HIGH LIFETIME SOLAR CELL PROCESSING AND DESIGN

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Introduction

In order to maximize efficiency a solar cell must, a) absorb as much light as possible in electron-hole production, b) transport as large a fraction as possible of the electrons to the n-type terminal and holes to the p-type terminal without their first recombining, and c) produce as high as possible terminal voltage. Step a) is largely fixed by the spectrum of sunlight and the fundamental absorption characteristics of silicon, although some improvements are possible through texturizing induced light trapping and back-surface reflectors. Steps b) and c) are, however, dependent on the recombination mechanisms of the cell. The recombination, on the contrary, is strongly influenced by cell processing and design. This paper presents some of the lessons learned during the development of the EPRI point-contact-cell [1].

Cell Dependence on Recombination

A useful way to visualize solar cell operation is through the following pair of equations:

$$I = I_{ph} - I_{rec} \tag{1}$$

$$V = (kT/q)\ln(pn/n_i^2) - V_{res} \tag{2}$$

The first equation is easily derived by integrating the continuity equation [1, p. A-1] and says that the terminal current, I, equals the photo-current of electron-hole pairs, I_{ph}, minus the recombination current, I_{rec}. In this case the recombination current must be defined as follows

$$I_{rec} = I_{bulk} + I_{surface} + I_{p,n\ cont} + I_{n,p\ cont} \tag{3}$$

The nature of each term in (3) will be described briefly here and then in more detail in the next section.

I_{bulk} is the bulk recombination throughout the entire volume of silicon. In otherwords, if the steady-state electron-hole volume recombination rate is R, then I_{bulk} is the volume integral of R throughout the entire device.

$I_{surface}$ is the recombination occuring at the surface in regions with no metal contact.

$I_{p,\ n\ cont}$ is the current of holes flowing into the n-type metal contact (ie, the minority carrier recombination current) and $I_{n,\ p\ cont}$ that of electrons flowing into the p-type metal contact.

To a first approximation the terminal voltage is simply related to the pn product through equation (2) which, in effect, assumes constant quasi-Fermi levels throughout the device. Even though the actual pn product varies with position in a real device, this equation reveals the essential element in device design because, along with voltage, all the recombination mechanisms increase with pn product. Thus the maximum power point occurs at that pn product which balances recombination loss with voltage gain. Improving efficiency comes down to reducing recombination as much as possible.

The last term in equation (2) is the resistive loss in the cell. In devices which rely on conductivity modulation to obtain low base region resisitive loss it is additionally important to maintain a high pn

product to provide as much conductivity modulation as possible. Thus these devices are particularly sensitve to recombinataion.

Reducing Recombination

Bulk recombination

Typically bulk recombination is a combination of devect related recombination (which is usually modeled by a Shockley-Read-Hall (SRH) type formula, without any real experimental justification), Auger recombination, and radiative recombination. In this case one has

$$R = v_{th}\, N_T \frac{pn - n_i^2}{\frac{1}{\sigma_p}\left[n + n_i exp\left(\frac{E_T - E_i}{kT}\right)\right] + \frac{1}{\sigma_n}\left[p + n_i exp\left(-\frac{E_T - E_i}{kT}\right)\right]}$$

$$+ B(pn - n_i^2) + C_n(n^2 p - n_o^2 p_o) +$$
$$C_p(p^2 n - p_o^2 n_o) \tag{4}$$

where

$B = 2 \times 10^{-15}\ cm^3/sec$ (radiative recombination)

$C_n = 3 \times 10^{-31}\ cm^6/sec$ (eeb Auger coefficient)

$C_p = 1 \times 10^{-31}\ cm^6/sec$ (ehh Auger coefficient)

The radiative term is usually negligible, except when discussing fundamental limits where the remaining recombination terms have arbitrarily been set to zero. The magnitudes of C_n and C_p are somewhat in dispute but are undoubtedly within an orger of magnitude of those shown in equation (.) which are from (2). The designer can control Auger recombination only by varying the doping density as a function of position in the device.

The defect related (SRH) term is strongly dependent on the nature and concemtration of process induced defects and contaminants. Typically a material will have both donor and acceptor type deep level defects. Under low level injection acceptors will usually dominate the recombination process in n-type material and vice-versa in p-type material. This is because hole capture in n-type material would be the rate limiting process and hole capture is an attractive process for acceptors. Under high level injection the SRH recombination lifetime becomes $\tau = 1/N_t v_{th}(1/\sigma_n + 1/\sigma_p)$. Since one of the capture processes (electron or hole) must be attractive and the other neutral one would expect that under high level injetion the lifetime would be considerably greater as the neutral capture becomes rate limiting for both acceptors and donors. We have found that high level bulk lifetimes over 1000 μs can be obtained in completed devices when high resistivity float-zone silicon is used as the starting material. The low-level lifetime is typically a factor of 3 to 10 less. Careful processing is required to routinely obtain high lifetime. We have found the following procedures sufficient (but not necessarily necessary) to this end

a) Never use metal tweezers to handle wafers.

b) Always perform a RCA (3) clean prior to high temperature steps.

