INTRODUCTION - COMPRESSIVE STRESSES

Evidence was presented in a recent publication indicating that the high voltages obtained from the MINP solar cell are due not only to its highly optimized emitter region but to improvements in its base region as well. (ref. 1) The analysis further suggested, albeit on the basis of indirect evidence, that the MINP cell base enhancement is due to a lower value of minority carrier mobility in that region as compared to cells of the same material but fabricated at other laboratories.

Subsequent measurement of the base region minority carrier mobility in the MINP cell as well as in other cells made from similar material, confirmed the suggestions of the preceding analysis (ref. 2). The MINP cells were indeed found to have a lower base mobility than the other cells tested. However, rather than finding a lower than normal mobility in the MINP cells, it was discovered that the other cells possessed anomalously high mobility values. Figure 1, taken from reference 1, shows these differences and indicates further that the anomalously high mobility (diffusivity) values are localized in the near-junction base region.

The MSD cell data in figure 1 can be fit quite well using a model that assumes a narrow region of high diffusivity (D) near the junction. Figure 2 shows such a fit assuming, for ease of calculation, an infinite value of D in a 15 μm thick region adjacent to the depletion region. A detailed calculation of the variation of the base component of the dark saturation current $J_{ob}$ as a function of the magnitude of D in the near-junction region indicates that an increase of only 12x is required to explain the measured factor of two difference between the MINP and the MSD base saturation current components. This is illustrated in figure 3 where $J_{ob}$ and $J_{ob}$ are the base components of the dark saturation current with and without the high D region, respectively. Although it was not possible to take measurements on samples thinner than 20 μm or so, extrapolation of the MSD cell data in figure 1 indicates that D increases of this magnitude are indeed feasible.

The mechanism responsible for the localized increases in D has been identified as the effect of diffusion induced stress (ref. 2). Emitter contraction due to phosphorus diffusion causes tensile stresses to be generated in that region. These stresses in turn cause compressive stresses to be generated in the adjacent lattice, i.e., in the near-junction base region. Since silicon is a piezoresistive material,
these base region stresses result in localized disturbances in the minority carrier diffusivity in that region.

If the above mechanism is correct, if the high diffusivity values measured in the base regions of these cells are due to stresses originating in the emitter, then it is reasonable to believe that removal of some or all of the highly stressed emitter should result in a lowering of the base diffusivity. When the emitter surface is chemically etched, however, just the opposite effect is found. When the surface of the emitter is removed the measured diffusivity shows an abrupt increase. Also, as seen in figure 4, the increase is not limited to the near-junction region. Diffusivity levels throughout the base are raised by the etching process. Concurrent with these changes in D are a sizable decline in the red response (fig. 5), confirming that the etching operation performed on the emitter does affect the base region, and a drop in the open circuit voltage.

Upon thermal annealing (110 °C, 30 min.) the etched cell characteristics return to normal. Diffusivity levels throughout the cell drop to values typical of an unetched thick base cell, and the voltage and the red response recover. Measurement of the activation energy for thermal recovery (fig. 6) yields a value close to the energy for divacancy migration, indicating that atomic motion (silicon self diffusion) is involved in the recovery process.

TENSILE STRESSES

While the mechanism of stress generation in an as-diffused cell is rather straightforward, an explanation of cell behavior subsequent to emitter etching and annealing appears to be somewhat involved. In order to describe the etch and anneal phenomenon it appears that we must postulate that as the cell is lowered from the diffusion temperature and is still in a plastic state, a limited amount of plastic deformation takes place to relieve some of the diffusion induced stress. The resulting room temperature situation is described schematically in figure 7(a). As shown, there is a region near the surface in a state of tension that is balanced by other regions in various states of compression.

When a part of the surface region (in tension) is removed by the etching process, the tension-compression couple becomes unbalanced, allowing the compressed region to expand (fig. 7(b)). The slipped region, being at room temperature and unable to flow plastically, merely transmits the expansion to the adjacent base region. The near-junction base region is thus put into a state of tension. It is this etch induced tensile stress that is proposed as the cause of the drastic post-etch increase in D. Further evidence supporting a tension based mechanism will be presented further on in the discussion.

When the etched cell is annealed at elevated temperatures, the stresses are relieved by a rearrangement of the lattice and the various cell characteristics return to, or close to, normal.

We can thus state at this point that both tensile and compressive stresses can be generated in the base region and that both types of stress degrade cell operation. It is also evident that tensile stresses are appreciably more damaging than compressive stresses.

