

Porous silicon formation and electropolishing

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Electrochemical etching of silicon in hydrofluoric acid containing electrolytes leads to pore formation for low and to electropolishing for high applied current. The transition between pore formation and polishing is accompanied by a change of the valence of the electrochemical dissolution reaction. The local etching rate at the interface between the semiconductor and the electrolyte is determined by the local current density. We model the transport of reactants and reaction products and thus the current density in both, the semiconductor and the electrolyte. Basic features of the chemical reaction at the interface are summarized in the law of mass-action-type boundary conditions for the transport equations at the interface. We investigate the linear stability of a planar and flat interface. Upon increasing the current density the stability flips either through a change of the valence of the dissolution reaction or by a nonlinear boundary condition at the interface.

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I. INTRODUCTION

Porous silicon was discovered in the 1950s trying to electropolish silicon in hydrofluoric acid [1,2]. For low current densities and high electrolyte concentrations, silicon is not electropolished but pores are formed. Increasing the current density over a threshold value, which decreases with the electrolyte concentration, results in electropolishing. In the beginning of the 1990s visible luminescence at room temperature was discovered [3,4]. The possibility to produce optoelectronic devices out of porous silicon started enormous research activity. Meanwhile many applications for porous silicon are in development. Most of these applications are based on the morphology of porous silicon; for a review see [5].

Porous silicon is formed by anodic dissolution of silicon in hydrofluoric acid. The silicon surface is in contact with the electrolyte, usually in a Teflon cell. Through the external potential an electric current is maintained across the cell and flows from the semiconductor to the acid. Defect electrons (i.e., holes) from the semiconductor and HF (or F^- ions) from the electrolyte combine at the fluid-semiconductor interface and dissolve silicon through an electrochemical reaction. The morphology of the unsolved silicon depends on the current. In the electropolishing phase the silicon surface is etched layer by layer and remains essentially flat, whereas in the porous silicon phase many holes are formed of a size ranging from a few nanometers to microns. Porosities of over 95% relative to crystalline silicon can be reached.

Despite its importance, there is little theoretical understanding of how porous silicon is formed; for a review see [6]. Even the basic issue why there is a transition from porous silicon formation to electropolishing is unresolved. The reasons are rather obvious, when one compares with other pattern formation processes like dendrites, viscous fingering, and colloidal aggregation. As in these systems, we have to understand the dynamics of a moving interface, here between a semiconductor and an acid. At the interface silicon is dis-

solved through an electrochemical reaction. Thus in contrast to the better understood systems mentioned above, we have to consider the transport of several species in the presence of an electric field. Moreover, since the species feedback into the electrical field and react with each other, the transport equations become nonlinear.

One approach to model the dissolution process is by a stochastic growth model, i.e. growth of the fluid into the semiconductor; see, for example, [7,8]. These models are inspired by the diffusion limited aggregation (DLA) model. While, in principle, such a model is on the atomic scale, because of numerical limitations in practice, larger spatial units are used. By suitable adjustments of model parameters structures qualitatively similar to porous silicon can be produced, but the quantitative connection of model parameters to physical parameters is lost and, in some cases, the coarsening introduces a new length scale into the system that obscures the physics.

A second approach, starting at much larger length scales, is to use a continuum description for both the motion of the interface and the ionic and electronic transport; see, e.g., [9–12]. These models include a depletion or passivation layer at the interface in a phenomenological way and assume an *ad hoc* surface tension to stabilize against small perturbations and to provide a length scale that can be compared with the pore formation. However, surface tension can only affect length scales of the order of the micropore diameter, i.e., nanometers. The above-mentioned models are not valid on these small scales since the mean free path, quantum effects, and the electrical double layer in the electrolyte would have to be taken into account.

We will use here also a description through continuum equations, but take care to model the actual chemistry and kinetics at the interface and the physical transport mechanisms. This results in a somewhat complicated set of evolution equations and we have to be satisfied with the more modest goal to understand whether continuum equations in general are able to predict the transition from electropolish-

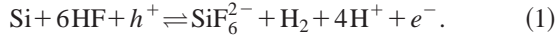
ing to pore formation. As a benchmark for the transition we use the dispersion relation as obtained from a linear stability analysis of the flat interface moving at a constant velocity. If the dispersion switches from unstable to stable, we interpret this as the transition from pore formation to polishing. Of course, if the continuum equations contain the information of the pore structure at all, it will not be unraveled in such a stability analysis.

In Sec. II we discuss the full nonlinear transport equations and their boundary conditions at the interface. We derive a simplified transport model that covers essential features of electrochemical etching of semiconductors and calculate the stability of the dissolution front in linear order in Sec. III. Our results are summarized in Sec. IV.

II. MODELING ELECTROCHEMICAL ETCHING

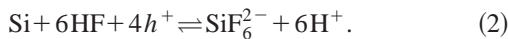
A. Electrochemistry

While anodizing silicon in hydrofluoric acid, silicon is dissolved in an electrochemical reaction. The detailed reaction mechanism is still a topic of actual research. However, during pore formation hydrogen evolution is observed whereas no hydrogen is formed during electropolishing. The valence ν of the chemical reaction (the number of unit charges needed to pass through the interface to dissolve one silicon atom) differs in both cases. During pore formation the dissolution steps for a single silicon atom add up to [13]



For each Si atom two positive charges are needed and the valence is $\nu=2$. To be more detailed, a defect electron (i.e., hole) h^+ is consumed and an electron is injected into the semiconductor. Two more charges are required to change the oxidation state of Si from 0 in the crystal to $4+$ in the SiF_6^{2-} ion in the solution. They originate from the reduction of the H atoms into two HF molecules, which leads to the production of H_2 . In the electrolyte only neutral molecules are consumed and a double negatively charged ion and four positively charged ions diffuse into the bulk, so their sum is just two positive charges.

For electropolishing the sum reaction is [14]



Since four holes are consumed the valence is $\nu=4$. All charges needed to oxidize the silicon atom are delivered by the electrical current and there is no hydrogen formation.

In both cases, pore formation and electropolishing, the local silicon dissolution rate is proportional to the local electrical current density component normal to the interface, denoted by \mathbf{j}_\perp . Thus the local interface velocity \mathbf{w} is

$$\mathbf{w} = -F\mathbf{j}_\perp , \quad (3)$$

where F is the volume of silicon per unit area dissolved by a unit charge. This number is inversely proportional to the valence ν of the chemical reaction. The valence doubles as the current density is increased over the threshold value for electropolishing [14].

B. Transport equations

The local current density is determined by the transport of reactants and reaction products in the semiconductor and the electrolyte as well as by the reaction kinetics. Modeling the transport and the interface reaction depends strongly on the considered length scale. In n -doped silicon, the pore spacing is typically some microns whereas in p -silicon nanometer sized pores are formed.

