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EFFECTS OF DIFFUSION REDISTRIBUTION OF PHOSPHORUS ON THE CHARACTERISTICS OF SILICON SOLAR CELLS

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16. Abstract

Shallow junction solar cells fabricated by redistribution, with and without final phosphorus exposure where compared to standard saturation diffused cells. Cells from both types of redistribution had higher short wavelength response than saturation cells of the same sheet conductance. Redistribution alone produced the highest response. All cells exhibit the low fill factors of shallow junctions. Redistribution in deep junction cells did not enhance short wavelength response. Redistribution cells exhibited similar forward resistances to saturation diffused cells and had higher sheet conductance.

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SUMMARY

A comparison was made of shallow junction silicon solar cells fabricated by diffusions employing a redistribution and redistribution plus final phosphorus source exposure with cells fabricated from standard saturation diffusions. All diffusions and final source exposures were performed with $POCl_3$ as source. The redistribution with and without final source exposure exhibited higher short wavelength response than saturation diffusion cells. The redistribution cells without final exposure showed the highest response. Shallow junction redistributed cells and redistributed plus final exposure cells had as low fill factors as shallow junction saturation cells. An attempt to improve deeper junction cells by redistribution was unsuccessful.

Redistribution cells without final source exposure exhibited similar forward resistance to saturation diffused cells and had higher sheet conductance.

INTRODUCTION

It has been well established that the response of silicon solar cells to the short wavelength (blue) end of the visible spectrum is strongly dependent upon the depth of the p-n junction below the illuminated surface and that the response to the long wavelength (red) end is independent of the junction depth.

Previous studies (ref. 1) have verified that the response of silicon solar cells to short wavelength light, as measured in terms of short circuit current, increases as the junction depth is made shallower. However, when very shallow junctions were made, the blue response fell off drastically. Another way to improve the blue response is to improve the collection of light generated carriers from the thin phosphorus diffused region at the illuminated surface. It seem likely (refs. 2 to 6) that the saturation diffusion conditions used in standard solar cell production result in some of the phosphorus occupying interstitial sites. It was suspected that this excess phosphorus was a major cause of poor collection from the diffused region, and that if it could be redistributed into substitutional sites the blue response would improve. In the present investigation, solar cells were made with a heat treatment following the standard saturation diffusion to redistribute the phosphorus. Performance of solar cells made in this manner was measured to determine how cell parameters, especially response to blue light, are affected by the redistribution.

These experiments were restricted to the diffusion temperature range of 800° to 1000° C where solar cell diffusions are generally performed. In all the experiments $POCl_3$ was used as the phosphorus source.

EXPERIMENTAL

The open tube diffusion method (ref. 1) was used in these experiments to form the solar cell junction. The phosphorus source employed was $POCl_3$. This is a liquid through which oxygen was bubbled and then this mixture was passed through a quartz tube containing the silicon wafers maintained at the diffusion temperature. The system provided fairly precise timing of the exposure of the silicon wafers to phosphorus. In all experiments the wafers were allowed to come to equilibrium at the desired diffusion temperature before exposure to $POCl_3$.

All silicon material used was 10 ohm-centimeter boron doped. The wafers were 1 by 2 by 0.35 centimeters cut from crucible grown material.

The initial experiments were designed to saturate the diffused region of the silicon with phosphorus as in typical solar cell fabrication procedure. These wafers were kept in contact with the $POCl_3$ continuously until they were withdrawn from the furnace. Some of the wafers from these diffusions were treated with concentrated HF, to remove the phosphorus-rich oxide layer developed on their surfaces, and rinsed with deionized water. After measurement of sheet conductance these uncoated wafers were placed in a furnace at 1000° C in a reducing atmosphere. Redistribution was continued until periodic removal and four point probe measurements (ref. 7) indicated that the sheet conductance was no longer changing. Other wafers from the initial diffusions were fabricated into solar cells to determine their photovoltaic properties.

The second set of experiments consisted of diffusions followed by redistribution at the diffusion temperature. The wafers were exposed to $POCl_3$ for various times and then left in the furnace with the $POCl_3$ source shut off but with the oxygen flow maintained. In most cases the wafers were withdrawn after an arbitrary total time of

60 minutes had elapsed from the beginning of $POCl_3$ exposure. Sheet conductance was determined on one wafer from each of these diffusions. The remaining wafers were fabricated into solar cells.

