IMPURITIES IN SILICON SOLAR CELLS

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We studied how metallic impurities, both singly and in combinations, impact the performance of silicon solar cells. Czochralski silicon web crystals were grown with controlled additions of secondary impurities. The primary electrical dopants were boron and phosphorus. The metal elements were selected because of their occurrence in silicon raw materials, possible introduction during subsequent device processing, or because there were common construction materials for process equipment or the cells themselves. Some 26 elements were examined including Ag, Au, Al, C, Cr, Co, Cu, Fe, Gd, Mn, Nb, Ni, Pd, Sn, Ta, Ti, V, W, and Zr. Impurity concentrations were in the range of 10^{11} to 10^{18} cm^{-3}.

All silicon ingots were grown under controlled and carefully monitored conditions from high-purity charge and dopant material to minimize unintentional contamination. Following growth, each crystal was characterized by chemical, microstructural, electrical, and solar cell tests to provide a detailed and internally consistent description of the relationships between silicon impurity concentration and solar cell performance.

Analysis of vacuum-cast melt samples provided an accurate determination of the melt impurity concentration at the completion of crystal growth. Melt concentrations coupled with reliable effective segregation coefficients in turn were used to calculate ingot impurity concentrations, which were in excellent agreement with the ingot impurity concentrations measured directly by spark source mass spectroscopy and neutron activation analyses. Deep-level spectroscopy measurements were used to measure impurity concentrations at levels below the detectability of the other techniques and to study thermally-induced changes in impurity activity.

Solar cells made using a conventional diffusion process optimized for repeatability and reliability were used to evaluate the effect of impurities. For the majority of contaminants, impurity-induced performance loss was due to a reduction of the base diffusion length. From these observations, we formulated a semi-empirical model which predicts cell performance as a function of metal impurity concentration. The calculated performance parameters agree well with measured values except for the impurities Cu, Ni, and Fe, which at high concentrations degrade the cell performance substantially by means of junction mechanisms. The model was used successfully to predict the behavior of solar cells bearing as many as 11 different impurities. The concentration of recombination centers identified by deep-level transient spectroscopy not only correlates directly with the concentration of metallurgically added impurity, but also with solar cell performance.

The effects of impurities in n-base and p-base devices differ in degree but can be described by the same modeling analysis. Some of the more deleterious impurities in p-base devices produce significantly less performance reduction in n-base silicon. For example, nearly ten times more Ti is acceptable in n-type silicon to produce the same cell efficiency as in a similarly contaminated p-base device. N-base cells containing V, Mo, and Mn exhibit somewhat smaller efficiency improvements.

When the model-calculated and measured cell performance for multiple impurities are compared, there is limited indication of interaction between impurities. For example, copper improves the efficiency of Ti- and V-doped cells, although the effect is small. Apparently, Cu diffuses to and combines with the second transition metal to reduce its electrical activity. Precipitated impurities have little or no effect on carrier-transport properties in the low-field base region of the solar cell, but do affect cell performance when they occur in or near the high-field junction region. The latter effect is manifested by large shifts in the lower segment of transformed dark I-V curves measured on cells containing the metal-rich precipitates. (The presence of precipitation was confirmed by X-ray topographic analysis of the devices.)

Extension of the impurity performance model to high-efficiency solar cells indicates, in general, that such devices will be more sensitive to impurities than are their more conventional counterparts. This increased impurity sensitivity will be exhibited in widebase cells and medium-base cells with back-surface fields or passivated surfaces, but may be significantly reduced by making cells with narrow ($\approx$ 100 μm) basewidths. For example, we calculate that raising the base diffusion length of our standard efficiency device (275 μm thick) to 450 μm from 150 μm lowers the impurity threshold for performance loss onset from 6 x 10^{11} Mo atoms per cm^{-3} to 9 x10^{10} atoms per cm^{-3}. The absolute efficiency of cells with the 450 μm diffusion length of course remains higher than that of cells with the 150μm diffusion length until the performance becomes dominated by impurity effects. Similar shifts in impurity sensitivity are calculated for passivated cells with back-surface fields using a one dimensional analytic model.

In addition to the direct impact on device performance, impurities also can degrade crystal structure. Crystal structure breakdown (constitutional supercooling) or precipitation effects largely affect junction behavior. Since the concentration thresholds are higher for structural impairment than for lifetime degradation, the latter is a dominant performance loss mechanism in solar cells.