The shorter the considered length scale the more detailed the model has to be. The mean free path of charge carriers in the semiconductor is of the order of some 10 nm. Transport on this length scale can be described by Boltzmann equations, but their nonlocality makes them difficult to analyze [15].

On the nanometer scale, quantum effects start to play a role [4] and the electrical double layer at the interface in the electrolyte, i.e., the Helmholtz layer, has to be taken into account [16]. At this level, details about the electrochemical reaction pathway have to be fed into electronic structure calculations to determine the boundary conditions. Such detailed knowledge is not available and the presence of an electrolyte makes the calculations even more complicated.

To avoid these difficulties we restrict our model to length scales, large as compared to the mean free path in the semiconductor, i.e., larger than 100 nm. Then, the transport in the semiconductor and in the electrolyte can be described by drift and diffusion, i.e., by Nernst-Planck equations. The current density of electrons, \mathbf{j}_n , and holes, \mathbf{j}_p , is given by

$$\mathbf{j}_n = eD_n \nabla n + e^2 \mu_n n \mathbf{E}, \quad (4)$$

$$\mathbf{j}_p = -eD_p \nabla p + e^2 \mu_p p \mathbf{E},$$

where $D_{n/p}$ is the diffusion constant, $\mu_{n/p}$ the mobility, e the elementary charge, and \mathbf{E} the electric field. The electron and hole concentrations n and p determine the local charge density and thus the electric field via the Poisson equation

$$\nabla \cdot \mathbf{E} = \frac{e}{\epsilon_{\text{Si}}} (p - n + N), \quad (5)$$

with N the density of ionized dopant atoms and ϵ_{Si} the dielectric constant of silicon. For p -doped silicon, N is negative and for n -doped silicon is positive. Since the electric field is determined by the charge carrier concentration, the products $n\mathbf{E}$ and $p\mathbf{E}$ in Eq. (4) represent nonlinearities. Another nonlinearity appears due to production and recombination of electron hole pairs in the continuity equation

$$\nabla \cdot \mathbf{j}_n = \frac{e}{\tau} \frac{pn - p_{\text{eq}}n_{\text{eq}}}{p_{\text{eq}} + n_{\text{eq}}} = -\nabla \cdot \mathbf{j}_p , \quad (6)$$

where τ is the lifetime of the charge carriers and n_{eq} and p_{eq} are the equilibrium electron and hole concentration, respectively [17]. We make the quasistatic approximation neglecting the time derivative of the concentration fields. This is justified if the relaxation time for any field involved in the dissolution process is much faster than the interface movement. The electrical charge is conserved due to

$\nabla \cdot \mathbf{j} = \nabla \cdot (\mathbf{j}_n + \mathbf{j}_p) = 0$. The source term in Eq. (6) is derived from a law of mass action for the recombination reaction $e^- + h^+ \rightleftharpoons 0$.

If convection is negligible, the transport of molecules and ions in the electrolyte can be described analogously. HF, H_2 , H^+ , and SiF_6^{2-} have to be considered as well as fluoride F^- and OH^- . For each component X a Nernst-Planck equation gives the particle current density, denoted by \mathbf{i}_X (in contrast to the electric current density \mathbf{j}),

$$\mathbf{i}_X = -D_X \nabla C_X + q_X \mu_X C_X \mathbf{E}, \quad (7)$$

with the particle's charge q_X . The reactions $\text{HF} \rightleftharpoons \text{H}^+ + \text{F}^-$ and $\text{H}_2\text{O} \rightleftharpoons \text{H}^+ + \text{OH}^-$ have to be taken into account in source terms for the continuity equations of the corresponding current densities

$$\begin{aligned} \nabla \cdot \mathbf{i}_{\text{OH}^-} &= \frac{1}{\tau_{\text{H}_2\text{O}}} \frac{C_{\text{OH}^-} C_{\text{H}^+} - K_w}{C_{\text{H}_2\text{O}}^2}, \\ \nabla \cdot \mathbf{i}_{\text{H}^+} &= -\frac{1}{\tau_{\text{H}_2\text{O}}} \frac{C_{\text{OH}^-} C_{\text{H}^+} - K_w}{C_{\text{H}_2\text{O}}^2} - \frac{1}{\tau_{\text{HF}}} \frac{\frac{C_{\text{F}^-} C_{\text{H}^+}}{C_{\text{HF}}} - K_{\text{HF}}}{C_{\text{H}_2\text{O}}}, \\ \nabla \cdot \mathbf{i}_{\text{F}^-} &= \frac{1}{\tau_{\text{HF}}} \frac{\frac{C_{\text{F}^-} C_{\text{H}^+}}{C_{\text{HF}}} - K_{\text{HF}}}{C_{\text{H}_2\text{O}}}. \end{aligned} \quad (8)$$

The equilibrium constants for the water dissociation and the HF hydration are $K_w = 10^{-14} \text{ mol}^2/\ell^2$ and $K_{\text{HF}} = 3.5 \times 10^{-4} \text{ mol}/\ell$ [19]. In Eq. (8) the water concentration, considered as a natural constant of unit mol/ℓ , has been added to correct the units [18]. In the electrolyte the Poisson equation is

$$\nabla \cdot \mathbf{E} = \frac{e}{\epsilon_{\text{Ele}}} (C_{\text{H}^+} - C_{\text{F}^-} - C_{\text{OH}^-} - 2C_{\text{SiF}_6^{2-}}), \quad (9)$$

with the electrolyte's dielectric constant ϵ_{Ele} . As in the semiconductor, the law of mass action-type source terms and the coupling of the ion concentrations to the electric field represent nonlinearities that make the transport equations considerably more complicated as compared to equations used to describe directed solidification or viscous fingering for example [20]. Moreover, especially in the description of the transport in the electrolyte, there are poorly understood features. First of all, there are many other ions in the electrolyte that do not take part in the dissolution reaction directly but affect the electric field and the transport properties. Second, during pore formation, silicon enters the solution as HSiF_3 and reacts to SiF_6^{2-} in the solution [13]. The reaction rate for this process is not known and it is possible that a considerable amount of HSiF_3 is present near the interface in the solution. Third, hydrogen bubble evolution is not modeled as well as convection. Nevertheless, we propose to proceed with the nonlinear transport Eqs. (4)–(9).