The third set of diffusion redistribution experiments was identical to the second set described previously except that an additional exposure to $POCl_3$ was made for either 5 or 10 minutes at the end of the redistribution. The total heat treatment was also 60 minutes. The short wavelength (blue) response of fabricated cells was measured in terms of the 0.4-micrometer short circuit current as determined with the Lewis Laboratory filter wheel solar simulator (ref. 8). No antireflecting coatings were applied to the cells discussed in this report. These currents were corrected to effective outer space currents as described in reference 8. Total short circuit currents were also determined with the filter wheel solar simulator. The fill factor of the cells was determined from the I-V characteristic (ref. 1). Reverse diode leakage and forward resistance were measured on a curve tracer oscilloscope. The reverse diode leakage is the value of the current for the unilluminated cell when biased in the reverse direction and read at a voltage of 0.6 volt. The forward resistance is the slope of the I-V curve of the unilluminated cell taken in the forward direction in the range of 300 to 400 milliamperes.

RESULTS

The results of the 1000° C redistribution experiment are summarized in table I. The second and third columns list values of sheet conductance after saturation diffusion and 1000° C redistribution, respectively. The ratio of these values in column five shows that an increase in sheet conductance by a factor of between two and six is caused by redistribution at 1000° C even though the blue oxide layer was removed from the wafers. Two undiffused P-type wafers were included in these redistributions. The change in their four-point probe conductance, if attributed to phosphorus in-diffusion from the furnace, is not large enough to account for the changes observed on the diffused wafers. This increase in sheet conductance indicates that either or both of two effects are caused by redistribution. The first is that phosphorus in the silicon lattice is converted to donors from some other form. The second is that the mobility of the donor electrons already present is increased by the redistribution.

The data for the 800° C diffusions and redistributions are summarized in table II and figures 1 to 7. The data are grouped according to diffusion procedure. The treatment of these wafers differs from those reported in table I in that they were not removed from the furnace between diffusion and redistribution, and redistribution was at 800° C. Results of measurements of sheet conductance, 0.4-micrometer short circuit current, total short circuit current, fill factor, reverse leakage, and forward resistance are discussed separately hereinafter.

Sheet Conductance

The saturation diffusion wafers in table II and figure 1 are typical of 800° C diffusions for solar cell fabrication. Observation of the sheet conductance after redistribution of the wafers show a rise, similar to the 1000° C redistribution of table I. It should be recognized, however, that a phosphorus-rich oxide layer was present on the surface during the redistributions reported in table II. This could have acted as a second source of donors.

The effect of a final $POCl_3$ exposure is to decrease sheet conductance. It may be noted in figure 1 that these wafers, if plotted as a function of final $POCl_3$ times rather than initial, would fall near the straight line drawn through the saturation diffusion data. The final exposure sheet conductances appear to depend primarily on final exposure time.

0.4-Micrometer Short Circuit Current

These data are presented in table II and in figure 2 as a function of sheet conductance. After redistribution the cells exhibit much higher blue response than saturation diffused cells over the same sheet conductance range. Indeed, they exhibit much higher blue response than any saturation diffused cells produced at Lewis. After final $POCl_3$ exposure, the sheet conductance and blue response are lower than with only a redistribution step. These cells do not show the drastic decrease in the blue response at low sheet conductance exhibited by saturation diffusion alone.

Reverse Leakage

In table II and figure 3 reverse leakage is observed to increase as sheet conductance decreases for the saturation diffused cells. This condition has been used in previous work (ref. 1) to explain the drop in blud response of such cells at low sheet conductance. After redistribution, reverse leakage is seen to be less by a factor of about ten than in saturation diffused cells at low sheet conductance values. Final exposure appears to increase leakage but not to the initial values.

Total Short Circuit Current

The total short circuit current for saturation diffused cells in table II and figure 4 exhibit a decrease with decreasing sheet conductance similar to the blue response data. Both the blue and total response current are higher after redistribution. This increase in total current comes entirely from the short wavelength half of the spectrum. Total currents after final exposure are degraded but not to the extent that they are after saturation diffusion.