We examined the redistribution of impurities during silicon web growth and found that, like Czochralski silicon growth, the segregation coefficients for metals are small, typically 10^{-7} to 10^{-5}. In addition, the performance loss of web cells due to impurities can be modeled in a fashion identical to that employed for devices made on Czochralski wafers. The predicted and measured cell performance values are in good agreement.
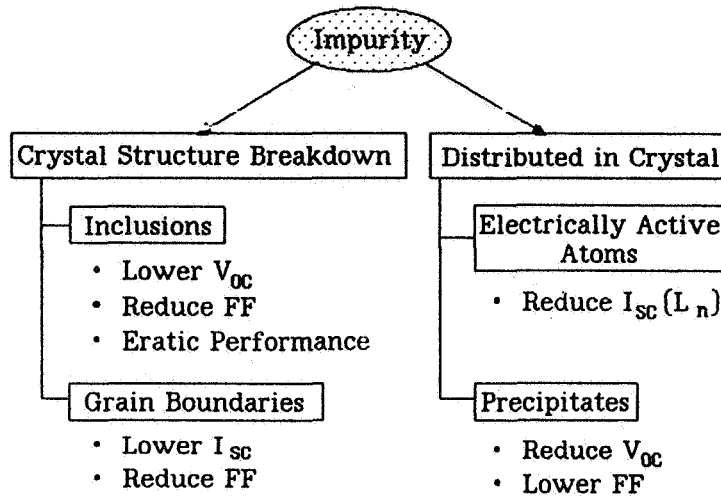
Solar-Cell Impurity Data Base

- 240 crystals

- 26 impurity species

- Over 7,000 solar cells.

Material Characterization

- Impurity Analysis
    - Neutron Activation
    - Spark Source Mass Spectroscopy
    - Infrared Absorption
    - Deep Level Transient Spectroscopy

- Electrical Properties
    - Four-point Resistivity
    - Spreading Resistance
    - Photoconductive Decay
    - Open Circuit Decay
    - Dark I-V Analysis
    - Laser-scanned Photoresponse

- Structural Characterization
    - Etch Pit Density
    - X-ray Topography
    - Optical/Electron Microscopy

- Solar Cell Characterization
    - Lighted I-V
    - Spectral Response

Impurity Degradation Mechanisms
in Silicon Solar Cells

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                    ┌───────────┐
                    │  Impurity │
                    └───────────┘
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Crystal Structure Breakdown	Distributed in Crystal

Inclusions
- Lower V_{oc}
- Reduce FF
- Eratic Performance

Grain Boundaries
- Lower I_{sc}
- Reduce FF

Electrically Active Atoms
- Reduce $I_{sc}(L_n)$

Precipitates
- Reduce V_{oc}
- Lower FF

Crystal Growth Conditions

Doping: boron 3—6 Ωcm
              or $\Big\}$ + metal
              phosphorus 1—3 Ωcm   impurities

Czochralski: <111> orientation
              3.5 cm diameter
              7 cm/hr growth rate
              10 rpm cw seed rotation
              3 rpm ccw crucible rotation
              argon atmosphere

Dendritic Web <211> orientation
Ribbon: 3 cm width
               1 cm/min growth rate
               argon atmosphere

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Effective Segregation Coefficients in Silicon

ELEMENT	SEGREGATION COEFFICIENT
Ag	1.7×10^{-5}
Al	3×10^{-2}
Au	2.5×10^{-5}
Co	2×10^{-6}
Cr	1.1×10^{-5}
Cu	8.0×10^{-4}
Fe	6.4×10^{-6}
Mn	1.3×10^{-5}
Mo	4.5×10^{-8}
Nb	4.4×10^{-7}
Ni	1.3×10^{-4}
Pd	5×10^{-5}
Sn	3.2×10^{-2}
Ta	2.1×10^{-8}
Ti	2.0×10^{-6}
V	4×10^{-6}
W	1.7×10^{-8}
Zr	1.6×10^{-8}

Solar-Cell Design and Fabrication: Standard Efficiency (SE)

Baseline Cell

- 1.03 cm^2, five finger grid (5.4% coverage)

- Ti − Pd − Ag contacts
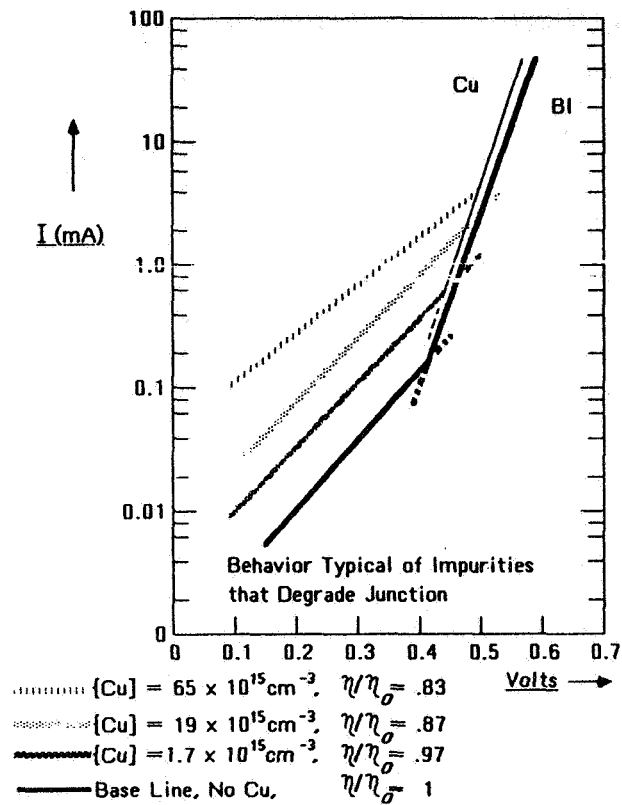
- Cell efficiency $14.1 \pm 0.7\%$ AM1 (2000 cells)