C. Boundary conditions

At the interface between the semiconductor and the electrolyte, the dissolution reaction Eqs. (1) and (2) have to be taken into account. In both equations, the electric current density component normal to the interface (denoted by the subscript \perp) is given by the difference of the forward and backward reaction rate. In a law of mass action type approximation, these rates are given by the concentration product of the reactants and the reaction products, respectively. Thus for the pore formation reaction we obtain

$$j_{\perp} = -\Gamma_{\text{pore}} (C_{\text{HF}}^6 p - \eta_{\text{pore}} C_{\text{SiF}_6^{2-}} C_{\text{H}_2} C_{\text{H}^+}^4 n), \quad (10)$$

with the reaction rate Γ_{pore} . The parameter η_{pore} is a measure for the equilibrium concentration product for this reaction. The current density is taken positive for currents flowing from the electrolyte into the semiconductor. For reaction Eq. (2) we obtain correspondingly

$$j_{\perp} = -\Gamma_{\text{polish}} (C_{\text{HF}}^6 p^4 - \eta_{\text{polish}} C_{\text{SiF}_6^{2-}} C_{\text{H}^+}^6). \quad (11)$$

In both cases, the concentration of crystalline silicon is a constant summarized in the parameters Γ and η . Surface tension could be accounted for by a curvature dependence of η but cannot play a role at the length scales discussed here. Obviously, these boundary conditions are highly nonlinear. The particle current density components normal to the interface represent the stoichiometry of the corresponding chemical reaction. In case of Eq. (1) this is

$$\begin{aligned} 4i_{\text{HF}\perp} &= 6i_{\text{H}^+\perp}, \\ j_{p\perp} &= j_{n\perp}, \\ \frac{1}{e} j_{p\perp} &= i_{\text{H}_2\perp}, \\ \frac{4}{e} j_{p\perp} &= i_{\text{H}^+\perp}, \\ \frac{1}{e} j_{p\perp} &= i_{\text{SiF}_6^{2-}\perp}, \end{aligned} \quad (12)$$

and for Eq. (2)

$$\begin{aligned} i_{\text{HF}\perp} &= i_{\text{H}^+\perp}, \\ \frac{1}{e} j_{p\perp} &= 4i_{\text{SiF}_6^{2-}\perp}, \\ \frac{6}{e} j_{p\perp} &= 4i_{\text{H}^+\perp}. \end{aligned} \quad (13)$$

Thus the current densities of all species taking part in the reaction are determined by fixing the current density of one of them. The normal current density component of species that do not take part in the dissolution reaction is zero.

The inner Helmholtz layer in the electrolyte is not described by the ion transport equations. This layer has a very

high capacity as compared to the diffuse part of the electrical double layer in the electrolyte and the depletion layer in the semiconductor [21]. For this reason, the main potential drop across the interface occurs in the depletion layer in the semiconductor. Thus the electrical potential V ($\mathbf{E} = -\nabla V$) is continuous at the interface in a first approximation. For the electric field boundary conditions as known from electrostatics are used, i.e., the tangential component of \mathbf{E} and the normal component of $\epsilon\mathbf{E}$ are continuous across the interface.

We do not specify the boundary conditions at the cathode or at the backside of the wafer, since no experimental evidence is reported for an influence of the cathode or the wafer backside on the dissolution process. Outside the depletion layer the semiconductor is electrically neutral and can be treated as an Ohmic conductor. The electron and hole concentrations have equilibrium values. In the electrolyte, there is more variety. Due to the consumption of reactants and the accumulation of reaction products, the composition of the electrolyte changes in time. However, usually the electrolyte is stirred. In a large container, this means, that in a certain distance from the anode, the electrolyte is homogeneous, approximately in equilibrium, and has a composition that hardly changes in time. Thus, a reasonable boundary condition for the model equations is to fix the concentration of the electrolyte components at a certain distance from the interface to the equilibrium values. This distance depends strongly on stirring and the current density and must remain as a free parameter. Such kind of boundary condition is a very crude approximation, since convection certainly plays a role even in the diffusion layer, i.e., the region near the interface where the electrolyte is not homogeneous due to the applied current. To include convection in the model is in principle possible. On the scale of the pores convection should not play a role because of the high viscosity of hydrofluoric acid.

The model described in this section should be reasonably close to the physics and chemistry of the etching process on length scales, large compared to the mean free path in the semiconductor. We have to deal with nonlinear transport equations and boundary conditions. However, the two cases, i.e., pore formation and electropolishing, are actually treated as two separate models. One would like to have a model that decides itself which reaction pathway (i.e., which law of mass action boundary condition) to take, depending on concentrations or current densities at the interface. Combining the two boundary conditions Eq. (10) and Eq. (11) to

$$j_{\perp} = -\Gamma_{\text{pore}}(C_{\text{HF}}^6 p - \eta_{\text{pore}} C_{\text{SiF}_6} C_{\text{H}_2} C_{\text{H}^+}^4 n) - \Gamma_{\text{polish}}(C_{\text{HF}}^6 p^4 - \eta_{\text{polish}} C_{\text{SiF}_6} C_{\text{H}^+}^6) \quad (14)$$

gives the correct normal current density. But the stoichiometry equations (12) and (13) have to be included, too. For that one needs to know the local fraction of silicon atoms that are dissolved by the pore reaction (1) and the polishing reaction (2), respectively.

Beside this constraint, analyzing the above developed model (analytically or numerically) would be a really demanding venture. The parameter space is large and even

though many parameters have a direct physical interpretation, experimental values are not available to fix them.

Our goal is to study the transition from pore formation to electropolishing, in particular to investigate the mechanism that can lead to such a transition. Therefore we study a simplified model that captures the key features of the above description of electrochemical dissolution of silicon, namely the interplay of more than one field determining the interface motion, a change of valence of the dissolution reaction, and law of mass-action-type boundary condition.

III. LINEAR STABILITY ANALYSIS

A. Simplified model

1. Model equations

To have a tractable model and to gain some experience we have to simplify and consider only one field, Ψ_E , in the electrolyte and one field, Ψ_S , in the semiconductor. These fields could be either the concentrations of one of the species in the electrochemical reaction, or the electrical potential, or a linear combination of fields as, e.g., the total amount of fluor per unit volume, which is the sum $C_{\text{F}^-} + C_{\text{HF}}$. For simplicity, we will work with concentration fields in the following. To account for the interaction between the various fields we include source terms in the continuity equations that drive the fields to their equilibrium values Ψ_E^{eq} and Ψ_S^{eq} in the electrolyte and the semiconductor, respectively. We assume only diffusive transport to keep the transport equations linear, which allows the stability analysis of a planar interface to be performed analytically. Nonlinear transport equations would lead to linearized equations for a flat and planar interface with nonconstant coefficients. The particle current densities in the electrolyte and the semiconductor, \mathbf{i}_E and \mathbf{i}_S , respectively, are assumed to be given by

$$\mathbf{i}_E = -D_E \nabla \Psi_E \quad \text{and} \quad \mathbf{i}_S = -D_S \nabla \Psi_S, \quad (15)$$

with the diffusion constants D_E and D_S . The continuity equations are then

$$\nabla \cdot \mathbf{i}_{E/S} = -D_{E/S} \nabla^2 \Psi_{E/S} = -\frac{1}{\tau_{E/S}} (\Psi_{E/S} - \Psi_{E/S}^{\text{eq}}), \quad (16)$$

with the time constants τ_E and τ_S for the electrolyte and the semiconductor, respectively [23].

