

# Oscillatory reaction involving structural changes in defects in silicon

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(Submitted 3 October 1986; resubmitted 23 February 1987)  
*Pis'ma Zh. Eksp. Teor. Fiz.* **45**, No. 7, 350–352 (10 April 1987)

Experiments reveal that an "oscillatory" reaction involving an interaction of defects may occur in silicon.

Oscillatory chemical reactions in liquid solutions are presently being studied actively.<sup>1</sup> In the present letter we report a study of thermal structural changes in radiation defects in silicon. We have observed changes in the states of defects which repeat in time and which can be identified with an oscillatory reaction.

The samples are *p-n* structures made from *n*-type silicon ( $n_0 = 10^{14} \text{ cm}^{-3}$ ), synthesized by the diffusion of boron in a medium containing oxygen. The defects are produced by bombardment with  $^{60}\text{Co}$   $\gamma$  rays. The concentration of defects, the positions of their energy levels, and the carrier-capture cross section are determined by time-varying capacitive spectroscopy.

In the oxygen-enriched samples, the most abundant radiation defects are *E* 1 centers with an energy level  $E_c - 0.18 \text{ eV}$  and an electron-capture cross section  $\sigma_n = 2 \times 10^{-14} \text{ cm}^2$ . This center is usually associated in the literature with an *A* center (a vacancy-oxygen or V–O complex).<sup>2</sup> This complex is thermally stable up to 600 K. Our measurements show, however, that even at  $T \gtrsim 373 \text{ K}$  one observes a decrease in the concentration of this center, which is accompanied by the appearance of *E* 2 defects, with a level  $E_c - 0.34 \text{ eV}$  and a carrier-capture cross section  $\sigma_n = 1 \times 10^{-15} \text{ cm}^2$ . This observation stimulated a study of the time evolution of the concentration of these defects at a fixed sample annealing temperature.

Figure 1 shows the time evolution of the concentrations of the *E* 1 and *E* 2 centers for a sample annealing temperature of 600 K; the concentrations have been divided here by the total concentration of these centers for the given annealing time:  $f = N_{1,2}(t) / [N_1(t) + N_2(t)]$ . This normalization was chosen in order to eliminate the effect of the decomposition of complexes which is observed at long annealing times. We see that during the first  $\sim (4-5) \text{ s}$ , the *E* 1 defects disappear completely; this disappearance is accompanied by the appearance of *E* 2 defects, in the same concentration. The process then reverses direction: the *E* 2 centers disappear and they are replaced by *E* 1 centers. The concentration of the basic radiation defects, with the level  $E_c - 0.18 \text{ eV}$  thus undergoes a complete cycle of oscillations (appearance-disappearance-appearance). The thermal decomposition of the V–O complex limits the possibility of observing the subsequent time evolution of this system of defects at  $t > 10^6 \text{ s}$ . Attempts to study the oscillatory regime of the changes in the structure of the defects at a lower temperature showed that the time required for the transition of the system

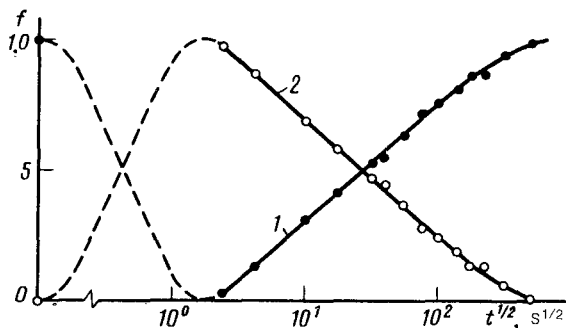
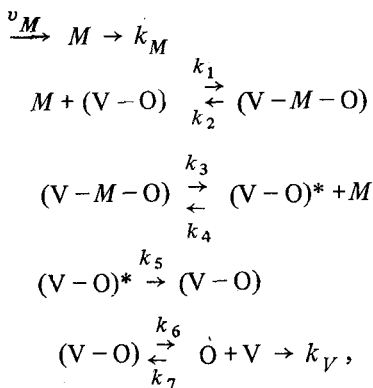


FIG. 1. Normalized defect concentration versus the duration of the isothermal annealing ( $T = 600$  K). 1— $E_c - 0.18$  eV ( $E_1$ ); 2— $E_c - 0.34$  eV ( $E_2$ ).

of defects from one state to the other increases by several orders of magnitude, making such experiments unfeasible.

