Long-Time Relaxation of Silicon Resistivity after Annihilation of Thermal Donors

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Grown-in thermal donors (TDs) are normally annihilated by annealing at 650°C or higher *T*, to restore the resistivity value corresponding to the dopant concentration (boron, in our case). We have found that immediately following such an anneal (followed by a quench) the resistivity drifts at the room temperature to a lower value – and, accordingly, the hole concentration p drifts to a higher value. The amplitude of this relaxation is appreciable, sometimes up to 50% (Fig.1).

To understand the reason for this phenomenon, we have monitored the relaxation process, by Hall effect and resistivity, in a number of samples of different boron concentration (in a range of $5\text{x}10^{12}$ to $5\text{x}10^{16}$ cm^{-3}) and of different oxygen content, (5 to 8)$\text{x}10^{17}$ cm^{-3} using the optical calibration coefficient $2.45\text{x}10^{17}$ cm^{-2}. The relaxation curve $p(t)$ can be well fitted by an exponential law p_o - δp $\exp(-t/\tau)$ characterized by an amplitude δp and a relaxation time τ. The latter parameter was found to be in a range of several hours to several days. The saturated hole concentration p_o was identified with the boron concentration N_a.

The dependence of the relaxation amplitude δp and the relaxation time τ on the boron concentration N_a and the oxygen concentration C_{ox} was found to be specific for the annealing temperature. For a conventional annealing temperature of 650°C (for 30 min), the amplitude δp was proportional to N_a (in a middle concentration range of boron, 10^{13} to 10^{16} cm^{-3}) and well correlated with C_{ox}. The amplitude, normalized by N_a, can be described by a power law $C_{ox}{}^m$ ($m \approx 5.5$). The relaxation time was less definitely correlated with the parameters N_a and C_{ox}, but on average it was an increasing function of C_{ox}.

Annealing of TDs at a higher *T*, 900°C for 5 min, also induced an appreciable room-temperature relaxation but with a stronger correlation to N_a, and –surprisingly – with a decreasing dependence of δp on C_{ox}.

In one of the samples the Hall effect was monitored down to a liquid helium temperature, to deduce separate values for the boron acceptor concentration N_a and the compensating concentration N_d of donors (phosphorus, and probably some residual TDs). This was done right after a quench (after a time of about 1 h necessary to apply the electric contacts), and several days after – when $p(t)$ was already saturated. It turned out that N_d was the same in both cases while N_a was increased.

The relaxation process is thus essentially re-activation of boron acceptors partially de-activated by annealing. A strong correlation with oxygen suggests that the de-activation is caused by mobile oxygen clusters inherited from the anneal. Within this model, the clusters O_n (of n oxygen atoms) are partially trapped by boron acceptors to become electrically inactive BO_n species (it is possible that these centers are also acceptors, but with a deeper energy level not felt in p-type material). The re-activation process implies that the O_n clusters are mobile even at room temperature. The proportionality between the amplitude δp and the boron concentration is accounted for if the equilibrium between the free and boron-trapped O_n species is maintained, and the concentration of BO_n species is smaller than that of boron and of O_n clusters. Re-activation is caused by a loss of O_n, most likely due to aggregation of O_n into larger clusters. The origin of the quenched-in O_n clusters can be the initial TD-clusters. It is well known that the TDs are not dissolved by 650°C anneal but transform into some other (inactive) clusters that later give rise to the New Thermal Donors (NTDs) [1]. These 'transient' oxygen clusters (already not TDs and not yet NTDs) can be the reason for the room-temperature relaxation of the resistivity.

In the final stage of this work, it was discovered that the relaxation time τ was very sensitive to the sample illumination level, decreasing essentially under deliberate illumination. The value of τ could be also reduced by keeping a sample at a slightly raised temperature (for example 30°C). The relaxation amplitude was insensitive to these factors. The effects of uncontrolled illumination (and, to a lesser extent, of a not precisely fixed temperature) are thought to be the main source of a scatter in the value of τ.

There is a remarkable similarity between the boron de-activation/re-activation of the present study and a well-known phenomena of lifetime degradation/recovery related to boron and oxygen impurities in photo-voltaic silicon materials [2,3].

References

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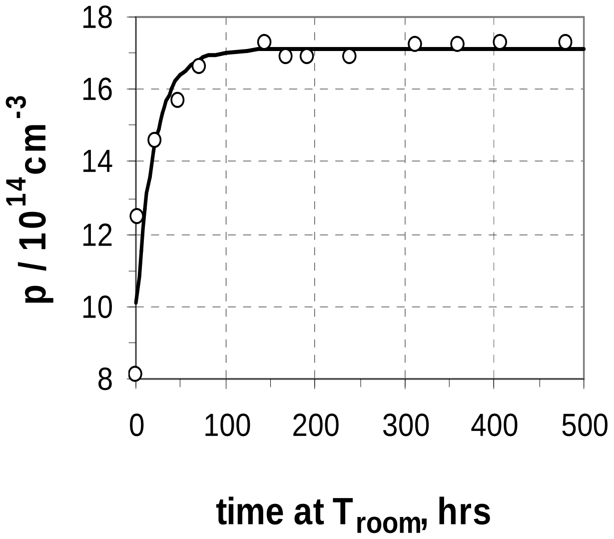

Fig.1 Room-temperature relaxation of the hole concentration (monitored by Hall effect) after anneal at 650°C for 30 min followed by a quench. Oxygen concentration is $7\text{x}10^{17}$ cm^{-3}.