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c) Process in a class 100 clean area.

d) Perodically clean furnace tubes with HCl.

surface recombination

Surface recombination appears to be more a function of the preparation procedure for forming the passivating oxide layer, rather than being highly sensitive to contamination as is bulk recombination. Those procedures that have been found to produce high quality Si-SiO$_2$ interfaces for MOS transistors appear to minimize the surface recombination velocity.

Dry thermal oxidation followed by a low temperature hydrogenation produces surfaces with a mid-gap interface state density of around 1×10^{10} /cm^{2}eV. Figures 1 and 2 show the measured interface state density for such an oxide in the upper and lower portions of the bandgap, respectively. These measurements, done using DLTS, show no evidence of the so called U shaped continuum but rather a monotonic decrease from conduction to valence band.

By performing an inert atmosphere anneal after oxidation the density of interface states can be reduced to about 1×10^9 /cm^{2}eV. Such a surface has a measured high level interface recombination velocity of 2 to 5 cm/sec. This rather low value can be understood by referring to figures 3 and 4 which show the measured electron and hole capture cross-sections (4). One finds that the electron capture cross section is generally orders of magnitude larger than that for holes. Under high level conditions most of the recombination will occur for those states where σ_n and σ_p are approximately equal. This occurs at about 0.2 eV below mid-gap where they are in the mid 10^{-16}/cm^{2}eV range. At higher energies σ_p becomes smaller and limits the recombination rate, and similarly for σ_n. Using the data of figures 1 through 4 to calculate the recombination velocity using SRH theory yields 2 cm/sec, in agreement with mesurements. (This calculation assumes that the interface charge is small enough to produce negligible band bending.)

The data of figures 3 and 4 indicate the surprising result that p-type surfaces should have a much larger recombination velocity than n-type because of the large differences in cross sections. We are currently investigating whether this is proves to be the case.

Further work is needed to deve   methods which produce MOS quality interfaces on very thin oxides suitable for use under anti-reflection layers.

contact recombination

Keeping carriers from the contact metal proves to be a most challanging problem of the cell design. The traditional approach is to create potential barriers by doping which are sufficiently wide to support a significant diffusion potential (ie., the gradient in pn product across the barrier does not cause too much minority carrier current).

Because of the well known confluence of heavy doping effects such as reduced bandgap and lifetime such barriers are not as effective as one might want. Never-the-less, it can be shown (1, p. A8) the recombination current in the barrier and contact can always be writen, so long as the doped barrier is not high level injected,

$$I_{rec} = I_0(pn/n_i^2 - 1) \tag{5}$$

where the pn product is evaluated in the space charge region at the edge of the barrier. I_0 will be called the barrier saturation current in analogy with the terminology of ideal diode theory. Indeed, if the separation of quasi Fermi levels at the space charge region equals the applied terminal voltage then equation (5) gives the typical

$$I_{rec} = I_0(\exp(qV/kT) - 1) \tag{6}$$

Calculated saturation currents appear in figures 5 and 6 for Gaussian n-type doping profiles (6). Notice that in regions which have a high recombination velocity such as under metal contacts, deep diffusions with surface concentration around 10^{20} cm_{-3} produce the best results. If such diffusions are used to keep carriers away from surfaces Our experwith low recombination velocity, then shallow diffusions with surface concentration around 10^{19} cm^{-3} give the best results. Our experience, however, is that in this case no diffusion at all is the best choice, provided the surface is well passivated. Of course, in a conventional cell the surface diffusion has the additional role of transporting majority carriers to the contacts and cannot be simply eliminated. In cells with high lifetime and hence long diffusion length, it is possible to rely on diffusion of carriers to the contact regions and dispense with the surface diffusion except under the contacts. This is the approach of the point-contact-cell (1).

It is interesting to compare the relative magnitudes of the various sources of recombination. Assuming that, a) we have a 100 μm thick undoped base with a high level lifetime of 1000 μs, b) the surface recombination velocity is 2 cm/sec, and c) the n and p barrier saturation currents are both 3 X 10^{-13} A/cm^2 the methods of the preceeding sections can be used to calculate the recombination currents.

When the pn product is $(10^{17}$ $cm_3)^2$, as might occur in a concentrator cell, one calculates the following:

	J_{rec} A/cm^2
bulk, SRH	0.160
bulk, radiative	0.032
bulk, Auger	0.160
surface	0.064
diffused regions	28.5

These results show the overwhelming influence of contact recombination on the operation of the cell when the other sources of recombination are reduced by careful processing. At a pn product of $(3$ X 10^{15} $cm^{-3})^2$, as might occur at one sun, these results become

	I_{rec} mA/cm^2
bulk, SRH	4.8
bulk radiative	2.9 X 10^{-2}
bulk, Auger	4.3 X 10^{-3}
surface	1.9
diffused regions	25.7

At one sun the contact recombination dominates the other sources of recombination , though not so completely as in the concentrator case.

