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KINETICS OF BOUND ELECTRONS IN Si:P

Peter Lawaetz and Warren G. Proctor

Physics Laboratory III
Technical University of Denmark
Lyngby
Denmark

Detailed experimental studies of the electric-field-induced breakdown of Si:P in the range 18-37 K yield information on the kinetics of bound electrons with and without electric field. This results in a completely revised picture of recombination with large time constants involved.

I. Introduction

In silicon lightly doped with phosphorus, the conduction electrons freeze out at temperatures below 50 K, and in thermal equilibrium most of them are found in the ground state of the donors. By application of a strong electric field it is possible to excite the bound electrons into the conduction band by hot-electron impact. With increasing field the concentration of free electrons exhibits an abrupt increase [1] . Recent theoretical investigations [2,3] indicate that the excited states of the donor play a crucial role in this breakdown.

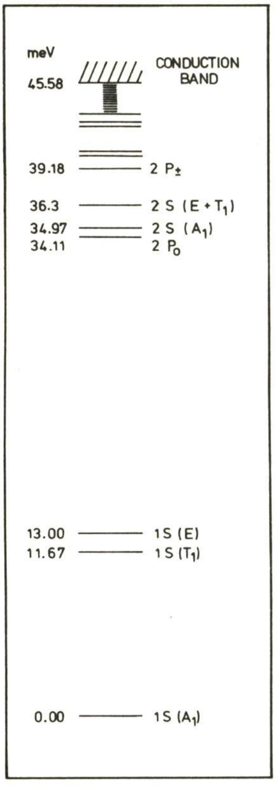

Fig. 1 The energy levels of P in Si

Experiments on Si:P by Lehto and Proctor [4] show a delay between the application of the breakdown field and the increase in free-carrier concentration, the delay t_b depending upon the time τ since the previous breakdown. They ascribe this phenomenon to decaying populations of the excited states, and a analysis of $t_b(\tau)$ measured under various conditions yields 4 different lifetimes ranging from 0.1 s to several hours at 20 K. The temperature dependence suggests certain activation energies, but the numbers make no sense in terms of the energy spectrum of Si:P shown in Fig.(1).

Similar to the excitation, the recombination of excess free carriers is supposed to proceed stepwise through the excited states down to the ground state [5]. Calculation [6] is somewhat at variance with experiment [7], and the recombination time observed by Asche et al. [8] on material similar to [4] is much below 1 μs and rather independent of temperature. The apparent contradiction between the two types of experiments as well as discrepancies in the subject of recombination have led us to refine the experimental study of delayed breakdown.

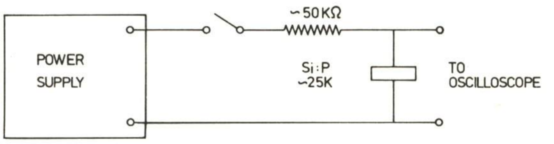

Fig. 2 Equivalent circuit used in breakdown experiments

II. Experiments

The simple principle of the experimental set-up [4] is sketched in Fig.(2). The sample is identical to the one used in [4]: 100 Ωcm phosphorus-doped ($5 \cdot 10^{13} cm^{-3}$ donors) with about 1% compensation. Apart from many more observations of $t_b(\tau)$ for each temperature and field, the present study significantly improves the measurement of sample temperature and extends the temperature range to 18-37 K. Typical pulse responses are sketched in the inset in Fig. (3) which also illustrates the two basic varieties of experiments: bias-breakdown and breakdown-breakdown. Our principal results are summerized as follows:

1. In the breakdown-breakdown experiments shown in Fig. (3), $t_b(\tau)$ exponentially approaches an asymptote for $\tau \to \infty$, the time constant T_2 in the long tail $\exp(-\tau/T_2)$ being independent of the electric field used to initiate the breakdown. The temperature dependence of T_2 is plotted in Fig. (4) giving an activation energy of 46 ± 2 meV.

2. After the switch-off of the breakdown pulse, the sample exhibits a decaying conductivity observed through a small decrease ΔV in the subsequent breakdown pulse top. A careful analysis of $\Delta V(\tau)$ shows that the decay is initially non-exponential with an exponential tail having the same time constant T_2 as above.

3. For very small time intervals ($\tau \to 0$), t_b approaches linearly a nonzero value. The ratio $t_b(\infty)/t_b(0)$ is typically 2000 at 22.5 K.

4. The results of a standard bias-breakdown experiment are shown in Fig. (3). $t_b(\tau)$ also has an exponential tail, but the corresponding time constant T_1 is smaller than T_2. By plotting T_1 as function of temperature in Fig. (4) we find again an activation energy around 46 meV. Contrary to [4], we observe no longer