Another means of reducing diffusion associated lattice stress, according to conventional wisdom, is to use a diffusant that is dimensionally compatible with the silicon lattice. One such element is arsenic, which has, according to the literature, a tetrahedral radius very close to that of silicon (ref. 3).

Following this line of reasoning we prepared a number of arsenic diffused solar cells from 0.1 ohm-cm float zone material. To ensure that the diffusant and the lattice were in as close to an equilibrium state as possible, we performed a low temperature deposition (850 °C, 150 min), and then subjected the wafers to a long (65 hr.), high temperature (950 °C) drive in with the arsenic source removed.
Upon measuring the base region diffusivity in these cells we found, to our surprise, that the situation was worse than it was with the phosphorus diffused cells. Figure 8 is a plot of the measured diffusivity as a function of base width for one of the arsenic diffused cells. For comparison the figure also shows the corresponding data for a MINP cell. As can be seen, not only is there a wide region of high diffusivity adjacent to the junction, but the high D values persist deep into the cell. The plot is quite similar to that found for the etched phosphorus diffused cell (fig. 4).

An estimate of the increase in the base component of the dark saturation current caused by the diffusivity profile of figure 8 can be made by assuming a base region composed of two regions of constant D. If we assume a base with a 30 to 40 μm thick near-junction region where D is 15 to 20 times that in the rest of the base, and assume (from fig. 8) a value of 35 cm²/sec in the rest of the cell, a 5x to 8x enhancement in J_{0b} should be expected. This is considerably greater than the twofold increase found for the phosphorus diffused cells.

These unexpected results prompted a return to the literature. What one finds upon closer scrutiny is that although arsenic is well matched dimensionally to the silicon lattice, a substantial fraction (as much as 35 to 40 percent (ref. 4)) of the absorbed material goes into the lattice non-substitutionally. At least a portion of this non-substitutional fraction becomes incorporated in the lattice in the form of lattice expanding precipitates (ref. 5), as evidenced by the increased lattice parameters which have been measured in arsenic diffused silicon. (ref. 6) Thus, contrary to the situation found in the phosphorus diffused emitter, the arsenic diffused emitter is a region of compressive stress, and as such should be expected to cause tensile stresses to be generated in the adjacent base region.

The evidence strongly suggests, therefore, that the extremely high values of D found in the base region of the arsenic diffused cell are due to the existence of tensile stresses in that region, in turn, are the result of compressive stresses in the emitter region. The similarity between the diffusivity versus base width plots of the arsenic diffused cells and those of the phosphorus diffused, emitter etched cells suggests that the same mechanism is active in both cases. The arsenic diffused cell data thus support the mechanism proposed earlier to explain the behavior of the emitter etched, phosphorus diffused cells.

Although an attempt to lower base stress levels in phosphorus diffused cells by chemically removing highly stressed emitter regions resulted instead in an unexpected increase in stress, a similar effort with arsenic diffused cells proved to be successful. Figure 9 shows plots of D versus base width for an arsenic diffused cell before and after the emitter etch procedure. As can be seen, the etching process reduces stress levels to such an extent that the measured diffusivity profile after etching is quite similar to that found in the low stress MINP cell (fig. 1).

Another major difference between the phosphorus and arsenic diffused cells is the fact that the dark saturation current of the former cell rose abruptly after emitter etching whereas for the arsenic diffused cell it remained constant. This is shown in table I where the etched arsenic diffused cell characteristics can be seen to be even slightly better than those of the unetched cell. This is in contrast to the sharp drop in the output characteristics of the etched phosphorus diffused cell.

The fact that the total dark saturation current of the arsenic diffused cell is not affected by the etching process while at the same time the base component undergoes a significant change, permits us to draw some interesting conclusions concerning the emitter region.
Up to this point we have limited our discussion to diffusivity changes taking place in the base region. While we cannot measure $D$ in the emitter region, it is obvious that similar, possibly even greater changes are taking place there. Fortunately, we can get some insight into what is happening from an analysis of the variation of the cell electrical characteristics during the emitter etching procedure.

As mentioned with respect to figure 9, the base diffusivity profile of the etched arsenic diffused cell is very similar to that measured for the low stress MINP cell. If we make the reasonable assumption that the etched arsenic diffused cell has a value of $J_{ob}$ comparable to that found in the MINP cell, we can, as shown in table II, separate the dark saturation current of the etched arsenic diffused cell into its base and emitter components.