references

1. R. M. Swanson, "Point Contact Silicon Solar Cells," EPRI report AP-2859, May 1983.

2. J. Dziewiour and W. Schmid, Appl. Phys. Lett. 31, p. 346 (1977).

3. W. Kerm and D. A. Poutinen, RCA Review, June 1970, pp. 187-207.

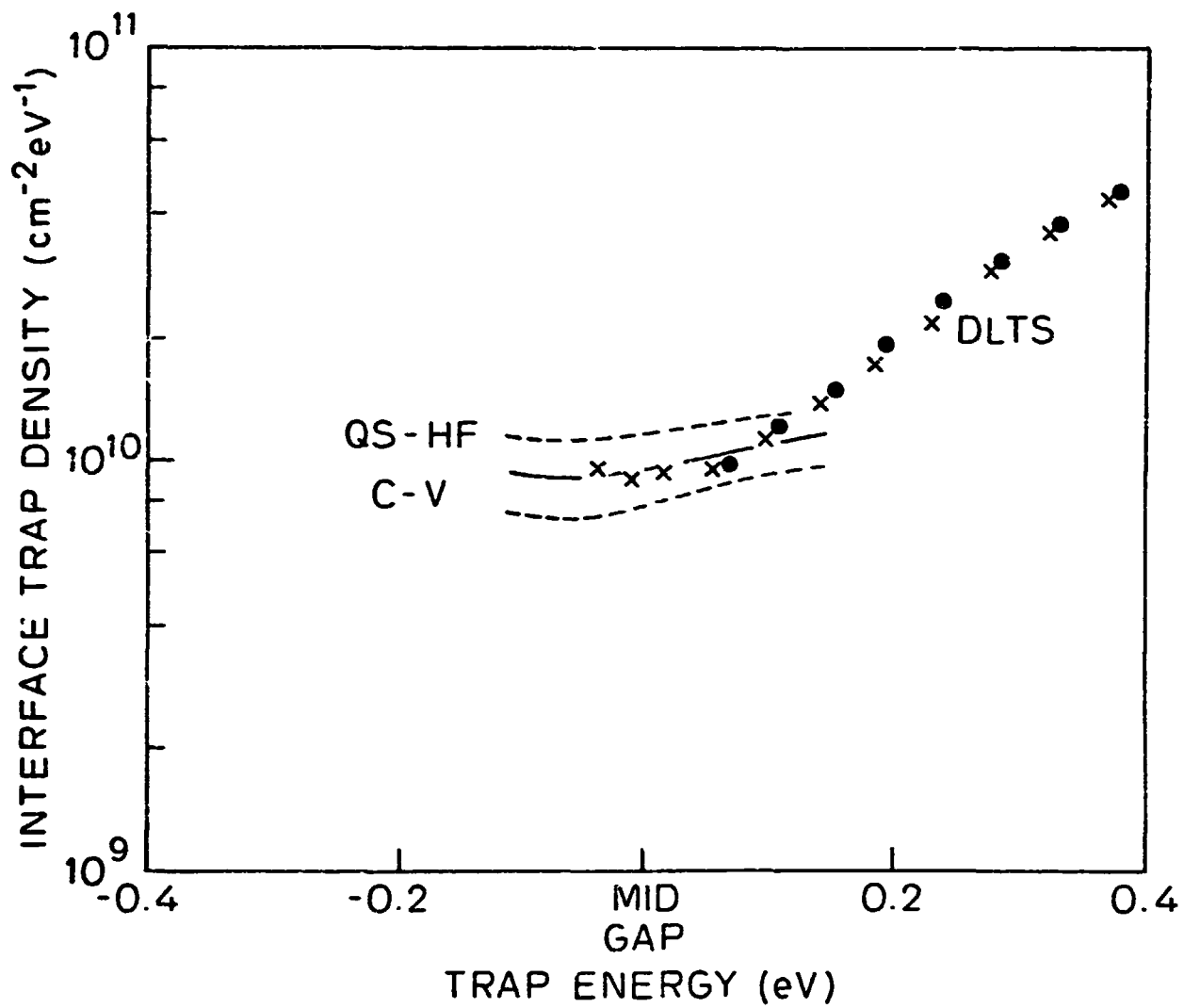4. R. M. Swanson and W. D. Eades, being prepared for publication.

