barrier layer. Further work in this area certainly appears to be warranted.

CONCLUSIONS

The major conclusions to be drawn from the preceding analysis are:

1. The flat-spot phenomenon is due to events occurring in localized regions under the front grid metallization.

2. These localized regions are regions in which the PN junction has been destroyed and replaced with a metal-semiconductor-like interface.

3. The localized structural changes are due to thermally activated metallurgical reactions between the silicon substrate and the contact metallization.

4. All metallization systems studied have been shown to be active in the production of FS behaviour.

5. Deep junction cells with TiPdAg contact metallization systems show less FS behavior after heat treatment than do shallow junction cells.

6. (111) and (100) oriented cells with TiPdAg contact metallization systems are equally susceptable to FS behavior.

7. Silicon-metal reactions under as-deposited TiPdAg metallization can be suppressed by overcoating the metal with Ta_2O_5. The overcoating effectively prevents the formation of vacancies at the free metal surface which are necessary to support the reaction.

8. The Ta_2O_5 overcoating is not effective if the metal surface is highly disordered.

9. The edges of the cell metallization have been found to be sites of considerable lattice disorder, probably due to thermal cycling during cell fabrication. The disorder renders these areas nonresponsive to Ta_2O_5 passivation.

10. Preliminary data indicates that the application of a TiN diffusion barrier between the cell and TiPdAg contact metallization is effective in preventing FS behavior.

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TABLE I. - METALLIZATION SYSTEMS STUDIED AND FOUND TO INDUCE FLAT-SPOT BEHAVIOR

Ti-Pd-Ag
Cr-Au-Ag
Al
Al-Ag
Ag
Zr-Ag
Ta-Ag
Hf-Ag
Ce-Ag
Ni-Cu-Au
SNO_2-Ti-Ag

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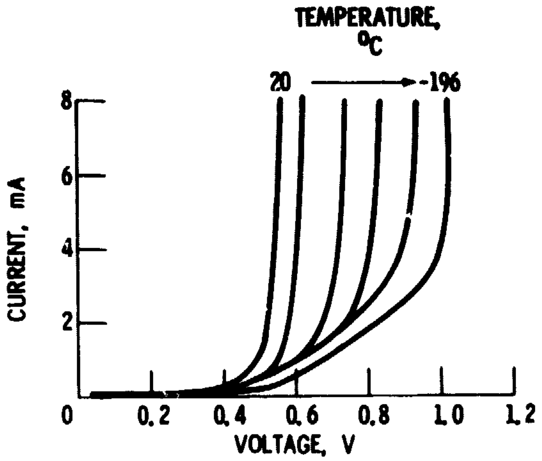

Figure 1. - Flat-spot development with decreasing temperature.

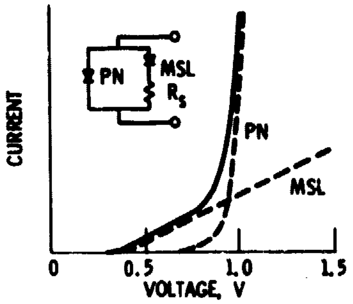

Figure 3. - Schematic diagram of FS mechanism. Solid curve is sum of PN and MSL characteristics.

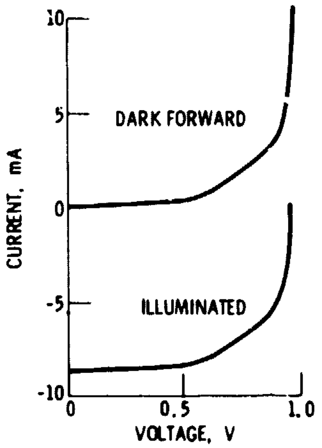

Figure 2. - Comparison of dark forward and illuminated characteristics at - 196° C.

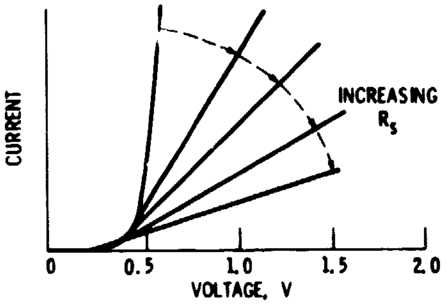

Figure 4. - Effect of varying resistance R_s on metal-semiconductor-like interface characteristics.