Forward Resistance

In figures 5 and 6 forward resistance is plotted against the reciprocal of the sheet conductance and the reciprocal of the initial $POCl_3$ exposure time, respectively. The figure 5 plot implies that redistribution of the wafers causes an increase in forward resistance. Figure 6 indicates however that, as a function of initial $POCl_3$ exposure, the redistribution has not affected forward resistance. The figure 5 relation appears to be that of the effect of redistribution on sheet conductance. As in figure 1 the points for final $POCl_3$ exposure are also plotted against final exposure time. Although the data are somewhat scattered, it appears that the forward resistance is more dependent on the final exposure time than the initial.

Fill Factor

The relatively deep junction (high sheet conductance) saturation diffused cells have by far the highest fill factors (fig. 7). Redistribution does not improve the low fill factors on the shallow junction (low sheet conductance) cells. In order to utilize the improved blue response of redistribution cells to increase solar cell efficiency, fill factors comparable to deeper junction saturation cells must be obtained.

In an attempt to obtain deep junction redistributed cells, diffusion plus redistribution was briefly investigated at a higher diffusion temperature. Data from such 900° C diffusions is listed in table III. The high sheet conductance values indicate that the higher temperature drove the junctions in much deeper than at 800° C. The low blue response with low reverse leakage observed are typical of deep junction saturation diffusions. It appears that even the longest redistribution times did not improve diffused layer collection in these cells.

One cell, the 2-minute $POCl_3$ exposure with 120-minute redistribution, exhibited a very high blue response. This cell, however, had a discolored surface which may have acted as a antireflecting coating thus invalidating comparison with the other cells. The 900° C redistribution cells exhibit much higher forward resistance than those at 800° C.

The 800° C diffusion plus redistribution experiments indicate that an increase in collection of current from the diffused layer of silicon solar cells can be achieved. However, this method also leads to degradation of other cell parameters such as fill factor. This latter effect must be corrected if the improved collection is to be utilized.

SUMMARY OF RESULTS

Comparison of silicon solar cells fabricated from saturation phosphorus diffused wafers with cells fabricated from diffused and redistributed wafers yielded the following results:

1. The 1000° C redistribution of phosphorus diffused silicon resulted in an increase of sheet conductance by a factor of two to six even though the blue oxide coating was removed from the wafers. This indicates that either or both of two effects are caused by this redistribution. The first is that phosphorus in the silicon lattice is converted to donors from some other form. The second is that the mobility of the donor electrons already present is increased by redistribution.

2. Redistribution of saturation diffused wafers at 800° C produced solar cells with higher response to short wavelength radiation than were produced from saturation diffusions alone.

3. Solar cells fabricated from silicon wafers that received the treatment, diffusion, redistribution, final 5- or 10-minute-source exposure, also exhibited improved short wavelength response, but not as much so as those described in point 2.

4. Cells made from redistribution wafers, and from redistribution plus final source exposure wafers, exhibited poor fill factors just as did saturation diffused cells with shallow junctions.

5. Redistribution at 800° and 900° C increased the sheet conductance of diffused wafers.

6. Final $POCl_3$ exposure reduced sheet conductance from its value after redistribution. The final sheet conductance appears to be primarily determined by the final exposure rather than the initial.

7. Redistribution reduced reverse leakage. The final $POCl_3$ exposure raised reverse leakage but not as high as with initial saturation diffusion alone.

8. Redistribution did not change forward resistance of cells. Final $POCl_3$ exposure, however, reduced forward resistance.

9. An attempt to improve deep junction cells by redistribution was unsuccessful. Heat treatments for up to 2 hours of wafers diffused at 900° C for 2 to 30 minutes did not enhance the short wavelength response.

Lewis Research Center,
National Aeronautics and Space Administration,
Cleveland, Ohio, September 16, 1970,
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TABLE I. - COMPARISON OF POST DIFFUSION SHEET CONDUCTANCE TO 1000° C REDISTRIBUTION IN A REDUCING ATMOSPHERE

