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ACCELERATED DEGRADATION OF SILICON METALLIZATION SYSTEMS

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INTRODUCTION

Clemson University has been engaged for the past five years in a program to determine the reliability attributes of solar cells by means of accelerated test procedures (1). The approach, as shown in Figure 1, is to electrically measure and visually inspect the cells, then subject them for a period of time to stress in excess of that normally encountered in use, and then to remeasure and reinspect the cells. Changes are noted and the process repeated. This testing has thus far involved 23 different unencapsulated cell types from 12 different manufacturers, and 10 different encapsulated cell types from 9 different manufacturers. Unencapsulated cells were subjected to a variety of tests: bias-temperature testing at 75, 135, and 150 C, bias-temperature-humidity testing at 85% relative humidity and 85 °C, pressure cooker testing at 121 °C and 15 psig steam, and thermal shock and thermal cycle testing from +150 to -65 °C. Encapsulated cells because of the limitations of organic pottants have been subjected mainly to 85/85 testing and to thermal cycle from +95 to -65 °C.

The basic structure of a solar cell is shown schematically in Figure 2. In an effort to simplify the manufacturing process the metallization on both sides of the cell is usually the same. The purpose of the metallization is twofold: to make electrical connection to the silicon and to transport the current to the leads. Solar cell metallization systems in general consist of a thick current carrying layer plus one or more thin barrier/strike layers which interface the conductive layer to the silicon. There are essentially four different generic metallization systems in use today, as shown in Figure 3 -- vacuum deposited silver (titanium/palladium/silver), electroplated copper, screen printed silver frit, and solder coated nickel. In this figure the thick conductive layers are shown approximately to scale and the effect of different electrical conductivities can be easily seen. The thick high conductivity layer primarily influences the cost of the system, while the barrier/strike layers primarily influence the reliability of the system. In a comprehensive study of metallization costs, which considered both materials and processing, Wolf and Goldman (2) showed the thick layer to be the cost driver and they concluded that the only system which could be considered truely low cost was the copper plated structure.

Reliability attributes of metallization systems can be classified as major or minor, depending on the severity of the effects observed. As a result of the accelerated testing conducted under the Clemson program, major effects have been observed related to contact resistance and to mechanical adherence and solderability. Increasing the contact resistance as a result of stress will cause a degradation of the cell's electrical output, while

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adherence and solderability problems can result in catastrophic failure through open circuits. Minor effects observed include diffusion of metallization into the bulk semiconductor resulting in decreased minority carrier lifetime and a consequent reduction of Isc and possibly increased series resistance. Dissolution of metallization through corrosion resulting in increased series resistance is also possible, but has not been identified as a significant problem in cells tested thus far.

As summarized in Figure 4, the thick layer has essentially only two functions -- to transport current and to provide a solder interface to the external lead -- whereas the thin layers have a number of functions. These include making an ohmic, low resistance connection to the silicon, serving as a non-penetrating diffusion barrier, providing a uniform and easily p. table surface, serving as the glue for good adherence of the thick layer, and providing a transition layer for any thermal mismatch.

The cells tested in the Clemson program had a wide variety of barrier/strike layers. Conductive layers could easily be identified as belonging to one of the four catagories shown in Figure 3, but more often than not the composition and thickness of the barrier/strike layers was unknown. Furthermore, manufacturers are naturally reluctant to release proprietary information on film composition and deposition techniques, which represents one of the key trade secrets of solar cell processing. Therefore, despite the numerous accelerated tests which have been run, it is difficult to interpret the data obtained on specific cell types as relating to generalized metallization systems. In addition to the uncertainty of the metals and the deposition methods involved, it is often difficult to attribute the degradation observed as a result of testing to the metallization, rather than to some other aspect of the solar cell. The loss of mechanical adhesion, for example, would appear to be a straightforward problem of metallization, but an increase in series resistance could be either a contact problem or a change in the bulk resistivity. This paper, therefore, does not attempt a generalized survey of accelerated test results, but rather concentrates on one particular attribute of metallization that has been observed to cause electrical degradation -- increased contact resistance due to Schottky barrier formation. In this example basic semiconductor theory was able to provide an understanding of the electrical effects observed during accelerated stress testing.

EXPERIMENTAL OBSERVATIONS

Most cell types when subjected to bias temperature testing in the unencapsulated mode show only a slight increase in series resistance. A few cell types, on the other hand, show a large increase in resistance accompanied by a pronounced non-linearity as shown in Figure 5. Construction of these cell types involved a flash of gold to provide a good plating surface, followed by electroless nickel plating, followed by a solder dip to provide the thick conductive layer. The cell itself was p+ on n. The non-linear shape of the IV characteristic implied the formation of a rectifying contact, and because the back was lightly doped, this would be the most likely location for its formation. To simulate this a discrete Schottky barrier diode was connected to the back of an unstressed cell with the result shown in Figure 6. When the diode by itself was connected into the circuit (using leads having 0.1 ohm resistance) curve B was obtained. In the power quadrant it can be seen that the effect of the forward diode drop was to push the IV characteristic to

lower voltages with a consequent reduction in power output. In the far forward region only the diode leakage current flowed. This gave rise to a pronounced non-linearity. If a 0.5 ohm resistor was placed across the diode, curve C was obtained which showed a less pronounced non-linearity, more nearly approximating the shape of Figure 5. Of course, any rectifying contact which would be formed as a result of accelerated stress would not be expected to be of ideal shape, but only to exhibit greater resistance in one direction than in the other. The presence of such a "poor" rectifying contact was further confirmed by fitting the IV characteristics of stress tested cells using the SPICE computer model. In this simple lumped constant model the solar cell was represented by a current source in parallel with a diode. The rectifying Schottky barrier contact was represented by a diode having a 0.69 eV band gap (vs 1.11 for Si) in series with the cell in exactly the same way as was physically performed for Figure 6. The contact diode's resistance in the reverse direction could then be adjusted to give the best fit to the characteristic. Additional resistance was introduced in series with the cell to simulate the cell's series resistance. Other more complicated models are also possible, but this one gave reasonable results as can be seen from the degree of fit achieved in Figure 7. Also shown is the contact diode characteristic which was required for this fit, illustrating its poor rectification shape. This same shape was also directly confirmed by probing small isolated areas of the back contact relative to the main area.