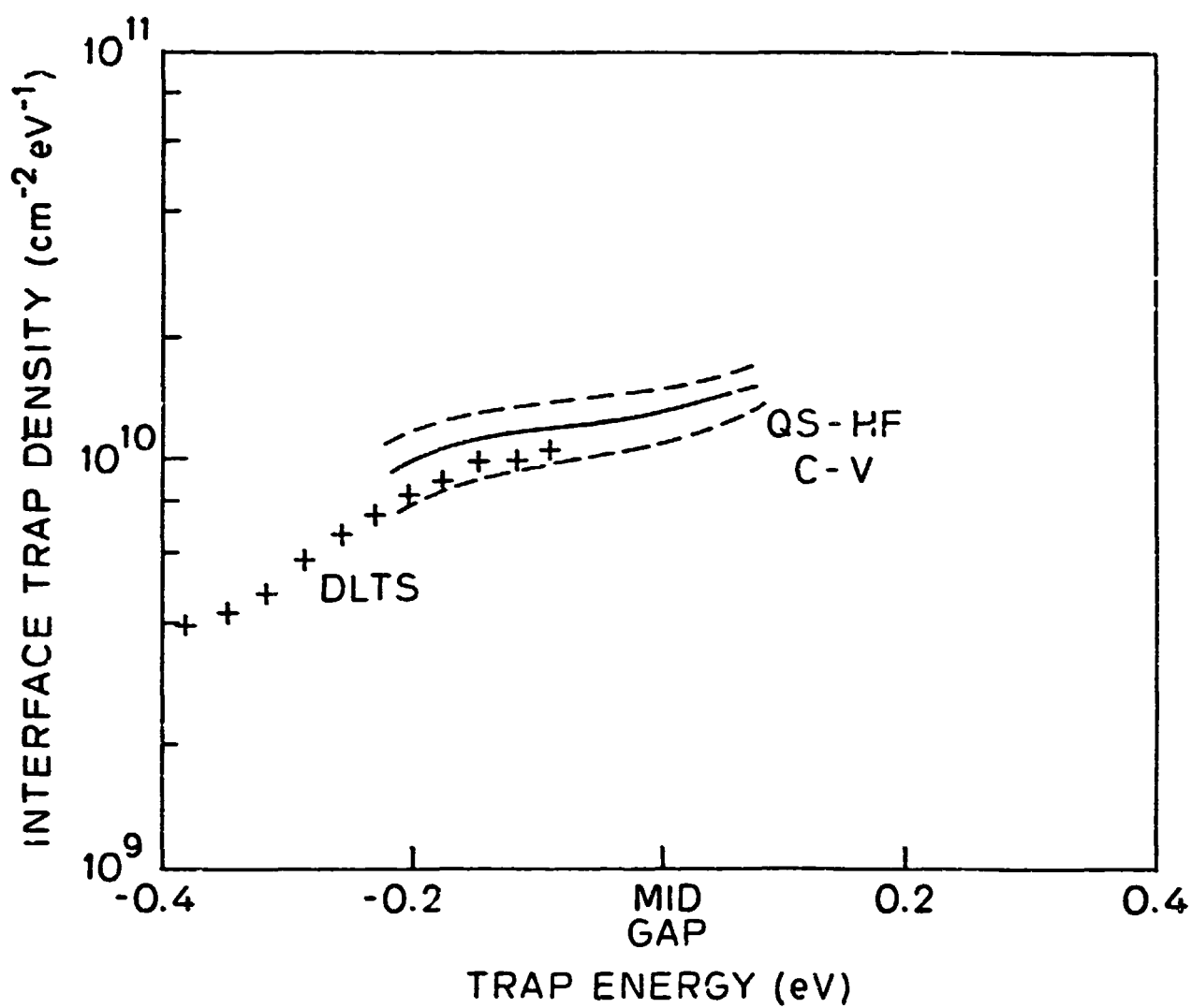Figure 1. Density of interface states in the upper portion of the bandgap.

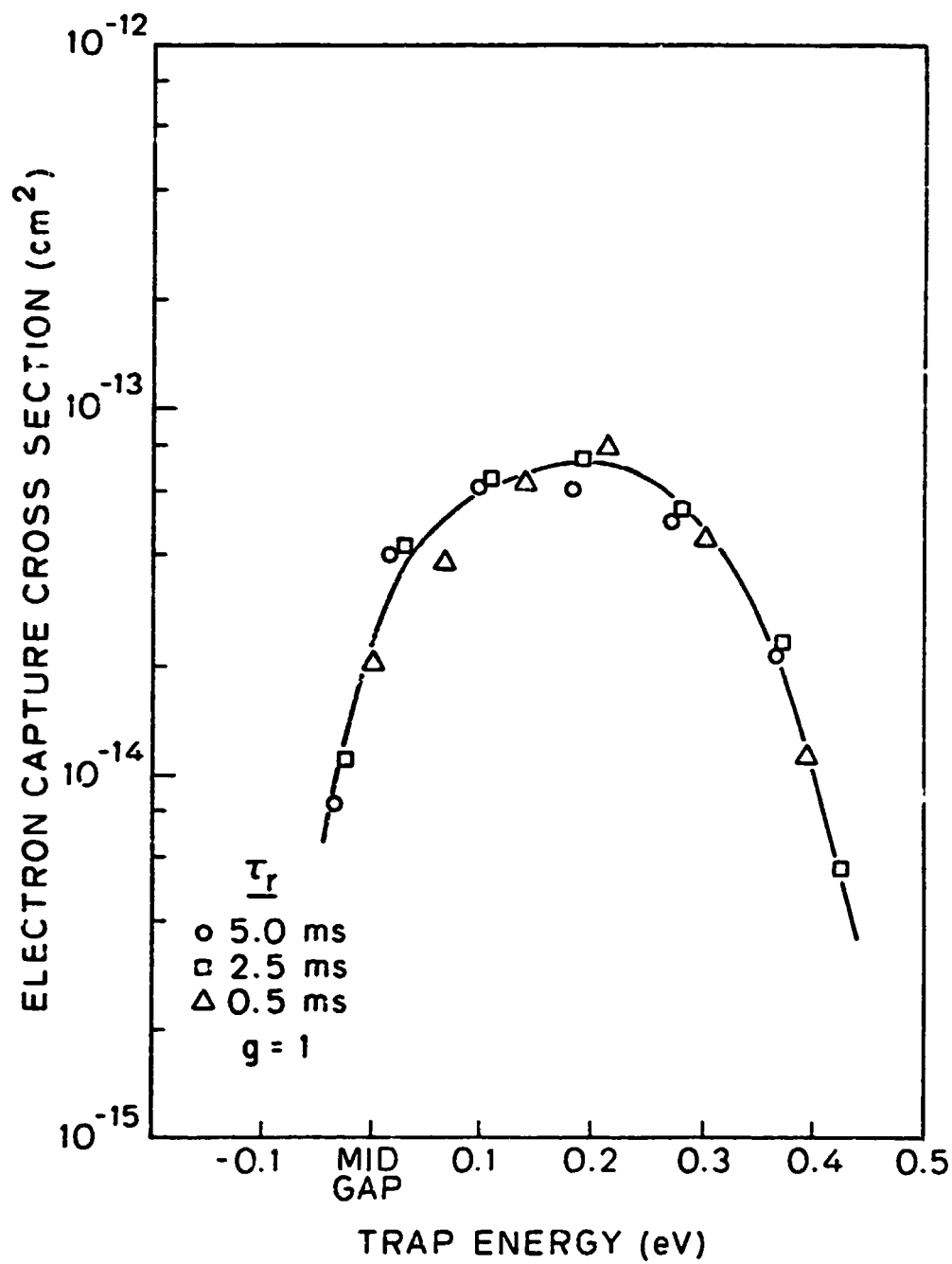Figure 2. Density of interface states in the lower portion of the bandgap.

