

2. State of the art

2.1. Introduction

Electrochemical etching of silicon in fluoride containing electrolytes, also named as anodization process, is a fascinating process which provides material for research for more than half a century. The first report on anodization of silicon (and germanium) was published by Uhler [78]. Further investigations of silicon anodization were performed ten years later by Memming and Schwandt [79]. The process was used firstly only as a technique to polish wafers [71, 72]. In the 1990s the process of silicon anodization got great interest of the scientific community after the publication of Canham about his discovery of photoluminescence from one of the products of the process - porous silicon [1]ⁱ. At that time other remarkable papers on silicon anodization and applications of porous silicon as a new material for photoluminescent devices, as well as adsorption material, insulating material, composition material, and sacrificial layer material for micro-electronic and micromechanical devices were published by Eddowes [81], Zhang et al. [76, 82], Lehmann et al. [32, 83–86], Lang et al. [5–7], and others [9, 12–14, 21, 27, 28, 33, 37, 38, 45, 66, 67, 87–103].

In this chapter, state of the art on theory and technology of the process is presented. An emphasis is given to the electrochemical backgrounds of the process and the role of process parameters. A short overview of other structuring techniques for semiconductor based smart systems is also presented.

2.2. Structuring techniques for semiconductor based smart systems

The history of semiconductors started in the first half of the 19th century with the discovery of first semiconductor material – silver sulfide – by

ⁱThe importance of this discovery for the scientific community is confirmed by the fact that for his discovery Canham was named as probable Nobel Prize candidate in physics by Thomson Reuters in 2012 [80].

Michael Faraday in 1833 [104]. After the discovery of the phenomenon of unilateral conduction of metal-sulfide by Karl Ferdinand Braun [105] and its practical application in the first semiconductor device – Cat’s-whisker detector – for radio wave detection [104] in the beginning of the 20th century, the next milestone of the semiconductor device technology came with the invention of the first transistor in 1947 [106], which led to the beginning of the microelectronics era of – mostly silicon based – very and ultra large scale integration (VLSI and ULSI) devices. Since then, the need for miniaturization of semiconductor devices encouraged the invention of numerous technologies for production of high-quality crystalline silicon wafers and structuring (mostly planar) of silicon and the accompanying materials.

Miniaturization technologies of microelectronics enabled also miniaturization of mechanical devices. The idea of miniaturization of mechanical systems was first pronounced by Richard Phillips Feynman in his famous lecture “There’s Plenty of Room at the Bottom” at an American Physical Society meeting in 1959. This talk is considered as a starting point of micromachining and nanotechnology [107] as well as the beginning of the era of micro- and nanoelectromechanical systems (MEMS and NEMS).

Characteristic length scale of MEMS and NEMS is considered to be in order from micrometer to few millimeters and below micrometer, respectively. Advantages of micromachining, such as reduction of costs due to batch processing and integration with electronic components on a chip, led to a rapid increase of popularity of MEMS and NEMS and based on them smart systems starting from 1980s.

At first, fabrication of MEMS devices was done with the technological processes of planar microelectronics. One of the first mass applications were accelerometers, pressure sensors, and ink-jet nozzles. Further advancements of the structuring techniques for fabrication of three-dimensional (3D) etch forms in 1990s allowed the fabrication of more complex systems. Today miniaturized mechanisms and devices can be found in many application fields.

The choice of materials for smart systems is typically limited to the materials compatible to the complementary metal-oxide-semiconductor (CMOS) technology, because this way integration of smart systems into electronic chips can be guaranteed [108]. Silicon was and remains the most popular material for smart systems due to its good mechanical properties, properties of its oxide, well-studied technological processes, and the fact that it is a second abundant material on Earth. This chapter provides an overview

of main fabrication strategies and structuring processes for silicon based MEMS and NEMS.

2.2.1. Principles and characteristics of structuring processes

Micromechanical structures are usually formed by removing/etching material in some regions of a substrate. An etching process is characterized by etch rate R_{etch} [length/time] (equal to etch front velocity v_{etch}) and etch time t_{etch} [time], which define together etch depth d_{etch} [length].

Localization of a structuring process can either be achieved by the process itself (e.g., laser beam machining) or by auxiliary masking layers working as a protection for areas which should remain after the process. In case of using protecting masking materials which provide good protection for the duration of the whole etching process, a masking material with better/higher chemical stability (low etch rate) compared to the underlying layer for the given etching process is required. Hence, the etching processes are classified according to their selectivity S for different materials. Selectivity is defined as etch rate ratio for material to be structured and masking material (s. eq. (2.1)). Selectivity defines how deep (or how long) the etch process can be run for a given thickness of the protecting mask.

$$S = \frac{R_{\text{etch (material)}}}{R_{\text{etch (mask)}}} \quad (2.1)$$

Other important issues for an etching process with a protective masking film are the adhesion of the masking film to the substrate and mechanical properties (internal stress) of the film. In case of low adhesion, the masking material can detach completely from the substrate before the etching process is finished. For example, this problem occurs during etching of silicon nitride in buffered hydrofluoric acid solution (BHF) with photoresist as a protecting mask. In this case, special adhesion promoters are applied before deposition of photoresist, and intermediate baking steps during the etch process are used in order to prevent the photoresist from detaching. Additionally, internal stress in the masking film might result in bending or breaking of the film in case of large underetching.

Etch shape during etching process is typically defined by vertical $R_{\text{etch V}}$ and lateral $R_{\text{etch L}}$ etch rates. Lateral etch rate defines underetching of a masking material. If $R_{\text{etch V}} = R_{\text{etch L}}$, etching process is called isotropic, otherwise

the process is anisotropic. Anisotropy of an etching process can be related to crystallographic orientation of a crystalline material (e.g., silicon etching in KOH or TMAH), or induced by the etching process itself (e.g., reactive ion etching, where more anisotropy can be achieved by directional electric field). Anisotropy factor A_f defines anisotropy of the process (eq. (2.2)) for simple shapes [7]. If $R_{\text{etch V}} \gg R_{\text{etch L}}$ (s. Fig. 2.1a), then $A_f \rightarrow 1$, meaning only vertical etching, as can be achieved, for example, with deep reactive ion etching (DRIE) [109]. For isotropic processes, $A_f = 0$ (s. Fig. 2.1b).

$$A_f = 1 - \frac{R_{\text{etch L}}}{R_{\text{etch V}}} \quad (2.2)$$

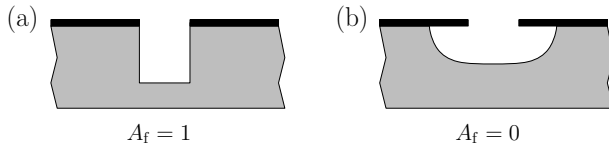


Figure 2.1.: Wafer cross-section showing (a) anisotropic and (b) isotropic etch structures.

Although for planar microelectronic devices etch shape is often not of main concern, it plays very important role in MEMS, where real 3D structures are required in order to fabricate particular mechanisms or structural elements. Anisotropic etching of silicon (e.g., DRIE) can result in vertical sidewalls, whereas isotropic (e.g., wet) etching results in spherical concave shapes. Thus the resulting shape and depth are determined by the anisotropy factor of the etch process. For conventional techniques with a fixed anisotropy factor, it is not possible to produce structures with different 3D shapes and depths in one step.

2.2.2. Fabrication strategies for smart systems

There are two main fabrication routes used for silicon-based smart systems: surface micromachining and bulk micromachining [108, 110].

Surface micromachining processes came from microelectronics technology. As the name suggests, the fabrication processes used in surface micromachining are performed on thin films on one side of a wafer. The starting point is normally a crystalline silicon wafer (substrate). Devices are

formed by many steps of deposition and subsequent structuring by etching of films on the substrate. Structuring processes in planar microelectronic technology are typically relying on sophisticated methods for transfer of two-dimensional (2D) patterns into 3D structures by lithography and subsequent etching. Whereas the lateral definition and resolution are mainly determined by the lithography as primary structuring step, the vertical dimension and shape depend on the etch process.

Examples of surface micromachined smart systems are RF capacitors [111], pressure sensors [112], angle sensors [113], and micromirror devices [114, 115]. In general, surface micromachined smart systems have limitations in depth of their structures.

In the bulk micromachining of smart systems, microelements are formed in volume of a silicon substrate. This way larger and deeper elements than in surface micromachining can be fabricated. In contrast to the surface micromachining technology, in bulk micromachining typically both sides of a wafer are processed, which makes the process less compatible to the CMOS technology. In order to overcome limitations of planar microelectronics technology and generate deep 3D cavities, several sophisticated approaches have been investigated, e.g., gray-scale lithography [116, 117] (s. also sec. 2.2.3.2) and stereo lithography [118–120]. In order to obtain reproducible etch results, it is important to have precise control of etching process parameters and/or apply special etch stop techniques [7]. One such etch stop technique which is very popular nowadays is based on the use of SOI wafers [121].

Examples of bulk micromachined smart systems are pressure sensors [122], accelerometers [123, 124], thermoelectric generators [125], tactile sensors [8], micro force sensor [126], focusing mirror device [127], and shear-stress sensor [128].

To decrease the production costs for MEMS, there is a trend in the last decade to replace silicon with cheaper materials, such as polymers. In this case, structures etched into silicon or other materials can be used as micro-molds to form plastic elements by some molding technique, such as injection molding or hot embossing [120]. A quite often used process here is the LIGA-technique (s. sec. 2.2.3.2) for high aspect ratio microsystems (HARMS), although silicon plays in this technology only a minor or no role [110, 129–136]. Another nanostructuring process based on replication is the nanoimprint process [137–139] which, however, relies on other structuring techniques for fabrication of the imprints.

2.2.3. Structuring techniques

2.2.3.1. Conventional wet and dry etch techniques

There are various conventional structuring techniques developed in micro-electronics and microsystems technologies for structuring silicon. In general, these processes can be divided in dry and wet processes.

In dry etch processes the material is removed by gaseous etchant in form of vapor or plasma. The principles of removing material are either chemical, physical or physical-chemical [7, 140]. Since the free mean path of a particle in a gas is inversely proportional to the gas pressureⁱⁱ, in general, increasing the gas pressure provides a more isotropic process.

An example of physical etching is sputter etching, where ions of chemically inert gases, such as argon, bombard the surface after being accelerated in high-frequency electric field. With this process, high anisotropy can be achieved due to directed attack of the surface by the accelerated ions. Selectivity in the process is provided by the fact that soft materials (e.g., resist) are etched slower than hard materials. The formed cavities, although showing high anisotropy, are subjected to the scattering effects, such as micro-trenching (high etch rate near the edges of cavities due to ion reflection from the cavity sidewalls), and redeposition of the removed material to the mask edges (Fig. 2.2a) [141, 142].

