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GETTERING IN MULTICRYSTALLINE SILICON - A DESIGN-OF-EXPERIMENTS APPROACH

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Design-of-experiment methods were used to study gettering due to phosphorus diffusion and aluminum alloying in four industrial multicrystalline silicon materials: Silicon-Film material from AstroPower, heat-exchanger method (HEM) material from Crystal Systems, edge-defined film-fed growth (EFG) material from Mobil Solar, and cast material from Solarex. Time and temperature for the diffusion and alloy processes were chosen for a four-factor quadratic interaction experiment. Simple diagnostic devices were used to evaluate the gettering. Only EFG and HEM materials exhibited statistically significant gettering effects within the ranges used for the various parameters. Diffusion and alloying temperature were significant for HEM material; also there was a second-order interaction between the diffusion time and temperature. There was no interaction between the diffusion and alloying processes in HEM material. EFG material showed a first-order dependence on diffusion temperature and a second-order interaction between the diffusion temperature and the alloying time. Gettering recommendations for the HEM material were used to produce the best-yet Sandia cells on this material, but correlation with the gettering experiment was not strong. Some of the discrepancy arises from necessary processing differences between the diagnostic devices and regular solar cells. This issue and other lessons learned concerning this type of experiment are discussed.

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Oral Presentation

Gettering in Multicrystalline Silicon - A Design-of-Experiments Approach

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It is well-known that phosphorus diffusion and aluminum alloying can have beneficial gettering effects in multicrystalline silicon (mc-Si). Because different types of mc-Si have different impurities and defect structures, one cannot devise a generic gettering procedure which will work on all materials. Design-of-experiment (DOE) techniques may be useful in efficiently developing an optimized gettering procedure for a particular material.

We used the DOE approach to investigate gettering effects on four industrial mc-Si materials: Silicon-Film from AstroPower, EFG ribbon from Mobil Solar, directionally solidified Heat Exchanger Method (HEM™) material from Crystal Systems, and cast material from Solarex Corporation. After an initial main-effects experiment, we settled on the time and temperature for the $POCl_3$ diffusion and aluminum alloy processes for inclusion in a four-factor quadratic interaction experiment. The parameters and ranges are shown in Table I. The total experiment required 13 processing lots in the Photovoltaic Device Fabrication Laboratory at Sandia. The four industrial materials were co-processed. Forty-two slices of each material had to be successfully processed to complete the experiment.

One-square-centimeter devices with a single front contact pad and no surface passivation were used for the experiment. These devices are appropriate only for open-circuit voltage (V_{oc}) and dark I-V measurements. The one-sided gettering diffusion was also used as the emitter diffusion, so that some of the devices had very heavily doped emitters. The open-circuit voltage is not as strongly affected as the short-circuit current by heavy doping effects. These approaches were taken to reduce the time and cost of processing and characterization. Thirteen devices were

Table I. Gettering Experiment Process Factors and Ranges

Process Factor	Low Setting	High Setting
$POCl_3$ Diffusion Temperature	850°C	950°C
$POCl_3$ Diffusion Time	10 min.	120 min.
Alloy Temperature	700°C	900°C
Alloy Time	10 min.	120 min.

produced and tested on each slice to gain information on the spatial uniformity of the various materials. After losing a few devices to breakage during processing, over 2,000 devices were tested during the course of the experiment!

The equation describing the wafer-average open-circuit voltage response ($<V_{oc}>$) is given below where b_0 is a constant term and the subscripts one through four refer to the process parameters.

$$< V_{oc} >= b_o + \sum_{i=1,4} b_i x_i + \sum_{\substack{i,j=1,4 \\ j\geq i}} b_{ij} x_i x_j$$

