TEXTURE ETCHING OF (100) SILICON FOR SOLAR CELLS

Lawrence D. Dyer
Texas Instruments, Incorporated
Sherman, Texas 75090

INTRODUCTION

In a solar cell it is desirable for the light-absorbing surface to consist of facets such that incident rays must undergo at least two reflections prior to escape. This can be accomplished by mechanical means (1) or by photolithographic protection of lines or arrays, but the former results in deeply damaged material and the latter requires polished surfaces and expensive processing. In 1974 Haynos, et al (2), reported an unspecified chemical means of creating the proper kind of light-collection texture on (100) silicon slices. This procedure converted the (100) silicon surfaces to random arrays of microscopic pyramids. Only 50 days later, Baraona and Brandhorst (3) reported nearly identical texturing with aqueous solutions of hydrazine hydrate, and showed that such behavior could be deduced from device fabrication etching experiments and observations of Lee (4). Soon thereafter similar texturing was accomplished by safer and less expensive sodium and potassium hydroxide solutions (5-7). In the meantime other benefits of this texturing had been realized: improved collection from lateral refraction (2) and internal reflection in the case of thin cells (3).

Various workers have reported studies, optimizations, and improvements of texturing using basic solutions (3-13). In 1977 Fissore, et al (7) proposed that the pyramid texture was generated in the case of KOH etching by nucleation sites covered by silicate salts precipitated at random. In 1977 Scott-Monck, et al, (9) proposed a similar situation for 2% NaOH etching with and without isopropyl alcohol (IPA). In 1978 Dyer (10, 11) proposed a similar model except that most protective sites were thought to be growths, not precipitates. An attempt was made to quantify the various promotional effects. The purpose of the present paper is first to explain in detail the attempt at understanding and quantifying texturing; second, to give an experimental description with observations on the proximity effect (8) and the effect of additions of water glass that were discovered during this work; and third, to show that the precipitate or growth models account for almost all of the known promotional effects.

PROCEDURE

QUALITATIVE.--Qualitative test runs were made in which concentration, temperature, pretreatments, ultrasonics, alcohol additions, containers, etc. were varied. Since similar procedures have been described in many texturing reports to date, they will not be repeated here.

QUANTITATIVE.--In order to quantify texturing it was first tried to measure the fraction of light reflected back from the textured surface. A simple apparatus consisting of a light source, a stereomicroscope, and an exposure meter was constructed and used to get relative numbers of merit for various treatments. This approach was abandoned when it was realized that the measurement lacked sensitivity in the final stages of texturing, as well as in the early stages where specular reflection swamps the readings. In addition this approach reveals nothing about the microscopic details of texturing.

The approach taken to quantify texturing was to measure the fraction of area covered by pyramids, as seen under the microscope, realizing that, for all practical purposes on (100) silicon, texturing is the degree to which the surface is converted to pyramids. Exceptions are 1) anomalous reflection when the pyramids have sizes comparable with the wavelength of light, 2) extra reflection when the large pyramids formed have lost their protective tops and begin dissolving from the apexes of the pyramids. The measurement of fractional area coverage has several advantages: it is versatile over a wide range of pyramid-producing capabilities because the etching time selected can be varied to produce convenient densities of pyramids, and the measurement is independent of pyramid size or magnification.

DETAILS OF QUANTITATIVE TESTS.--Texturing was done at 90 deg. C. at two concentrations, 1 and 4 wt. % NaOH. Isopropyl alcohol (IPA) was semiconductor grade, and water glass ($Na2SiO3.xH2O$) was reagent grade 40-42 deg. Be'. The proximity of the test surface to another surface was established by either of two methods. In the first, simple jigs were constructed, each consisting of a stainless paddle and Teflon® or Delrin® screws. The screws protruded through the paddles at three positions around the slice and were located radially such that slices with flats could be wedged into place by rotating the slice until the flat was out of alignment with the screw. Proximities were controlled by choice of screw thread for a given thickness of slice. In the second method the slices were placed between glass slides with suitable spacers. Ordinary rubber bands were used to hold each pack together, and the angle of the slice from the horizontal was measured. Three-inch silicon wafers, p-type, 1 ohm-cm, (100) were used. Polished wafers were used for the fractional coverage studies to eliminate the enhancement of pyramid formation by rough surfaces (3, 10). Pyrex and stainless steel containers were used and each wafer was etched 3 min. in 30% aqueous NaOH at 100 deg.C. prior to texture etching.

MEASUREMENT METHOD.-- A compound incident-light microscope with 10x10 counting reticle was used. A convenient method of assessing the area covered by pyramids was to count the pyramids in each row of the grid in size groups: 0.1-0.2, 0.2-0.3, etc. (Fractional sizes of a unit square on the grid.) This assessment of pyramid size can be done surprisingly rapidly and accurately. The numbers for the ten rows in the grid were totaled in each size group and converted to relative areas by the appropriate size factors. The fractional coverages were summed to obtain the total pyramid coverage. These values were measured at two or more places on the slice and averaged.

RESULTS

QUALITATIVE OBSERVATIONS.--Results of previous workers will be listed as well as those of the present study.

POSITIVE INFLUENCES.--The following chemical additions to KOH or NaOH solutions enhance texturing of (100) silicon:

- o Alcohols (5-9)
- o Methyl ethyl ketone (MEK) (9)
- o Films of long-chain carboxylic acids (9)
- o Fingerprints (11)
- o Water Glass (10)

The following physical conditions promote texturing:

- o As-cut or lapped surfaces (3)
- o Terraces in NaOH-etched as-cut surfaces (10)
- o Proximity to another surface (8). This effect was discovered by noticing that the places where the slices were wedged into holders were often textured better than the remainder of the slices. Optimum proximity for developing pyramids was found to be 0.4-1.0 mm. The controlling factor appears to be the entrapment of hydrogen bubbles between the two surfaces, and thus viscosity, flow, and angle of the surfaces from the horizontal are all factors. The observation of the beneficial effect of the bubbles is in contrast to previously-reported ideas about the effect of bubbles (9,13).
- o Repeated use of texturing solution (11)
- o Adherent growths or particles left after NaOH or KOH pretreatment. In fact, some growths or precipitates remain attached to the tops of the pyramids after texturing, even after rinsing with D.I. water. Figure 1 shows such a growth as seen by the scanning electron microscope (11).

NEGATIVE INFLUENCES.--In the present work it was noted that texturing was inhibited by polyvinyl chloride cement and by certain plastic slice holders. In addition, the following observation was made by Baraona and Brandhorst (3):

> "For a given etch composition and temperature, there appears to be an optimum etch time to achieve maximum structural perfection and uniformity. If etching continues beyond this time the pyramids begin to disappear, and flat, shiny regions_____begin to emerge."

NEUTRAL FACTORS.--If a texturing bath was used repeatedly, visible precipitates accumulated in it, but had no apparent effect on texturing.

RESULTS OF QUANTITATIVE TESTS.--Figure 2 compares the results of various treatments in 1% NaOH on percentage of surface coverage by pyramids. The result was that each additive or promoting condition (proximate surface) caused a 2 to 20-fold increase in pyramid coverage. Also a threshold concentration exists for $Na2SiO3.xH2O$. Figure 3 compares the results of various treatments in 4% NaOH. Similar results to those at 1% were seen. The proximity effect exerted a strong influence at both concentrations.

INTERPRETATION OF RESULTS

Several authors have reached the conclusion that texturing of (100) silicon occurs by the formation of protected spots on the surface (7,9). This conclusion could, in fact, be reached from the knowledge in device fabrication on (100) silicon that any masking material will generate pyramidal mesas. The following is a line of reasoning from the atomic model that allows the same conclusion. After that, the protective mechanism will be discussed.