In chemical plasma etch processes, chemically active gases, such as the halogens F, Cl or Br [140], are used, and the processes run with chemical reaction of the radicals generated in the plasma, when they are transported to the etch site, adsorbed there, and then react with the surface atoms. Another examples of dry chemical etching are vapor-phase etch processesⁱⁱⁱ, where etchants in vapor/gas phase, e.g., HF for silicon dioxide etching or XeF₂ for silicon etching, are used [132, 143, 146–149]. The process selectivity of dry chemical etch processes is defined by the chemical reactions and the phase of the products: volatile products can move away from the reaction site without disturbing the reaction; solid products, in contrast, passivate the

ⁱⁱIn an ideal gas when the particle speed is given as Maxwell-Boltzmann distribution, the mean free path l for a given diameter of the particles d and the gas pressure p can be calculated with the formula: $l = \frac{k_b T}{\sqrt{2} \pi d^2 p}$, where k_b is the Boltzmann constant and T is the absolute temperature in Kelvin.

ⁱⁱⁱThere are also classifications of etch processes, where only plasma/discharge etch processes are meant as dry etch processes, and vapor etching is considered as a separate class [132].

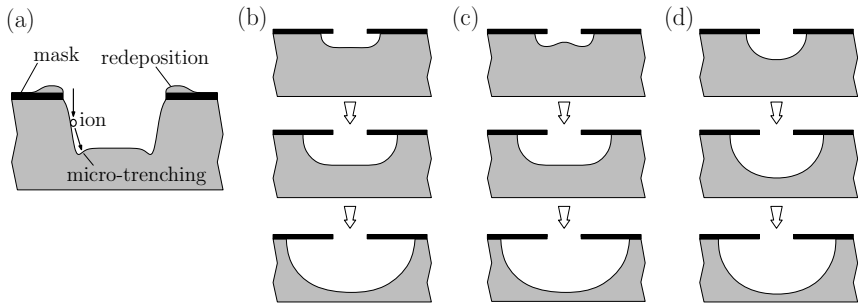


Figure 2.2.: Schematic cross-section of etch forms for (a) sputter etching with micro-trenching and material redeposition [142], (b) isotropic etching without diffusion-limitation (e.g., with slow etch rate) [143], (c) diffusion-controlled isotropic wet etching without agitation [144,145], and (d) isotropic wet etching with agitation [143].

surface, and the process might stop. The process of chemical dry etching is load-dependent, i.e., for larger exposed wafer areas slower etch rates are observed. Typically, high pressure is used, and the process results in isotropic shapes.

In physical-chemical processes (for example, reactive ion etching - RIE), the reaction is additionally activated with ion bombardment (physical action). The more physical component, the more anisotropic is the etch process. Therefore, the anisotropy of such a process can be to some extent controlled by the process parameters. During the process, at specific operation conditions the surface can get passivated by polymer layers formed from present halogens and carbons inside the reactor gases. The subsequent etching step results in vertical etching of the passivating layer and the material, leaving the vertical sidewalls passivated. This way, switching between etching and passivating steps can provide nearly anisotropic etching in the DRIE Bosch process.

In wet etch techniques, etchants in liquid phase are used. Although in many fabrication processes wet etch processes have been replaced with dry etch processes, wet etch processes are still widely used as structuring techniques for smart systems because of their advantages such as setup simplicity and low cost. An example of isotropic silicon etchant is HNA, that is a mixture of HF, nitric acid (HNO_3), and acetic acid (CH_3COOH) in water [150,151].

In this solution, silicon is first oxidized in nitric acid and subsequently etched away by hydrofluoric acid [143].

For an isotropic wet etch process, where diffusion does not control the process (due to high diffusion constants of the reactants and reaction products, or due to slow etch rates), the isotropic shape develops from a shape with flat bottom to a concave shape, when the etch depth increases over the width of the opening in the mask (s. Fig. 2.2b). With diffusion limitation, the isotropic etch process might result in pronounced etching of the structures near the edges of the mask in the beginning of the process, giving convex etch form, with later transformation of the etch form to the concave form (s. Fig. 2.2c) [144, 145]. When agitation of the etch solution, e.g., stirring, is applied to overcome diffusion limitation, concave forms from the beginning of the process can be obtained (s. Fig. 2.2d) [143]. Thus, certain etch shape control for the isotropic wet etch process can be done and has been used in the past.

Anisotropy in a wet etch process can be also caused by anisotropic properties of the material to be etched. For monocrystalline silicon, such anisotropy can be provided by its crystal lattice. Typical anisotropic silicon etchants are KOH and TMAH. These solutions show very slow etching of (111)-planes in comparison to the etch rate for (100)-planes^{iv}, resulting in well controlled V-groove shapes for (100)-oriented silicon wafers (s. Fig. 2.3a) and perpendicular (vertical) sidewalls for (110)-oriented silicon wafers (s. Fig. 2.3b) [143].

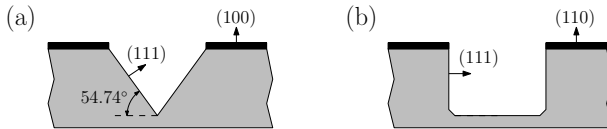


Figure 2.3.: Schematic cross-section of etch forms in anisotropic silicon etching for (a) (100)-substrate resulting in V-groove and (b) (110)-substrate resulting in vertical walls [143].

Electrochemical etching processes, as a special group of wet chemical processes, provide additional degree of control through dependence of their etch

^{iv}The etch-rate ratio $R_{\text{etch (111)}}/R_{\text{etch (100)}}$ is concentration and temperature dependent [152].

rates on charge flow. This way, for example, in anisotropic etching of silicon in alkaline solutions, the etch rate of the process can be controlled by applying anodic potentials to the silicon [153].

Silicon etching in hydrofluoric acid as a specific example of electrochemical etching processes for silicon structuring, and as main topic of this work will be covered in detail in sec. 2.6. It is worth noting that although silicon was and remains the material for most of studies of the anodization process, there are also other semiconducting and conductive materials that can be anodized, such as GaAs and other compound semiconductors [154] or metals, e.g., aluminum [155].

2.2.3.2. Micromachining methods

The conventional wet and dry etch techniques are typically applied to the full area of a wafer, therefore they provide high throughput. However, they are limited in definition of real 3D shapes. Several advanced techniques for 3D structuring at wafer-level have been developed. For example, with grayscale lithography, 3D shapes formed in photoresist by exposure with locally modulated light intensity are transferred into the underlying material during RIE process (s. Fig. 2.4) [117]. Another technique for real 3D shapes is 3D micro-stereolithography, where polymer is cured with focused UV light at very small energy, at which hardening of the polymer only occurs at the focal point, and complex 3D structures as small as several micrometers are defined [156]. In the LIGA process utilizing X-ray lithography, quasi-3D or 2.5D structures (i.e., 2D layout in x, y -plane projected to a fixed depth in z -axis) with typical feature size of $1\text{ }\mu\text{m}$ are formed in thick photoresist and transferred to another material, for example, with electroplating [110, 129–136, 138].

Besides these wafer-level processes, there is a number of micromachining techniques for local material removal, which can provide very high precision in nanoscale, however, they require processing of structures in a sequence one after another^v. Whereas well established for macrostructuring, for microstructuring such processes are mostly in the research-and-development stage. These processes can be considered as a separate class of structuring techniques. Examples of such techniques are laser beam machining (LBM),

^vBatch processing with wet microstructuring processes (e.g., micro-ECM) is also possible, to some extent, by using arrays of tool-electrodes.

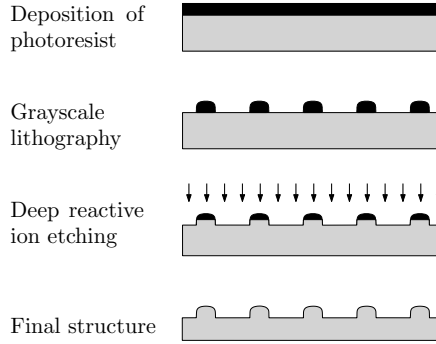


Figure 2.4.: Process flow for grayscale lithography with structure transfer process from photoresist to substrate.

electrochemical micromachining (micro-ECM), electro discharge micromachining (micro-EDM), etc.

Dry microstructuring processes are listed in Tab. 2.1. The overview of wet microstructuring processes (s. Fig. 2.5) is given in Tab. 2.2.

Conventional mechanical material processing techniques, such as drilling and milling [157], or micro ultrasound machining (USM) [138, 158], which require mechanical contact between the workpiece and a tool or abrasive particles, as well as electrochemical cutting techniques (e.g., wire electro-discharge grinding - WEDG, wire-ECDM - WECDM [159–161], wire-ECM - WECM [162]) are excluded from this overview. Excluded are also variations of the microstructuring processes for nanomachining, such as application of scanning tunneling microscope, where the tip plays the role of the tool for nano-ECM [138, 139, 163, 164].

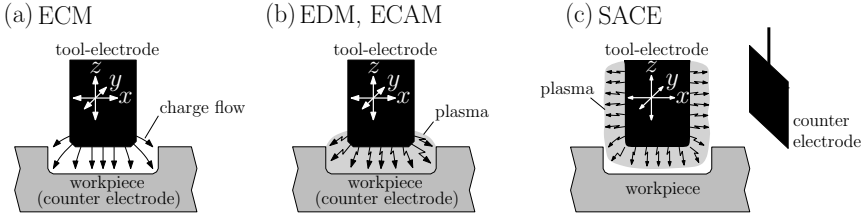


Figure 2.5.: Wet micromachining methods shown in schematic cross-section (electrolyte not shown): (a) ECM, (b) EDM or ECAM, (c) SACE.

Table 2.1.: Dry micromachining methods

Structuring method	Principle	Processed materials	Resolution	Typical applications
RAP ^a [165]	chemical	silicon, quartz, silicon nitride, silicon carbide, etc.	micrometers	optical components in glasses and ceramics
EBM ^b [138, 165, 166]	thermal vaporization via electron impact	any	5 nm	structures with very high aspect ratio, microholes, molds
FIB ^c [138, 165, 167–169]	mechanical (ion impact)	any	10 nm	MEMS, AFM tips, microtools, molds
Long-pulse-LBM and CW-LBM ^d [165, 166, 170]	photon absorption, thermal evaporation or melting	light absorbing materials	50 μm	cutting, scribing
Ultrashort-LBM ^e [138, 170–172]	evaporation through ionization	any	100 nm	microstructures, microtools

^aRAP - reactive atom plasma machining.