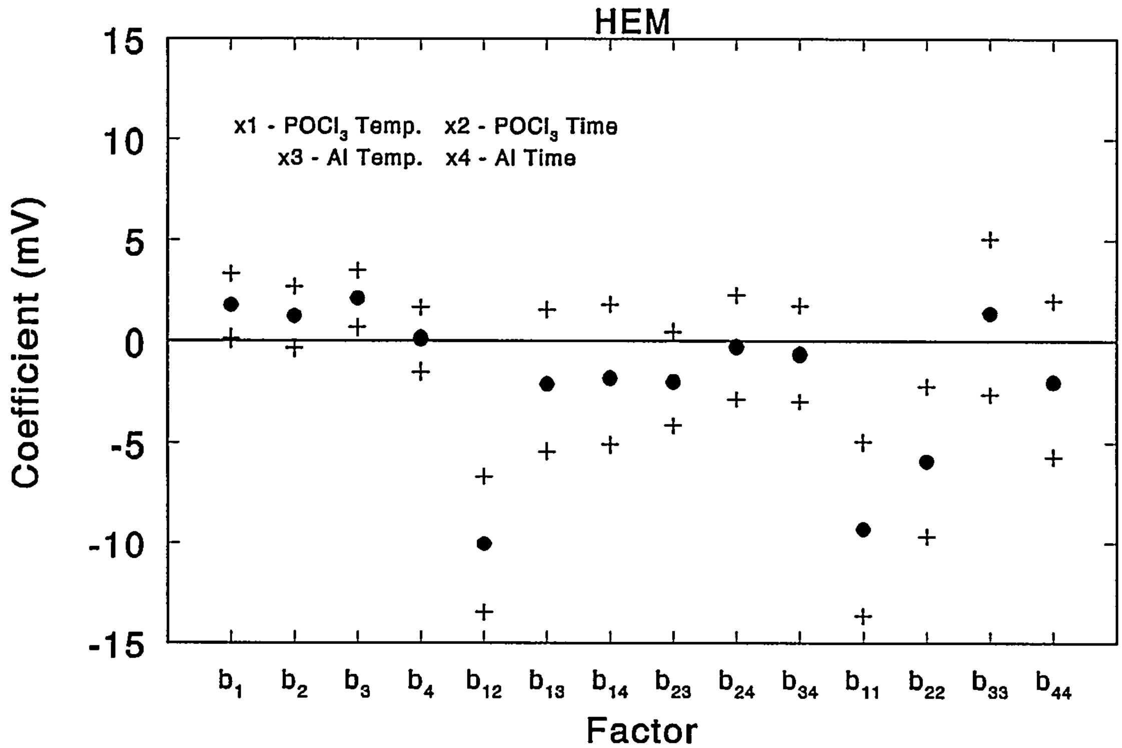
Only EFG and HEM materials exhibited statistically significant gettering effects with the factors and ranges used. Figure 1 shows the coefficients for the various factors and interactions for these two materials. Statistically significant coefficients are indicated when the confidence limits do not straddle the zero line. A contour plot for $<V_{oc}>$ based on the HEM results is shown in Figure 2. There were no interactions between the $POCl_3$ and alloy processes, indicating that the two can be optimized separately in silica crucible HEM material.

In contrast, a second-order interaction between the diffusion temperature and the alloying time was detected for EFG material. The EFG material preferred a combination of short, higher temperature diffusions with a short, low temperature alloy process or longer, lower temperature diffusions with a longer, higher temperature alloy process. The second order interaction for EFG material indicate that the diffusion and alloying processes should be optimized simultaneously for the best results.

The gettering recommendations for HEM material were tested with 4-cm^2 solar cells (eight/wafer). In the cell lot, we removed the gettering diffusion and re-diffused the emitter to avoid heavy-doping effects. Wafer average (<>'s) and best cell results for the various splits are shown in Table II. All of the gettering splits produced higher efficiency cells than we produced without intentional gettering before the experiment, and differences between them are statistically insignificant. The lessons learned from this experiment and possible improvements to our approach will be discussed in the presentation.

Table II. HEM Cell Results Using Gettering Experiment Recommendations

$POCl_3$ Split Temp.(°C) /Time(min.)	$<V_{oc}>$ (mV)	$<I_{sc}>$ (mA)	<FF> (%)	<Eff.> (%)	Best Cell Eff. (%)
900 /60	609	134.5	77.0	15.7	15.8
950/120	600	135.9	75.7	15.5	16.4
850/10	602	133.9	77.6	15.6	16.0
850/10	602	133.5	77.4	15.5	16.0
850/120	601	133.5	78.1	15.6	16.1
850/120	601	134.1	77.1	15.5	15.9
950/10	603	135.5	78.1	15.9	16.6
950/10	605	136.1	77.6	16.0	16.3