At the moving interface $\mathcal{I} = \{(x, y, z) | z = h(x, y, t)\}$ we assume a law of mass-action-type boundary condition for the reaction

$$\Psi_E + \Psi_S \rightleftharpoons 0, \quad (17)$$

similar to Eq. (10) or (11). The setup is illustrated in Fig. 1. Since we want to perform a linear stability analysis of a flat and planar interface the restriction to single valued interfaces is no real limitation for our analysis. Another choice of the interface reaction would be $\Psi_E \rightleftharpoons \Psi_S$, leading to linear law of mass-type boundary conditions, see [22]. This type of boundary conditions does not lead to the desired properties. The law of mass action for Eq. (17) is

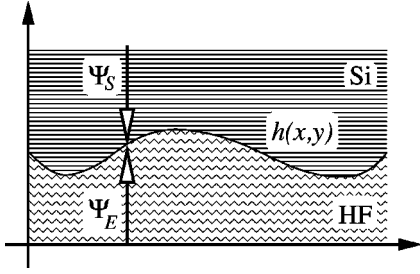


FIG. 1. Sketch of the simplified model. The semiconductor is above the interface $h(x,y)$ and the electrolyte below. Particles move to the interface from both sides and react with each other, dissolving the semiconductor.

$$i_{S\perp}|_{\mathcal{I}} = -\Gamma(\Psi_S \Psi_E|_{\mathcal{I}} - \eta) \quad (18)$$

and the stoichiometry is represented by

$$i_{S\perp}|_{\mathcal{I}} = -i_{E\perp}|_{\mathcal{I}}. \quad (19)$$

At some distance d_E and d_S from the interface \mathcal{I} , either the current density $\mathbf{i}_{E/S}$ or the field $\Psi_{E/S}$ can be fixed. However, at least at one side the field has to be fixed to eliminate all gauge freedom. We will fix the current density in the semiconductor and the field in the electrolyte, i.e., $i_{S\perp}|_{z=d_S} = I$ and $\Psi_E|_{z=-d_E} = \Psi_{d_E}$. The normal velocity \mathbf{w} of the interface is given by the normal current density

$$\mathbf{w} = -F i_{S\perp}|_{\mathcal{I}}. \quad (20)$$

With the choice of sign in the above equation and interface reaction (17) the particle current in the semiconductor has to flow to the interface to dissolve the silicon. This means that Ψ_S has to be the hole concentration.

A change in the valence of the dissolution reaction can then be modeled by a current dependent $F(i_{S\perp})$, which is inversely proportional to the valence $\nu \propto 1/F$, i.e., the number of particles $\Psi_{E/S}$ needed to dissolve a certain amount of semiconductor material. Geometric considerations lead to the growth rate of the height function $h(x,y;t)$

$$\dot{h}(x,y;t) = -F(i_{S\perp}) \begin{pmatrix} -\nabla h \\ 1 \end{pmatrix} \cdot \mathbf{i}_S|_{\mathcal{I}}, \quad (21)$$

where \dot{h} denotes the time derivative of h .

2. Linearized theory

For a flat and planar interface $h_0(t)$, the transport equations (16) become ordinary linear differential equations with constant coefficients in the independent variable z . The solutions, which can be obtained analytically, depend on the boundary conditions at $z=d_E$ and $z=d_S$ and will be discussed later. They are linear combinations of exponentials or, in the limiting case $\tau_{E/S} \rightarrow \infty$, affine functions of z .

Now we assume a small perturbation $\delta h(x,y;t)$ of a certain wavelength $\lambda = 2\pi/k$ of the interface and expand the fields (and correspondingly the current densities) up to first order in δh ,

$$\Psi_{E/S} = \Psi_{E/S}^0 + \delta \Psi_{E/S} + O(\delta h^2), \quad (22)$$

$$\mathbf{i}_{E/S} = \mathbf{i}_{E/S}^0 + \delta \mathbf{i}_{E/S} + O(\delta h^2). \quad (23)$$

From Eq. (21) the time evolution of the perturbation can be derived

$$\delta \dot{h} = -F(i_{S\perp}^0) (\delta h i_{S\perp}' + \delta i_{S\perp}) \underbrace{\left(1 + i_{S\perp}^0 \frac{d \ln F}{d i_{S\perp}} \right)}_{(*)} \bigg|_{\mathcal{I}}, \quad (24)$$

with the prime abbreviating the derivative with respect to z . The last term $(*)$ is independent of the shape of the perturbation δh . In terms of the valence ν it can be written as

$$(*) = \left(1 - i_{S\perp}^0 \frac{d \ln \nu}{d i_{S\perp}} \right) \bigg|_{i_{S\perp}^0}. \quad (25)$$

The growth speed of the perturbation δh is thus proportional to δh and Eq. (24) can be written as $\delta \dot{h} = \omega(k) \delta h$ with the dispersion relation $\omega(k)$. Perturbations with $\omega(k) > 0$ will grow exponentially and are called unstable, whereas modes with $\omega(k) < 0$ are damped and stable.

From the continuity equations (16) it follows

$$-D_{E/S}(\delta \Psi_{E/S}'' - k^2 \delta \Psi_{E/S}) = -\frac{1}{\tau_{E/S}} \delta \Psi_E, \quad (26)$$

by comparing powers of δh . The first order terms in the boundary condition Eqs. (18) and (19) for the perturbed fields $\delta \Psi_{E/S}$ are

$$\begin{aligned} (\delta i_{S\perp} + \delta h i_{S\perp}')|_{\mathcal{I}} &= -\Gamma((\Psi_S^0 + \Psi_S^{\text{eq}})(\delta \Psi_E + \delta h \Psi_E') \\ &\quad + (\Psi_E^0 + \Psi_E^{\text{eq}})(\delta \Psi_S + \delta h \Psi_S'))|_{\mathcal{I}}, \end{aligned} \quad (27)$$

$$(\delta i_{S\perp} + \delta h i_{S\perp}')|_{\mathcal{I}} = -(\delta i_{E\perp} + \delta h i_{E\perp}')|_{\mathcal{I}}. \quad (28)$$

At the lines $z=d_E$ and $z=d_S$ the fields satisfy Dirichlet boundary conditions.