ATOMIC MODEL.--In order to more clearly appreciate the surface orientation aspect of the texturing problem, atomic models are shown. Figure 4 shows a Fisher- Hirschfelder-Taylor model or "sphere" model of a perfect (100) surface of silicon. The surface consists of an array of pyramid tips having <111> sides. Each surface atom has an equal chance to become the tip of a pyramid. Therefore, some external influence selects the preferred sites of pyramid formation. Figure 5 shows a model of a pyramid on the (100) face. The selectivity of etchants, including sodium and potassium hydroxides, can be explained by considering the two ways in which atoms are held into the illustrated surfaces: One type is bonded only twice and is typified by the perfect (100) surface and by the tip of a pyramid, the other kind is bonded three times and is typified by the perfect (111) surface and by the sides and edges of the pyramids. The perfect (111) surface etches very slowly compared with the (100) surface in preferential etchants (14). Clearly, if a means can be found to protect small areas of the (100) surface, each area will become the tip of a pyramid as the (100) surface is progressively dissolved.

MECHANISM OF FORMING PROTECTED SITES ON (100) SILICON IN SODIUM OR POTASSIUM HYDROXIDES.

The chemical reaction for texturing in NaOH or KOH solutions is as follows:

$$2MOH + Si + H_2O \longrightarrow M_2SiO_3 + H_2 \uparrow,$$

where M represents sodium or potassium. Since pyramid formation is enhanced in dilute (1/2-4%) and not in concentrated (30-40%) aqueous NaOH solutions, the protective factor is related either to product insolubility in the etchant or to its low dissolution rate. Third, since addition of small amounts of $Na_2SiO_3.xH_2O$ to NaOH solutions enhances pyramid formation; and the Na_2SiO_3 produced in the reaction has limited solubility in aqueous NaOH and even lower solubility in NaOH-H_2O-IPA mixtures, some reaction product like M_2SiO_3 must be the protective factor and it must be grown or precipitated at random sites. Figure 6 shows a schematic diagram of the stages in the process for texturing with NaOH, with and without enhancement effects.

The reasons for favoring the idea that the protective products are growths rather than precipitates are: first, it is difficult to see why precipitates would occur preferentially on the terraces of pitted surfaces. Second, precipitates have only a slight tendency to bond to the silicon under a liquid, particularly one under agitation from gas development. Third, the neutral effect of the precipitates that accumulate from extended use of the texturing bath favors the growth hypothesis.

The positive influences can now be explained as follows: Alcohols and MEK decrease the solubility of the reaction product. Water glass suppresses dissolution of growths of reaction products by the mass-action principle. Fingerprints and films of long-chain carboxylic acids slow the vertical diffusion of reaction product; proximity (intermittent bubble-entrapment) acts the same way by providing a gas barrier to product diffusion. As-cut or rough surfaces texture better because they are already closer to the textured state. Repeated use of the texturing solution works progressively better because of build-up of reaction product.

The negative influences are explained as follows: PVC cement stops the reaction instead of slowing it. Too long texturing eventually removes the protective growths from tops of the pyramids, which leaves them free to dissolve down to base level.

PRACTICAL USES OF RESULTS.--The variety of agents that promote texturing make it possible to select a wide variety of texturing solutions. The synergistic effect of combined additives or physical conditions broadens the possibilities further. By more rapid pyramidization, a smaller range of sizes for pyramids is possible. If a texturing process has stopped producing adequate absorption of light, one can look for inhibiting agents such as PVC cement residues, or examine the pyramid tops to see if they are dissolving away either from some contaminant like a fluoride, or from over-etching.

CONCLUSIONS

- Texturing of (100) silicon surfaces in sodium or potassium hydroxides occurs by the growth of a reaction product in a random array of surface sites, which leads to pyramids remaining at the sites after other parts of the surface dissolve away.

- Various additives and conditions promote texturing by increasing the probability of localized growth of reaction product.

- A new texture-promoting influence--a proximity effect--was discovered in this work. This effect was found to further enhance texturing in the presence of promotional additives.

- A method of quantifying the pyramid-producing capabilities of each texturing solution was developed.

- Combined effects of additives or physical conditions are synergistic with respect to pyramid density.

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APPENDIX

VERTICAL METALIZATION IN SOLAR CELLS AND OTHER SEMICONDUCTOR DEVICES

One of the factors that reduces solar cell efficiency (and device packing density) is that a fraction of the active area (about 10%) must be metalized to collect current from the remainder of the device area. This metalization is in the form of "fingers" and "bus bars" that are much thinner than their breadth, and is placed parallel to the slice surface. The metal is at least 2 microns thick so that light is prevented from entering and generating carriers in the underlying volume beneath the metal. The present proposal is to place the metallization vertically so that much of the area formerly beneath metal can generate carriers. A gain in efficiency of almost all that lost to metallized area can be expected, i.e. perhaps 9.5% if 10% was metal.

The proposed method consists essentially of metalizing deep, narrow grooves in silicon that have been introduced by the orientation-dependent etching of (110) surfaces (15). In a solar cell, the collection junction would be formed after the grooves were installed, and metalization would then be carried out.

The metalization could be accomplished by various techniques: ion plating, electroless deposition, low temperature chemical vapor deposition, or sputtering. It would preferably coat both sides of a groove; filling up the groove might give problems with mismatched thermal expansion coefficients. Connection of the several collection fingers could either be accomplished by metalization of the solar cell edges or by introducing a second set of groove directions that lie 70.53 deg. from the first set. Contacts could be made to the edges or to small horizontal patches of metalization. The foregoing idea may also be used in device manufacture in which the goal is to conserve area that is presently used in horizontal metalization.

If this method is successful, the benefit to earth-based solar cells will be offset by the inability to texture-etch the required (110) silicon surfaces; on the other hand, space-based solar cells may still benefit because of difficulties with the textured cells in this application (16).