^bEBM - electron beam machining.

^cFIB - focused ion beam machining.

^dLong-pulse-LBM and CW-LBM - long-pulse and continuous wave laser beam machining with pulses of nanosecond and longer width.

^eUltrashort-LBM - ultrashort-pulse laser beam machining with pulses of femtosecond and shorter width.

Table 2.2.: Wet micromachining methods

Structuring method ^a	Principle	Processed materials / workpiece	Electrolyte	Working electrodes	Resolution
ECM ^b [138, 162, 163, 173–178]	electrochemical etching, anodic dissolution	(semi-)conducting materials	conductive, chemically active	tool and workpiece	0.5 μm
EDM ^c [138, 156, 163, 165, 181–194]	thermal vaporization via spark discharge plasma between the tool and workpiece	non-conducting materials with conductive carbon film formed after discharge or (semi-)conducting materials	non-conductive (hydrocarbon oils, e.g., kerosene, or deionized water)	tool and workpiece	0.5 μm
ECAM ^d [138, 195–199]	s. ECM + EDM	(semi-)conducting materials	low-resistivity deionized water	tool and workpiece	15 μm
SACE ^e [198–216]	thermal vaporization of workpiece in close vicinity to the tool, on which a plasma layer is formed by discharge between the tool and electrolyte in a surface gas layer (hydrogen and water vapor)	any material	conductive, e.g., aqueous solutions of salts	tool and electrolyte (with a counter big area electrode remotely located in the electrolyte)	10 μm

^aThe word “micro” is omitted in the names of the micromachining techniques here, because the discussed processes can be performed on both macro- and microscale.

^bECM - electrochemical machining; other variations: pulse electrochemical machining (PECM), jet electrochemical machining (JECM), laser assisted ECM, vibration/ultrasonic assisted ECM.

^cEDM - electrical discharge machining; typically (semi-)conducting materials can be structured with EDM. However, structuring of non-conductive materials have been also demonstrated [179, 180]: in this case, a carbon film on a non-conducting workpiece is formed after discharge in electrolyte (oil), and works as counter electrode for a next discharge, after which again the carbon film is formed, and the process repeats.

^dECAM - electrochemical arc machining (ECAM); other names: electrochemical discharge machining (ECDM), simultaneous ECM and EDM (SECDM). The name ECDM is also used to describe the microstructuring process SACE for non-conductive and conductive materials (s. below). In general, literature review in the field reveals lack of unified conventions on names of various wet micromachining processes.

^eSACE - spark assisted chemical engraving; other names: electrochemical spark machining (ECSM), electrochemical discharge micromachining (ECDM).

2.2.4. Conclusions

In this section, an overview of microstructuring methods, with emphasis on structure shape, has been presented. Conventional wet and dry etch

techniques provide only specific etch shapes of fixed anisotropy. From the other point, the techniques giving real 3D shapes require expensive facilities, such as micro-stereolithography or FIB, and are typically suffering from very long processing times and associated costs of final product.

Electrochemical etching of silicon in hydrofluoric acid based electrolytes can be applied as an alternative structuring method for fabrication of 3D forms in silicon, where etch profile (shape and surface quality) can be controlled with various localization techniques (electric potential, doping, light, and more) and a precision in the nanometer range. As common for wet chemical processes, silicon anodization does not require costly equipment, and can be performed at wafer-level, providing high throughput. In the next sections, this process will be described in detail.

2.3. Mass and charge transfer in silicon and electrolyte

2.3.1. Band diagram and transfer of charge and mass in bulk p-type silicon

The schematic band diagram of p-doped silicon at room temperature is shown in Fig. 2.6, where E_F is the Fermi level, E_C is the energy at the bottom of the conduction band, E_V is the energy at the top of the valence band, $E_G = E_C - E_V$ is the band gap ($E_G = 1.12$ eV for silicon at 300 K [106]), and E_A is the acceptor level^{vi}. The difference $E_A - E_V$ defines the ionization energy required to excite holes from the acceptor energy level to the valence band.

Transport of electrons and holes in silicon with concentrations n and p , respectively, can be described by Nernst-Planck equation accounting for drift and diffusion [106, 221–223]^{vii}:

$$\mathbf{j}_n = e\mu_n n\mathbf{E} + eD_n \nabla n, \quad \mathbf{j}_p = e\mu_p p\mathbf{E} - eD_p \nabla p \quad (2.3)$$

where $\mathbf{E}$ is the electric field, $\mathbf{j}$ is the current density field, e is the elementary charge, $\mu_{n/p}$ are the carrier mobilities, and $D_{n/p}$ are the diffusion constants of electrons (subscript n) and holes (subscript p).

^{vi}In the work an effort was made to write symbols according to the rules of the Le Système International d'Unités (SI) [217], International Union of Pure and Applied Chemistry (IUPAC) [218, 219] and the international standard ISO 80000-9 [220]. In some cases, conventional symbols are used, which are not SI-conform.

^{vii}These references are used through this section.

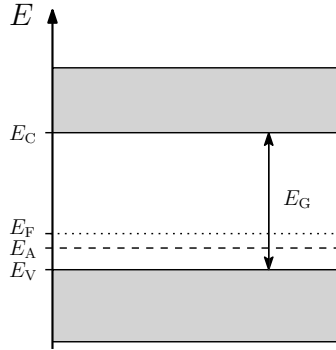


Figure 2.6.: Band diagram of p-type silicon.

At 300 K, $\mu_n = 1450 \text{ cm}^2/(\text{V}\cdot\text{s})$, $\mu_p = 500 \text{ cm}^2/(\text{V}\cdot\text{s})$, $D_n = 37.5 \text{ cm}^2/\text{s}$, and $D_p = 13 \text{ cm}^2/\text{s}$ [221].

The total current density is

$$\mathbf{j} = \mathbf{j}_n + \mathbf{j}_p \quad (2.4)$$

For non-degenerate semiconductors (i.e., for semiconductors with $E_C - E_F \gg k_b T$) the mobility of charge carriers is related to their diffusion constants according to the Einstein relation:

$$D = \left(\frac{k_b T}{e} \right) \mu \quad (2.5)$$

The conductivity σ is defined by the mobilities and the concentrations of the carriers:

$$\sigma = e\mu_n n + e\mu_p p \quad (2.6)$$

In the models of silicon anodization, transport of holes in p-type silicon substrate is often described by current density distribution, assuming that holes as major carriers almost solely provide this current density [3, 13, 29, 30, 45, 62, 96, 110, 224]. In this case, simplified description of silicon substrate as a material with isotropic conductivity defined by doping level is sufficient. For the silicon substrates with resistivity in the ranges $10\text{--}20 \Omega\text{cm}$ and $0.01\text{--}0.1 \Omega\text{cm}$ used in the models in this work, the conductivity σ_{Si} is in the ranges $5\text{--}10 \text{ S/m}$ and $10^3\text{--}10^4 \text{ S/m}$, respectively.

2.3.2. Band diagram and transfer of charge and mass in bulk electrolyte

2.3.2.1. Band diagram

An electrolyte contains reduced and oxidized species characterized with the corresponding energy levels E_{Red} and E_{Ox} reflecting the average energy levels of all individual redox species in reduced or oxidized form, respectively (Fig. 2.7). These energy levels E_{Red} and E_{Ox} are the most probable energy levels for the reduced and oxidized species, and together they determine the redox potential $E_{\text{redox}} = 0.5 \cdot (E_{\text{Red}} + E_{\text{Ox}})$, which can be considered as the effective Fermi level of electrolyte similarly to the Fermi level in semiconductors. The redox potential describes the tendency of the species to accept or give up electrons [4].

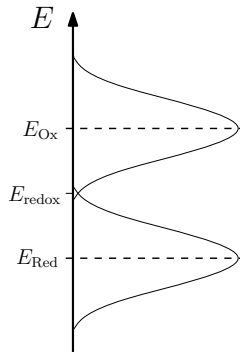


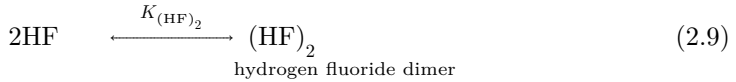
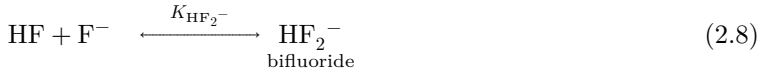
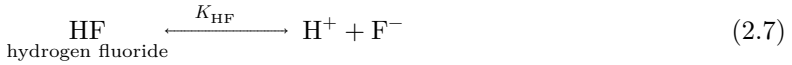
Figure 2.7.: Electron energy levels of a redox couple in electrolyte [4].

2.3.2.2. Composition of an HF-based electrolyte

Anodization of silicon is conducted in fluoride containing electrolytes, typically based on hydrofluoric acid (HF). According to Föll et al. [22], electrolytes for silicon anodization can be classified in aqueous electrolytes and organic electrolytes. The aqueous electrolytes, as the name suggests, include mixtures of HF and water in various proportions. Additionally, such electrolytes might contain ethanol, acetic acid or some other surfactants which are applied in order to reduce surface tension or to adjust pH-value or viscosity. In the organic electrolytes, mixtures of HF with organic substances

such as acetonitrile (MeCN) or dimethylsulfoxide (DMSO) are applied. This classification might be not quite obvious at first sight, however is well justified by Föll and co-authors, and both classes of electrolytes provide peculiar features distinguishing them in anodization process [22]. Most commonly used electrolytes for silicon anodization are aqueous electrolytes based on HF and water with or without addition of ethanol, and such electrolytes are meant through this report, unless otherwise stated.