B. Change of valence

Independent of the solution of the first order equation (26), the third term $(*)$ in the right-hand side of the time evolution equation (24) changes sign with the current density $i_{S\perp}^0|_{\mathcal{I}}$ passing through the interface if F (or the valence ν) varies strongly enough. A change of sign of this term changes the sign of $\omega(k)$ for all k , making stable modes unstable and vice versa. A similar mechanism has been proposed to explain the stability of the macropore front [24].

A sharp change of the valence of the electrochemical dissolution reaction from 2 to 4 electrons per Si atom at the critical current density for electropolishing has been found experimentally. Estimating the valence change from ([14], p. 39, Fig. 3.8) leads to $i_{S\perp}^0 (d \ln \nu / d i_{S\perp}) \approx 1.18$, i.e., enough to change the sign of $\omega(k)$.

This change of sign leads only to a stabilization of the interface if there have been no stable modes for lower current

densities, since these would become unstable. Moreover, our analysis cannot explain, why the interface remains stable for high current densities, i.e., for electropolishing, where the valence does not change anymore.

C. Transport and boundary conditions

The linearized interface growth model as described in Sec. III A can in principle be solved analytically for all types of boundary conditions far away from the interface. Among the many possibilities we discuss some instructive limiting cases and infer the general behavior from them. In this section we assume for simplicity that F , and thus the valence ν , is independent of the current density.

1. Infinite lifetime—double Laplacian growth

The simplest case is the limit of infinite lifetime $\tau_{E/S} \rightarrow \infty$. Both fields, Ψ_E and Ψ_S , solve the Laplace equation and this simplified model is a straight forward extension of the well studied Laplacian growth model [20]. The solutions for the planar interface are then

$$\begin{aligned}\Psi_S^0 &= -\frac{I}{D_S}z + \frac{D_E(-I + \Gamma\eta)}{\Gamma(Id_E + D_E\Psi_{d_E})}, \\ \Psi_E^0 &= \frac{I}{D_E}(z + d_E) + \Psi_{d_E}.\end{aligned}\quad (29)$$

After solving the first order equations (26) one obtains for the dispersion relation

$$\omega(k) = \frac{FIk \left(\Psi_E^0(0) - \frac{D_S}{D_E} \Psi_S^0(0) \right)}{\Psi_E^0(0) \coth kd_S + \frac{D_S}{D_E} \Psi_S^0(0) \tanh kd_E + \frac{D_S}{\Gamma} k}.\quad (30)$$

For small k , the sign of $\omega(k)$ is basically determined by the ratio of the diffusivities and the current direction and goes quadratically to zero

$$\omega(k) \sim FI \left(\frac{D_S \Psi_S^0(0)}{D_E \Psi_E^0(0)} - 1 \right) d_E k^2 + O(k^4).\quad (31)$$

In the limit of $d_E \rightarrow \infty$ the dispersion relation goes linearly to zero for $k \rightarrow 0$ with the same prefactor as above (i.e., substitute $d_E k^2$ by k).

For large k , the dispersion relation saturates at

$$\omega(k) \sim FI \Gamma \left(\frac{D_S \Psi_S^0(0)}{D_E \Psi_E^0(0)} - 1 \right) \frac{\Psi_E^0(0)}{D_S} + O\left(\frac{1}{k}\right).\quad (32)$$

Again the term $[D_S \Psi_S^0(0)/D_E \Psi_E^0(0) - 1]$ determines the sign. For $D_E \gg D_S$ the dispersion relation is positive for all k but changes sign as $D_E \ll D_S$. In other words, the interface is unstable if the front propagates into the medium with the much lower diffusion constant. The ratio of diffusion constants at which the sign changes is determined by the other

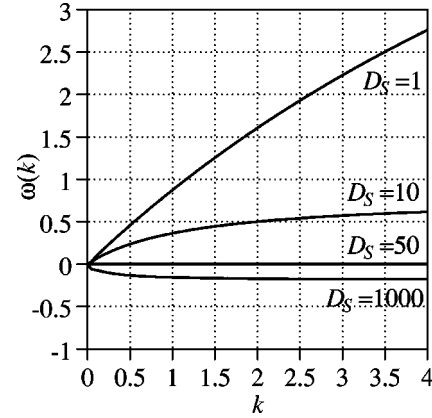


FIG. 2. Dispersion relation in case of infinite lifetime and for several values of D_S . Note the sign change at $D_S=50$. The other parameters are set to $\Gamma=1$, $D_E=1$, $d_E=10$, $d_S=20$, $\eta=1$, $I=-1$, and $\Psi_{d_E}=20$.

parameters, e.g., by $D_E/D_S=1/50$ in the example in Fig. 2. The reason for the dependence of the stability on the diffusion constant is the following. Reactants from the semiconductor (e.g., holes) reach the pore tips first. The diffusive transport in the semiconductor thus destabilizes the interface. On the other hand, the reactants in the electrolyte reach the pore walls easier than the tips and thus stabilize the interface. If the diffusion in the semiconductor is much slower than in the electrolyte, then the growth speed is solely determined by the transport in the semiconductor and the interface is unstable. This is the standard DLA scenario [20]. In the opposite case, the transport in the electrolyte determines the local dissolution rate and the interface is linearly stable. This anti-DLA limit has been studied in [25].

The term $[D_S \Psi_S^0(0)/D_E \Psi_E^0(0) - 1]$ also has two zeros as a function of I since the numerator is a quadratic polynomial in I . For $D_E \gg D_S$ and a small negative I the dispersion relation is positive for all k and changes sign at the first zero I_1 . Figure 3 illustrates this property of $\omega(k)$. This means that the law of mass action boundary conditions provide a mecha-

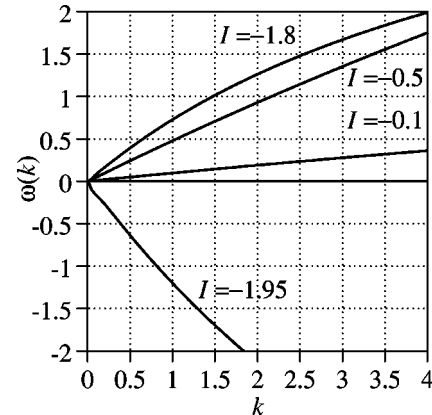


FIG. 3. Dispersion relation in case of infinite lifetime and for various current densities. Note the sign change between $I=-1.8$ and $I=-1.95$. The other parameters are $\Gamma=1$, $D_E=1$, $D_S=0.5$, $d_E=10$, $d_S=20$, $\eta=1$, and $\Psi_{d_E}=20$.

nism to stabilize an interface simply by changing the current density. The second zero I_2 is smaller than $I_0 = -D_E \Psi_{d_E}/d_E$ where $\Psi_E^0(0)$ changes sign. This leads to an unphysical pole in the dispersion relation. Since we interpret the fields $\Psi_{E/S}$ as concentrations, $\Psi_E^0(0)$ has to be positive.

