# Model of breakdown of MOS-structures by the mechanism of anode hydrogen release

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A quantitative model of the breakdown of MOS-structures with relatively thick (10−100 nm) gate dielectric by the mechanism of anode hydrogen release from interphase boundary Si-$SiO_2$ is proposed. The breakdown delay time is determined by dispersion transport and accumulation of hydrogen ions in the gate dielectric. It is shown that at a high concentration of hydrogen in MOS structures and electric field strength of less than $\sim 10$ MV/cm, the model satisfactorily describes breakdown delay times significantly shorter than those expected from the $1/E$ model. At higher field strengths, the breakdown is described by the anode hole injection model.

**Keywords:** MOS-structure, breakdown, anode hydrogen release, anode hole injection.

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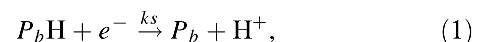
## 1. Introduction

In modern MOS integrated circuits (MOS IC), high performance is achieved by reducing the dielectric thickness to 1−4 nm and using dielectrics with high permittivity (high-k) with a sublayer of silicon dioxide [1,2]. At the same time, an increase in tunnel leakage currents (stress-induced leakage current (SILC)) is observed, the operating voltage and noise immunity of the MOS IC decrease [3]. Due to the processes of degradation of a two-layer dielectric and electromigration of metallization, reliability and operating time may decrease [4,5]. Due to these circumstances, MOS IC with a thicker (10−100 nm) traditional dielectric such as silicon dioxide are still widely used in both civilian and military equipment [6]. The operating time for failure for such MOS structures is determined by the delay time of the breakdown of the gate insulator [3].

Several mechanisms of breakdown of MOS structures are considered in the literature [2,3,7–9]: avalanche ionization, anode hole injection (ADI), thermochemical model and anode hydrogen release. It is believed that avalanche ionization occurs at high fields ($E > 8-10$ MV/cm) in sufficiently thick layers of silicon dioxide ($d \geq 20$ nm). The anode hole injection underlying the $1/E$ model is the cause of breakdown in the presence of hole traps near the cathode at fields $E > 6-8$ MV/cm. The thermochemical $E$-model provides a better description of the delay time for a breakdown at low field strengths than $1/E$ ADI model. However, the thermochemical model does not explain the dependence of the breakdown delay time on the thickness of the gate insulator, as well as the relative constancy of the injected breakdown charge on the field strength.

A qualitative model of hydrogen release from the anode interface boundary (IPB) Si-$SiO_2$ was proposed in [10]. According to this model, the electrons injected by the cathode in the electric field of the dielectric acquire energy sufficient to release hydrogen ions from boundary traps and form surface states:



$$P_b\mathrm{H} + e^- \xrightarrow{ks} P_b + \mathrm{H}^+, \qquad (1)$$

where $P_b$H and $P_b$ — passivated and unpassivated $P_b$-centers on IPB Si-$SiO_2$, $k_S$ — reaction rate constant. The released hydrogen ions $H^+$ migrate to the cathode, where they form defects affecting the breakdown of MOS structures.

MOS structures manufactured using conventional planar technology may contain a significant amount of hydrogen up to $10^{14}-10^{15}\,\mathrm{cm}^{-2}$, which is concentrated mainly at the interface boundaries of $SiO_2$-Si (substrate) and $SiO_2$-gate [11]. When avalanche injection of electrons from a silicon substrate is implemented in the MOS structure, hydrogen moves to the cathode, where it accumulates at the $SiO_2$-gate in a thin layer with a width of the order of the monolayer [11]. The introduction of hydrogen by annealing in a hydrogen-containing medium or from a protective layer leads to a decrease in the breakdown delay time of MOS structures [12,13]. The release of hydrogen from IPB Si-$SiO_2$ and the associated generation of surface states occur at electron energy $> 2$ eV [14], which corresponds to the field strength $> 3-4$ MV/cm. The mechanism of hydrogen release is explained by the inelastic interaction of electrons with local modes of Si-H bonds on the surface of the silicon anode [8]. Thus, in the presence of hydrogen in the MOS structure, the breakdown with relatively low fields ($E > 3-4$ MV/cm) may be caused by the mechanism of anode hydrogen release.

Defects caused by released hydrogen in the thin layers of the dielectric ($d < 10$ nm) line up randomly along the thickness of the dielectric, forming conductive paths and SILC leaks, causing the so-called soft breakdown. Such a breakdown is believed to occurs when the critical density of defects is reached (percolation model [2,8]).