Hydrofluoric acid based aqueous electrolyte is a complex system of ions and not dissociated molecules. Because HF is a weak acid, besides undissociated HF molecules, there are small amounts of HF_2^- , F^- , and $(\text{HF})_2$ species present in such electrolyte according to the following dissociation (ionization) and association reactions [2, 225–228]:



with

$$K_{\text{HF}} = \frac{a_{\text{H}^+} \cdot a_{\text{F}^-}}{a_{\text{HF}}}, \quad K_{\text{HF}_2^-} = \frac{a_{\text{HF}_2^-}}{a_{\text{HF}} \cdot a_{\text{F}^-}} \quad \text{and} \quad K_{(\text{HF})_2} = \frac{a_{(\text{HF})_2}}{a_{\text{HF}}^2} \quad (2.10)$$

where K_{HF} , $K_{\text{HF}_2^-}$, and $K_{(\text{HF})_2}$ are the equilibrium constants for the reactions^{viii}, and a is the activity of species given in subscript. The smaller the

^{viii}For a reaction in equilibrium of the form $\alpha\text{A} + \beta\text{B} \dots \xrightleftharpoons{K_{\text{eq}}} \rho\text{R} + \sigma\text{S} \dots$, the equilibrium constant is $K_{\text{eq}} = \frac{a_{\text{R}}^{\rho} \cdot a_{\text{S}}^{\sigma} \dots}{a_{\text{A}}^{\alpha} \cdot a_{\text{B}}^{\beta} \dots}$, where the symbol of the form a_{X} is the activity of a species X, which can be defined in relation to the concentration of the species X (concentration $c_{\text{mol X}}$) through the activity coefficient γ_{X} : $a_{\text{X}} = \gamma_{\text{X}} \cdot c_{\text{mol X}}$. Activity defines how much of the available species actually take part in the reactions, i.e., how close the solution behaves to the ideal solution. Since for diluted solutions activity coefficients approach 1, concentrations are often used instead of activities to find equilibrium constant. In practice values of activity coefficients are mostly unknown, and concentrations are applied also for concentrated solution [229]. Therefore, in further equations for simplicity also concentrations will be used instead of activities in this work. Dissociation constant (also called as ionization constant) is a specific type of equilibrium constant for reactions of dissociation [230].

equilibrium constants, the less amount of the reaction products is available in a solution in equilibrium.

The equilibrium constants in an electrolyte depend on the concentration of the electrolyte^{ix}, or, more exactly, on the ionic strength of the electrolyte [225, 231], however, according to Warren [226] this effect is small.

Up-to-date publications on the topic provide the following values of the equilibrium constants corrected for zero ionic strength at 25 °C: $K_{\text{HF}} = 6.71 \times 10^{-4} \text{ mol/dm}^3$, $K_{\text{HF}_2^-} = 3.861 \text{ dm}^3/\text{mol}$, and $K_{(\text{HF})_2} = 2.703 \text{ dm}^3/\text{mol}$ [2, 227]. With these constants, equilibrium concentrations of all components in a HF:water solution can be calculated (s. Appendix, sec. A.1.3.4 and sec. A.1.3.5). The dimerization reaction (2.9) is not always taken into account. However, as can be seen from the calculations in sec. A.1.3.5, this reaction changes significantly the equilibrium concentrations in the solution.

Besides the above mentioned species, a concentrated HF solution might contain other species, such as more complex polymers of HF (e.g., hexamer $(\text{HF})_6$, tetramer $(\text{HF})_4$) [2, 226] or the fluoronium ion H_2F^+ [231–234]. It is often assumed that these species are present in very small concentrations, and can therefore be neglected^x. The role of other substances added to the electrolyte in chemical reactions is also often neglected. However, ethanol, for example, can reduce dissociation of HF and decrease the activity of F^- [2, 236]. For example, $K_{\text{HF}} = 3.214 \times 10^{-5} \text{ mol/dm}^3$ and $K_{\text{HF}_2^-} = 12.882 \text{ dm}^3/\text{mol}$ for the solution with 50 m% ethanol at 25 °C and zero ionic strength [237]. The effect of the ethanol mass fraction on the equilibrium constants and calculation of the equilibrium concentrations of the components in HF:water:ethanol mixture are shown in Appendix, sec. A.1.4.4.

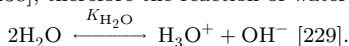
There is also water dissociation reaction in the electrolyte^{xi}:



^{ix}There are various concentration units with multiple different notations introduced in chemistry through the history of its development and for ease of calculations in certain cases. An overview of different concentration units and conversions between them used in the work are explained in Appendix, sec. A.1.

^xPolymerized species of the form $(\text{HF})_x\text{F}^-$ start playing an important role in solutions with the total F concentration above 15 mol/l [235].

^{xi}Proton H^+ after the ionization quickly connects to a molecule of water to form H_3O^+ [238], therefore the reaction of water dissociation is often written in the form



where $K_{\text{H}_2\text{O}} = 1.8 \times 10^{-16} \text{ mol/dm}^3$ at 25°C , which is very small, meaning almost no dissociation in pure water [238, 239].

Additionally, during electrochemical dissolution of silicon according to the reactions (2.29) and (2.34) which will be discussed in sec. 2.4, there is also silicon hexafluoride (hexafluorosilicate anion) SiF_6^{2-} as final stable reaction product in the electrolyte [94].

2.3.2.3. Mass and charge transfer phenomena in bulk HF-electrolyte

The transport of species X in an electrolyte by drift and diffusion, and neglecting convection can be described with the Nernst-Planck equation [240]:

$$\mathbf{i}_X = z_X \mu_X c_X \mathbf{E} - D_X \nabla c_X \quad (2.12)$$

where $\mathbf{i}_X$ is the flux, μ_X is the mobility, z_X is the charge number, D_X is the diffusion constant, and c_X is the concentration of the species X [$1/\text{m}^3$], and the current density is

$$\mathbf{j}_X = e z_X \mathbf{i}_X \quad (2.13)$$

Different values of the diffusion constants for the species in HF-based electrolytes have been reported. Monk reported $D_{\text{HF}} = 3.1 \times 10^{-5} \text{ cm}^2/\text{s}$ for the experiments of diffusion-limited etching of sacrificial silicon dioxide layers in HF-water solution at 25°C [241, 242]. J. van den Meerakker found experimentally with rotating disk electrodes $D_{\text{HF}} = 2.2 \times 10^{-5} \text{ cm}^2/\text{s}$ in HF-water-ethanol solution at 20°C [243]. Values for other species are: $D_{\text{F}^-} = 1.473 \times 10^{-5} \text{ cm}^2/\text{s}$, $D_{\text{HF}_2^-} = 2.35 \times 10^{-5} \text{ cm}^2/\text{s}$, $D_{\text{H}^+} = 9.315 \times 10^{-5} \text{ cm}^2/\text{s}$ [2], $D_{\text{OH}^-} = 5.3 \times 10^{-5} \text{ cm}^2/\text{s}$ [228]. It is important to note that the diffusion constants depend on the concentration of the components in the electrolyte [228]. For silicon hexafluoride SiF_6^{2-} , Suratwala et al. provide concentration independent diffusion constant of $5 \times 10^{-8} \text{ cm}^2/\text{s}$ “based on the values described for oils with similar viscosity” [244], which is suspiciously much smaller than typical values of diffusion constants in the order of $10^{-5} \text{ cm}^2/\text{s}$, and cannot be taken for granted. Lehmann [2] provides from [245] values of $D_{\text{SiF}_6^{2-}}$ at room temperature (RT) to be from $1.2 \times 10^{-5} \text{ cm}^2/\text{s}$ for 0.83 mol/dm^3 to $0.45 \times 10^{-5} \text{ cm}^2/\text{s}$

for 2.5 mol/dm^3 which are more trustworthy, considering that diffusion constants in a system are typically of similar magnitude.

The Einstein relation (eq. (2.5)) connecting diffusion constant of species to its mobility in thermodynamic equilibrium is also applicable for electrolytes.

Diffusion limitation of reactants to and products from the reaction site can be neglected for concentrated electrolytes (meaning high supply of the reactants) with high diffusion constants and low etch rates provided by low applied current density. Then, neglecting also convection, a simplified representation of such electrolyte as conductive media with isotropic conductivity σ_l defined by concentration of ions can be used. Hill and Sirkar provided the values of conductivity of water-based HF mixture at 18°C [246]: the conductivity increases nearly linearly with increase of HF concentration from 5.93 S/m for $4.8 \text{ m\% HF}$ to 34.11 S/m for $29.83 \text{ m\% HF}$.

2.3.3. Interface silicon-electrolyte

2.3.3.1. Band diagram and models of the silicon-electrolyte interface

When silicon with native oxide is immersed into HF-based electrolyte, the native oxide is etched, and the surface is predominantly terminated with hydrogen forming hydride Si-H or trihydride Si-H₃ for ideal (111) surface and dihydride Si-H₂ for ideal (100) surface differentiated due to the difference in the number of dangling bonds [2, 4, 35, 247]. Non-ideal silicon surface is rough on an atomic scale, therefore all three hydrides may be present, as well as other adsorbed impurities, such as metals [4].

After immersion in the electrolyte, thermodynamic equilibrium between the electrolyte and silicon is achieved when their Fermi levels become equal, i.e., $E_F = E_{\text{redox}}$ (s. Fig. 2.8) [4, 13, 87]. In this situation for p-type silicon holes will move deeper into silicon away from the electrolyte, leaving negatively charged acceptor ions, as shown in Fig. 2.8b for generated electron-hole pair. Thus, excess charge (negative) is built in the silicon near the contact to the electrolyte. This region is called space charge region (SCR). Electric field resulting due to the charge redistribution in SCR is shown by bending of the bands. Typical thickness of the SCR is in order of micrometer for moderate/low doped silicon [4].

On the electrolyte side, an ionic layer is established in order to compensate the excess charge in the semiconductor, and an interfacial electric double layer (EDL) between the silicon surface and the electrolyte is formed.

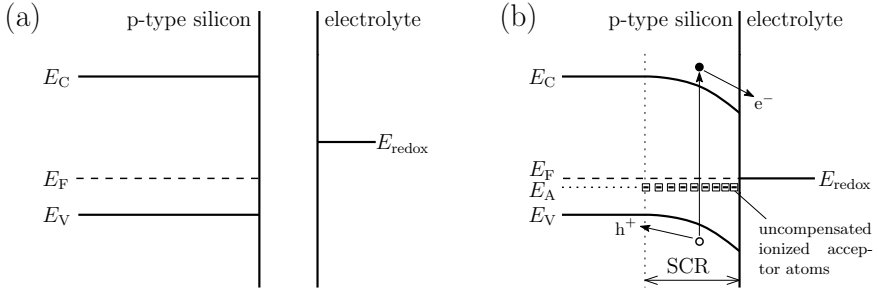


Figure 2.8.: Band diagram (a) before and (b) after the contact of p-type silicon with electrolyte.

There are various models of the ionic electric double layer at the interface solid-electrolyte [248]. In the classical Helmholtz model, the EDL is formed by layer of ions packed at the interface, forming with the solid surface two oppositely charged planes representing a capacitor separated by distance δ which is defined by radius of ions (s. Fig. 2.9a).