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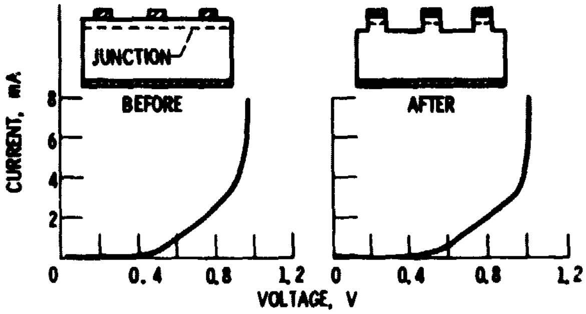

Figure 5. - Comparison of I-V characteristics before and after emitter etching.

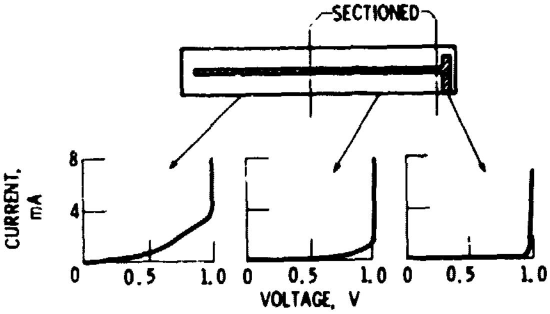

Figure 6. - Determination of location of flat-spot-causing centers.

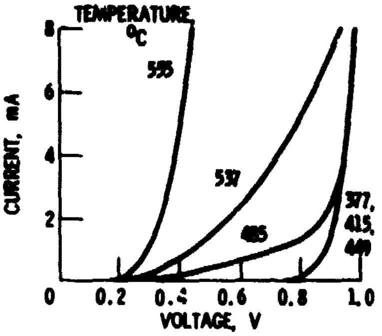

Figure 7. - Effects of isochronal (20 min) heat treatment at various temperatures on low-temperature (-196° C) I-V characteristic.

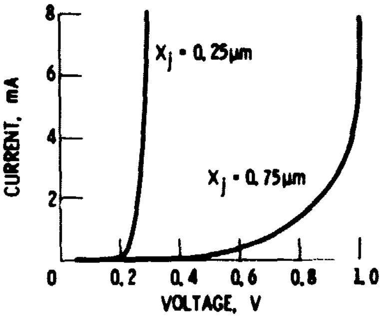

Figure 8. - Comparison of deep- and shallow-junction cells after heat treatment.

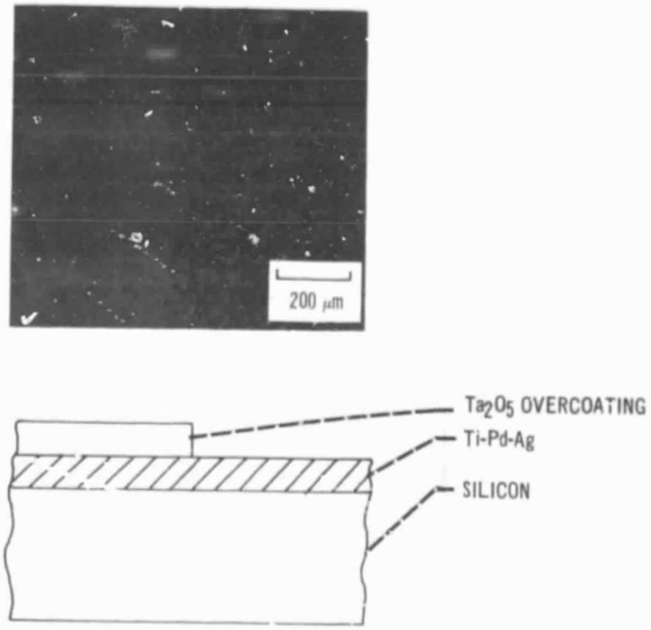

Figure 9. - Effect of Ta_2O_5 overcoating on silicon surface pitting heat treatment, 560° C for 2 hr; inert atmosphere.

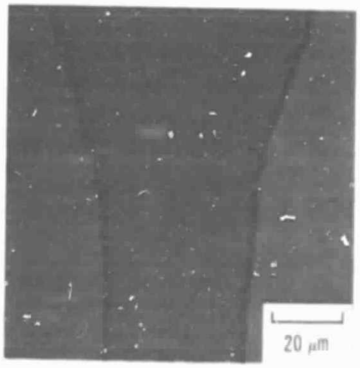

Figure 10. - Pitting observed at metallization edges after 2-hr, 560° C heat treatment with Ta_2O_5 overcoat applied.