$POCl_3$ GETTERING OF TITANIUM, MOLYBDENUM AND IRON-CONTAMINATED SILICON SOLAR CELLS

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SUMMARY

The effect of Ti, Mo, and Fe on silicon solar cell performance and the response of the contaminated material to $POCl_3$ gettering has been investigated. Mo, Ti and Fe all degrade cell performance, but Mo exhibits the most serious effect. Mo induces a recombination center in silicon at E_V+ 0.30 eV; the onset of efficiency degradation occurs at metal concentrations in only the mid $10^{10}cm^{-3}$ range. $POCl_3$ gettering of Mo-doped ingots prior to cell fabrication, has very little effect on the cell performance. Ti reduces cell performance when the metal concentration exceeds about $10^{11}cm^{-3}$; it induces two deep levels in silicon, E_V+0.30eV and E_C-0.26eV. $POCl_3$ gettering appreciably improves the efficiency of Ti-doped cells but complete recovery to the baseline (uncontaminated) efficiency value would require prolonged times and high temperatures. Fe degrades solar cell performance above a concentration of $2x10^{14}cm^{-3}$ due to a recombination center at E_V+0.40 eV; $POCl_3$ gettering of Fe-doped ingots improves the cell performance significantly

1. INTRODUCTION

The behavior of transition metals, common contaminants in partially refined silicon, and their deleterious effect on silicon solar cell performance has been an area of major concern (1,2). Crystals grown from contaminated silicon may develop inclusions and precipitates which lead to polycrystalline structure. The incorporated impurities also may give rise to recombination centers due to the perturbation of the electronic and geometric periodicity of the silicon lattice (3). These centers may reduce the diffusion length of the minority carriers (4) and, thereby, lower the solar cell efficiency.

The elevated temperature treatment of silicon wafers in an ambient containing $POCl_3$ (5) provides a mechanism to neutralize, or getter, contaminants subsequent to crystal growth. In principle, the method may be used to improve the performance of solar cells fabricated on impurity-bearing material. We report here the influence of Ti, Mo and Fe on silicon solar cell efficiency and the response of the contaminated silicon to $POCl_3$ gettering.

2. EXPERIMENTAL

The studies were conducted on 4 Ω-cm <111> silicon crystals which were doped with boron and a secondary metal impurity during Czochralski growth. The metal impurity concentrations in the as-grown crystals, typically in the range of 10^{11}-$10^{16}cm^{-3}$, were determined by spark source mass spectrometry or by neutron activation analysis.

Wafers from the impurity-doped material along with uncontaminated baseline wafers were heat treated in $POCl_3$-bearing ambients. The gettering temperature ranged from 950° to 1100°C and the time was varied from 1 to 5 hours. Following removal of the gettered surface (phosphorous glass) and about 12 μm of the silicon beneath it by etching, the wafers were fabricated into n+p solar cells by 50 minute phosphorous diffusion at 825°C. The one cm^2 cells were mesa etched and metallized with Ti-Pd-Ag. The front pattern was a five finger grid with 5.4% area coverage. Neither back surface field nor anti-reflective coating were employed.

Current-voltage measurements were made using a quartz-iodine AM2 simulator whose light level was set at 91.6 mw/cm^2. Peak power point, fill factor and cell efficiency were determined with the help of a computer program using a single exponential model (1). The average efficiency of the uncontaminated baseline cells was 10% which is about 14% with a typical AR coating. The carrier lifetime was determined by the open-circuit voltage decay method using a 20 mA/cm^2 injection current.

Deep level transient spectroscopy (DLTS) was used to examine the impurity-induced recombination centers and any changes in the active center density with gettering. The DLTS technique is well documented in the literature (6,7). DLTS measurements on the wafers were performed by fabricating 30 mil diameter Ti-Si Schottky barrier diodes with gold evaporation on top of Ti. For the DLTS studies on solar cells, the front metal grid was removed and then the cell was subdivided into an array of 30 mil diameter mesa diodes with Ti-Au contact on the front side. These measurements were performed with the help of a lock-in amplifier DLTS system. To determine the effect of gettering deep in the bulk wafer, the phosphorous glass and the adjacent n+ region was removed after gettering. The active impurity concentration at various depths was then determined by etching a series of steps into the silicon which were followed by fabrication of Schottky barrier diodes. DLTS measurements made on the diodes provided a profile of the active impurity concentration as a function of depth.