Having shown that non-linear degradation is diode related, a very simple model of a metal to semiconductor contact will now be developed in order to examine conditions under which a rectifying contact could be formed at the back surface of the cell.

METAL TO SEMICONDUCTOR CONTACT THEORY

Figure 8 shows idealized energy band diagrams for an n-type semiconductor and a metal, both when seperated and when joined. The work function of a metal is the amount of energy required to remove an electron from the Fermi level of the metal to infinity, whereas the electron affinity of a semiconductor is the energy required to remove an electron at the conduction band edge to infinity. When the metal is far removed from the semiconductor, as in Figure 8(a), both the work function and the electron affinity are referenced to infinity and, in the absence of surface effects, the bands will be flat as shown. When they are brought together in thermal equilibrium, however, the Fermi levels must line up and the difference between the metal's work function and the semiconductor's electron affinity causes the bands to bend as shown in Figure 8(b). Such band bending requires an electric field which comes from negative charge accumulating on the metal and positive charge on the semiconductor. The positive charge in the semiconductor is the result of "uncovered" donor atoms in the space charge region. As a consequence a potential barrier (ϕ_B) exists between the metal and the semiconductor much as occurs at a semiconductor p-n junction. This is a Schottky barrier and the junction will exhibit rectification properties. In this simple theory the barrier height is the difference between the work function and the electron affinity.

At actual metal-semiconductor contacts the situation is more complicated as shown in Figure 9. As shown in this diagram, a thin insulating layer (oxide) may exist between the metal and the semiconductor. This layer can be so thin as to be transparent to electron conduction, but at the same time

contain charged surface states. Thus, in addition to the charge on the metal (Qm) and the semiconductor (Qsc), charge will exist in surface states (Qss) at the semiconductor-oxide interface. The presence of these surface states clamps the barrier height and makes it essentially independent of both the metal work function and the bulk doping of the semiconductor (for light to moderate doping). The barrier height in a practical case thus depends on such factors as the surface preparation (cleanliness) performed prior to deposition of the metal, the presence of a thin layer of native oxide, and the deposition technique used.

When a forward bias is applied across the barrier, conduction may occur by either or both of two mechanisms, as illustrated in Figure 10. Electrons may have sufficient energy to surmount the barrier (which is now slightly rounded as a result of image force effects), or if the barrier is suffiently thin, they may tunnel through it quantum mechanically. In either case the thin oxide is considered to be essentially transparent to electrons. Thus a metal semiconductor contact may be either ohmic or rectifying depending on the barrier's height and thickness. This is illustrated in Figure 11, where the oxide layer has been omitted for simplicity. If the barrier is low enough electrons are able to pass freely over it and an ohmic contact results. If the barrier is thin enough, as will occur when the substrate is highly doped, as by the n+ layer of Figure 11a, electrons will tunnel through the barrier and the contact will also be ohmic. Thus either a low barrier, a thin barrier, or a combination of the two results in an ohmic contact. On the other hand, if the barrier is high and thick, as will occur with a lightly to moderately doped substrate having the proper surface state conditions, a rectifying contact can occur as shown in Figure 11b.

The final pieces of information needed to analyze solar cell contacts concern the polarity of the surface states that can be expected on silicon and their effect on the barrier height. As was mentioned, a number of variables can contribute to the magnitude and polarity of the surface states, but recent work (3) using low-energy, ion-scattering spectrometry on thin oxides such as would be expected to form naturally at room temperature, has determined that the silicon atoms in the oxide adjacent to the interface are deficient in oxygen. A silicon atom with an unsatisfied (dangling) bond represents a positive charge. Hence the effect of this non-stoichiometric layer is to place a positive charge on the oxide side of the semiconductor-oxide interface as was illustrated in Figure 9. It has been demonstrated experimentally (4) that it is possible to control Schottky barrier height over a wide range by using very shallow, highly doped ion implanted layers. The effect of such artifically produced layers will be similar to the naturally occurring surface charge layers we are postulating. It was found in this work that positive charge on n-type silicon reduced the barrier height while positive charge on p-type silicon increased the barrier height. We are now in a position to analyze the non-linear degradation observed after stress on some types of cells.

ANALYSIS OF TEST RESULTS

Since the cells in question have a moderately doped n-type substrate the theory presented above would indicate that the contact formed initially to the back should be ohmic because the positive surface state charge at the interface will result in a low barrier height. This agrees with our

experimental observations. In order for the contact to become rectifying under stress testing neutralization of the positive charge at the surface is postulated. The most probable method of neutralization would be for oxygen atoms to complete the dangling silicon bonds (achieve stoichiometry) at the interface. In order for this to occur oxygen must diffuse to the interface from elsewhere in the structure. It would appear difficult for oxygen to diffuse through the thick metal contact from the ambient, and it is more likely that it would come from oxygen dissolved in the metal or in the silicon. The ability of oxygen to diffuse in a metal is related to the free energy of formation of its most stable oxide. If the free energy (ΔF^o) is low (small negative value or positive) then oxygen does not react easily with the metal and it can diffuse with ease. As can be seen from the data of Table 1, this would be true for such metals as Au, Cu, Pb, Ni, and Ag. On the other hand, when the free energy is high (large negative values) a strong reaction between the metal and oxygen occurs and diffusion is difficult. Examples are Al, Cr, Mg, Mo, Si, Ta, and Ti. Thus the Si/Au/Ni/Solder structure being considered would allow oxygen dissolved in the metals to freely diffuse to the interface, but not oxygen dissolved in the silicon. Oxygen diffusing to the interface will neutralize the dangling silicon bonds causing the barrier height to increase and the contact to become rectifying. This agrees with the experimental observations shown in Figures 12 and 13. A comparison of the curvature of the far forward characteristics of the two figures indicates that 2300 hours at 135 °C is equivalent to roughly 100 hours at 150 °C. This would correspond to an activation energy of approximately 3 ev., a reasonable value for a diffusion process.