n^+p Cell

$POCl_3$ diffusion
850° C, 50 min
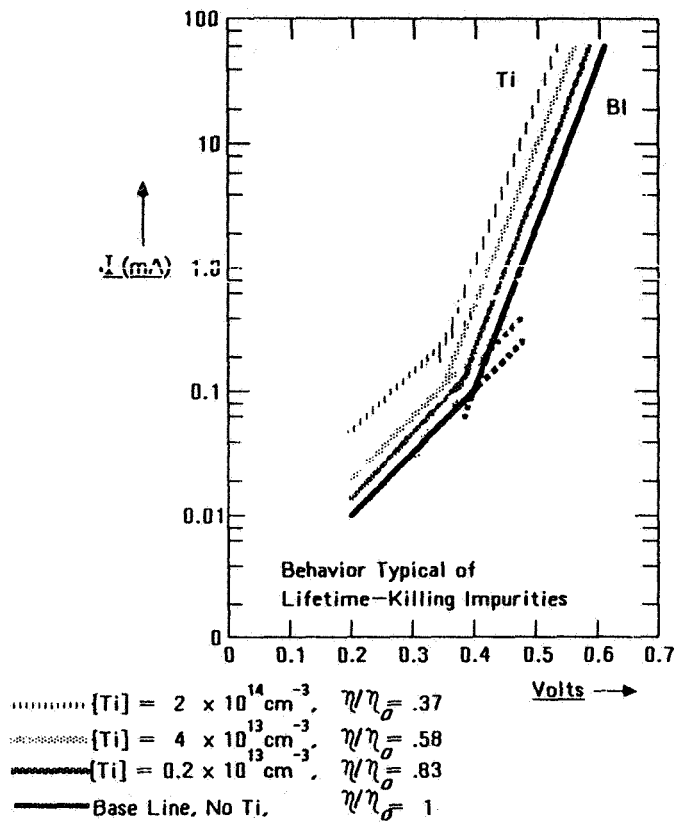0.35 µm junction depth
Contacts sintered @
   400° C, H_2

p^+n Cell

BBr_3 diffusion
875° C, 30 min
0.35 µm junction depth
Contacts sintered @
   350° C, H_2

Transformed Dark I-V Curves for Cu-Doped Solar Cells

Figure legend:

$[Cu] = 65 \times 10^{15} cm^{-3}$, $\eta/\eta_o = .83$

$[Cu] = 19 \times 10^{15} cm^{-3}$, $\eta/\eta_o = .87$

$[Cu] = 1.7 \times 10^{15} cm^{-3}$, $\eta/\eta_o = .97$

Base Line, No Cu, $\eta/\eta_o = 1$

Transformed Dark I-V Curves for Ti-Doped Solar Cells

.... $[Ti] = 2 \times 10^{14} cm^{-3}$, $\eta/\eta_o = .37$

$[Ti] = 4 \times 10^{13} cm^{-3}$, $\eta/\eta_o = .58$

$[Ti] = 0.2 \times 10^{13} cm^{-3}$, $\eta/\eta_o = .83$

Base Line, No Ti. $\eta/\eta_o = 1$

Impurity Behavior

- Degrade Junction

  Cu, Ni

- Reduce Diffusion Length

  Nb, Ti, V, Ta, W, Mo, Pd, Au, Zr, Mn, Al, Sn

- Both

  Fe, Co, Ag

Impurity Model Assumptions

1. Device can be modeled as if the cell consisted wholly of a single base region with uniform electrical properties.

2. Impurity effect is exclusively to reduce carrier diffusion length in the effective base region.

3. Impurity-induced diffusion length reduction is due either to carrier recombination at deep centers or mobility loss by ionized impurity scattering.

4. The number of electrically active centers is a species-dependent linear function of the total metallurgical concentration of that impurity.

Impurity Model Equations

$$\left[\frac{I_{n\infty}}{I_n} - 1\right]^2 = C_1 \left[1 + \frac{N_x}{N_{ox}}\right] \quad \text{Normalized } I_{sc}$$