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3. RESULTS

Figure (1) and Table (1) illustrate how Ti, Mo and Fe affect solar cell performance. The threshold impurity concentrations for the onset of performance degradation are about $5x10^{10}cm^{-3}$, $2x10^{11}cm^{-3}$ and $2x10^{14}cm^{-3}$ for Mo, Ti and Fe, respectively.

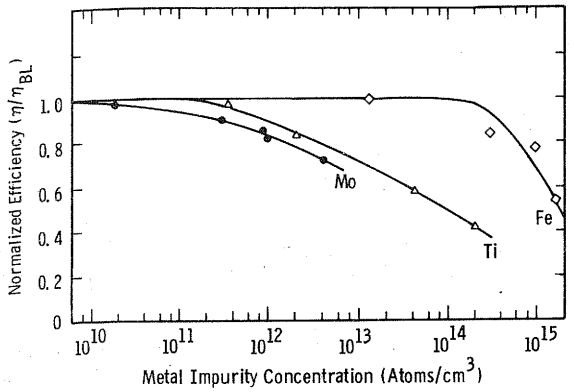

Figure 1. Normalized silicon cell efficiency versus the content of molybdenum, titanium and iron in silicon

Table 1

Effect of Titanium, Molybdenum and Iron on Silicon Solar Cell Performance and OCD Lifetime

Ingot ID	Impurity Concentration* (cm-3)	Short Circuit Current (mA)	Open Circuit Voltage (volts)	Normalized Cell Efficiency η/η_{BL}	Open Circuit Decay Lifetime (μsecs)
BL-03	0	22.50	0.556	1.0	4.50
Ti-48	$3.6x10^{11}$	22.50	0.550	0.98	3.97
Ti-33	$2.0x10^{12}$	19.45	0.536	0.83	2.02
Ti-42	$4.0x10^{13}$	16.39	0.494	0.58	0.53
Ti-137	$2.0x10^{14}$	12.63	0.463	0.42	0.17
Mo-124	$1.8x10^{10}$	21.60	0.546	0.96	4.20
Mo-125	$3.0x10^{11}$	21.00	0.543	0.90	1.95
Mo-98	$9.0x10^{11}$	20.90	0.522	0.85	1.12
Mo-138	$1.0x10^{12}$	20.83	0.529	0.82	1.08
Mo-139	$4.2x10^{12}$	18.43	0.507	0.72	0.63
Fe-44	$1.3x10^{13}$	22.50	0.556	1.0	4.30
Fe-136	$3.0x10^{14}$	20.04	0.536	0.82	2.00
Fe-16	$9.0x10^{14}$	20.69	0.533	0.86	2.60
Fe-18	$1.7x10^{15}$	14.21	0.495	0.54	0.30

current density used in the open circuit voltage decay measurement was 20 mA/cm^2

* impurity concentration is total and not the active

Table (2) shows that Ti produces two deep levels, Ev + 0.30 eV and Ec-0.26 eV, Mo induces a level at Ev + 0.30 eV, and Fe a level at Ev+0.40 in the cells.

Table 2

Impurity-induced Trap Levels in solar cells

Sample ID	Metallurgical Concentration (cm^{-3})	Trap Level (eV)
Ti-08	$2.0x10^{14}$	E_V+0.30
		E_C-0.26
Mo-139	$4.2x10^{12}$	E_V+0.30
Fe-18	$1.7x10^{15}$	E_V+0.40

The concentration of these centers will be used to designate the electrically active impurity concentration for each species. In the case of Ti the two levels have nearly the same concentration but the concentration of EV+0.30 eV trap will be used because it is a majority carrier trap which can be determined more accurately.

The metallurgical impurity concentrations of the wafers subjected to gettering were $2x10^{14}cm^{-3}$ Ti, $4.2x10^{12}cm^{-3}$ Mo and $3x10^{14}cm^{-3}$ Fe. The data in Table (3) show the effect of gettering time and temperature on the solar cell performance and the concentration of the Ti-induced Ev+0.30 eV trap.

Table 3

Variation in cell efficiency and trap concentration (N_T) as a function of gettering treatment for silicon containing a metallurgical Ti concentration of $2.0x10^{14}cm^{-3}$

Gettering Condition	Normalized Cell Efficiency (η/η_B), (%)	Concentration (N_T) of E_V+0.30 eV TRAP (cm^{-3})
None (starting wafer)		$8.0x10^{13}$
None (solar cell)	42.8	$1.76x10^{13}$
950°C/1 hr.	46.7	$6.35x10^{12}$
1000°C/1 hr.	51.0	$3.94x10^{12}$
1100°C/1 hr	52.9	$2.99x10^{12}$
1100°C/2 hr.	55.4	$2.50x10^{12}$
1100°C/3 hr.	59.1	$2.39x10^{12}$
1100°C/5 hr.	66.2	$1.49x10^{12}$

The 1100°C/5 hr $POCl_3$ gettering treatment improves the normalized cell efficiency by 23% and reduces the active Ti concentration near the junction by an order of magnitude compared to that in the as grown ingot. Figure (2) illustrates how the active Ti concentration changes with depth in the bulk silicon wafer as a result of the cell diffusion step (825 °C)and two different 1100°C $POCl_3$ treatments.

