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Publication Date
1965-06-15
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R. Y. Deshpande

June 15, 1965
OBSERVATION OF DOUBLE INJECTION IN LONG p⁺pn⁺ DIFFUSED SILICON JUNCTIONS AND SOME RELATED EFFECTS*

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ABSTRACT

Double injection has been observed in long p⁺pn⁺ diffused silicon junctions. The compensation of acceptors in silicon after diffusion and heat treatment increases the resistivity of the starting p-type material and makes the observation of double injection in the device possible. A model based on the formation of donor-like complexes is suggested to explain the results. The density of the donors and their activation energy have been experimentally determined. The electrical properties of the diffused devices are examined in the light of these results.

Work done under the auspices of the U.S. Atomic Energy Commission.

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1. INTRODUCTION

The concept of two-carrier (double) injection in semiconductors has received considerable attention in both theoretical and experimental investigations. (1-4) In the earlier studies of double injection into solids, only space-charge-limited currents in a trap-free semi-insulator were investigated. Subsequently Lampert (2) extended this early analysis to the case of double injection in the presence of deep-lying traps in the forbidden band of the solid. His analysis, based on the recombination kinetics and the space-charge effects, predicts three regions in the current-voltage characteristics of a sample of length L: (i) an ohmic region for low applied voltages $V$, (ii) $V^2/L^3$ region determined by the recombination kinetics, and (iii) $V^3/L^5$ region at high injection levels, determined both by the recombination kinetics and the space-charge effects. The possibility of negative resistance, because of the variation of lifetimes of holes and electrons with the injection level, is also predicted by this analysis. However, as pointed out by Lampert, his analysis neglects the carrier diffusion effects.

A general experimental confirmation of Lampert's model has been obtained by several authors. (3-10) However, Baron et al. (7) find that when Lampert's theory is applied, the carrier diffusion effects must be taken into account. In fact, Baron (11) has extended Lampert's analysis and included the effects of diffusion; Baron's model has been verified by Mayer et al. (12) who used silicon p-i-n structures fabricated by means of the Li-ion drift techniques.
We used some of these ideas to investigate the properties of silicon subjected to different heat and ambient treatments. The technology of diffused silicon devices employs various diffusions of impurities, growth of oxide films as diffusion masks, and several heat-cycles in different ambients. These treatments can profoundly modify both the bulk and surface properties of silicon.\(^{(13-15)}\) The modifications in the properties can be explained on the assumption that certain heat and ambient treatments introduce donor-like complexes in silicon. If this assumption is true, then it should be possible to detect their presence by the double-injection method and the occurrence of negative resistance in the I-V characteristics of the device. That such is indeed the case is shown in the following.

2. PRINCIPLE OF THE METHOD

Let us consider a long bar of high-resistivity p-type silicon (acceptor concentration \(N_A \text{ cm}^{-3}\)) with \(p^+\) and \(n^+\) diffused contacts at two ends. Assume that deep donors, \(N_D \text{ cm}^{-3}\), are introduced in the material as a result of diffusions and heat treatments. When all the donors are ionized their effect will be to partially compensate and thereby increase the resistivity of the p-type silicon. The increase in the resistivity makes the observation of double injection in the device possible. But the nature of the double-injection current density will be determined by the actual values of \(N_A\) and \(N_D\).

The effect of making \(N_D\) comparable to \(N_A\) will be suppression of the \(v^2/L^3\) region from the I-V characteristics. That is, in the intrinsic material the ohmic region would merge into the \(v^3/L^5\) region where both
the recombination kinetics and the space-charge effects become dominant. On the other hand, when $N_D < N_A$ the ohmic region of the I-V characteristics will be followed by the $V^2/L^3$ region. In this latter region only the recombination kinetics dominate the current-flow mechanism. These kinetics present a possibility for one to observe negative resistance if the electron and hole-capture cross sections -- $\sigma_n$ and $\sigma_p$, respectively -- of the recombination centers are unequal. This observation is possible, for instance when the donors are neutral, i.e., when the device is operated at temperatures low enough to freeze the donors. That such a situation -- $\sigma_p > \sigma_n$ -- leads to the occurrence of negative resistance can be seen in a simpler way: At low voltages the current is given by Ohm's law, the applied field giving a net directional velocity to the carriers. As the injection level is increased, the recombination mechanism starts operating. At moderate levels $\sigma_p > \sigma_n$. Accordingly, if the increase in the electron density in the region near the $n^+$ contact more than compensates for the decrease in the hole density in the region near the $p^+$ contact, then the net conductivity of the device increases. With further increase in the injection level, this phenomenon sweeps across the whole semiconductor and effectively turns it into an n-type semiconductor. Of course, after a certain stage both the capture probabilities become equal and the negative-resistance regime is terminated. At high injection levels both the recombination mechanism and the space-charge effects govern the conduction process.