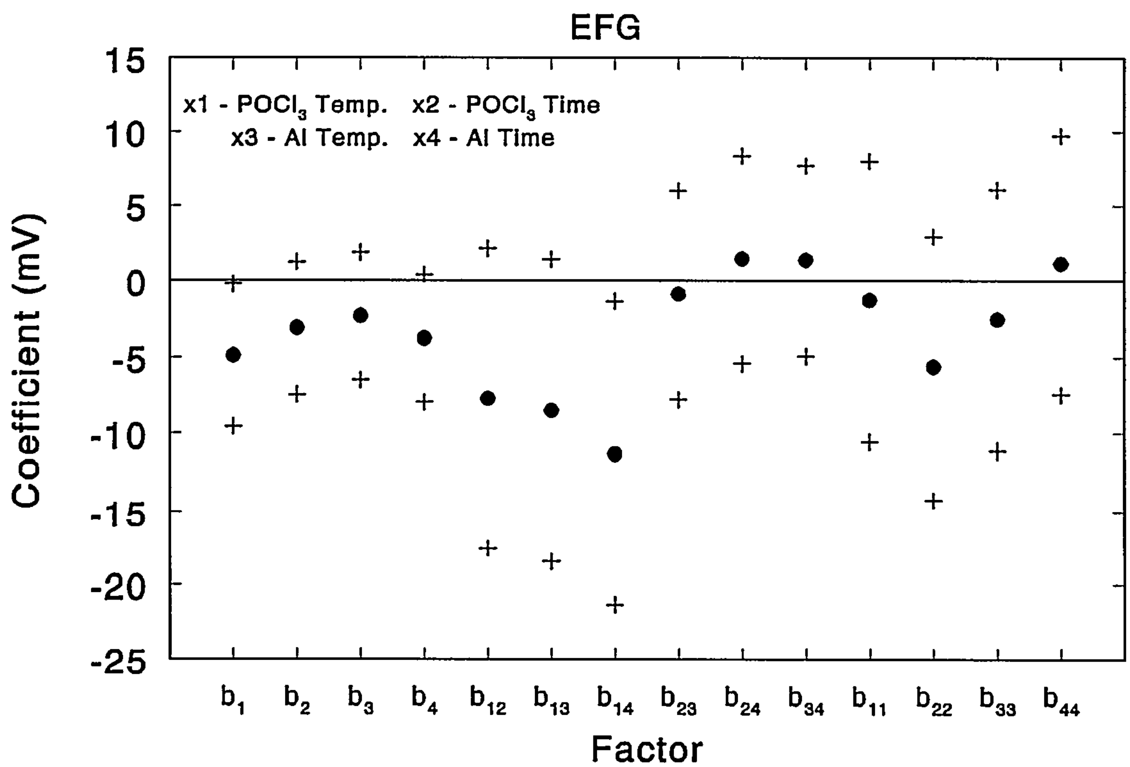


Figure 1. Coefficients for $\langle V_{oc} \rangle$ response on HEM and EFG material. A factor is statistically significant at the 95% confidence level if the plus symbols associated with the central dot do not straddle the zero line. Coefficients with double subscripts refer to second-order interactions.

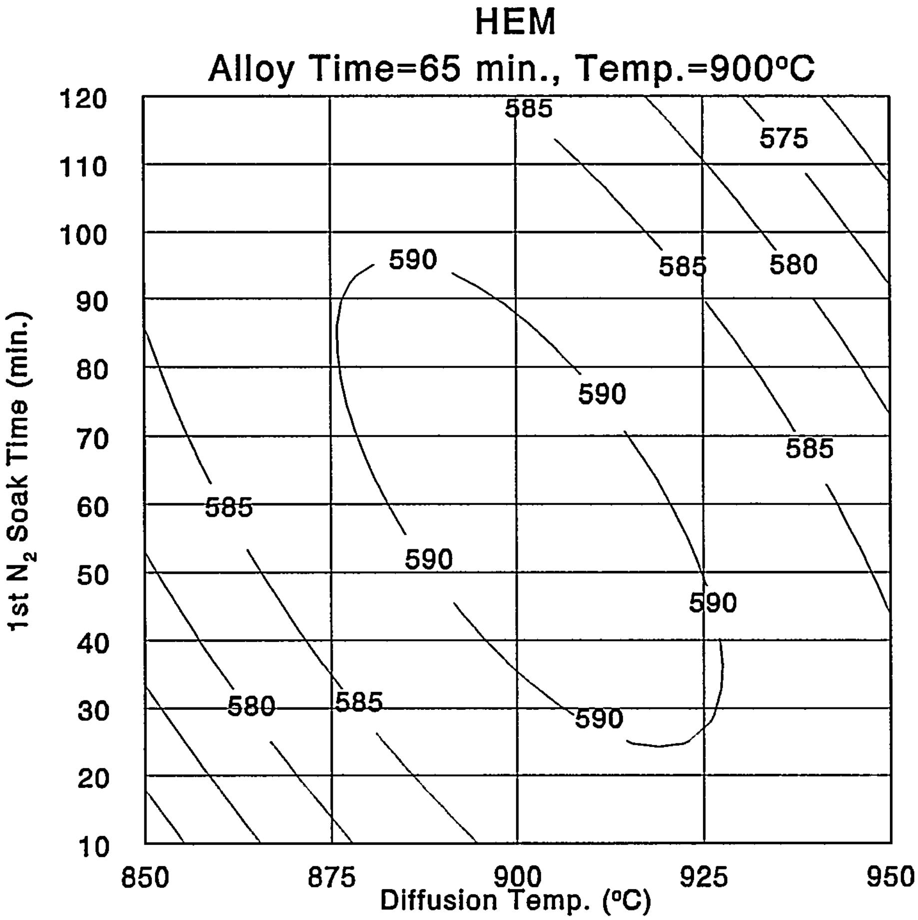


Figure 2. <V_{oc}> contour plot for HEM material. The 95% confidence limits on this plot range from less than +/- 5 mV near to center to +/- 10 mV at the corners.