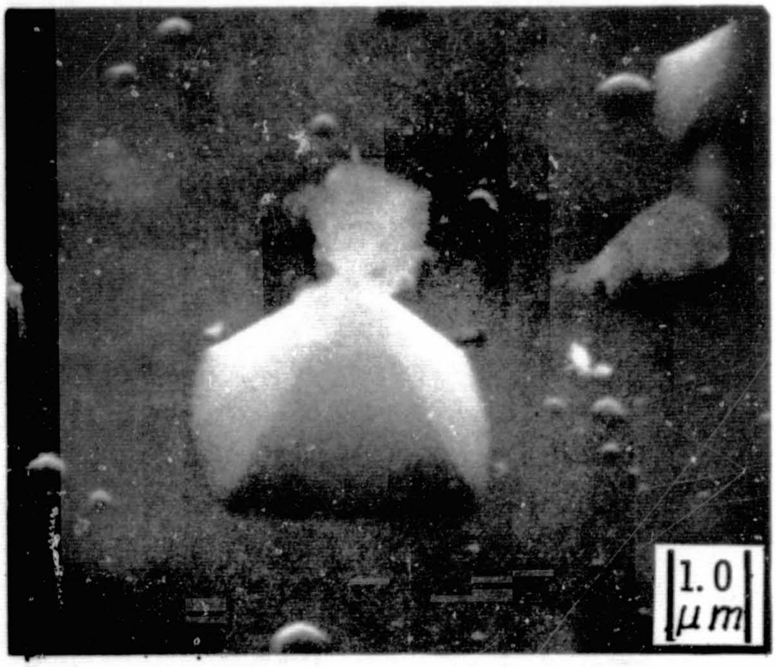

Figure 1. Reaction Product Growth at Top of Texturing Pyramid on (100) Silicon

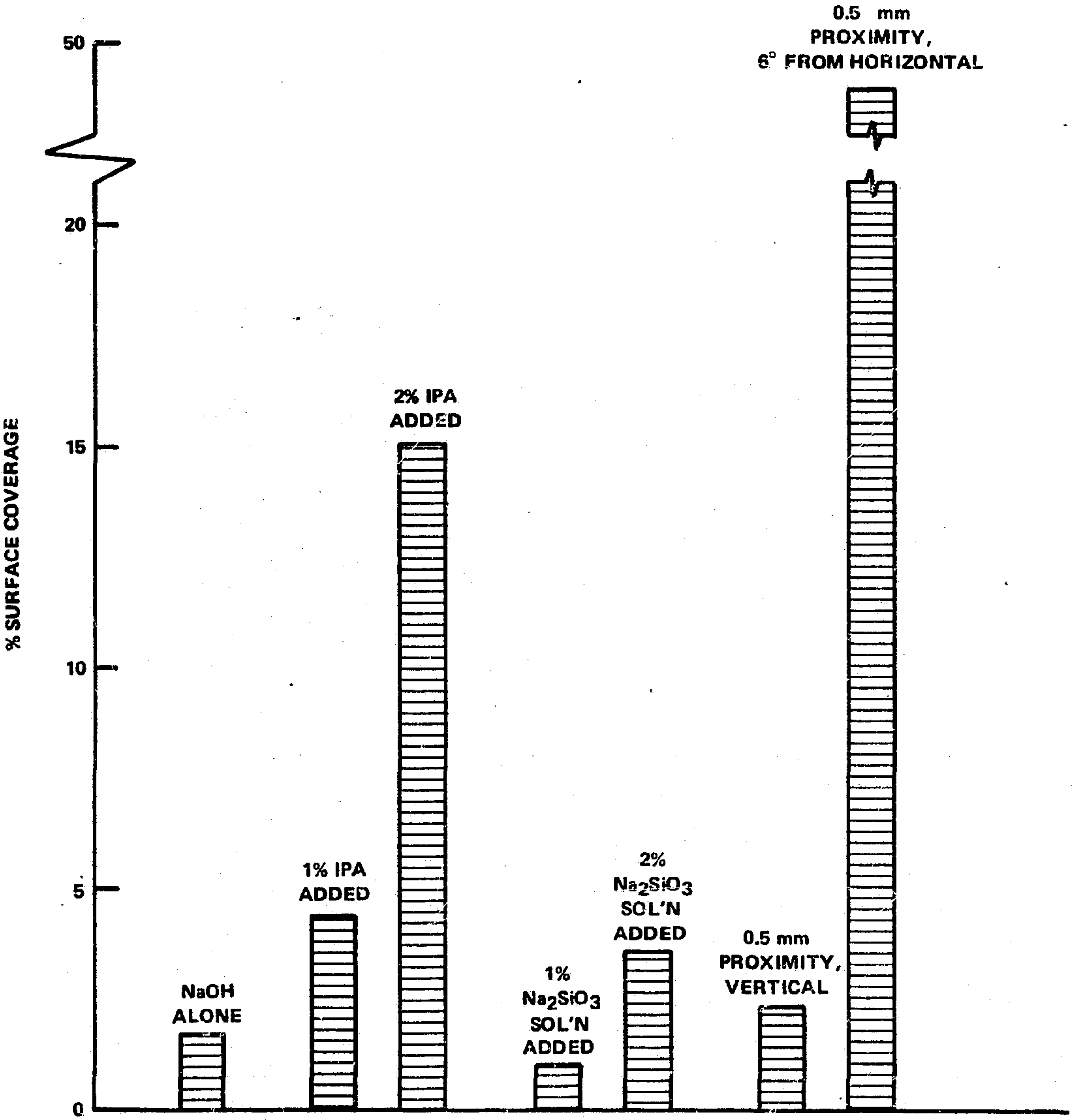

Figure 2. Effects of Various Enhancement Conditions on % Coverage by Pyramids After Texturing in 1% NaOH for 5 min. at 90 deg. C.

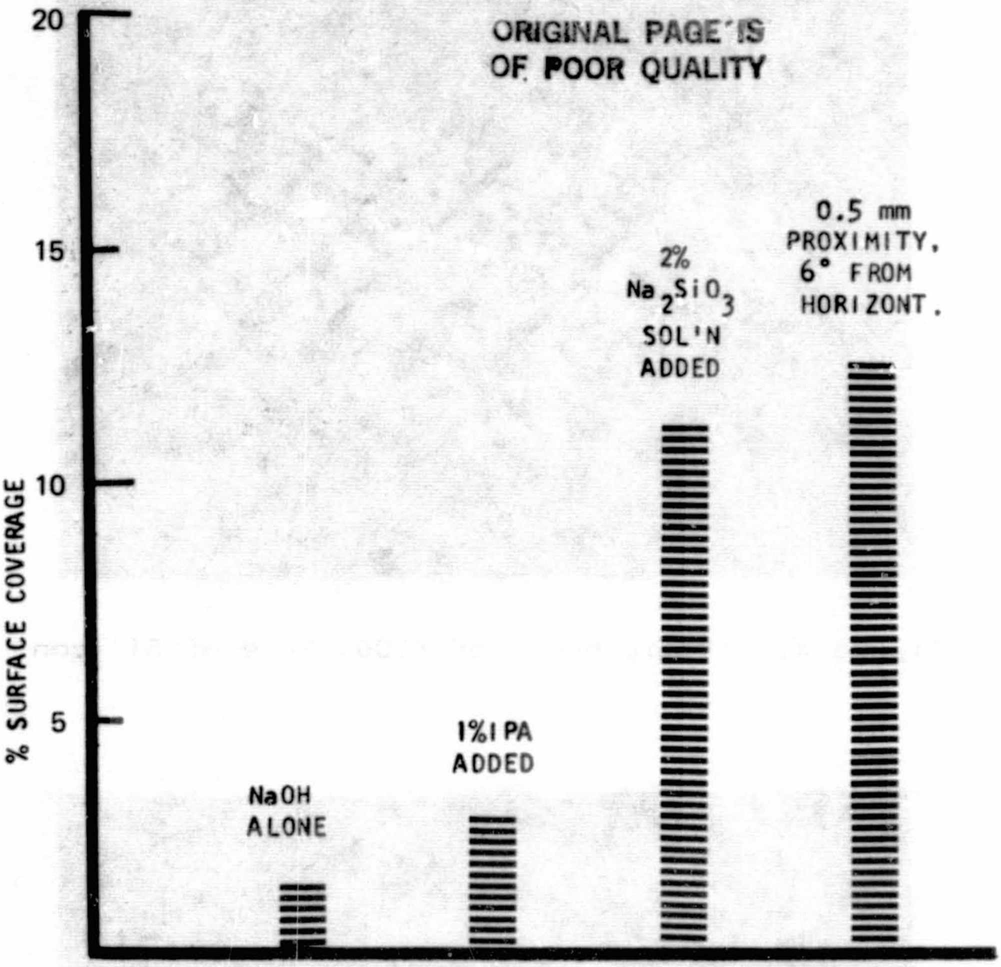

Figure 3. Effects of Various Enhancement Conditions on % Coverage by Pyramids After Texturing in 4% NaOH for 10 min. at 90 deg. C.