The finite distances $d_{E/S}$ have basically the effect that they provide an infrared cutoff changing the dispersion relation from linearly to quadratically for $k \rightarrow 0$ (besides changing the numerical values of $\Psi_{E/S}^0$). Therefore we set $d_E \rightarrow \infty$ for the discussion of the model with finite lifetimes in the electrolyte.

2. Helmholtz equation in the electrolyte

To study the effect of a finite lifetime for the diffusing species, we take τ_E finite while keeping τ_S infinite. The choice is motivated by the high background ion concentra-

tions in the electrolyte that provide a buffer/reservoir for particles. Since we set $d_E \rightarrow \infty$, equilibrium is the only choice for the boundary condition in the electrolyte far away from the interface, i.e., $\Psi_E \rightarrow \Psi_E^{\text{eq}}$ for $z \rightarrow -\infty$. The solution for the flat interface is then

$$\Psi_S^0(z) = -\frac{I}{D_S}z + \frac{\eta - \frac{I}{\Gamma}}{\frac{I}{D_E \kappa_E} + D_E \kappa_E \Psi_E^{\text{eq}}},$$

$$\Psi_E^0(z) = \frac{I}{D_E \kappa_E} e^{\kappa_E z} + \Psi_E^{\text{eq}}, \quad (33)$$

where $\kappa_E = 1/\sqrt{D_E \tau_E}$ is the reciprocal diffusion length. The dispersion relation for this case is

$$\omega(k) = -FIk \frac{\Gamma \left(\frac{I}{\kappa_E} + \Psi_E^{\text{eq}} \right) \sqrt{\kappa_E^2 + k^2} - D_S D_E \frac{\Gamma \eta - I}{\frac{I}{\kappa_E} + \Psi_E^{\text{eq}}} (\sqrt{\kappa_E^2 + k^2} - \kappa_E)}{\left[D_E D_S k + \Gamma \left(\frac{I}{\kappa_E} + \Psi_E^{\text{eq}} \right) \coth kd \right] \sqrt{\kappa_E^2 + k^2} + D_S \frac{\Gamma \eta - I}{\frac{I}{\kappa_E} + \Psi_E^{\text{eq}}} k}. \quad (34)$$

For small k , the sign of the dispersion relation is determined by the sign of the current density I ,

$$\omega(k) \sim -FI d_S k^2. \quad (35)$$

For $d_S \rightarrow \infty$, $\omega(k)$ goes linearly to zero with the same prefactor (i.e., substitute $d_S k^2$ by k).

The dispersion relation has a limit for $k \rightarrow \infty$, which is a nonlinear function of the current density I

$$\omega(k) \sim -FI \frac{\Gamma I^2 + D_S \kappa_E (D_S \kappa_E + 2\Gamma \Psi_E^{\text{eq}}) I + D_S \Gamma \kappa_E^2 (D_S \Psi_E^{\text{eq}2} - D_S \eta)}{D_S D_S \kappa_E (I + D_E \kappa_E \Psi_E^{\text{eq}})} + O\left(\frac{1}{k}\right). \quad (36)$$

The sign of this limiting value changes with the current density in the same way as the sign of the dispersion relation in the previous section. The difference here is, that the sign for small values of k is independently fixed by the sign of I . For $I < 0$, i.e., in the case of dissolution of the semiconductor, the dispersion relation is positive for small k and positive or negative for large k . The change in the stability of small wavelength modes is illustrated in Fig. 4.

The reason why the sign of the dispersion relation for small k is given by the current density I only is, that in this limit the electrolyte does not influence the stability of the interface. The diffusion length $1/\kappa_E$ is a cutoff for the wavelength up to which the electrolyte can stabilize the interface. Longer wavelength perturbations are controlled only by the semiconductor.

3. Finite lifetime in semiconductor and electrolyte

The findings in the above section lead to the conjecture that the stability of long wavelength perturbations is deter-

mined by the medium with the longer diffusion length. To verify this we assume a semi-infinite electrolyte and semiconductor to keep formulas simple. With this type of equation and boundary condition it is no longer possible to fix the current density I but by changing the ratio of $\Psi_E^{\text{eq}}/\Psi_S^{\text{eq}}$ the current through the interface can be controlled indirectly. The solutions for the flat interface are then

$$\Psi_S^0(z) = B e^{-\kappa_S z} + \Psi_S^{\text{eq}},$$

$$\Psi_E^0(z) = \frac{D_S}{D_E \kappa_E} B e^{\kappa_E z} + \Psi_E^{\text{eq}}, \quad (37)$$

where B is the positive root of

$$0 = \Gamma D_S \kappa_S B^2 + [\Gamma (D_S \kappa_S \Psi_S^{\text{eq}} + D_E \kappa_E \Psi_E^{\text{eq}}) + D_S D_E \kappa_S \kappa_E] B + \Gamma D_E \kappa_E (\Psi_S^{\text{eq}} \Psi_E^{\text{eq}} - \eta). \quad (38)$$

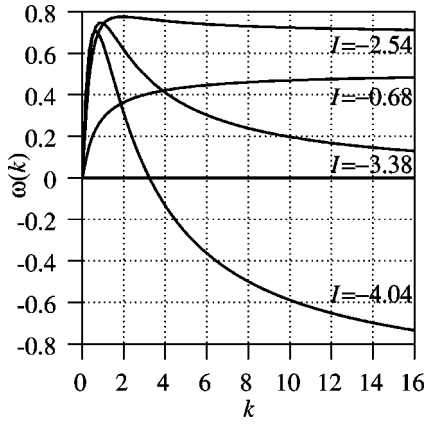


FIG. 4. The dispersion relation in case of finite lifetime in the electrolyte and infinite lifetime in the semiconductor for various current densities. The sign of $\omega(k)$ for $k \rightarrow \infty$ changes at $I = -3.38$. The other parameters are $F=1$, $\Gamma=1$, $D_E=10$, $D_S=1$, $d_S=10$, $\eta=1$, $\kappa_E=1$, and $\Psi_E^{\text{eq}}=1$.