The Helmholtz model explains capacitance observed on the interface solid-electrolyte, but does not show any influence of the electrolyte concentration and other factors [248]. Further improvements were introduced by Frumkin, Gouy, Chapman, Stern, Grahame, Bockris, and others [248, 251]. The comprehensive model of the EDL consists of the following regions (s. Fig. 2.9b):

- The Helmholtz layer of ions attracted to the solid electrode by the excess charge in the SCR and also by the polar water (or, in general, solvent) molecules. The outer border of the Helmholtz layer at the distance δ defines the outer Helmholtz plane (OHP). The region from the OHP till the solid surface is also called the compact layer of the EDL.
- Further in the electrolyte after the compact layer lies the diffuse ionic layer (Gouy-Chapman layer) which is formed by both anions and cations under the effect of thermal motion.
- Directly on the solid surface specifically adsorbed cations and anions are located. The locus of these ions is called the inner Helmholtz plane (IHP).

The compact layer is typically few angstroms thick. Thickness of the diffuse ionic layer is strongly dependent on the concentration of the electrolyte, and

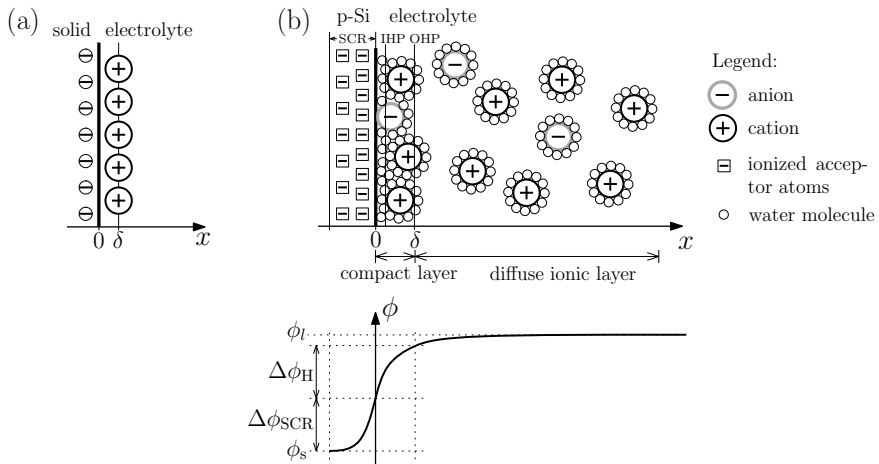


Figure 2.9.: Electric double layer models: (a) Helmholtz model for solid-electrolyte interface; (b) general electric double layer model with potential distribution ϕ for p-Si, where $\Delta\phi_{SCR}$ and $\Delta\phi_H$ are the potential drops in the SCR and the Helmholtz layer, ϕ_s and ϕ_l are the bulk potentials of the solid (silicon) and liquid (electrolyte), not in scale; increase of potential in silicon and electrolyte due to finite conductivity is not shown [88,248–250]; the legend is for the figure (b) only.

is typically below $300 \text{ \AA}$ [4,250]. For electrolytes with a high concentration ($> 0.1 \text{ M}$), the potential drop in the diffuse ionic layer can be neglected [4], thus the main potential drop on the solution side of the EDL occurs in the Helmholtz layer (s. at the bottom in Fig. 2.9b). The potential difference between the potential in the bulk solid (silicon) ϕ_s and the potential in the bulk liquid (electrolyte) ϕ_l determines the total potential drop in the EDL $U = \phi_s - \phi_l$ which is also called the Galvani potential [252].

Due to the small thickness of the EDL, the capacitance at the interface silicon-electrolyte, although smaller than for metal-electrolyte interface, is rather high (few Faradays per square centimeter [4]) and must be taken into account when working in a time-dependent power supply mode.

2.3.3.2. Polarization of silicon electrode

The electrochemical reactions of the silicon anodization involve a charge transfer between silicon and electrolyte. The silicon-HF system forms an electrolytic cell, i.e., a cell in which a non-spontaneous reaction is driven by an external source of current, in contrast to galvanic cells producing electricity as a result of spontaneous reaction occurring in them. Therefore, in order to proceed, the silicon electrode anodization reactions require the driving force provided by the surface overpotential^{xii}, and the rate of the electrode reaction and, consequently, the current density are related to the surface overpotential. On the other hand, the reaction rate is also dependent on the surface concentrations of reactants from both solid (e.g., holes in forward biased p-Si) and liquid (e.g., HF_2^- , F^- , and HF in HF-based electrolyte). Two specific cases can be distinguished with limitation of charge transfer at the interface (charge transfer controlled) or in the electrolyte (mass transfer controlled) as described below.

Control by the rate of the charge transfer - activation polarization

Excess fluoride components induced by the concentrated electrolyte at relatively low applied current density (and with sufficiently high diffusion constants for the reactants and the product) provide the process where mass transport limitation phenomena in the electrolyte can be neglected and the reactions are controlled by the rate of charge transfer. In this case, the current-voltage curve of the silicon-electrolyte junction is very similar to the current-voltage curve of the silicon-metal junction (Schottky diode) (s. Fig. 2.10) [2, 79, 81, 98].

This exponential increase of current I with increase of applied overpotential η can be described with Tafel expression which is characteristic for activation-controlled reactions [4, 248, 253]:

$$\eta = a - b \log I \quad (2.14)$$

where a is the value of polarization at the unit current and b is called the Tafel slope (s. Fig. 2.11b):

$$b = 2.303 \cdot \frac{RT}{\alpha n_e F} \quad (2.15)$$

^{xii}also called overvoltage [253]

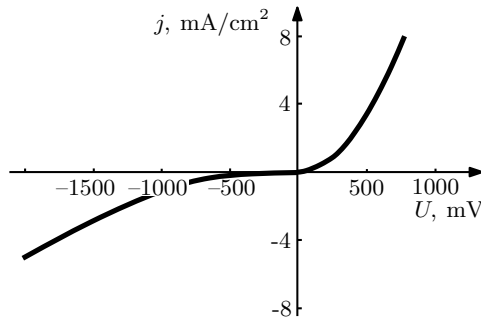


Figure 2.10.: Current density vs. electrode potential for a p-type ($1\ \Omega\text{ cm}$) silicon electrode in 10 M hydrofluoric acid electrolyte measured in the dark; reproduced from Memming and Schwandt [79] © 1966 with permission from Elsevier.

where R is the universal gas constant, α is the dimensionless charge transfer coefficient (between zero and unity), n_e is the reaction valence, and F is the Faraday constant.

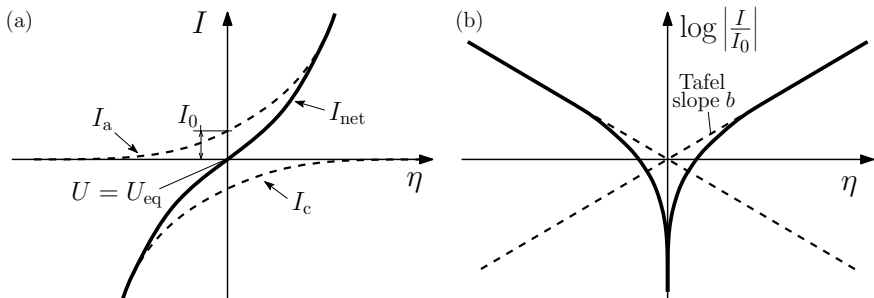


Figure 2.11.: Polarization curve for the redox process $\text{Ox} + n_e\text{e}^- \leftrightarrow \text{Red}$ in charge transfer limited mode, assuming equal concentrations of the oxidized Ox and reduced Red forms of the redox couple, and $\alpha = 0.5$; the dashed lines show the anodic I_a and cathodic I_c components: (a) in linear scale, (b) with the ordinate showing absolute values of normalized current in logarithmic scale [253].

More complicated polarization curves might have several Tafel sections, each with a specific slope. Typical values of Tafel slope b for p-Si in pore formation regime are in the range 40–110 mV/decade [4] corresponding to αn_e in the range 0.53–1.45.

In general, for a redox half-reaction $\text{Ox} + n_e e^- \leftrightarrow \text{Red}$ (s. Fig. 2.12) on an electrode with the oxidized Ox and reduced Red forms of species in the charge transfer limited mode both reactions, forward and backward^{xiii}, are running at the same time, meaning non-zero anodic and cathodic currents I_a and I_c even when the net current $I = I_a + I_c$ is equal to zero at the equilibrium potential $U = U_{\text{eq}}$ (s. Fig. 2.11a) [253]. The equilibrium potential depends on the surface concentrations (i.e., the concentrations near the electrode) $c_{\text{Ox S}}$ and $c_{\text{Red S}}$ of the oxidized Ox and reduced Red species according to the Nernst equation [253]:

$$U_{\text{eq}} = U_{\text{eq}}^0 + 2.303 \cdot \frac{RT}{n_e F} \cdot \log \frac{c_{\text{Ox S}}}{c_{\text{Red S}}} \quad (2.16)$$

where U_{eq}^0 is the standard electrode potential, which is the electrode potential at the unit concentrations.

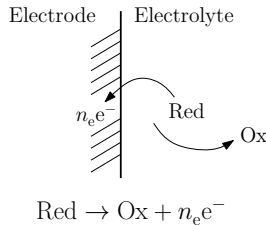


Figure 2.12.: Oxidation half-reaction on an electrode.

The potential difference of the solid-liquid half-cell is given by $U = \phi_s - \phi_l$. In terms of the overpotential

$$\eta = U - U_{\text{eq}} = \phi_s - \phi_l - U_{\text{eq}} \quad (2.17)$$

^{xiii}In the text here *forward* for a reaction or current means the same as *anodic*, and *backward* means the same as *cathodic* according to Wang [253]. Another notation can be found in the literature, e.g., in Bagotsky's book [248]: *forward* and *backward* denote there the partial reactions and the corresponding partial currents as in the Wang's book [253]; *anodic* and *cathodic* describe, in contrast, net properties of the redox system (overpotential or net current) in the corresponding quadrants of the current-voltage plot.

and for the equilibrium case $U = U_{\text{eq}} = \phi_{\text{s eq}} - \phi_{\text{l eq}}$ this means $\eta = 0$. The absolute magnitude of I_{a} and I_{c} at $U = U_{\text{eq}}$ defines the exchange current $I_0 = |I_{\text{a}}|_{U=U_{\text{eq}}} = |I_{\text{c}}|_{U=U_{\text{eq}}}$ for the electrode area A , and the exchange current density $j_0 = I_0/A$. The exchange current in the silicon anodization process is very sensitive to trace amounts of metals such as Cu or Au in the electrolyte, which can give change of I_0 in order of 10^3 [4]. For low-doped p-type silicon with resistivity 1–10 $\Omega \text{ cm}$, $j_0 = 7 \times 10^{-6} \text{ A/cm}^2$ was reported [98].