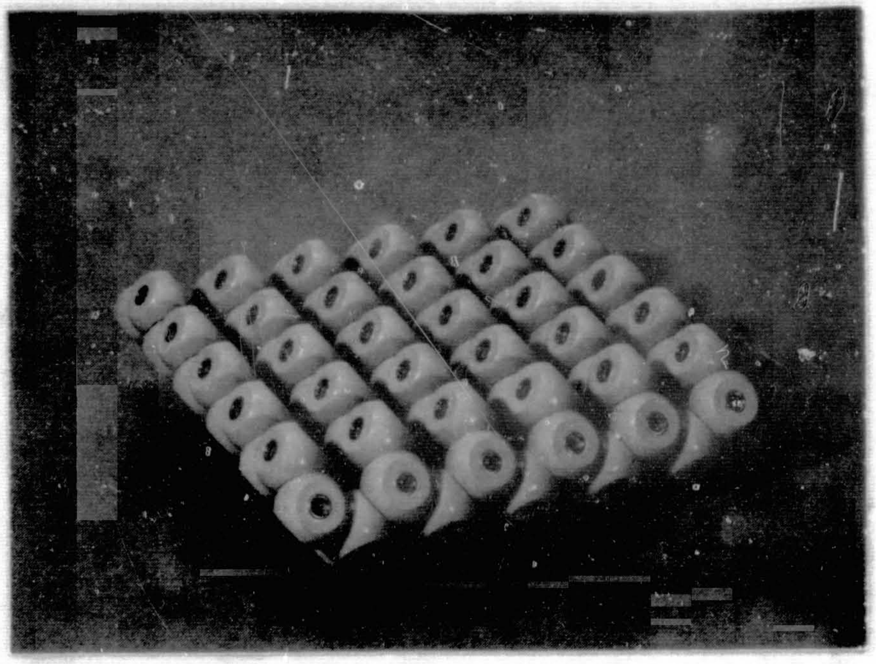

Figure 4. Atomic Model of (100) Face of Silicon

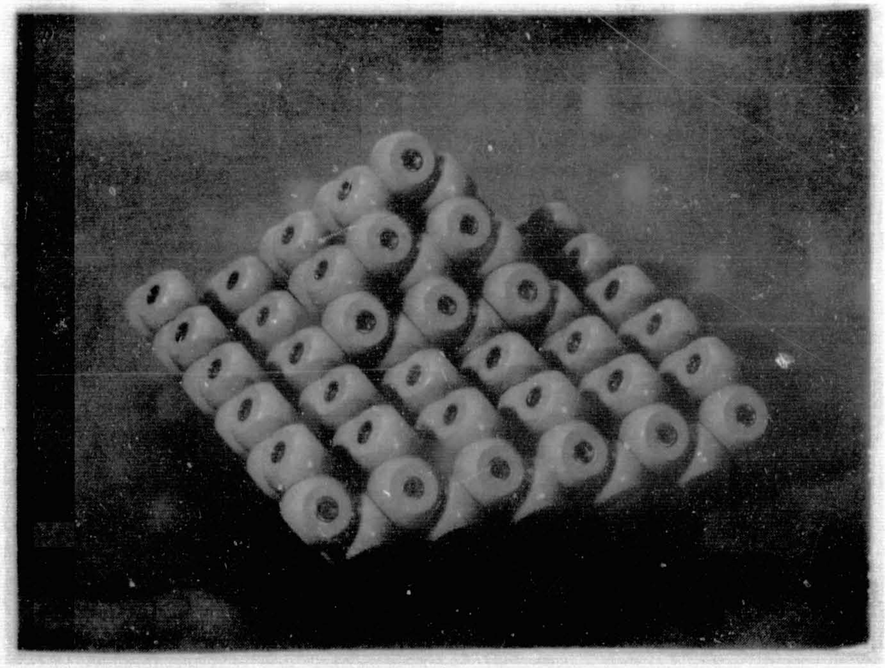

Figure 5. Atomic Model of Texturing Pyramid on (100) Face of Silicon

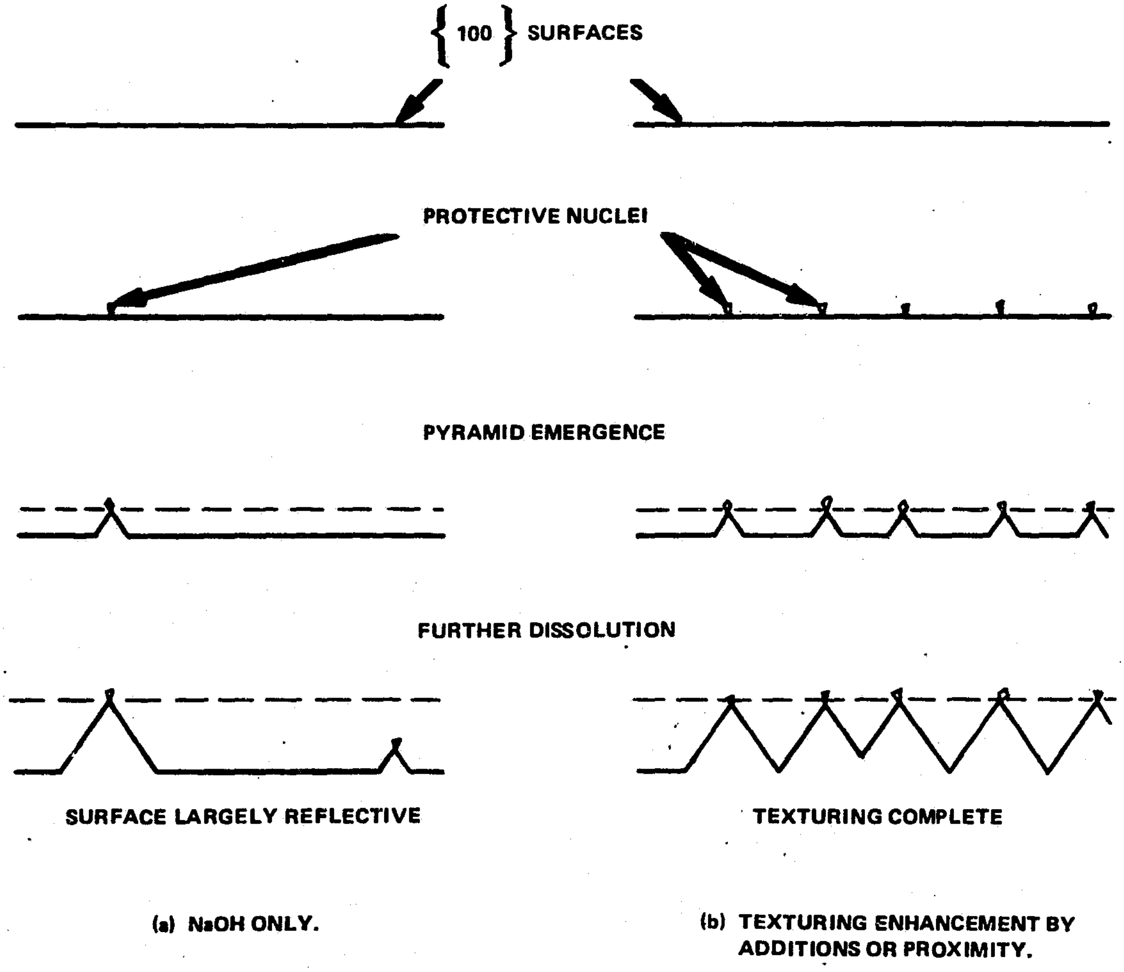

Figure 6. Schematic Diagram of Stages in Texturing Process with and without Enhancement Effects

DISCUSSION

QUESTION: Is there any difference between that structure and the DMVJ cell? With Sandia's support, the development of that kind of metallization, we are probably six or seven years . . .