Table (4) shows the gettering effect on Mo-doped cells. All the Mo in the starting material is active. Neither the solar cell diffusion step nor a one hour $POCl_3$ treatment at various temperatures appreciably changes the cell performance or the active Mo content. After extensive gettering (1100°C/5 hr) there is a factor of 4-5 reduction in the Mo concentration near the junction but relatively little improvement in the cell performance. Except in the case of 1100°C/5 hr $POCl_3$ gettering the active Mo concentration returned nearly to its

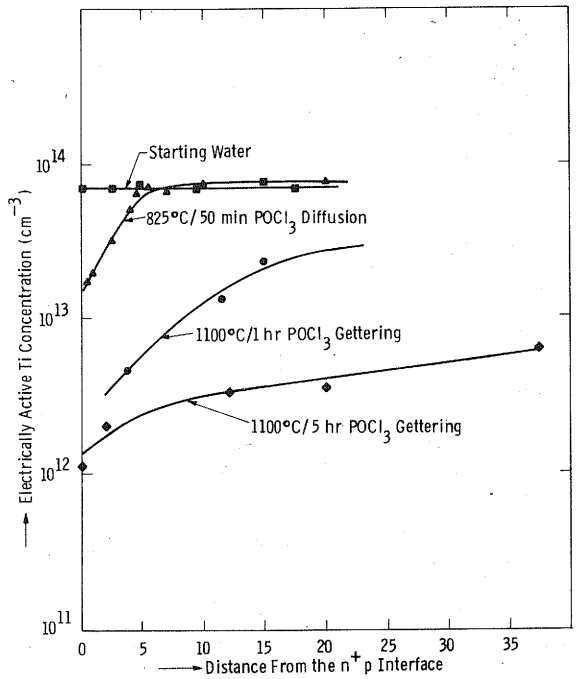

Figure 2. Electrically active titanium concentration as a function of the distance from n+p interface

Table 4

Variation in cell efficiency and trap concentration (N_T) as a function of gettering treatment for silicon containing a metallurgical Mo concentration of $4.2x10^{12}cm^{-3}$.

Gettering Condition	Normalized Cell Efficiency (n/n_B), (%)	$N_T(cm^{-3})$ of E_V+0.30eV Trap near the junction	$N_T(cm^{-3})$ of E_V+0.30eV Trap 4-6μm below the junction
None- (Starting wafer)	-	$4.45x10^{12}$	$4.5x10^{12}$
None (Solar Cell)	72.3	$4.4x10^{12}$	$4.0x10^{12}$
950°C/1 hr.	76.4	$4.7x10^{12}$	$4.3x10^{12}$
1000°C/1 hr.	72.2	$4.5x10^{12}$	$4.5x10^{12}$
1100°C/1 hr.	75.7	$4.4x10^{12}$	$4.3x10^{12}$
1100°C/2 hr.	66.7	$2.2x10^{12}$	$4.5x10^{12}$
1100°C/3 hr.	77.4	$1.35x10^{12}$	$3.1x10^{12}$
1100°C/5 hr.	75.3	$1.0x10^{12}$	$2.0x10^{12}$

original value within 6 μm, Table 4.

The data in Table (5) show that $POCl_3$ gettering is very effective when applied to Fe-doped silicon. A 1000°C/1 hr. gettering raises the normalized cell efficiency from 0.824 to 1.0. The active Fe concentration in these cells was too small to be detected by DLTS.

Table 5

Variation in cell efficiency as a function of gettering treatment for silicon containing a metallurgical Fe concentration of $3x10^{14}cm^{-3}$.