We write the dispersion relation in terms of the zeroth order fields and current density at the interface and we use the abbreviation $\mathcal{K}_{E/S} = \sqrt{\kappa_{E/S}^2 + k^2}$

$$\omega(k) = -F\Gamma i_{S\perp}^0(0) \times \frac{D_E \mathcal{K}_E (\mathcal{K}_S - \kappa_S) \Psi_E^0(0) - D_S \mathcal{K}_S (\mathcal{K}_E - \kappa_E) \Psi_S^0(0)}{\Gamma [D_E \mathcal{K}_E \Psi_E^0(0) + D_S \mathcal{K}_S \Psi_S^0(0)] + D_E D_S \mathcal{K}_E \mathcal{K}_S}. \quad (39)$$

For long wavelength, the dispersion relation is

$$\omega(k) \sim -F\Gamma i_{S\perp}^0(0) \times \frac{1}{2\kappa_E \kappa_S} [\kappa_E^2 \Psi_E^0(0) - \kappa_S^2 \Psi_S^0(0)] \times \frac{1}{\Gamma [D_E \kappa_E \Psi_E^0(0) + D_S \kappa_S \Psi_S^0(0)] + D_E D_S \kappa_E \kappa_S} k^2 + O(k^4). \quad (40)$$

If the semiconductor has a much longer diffusion length (i.e., $\kappa_S \ll \kappa_E$), the leading term is stable and it is unstable if the diffusion length in the electrolyte is much longer. The value of the ratio κ_E/κ_S at which the sign changes depends on the values of the other parameters. In the example of Fig. 5 the critical ratio is $\kappa_E/\kappa_S = 1.83$.

For large $k \rightarrow \infty$, the dispersion relation has a limit

$$\omega(k) = -F\Gamma i_{S\perp}^0(0) \left(\frac{\Psi_E^0(0)}{D_S} - \frac{\Psi_S^0(0)}{D_E} \right) + O\left(\frac{1}{k}\right). \quad (41)$$

Like in the previous sections, the stability of small scale perturbations is determined by the ratio of diffusion constants. They are stable if the diffusivity in the semiconductor is much larger than in the electrolyte and unstable if $D_S \ll D_E$. For the parameters in Fig. 6, the critical ratio of diffusion constants is $D_S/D_E = 0.90/2.0$.

With the boundary conditions discussed in this section, the current through the interface is controlled by the ratio

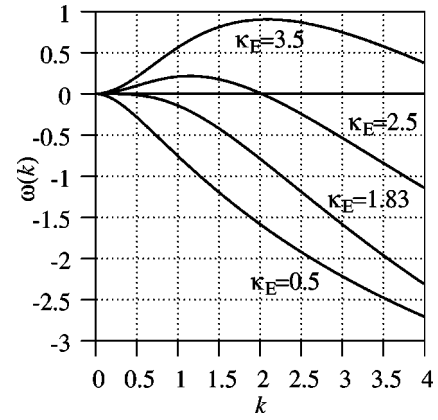


FIG. 5. Dispersion relation in case of finite lifetime in semiconductor and electrolyte for different values of κ_E . Note that the sign of $\omega(k)$ for small k changes at $\kappa_E = 1.83$ but not the sign for large k . The other parameters are $F=1$, $\Gamma=1$, $D_E=2$, $D_S=1$, $\kappa_S=1$, $\epsilon=1$, $\Psi_E^{\text{eq}}=2$, and $\Psi_S^{\text{eq}}=10$.

$\Psi_S^{\text{eq}}/\Psi_E^{\text{eq}}$. Like in the last section, short wavelength perturbations can be stabilized by increasing the current over a certain threshold, i.e., increasing the ratio of $\Psi_S^{\text{eq}}/\Psi_E^{\text{eq}}$. In the example in Fig. 7 this value is $8.58/2.0$.

Reducing the ratio $\Psi_S^{\text{eq}}/\Psi_E^{\text{eq}}$ to the equilibrium value, i.e., for $\Psi_S^{\text{eq}}\Psi_E^{\text{eq}} = \eta$, the zero order current density $i_{S\perp}^0(0)$ vanishes and the interface becomes marginally stable. Below that value semiconductor material is deposited and $\omega(k)$ changes sign for all k . In Fig. 8 the growth rate of the flat interface \dot{h}_0 and the limit of the dispersion relation for large k are plotted against Ψ_S^{eq} for the same parameters as in Fig. 7, showing the two sign changes of $\omega(k \rightarrow \infty)$. The sign change at $\Psi_S^{\text{eq}} = 0.5$ is accompanied by a reversion of the growth direction whereas at $\Psi_S^{\text{eq}} = 8.58$ only the stability properties change.

IV. DISCUSSION

Motivated by the discussion of electrochemical etching of silicon in HF solutions we developed a simplified model in

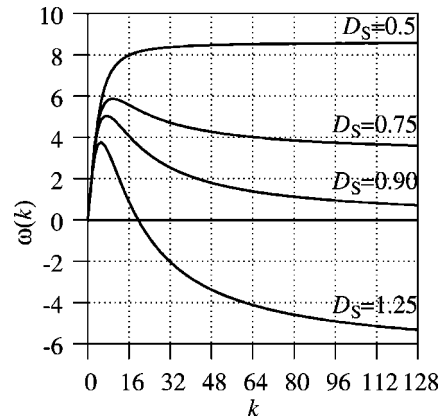


FIG. 6. Dispersion relation in case of finite lifetime in semiconductor and electrolyte for different values of D_S . Note that the limit of $\omega(k)$ for $k \rightarrow \infty$ changes sign at $D_S = 0.90$. The other parameters are $F=1$, $\Gamma=1$, $D_E=2$, $\kappa_S=1$, $\kappa_E=10$, $\epsilon=1$, $\Psi_E^{\text{eq}}=2$, and $\Psi_S^{\text{eq}}=10$.

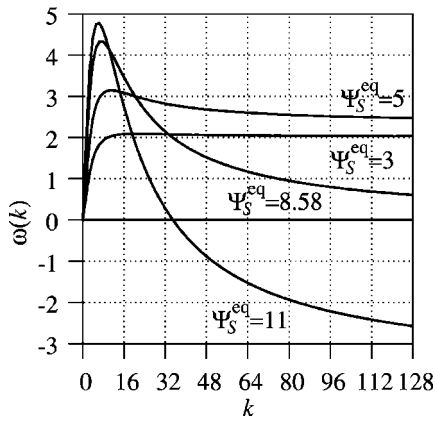


FIG. 7. Dispersion relation in case of finite lifetime in semiconductor and electrolyte for different values of Ψ_S^{eq} , i.e., different current densities. Note that $\omega(k)$ for $k \ll 1$ remains positive. The other parameters are $F=1$, $\Gamma=1$, $D_E=2$, $D_S=1$, $\kappa_S=1$, $\kappa_E=10$, $\epsilon=1$, and $\Psi_E^{\text{eq}}=2$.

Sec. III. This model has more than one field determining the interface motion, includes a change of valence in the dissolution reaction, has nonlinear law of mass-action-type boundary condition, and includes a background reservoir for the reactants. The transport in both, the semiconductor and the electrolyte is diffusive. We performed a linear stability analysis of a flat interface for three limiting cases of a simplified model and found two mechanisms that can cause a stabilization of the interface at high current densities.