In terms of the exchange current I_0 , the constant a in eq. (2.14) is given as:

$$a = 2.303 \cdot \frac{RT}{\alpha n_e F} \log I_0 \quad (2.18)$$

The exchange current density j_0 is proportional to the standard heterogeneous rate constant k° [cm/s] for the particular reaction of the reactants with the electrode material and the concentration of the species [253, 254]:

$$j_0 = n_e F k^\circ c_{\text{Ox V}}^{(1-\alpha)} c_{\text{Red V}}^\alpha \quad (2.19)$$

where $c_{\text{Ox V}}$ and $c_{\text{Red V}}$ are the bulk concentration of the oxidized Ox and reduced Red forms of the redox couple. The formula is valid for first-order reactions.

The charge transfer coefficient α defines the symmetry of both forward and backward reactions, with typically assumed $\alpha = 0.5$ meaning symmetric curves as shown in the example in Fig. 2.11a. It is worth noting that in some literature, as for example in the Bagotsky's book [248], the charge transfer coefficient is defined as the product of α and the reaction valence, i.e., (αn_e) , with the range from zero to n_e .

The Tafel equation can be also written in the following form [253]:

$$I = I_0 \cdot \exp\left(\pm \alpha \cdot \frac{n_e F \eta}{RT}\right) \quad (2.20)$$

where the minus sign refers to the cathodic reaction (*cathodic Tafel curve*), and the plus sign to the anodic reaction (*anodic Tafel curve*).

The Tafel equation is valid for relatively high overpotentials ($\eta > 118 \text{ mV}/n_e$), when the electrode reaction becomes irreversible, meaning that there is only forward or backward reaction on the electrode with the

corresponding anodic or cathodic current depending on the sign of the applied overpotential (s. Fig. 2.11b) [253]. The Butler-Volmer equation is the generalized equation for polarization curve of a redox process in the charge transfer limited mode, that describes the current-voltage dependence also at low overpotentials and for both cathodic and anodic reactions [253]:

$$I = I_0 \left[\exp \left(\alpha \cdot \frac{n_e F \eta}{RT} \right) - \exp \left(-(1 - \alpha) \cdot \frac{n_e F \eta}{RT} \right) \right] \quad (2.21)$$

In the region of low polarizations eq. (2.21) can be reduced to the linearized form [253]:

$$I = I_0 \cdot \frac{n_e F \eta}{RT} \quad (2.22)$$

The concentration dependent form of the Butler-Volmer equation takes into account concentration dependence of the exchange current density [254]:

$$I = I_0 \left[\frac{c_{\text{Red S}}}{c_{\text{Red V}}} \cdot \exp \left(\alpha \cdot \frac{n_e F \eta}{RT} \right) - \frac{c_{\text{Ox S}}}{c_{\text{Ox V}}} \cdot \exp \left(-(1 - \alpha) \cdot \frac{n_e F \eta}{RT} \right) \right] \quad (2.23)$$

Control by the mass transport of reactants - concentration polarization

If the reactants or the products have small diffusion constants, or the concentration of the reactants in the electrolyte is low, or etch rate is high due to high applied current density, the electrochemical process can become controlled by the mass transport^{xiv} of the products and reactants in the electrolyte.

In case of pure diffusional concentration polarization, with increase of the applied potential, current approaches the limiting value I_{lim} (s. Fig. 2.13, curve 2) [248]. This limiting diffusion current neither depends on the electrode potential nor on the rate of the electrode reaction, but on concentrations and diffusion constants of species, and geometry of the electrode. The polarization curve under mass transport control is strongly dependent on the scan rate at which it was measured.

^{xiv} As described in sec. 2.3.2.3, only mass transport by diffusion and electromigration is considered in the whole work, neglecting convection.

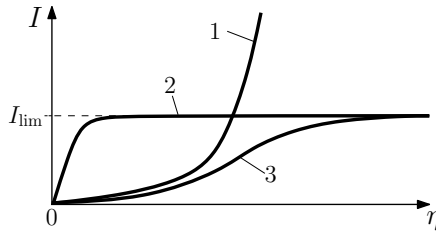


Figure 2.13.: Current-voltage curves for 1 - activation polarization, 2 - diffusional concentration polarization, and 3 - combined polarization; figure adapted by author from Bagotsky [248].

Virtually every real electrochemical reaction of dissolution is the combination of at least two steps in series, which are (a) the chemical dissolution step defined by reaction kinetics and (b) the mass transport of the products and the reactants in the electrolyte [227]. This means mixed regime of activation polarization and concentration polarization, where the current-voltage curve cannot follow the exponential behavior of the Butler-Volmer and the Tafel equations and limits itself with I_{lim} (s. Fig. 2.13, curve 3). The corresponding current densities of the single reaction steps of mass transport (diffusion) j_d and reaction kinetics j_k are contributing to the total current density j according to the following equation [248]:

$$\frac{1}{j} = \frac{1}{j_d} + \frac{1}{j_k} \quad (2.24)$$

If the limiting diffusion current I_{lim} is known for electrochemical system with mixed polarization, the polarization curve for this system (s. Fig. 2.13, curve 3) can be described applying the activation polarization equations in the following form:

$$I = \frac{I_{\text{lim}} I_{\text{act}}}{I_{\text{lim}} + I_{\text{act}}} = \frac{I_{\text{lim}}}{1 + \frac{I_{\text{lim}}}{I_{\text{act}}}} \quad (2.25)$$

where I_{act} is obtained according to the Tafel equation (2.14) or Butler-Volmer equation (2.21). In this case, explicit description of the concentration distribution according to the Nernst-Planck equation (2.12) is not necessary, which helps to reduce numerical calculations of electrochemical systems.

It is important to note that the described idealized polarization curves account only for the diffusional mass transport in electrolyte, neglecting movement of species due to migration and convection. For neglecting convection, this simplified case is achieved in analytical electrochemistry by ensuring steady conditions without steering. To neglect effect of migration of the reacting ions, a supporting electrolyte is added. Such a supporting electrolyte contains much more ions which participate in charge flow in the electrolyte but do not participate in the charge transfer at the interface electrode-electrolyte, i.e., do not participate in the electrode reactions. In real systems such simplification are not always possible, therefore more complex polarization curves are observed.

Classification of electrochemical systems on current distribution

Summarizing the theory on mass and charge transfer phenomena in the electrolyte, electrode, and their interface, for modeling of an electrochemical cell the following classification of current distributions in electrochemical systems is applied [219, 255, 256]:

- *Primary current distribution* takes into account only current conduction according to the Ohm's law in the electrolyte and in the electrode neglecting the mass transport phenomena and activation polarization at the interface electrode-electrolyte. Prerequisites are that the electrochemical reactions are so fast that the losses on reaction activation can be neglected (assuming activation overpotential $\eta = 0$) and the electrolyte is homogenous meaning concentration gradients can be also neglected. Then:

$$\mathbf{j}_l = -\sigma_l \nabla \phi_l, \quad \nabla \cdot \mathbf{j}_l = -\frac{\partial \rho_q}{\partial t} \quad (2.26)$$

$$\mathbf{j}_s = -\sigma_s \nabla \phi_s, \quad \nabla \cdot \mathbf{j}_s = -\frac{\partial \rho_q}{\partial t} \quad (2.27)$$

$$\eta = 0, \quad U_{eq} = \phi_s - \phi_l \quad (2.28)$$

where subscript l denotes the electrolyte (liquid) and s the electrode (solid), ρ_q is the density of charge, and $\mathbf{j}$ is the current density vector field. In other words, the distribution is primary, when the solution bulk resistance is much higher than the interfacial impedance.

- *Secondary current distribution*: in this case the mass transport is still neglected (homogenous electrolyte), but the interfacial overpotential is taken into account. Then, for the electrode and the electrolyte equations (2.26) and (2.27) are still valid, and the overpotential is described according to equations (2.17) and (2.23). Secondary distribution is observed when the interfacial impedance is determined by processes of charging or charge transfer, or when the overpotential of the interfacial processes and the ohmic voltage drop in the solution bulk are comparable.
- *Tertiary current distribution* considers both interfacial overpotential at the interface solid-liquid as well as the mass transport phenomena in the bulk electrolyte according to the Nernst-Planck equation (2.12) and further equations discussed above in this section.

2.4. Silicon anodization: current-voltage characteristics and dissolution mechanisms

In this section, the basic theory explained above will be applied to discussion of the current-voltage curve and dissolution mechanisms in the silicon anodization process.

Silicon as a semiconductor shows rectifying behavior in any electrolyte [257]. However, the polarization curves for p-type and n-type silicon in aqueous HF electrolytes are more complex than the ones presented in Fig. 2.13. Typical polarization curves for p-type and n-type silicon in aqueous HF electrolytes are shown in Fig. 2.14. On these curves, distinct regions of various polarization types can be detected, as will be discussed in the subsections below.

2.4.1. Cathodic polarization and open circuit

At negative potentials $U \leq U_{OC}$ the polarization curves for p-type silicon and for n-type silicon with sufficient illumination show to some extent basic similarities to normal Schottky diode behavior expected from a semiconductor/electrolyte interface [89]. When p-type silicon gets in contact with HF electrolyte, band bending occurs in silicon, with the space charge region of ionized acceptor atoms (negative) being formed in silicon near the

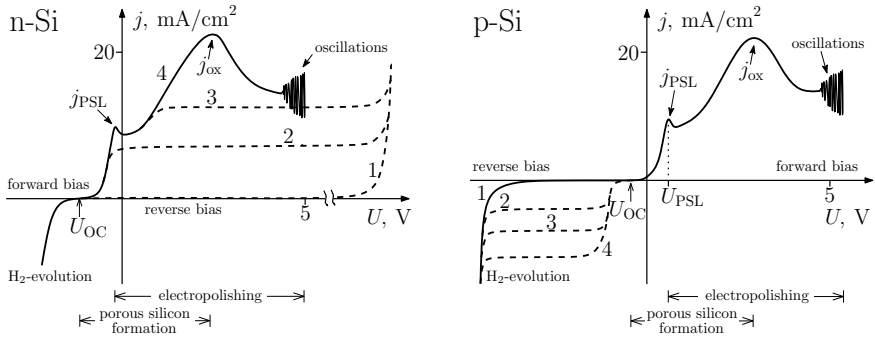


Figure 2.14.: Typical current-voltage relationships for n- and p-type silicon in contact with aqueous HF; U_{OC} - open-circuit potential; 1 – no illumination; 2–4 – with illumination of intensity I_v ($I_{v4} > I_{v3} > I_{v2}$); SCE - saturated calomel electrode; reproduced from Föll et al. [22] © 2002 with permission from Elsevier, with minor changes.

junction (depletion region), and the open-circuit potential U_{OC} is formed^{xv}. Under cathodic polarization ($U < U_{OC}$), the band bending increases. The depletion region increases in depth, and the Schottky diode remains reverse-biased. Electrons generated in the conduction band (e.g., due to photo- and thermogeneration) determine the reverse current. For n-type silicon, cathodic polarization provides forward bias for the Schottky diode, and exponential increase of current is observed. Both n- and p-type silicon remain mostly stable to the HF solution, however, there might be surface modifications (up to 0.1 μm in depth) due to the formation of silicon hydrides, especially at higher cathodic potentials, as shown in Fig. 2.15 [4,35]. At high cathodic overpotentials, the reduction of water at Si/HF interface with evolution of hydrogen gas also takes place [4,77,89].