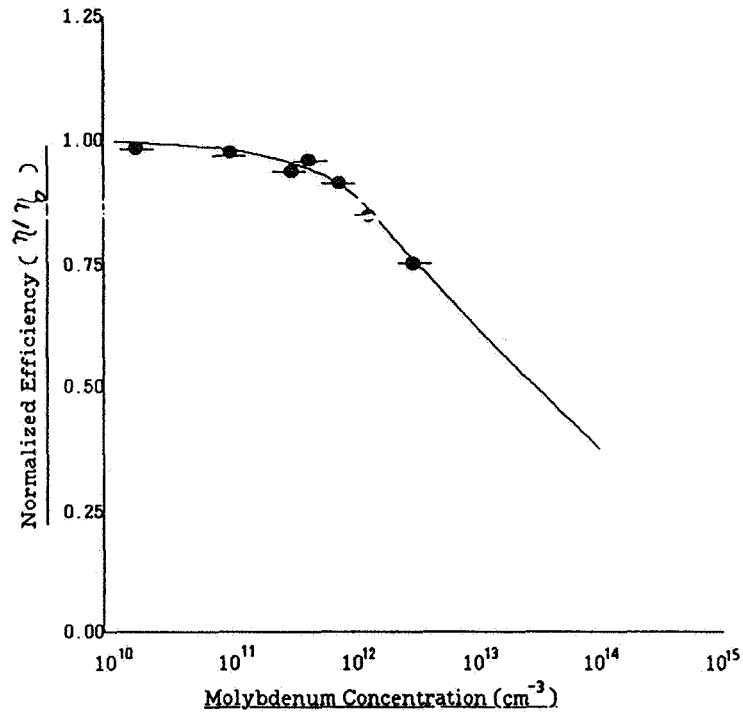N_{ox} : Impurity Thresold Degradation Concentration

N_x : Total Impurity Concentration in Cell.

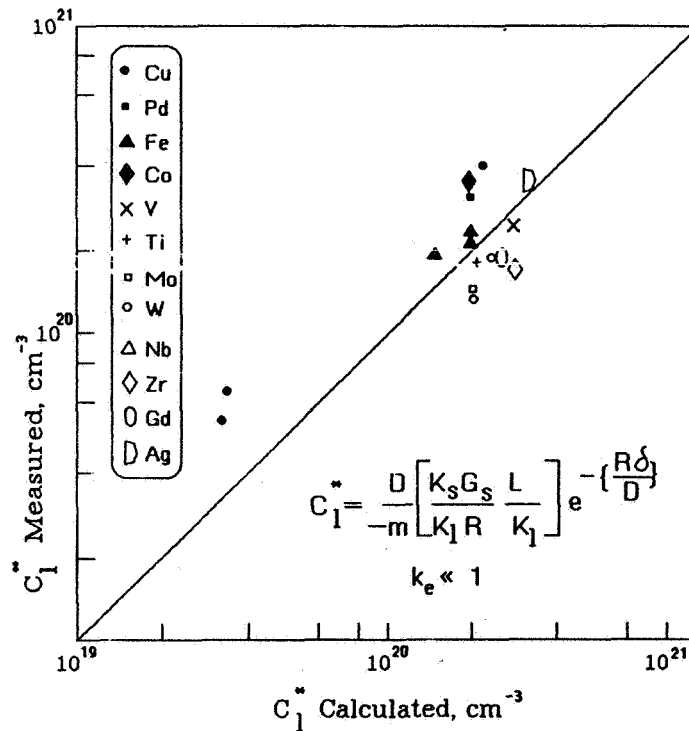$$\frac{\eta}{\eta_o} = \frac{i_p V_p}{i_{po} V_{po}} \quad \text{Normalized efficiency.}$$

$$\frac{\eta}{\eta_o} = 0.872 \, I_n^{1.128} + 0.128 \, I_n^{12}$$

[After J.R. Davis, R.H. Hopkins, and A. Rohatgi, IEEE Transactions Elec. Devices, ED-27, 677 (1980)]
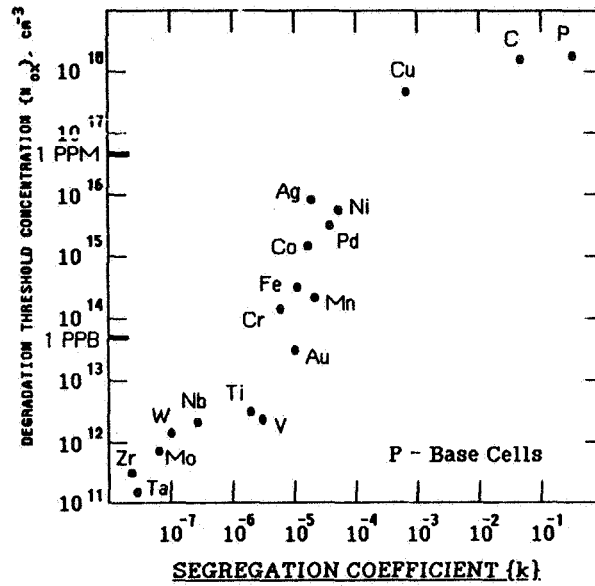
Normalized Silicon Solar-Cell Efficiency
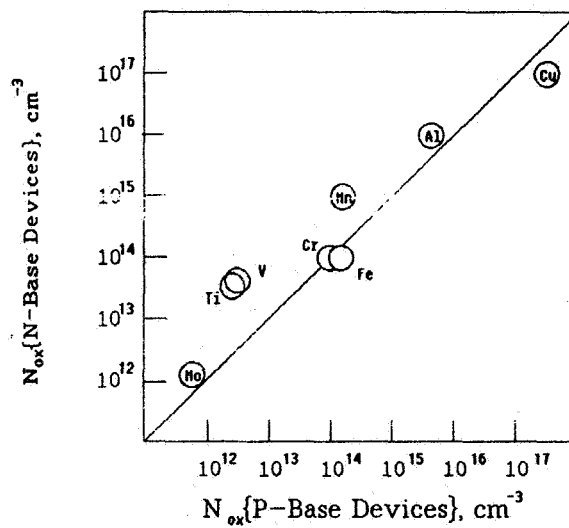## versus Content of Molybdenum in the Silicon