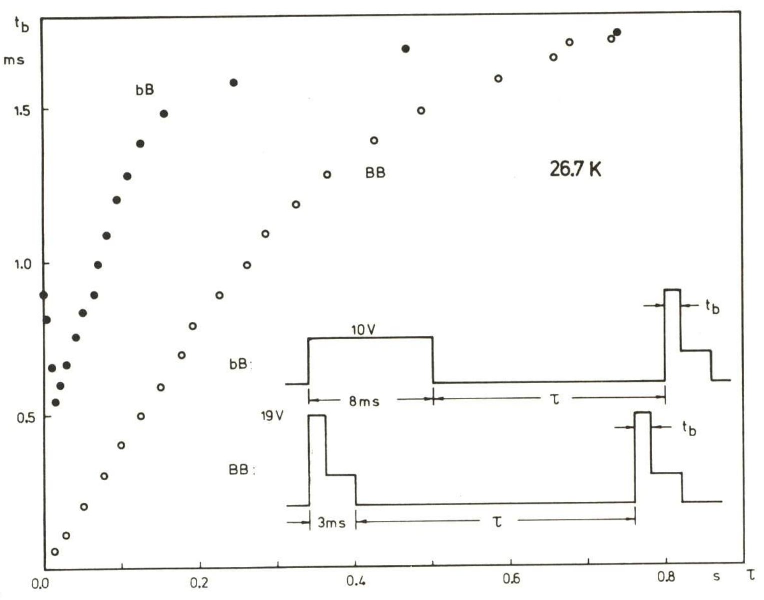

Fig.3 Dependence of the breakdown delay t_b upon the time interval for excitation either by a breakdown (BB) or a bias pulse (bB): 10 volts applied across the sample corresponds to a field of 125 V/cm

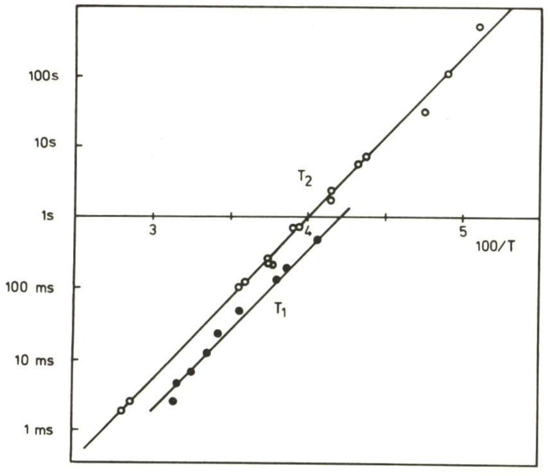

Fig. 4 Plots of the time constants T_1 and T_2 against the inverse temperature: The solid lines have been drawn with a slope corresponding to an activation energy of 46 meV

time constants than T_2.

III. Interpretation

As shown by the observation (2), the time constant T_2 is associated with the decay of free electrons. Reconciliation of this giant lifetime with the earlier more "normal" recombination times [8] can only be achieved if there is a fast communication between the conduction band and an excited state less than 20 meV above the ground state with very small transition rate downward. In thermal equilibrium between these states, the ratio of the populations n in the conduction band and N_2 in this excited level is much smaller than unity. In the broken-down situation, these populations are nearly in relative thermal equilibrium, and so we see the large decay time T_2, whereas in very high-field excitations as in [11], the observed small time constant reflects the fast approach to such an equilibrium.

Inspection of the Si:P level diagram Fig. (1) shows that electrons can easily cascade through the upper excited states by emission of low-energy acoustic phonons, but that the jump down to the 1S-levels requires a high-energy phonon. The only relevant phonon which conserves momentum approximately and energy exactly is an LA intervalley f-phonon of 26·2 meV. The corresponding electron transition is from $2P_{\pm}$ to the upper 1S-level, henceforth labelled 2. Intervalley phonons have not been included in previous recombination calculations [6], thus offering a possible qualitative explanation for the earlier discrepancies. We conclude that T_2 is connected with downward transitions from level 2, and that n and N_2 are in relative thermal equilibrium during this slow decay.

Observation (1) then demonstrates that the breakdown delay t_b is mainly governed by the number of free electrons present initially, and to some approximation $t_b \propto n^{-1}$. This is clearly indicative of impact excitation.

The nearly exponential behaviour of $t_b \propto n^{-1}$, the nonexponential form of $\Delta V(\tau)$, and the temperature dependence of T_2 prove that the decay associated with T_2 is an impact-induced deexcitation from level 2. One-phonon-assisted transitions among the 1S-levels are obviously very weak, the $1S(E) \leftarrow 1S(T_1)$ apparently forbidden for low-energy phonons, and transitions to the ground state excluded by energy conservation.

As observed in Fig. (3), $t_b \propto n^{-1}$ does not hold for all τ, and this is due to the role played during breakdown by the population N_1 of the lower excited

1S-state, labelled 1. Indeed, the constancy of n and N_2 during the breakdown delay as well as the abruptness of the actual breakdown imply an intermediate state, the population of which slowly builds up from the ground state during the delay. The barrier to impact transitions from 1 to 2 is caused by the small energy difference which diminishes the efficiency of impact by hot electrons up to a certain point.

The influence of N_1 is corroborated by observation (3). According to the present model, the maximum relative increase in n following breakdown is determined by the increase in N_2, which cannot exceed the total number of electrons. At 22.5 K, this increase is less than a factor of 100, whereas the observed t_b is reduced by a factor of 2000. Thus t_b depends on the population N_1 at the onset of the breakdown pulse.

The bias experiments described as observation (4) are believed to involve excitation to level 1 during the bias pulse. The existence of another time constant $T_1 < T_2$ is evidence for a faster decay of electrons in level 1 also by impact.

VI. Conclusion

By refinement of previous experiments [4] we have substantiated the existence of long-lifetime excited states of P-donors in Si. Our interpretation implies a new recombination model closely connected with the energy spectrum of the donor states and thus with the multivalley nature of the conduction band. The main features are the importance of intervalley phonons and the dominant impact de-excitation from excited 1S-states with a time constant T_2 depending only on the equilibrium concentration of free electrons. A more detailed account will be published elsewhere.

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