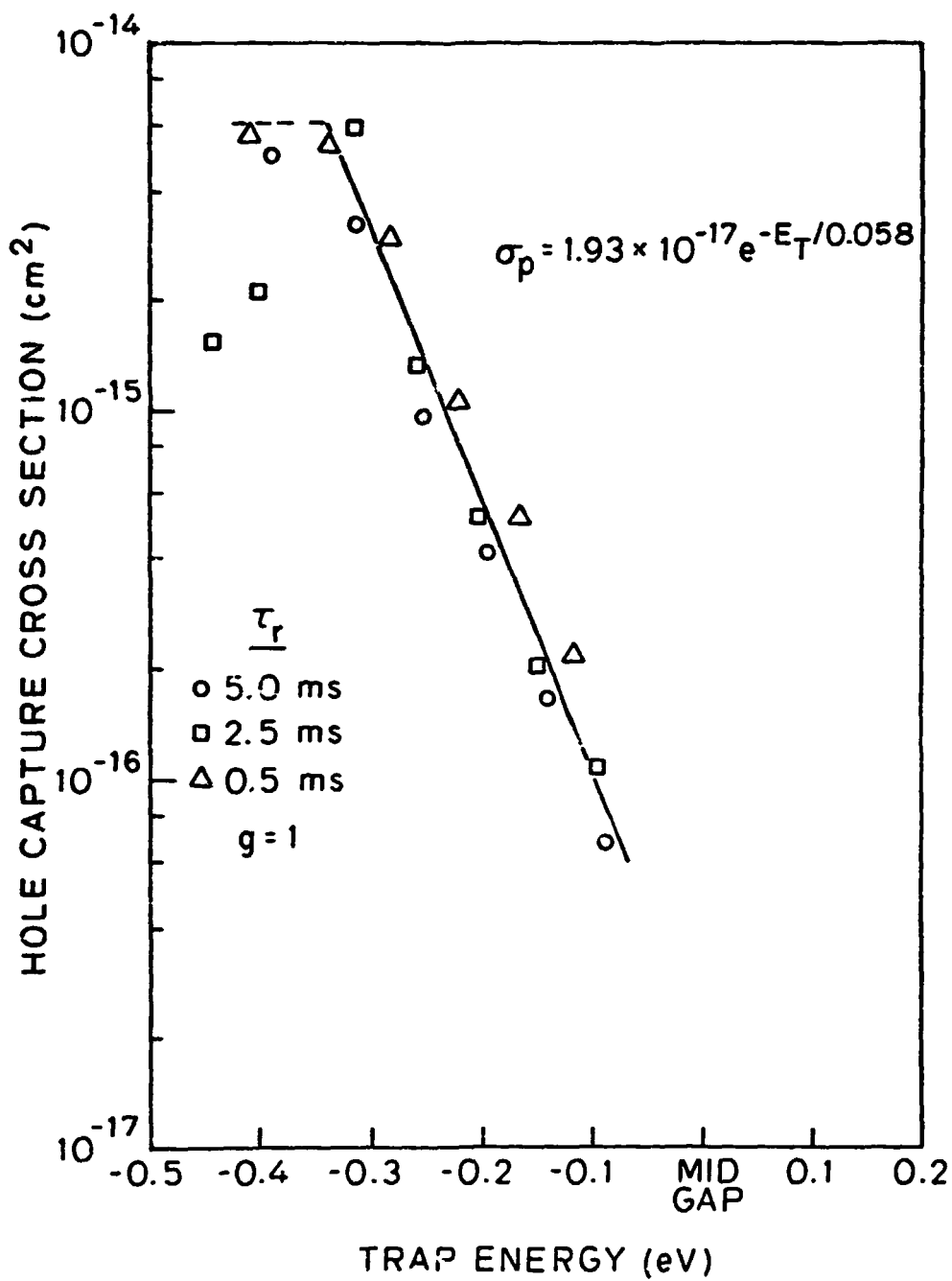Figure 3. Electron capture cross section of Si-SiO$_2$ interface states.