In the experiments described below we have observed most of these effects. This lends support to the assumption that deep donors are introduced in silicon when it is subjected to various treatments. Our model also explains a few of the difficulties encountered in the fabrication and operation of some oxide-passivated devices.
3. PREPARATION OF DEVICES AND MEASUREMENTS

Diffused p⁺pn⁺ silicon diodes were fabricated by the oxide-masking techniques used in the technology of oxide-passivated and planar devices. Rectangular blocks 270 by 120 by 120 mil were sawed from high-resistivity vacuum float-zoned p-type silicon (resistivity 6000 ohm-cm, lifetime 1000 µsec, EPD is $10^4$ cm⁻²). They were then lapped; etched in a 3:1 mixture of HNO₃:HF; cleaned with deionized water, methyl alcohol, and trichloroethylene; and blast-dried. Next they were loaded in a quartz furnace (1000°C) in order for boron diffusion to give the p⁺ contact. The boron source was BCl₃ and the carrier gas was dry nitrogen plus 5% hydrogen. A predeposit of 1 hour followed by a diffusion of 2 hours were carried out at the same temperature before the furnace was turned off. The devices were pulled out when the furnace cooled to < 600°C. One of the faces of each device was masked with picein in trichloroethylene, and the devices were then etched in 3:1 for 45 sec and cleaned as above. Steam-quartz, 0.7 µ thick, was then grown at 1000°C for 2 hours. The devices were again masked, with the side opposite to the boron side exposed so that the oxide from this side could be removed with NH₄F·HF. They were then given a quick etch in CP₄ and cleaned.

The devices were now ready for phosphorus diffusion to be provided with the n⁺ contact. Phosphorus diffusion was carried out in a furnace at 900°C. Here PCl₃ was the source and oxygen the carrier gas during the pre-deposit period of 60 sec. A 30-min diffusion was then carried out in three dry ambients -- (i) nitrogen, (ii) oxygen, and (iii) nitrogen for first 5 min followed by nitrogen plus 5% hydrogen. The furnace was then allowed to cool in the respective ambients to 600°C (45 min) or 500°C (90 min) before the
devices were removed. Finally the oxide from the devices was dissolved in HF. The finished diodes were \( \approx 6.5 \times 2.8 \times 2.8 \) mm.

The devices were mounted in a vacuum chamber and the I-V characteristics measured and plotted on a log-log scale. Although most of the measurements were made at room temperature, the negative resistance was observed at \( 100^\circ \text{K} \). About a hundred devices were prepared and tested with results described in the following sections.

4. EXPERIMENTAL RESULTS

Several \( p^+pn^+ \) diodes, prepared with nitrogen as the ambient in the last diffusion step, were annealed to either \( 600^\circ \text{C} \) or \( 500^\circ \text{C} \). Typical I-V characteristics plotted for them are shown in Fig. 1: the ohmic and the square-law regions are clear from the figure. The effect of carrier diffusions is also clear at low applied voltages. Changing the annealing temperatures did not make any difference in these characteristics.

Similar results were obtained when the devices were annealed in the other two ambients, oxygen, and hydrogen (ambient iii). Again, the annealing temperatures did not seem to matter.

In all these devices the resistivity, measured in the linear portion of the I-V characteristics, increased. The resistivity of the starting p-type material was about 6000 ohm-cm. The range of final resistivity was generally between 15000 and 30000 ohm-cm, though in a few cases it was as high as 50000 ohm-cm. From this increase we can estimate the concentration of donors introduced as a result of these processes. We have determined \( N_D \), assuming that

\[
N_A - N_D = \frac{1}{\rho} q \mu_p
\]

where \( N_A \) is the acceptor concentration in the original material, \( N_D \) the concentration of donors introduced in silicon as
a result of diffusions, \( \rho \) the final resistivity, \( q \) the electronic charge, and \( \mu_p \) the hole mobility. These values along with other parameters are given in Table I. The various annealing conditions are also given there.