DYER: I was on one of the DMVJ contracts so I know something about the structure. The making of the grooves is the same idea, you have to do masking, and you have to use a substrate with [110] orientation. It has disadvantages: you can't texture it then if it's [110] unless someone discovers some new way of texturing a non-[110] orientation. That may be, then, only an advantage for space, where you can't use the texturing.

ROSE: We supported it from a concentrator point of view, because you can etch those grooves deep, and the way you extract the current out of it at very high concentrations is no different from dragging out through a thin layer. The reason we gave it up -- it's still a good operating cell, even up in 800-sun concentration -- the reason we gave it up, is it is a large-emitter-area cell and there's limitations on V_{OC} involved in it. All I do is bring it up because it doesn't seem to me like it is a new idea, it's something we have supported and given up.

DYER: Except that here you are putting the metallization down here. In other words, there's no metal contact on the top; there is no shadowing.

ROSE: That's right. That is the DMVJ cell.

DYER: Well, you still had to have bus-bars come across and collect from that.

ROSE: No, you run them out the ends.

DYER: Well, I was involved with the VMJ concept, and it had this idea in about 1976 after a contract like that and there are some differences, which I guess we can talk about. Of course you don't have shadowing and shingling.

RAI-CHOUDHURY: If this texturizing takes place by these reaction products, masking the reaction, why does it not work on [111]? Can you comment? People always have difficulty texturizing.

DYER: We already have the low-energy face there; you are stuck.

MARTIN WOLF: I have been requested to prepare a summary of this meeting, not here, at some later time, and I would like to ask the presenters of all the sessions, not just this one here, to be so good as to supply me with perhaps four to six of their slides or viewgraphs, namely those that they think are either the most instructive or the most impressive-looking, which might help me then to perhaps select one or two from among them to use in the summary. So it doesn't have to be here that you get me the slides or viewgraphs, but if you could send them to me, the address is in the attendees list. I would appreciate this very much. Thank you.

SUMMARY AND DISCUSSION SESSION

R. Kachare, Moderator

SUMMARY AND DISCUSSION SESSION

PRINCE: Anything you want to say? The major problem we have in the Department of Energy, as I mentioned the other day, is that we are being squeezed again. We will not have as much money to spend on each of the areas as we originally thought we were going to have. So the question is, what should we be doing in the Department of Energy to improve the efficiency of solar cells? We have heard all sorts of different approaches to things: modeling of various types, general theoretical analyses, some experimental work that has resulted in moderately high-efficiency cells, and so on. We heard also about measurements of various types that will enable us to evaluate what we are getting out of these devices. So, I thought we would just start off by -- well, actually, I don't know where to start off. Perhaps by explaining what I think I heard during the session that I headed. I think that's what we all were asked to do, but I think I'm going to forego that. I'll tell you one thing that did bother me: I heard several comments about the importance of the emitter region -- and in one talk, that the emitter region has very little effect on the efficiency of solar cells. On the other hand, I heard in other talks that unless you have very low surface recombination velocity on the emitter surface, you're never going to get 20% cells. That's inconsistent. I've heard a lot of other inconsistencies during the last three days. I'd like to clarify these inconsistencies.

QUESTION: May I comment on that? That's not inconsistent at all. I think what you're seeing is, it depends on what the limiting mechanism is in the cell that you're looking at, and it's clear that if you're base limited, it really doesn't make any difference whether you passivate the surface. If you are emitter-limited, and Auger isn't large, and band-gap narrowing isn't killing, you then emitter is very important. I thought it was very healthy, this conference, because I think that realization is now getting to a lot of people that simply running an experiment -- passivation, not passivation -- and observing that it did not make any difference, doesn't tell you anything. As a number of people have said, you really have to optimize the entire cell and that is what really is important. I don't think any of those things are inconsistent.

SCHWUTTKE: I'm challenging. I'd like to see if I can say something without getting into trouble. I think the question, as I see it, is: where do we go from here? In that sense, I think the problem has a couple of different facets. From my point of view, certainly; I think I have already expressed the idea that we need to have a complete understanding of what it takes to get to a specified level of efficiency in terms of the best-first-principles kinds of things we can do. I think there are people who are working on that problem, and I think they are going to give us some pretty impressive results in the near future. I think the other thing that really matters is the industrial participants in the program doing those things that allow their product to be a better product. Because that's really what this entire program is all about. From that point of view, I have tried to make available to DOE participants, and to people who are not participating in DOE programs at this stage of the game, that information that we have. I would hope that kind of thing would continue; I would hope that the information that we are finding will be used. In terms of the critical issues, I would totally agree that the material issue is one that needs to be resolved: how do you get a real-world material that is good enough to be able to make cells consistently that are worthy of the processing we are finding out about? If there has to be something done in that area, then maybe it behooves us to think about that kind of a question. I think materials questions in general, in all photovoltaics, are a major issue.

SIRTL: Do you expect me to say something as a part of the wrapup of we have been listening to for several days? It may be a kind of egotistical wish. I already mentioned that to make gettering or gettering systems a science, he situation now, and the situation in other areas that have nothing to do with solar technology, is that so many different companies have their "black boxes" of what they call gettering processes. They never would like to disclose anything on that. On the other hand, we need to make it a more consistent technology in later years. We need a kind of well-understood buffering system that prevents the outbreak of blaming each other for being the culprit. The manufacturer of the material, or the device maker; if we would have reached some kind of gettering science, we would be much better off, and that of course includes a better knowledge of what direct combinations that predominate what recombination centers may look like. We really are at the very beginning of any understanding, and my feeling is, that is included in the science of gettering.

KOLIWAD: I have three observations. One is in the same line that you talked about, emitter importance. I have this concern about the work in the process-related area, process research area, as an example: do we have optimum emitter profile? It concerns me especially because of the heavy doping effects, and the field, as a result of the band gap or the band-gap tailing. Dick commented this morning that in a static field they distribute in ways that are complementary to each other, so we are not doing any research at all in tailoring the profiles. The second observation I have, I would again emphasize what Fred mentioned this morning, on the contacts -- the importance of contacts for high efficiency. There are a couple of areas that I think are in the area of process research, if you will, or process technology research, and I think some emphasis should be given to those areas.

LOFERSKI: I guess the thing that struck me particularly was Peter's discussion. I have heard him say this before, that the space cells may have been 18%, the stuff that they normally make, and of course by changing resistivity they would probably have been there. That's a question of many different steps and high-quality processing all along the road, I guess. Like the gap between what's possible in cells and what exists in commercial cells for space, I think, is rather small -- the things that are found in the laboratory and up in those space cells. But that is not so for terrestrial cells; there is a gap, and I guess what Peter is saying is that it's pretty much the same cell, that it's a space-quality cell that you are asking for, different resistivity and the higher quality material to get beyond the 18%. Like Mark Spitzer was saying: just give us better material, and pretty much the same processing that we are using to make the 18% cell will get us to 20%. But the big problem is that gap between what's demonstrated as possible and what comes out of the manufacturers. That is an economic problem. Like Martin says, we'll make a good cell and then learn how to make it cheap. I have heard someone else in the course of the talks say that's not the way to go, but that's basically it. For space the price is not what people are worrying about when they are manufacturing the cells, but for terrestrial application it's price -- economics -- that finally get in there. Now you said we shouldn't talk economics here, it's high efficiency that we are talking about, but there is that gap somehow in communication, perhaps not communication so much as the feeling of the terrestrial people that you cannot make these high-quality cells cheaply. I don't know how you change that.