In thicker ($d = 10-100$ nm) dielectric layers, the so-called hard breakdown occurs. Such a breakdown can be described by the ADI quantitative model in the presence of hole traps near the cathode [15]. However, the ADI model does not take into account the presence of hydrogen in MOS structures and its anode release.

The purpose of this work is to develop a quantitative model of breakdown of MOS structures with a relatively thick gate insulator by the mechanism of anode release of hydrogen, taking into account the dispersive nature of hydrogen ion transport.

## 2. Model description

When a negative bias is applied to the gate of a MOS structure with a relatively thick ($d = 10-100$ nm) insulator, electrons are injected by the Fowler–Nordheim tunneling mechanism:

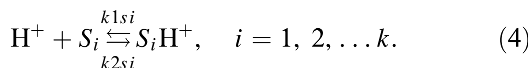
$$I_n = AE_c^2 \exp(-B/E_c), \tag{2}$$

where $I_n$ — electron flux, $E_c$ — electric field strength near the gate (cathode), $A$ and $B$ — constants determined by the effective mass of the electron in silicon dioxide $m_{ox}$ and the height of the potential barrier $SiO_2$-gate $\phi$ ($m_{ox} = 0.5m_e$, $\phi = 3.2$ eV for $n^+$-polycrystalline silicon (PC) gate). The electrons injected by the cathode in the electric field of the dielectric acquire energy sufficient to break the weak hydrogen bond in $P_b$H-centers at IPB Si-$SiO_2$ and release hydrogen ions by reaction (1). The rate of hydrogen release in this case, it will be determined by the rate of depassivation of $P_b$Hcenters:

$$\frac{\partial Q_{\mathrm{H}}^+}{\partial t} = \frac{\partial Q_{P_b}}{\partial t} = k_s Q_{P_b\mathrm{H}} n, \tag{3}$$

where $t$ — time, $Q_{\mathrm{H}}^+$ — number of released hydrogen ions, $Q_{P_b\mathrm{H}}$ and $Q_{P_b}$ — densities of passivated and unpassivated $P_b$-centers, respectively, $n$ — electron concentration on IPB Si-$SiO_2$. Hydrogen ions released in the reaction (1) move through the dispersion mechanism to the cathode, where they accumulate on IPB $SiO_2$-$Si_{pc}$ (PC gate).

The dispersive transport of hydrogen ions is described using a multiple capture model for localized states $S_i$ [16]:



$$\mathrm{H}^+ + S_i \underset{k2si}{\overset{k1si}{\leftrightarrows}} S_i\mathrm{H}^+, \quad i = 1,\ 2, \ldots k. \tag{4}$$

Hydrogen ion transport equations together with Poisson equation are written as:

$$\frac{\partial C_{\mathrm{H}}^+}{\partial t} = D_{\mathrm{H}}^+ \frac{\partial^2 C_{\mathrm{H}}^+}{\partial x^2} - \mu_{\mathrm{H}}^+ E \frac{\partial C_{\mathrm{H}}^+}{\partial_x} - C_{\mathrm{H}}^+ \sum_{i=1}^{k} k_{1si} C_{SHi}^0 + \sum_{i=1}^{k} k_{2si} C_{SHi}^+, \tag{5}$$

$$\frac{\partial C_{SHi}^+}{\partial t} = -\frac{\partial C_{SHi}^0}{\partial t} = k_{1si} C_{SHi}^0 - k_{2si} C_{Pi}^+, \quad i = 1, 2 \cdots k, \tag{6}$$

$$\frac{\partial^2 V}{\partial x^2} = -\frac{q}{\varepsilon \varepsilon_0} \left( p - n + C_{\mathrm{H}}^+ + \sum_{i=1}^{k} C_{SHi}^+ \right), \tag{7}$$

where $x$ — coordinate measured from IPB with silicon substrate ($x = 0$ on IPB with substrate, $x = d$ on IPB with gate, $d$ — dielectric thickness); $p$ — concentration of holes, $C_{\mathrm{H}}^+$ — concentration of free hydrogen ions; $C_{Si}^0$ and $C_{SHi}^+$ — concentrations of $i$-empty and filled hydrogen states, respectively; $D_{\mathrm{H}}^+$ and $\mu_{\mathrm{H}}^+$ — diffusion coefficient and mobility of free hydrogen ions, respectively ($D_{\mathrm{H}}^+ = 1 \cdot \exp(-0.73/(k_{\mathrm{B}}T)$ cm$^2$/s, $\mu_{\mathrm{H}}^+ = D_{\mathrm{H}}^+/(k_{\mathrm{B}}T)$); $V$ — potential, $E$ — electric field strength, $E = -dV/dx$, $q$ — electron charge; $\varepsilon$ — relative permittivity of silicon oxide ($\varepsilon = 3.9$), $\varepsilon_0$ — electrical constant.