When the potential is increased to the negative (vs. SCE) open-circuit value U_{OC} , current decreases to zero, and chemical processes are in equilibrium.

^{xv}In the text, the term open-circuit potential U_{OC} is used in the same sense as the equilibrium potential U_{eq} introduced in sec. 2.3.3, which is true only for the electrode-electrolyte systems where the open-circuit potential is at the equilibrium condition (reversible reactions), s. more in sec. 1.6 in [4], in sec. 8.3 in the Memming's book [250], and in sec. 16.1 in Bagotsky's book [248], where non-equilibrium open-circuit potential causes dissolution (corrosion) of metals.

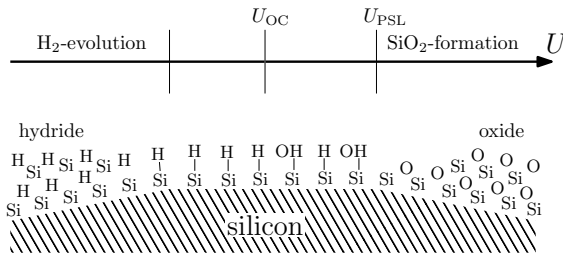


Figure 2.15.: Schematic representation of the surface condition of silicon in fluoride-containing aqueous electrolyte as a function of applied voltage; Si - silicon atom, H - hydrogen atom, O - oxygen atom; reproduced from Zhang [4] © 2001 with permission of Springer.

2.4.2. Pore formation

2.4.2.1. Current-voltage region

Dissolution of silicon in aqueous HF electrolytes occurs only under anodic polarization [227].^{xvi} For p-type silicon this means forward-biased Schottky contact. Illumination of the p-type silicon under anodic polarization does not influence much the I-V curve. For low- and moderately-doped n-type silicon illumination plays a significant role under anodic polarization. If the process runs without illumination, the I-V curve represents the reversed-biased Schottky contact, with breakdown taking place at a certain high potential. If illumination is applied to backside or frontside of the n-type silicon wafer, there is an additional photogenerated current, and for high illumination levels the curve follows the one for p-type silicon (s. Fig. 2.14). The fact that the dissolution of silicon is quite intense for p-type material where holes are majority carriers, whereas for n-type silicon the reaction is very slow without illumination or other hole generation mechanisms, is an indication that holes are required for silicon dissolution process.

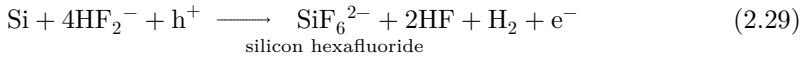
For low applied voltage, for both p-type and n-type silicon samples, and assuming high illumination intensity for n-Si, the polarization curve (s. Fig. 2.10 and Fig. 2.14) can be well described with the Tafel expression (2.15) or the Butler-Volmer equation (2.21) as explained in sec. 2.3.3.2 [79, 81, 89, 98].

^{xvi}The very slow process of chemical dissolution of silicon in HF electrolytes [75, 77, 258] is neglected here.

This exponential increase of current ends with the *first current peak*, or porous silicon layer peak, at potential U_{PSL} and current density j_{PSL} (s. Fig. 2.14). The first current peak defines the end of the pure pore formation regime.

2.4.2.2. Reaction

In the region $U_{\text{OC}} < U < U_{\text{PSL}}$ (which is also referred to as region $j < j_{\text{PSL}}$ or Tafel region), direct dissolution of silicon occurs at the silicon surface representing the secondary anode, with consumption of one hole h^+ and release of one electron e^- per silicon atom, which gives the reaction valence (dissolution valence) $n_e = 2$ [2]:



However, the actual measured effective dissolution valence in the pore formation mode is typically varying between 1.3 and 2.8 [4, 30, 71, 78, 259] (for example $n_e = 2.7$ for n-macropores [77]), which means that other parallel reactions take place during the anodization. For example, Balagurov distinguishes in the anodization process between the electrochemical dissolution and pure chemical etching that can reduce the effective dissolution valence and is temperature-dependent [259].

Considering the reaction (2.29), one can see that supply of holes coming from the silicon substrate and F-ions in form of bifluoride anions HF_2^- are required. Strong dependence of j_{PSL} on HF concentration was shown by many researchers [12, 71, 76, 81, 85, 90, 94, 243]^{xvii}. This indicated that the pore formation regime is favored when supply of holes from the silicon substrate is the limiting factor, and not the supply of F-ions from the electrolyte.

Many mechanisms of silicon dissolution in the pore formation regime have been proposed. One of the most accepted theories is the Gerischer mechanism revised and extended by Kolasinski [247]. The silicon surface covered with hydrogen (Fig. 2.15) is very inert, and according to Gerischer/Kolasinski the substitution of hydrogen atom with fluorine occurs after a hole comes from the silicon bulk and is captured near the surface in Si-Si bond. After

^{xvii}More on this is given in sec. 2.4.4.

some intermediate steps this leads to dissolution of a silicon atom leaving again hydrogen-terminated silicon surface.

Dissolution of silicon atoms occurs selectively in this mode. This way, pores of various shapes are etched into silicon, and porous silicon is formed. The dark layer of porous silicon was at first considered to be amorphous re-deposited silicon layer [71, 79]. Further studies with X-ray analysis showed that the skeleton of porous silicon remains mostly crystalline [260], although evidence of some amorphous material was also detected with Raman spectroscopy [261].

2.4.2.3. Classification of pores

Generally, pores are etch pits with their depth exceeding their width/diameter. There are different classifications of pores in porous silicon. The generally used classification is based on pore size (diameter) according to the IUPAC specifications for conventional porous materials. According to this classification, there are three types of pores:

- *micropores* (pore diameter < 2 nm)^{xviii}
- *mesopores* (pore diameter from 2 nm to 50 nm)
- *macropores* (pore diameter > 50 nm)

Pore size, specific surface area, and pore size distribution can be evaluated using Brunauer-Emmett-Teller (BET) and the Barrett-Joyner-Halenda (BJH) theories from measured adsorption/desorption isotherms [262, 263].

The classification based on pore size takes into account only the size of pores, without considering their morphologies, which in case of porous silicon can vary significantly depending on process conditions, even within one sample. Two distinguished morphologies of porous silicon are straight cylindrical pores (mostly in macropore-size) with very large aspect ratios (s. Fig. 2.16a) and 3D sponge-like (mostly microporous or mesoporous) structures (s. Fig. 2.16b) [22, 77, 264]. Various intermediate cases possessing features of these two morphologies (e.g., macropores with extra branching) have been reported [2, 77]. Typically, micropores and mesopores of sponge-like morphology are obtained from p-Si, and straight macropores (with backside illumination) from n-Si. More exotic cases like macropores

^{xviii} Microporous and mesoporous materials sometimes are also called *nanoporous* due to pore size in nanometer range.

in p-Si (s. Fig. 2.16a) require special process conditions (e.g., organic electrolytes).

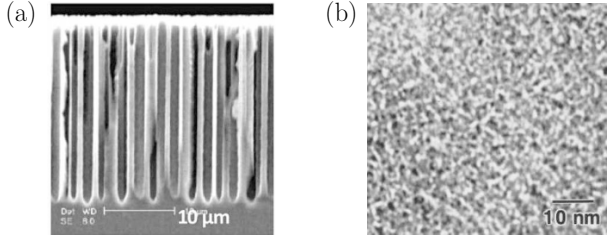


Figure 2.16.: Two specific types of porous silicon morphologies: (a) p-Si macropores with straight cylindrical pores, reprinted from Föll et al. [22] © 2002 with permission from Elsevier; (b) p-Si micropores with sponge-like morphology, reprinted from Cullis et al. [264] © 1997 with permission from AIP Publishing LLC.

There are also other classifications of pores in silicon based on process conditions (electrolyte, illumination, etc.), on crystallographic dependence, etc. [22, 77].

2.4.2.4. Characterization of the pore formation process and the porous silicon

The main parameter characterizing porous material is porosity $P_{\%}$ in percent, which for porous silicon can be found with the gravimetric method according to the following equation:

$$P_{\%} = \frac{m_1 - m_2}{m_1 - m_3} \cdot 100 \quad (2.30)$$

where m_1 , m_2 , and m_3 are the mass of silicon sample before anodization, after anodization, and after removal of porous silicon, respectively.

Porosity defines the effective refractive index of the porous silicon according to the effective-medium-approximation models, e.g., the Bruggeman's model [68], which is applied in fabrication of porous silicon based photonic crystals consisting of multiple layers with modulated refractive index.

When the values m_1 , m_2 , and m_3 are known, additionally, the growth rate R_{PS} and the dissolution valence n_e of the anodization process can be found:

$$R_{PS} = \frac{m_1 - m_3}{\rho_{Si} \cdot A \cdot t_{etch}} \quad (2.31)$$

$$n_e = \frac{I \cdot t_{etch}}{e} \cdot \frac{M_{Si}}{(m_1 - m_2) \cdot N_A} \quad (2.32)$$

where A is the anodization area, I is the current during the anodization of time t_{etch} , e is the elementary charge, ρ_{Si} and M_{Si} are the density and the molar mass of silicon, and N_A is the Avogadro constant. The expression for the growth rate in this form is valid for the quasi-3D case, where the anodization process runs strictly in depth with flat etch front plane, meaning almost constant value of the anodization area during the process. The expression is applicable, therefore, for anodization of large area samples (with *etch depth* $\ll$ *area sidelength*), and not suitable for samples with the etch depth comparable to the area sidelength, where significant part of anodization process is running laterally, and thus the anodization area increases significantly during the process.