Figure 4. Hole capture cross section of Si-SiO$_2$ interface states.

The figure shows a plot of HOLE CAPTURE CROSS SECTION (cm^2) versus TRAP ENERGY (eV). The y-axis ranges from 10^{-17} to 10^{-14}, and the x-axis ranges from -0.5 to 0.2 with MID GAP marked. The fitted equation is:

$$\sigma_p = 1.93 \times 10^{-17} e^{-E_T/0.058}$$

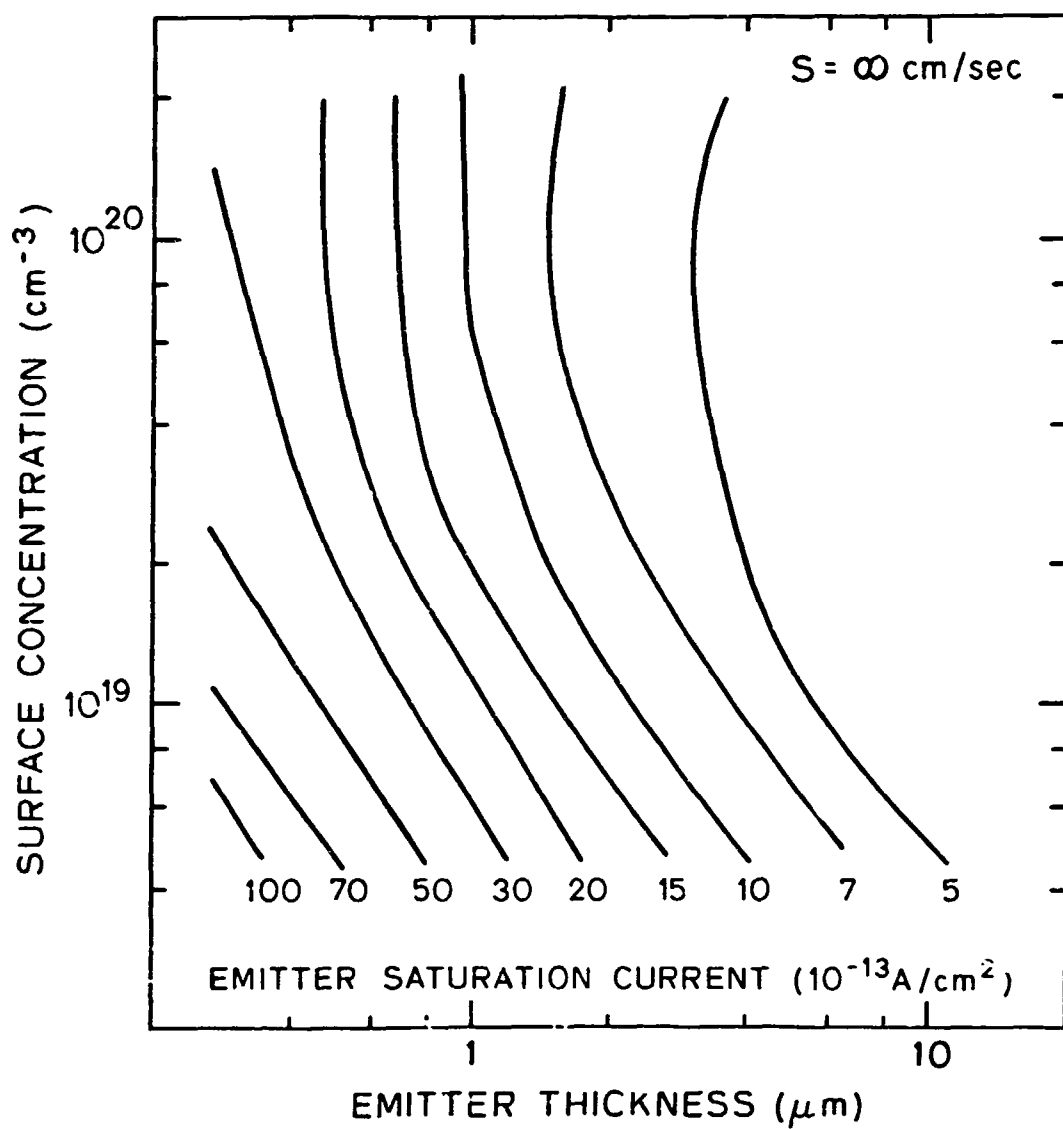Legend:
τ_r
○ 5.0 ms
□ 2.5 ms
△ 0.5 ms
g = 1