The density distribution of localized states for hydrogen ions has an exponential energy form characteristic of amorphous materials:

$$C_{Si}^0(E_{Si}) = N_S^0 \exp\left(-\frac{E_{Si}}{E_{SS}}\right), \quad i = 1, 2, \cdots k, \tag{8}$$

where $N_S^0$ — the total concentration of empty and filled hydrogen localized states,

$$N_S^0 = C_{SH}^0 + C_{SH}^+, \quad C_{SH}^0 = \sum_{i=1}^{k} C_{SHi}^0, \quad C_{SH}^+ = \sum_{i=1}^{k} C_{SHi}^+$$

$E_{Si}$ — energy of the $i$-level of the localized state; $E_{SS}$ — characteristic energy associated with the dispersion parameter $\alpha_S$ ratio $\alpha_S = k_{\mathrm{B}}T/E_{SS}$.

At the initial moment of time, the concentration of hydrogen ions and their filled localized states is zero:

$$C_H^+(x, 0) = 0, \quad C_{SHi}^+(x, 0) = 0, \quad i = 1, 2 \ldots k. \tag{9}$$

The boundary condition for electrons at $x = 0$ is determined by the rate of their runoff at IPB Si-$SiO_2$ in accordance with (3):

$$j_n = \frac{\partial Q_{P_b}}{\partial t}, \tag{10}$$

where $j_n$ — electron flow, $j_n = -D_n \frac{\partial n}{\partial x} + \mu_n n E$.

Free hydrogen ions flow down to the IPB $SiO_2$-$Si_{pc}$ (gate), therefore, at $x = d$, we assume an absorbing boundary for them:

$$C_{\mathrm{H}}^+(d, t) = 0. \tag{11}$$

A voltage of $V_G$ is applied to the gate at $x = d$:

$$V(0, t) = 0, \quad V(d, t) = V_G. \tag{12}$$

The following parameters were used in the calculation. Reaction rate constant (1), $k_S = \sigma_n V_{th}$, where $\sigma_n$ — electron capture cross section at $P_b$H-centers, $V_{th}$ — thermal velocity of electrons ($V_{th} = 10^7$ cm/s). The dependence of the electron capture cross section on the field strength was taken into account [17]:

$$\sigma_n(E) = \sigma_{n0}(1 + 8.7 \cdot 10^{-17} E^{2.865})^{-1} \text{ by } E > 7 \cdot 10^5 \text{ V/cm}, \tag{13}$$

where $\sigma_{n0}$ — electron capture cross section in weak fields ($\sigma_{n0} = 1.6 \cdot 10^{-12}\,\text{cm}^2$ [17]). The values of the remaining parameters for the dispersive transport of hydrogen ions in $SiO_2$ were taken from those previously defined in [18]: $N_S^0 = 6 \cdot 10^{22}\,\text{cm}^{-3}$, $E_{S1} = 0.65\,\text{eV}$, $E_{Sk} = 0.98\,\text{eV}$, $E_{SS} = 0.07\,\text{eV}$. The variable parameter of the model is the initial density of passivated $P_b$H-centers at the anode $Q_{P_b\text{H}}$.

## 3. Model calculation

System of equations (5)−(7) with initial conditions (8) and (9), the boundary conditions (10)−(12), taking into account (13), was solved numerically using an implicit difference scheme.

Figure 1 shows the depth distribution of the concentration of free hydrogen ions (curves *1*−*3*) and hydrogen ions in localized states (curves *1'*−*3'*) at different breakdown voltages at the gate. As can be seen from the figure, the concentrations of free hydrogen ions and hydrogen ions in localized states decrease from the anode (at $x = 0$) to the cathode (at $x = d$). With the dispersion mechanism of transport, the concentration of hydrogen in localized states exceeds the concentration of free hydrogen ions.