QUESTION: I don't feel that way at all, Joe. I think many of us have been in the semiconductor industry for many years and we have learned from experience that you do the best you can. And when you learn how to do those things well, you push your yields up and you get your cost way down, now that we have gotten up to this 15%, 16%, 17% range.

LOFERSKI: I think we have gone through this cycle of "Well, it can't be that it's that space cell that will be the terrestrial cell." There was the business about solar-grade silicon that was going to be a lower-grade silicon and not the best silicon there is, and now we have come around to "It's got to be this solar-grade silicon for high-quality cells, it's the best kind of silicon there is, and it's the best for processing all along the way." It's a question of doing all those things inexpensively or at an acceptable price.

QUESTION: Just a comment. I think everything is going in the right direction, and what we are learning in high efficiency is being applied to making the cells for the commercial market today. Their cost is important, as it always will be. You have to compete at $6 a watt or whatever it happens to be at the present time. These things are applicable; we are not going to be selling that kind of cell right away. I think there is one thing perhaps where DOE is a little off, in my opinion, of dead center, and that's in specifying efficiency on a module-sized basis. In other words, a 15% module requires 18% cells. What is important is the efficiency of the cell under glass. You could make 30% cells and fill up half a module and you have a 15% module. But that's not going to do it. It is not very important to a first approximation whether the module is 20% bigger or smaller than the average size. It may be for central-power systems, where everything has to be squeezed together. We are not going to be in that business for many years in this country because there are many other technologies that may dominate that market. What is important is the world-wide market for small systems. I think that's the real market that we are facing today. For that it's not so important, now; whether DOE's objective is that or not, perhaps, does not make any difference to the world market, but for American industry it may have some effect. I think we should be realistic and say what's important. We need efficient cells. We want to get the most we can. But what is more important is the cell efficiency under glass, cell efficiency in the module. We can worry about whether 10% is more crowded or not but thats not important, in my opinion, to the world market today.

DYER: I want to make a comment on something that someone else brought up in this conference about Czochralski vs float-zone. I want to expand on that. Czochralski growth is not optimized for solar cells at all and the economic question does come into it. Because whoever makes the silicon -- and in our case, we make it for our own divisions, our own front ends -- has to make it as cheaply as they can, and right now they are asked by front ends to make it optimized in several ways. They, of course, want to have a very constant resistivity over the whole thing. The segregation laws make it so that you have to, I mean the resistivity changes from one end to the other, so they are going to lose something there. It would be very nice if you could have one front end want the top part of the crystal and another one want another part and so on down to the tail. But when one device engineer decides that so-and-so ohm-centimeters is right, they all do. So you are putting the manufacturers in that bind. Then, in recent years, it has been realized that to have oxygen in the crystal is a good thing, and they don't want the oxygen to be measured just in one place, but both radially and axially along the crystal. So there is another restraint put on again, not by the solar-cell industry but by the device industry. No one has ever asked "make us some material for solar cells." It seems to me that in addition to all of these other requests someone has to sit down with people in the growth and selling of Czochralski silicon to see if they can't also do something else and provide a material that is good for solar cells. And that could be done, but the economic question has to be brought up and addressed. I rest my case there, I don't think they have gone as far as they can on it, because that isn't the one who is paying the bills.

QUESTION: I want to take up on Kris Koliwad's comment. Correct me, somebody, if I'm wrong. Most of the solar cells that we make, with the exception of float-zone silicon, seem to be base-limited. Hence, again the emphasis on bulk material is so much more urgent than the process. Tailoring of the emitter, if you leave the process in the hands of those who have good experience in semiconductor processing, not just solar-cell. Ion implantation diffusion from solid source, liquid dopant, you name it, more than one way. More than one way to tailor the emitter profile and I don't think we have run out of steam there yet. I think there are problems still: in the high-efficiency area is one, of the starting material -- Czochralski, of course, we talked about it; the recombination center in Czochralski, especially as a result of heat treatment. One has to address it; it is really a materials issue. Hence, how do you get around it so that you can apply the knowledge to a cheaper sheet growth process?

QUESTION: Maybe I should comment a little bit on the same question. It seems to me that there are two basic reasons why we live today with this emitter profile. The one is that we have not learned really to bring the surface recombination velocity to very low values, so that we need what I called, in my talk yesterday, the potential step, or in other words a large drift field that the profile gives us. It helps to reduce the effect of the high surface recombination velocity. The second is just strictly process historical. We have learned how to control diffusions, we have learned how to do ion implantations. Both leave us with a steep impurity gradient in the layer that we generate by this process, so we automatically end up with this type of profile just because of the process we use. Okay, what's the other alternative? Really, it could be alloying, a liquid face regrowth; we don't have those very well under control. We have gas-phase CVD epitaxy. We seem to have problems with that. That would give us different profiles, then we could live with something else. We haven't learned as well to use these processes for solar-cell fabrication. So to some degree it is historical. Again, if you could make one of these other processes work, we would not necessarily -- probably we wouldn't at all -- want such a high surface concentration, and we probably would have other means available to control the surface recombination velocity better, if you don't have such a high surface concentration of impurity. So we could move into a quite different technology here, but we don't quite know how to do it. So that's my response to Kris's question.

I have two other things I wanted to mention. I think this meeting has shown us very clearly that we really have moved to a new technology level. People have made use of modeling, of the the available analytical measurements, to understand exactly what the devices they are making are like, where their limitation are. They have analyzed where the next step for improvement has to be. They have moved along and made improvements in understanding of device physics, modeling, and the analysis of devices through measurements, and they have reached this new level of 18% to 19% efficiency. And we see that it can be done by quite a few people. It's not that just one individual that has this capability, and we also see that each one has put emphasis a little bit differently in how he got to this 18% to 19% level and through the modeling and analysis has seen what else, with today's technology, he can do to design this device better, to process it a little bit better, so that he probably can get to 20%. So we have heard a number of people who felt that 20% is essentially just around the corner. That seems to be the level of today's technology, and I think it's a good move ahead from where we were a couple of years ago. The question then becomes, what's the next thing? How do we get significantly beyond that point? It looks like, from everything that we have been hearing here, that that's not exactly accomplishable with today's technology. Again and again we heard that really to get significantly beyond, we need better material, and it seems to me, with that, we come pretty much to the talks we heard yesterday about what do you do with surfaces, what's happening with surfaces. We saw some very impressive pictures of what we have learned about how surfaces are reconstructed, for instance, and so on. What are the defects in materials, where do defects come from in the material? The question then comes, okay, since we start to understand what the surfaces are like, we start to understand how they reconstruct themselves, how can we foster it, how can we develop processes that will give us this desirable type of surface practically all the time? It seems to me we have made considerable research progress in understanding but we haven't yet learned really how to apply it. I don't know whether my understanding is right or not, but that's the impression I got. So I think this might be perhaps a subject we might want to discuss a little further here.

I have an answer for Erhard Sirtl. I didn't like his comments so much; let me tell you why. To me, it looks like gettering is something to repair what you didn't do well enough before. So, shouldn't we learn first to do the things as well as we can or better than we do it now? And maybe then still do some gettering, but maybe the first emphasis should be to reduce the defects in the material rather than afterwards try to repair it; make it right the first time out on the production line, and don't send it to the repair shop before you sell it. Those are my comments. Let's see whether we can get some good discussion from those.