Diffusion temperature, $^{\circ}C$	Diffusion time, min	Diffusion sheet conductance, σ_s, squares/ohm	Post 1000° C redistribution, σ_s, squares/ohm	Redistributed σ_s - diffusion σ_s	Redistribution σ_s/diffusion σ_s	Time to reach equilibrium in σ_s at 1000° C, min
(a)	(a)	----------	2.16×10^{-3}	------	----	120
(a)	(a)	----------	1.32	------	----	120
800	20	3.92×10^{-3}	10.33×10^{-3}	6.41	2.64	30
	45	7.69	19.84	12.15	2.58	30
900	1	0.69×10^{-3}	2.66×10^{-3}	1.97	3.87	60
	$1\frac{1}{2}$	8.28	39.1	30.8	4.73	60
	2	10.58	49.0	38.4	4.64	90
	$2\frac{1}{2}$	12.97	62.9	49.9	4.85	60
	3	13.23	75.2	62.0	5.68	60
1000	1	15.06×10^{-3}	29.1×10^{-3}	14.0	1.94	60
	$1\frac{1}{2}$	36.63	124.1	87.5	3.39	75
	2	52.36	187.6	135.2	3.59	60
	$2\frac{1}{2}$	68.97	243	174	3.52	75

[a]Undiffused.

TABLE II. - CHARACTERISTICS OF SILICON SOLAR CELLS FABRICATED FROM 800° C DIFFUSED AND REDISTRIBUTED WAFERS

	Initial $POCl_3$ time, min	Final $POCl_3$ time, min	Total heating time, min	Sheet conductance, σ_s, squares/ohm	0.4 Micrometer current, mA	Total current, mA	Fill factor, percent	Reverse leakage, μA	Forward resistance, ohm
Saturation diffusions	3	---	3	1.0×10^{-3}	0.16	2.15	15.8	Very high	0.75
	5	---	5	1.2	.48	9.85	35.3	24×10^{3}	.82
	10	---	10	2.7	1.12	21.85	37.8	16×10^{3}	.82
	20	---	20	4.7	3.20	46.84	45.8	440	.34
	20	---	20	4.7	3.67	51.14	56.2	104	.30
	45	---	45	7.3	3.34	49.92	60.7	134	.26
	45	---	45	7.3	3.41	51.03	69.9	200	.22
	420	---	420	13.5	2.64	50.17	75.0	3	.22
Diffusion and redistribution	3	---	60	3.0×10^{-3}	4.81	54.45	22.2	32	3.5
	3	---		4.7	4.90	55.75	30.1	3	.9
	4	---		3.28	4.85	57.10	29.4	12	1.2
	5	---		7.65	4.81	55.68	37.0	12	.63
	10	---		5.1	4.54	54.38	44.5	3	.72
	20	---		9.5	3.89	52.75	----	83	.33
Diffusion, redistribution, and final $POCl_3$ exposure	5	5	60	1.28×10^{-3}	4.27	50.03	34.6	51	0.7
	3	10		2.35	3.03	44.78	56.5	130	.32
	4	10		3.13	3.74	46.11	40.2	186	.39
	5	10		2.67	3.77	45.78	35.3	220	.43

TABLE III. - CHARACTERISTICS OF SILICON SOLAR CELLS

FABRICATED FROM 900° C DIFFUSED WAFERS

	Initial $POCl_3$ time, min	Final $POCl_3$ time, min	Total heating time, min	Sheet conductance, σ_s, squares/ohm	0.4 Micrometer current, mA	Total current, mA	Fill factor, percent	Reverse leakage, μA	Forward resistance, ohm
Saturation diffusion	2	---	2	9.0×10^{-3}	3.47	50.05	71.7	14	0.26
	30	---	30	42.1	1.25	49.02	76.8	23	.19
Diffusion and redistribution	2	---	15	32.1×10^{-3}	2.28	(a)	(a)	62	5.5
	3	---	15	37.7	1.48	(a)		12	5.5
	15	---	15	35.5	1.37	(a)		5	1.6
	2	---	30	48.8	1.37	48.43		22	4.4
	3	---	30	52.9	1.02	47.09		102	3.3
	15	---	30	50.8	.86	46.15		166	.9
	30	---	30	46.3	.85	44.98		114	1.3
	2	---	60	60.2	1.28	(a)		184	5.2
	3	---	60	64.9	.68	(a)		51	11.0
	15	---	60	64.9	.61	(a)		7	1.3
	2	---	120	29.3	5.34	63.37		3	5.8
	3	---	120	81.4	.42	(a)		43	4.6

[a]Not measured.