The space charge produced by free and localized hydrogen ions affects the distribution of the electric field strength (Figure 2, curves *1*−*3*), leading to a deviation from the initial homogeneous field $E_0 = V_G/d$ (Figure 2, curves *1'*−*3'*). Moreover, the field strength decreases near the anode and increases towards the cathode. An increase of the field strength at the cathode results in an increase of the current of tunneling injection of electrons from the cathode. This causes an increase of the rate of release of hydrogen ions from the anode, which in turn increases the concentration of hydrogen ions and the field strength near

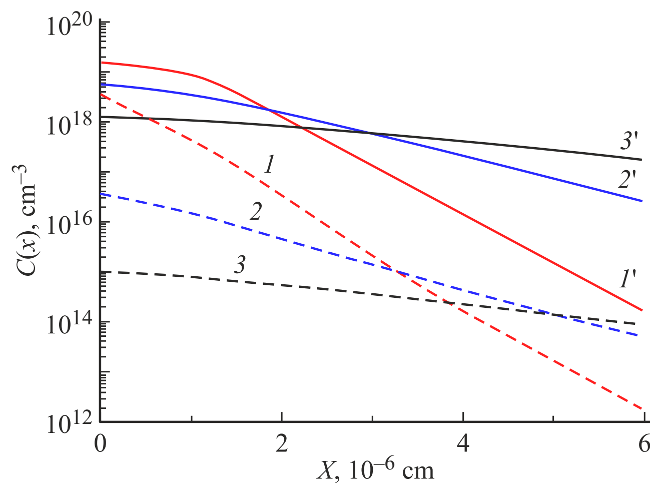



**Figure 1.** Depth distribution of the concentration of free hydrogen ions (*1*−*3*) and hydrogen ions in localized states (*1'*−*3'*). Breakdown voltage, V: *1, 1'* — 66.0; *2, 2'* — 58.3; *3, 3'* — 52.4. Breakdown delay time, s: *1, 1'* — 1; *2, 2'* — 10; *3, 3'* — 100. ($Q_{P_b\text{H}} = 8 \cdot 10^{14}\,\text{cm}^{-2}$).

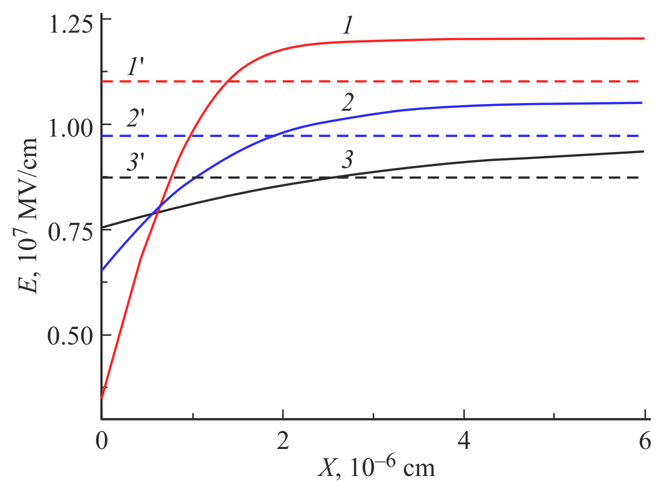



**Figure 2.** Depth distribution of electric field strength (*1*−*3*) and the initial field (*1'*−*3'*). Breakdown voltage, V: *1, 1'* — 66.0; *2, 2'* — 58.3; *3, 3'* — 52.4. Breakdown delay time, s: *1, 1'* — 1; *2, 2'* — 10; *3, 3'* — 100. ($Q_{P_b\text{H}} = 8 \cdot 10^{14}\,\text{cm}^{-2}$).