Critical Impurity Concentration
for Crystal Structure Breakdown

$$C_1^* = \frac{D}{-m}\left[\frac{K_s G_s}{K_l R} \frac{L}{K_l}\right] e^{-\left(\frac{R\delta}{D}\right)}$$

$$k_e \ll 1$$

Relation of Cell Degradation Threshold
to Impurity Segregation Coefficient

Degradation Threshold Concentrations,
n-Base versus p-Base Devices
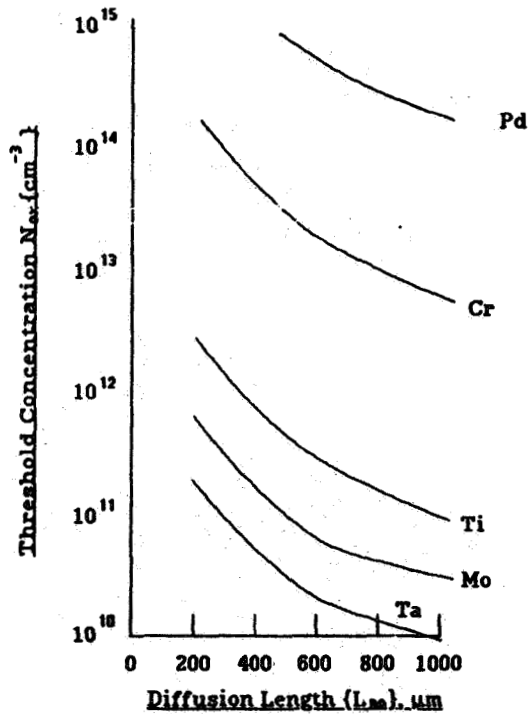
Impurity Model Extension to High-Efficiency Cells

$$N_{ox}(HE) = N_{ox}(SE) \left[\frac{L_{no}(SE)}{L_{no}(HE)} \right]^2 \left[\frac{D_{nb}(HE)}{D_{nb}(SE)} \right]$$
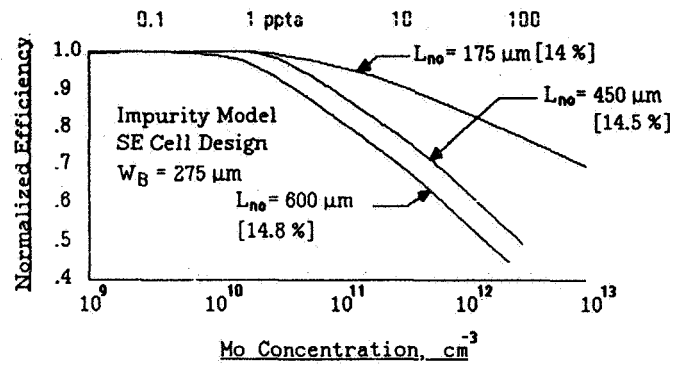
N_{ox}: Impurity Degradation Threshold

L_{no}: Diffusion Length of Uncontaminated Baseline Cell
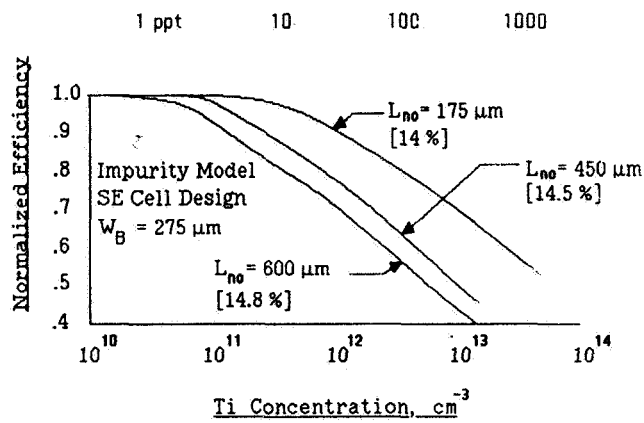
D_{nb}: Minority Carrier Diffusion Constant