As discussed earlier, there is a difference of a factor of at least 5 between the $J_{ob}$ values of the etched and the unetched arsenic cells. If this is true, and if $J_{ob}$ in the etched cell is $0.85 \times 10^{-13}$ A/cm$^2$, then in the unetched cell (table II) $J_{ob} = J_0$. The emitter component ($J_{oe}$) must therefore be negligibly small. It thus appears that the stresses in the unetched arsenic diffused cell are capable of producing an emitter with characteristics as good as those found in the MINP cell emitter without requiring MINP-type surface passivation.

As is evident in table II, however, the good news of an improved emitter region is accompanied by the bad news that the emitter improvement is coupled with a degradation in base characteristics. To realize the potential gains involved here, a means would have to be developed to decouple base and emitter stresses, eliminating the harmful base region stresses while at the same time maintaining the beneficial emitter region stresses.

BIPOLAR DEVICES

While the unetched arsenic diffused device in figure 9 would not make a very good solar cell, it would have a distinct advantage if it were incorporated into a bipolar transistor.

It is well known that the common emitter current gain of a bipolar transistor is directly proportional to the ratio of the minority carrier diffusivity in the base to that in the emitter. It is reasonable to assume that the extremely low value of $J_{oe}$ found for the unetched arsenic cell in table II is due to a stress induced reduction in the emitter diffusivity. The exact magnitude of the reduction is hard to determine but an estimate of about 10x would certainly be compatible with the data in table II. Conversely, for the same cell a 10x diffusivity increase in the near-junction base region would not be excessive. A ratio of the diffusivities thus indicates a two order of magnitude increase in transistor current gain should be possible through the use of a properly diffused arsenic emitter.

SUMMARY

The results of the preceding analysis can be summarized as follows:

1) Anomalously high values of minority carrier diffusivity have been measured in both phosphorus and arsenic diffused silicon.

2) The cause of the diffusivity anomalies is diffusion induced stress.

3) Both tensile and compressive stresses can be generated in the base region, tensile stresses being more degrading.
4) Arsenic related stresses can greatly improve emitter characteristics.
5) Emitter improvements in present cells are coupled with base degradation. There is a need to develop techniques to decouple base and emitter stresses.
6) Current gain increases of 100x are possible in bipolar transistors incorporating properly designed arsenic diffused emitters.

REFERENCES


TABLE I. - AMO OUTPUT CHARACTERISTICS FOR AN ARSENIC DIFFUSED CELL, BEFORE AND AFTER EMITTER ETCHING

<table>
<thead>
<tr>
<th>Etched</th>
<th>$V_{oc}(V)$</th>
<th>$I_{sc}(A)$</th>
<th>$J_0(A/cm^2)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Yes</td>
<td>0.648</td>
<td>0.127</td>
<td>$3.52 \times 10^{-13}$</td>
</tr>
<tr>
<td>No</td>
<td>0.644</td>
<td>0.122</td>
<td>$3.95 \times 10^{-13}$</td>
</tr>
</tbody>
</table>

TABLE II. - CALCULATED BASE AND EMITTER DARK SATURATION CURRENT COMPONENTS

<table>
<thead>
<tr>
<th></th>
<th>$J_0(A/cm^2)$</th>
<th>$J_{ob}(A/cm^2)$</th>
<th>$J_{oe}(A/cm^2)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>MINP cell</td>
<td>0.85</td>
<td>0.85</td>
<td>(0)</td>
</tr>
<tr>
<td>Arsenic emitter - etched</td>
<td>3.52</td>
<td>.85</td>
<td>2.67</td>
</tr>
<tr>
<td>Arsenic emitter - unetched</td>
<td>3.95</td>
<td>3.95</td>
<td>(0)</td>
</tr>
</tbody>
</table>

All values x 10^{-13}
Figure 1. Measured base diffusivity as a function of base width for MINP and MSD cells.

Figure 2. Theoretical fit to MSD cell diffusivity data.
Figure 3. Calculated variation of base saturation current component with diffusivity ratio.

Figure 4. Effect of emitter surface etch on base diffusivity.
Figure 5. Measured spectral response changes with emitter surface etch.

Figure 6. Thermally activated recovery time as a function of reciprocal temperature.
Figure 7. Schematic description of etch induced stress generation mechanism.

(a) Before emitter etch. (b) After emitter etch.

Figure 8. Measured base diffusivity as a function of base width for arsenic diffused cell.
Figure 9. Effect of emitter surface etch on base diffusivity in an arsenic diffused cell.