Figure 5. Calculated saturation current density for Gaussian profile emitters with infinite surface recombination velocity
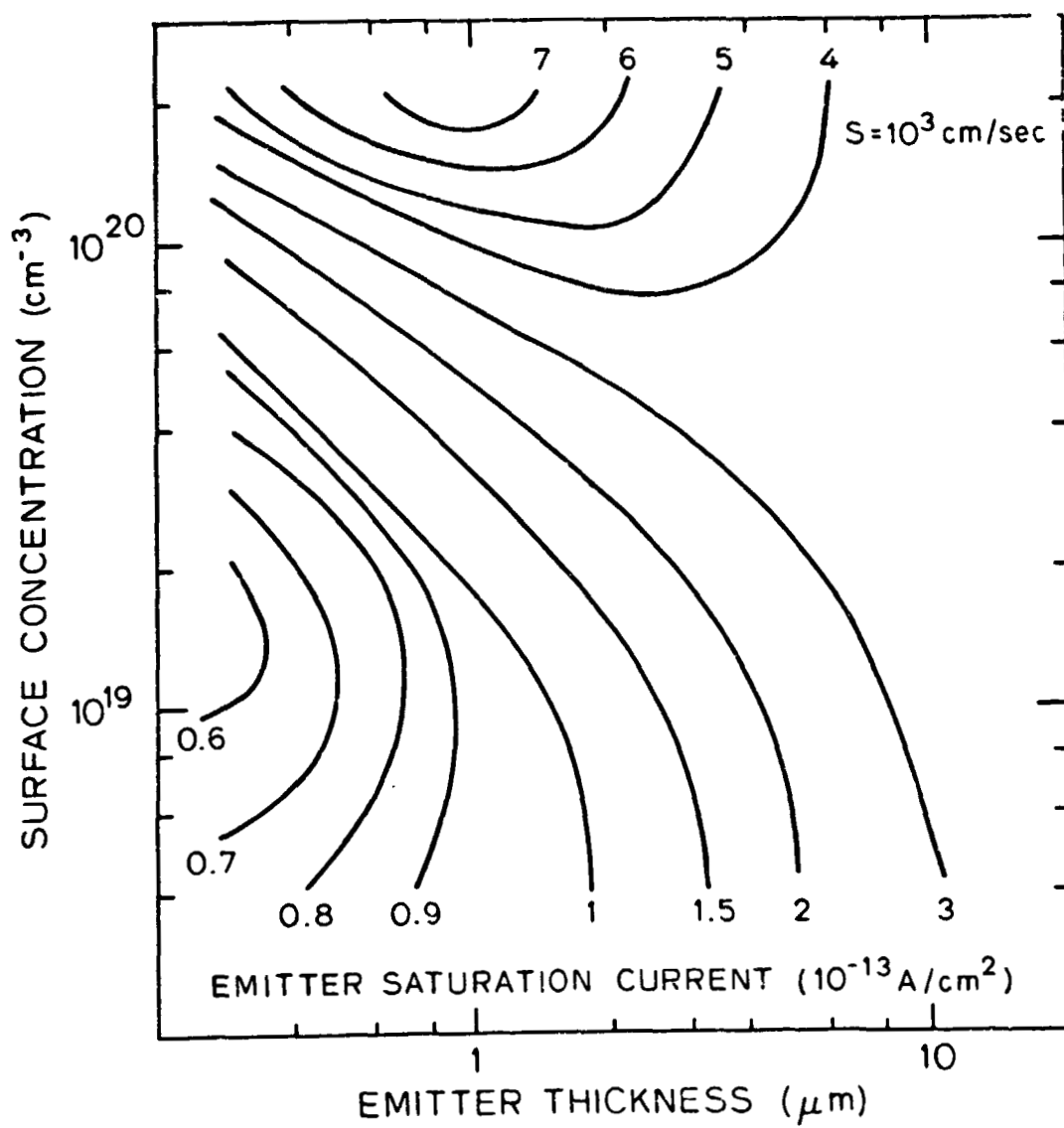
Figure 6. Calculated saturation current density for Gaussian emitters with s = 10^3 cm/sec.

LINDHOLM: Dick, I have a couple of questions. The first is in connection with your last remark. Do you think you need a two-dimensional code or a three-dimensional code?

SWANSON: For the point contact cell I think you need a three-dimensional code. If you made the lines as stripes, a two-dimensional code would be adequate.

LINDHOLM: Would you comment on your preference for the open voltage over the conductivity method for determining high injection lifetime? Why you use it at the end, and also say a little more on the photoconductive decay method for in-process lifetime?

SWANSON: The open-circuit voltage decay: I like it because it is very easy to do, and once you understand what it is doing it is easy to extract data from it. In the type of cell we are talking about, where the diffusion length is much greater than the thickness of the device: after interrupting the current, a very short period of time later the carriers are more or less uniformly distributed from the front to the back of the device, and this makes the analysis of the transient very simple. Basically you have one recombination term that is going as n^2, that is the diffused areas, and that gives you a steeper slope in the beginning. It allows you to extract the J_0's and then it goes into a linear region where the recombination going is n, and there is a straight line on the decay, and you pick the lifetime off that.

LINDHOLM: Have you written something on that? Published?

SWANSON: No. There is, but I am just using things from the literature on it.

LINDHOLM: How about the photoconductivity decay in process lifetime monitoring?