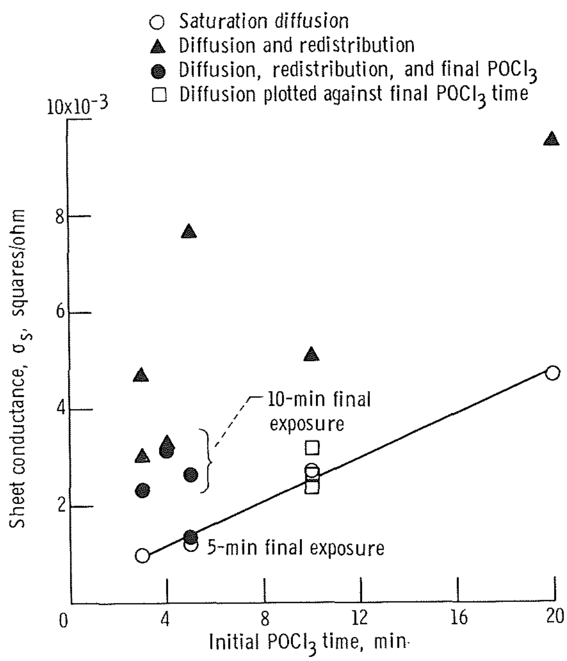

Figure 1. - Effect of redistribution on σ of 800° C diffused wafers.

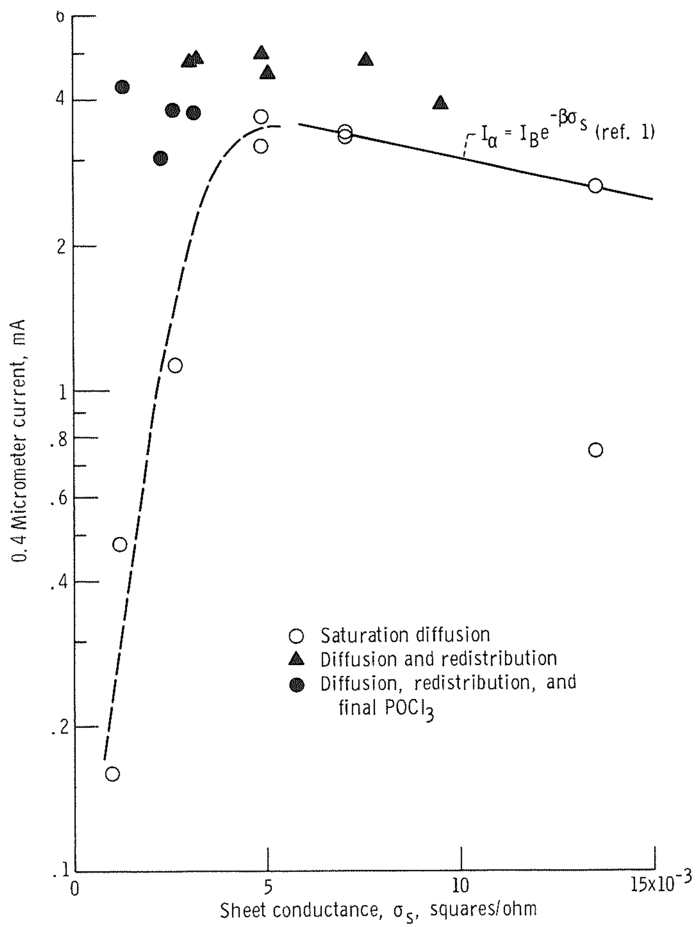

Figure 2. - 0.4-Micrometer current plotted against sheet conductance diffusions with $POCl_3$ at 800° C.