Variation in Degradation Threshold With Diffusion Length of Baseline SE Cell
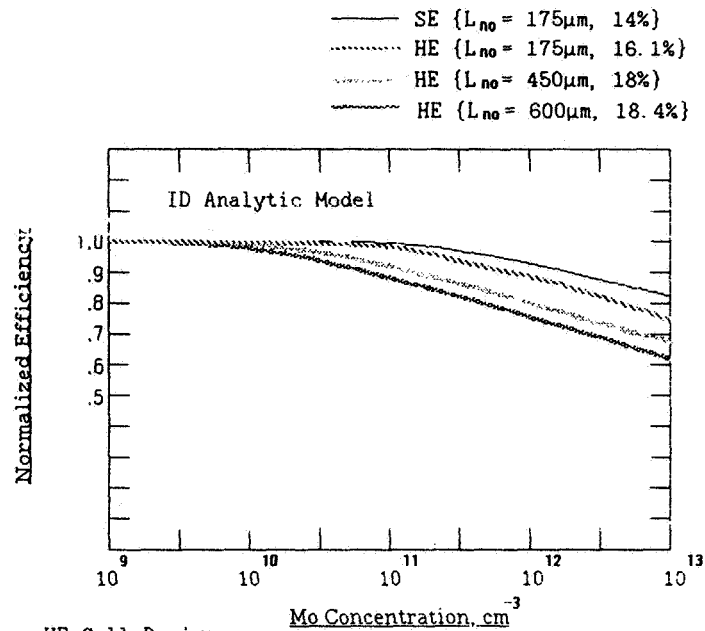
Cell Efficiency Change With Mo Concentration
for Various Initial Base Diffusion Lengths

Impurity Model
SE Cell Design
$W_B = 275 \ \mu m$

$L_{no} = 175 \ \mu m \ [14 \ \%]$

$L_{no} = 450 \ \mu m$
$[14.5 \ \%]$

$L_{no} = 600 \ \mu m$
$[14.8 \ \%]$

Normalized Efficiency

Mo Concentration, cm^{-3}

Cell Efficiency Variation With Ti Concentration
for Various Initial Base Diffusion Lengths