CONCLUSIONS

Two routes are thus open for the fabrication of ohmic contact to the back surface of a solar cell -- a safe route using a heavily doped substrate (e.g. back surface field) which permits electrons to tunnel through the potential barrier, or a more dangerous route which utilizes a moderately doped substrate plus a low barrier height. The reason the latter route is considered dangerous is that conditions for achieving a low barrier height depend on the density of surface states, which can change under stress. For the particular cells described in this paper it is hypothesized that the surface states were originally positive charges, occurring as a result of dangling silicon bonds, and were later neutralized under high temperature stress by diffusion to the interface of oxygen dissolved in the metal. Modification of surface states in this fashion will tend to make a contact which was originally ohmic become rectifying, and one which was originally rectifying become ohmic.

The effect depends on the existance of a thin oxide layer and will only occur when the metals used do not react with oxygen, i.e. have a low free energy. If a metal is used having a high free energy, and is heat treated, it will react with the oxide and either change the surface states or dope the semiconductor so that a Schottky barrier may no longer exist. A good example is aluminum which has been used for more than two decades in the fabrication of integrated circuits. Aluminum can make a rectifying Schottky barrier contact to either n- and p-type silicon (moderately doped) when originally deposited. Heating to 400 °C, as is normally done during integrated circuit fabrication, allows the aluminum to reduce the native oxide. The solid solubility of silicon in aluminum is sufficiently high that a thin p-type epitaxial layer is produced upon cooling down even though the eutectic

temperature was not reached. On moderately doped n-type silicon this will result in a rectifying Schottky barrier, while on moderately doped p-type silicon an ohmic contact will result (5). It should be pointed out, however, that random fluctuations in the thickness and doping of the precipitated silicon layer can cause fluctuations in the barrier height, which in turn translate into fluctuations in diode characteristics, so that aluminum is not considered a suitable metal for Schottky barriers in integrated circuits. Platinum silicide which forms a high barrier height (0.84 ev) on n-type silicon and which, by virtue of being an in situ formed compound, is insensitive to interface conditions is now used instead.

The cells described in this report which exhibited non-linear behavior, and consequent loss of power output, after B-T testing, appeared to have been made in exactly the wrong manner. A moderately doped substrate was used which resulted in a wide barrier not favoring tunneling . The substrate was n-type so that neutralization of the interface charge as a result of stress testing raised the barrier height and made the contact become rectifying. The metals chosen had low values of free energy favoring rapid diffusion of neutralizing oxygen atoms. Finally, although not directly related to Schottky barrier formation, the gold flash used to insure uniform plating was able to diffuse to the junction from the top under some conditions of stress, reducing the minority carrier lifetime and resulting in lower Isc as seen in Figure 13.

It should be noted that the analysis presented in this paper is based on circumstantial, but self-consistant evidence. The ideas were based on concepts developed over years of single crystal silicon device investigations, but in order to prove (or disprove) the model, micro analytical techniques utilizing methods such as scanning Auger analysis and secondary ion mass spectrometry will need to be used. While many of the ideas presented here should be applicable to other constructions, such as amorphous cells, interpretation will undoubtably be more difficult since the materials are less well understood than those in silicon cells.

REFERENCES

1. Lathrop, J.W. et al, "Accelerated Stress Testing of Terrestrial Solar Cells," IEEE Transactions on Reliability, vol. R-31, p.258 (1982)
2. Wolf, M. and Goldman, H., "Assesment of Metal Deposition Processes," DOE/JPL Report 954976-81/12, January 1981.
3. Harrington, W.L. et al, "Low-energy Ion-scattering Spectrometry (ISS) of the SiO2/Si Interface," Applied Physics Letters, vol. 27, p.644 (1975).
4. Shannon, J.M., "Control of Schottky Barrier Height Uing Highly Doped Surface Layers," Solid State Electronics, vol. 19, p. 537 (1976).
5. Card, H.C., "Aluminum-Silicon Schottky Barriers and Ohmic Contacts in Integrated Circuits," IEEE Trans. Electron Devices, vol. ED-23, p.538 (1976)

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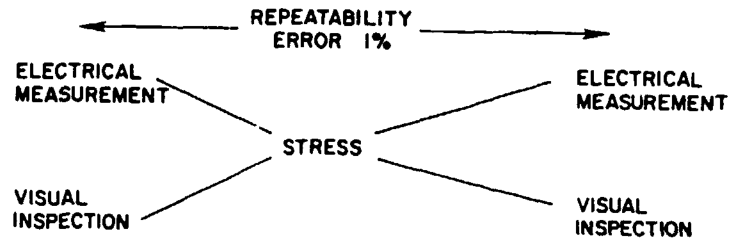
Figure 1.