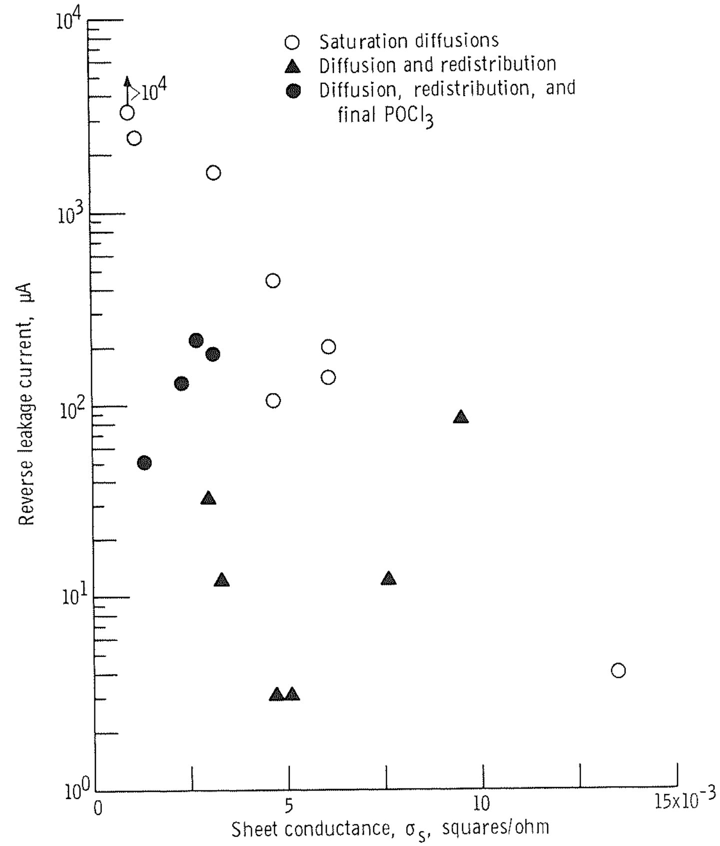

Figure 3. - Reverse leakage plotted against sheet conductance diffusions with $POCl_3$ at 800° C.

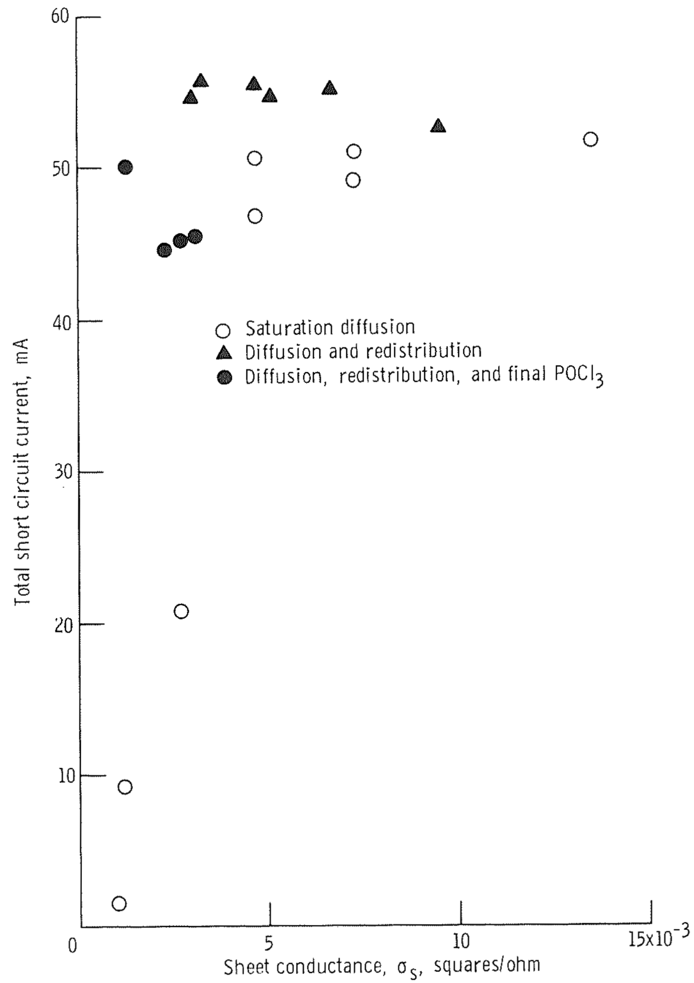

Figure 4. - Total short circuit current plotted against sheet conductance. Diffusions with $POCl_3$ at 800° C.