QUESTION: I always used to say gettering is an act born out of desperation but at some time it is necessary, but on the other side, it spoils manufacturing to be sloppy. I would really like to pick up on the comment made by Larry Dyer and also by Marty. Not too long ago the solar-cell industry used silicon that the IC industry was throwing away. Maybe, just over the last couple of years, they have become more conscious, and they buy Czochralski silicon; and then they heard about float-zone silicon, so they all rush out and want the float-zone silicon, because somebody told them that it's a lot better. Shortly before that everybody was hot on sheet silicon because you didn't have to slice it; now we cast for the kilo silicon and nobody asks about slicing any more. So there are a lot of contradictions in that particular field. What I believe we have to do now is come out aggressively and specify the material we would like to have and then go after the vendor to develop it. So far, we just take what we get. I would like to say we really don't know what your process can do, we don't know what float zone can do and we don't know what sheet technology can do for us. We have never taken the time to sit down, and we have done a lot of modeling, but the hell with it, I'd like to sit down with you guys and draw up the specs of the material for a high-efficiency cell. You tell me what you want and then we go and find somebody who is going to make it.

QUESTION: Let me now give the answer to Martin Wolf and maybe dwell on some inconsistencies in thinking. Let's comment briefly on Schwuttke's comment. Presently we have to live in microelectronics exclusively with gettering. Whether it's oxide gettering, whether it's internal or intrinsic gettering, whatever you may call it, we have to live with it until somebody comes up with a better understanding to make good and cheap Czochralski materials that don't need all that, including the device processing. Let's talk about solar cells now. What has been the reason I so strongly would like to see gettering becoming a science? What is the situation we are in right now? On the one hand we are striving for the highest-efficiency cells possible. That's something else, that's special research, and we want to give it all the support possible . . . we may learn a lot more about the mechanism of a solar cell in general, the mechanism of different device concepts and the like. But we must never forget that this type of solar cell nearly exclusively is made from a material that I would call exotic. Exotic means that I don't see, in the near future, ways to realize a production of some sizeable quantity. That means it's good to have found out how we can make high-efficiency cells, but later on we have to learn to live with a material that's economically available, and that we can scale up, and it's done best in connection with the device maker in a way where I think we need gettering. But that may not be the only solution. And by gettering, I mean it in all senses; it means that could include hydrogen passivation, that may even include some kind of intentional complexing in the original material. When we now talk about something that has not gotten the share of attention in this meeting that it should have, about all the terrestrial approaches to make real cheap solar cells and real cheap material, I think we haven't come to a point yet where we can talk about the standard final quality of material that may have come out from any kind of process. Developing some special additional treatment to improve things here means just a temporary situation, because we have not reached maturity in whatever the process may look like. In my feeling, gettering can be an early solution to improve things at least to a point where the efficiency that can be seen as possible by the device maker has reached a certain attractiveness already. But we still have this gap between high efficiency of space types of solar-cell technology and the technology we mostly are talking about, namely for terrestrial application. That's where we need help to get into shape early to make solar cells attractive and efficient -- but it cannot be the maximum efficiency that we may reach during the next five years.

QUESTION: The question about gettering. I think that your comparison is not a better comparison with microelectronics, where all the action is on the surface. One-dimensional, two dimensional-device. Better compared with power devices, where current flows through the thickness of the material. A solar cell is essentially such a device. When you have a device such as that, you can getter but you have to have a material that does not have bulk precipitation, something going on in the bulk as a result of gettering, because in my experience, or that of all the people I know in the processing area, we never even dream of starting with a bad material and getter it and then make a device. The only purpose of gettering is to prevent contamination during processing. It's not really an answer. Can one take a material that is not so good, and getter-improve it, and make solar cells? I think the whole area needs to be examined.

QUESTION: I would like to just follow on what Ajeet made a point about. I think it's an excellent point, because if you try to getter something within the bulk, it's going to kill you . . . Now, the other choice is to go to the surface, which is like back-surface damaging, and that is going to kill you again because now you are going to raise your surface recombination velocity. So it becomes very difficult. And the third point is that generally the best gettering is achieved at high temperatures. All those things stand to hurt solar cells, so how you are going to do it and apply it to solar cells is going to be a slightly difficult question.

SCHWARTZ: I'd like to switch topics for a moment and talk about modeling. I think Martin Wolf probably said it best, near the end of his session: he stood up and said this sounds like a modeling session that we have. The one thing that struck me was that there were very few device papers presented that didn't either use as a guide, or rely upon as an interpretive tool, some sort of a model. There are all levels of sophistication. But almost everyone had some sort of a model that they were using, and I was very pleased to see this because I think that the device is deceptively simple-looking and still very sophisticated. The realization that the model is a design tool, an interpretive tool, seems to be widespread, and

I was very pleased to see that. The current status, I think, of the device codes is that they really are very good in spite of all the time I spent last night talking about the things that need to be done. In fact, one can show large numbers of plots of all kinds over wide ranges of operating conditions and over wide design ranges for which the predictions fall dead on the measurements, within the experimental accuracy of the measurements. The codes are designed to do it, really do an outstanding job of fitting what's there. In fact, they really do a very good job of predicting of what will happen under changes before the experiments are made. The status is really very good. So what does it need? There were needs: maybe three dimensions, time -- actually, time is very easy to do, that's a very small extension from where we really are. There are some needs, and they were not very well expressed directly, but it was implied by a number of questions, and that was the codes are only good, useful and easy to use. Therefore, the output is very important, and good graphical output, where you can sit down and look at things very quickly and understand what is going on, is very important to the use of modeling. I have one other comment: it seems to me that there should be larger, wider access to some of the more sophisticated codes. At the present time they really aren't widely available for people to use, and that's probably something JPL has been looking into. That in fact would help a great deal if there were wide access to some of the existing codes.

QUESTION: Perhaps we could resolve the controversy between Martin Wolf and Sirtl if we made the gettering part of the wafer manufacturing process. You know your material the best of anybody. If you feel it can profit from gettering, you can make a better wafer, include it in the production process and maybe get more money for it.

QUESTION: I think I have to give a better definition of what I understood about gettering. It finally, very clearly, should be a help for the device maker to get the best quality of his specific device after having done, at a fairly late stage of his process, some kind of gettering. I'm just speaking for the material supplier because in general, the device maker has not had as good an understanding of materials problems as the materials maker in general. So we have to live with a situation that there are many device production areas that just have to have a very simple recipe available that, of course, needs a lot of exploration before we get to that point in terms of gettering science, as I call it. Later on it should be particularly a help for the device maker to get the best device possible.

SIRTL: If you want to getter wafers downstream in the process it has to be at low temperature, unless you know some miraculous way of making the atoms move faster at low temperature. The problem then is to make a junction device. How do you getter downstream without disturbing the device?

WOLF: One thing bothered me a little on Schwuttke's comment, which is basically a very desirable one, but it's somewhat a chicken-and-the-egg problem. The solar-cell industry is a very small industry in comparison with the integrated-circuit industry, and probably even the power-devices industry. So can we even move the material manufacturers at this point.

QUESTION: I don't think you have to move it at the present point, but what does prevent you from sitting down and drawing up the specs you would like to see? That's the first step, and if we do we will move the guy who is going to make it. If you have the specs, maybe you'll find the guy who wants to do it.