First, a change of valence of the dissolution reaction with current density can stabilize the interface. The sign of the dispersion relation flips when the change of the valence with current density is large enough, namely, if $i_{S\perp}^0(0)[d \ln \nu(i)/di]_{i_{S\perp}^0(0)} > 1$. This is true in general, independent of the transport mechanisms in the semiconductor and electrolyte, the number of reactants and reaction products, and the type of boundary conditions. For electrochemical etching of silicon in hydrofluoric acid the change of valence at the transition from pore formation at low current densities to electropolishing at high current densities is large enough. The stability of the interface at high current densities, after the valence settled at the electropolishing value, cannot be explained with this mechanism. However, there an oxide layer is formed that has to be dissolved chemically. At low current densities, when pores are formed, silicon is dissolved directly. This oxide layer reduces the diffusivity in the electrolyte considerably, leading to a stabilization of the interface. Our model shows, that an interface propagating into a much more diffusive medium is stable (given that the reactants are the rate limiting species, not the reaction products).

A second mechanism that at least partially stabilizes an interface are nonlinear law of mass-action-type boundary conditions. While the sign of the dispersion relation $\omega(k)$ at small k is determined by the ratio of diffusion lengths in semiconductor and electrolyte, the value at high k as a func-

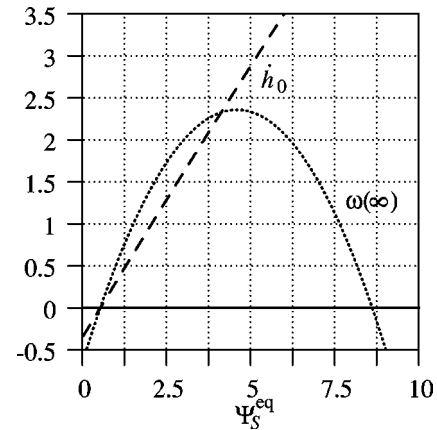


FIG. 8. The growth velocity of the flat interface (dashed line) and the limiting value of $\omega(k)$ for $k \rightarrow \infty$ (dotted line) are plotted against Ψ_S^{eq} . The growth velocity and $\omega(\infty)$ change sign at $\Psi_S^{\text{eq}} = 0.5$. At $\Psi_S^{\text{eq}} = 8.58$ only $\omega(\infty)$ changes sign. The other parameters are the same as in Fig. 7.

tion of the current density can change sign from positive to negative. The sign of $\omega(k)$ for small k is determined by the ratio of diffusion lengths. The side with the larger diffusion length $1/\kappa$, i.e., the larger lifetime τ , determines the stability of long wavelength perturbations. If the diffusion length of the semiconductor is much longer than the one of the electrolyte, the interface is unstable for long wavelengths. If the diffusion length in the electrolyte is much larger, $\omega(k)$ is negative for small k .

Our analysis shows, that a continuum model of surface growth, i.e., a moving boundary value problem for partial differential equations, can have a transition from linear stability to instability with increasing current density. The two mechanisms discussed here are particularly interesting from a theoretical point of view in that the effects of nonlinearities in the model equations can still be handled analytically through a linear stability analysis.

It is questionable whether the transition from porous silicon formation to electropolishing can be described by one of the discussed mechanisms alone. The valence of the dissolution reaction of silicon does change in this transition. But the implementation in the model of Sec. III A is oversimplified. A more realistic model would include two alternative reaction pathways for the species at the interface in the spirit of Eq. (14). The analysis in this paper should be regarded as a stepping stone for the development of such models.

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- [1] A. Ulhir, *Bell Syst. Tech. J.* **35**, 333 (1956).
- [2] D. R. Turner, *J. Electrochem. Soc.* **105**, 401 (1958).
- [3] L. T. Canham, *Appl. Phys. Lett.* **57**, 1046 (1990).
- [4] V. Lehmann and U. Gösele, *Appl. Phys. Lett.* **58**, 856 (1991).
- [5] V. Parkhutik, *Solid-State Electron.* **43**, 1121 (1999).
- [6] G. C. John and V. A. Singh, *Phys. Rep.* **263**, 93 (1995).
- [7] J. Erlebacher, K. Sieradzki, and P. C. Searson, *J. Appl. Phys.* **76**, 182 (1994).
- [8] R. L. Smith and S. D. Collins, *Phys. Rev. A* **39**, 5409 (1989).
- [9] V. P. Parkuthik *et al.*, *Appl. Phys. Lett.* **62**, 366 (1993).
- [10] Y. Kang and J. Jorné, *J. Electrochem. Soc.* **140**, 2258 (1993).
- [11] A. Valance, *Phys. Rev. B* **55**, 9706 (1997).
- [12] H. Föll, J. Carstensen, M. Christophersen, and G. Hasse, *Phys. Status Solidi A* **182**, 7 (2000).
- [13] H. Gerischer, P. Allongue, and V. Costa Kieling, *Ber. Bunsenges. Phys. Chem.* **97**, 753 (1993).
- [14] V. Lehmann, Ph.D. thesis, Friedrich-Alexander-Universität, Erlangen-Nürnberg, 1988.
- [15] C. Cercignani, *The Boltzmann Equation and Its Applications*, Applied Mathematical Science Vol. 67 (Springer, New York, 1988).
- [16] J. O'M. Bockris and A. K. N. Reddy, *Modern Electrochemistry* (Plenum Press, New York, 1970), Vols. 1 and 2.
- [17] H. K. Henisch, *Semiconductor Contacts* (Clarendon, Oxford, 1985).
- [18] In the literature on physical chemistry, K_w and K_{HF} are dimensionless, since not the concentrations but the dimensionless activity defines the equilibrium constants. However, in linear approximation, the chemical activity is proportional to the concentration.
- [19] P. W. Atkins, *Physical Chemistry*, 3rd ed. (Oxford University Press, Oxford, 1986/1987).
- [20] P. Pelcé, in *Dynamics of Curved Fronts*, edited by P. Pelcé (Academic Press, London, 1988), Pt. I.
- [21] D. Vanmaekelbergh and P. C. Searson, *J. Electrochem. Soc.* **141**, 697 (1994).
- [22] M. Rauscher and H. Spohn, *J. Porous Mater.* **7**, 345 (2000).
- [23] If $\Psi_{E/S}$ is interpreted as the electrostatic potential V (or as $-V$), $\sqrt{D_{E/S}\tau_{E/S}}$ is the electrostatic screening length.
- [24] V. Lehmann, *J. Electrochem. Soc.* **140**, 2836 (1993).
- [25] J. Krug and P. Meakin, *Phys. Rev. Lett.* **66**, 703 (1991).