ELECTRICAL PARAMETERS

V_{oc} I_{sc} R_s V_m I_m P_m

INSPECTION

LOW POWER MAGNIFICATION

PHOTOGRAPHY

Figure 2. Basic Solar Cell Structure

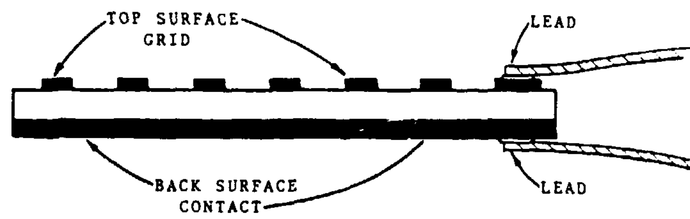


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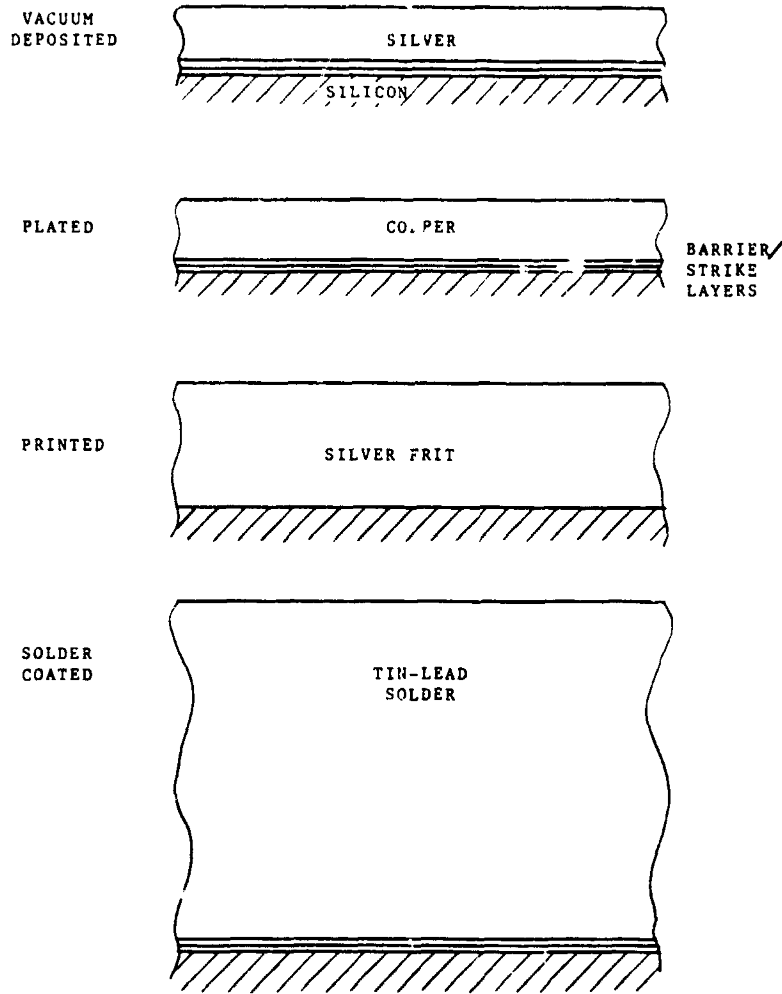
Figure 3. Common Solar-Cell Metallization Systems



(THICK CONDUCTIVE LAYERS APPROXIMATELY TO SCALE)

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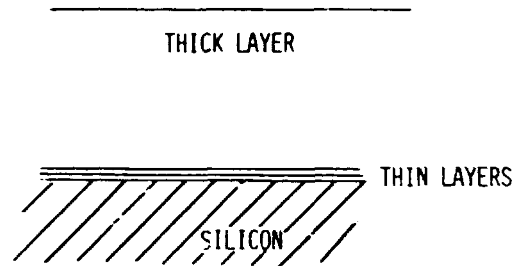
Figure 4. Metallization Layer Functions



<u>THICK LAYER</u>

- TRANSPORT CURRENT
- SOLDER INTERFACE TO LEAD

<u>THIN LAYERS</u>

- OHMIC LOW R_c CONNECTION TO SILICON
- NON PENETRATING DIFFUSION BARRIER
- UNIFORM PLATING SURFACE
- ADHESION (GLUE)
- THERMAL EXPANSION MATCH

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Figure 5. Nonlinear I-V Characteristics After Stress

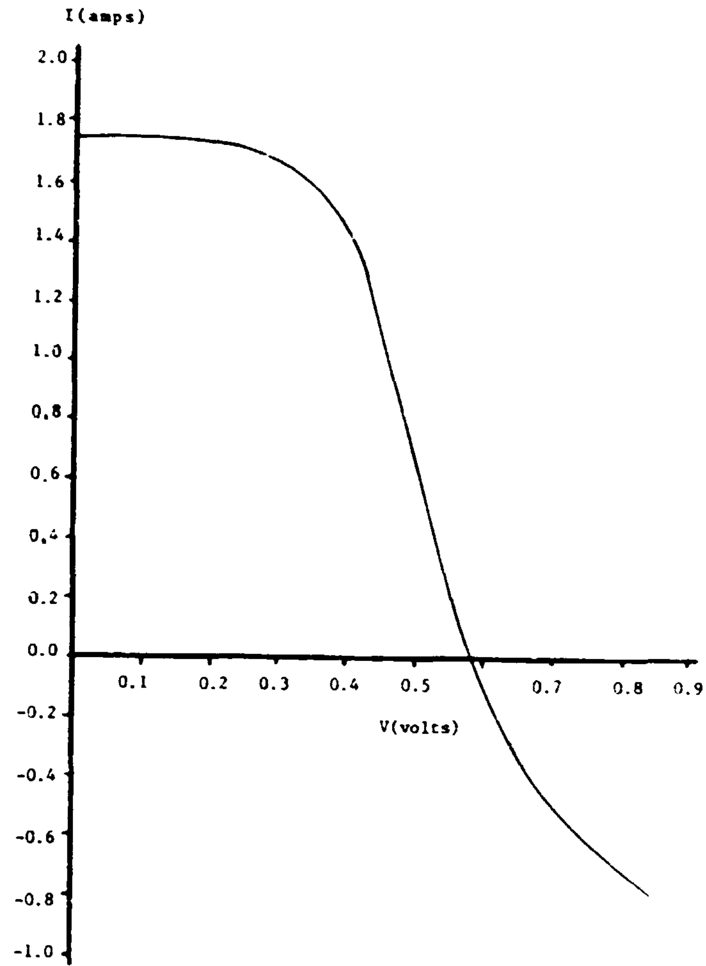

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Figure 6. Contact Degradation Simulated by Lumped Constant Method