For a few devices both the \( n^+ \) and \( p^+ \) junctions were masked and the sides successively etched in a 3:1 mixture of \( HNO_3:HF \) to a depth of several mils from the surface. The I-V characteristics were plotted after etching. A typical case is shown in Fig. 2, where the etching depth was 16 mils. The results clearly show that after heat and ambient treatments the properties of silicon are modified uniformly throughout the bulk.

We also prepared a few \( n^+p^+ \) diodes, for which the diffusion cycle was completely reversed. Phosphorus diffusion, carried out at 1000\(^\circ\)C for 30 min was followed by 2 hours of oxidation, and finally by boron diffusion -- at 900\(^\circ\)C with a predeposit period of 5 min in ambient (iii) and 25 min diffusion in any of the three ambients. The devices were removed when the furnace cooled to 600\(^\circ\)C. The characteristics of \( n^+p^+ \) devices treated in nitrogen are similar to those of \( p^+pn^+ \) devices under similar conditions (see also Table I). However, some differences in characteristics were found for the two types of devices treated in the other two ambients. A typical case of a device treated in ambient (iii) is shown in Fig. 3. It appears that either (a) the formation of donors is considerably suppressed or (b) the energy level is reduced, thereby modifying the recombination kinetics or that (c) both happen. What does happen however, cannot be definitely established at this stage.

In two groups of experiments we varied the length \( L \) of the diode structure and measured the I-V characteristics. The results for one group
are shown in Fig. 4. In Table II, the current density $J$, and $V^2/L^3$, are listed for the square-law case. The effect of carrier diffusion at low applied voltages and for shorter structures is obvious from these results.

This diffusion effect can, however, be made use of to measure the activation energy of the donors introduced in the p-type silicon. In several cases we measured the diode current as a function of temperature at low applied voltages, and from the log $I - 1/T$ plot determined the activation energy $\Delta E$ (eV) of the donors. These $\Delta E$ values are given in Table I and a typical case is shown in Fig. 5. In a few cases the results were checked by measuring the diode reverse current as a function of temperature.

Negative resistance in the I-V characteristics was observed on cooling of the devices. In our set up this measurement was made at $100^\circ K$, a typical example of which is given in Fig. 6. The appearance of two regions of negative resistance is surprising and could be due to the presence of two types of recombination centers, one strong and the other weak. Or perhaps $\sigma_n > \sigma_p$ in one region and $\sigma_p > \sigma_n$ in the other.

5. DISCUSSION

Several studies in the past have dealt with modifications in the properties of silicon subjected to various heat and ambient treatments; deep donors were introduced in silicon after these treatments. The effect of the donors on the carrier lifetime, generation-recombination current in p-n junctions and their reverse breakdown characteristics, and on the properties of silicon-silicon dioxide interface have been investigated by several authors. To explain these effects, it is generally postulated that donor-like complexes are formed through the diffusion reactions,
kinetics, and precipitation of oxygen in silicon. Many processes can take place simultaneously: fast diffusion of certain metal impurities; defects; strain fields associated with such things as dislocations; enhancing or inhibiting these processes.

From this description it is evident that a model based on the formation of donor-like complexes in silicon can very well explain our results. From the increase in resistivity of p-type silicon we estimate the average concentration of these donors to be about $1.8 \times 10^{12} \text{ cm}^{-3}$, with an activation energy equal to 0.32 eV. An estimate of the carrier lifetime can also be made as follows. Defining $V_{12}$ as the cross-over voltage from the ohmic to the square-law region of the I-V characteristics, we can take the electron transit time $t_n \approx \frac{L^2}{\mu_n V_{12}}$ as a measure of the lifetime.

Assuming $\mu_n = 1500 \text{ cm}^2/\text{V-sec}$ and taking $V_{12} = 15 \text{ V}$ and $L = 0.65 \text{ cm}$, we get $t_n = 18 \mu\text{sec}$. This will of course be the minimum lifetime of the carrier.