SWANSON: That is essentially a similar circuit to the one in High Lifetime Factors in Silicon Processing, which is a book from ASGF. Our particular implementation of it is simply a three-turn coil with 10 megahertz of RF flowing through it that is laid near the sample, and then we use a General Radio strobe attached to it to excite the carriers. We look at, essentially, the back EMF across the coil as a function of time, which -- in effect the silicon looks like a single-turn secondary, coupled to this, whose resistance is a function of time, and that gets reflected into the impedance looking into the coil, so that the real part of the impedance of the coil is a function of the conductivity, etc. I will send you a writeup we have on that. I wrote it up because the people from Westinghouse wanted to see it, so I made a bunch of copies. We had no intention of publishing because it really is the same - -

SPITZER: I am interested in hearing some more about your tips for high-lifetime processing. That is something we are working hard on. The first question is: did you find it necessary to use double-wall furnaces,

or do you use those?

SWANSON: Well, Mark, you will have to understand: being in the University environment, I have no secrets at all. However, we have tried silicon tubes, silicon carbide tubes, double-wall quartz tubes, double-wall quartz tubes inside of silicon carbide tubes, and plain silicon tubes with and without alumina liners.

SPITZER: We can't afford that in industry.

SWANSON: We couldn't afford that either. They were all given to us by interested parties. What I can say in retrospect is, though, that the system we are using now, which has given us the best results, is a plain quartz tube inside an alumina liner.

SPITZER: What about processing gases? Did you spend a lot of time judging various suppliers and things like that?

SWANSON: We did. We just used boil-off nitrogen and oxygen but we have had about five major lifetime crashes in the history of the program. At one time we thought it was gas. We hooked up a residual gas analyzer to our gas system and saw sulplur dioxide in the nitrogen and thought it was sulphur but then it turned out that was an artifact of the residual gas analyzer, and it turned out not, in that particular case, to be from the gas but to be from bacteria in the water. So we have never seen any evidence in boil-off that there was any need for more purity than we are obtaining routinely in the boil-off.

SPITZER: Do you use boil-off hydrogen?

SWANSON: We don't use hydrogen.

SPITZER: No hydrogen.

SCHRODER: How do you measure S of 2 cm/second?

SWANSON: We measured that by the photoconductivity decay method.

SCHRODER: These are surface recombinations velocities, right?

SWANSON: These are high-level surface recombinations velocities, which were measured by taking samples of different thicknesses, ranging from around 20 micrometers to 300 micrometers, and their high-resistivity float-zone material, oxidizing both sides and measuring the recombination lifetime, with our standard, as a function of thickness.

WOLF: Do these lifetimes then include the effect of the accumulation layer?

SWANSON: To measure effective recombination lifetime. However, the oxides we have produced, which are standard MOS-type oxides, have fixed charge densities under 10^9, I think, and when they are injected at 10^{17}, any kind of potential band due to that is very, very small. One of the challenges that faces one in this, one we have not fully resolved, is how

to get similar performance on very thin oxides suitable for putting under an antireflection coating. These are all state-of-the-art MOS-type oxides, high-temperature dry oxidation followed by nitrogen atmosphere anneal and low-temperature hydrogenation.

WOLF: Now, what you mentioned about the DI water and the bacteria sounds extremely interesting and it seems to me that you said if you have really pure water then there are no bacteria. So the bacteria comes with the indication whether your water is basically purified well or not. Is that right?

SWANSON: No. The problem is that most people monitor -- at least, in our laboratory until we discovered this -- we routinely monitor resistivity but not bacteria count. The resistivity can be in real good shape and have a very high bacteria count.

WOLF: DI water generally does not contain ions, and still bacteria can thrive on that?

SWANSON: I really don't know how they live in there but they do. They metabolize the plastic pipe, or that is what I have been told. They are anaerobic and whatever.

TAN: Allow me to make a comment on your last. Except for the first item, which is the float-zone silicon, the rest is standard practice of the integrated circuit industry. Off the record, I can also support him about the bacteria business. It is all true.

SWANSON: I don't know how you can go about getting these kinds of lifetimes in Czochralski or other materials. We were misled because, being a poor university, we were in one of those periods where silicon was hard to get. Wacker gave us silicon in boxes that said it was Czochralski material. But it turned out that it was mislabeled. It was actually float-zone material. We worked on that for a year, and we then ordered new material from them thinking they have got the hot stuff. It came back that we were getting 20 to 50 microseconds, and that is when we had the material analyzed and found that it was indeed float-zone material. Then we worked with the Czochralski material for over a year and were unable to get the lifetime.

SCHWARTZ: How did you measure the capture cross sections in surface states? To me it is a very surprising result.

SWANSON: It was to us too, and these data are being prepared for publication. It was done using DLTS in a capture mode. Just like you would use DLTS for bulk levels by shortening and filling the pulse width. We used essentially small-signal DLTS, where we wiggled the interface a little bit, so we filled emptying traps in a ΔE about a known point, and then varied the filling pulse time and watched the decay signals.

SCHWARTZ: It appears to me that your fall-off in capture cross section is so rapid that one would not see it, so that experiment doesn't seem to fit.

SWANSON: Right now we are making measurements of recombination velocity
            versus doping levels to see if we get the results predicted by
            integrating the SRH equation over those.