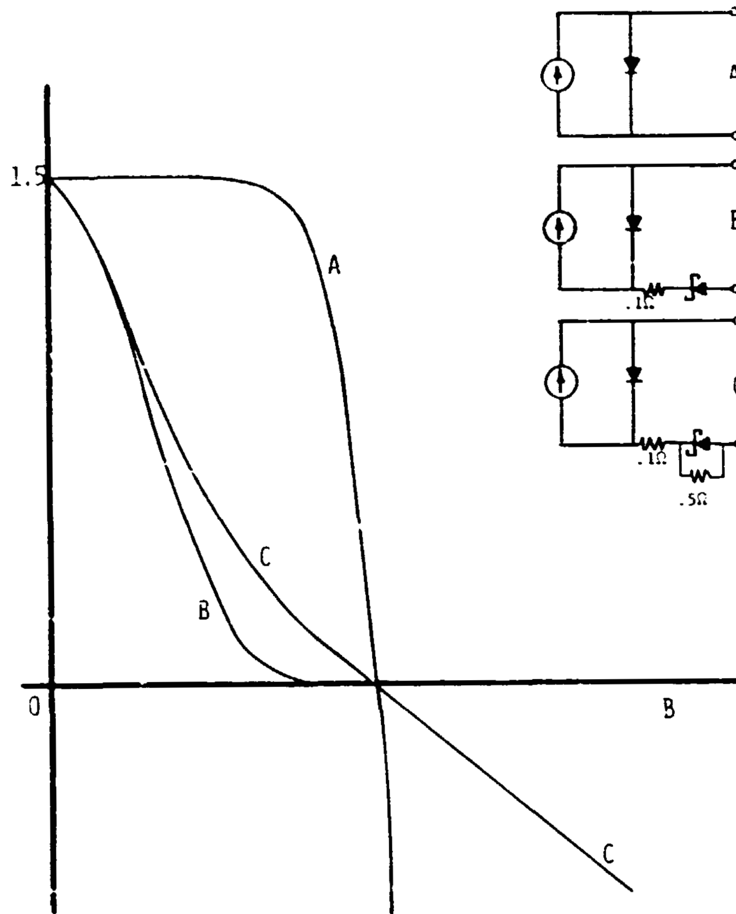

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Figure 7. Characteristics of PV Cell After 600 Hours at 150°C as Fitted by Spice Model Incorporating Rectifying Contact

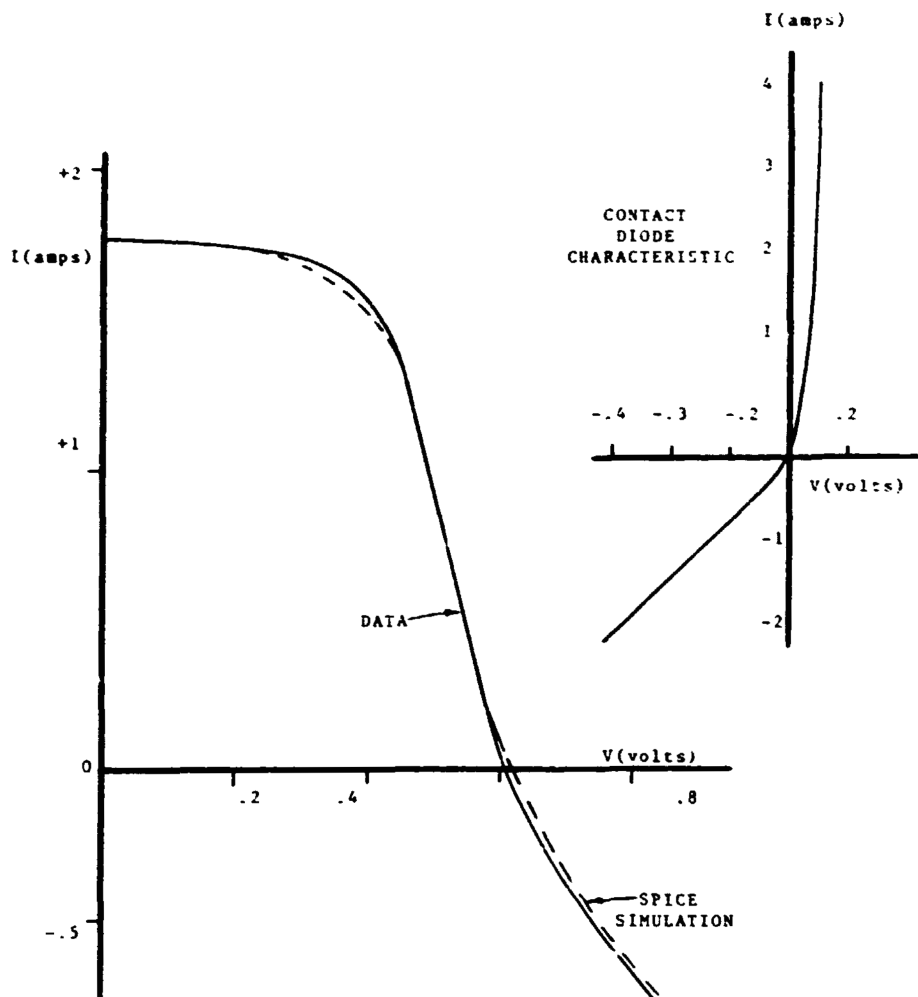

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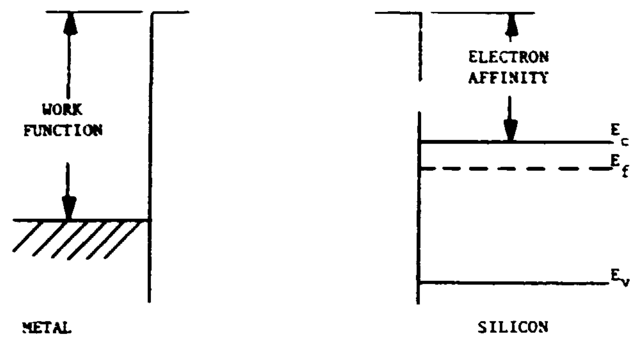
Figure 8. Idealized Energy Band Diagram Without Surface States



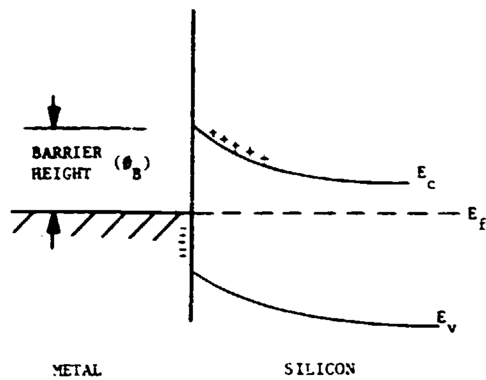


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Figure 9. Energy Band Diagram With Thin Interfacial Layer Containing Positive Charge