Here we compare the bulk properties of silicon with the properties of the silicon-silicon dioxide interface. When the latter is treated under oxygen, the concentration of donors is $\approx 1.6 \times 10^{12} \text{ cm}^{-2}$ with an activation energy of 0.31 eV. It is interesting that the value found for the activation energy tallies very closely with that of the donors in the bulk. This correlation strongly suggests formation of Si-0 complexes both throughout the bulk and at the interface. The interaction of the residual oxygen in the crystal with various metal impurities, defects, and dislocations would govern the process of formation of the donor-like complexes.

By the same reasoning, one would also expect that some of these bulk properties would be transferred to the surface, thus considerably affecting the electrical nature of the silicon-silicon dioxide interface.
As mentioned above, the presence of deep donors and the consequent reduction in their lifetime will considerably affect the properties of diffused silicon devices. That they can be a source of generation-recombination noise in these devices is obvious. They will also present a serious problem in the operation of devices such as the diffused silicon p-n junction nuclear-radiation detectors\(^{(17)}\) at low temperatures. Trapping of holes by the frozen donors will interfere with the charge collection and thus spoil the energy resolution.\(^{(18)}\) A similar problem arises in the preparation of oxide-passivated Li-drifted silicon p-i-n junctions. Several attempts to prepare such devices in this Laboratory were failures.\(^{(19,20)}\)

Naturally at this stage the question arises whether it is possible to suppress the formation of donors in silicon subjected to various treatments. Some gettering of these donors might take place by controlling the temperature, the ambients, and the predeposited period during the diffusions.

6. SUMMARY

We have shown that considerable compensation in high-resistivity p-type silicon occurs due to the introduction of donors after various heat and ambient treatments. This makes the observation of double injection in long diffused silicon diodes possible.

From the results the concentration of donors and their activation energy are determined.

A model based on the formation of donor-like complexes is suggested to explain the results.

The properties of a few diffused silicon devices are discussed in the light of these observations.
ACKNOWLEDGEMENTS

The author thanks the International Atomic Energy Agency, Vienna, for providing him a Fellowship. He also thanks William L. Hansen for several discussions, Robert P. Lothrop and Morris D. Roach for informing him about their results on Li-drifted and diffused silicon p-n-junction radiation detectors. The interest of Fred S. Goulding is gratefully acknowledged.
REFERENCES

16. N. B. Hannay, Semiconductors, Chs. 5 and 6, Reinhold Pub. Corp., N.Y. (1959);
   R. G. Rhodes, Imperfections and Active Centers in Semiconductors, Ch. 7, MacMillan and Co., London (1964)
Table I. Properties of long diffused silicon-diode structures.
(starting material, p-type silicon, resistivity 6000 ohm-cm,
lifetime 1000 μsec, \( N_A = 2.2 \times 10^{12} \text{ cm}^{-3} \), EPD is \( 10^4 \text{ cm}^{-2} \)).