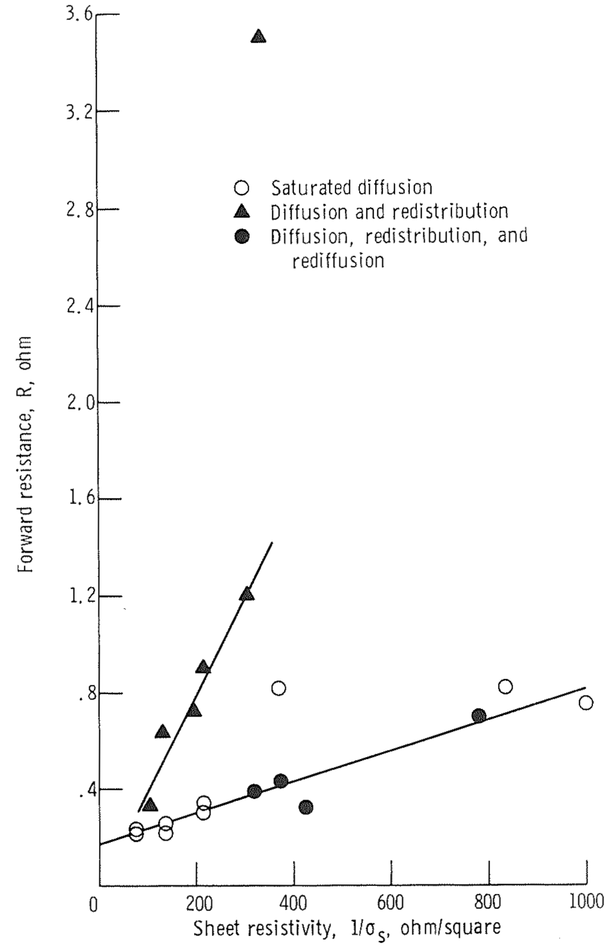

Figure 5. - Measured forward resistance. Diffusions with $POCl_3$ at 800° C.

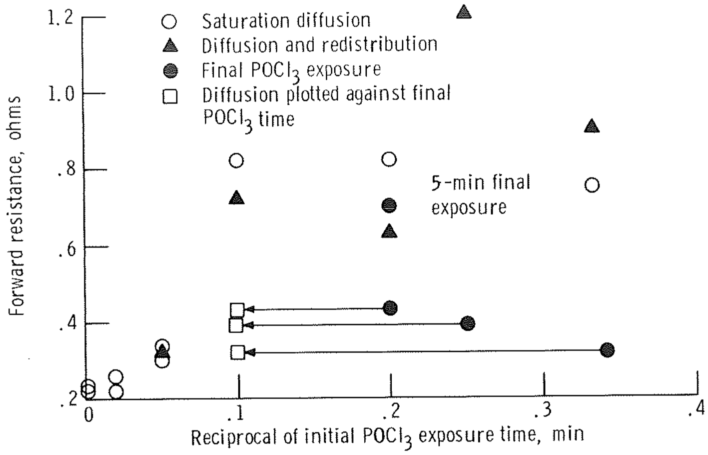

Figure 6. - Forward resistance plotted against initial $POCl_3$ exposure for 800° C diffusion.

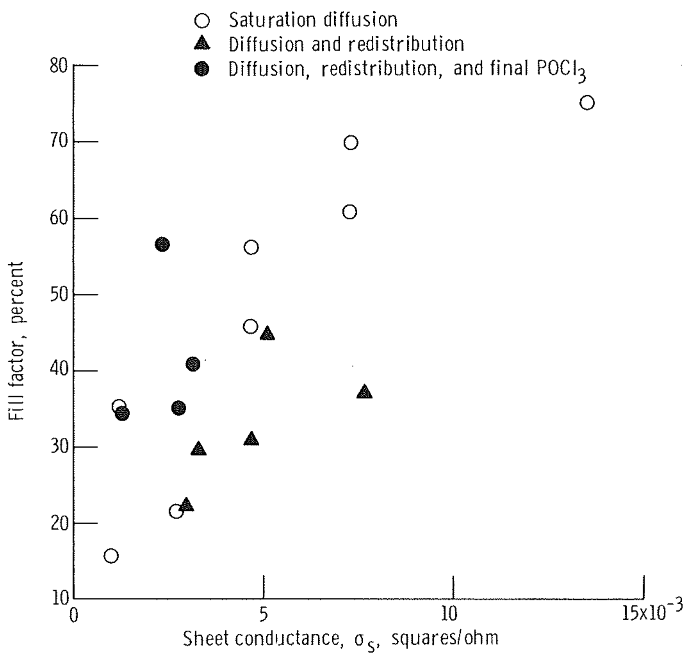

Figure 7. - Fill factor plotted against sheet conductance diffusions with $POCl_3$ at 800° C.

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