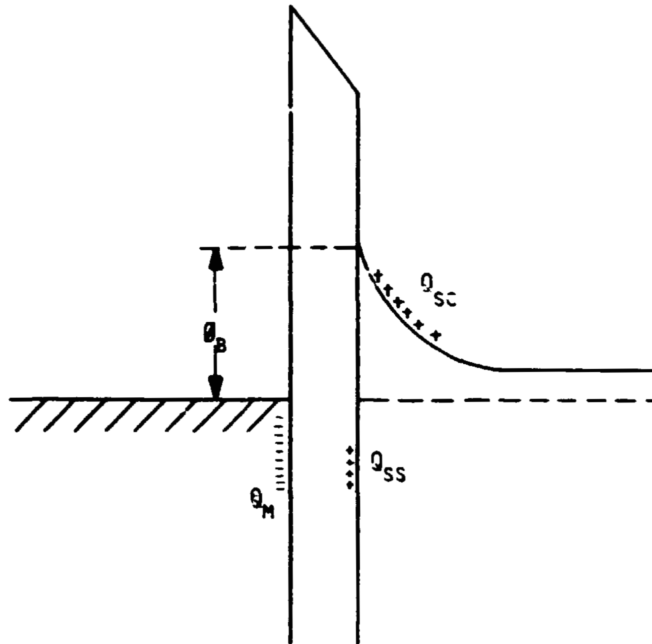

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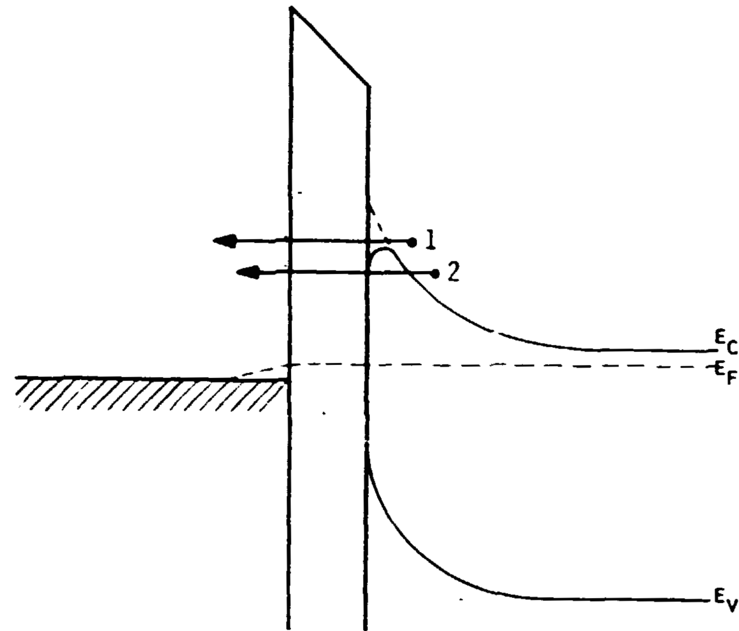
Figure 10. Nonrecombination Transport Mechanisms



1) OVER BARRIER TRANSPORT

2) QUANTUM-MECHANICAL TUNNELING

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Figure 11. Rectifying (Schottky) Contact Ohmic and Rectifying Barrier Configurations

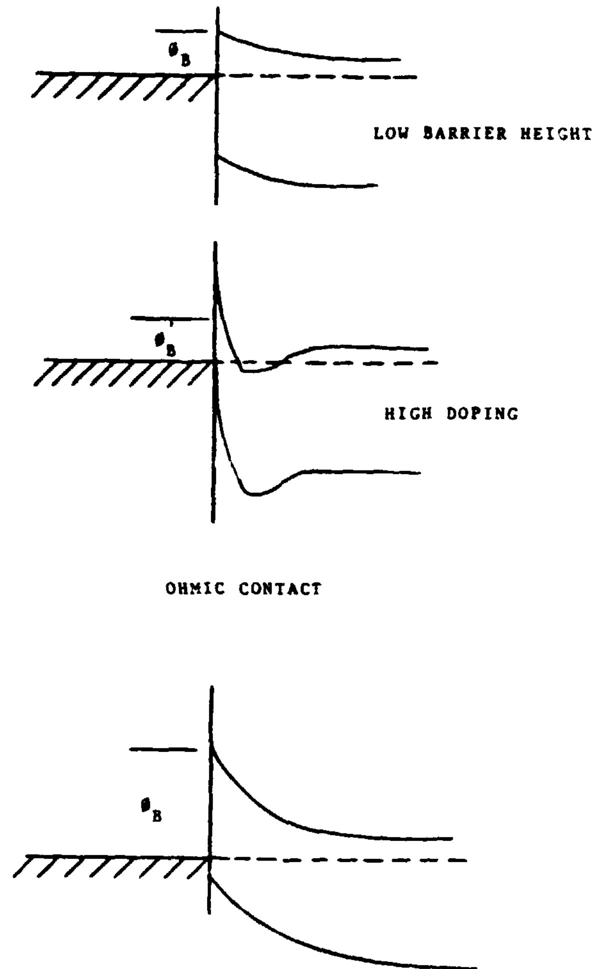

Figure 12. I-V Characteristics for Typical $p^{+}n$ Solar Cell Having Au-Ni-Solder Contacts Subjected to 135°C Bias-Temperature Stress