Impurity Model
SE Cell Design
$W_B = 275 \ \mu m$

$L_{no} = 175 \ \mu m$
$[14 \ \%]$

$L_{no} = 450 \ \mu m$
$[14.5 \ \%]$

$L_{no} = 600 \ \mu m$
$[14.8 \ \%]$

Normalized Efficiency

Ti Concentration, cm^{-3}

Variation in Cell Performance With
Mo Concentration: HE Cell Design
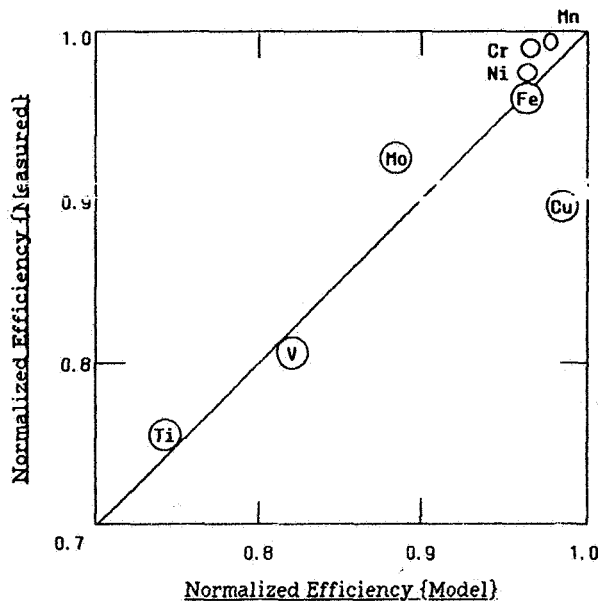
───── SE {L_{no} = 175μm, 14%}
············· HE {L_{no} = 175μm, 16.1%}
~~~~~ HE {L_{no} = 450μm, 18%}
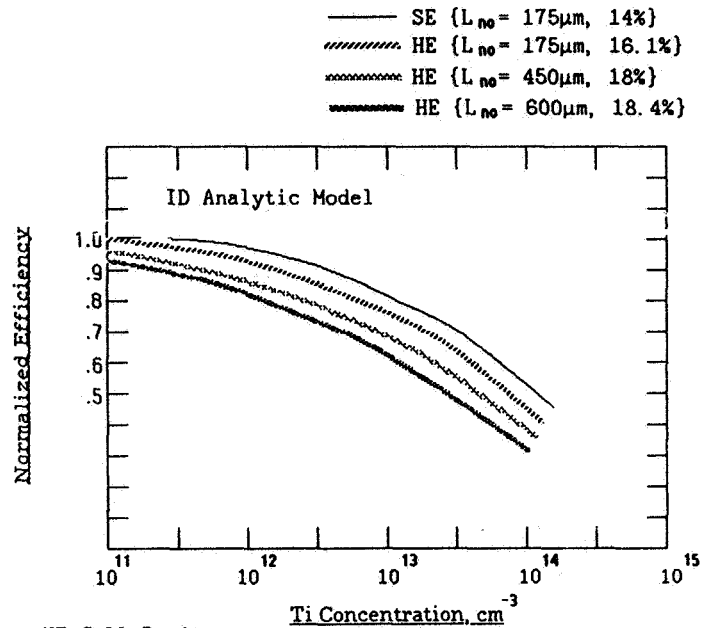~~~~~ HE {L_{no} = 600μm, 18.4%}

HE Cell Design
SiO_2 Passivated{S_{on} + = S_{op} + = 500 cm/sec}
Back Surface Field
Double Layer AR Coating (1.5)
W_B = 275 μm

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Variation in Cell Performance With
Ti Concentration: HE Cell Design

——— SE {L_{no}= 175μm, 14%}
〃〃〃〃〃 HE {L_{no}= 175μm, 16.1%}
∞∞∞∞∞ HE {L_{no}= 450μm, 18%}
━━━━━ HE {L_{no}= 600μm, 18.4%}

ID Analytic Model

Normalized Efficiency

Ti Concentration, cm^{-3}

HE Cell Design
Passivated{S_{on}+ = S_{op}+ = 500 cm/sec}
Back Surface Field
Double Layer AR Coating (1.5)
W_B = 275 μm
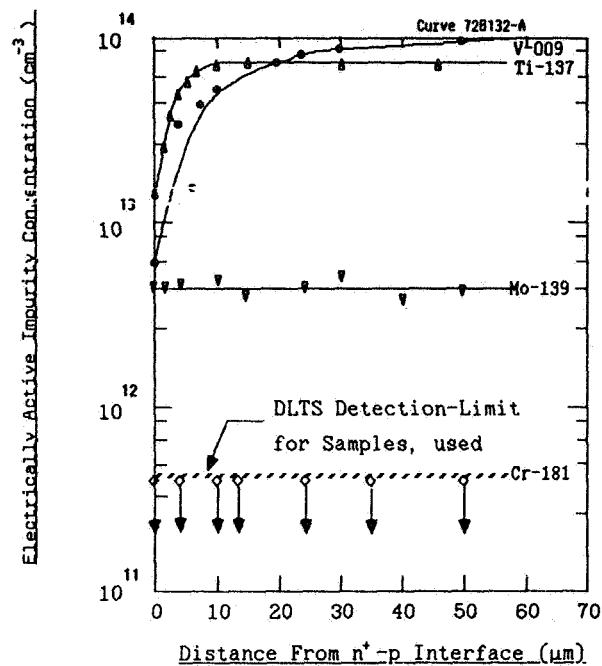
Calculated and Measured Performance
of Contaminated Web Cells

Normalized Efficiency {Measured}

Normalized Efficiency {Model}

Electrically Active Impurity Profiles for Several Species After an 825°C, 50-min $POCl_3$ Treatment

Curve 728132-A

V-009
Ti-137
Mo-139

DLTS Detection-Limit for Samples, used

Cr-181

Electrically Active Impurity Concentration (cm^{-3})

Distance From n^+-p Interface (μm)

Summary

1. Impurities Depreciate Cell Performance
   - Reduce Diffusion Length by Trap Formation
   - Degrade Junctions via Precipitates/Inclusions

2. Impurity Model Describes Well the Behavior of Conventional Cells (SE)with Single and Multiple Contaminants

3. Models Can be Used to Understand Impurity Effects in:
   - High Efficiency Designs
   - Polycrystalline Material
   - Sheet or Ribbon Crystals

4. High Efficiency Devices More Sensitive to Impurities than Conventional Devices

5. Improved Data on Impurity Effects Required to Quantify Model Predictions for High Efficiency

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    At Westinghouse: Ajeet Rohatgi, Phil Blais,
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        Jit Rai-Choudhury, Bob Campbell, Al
        Stewart, Dennis Schmidt, Steve Karako,
        and Carl Seiler.
    At Hemlock Semiconductor Corp.: Jim
        McCormick and Howard Mollenkopf.
    They turned ideas into solid results.

- To many colleagues at the Jet Propulsion Laboratory, especially Ralph Lutwack and Alan Yamakawa whose enthusiastic support made the work possible.

- To our friends in the photovoltaic community for their positive feedback and constructive criticisms.

- To DOE/NASA/JPL for the financial resources to do the job well.

DISCUSSION

DAVISON: You mentioned that you turned your models on polysilicon. Could you describe some of that work briefly?

HOPKINS: What you have to do is to model the grains as though they are silicon single crystals, and then do some calculations that allow you to take into account the recombination at the grain boundaries. Ajeet Rohatgi at our lab has done a lot of this work.

DYER: Since the sensitivity to impurities is offset by the segregation coefficient, it would seem that you could get a normalized danger factor by multiplying the two together -- that is, the sensitivity and the segregation coefficients. It ought to apply to the ones that reduce diffusion length.

HOPKINS: In the old JPL reports, like our final report, you'll see some calculations of that kind at the back of the report. What we did was to calculate the feedstock concentrations and rate one to the other as a function of the K value of the impurity and as a function of recharging or continuous feeding of impurity-laden silicon into the melt, so that you can build up exactly that kind of estimate or rating scheme for these impurities.

ILES: Do you have any general statements on gettering?

HOPKINS: We looked at backside damage. We looked at HCl gettering. We looked at the effect of phosphorus oxychloride. This is a plot of the electrically active titanium concentration measured by DLTS as a function of depth into a wafer that has undergone a phosphorus oxychloride gettering at different temperatures (1100°C and so on). You find these curves generally fit an out-diffusion model in which you assume that the impurity is diffusing into that phosphorus-rich layer because its site in that layer is a lower energy site. As you go to higher temperature, these curves shift farther and farther into the bulk. What we did after that was to strip off the phosphorus oxychloride-rich layer and make a solar cell on it. You find that you can improve the efficiency of the solar cell by doing something like this. I think for the case of 2×10^{14}, where the solar cell efficiency is down around 8%, you can gain 1% or 2% by doing this kind of thing. It's not clear whether it's a totally practical thing to do. While you buy a couple of percent, the cell efficiency is still so poor that it would never make a high-efficiency device. But yes, you can getter these things. We looked at other kinds of thermal processing as well, and, for those of you who are interested I refer you to the three summary reports on that program where a lot of these data are presented in exquisite and gory detail.

KALEJS: At 1100°C, if you do process it or anneal it under a phosphorus source, do you not get some degradation of the bulk lifetime that gives you a problem in recovering some of the efficiency?