SCHMIDT: I would like to agree, and perhaps elaborate a little bit on Schwartz's comments. I think it is very encouraging that we have computer codes that are in agreement in many cases with the performance from the terminals of existing devices. That's a real plus, and the codes have been very useful for a number of years, in lending the kind of understanding that has helped more people drive the efficiency up. On the other hand, I recall that in 1978 Paul Stella gave a paper at the Photovoltaics Conference in which he reported a 16+% AMO cell, which I'm fairly sure was an 18% AM1 cell. That was a very expensive cell. The point that I am going to make is that we have also heard some talks, particularly earlier in this Research Forum, concerning 25% cells, which is sort of No Man's Land. They are pretty easily designed on paper and with computer codes. The problem is that the physical parameters are probably not available to enable those designs to be achieved in the laboratory. Assuming some good lifetime in the base, there is probably something that will creep in when you do some heavy doping things. Secondly, I would guess there are probably a large number of ways of getting high-efficiency cells. I'm now going to say maybe 20% in a year or two and I think we have to pay a lot of attention to the multitude of different ways, because not all of those will be easily manufacturable. There the device codes are going to come in very handy as we explore different ways, for example, of emitter profiling, of contacting, and other things that will lend themselves to cells of high efficiency that can be manufactured in large volume as economically as possible. Which also brings up the utilization of computer codes for the purposes of monitoring the manufacturing process by enabling a very sophisticated and detailed interpretation of experiments that are going on in fabrication processing, as well as those after the cell has been made. At the same time I would agree with Dick that the codes are working very well and that we have some physics in there that will predict existing 18% cells, I think that there is an awful lot more work that needs to be done in fundamental understanding, particularly at the physics end of the spectrum. I'm not speaking as a software person, but I think Dick's comment last night was that if we can get the physics understood, then the software will probably take care of itself, because there are some capable people around doing the software. I'm interested in trying to work on some of these fundamental problems, but I think that it's very urgent that we think of not just achieving a 20% cell but of achieving a 20+% cell in a multitude of different ways so that we can evolve one or two or three different ways of manufacturing such cells in large volume and fairly inexpensively, and keeping the production line up with appropriate monitoring. So this is a much larger view of the computer codes than many people think of them.

DAUD: I guess Fred touched a little bit on what I was going to say of going beyond 20%, and I wanted to ask a question: if one wanted to go beyond 20%, what does the panel or audience think is the prime issue? Like do we have to go for different design of contacts or different design of the cell itself, go to plasma on cell or whatever? What would be the comments of the chairmen, as well as anyone from the audience?

QUESTION: While everybody is thinking of a good answer, I would like to make one remark. Of course, I don't actually make any of these cells, so I am just an outsider and therefore don't know quite what's going on. But I would like to concentrate on the notion of a defect because that really seems to be badly understood. First of all you start with the original material. What are the defects in there? You then have processing; thermal defects are produced, and then the materials cool down and some of these defects are annihilated and others survive and get frozen into the material. This whole area seems to be where metallurgists and engineers and physicists could really usefully work together. But it is an area of considerable ignorance. In one of the talks somebody put up energy levels, and how they changed with time . . . . It seems to me that if you want to improve these solar cells and get long lifetimes and get rid of these defects, one really has to be very scientific and extremely careful about each of these steps that introduce new defects or get rid of others. I am now including in my remarks what Sirtl said about gettering, because that's also got defects, and how to get rid of them. So it seems to me that there we have an area where I feel we are at a very early stage and really surprisingly ignorant. All these defects contribute to recombination, and so to understand that, the defect really comes first. Then we have to understand the recombination mechanisms. There is a lot of work to be done.

QUESTION: You know that for so-called good cells, that make say 18%, or for that matter 15%, 16% cells, we really don't have any technique of determining what defects are in them. Nothing we have on hand is sensitive enough, absolutely nothing electrically. You can detect only 17%, 18% cells. Clean as anything, no deep levels of any kind. With the kind of techniques we have on hand, we have to find some methods that can determine defects in those good cells we are producing now. If anybody has any ideas or anything they are working on, I would like to hear about it.

SCHWUTTKE: Obviously I agree 100% what was said about the tremendous need of such detailed characterization before and after processing, and its final correlation with device performance. And I'm in this field now for 20 years, and all I have learned is that it is tremendously complex and extremely expensive. And that the instrumentation that has been developed over the last 20 years is so extremely sophisticated that it is very difficult for a smaller laboratory to have access to such instrumentation. And then, the major problem is to get people interested in working in this field, because you cannot get very famous by doing this type of work. There is no fast reward, only a lot of sweat and long hours, and these guys are tough to find. Nevertheless, I think there are dedicated people who are working exactly along these lines and there may not be enough around, so maybe we can motivate some more to assist us in solving these extremely complex problems. You know, material science has always had the short end of the stick, compared with device science. The money is made on the device side, not on the material side.

QUESTION: I think I would say talking about good-quality silicon, float-zone and that sort of thing, you cannot specify anything but electrical stuff, you can specify oxygen, carbon, and then what do you specify is the diffusion length, the lifetime, the resistivity uniformity, things that we can measure. Now, how come this thing has a 100 microsecond lifetime? I want a millisecond lifetime. There is no good way of measuring what's the cause of it, so a crystal grower does not know what to do.

QUESTION: Let me respond to that. Usually the crystal grower is not expert in those ways to have the ability to guess, out of the periodic table, these things that will be likely to be in my puller and would be affecting his material that way. Usually he doesn't know that. Do we know what we are gettering? If we knew what we were gettering we could watch out for it in the reactors, in the pullers, it seems to me somebody ought to pin down what element or elements it is we are gettering.

PRINCE: I'm going to let our chairman close out our session.

KACHARE: One thing for sure, all of us agree that in the last two and half days, we learned a lot. I believe that with this High-Efficiency Research Forum we are really entering into a new technology. I think most of us also accept the fact that basic material requirements need to be defined. When we say that, I believe that gettering became a major issue also, and some element of research is needed there. But if I can summarize that in one sentence, basically we need to understand the loss mechanisms -- not only in the bulk; we also should know what are the defects, what are the chemical impurities, what are the dislocations, and also the loss mechanisms between silicon surface and metal, silicon surface-passivant interfaces. To understand these loss mechanisms, I believe that we have to have reliable measurement techniques. I think Lindholm said "let us use the effective parameters," but I have a lot of reservation about them because effective parameters may mislead us. So, basically, I am saying that to understand these loss mechanisms we have to have reliable measurement techniques. Cell fabrication research also needs additional efforts, whether we should use ion implantation, whether we should use diffusion, or whether we should have shallow junctions, whether we have this kind of emitter, whether we should have high or low junction -- all these issues are again for research. Furthermore, I think modeling is very useful and I feel that we just started using it. We have a tool now, I believe. It's not yet a perfect tool, but at least gives some kind of information. We can use it to refine our processing, refine our device design. As of today, float-zone material is a research material and not final material for our 15% module, $\$90/m^2$ kind of requirement for DOE goals. But that material is still useful because by using it, it is at least possible to make a 20% cell, so we are at least establishing some upper limit or a proof-of-concept. Can we bring low-cost sheet materials or any other cast material by gettering or by some other techniques to the level of float-zone? I have serious doubts about that, but at least we know that if you have some kind of material of excellent quality, it is possible to make 20% cells. I believe that measurement techniques are needed to enhance our basic understanding of, for example, heavy doping effects and Auger recombination coefficients. I had a lengthy discussion with Swanson from Stanford about the Auger recombination coefficients measurement that has been made in Germany. We are using those particular numbers as if they are reliable numbers. Many people are now questioning those numbers. So to understand the heavy doping effects, to understand device performance, to understand loss mechanisms, we need to have reliable measurement techniques. In short, I have tried my best to summarize two areas for obtaining high-efficiency cells: one is from the material end, and one from the design and device processing end -- and then bringing the material end and the device end together to achieve the 20% solar cell, at least in the lab. I think it is possible.

On behalf of DOE, SERI, FSA and the organizing committee, I want to thank all of you. I hope the conference was useful for all of us.