Gettering Condition	Normalized Cell Efficiency (n/n_B), (%)
None (Solar Cell)	82.4
950°C/1 hr.	96.5
1000°C/1 hr.	101
1100°C/1 hr.	100

4. DISCUSSION

The data in Table (1) and Figure (1) indicate that Mo degrades the silicon solar cell performance even at concentrations below $10^{11}cm^{-3}$. At a concentration of $4.2x10^{12}cm^{-3}$, Mo causes a 28% reduction in the cell performance compared to the uncontaminated cell efficiency. Ti is also a very harmful impurity, initiating a degradation in the solar cell performance above a concentration of $2x10^{11}cm^{-3}$. At a concentration level of $2x10^{14}cm^{-3}$, Ti lowers the absolute uncoated cell efficiency from 10% to 4%. Fe is comparatively less harmful and can be tolerated up to a concentration of about $10^{14}cm^{-3}$ without appreciable loss in the cell performance. At a concentration of $3x10^{14}cm^{-3}$ it depresses cell performance by 18%. The primary reason for the cell performance degradation due to these impurities is the reduction in the minority carrier diffusion length. This can be seen clearly from the decreased short circuit currents and OCD lifetimes compiled in Table (1).

Figure (2) shows that $POCl_3$ diffusion alone can reduce the active Ti concentration by almost a factor of 4 near the junction (DLTS measures the trap concentration only in the depletion region of the device). This concentration reaches its saturation value of $\sim 8x10^{13}cm^{-3}$ within 8-10 μm below the surface. More intense gettering reduces the cumulative active Ti concentration further. After 1100°C/5 hr $POCl_3$ gettering the active Ti concentration remains below the starting concentration even at a depth of 50 μm from the surface, Figure 2. Table (2) shows that increasing the gettering intensity from 950°C/1 hr to 1100°C/5 hr systematically increases the normalized cell efficiency from 0.43 to 0.66. The increase in efficiency is coupled with the monotonic drop in the active Ti concentration near the junction from $1.76x10^{13}cm^{-3}$ to $1.49x10^{12}cm^{-3}$, which is also a reflection of the decrease in the cumulative active Ti concentration in the bulk. This implies that gettering-induced improvement stems from the decrease in the active impurity center density. These observations are consistent with Nakamura (5) and Lecrosnier (11) who have shown that $POCl_3$ gettering of gold in silicon results in substantial reduction of Au concentration in the bulk and accumulation in the n+ region. Lecrosnier et. al. have shown by neutron activation analysis that Au and P profiles have the same shape in the n+ region indicating strong interaction between the two. Meek and Seidel (12) have calculated the increased solubility due to

metal-donor pairing. The measured profiles of electrically active Ti impurity in the p-base, beyond n^+ region, can be described by a diffusion process if we assume that Ti forms a complex with phosphorous and acquires a different energy state where it is no longer a part of the electrically active population. This would result in a concentration gradient directed toward the phosphorous rich region and lead to depletion of the impurity in the p region.

Unlike Ti, Mo-doped cell performance was insensitive to the $POCl_3$ gettering, Table 4. The Mo concentration in the bulk remains unaffected even after a 1100°C/1 hr $POCl_3$ gettering. Two to three hours gettering at 1100°C reduces the active Mo concentration by a factor of 2 to 3 near the junction which returns to its bulk value within 6 μm, indicating the steepness of the profile.

We have obtained (10) a diffusion constant for Ti in silicon at 825°C by fitting the experimental data to an out diffusion model. This value, $1.3 \times 10^{-11} cm^2/sec$, is in fairly good agreement with the literature (8) indicating that gettering process is diffusion controlled.

$POCl_3$ gettering is very effective on Fe-doped silicon. An hour gettering treatment at 1000°C was sufficient to remove the adverse affect of a 3×10^{14} cm^{-3} concentration of Fe on the cells. Fe is known to diffuse rapidly in silicon (9) and the rapid response of the Fe-doped wafers to the $POCl_3$ treatment supports that the gettering process is diffusion controlled.

5. CONCLUSIONS

Mo, Ti and Fe each degrade silicon solar cell performance but Mo is most harmful, producing efficiency degradation above a concentration of only about $5 \times 10^{10} cm^{-3}$. Mo induces a recombination center in silicon at Ev+0.30 eV, and it is relatively insensitive to $POCl_3$ gettering. Ti above a concentration of about $2 \times 10^{11} cm^{-3}$ impairs the cell performance; it induces two deep levels in silicon, Ev+0.30 eV and E_c 0.26 eV. $POCl_3$ gettering improves the efficiency of Ti-doped cells but complete recovery to the baseline efficiency value would require prolonged time and high temperatures. Fe degrades the cell performance above a concentration of $2 \times 10^{14} cm^{-3}$ due to a level at Ev+0.40 eV in the cell; $POCl_3$ gettering significantly improves the performance of the cells fabricated on Fe-contaminated wafers.

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