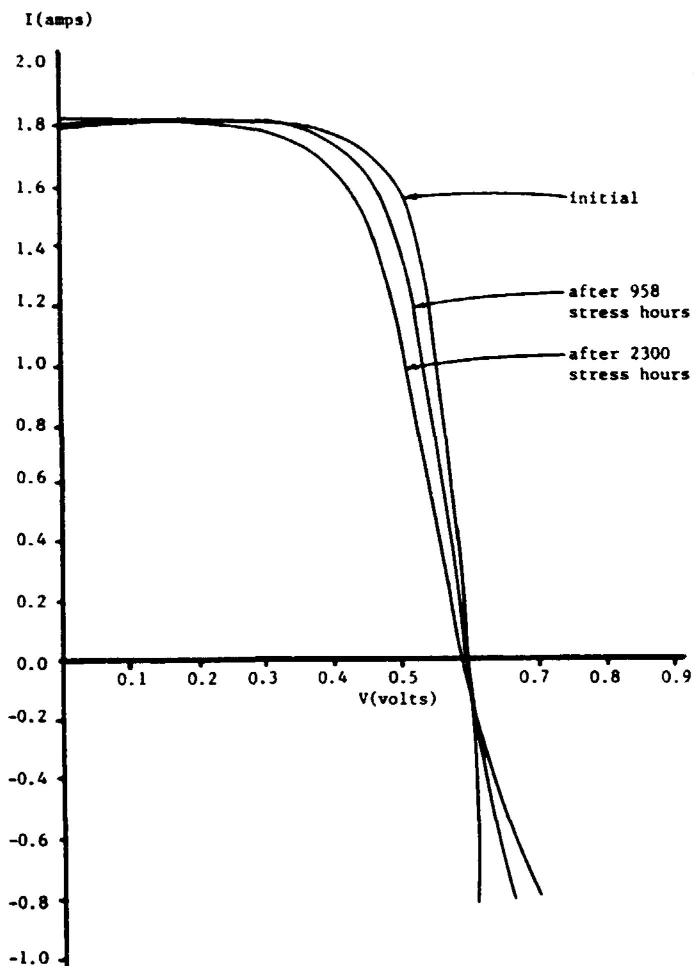

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Figure 13. I-V Characteristics for Typical $p^{+}n$ Solar Cell Having Au-Ni-Solder Contacts Subjected to 150°C Bias-Temperature Stress

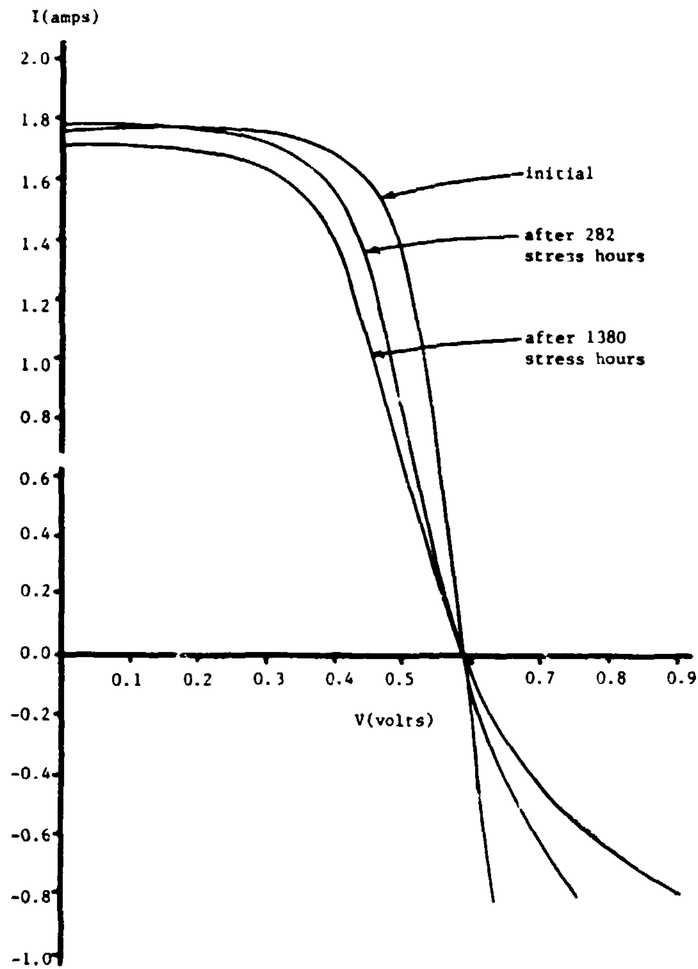

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Table 1. Measured Ionization Energy of Various Impurities in Silicon and the Free Energy of Formation of Their Most Stable Oxides

	P-TYPE $E-E_v$ (eV)	N-TYPE $E_c - E$ (eV)	ΔF° (KCAL)		P-TYPE $E-E_v$ (eV)	N-TYPE $E_c - E$ (eV)	ΔF° (KCAL)
Al	.067		-376.7	Hg	.76,.81	.79,.87	
Sb		.039		Mo	.33,.78,.82		-161.95
As		.054		Ni	.23,.77		-51.7
Ba	.5	.32		O	.41,.74	.16,.51	
Be	.17,.42			Pd	.34		-52.2
Bi		.069		P		.045	
B	.045			Pt	.36,.87	.82	
Cd	.3,.55,.67,.92		-.53.79	K		.26,.77	
C		.25		Se		.25,.4	
Cs	.5	.3		Si	.87	.63,.93	-192.4
Cr		.41	-250	Ag	.76	.79	-2.59
Co	.35,.49,.59		-51.0	Na		.77	
Cu	.24,.4,.53			Sr		.28.62	
Ga	.072			S	.48	.26	
[illegible]		.27,.62		Ta		.14,.43	-471
Au	.58	.83	+39.0	Te		.14	
In	.16			Tl	.3		
Fe		.14,.51,.72	-177	Sn	.25	.85	-124.2
Pb	.37	.17	-45.25	Ti		.21	-204
Li		.033		W		.22,.3,.37,.78,.81	-182.47
Mg	.87,1.01		-136.13	V	.4	.49	-271
Mn	.45	.43,.59		Zn	.26,.57		-76.0

DISCUSSION

RIEL: Were all the cells fabricated with single-crystal material?

LATHROP: Yes, as far as I know. It's single-crystal, and that is the only way of growing crystals this size.

REIL: I guess the next question is, what was the size of the cell you were using.

LATHROP: There were a couple of sizes, three-inch and four-inch. It was not one cell that showed this, there was --

REIL: Do you know anything about the oxygen concentration that they had in the original materials?

LATHROP: No, I don't, but I don't believe that oxygen will diffuse through silicon very rapidly, because it has high free energy of formation so I don't believe that is the phenomenon that is occurring.