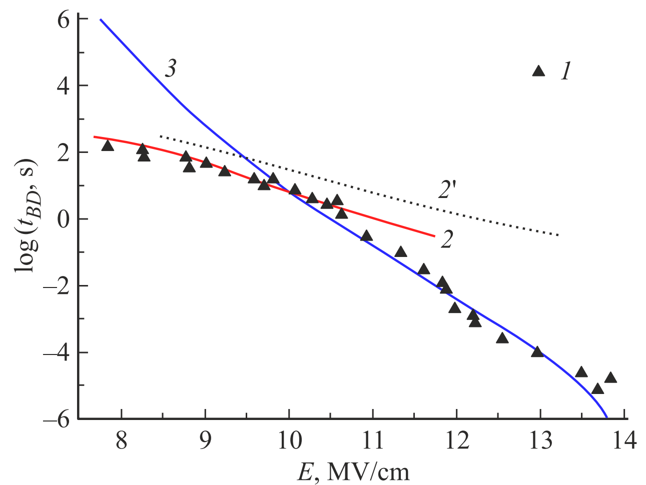



**Figure 3.** The dependence of the breakdown delay time on the field strength: *1* — experiment [19], *2* — calculation using this model with $Q_{P_b\text{H}}$, cm$^{-2}$: *2* — $8 \cdot 10^{14}$, *2* — $1 \cdot 10^{14}$; *3* — calculation using the ADI model [10] with $Q_T^0 = 5 \cdot 10^{12}\,\text{cm}^{-2}$. ($d = 60\,\text{nm}$, $T = 300\,\text{K}$).

the cathode. This positive feedback leads to a sharp increase in current and a hard breakdown of the MOS structure. The breakdown delay time is determined by the accumulation time of hydrogen ions at the anode of the MOS structure and its dispersion transport to the cathode.

Calculations based on the model were compared with the experimental dependence of the breakdown delay time $t_{BD}$ on the electric field strength from the work [19] (icons *1* in Figure 3). A silicon dioxide with a thickness of $d = 60\,\text{nm}$, obtained by thermal oxidation of silicon in dry oxygen at a temperature of 1050°C was a gate insulator in the MOS structures studied in [19]. The calculated dependencies are shown by lines in Figure 3 (curves *2, 2'* and *3*).

A 10-fold increase of the injection current was selected as the breakdown criterion. As can be seen from the figure, the dependence calculated by the mechanism of anode release of hydrogen with a density of $P_b$H-centers of $Q_{P_b\mathrm{H}} = 8 \cdot 10^{14}\,\mathrm{cm}^{-2}$ (curve *2*) satisfactorily describes experimental data at electric field $E$ less than $\sim 10$ MV/cm and breakdown delay times $t_{BD}$ of over $\sim 10$ s. Breakdown delay times increase with a lower density of $P_b$H-centers $Q_{P_b\mathrm{H}} = 1 \cdot 10^{14}\,\mathrm{cm}^{-2}$ (curve *2′*).

The experimental dependence becomes steeper with a higher electric field strength higher than $\sim 10$ MV/cm and breakdown delay times less than $\sim 10$ s. This steeper section is described by the quantitative $1/E$ breakdown model developed earlier using the ADI mechanism [15] with an exponential distribution of hole traps near the cathode with an integral concentration $Q_T^0 = 5 \cdot 10^{12}\,\mathrm{cm}^{-2}$ (curve *3*). Thus, the breakdown delay times at $E < 10$ MV/cm are significantly less than expected according the $1/E$ ADI model with a high concentration of hydrogen in the MOS structure.

It should be noted that a space charge is produced by free and localized hydrogen ions in the described mechanism of anode hydrogen release. It does not require the presence of hole traps near the cathode, as in the ADI mechanism. There is some symmetry in MOS structures with a polysilicon gate with respect to the presence of $P_b$H-centers on both IPBs $SiO_2$-Si (substrate) and $SiO_2$-$Si_{pc}$ (gate). Therefore, it is possible to expect a weak effect of polarity and the presence of traps with the breakdown voltage. Such an absence of dependence of the breakdown voltage of MOS structures on the polarity of the gate voltage, as well as on the magnitude and sign of the charge trapped on hole and electronic traps after ionizing irradiation, was observed in work [20], which supports the breakdown of MOS structures by the mechanism of anode release of hydrogen.

## 4. Conclusion

A quantitative model of breakdown of MOS structures with a relatively thick (10–100 nm) gate insulator is proposed based on the anode hydrogen release mechanism with IPB Si-$SiO_2$, in which the breakdown delay time is determined by the accumulation of hydrogen ions at the anode and its dispersion transport to the cathode. It is shown that the model of anode hydrogen release with a high concentration of hydrogen in MOS structures and fields less than $\sim 10$ MV/cm satisfactorily describes experimental breakdown delay times which are significantly lower than expected in the $1/E$ model. The breakdown delay times are satisfactorily described by the $1/E$ model of anode hole injection in case of higher field strengths.

### Conflict of interest

The author declares that he has no conflict of interest.

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