It can be seen from Fig. 1 that the time required for the structural change  $E_1 \rightarrow E_2$  is  $\sim 5$  s, while that for the inverse process,  $E_2 \rightarrow E_1$ , is  $\sim 10^6$  s. This result indicates a substantial increase in the reaction "period" due to a decrease in the "quality" factor of the system over time. It follows from Ref. 3 that a situation of this sort could arise in the rate constants of the chemical reactions do not remain constant over time. In our case the observed time dependence of the concentrations of defects can be described by the following scheme:



where  $M$  is a defect which is mobile at  $T \gtrsim 373$  K, which is generated with a rate  $v_M$ , and which moves off to a sink at a constant rate  $k_M$ . The rates at which this defect is generated and moves off to the sinks depend on the time. The capture of a mobile component  $M$  by a  $(V-O)$  complex results in a structural change of the center into the state  $(V-O)^*$ , which introduces a level in the energy gap at  $E_c - 0.34$  eV. This structural change is accompanied by the liberation of the component  $M$ . In turn, the  $(V-O)^*$  configuration is metastable. That centers can exist in several structural configurations was demonstrated in Refs. 4–6. The last equation describes the thermal decomposition of the  $(V-O)$  complex, accompanied by a runoff of vacancies to sinks. Important to the appearance of the oscillations in this model as in the case in Ref. 3, is

the binding of the component  $M$  by the (V–O) complex and the subsequent liberation of this component.

What might be playing the role of the defect  $M$ ? A study of the kinetics of the structural changes under the assumption of a first-order reaction yields the activation energy for the  $E1 \rightarrow E2$  process:  $\cong 0.7$  eV. In a first approximation, the activation energy for the transformation of a defect can be related to the migration energy of defect  $M$ . A comparison of the value found here for the activation energy for the process with data on the migration energies of interstitial host atoms ( $\cong 0.85$  eV) and carbon atoms ( $\cong 0.80$  eV) in silicon reveals a satisfactory agreement. This agreement suggests that in this case the mobile defect  $M$ , which leads to the oscillation in the concentration of  $A$  centers, is a carbon atom or an interstitial host (silicon) atom.

<sup>1</sup>D. Garel and O. Garel, *Oscillatory Chemical Reactions* (Russ. transl. Mir, Moscow, 1986).

<sup>2</sup>W. Corbett *et al.*, *Phys. Rev.* **121**, 1015 (1961).

<sup>3</sup>E. E. Sel'kov and V. G. Nazarenko, *Biofizika* **25**, 1006 (1980).

<sup>4</sup>M. Levinson, M. Stavola, and P. Besomi, *Phys. Rev.* **B 30**, 5817 (1984).

<sup>5</sup>J. Bourgoin and M. Lannoo, *Point Defects in Semiconductors II: Experimental Aspects*, Springer-Verlag, New York, 1983 (Russ. transl. Mir, Moscow, 1985, p. 304).

<sup>6</sup>P. V. Kuchinskii, V. M. Lomako, and L. N. Shakhlevich, *Pis'ma Zh. Eksp. Teor. Fiz.* **43**, 423 (1986) [*JETP Lett.* **43**, 544 (1986)].

<sup>7</sup>V. V. Emtsev and T. V. Mashovets, *Primesi i tochechnye defekty v poluprovodnikakh* (Impurities and Point Defects in Semiconductors), *Radio i svyaz*, Moscow, 1981, p. 248.