GARCIA: Would it be possible to make a rectifying contact and watch it get better with time to sort of prove this?

LATHROP: In my theory it should be. You have a good point there. This is all based on self-consistent but rather circumstantial evidence. In order to prove it, one would have to go to Auger analysis or low-energy ion mass spectrometry or something like that. It would be very interesting also to look for oxygen, to look for neutralization, to look for diffusion.

GARCIA: I think I can give you a lot of rectifying contacts I have made.

WONG: In your abstract you mentioned the role of encapsulants in encapsulated and unencapsulated cells. Do you have any data?

LATHROP: Yes. We have a lot of data on both. But I did not want to present that in this talk because I really had no way of making a general conclusion, so I thought it would be more interesting to go to a specific thing we saw. I would be happy to talk with you about what we have found in our general testing procedures afterwards.

WONG: Are they all terrestrial cells?

LATHROP: Yes. They are all commercial state-of-the-art terrestrial cells. Not experimental.

WOLF: You mentioned primarily the gold-nickel system as the one that shows the formation of the Schottky barriers. You must have tested other cells and other methods.

LATHROP: That is right.

WOLF: Is that always a predominant failure mechanism that the Schottky barrier develops during various heat treatments --

LATHROP: Not at all. The only one with lightly doped substrate we looked at had gold-nickel, so I can't draw any conclusions about anything else that would happen. All I can say is that had the manufacturer gone to heat treatment of one sort, that probably would have changed things. It might have changed things for the worse. In other words, heat treating with nickel silicide, to form a nickel silicide, I don't know what that is going to do. Bill Taylor could probably tell you but I'm not sure in my own mind whether that is going to make things better or worse than just a plain low-high Schottky barrier. But anyway, the only things that we saw it on were moderately doped substrates. The other cells, in general, had a p^+ substrate, p^+ on p back-surface field. In these we don't see this rectification. We have never seen rectification on p^+ and so my advice is always use a back-surface field, not for better efficiency but for better reliability.

WOLF: Then the other trends have always given you different material for blackmail other than formation of Schottky barriers.

LATHROP: That's right. I have something on them too. Next meeting, we will talk about that. No. I have something on everybody.

SOMBERG: You mentioned at the beginning of your talk that a lot of your tests were at fairly high or low temperature extremes. It seems, in the FSA program, that most of the thermal cycling is from -40° to +90°C and in real-life situations out in the field modules were sitting typically at relatively moderate temperatures. Would you care to comment about the temperature extremes and any extrapolation you have done in terms of this new 30-year lifetime?

LATHROP: It is very difficult to try to relate accelerated testing to real life unless you have some way to get there. You know you have to have field data and you have to have some way of extrapolating the field data. For example, in bias-temperature testing you can go through a bunch of different temperatures and you can attempt to get some sort of activation energy, which you extrapolate back to room temperature. This is more difficult than something like thermal cycling. I don't know how to do it. The only thing that I can say is that if cell A goes through the thermal cycling with no problems, and then cell B has all kind of problems, cell B is worse than cell A. But both cell A and cell B may last for 30 years. I just don't know. But it behooves the manufacturer of cell B to take a look at it and try to improve it. That's all I can say. All I can talk about at the moment with regard to this is the relative aspects with regard to other cell types, but not with regard to an absolute "will it last 30 years?"

SCHWUTTKE: I have one question. I am interested in your model based on the oxygen. What you say very simply is that the property of the contact depends very much on whether you have an oxygen-rich or an oxygen-poor surface, is this correct?

LATHROP: That's my thinking, yes. Except that --

SCHWUTTKE: Now I would like to bring to your attention that this may not be generally known and I would like to know your thinking how this would tie in. You have very little control on what the oxygen concentration is in a wafer after processing. This depends on, and ties in readily with, the original oxygen content in your wafer. After one heat treatment, depending on the atmosphere -- be it oxygen, be it nitrogen, or whatever -- you may have a surface which is oxygen rich or oxygen poor. Now this would lead to great variety in your contact formation.

LATHROP: Except that in my simple-minded theory I feel that the oxygen is coming from the metal, not from the silicon.

SCHWUTTKE: Yes, but you must have some kind of equilibrium, whether it is coming through the metal, through the interface, and depending on what the oxygen content is in the silicon at the interface. Don't you think so?

LATHROP: Yes. I would think so. Whether we have reached that equilibrium or not, I am not sure.

SCHWUTTKE: This may vary considerably from wafer to wafer. All that I am saying is that you have basically no control at the present time, for the oxygen concentration is in the surface of the wafer before you start putting down your metallization.

LATHROP: That is correct, yes.

SCHWUTTKE: What would be now the interaction? Nevertheless, I find your model very interesting.

LATHROP: I have a feeling that it is not the oxygen in the silicon that is the problem, it's the oxygen--

SCHWUTTKE: If it is the interface, then both sides contribute.

LATHROP: Well, except that the oxygen has got to get into the silicon dioxide, the thin silicon dioxide layer, there and if you have a lot of oxygen on the metal side, which is capable--

SCHWUTTKE: Yes, but the silicon dioxide layer formation will depend on the presence of oxygen in the wafer.

LATHROP: That oxide has already been grown.

SCHWUTTKE: Yes, but --

BICKLER: Would you imagine more than 10^{16} oxygen in the silicon?

SCHWUTTKE: Oh, definitely.

BICKLER: The chemical reaction to give you free bonds at the interface that Jay (Lathrop) is describing is going to be up in the chemical range, up to the 10^{20}'s, so I submit that the background oxygen in the silicon crystal is so slight an influence that . . . .

SCHWUTTKE: That is an order of magnitude difference, so--

BICKLER: More than one magnitude.

WOLF: Yes, there will always be on the free silicon surface something like 20 or more Angstroms of oxide. It depends on the chemical treatment that is being used in getting the metal there. How much of the oxide may or may or not be removed, and what is the state exactly of the surfaces, are probably really more important than the 10^{18} oxygen atoms in the bulk below.

COMMENT: I think that is a good point.