<table>
<thead>
<tr>
<th>Device</th>
<th>Length (#,ambient\textsuperscript{a},temp\textsuperscript{a})</th>
<th>( V_{12} ) (volts)</th>
<th>( J_{12} ) (amp/cm\textsuperscript{2})</th>
<th>( \rho ) (ohm-cm)</th>
<th>( N_{D3} ) (cm\textsuperscript{3})</th>
<th>( \Delta E ) (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>p\textsuperscript{+}pn\textsuperscript{+}</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1 N 600</td>
<td>6.5</td>
<td>17</td>
<td>( 6.1 \times 10^4 )</td>
<td>( 3.7 \times 10^4 )</td>
<td>( 1.86 \times 10^{12} )</td>
<td>0.32</td>
</tr>
<tr>
<td>2 N 600</td>
<td>6.5</td>
<td>15</td>
<td>4.5</td>
<td>4.9</td>
<td>1.95</td>
<td>0.30</td>
</tr>
<tr>
<td>3 N 500</td>
<td>6.5</td>
<td>12</td>
<td>6.4</td>
<td>2.8</td>
<td>1.75</td>
<td>0.29</td>
</tr>
<tr>
<td>4 N 500</td>
<td>6.5</td>
<td>13</td>
<td>7.4</td>
<td>2.5</td>
<td>1.71</td>
<td>0.33</td>
</tr>
<tr>
<td>5 H 600</td>
<td>6.4</td>
<td>18</td>
<td>7.0</td>
<td>3.9</td>
<td>1.87</td>
<td>0.32</td>
</tr>
<tr>
<td>6 H 600</td>
<td>6.6</td>
<td>21</td>
<td>7.9</td>
<td>4.0</td>
<td>1.88</td>
<td>0.33</td>
</tr>
<tr>
<td>7 H 500</td>
<td>6.5</td>
<td>18</td>
<td>10.2</td>
<td>2.8</td>
<td>1.74</td>
<td>0.30</td>
</tr>
<tr>
<td>8 H 500</td>
<td>6.5</td>
<td>16</td>
<td>9.2</td>
<td>2.8</td>
<td>1.74</td>
<td>0.30</td>
</tr>
<tr>
<td>9 0 600</td>
<td>6.4</td>
<td>14</td>
<td>7.1</td>
<td>3.1</td>
<td>1.79</td>
<td>0.36</td>
</tr>
<tr>
<td>10 0 600</td>
<td>6.4</td>
<td>15</td>
<td>6.6</td>
<td>3.8</td>
<td>1.87</td>
<td>0.32</td>
</tr>
<tr>
<td>11 0 500</td>
<td>6.2</td>
<td>12</td>
<td>6.9</td>
<td>2.4</td>
<td>1.68</td>
<td>0.36</td>
</tr>
<tr>
<td>12 0 500</td>
<td>6.4</td>
<td>15</td>
<td>7.0</td>
<td>3.3</td>
<td>1.82</td>
<td>0.34</td>
</tr>
<tr>
<td>n\textsuperscript{+}pp\textsuperscript{+}</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1 N 600</td>
<td>6.3</td>
<td>20</td>
<td>( 13.0 \times 10^4 )</td>
<td>( 2.4 \times 10^4 )</td>
<td>( 1.69 \times 10^{12} )</td>
<td>0.32</td>
</tr>
<tr>
<td>2 N 600</td>
<td>6.3</td>
<td>24</td>
<td>12.7</td>
<td>3.0</td>
<td>1.78</td>
<td>0.29</td>
</tr>
</tbody>
</table>

\textsuperscript{a}Ambient and temperature at which device was removed from furnace in the last diffusion step.
Table II. Effect of diode length on the I-V characteristics in the square-law region (calculated for the current density \( J = 6 \times 10^{-2} \text{ amp/cm}^2 \)).

<table>
<thead>
<tr>
<th>( L ) (cm)</th>
<th>( V ) (volts)</th>
<th>( V^2/L^3 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.52</td>
<td>90</td>
<td>5.75 \times 10^4</td>
</tr>
<tr>
<td>0.42</td>
<td>60</td>
<td>4.85</td>
</tr>
<tr>
<td>0.32</td>
<td>44</td>
<td>5.86</td>
</tr>
<tr>
<td>0.22</td>
<td>16</td>
<td>2.40</td>
</tr>
<tr>
<td>0.12</td>
<td>3.7</td>
<td>0.80</td>
</tr>
</tbody>
</table>
FIGURE CAPTIONS

Fig. 1. I-V characteristics for $p^+p_n^+$ devices treated in nitrogen.

Fig. 2. I-V characteristics after successive etching of the sides in 3:1 $\text{HNO}_3:HF$. Etching time in minutes was: 0 (2); $\bullet$ (2); $\times$ (4); $\Theta$ (6); and $\Box$ (8).

Fig. 3. I-V characteristics for $n^+p_p^+$ devices treated in hydrogen (ambient iii)

Fig. 4. Current density as a function of the applied voltage and the length of the device. The lines with dots represent experimental data and the lines without dots theoretical data.

Fig. 5. Temperature dependence of the diode current at low applied voltages.

Fig. 6. Observation of negative resistance at $100^\circ$K.
Fig. 1
Fig. 3
Fig. 4

CURRENT DENSITY, J (AMPS/CM²)

VOLTAGE, V (VOLTS)
Fig. 5

MUB-6670

SLOPE 0.32 eV
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