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HOPKINS: The problem I have with giving an answer to that is that the bulk
           lifetime of these devices is already very low because of the
           titanium present, and bulk lifetime gets better when you getter, but
           it's not good because you still have a fair amount of titanium left.

KALEJS: You didn't do any low temperature treatment, 500°C, 600°C,
           afterwards?

HOPKINS: No, we did some very crude experiments but I don't think I would hang
           much on those results.

SUREK: Would the effective segregation coefficient in web eventually go to
           unity if you do continuous growth?

HOPKINS: I don't see why it would. We measured those on strips that were a
           meter or two long, which would still represent a small part of the
           volume. If you keep pushing the volume down until there is not very
           much left, the segregation is going to build up. We have never seen
           anything that suggested to us when we grew multiple strips that we
           were reaching anything like K equals one. We did molybdenum,
           titanium, and a number of others where we ran several crystals from
           the same melt and we never saw any behavior that suggested that.

SUREK: What would you predict would be the effect of impurities in cases like
           EFG where the K_{eff} is supposedly unity all the way through the
           process?

HOPKINS: I think the effect of impurities, if you getter with concentrations
           like this, is going to be to degrade the cell performance. Both by
           virtue of their presence in the grains themselves and also by virtue
           of the fact that you have grain boundaries in the material to start
           with.

KALEJS: In connection with Tom's [Surek] first question, I think the only way
           that you can get K_{eff} down is to imply that the stirring under the
           meniscus is equally as strong in your case as it is in Czochralski.
           That's the only physical way you could produce it.

HOPKINS: There is definitely stirring in the melt. There is no doubt about
           it. If you look at the paper that Ray [Seidensticker] and I did, we
           postulated a relatively simple model in which you have a 7 mm-high
           meniscus which is effectively a cone through which the impurities
           diffuse. Once they have diffused through that cone they then mix in
           the melt. Some recent calculations by Julian Szekely on fluid flow
           in the web system indicate that you do have fluid flow. It does mix.

KALEJS: Does that not bring hot fluid up to the interface and give you
           problems with stability?

HOPKINS: It depends on how fast the fluid moves.

KALEJS: It has to move fairly fast to reduce K_{eff} down to Czochralski levels.

HOPKINS: We can grow web 10 or more meters, and that doesn't seem to be the biggest problem by any stretch.

JEWETT: You showed results for carbon and oxygen. Were these measured results or an extension of the model?

HOPKINS: We did relatively little with oxygen and I think the values that Ranny Davis plotted were simply concentrations that were known to be in the melt. We did a little bit with carbon and that probably represents some real data. I think we did two or three purposely carbon-doped runs. I wouldn't want to say that we know anything about carbon and oxygen to the degree of confidence that we know things about the metal contaminants. I think one of the interesting studies to be done yet is the interaction between the metal contaminants and the carbon and oxygen, in the context of a solar cell, along the lines of what we have done. I think that is a very fertile area for research.

BROWN: I'd like to go back to this problem of melt convection in web. Since you are seeing the same kind of convective patterns that you'd seen in Czochralski, then I would expect that you would see essentially time-dependent fluctuations in the melt.

HOPKINS: We do have some.

BROWN: Do you see those kinds of striation fluttering in the crystal?

HOPKINS: We use boron as a primary dopant and you see very little effect on the borane concentration.

BROWN: Because K is close to one. Have you looked at any other dopant?

HOPKINS: We looked at phosphorus but I don't think we ever looked for striations. It's not really a concern, because we are not making devices of that kind.

BROWN: I'm not really worried about the striations. I'm worried about the back melting that they imply, because the thermal mass of your system is so small.

HOPKINS: One potential retardant to the back-melting problem is that as far as we can guess the web interface is a faceted one, requires an undercooling to propagate it, and I think it is a relatively stable interface in that sense. I know there is a small amount of back melting but you also have that 7-mm-high meniscus that's a thermal buffer as well. The fluid flow is in the melt itself. I don't know to what extent there is much fluid flow in the meniscus unless it's Marangoni, and we don't have any way of estimating that.

BROWN: I would agree that it's buffered against it but I also would think the fluctuation would propagate through it.

HOPKINS: I'm interested in seeing those data myself. It's something that would be satisfying in a scientific sense but we have never really had the time to do it.