The growth rate and the dissolution valence can be also found by etching porous silicon away and measuring the etch depth. This method, as well as the gravimetric method, is destructive, however, there are also non-destructive characterization methods. One such non-destructive optical technique – spectroscopic liquid infiltration method (SLIM) – was described by Segal et al. [265]. In this method, interferometric reflectance spectrum of the porous layer is measured for different filling liquids with known refractive indices. Then, the data are fitted to the Bruggeman's effective-medium approximation. This way, porosity and thickness of the porous layer can be determined.

2.4.2.5. Pore formation mechanisms

Two phases during pore formation can be distinguished: pore initiation (nucleation) and pore growth. Since the discovery of porous silicon formation in anodization process, different models for the two phases have been suggested. Although the proposed mechanisms could not succeed explaining all effects, they helped to understand influence of various process parameters and, to some extent, to predict the results.

As was discussed in sec. 2.3.3, upon contact of electrolyte to silicon, space charge region depleted from free charge carriers forms in silicon. According to Theunissen [266] and, later, Beale et al. [87], the driving factor for pore initiation and growth is current focusing on surface inhomogeneities, where a breakdown voltage of the SCR is expected to be lower. Later, Searson et al. [267] have showed analytically that the depletion layer at the tip of an elliptical pore is indeed thinner. Thus, according to Beale et al., the dissolution process starts at surface defects. Once the first silicon atoms are removed, current focusing on the pore tips provides further growth of the pores in a positive feedback mechanism. SCR passivates already porosified material and defines distance between single pores, i.e., thickness of pore walls [83]. Zhang [82] showed that when the distance between two neighboring pores gets larger than the double thickness of SCR, then a new pore between the existing two should grow. Thus, porous silicon layer is fully depleted from free carriers, and the dissolution process continues only at the interface between bulk silicon and porous silicon, where holes coming from bulk silicon reach pore tips by tunneling or avalanche breakdown through the SCR [89, 268]. The effect of pore wall passivation by SCR matches well with experiments and explains very good growth of macropores in n-type silicon [59, 83, 269]. However, the mechanism of pore initiation by current focusing on surface defects was later questioned with the in-situ study by Allongue et al. of KOH etching with scanning tunneling microscope [154, 270]. The authors have demonstrated that pore pits on silicon surface occur independently of atomic defects at the initial stages. On the other hand, the effect of current focusing is successfully applied for growth of regular arrays of macropores in n-type silicon, where controlled pore initiation is achieved with inverted four-sided pyramidal etch-pits formed with photolithography and anisotropic KOH etching [83, 271].

Smith et al. [89, 95] have proposed the diffusion-limited model of pore initiation and growth, where a hole in a process of stochastic random walk diffuses to the surface and initiates silicon atom dissolution. Next holes, with higher probability, will come to the formed pits and provide further pore growth.

The Beale's field effect model and the diffusion-limited model can explain both pore initiation and pore growth. Another proposed model for pore growth is based on quantum effects in nanometer-sized features of porous silicon [84, 89, 272, 273]. It is known that small silicon crystallites have larger band gap than bulk silicon. This effect was used to explain strong photoluminescence in visible range in porous silicon, with nanocrystalline porous

material consequently called “nanowires” or “nanodots”. Due to difference in band gaps between porous silicon and bulk silicon, holes from bulk silicon are blocked from penetrating small crystallites of porous silicon, and no holes are generated in the pore walls^{xix}. This way, already formed nanoporous structures remain passivated during further anodization. The model originally was applied to explain formation of microporous silicon. However, Föll [272] applied the quantum model to explain growth of macropores in n-type silicon. According to Föll, in case of macropores of micrometer-size, where no quantum effects are expected, pore walls are covered with thin layer of micropores which passivate the macropore-walls.

A model that attempts to explain all processes of the silicon anodization on the microscale (formation of all kinds of pores, and current oscillations in the electropolishing regime, s. sec. 2.4.3) was developed at the University of Kiel by Föll, Carstensen, Christophersen et al. [101, 274–276]. The model named current burst model (CBM) assumes that all silicon dissolution or oxidation processes during anodization process occur inhomogeneously in time and space as current bursts (CB). Interaction between single CBs is described by surface passivation with hydrogen (in case of direct silicon dissolution - pore formation) or oxide (in case of electropolishing), which defines the probability of the next CB at a given location. Effect of SCR is also included in the model. Besides silicon, the model covers also anodization of III-V semiconductors.

Martín-Palma et al. [277] have performed examination of porous silicon with high resolution electron microscope, and proposed another mechanism of pore growth. They observed that dissolution of silicon atoms during pore formation causes dislocations in the silicon matrix, which are more electronically active, thus the dissolution continues through these areas.

The anodization process is not always a stable process. For example, for p-type silicon, micropores can occur first, and later develop into macropores [85, 278]. The question of process stability was studied by several research groups with help of etch front stability analysis. The stability analysis was initially applied for growth of a sphere precipitate particle in a uniformly saturated solution [279]. In 1990s the stability analysis approach was applied to silicon anodization process. Kang and Jorné [280] studied morphology of porous silicon with stability analysis according to the Mullins-Sekerka theory [279], taking into account diffusion of holes in silicon, diffusion of ions in electrolyte, and surface tension. They showed for

^{xix}The effect is also called *charge confinement* or *quantum-wire effect*.

n-type silicon, that porous silicon formation is favored when the process is controlled by the supply of holes from silicon bulk. Wehrspohn et al. [103] proposed an electrostatic model aimed on explanation of macropore formation in low-doped p-type silicon. There the role of difference between resistivity of silicon and of electrolyte on mechanism of pore formation was studied. It was shown that for low-resistive silicon (high and moderate n-type or p-type doping, with sufficient illumination for moderate n-type doping), micropores are formed substantially, and in opposite case (low-doped n-silicon and low-doped p-type silicon) macropores are observed. Additionally, in case silicon is more conductive than electrolyte, the growth front is more stable. In their further paper they extended the model and showed conditions for instability of the interface “bulk silicon - porous silicon” for p-type silicon of resistivities in the range 10^{-1} – $10^4 \Omega \text{ cm}$ [278].

Stability analysis was also used to study how the process switches between pore formation (divalent etching) and electropolishing (tetravalent etching, s. sec. 2.4.3). Valance [94, 99] has further developed the model of Kang and Jorné [280], and showed that the electrolyte-silicon interface gets unstable when the dissolution current is below a critical value which depends linearly on the HF concentration. In their model, unstable electrolyte-silicon interface indicated pore formation and stable interface meant electropolishing. The stability criteria fits to some extent to the experimentally observed dependence of limiting current density j_{PSL} on HF-concentration (s. Fig. 2.17). Rauscher and Spohn in their Laplacian growth model also showed that instability is maximal for small current densities (pore formation), and a transition to a stable interface at high current takes place [228, 281, 282].

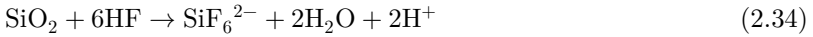
2.4.3. First and second plateaus of electropolishing

At potentials larger than the first peak on the polarization curve ($U > U_{\text{PSL}}$), two regions can be distinguished - first and second plateaus of electropolishing, separated from each other by the second peak with current density j_{ox} at potential of few volts vs. SCE (s. Fig. 2.14).

The reactions in the first plateau of electropolishing are considered to be under mixed control conditions described with Koutecky-Levich equation (2.24) [257], and the dissolution reaction gradually changes from the divalent reaction of direct silicon dissolution (s. eq. (2.29)) to tetravalent reaction of silicon oxidation [2]:

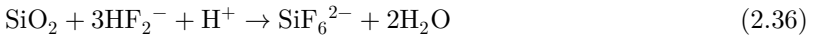
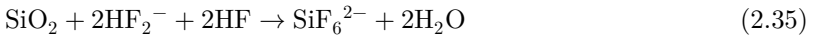


The formed anodic oxide is etched in hydrofluoric acid [283]:



Thus the reaction of tetravalent silicon dissolution has a two-step mechanism. The oxide etching step (2.33) is considered to be the rate-determining step (RDS). The limitation of the oxide etching step comes not due to the reaction kinetics but due to diffusion-limited transport of fluoride species to the reaction site. This way, hillocks of the oxide are etched faster, and electropolishing of the surface occurs.

The reaction of oxide dissolution shown above is only one possible reaction. Alternative reactions with other (minor) components of the aqueous HF solution, for example $(\text{HF})_2$ and HF_2^- , were also proposed [2, 284]:



The reactions of oxide dissolution involving HF_2^- are considered to be more likely because of higher reactivity of HF_2^- in comparison to HF [247]. Good overview of various mechanisms of silicon oxide dissolution is given in the work of Mitra and Rimstidt [285].

The silicon surface at the first plateau of electropolishing is covered with porous “wet” hydroxylated oxide, and the surface remains rough on the nanometric scale [257, 286, 287].

In the second plateau of electropolishing, the reaction is nearly tetravalent, and the surface is covered with “dry” compact oxide which thickness increases with increase of potential [257, 286]. At this conditions, electropolishing takes place in the diffusion-controlled regime, which leads to smoothing of the surface [71]. That electropolishing occurs in the plateau region of the anodization polarization curve, where current is assumed to be independent of voltage, is not unexpected, and is common for many other electropolishing processes [284]. The dissolution rate in this region may be expressed in terms of current according to the Faraday’s law of electrolysis, although the chemical step of oxide dissolution in HF is dependent on the kinetic constants. At higher potentials in the second plateau of electropolishing, additionally oscillations of current or voltage (depending on which

parameter is fixed) are observed. Good explanation of these oscillations gives the current-burst model described above (s. sec. 2.4.2.5).

At even higher potentials typically between 10 V and 20 V (not shown in Fig. 2.14), again strong increase of current is observed. In this region increased silicon dissolution occurs with formation of mesoporous silicon oxide (silica) layer [257, 288]. Further increase of potential leads to formation of macrostructures of silica and evolution of oxygen [289, 290].

2.4.4. Position of the first and the second current peaks

There is some controversy in the reviewed papers on the observations of the first and the second peaks on the polarization curves shown in Fig. 2.14. For example, Turner [71] observed only one peak dividing the process between pore formation and electropolishing. He found that the value of this limiting current density peak (named in the work as critical current density) is determined by the mass transport of HF to the reaction site. He showed that this critical current density for the horizontally arranged silicon electrodes was linearly dependent on HF concentration and temperature and inversely dependent on the fourth root of the electrolyte viscosity. Turner also reported that the role of electrolyte agitation due to natural convection and hydrogen bubbles has a significant influence on the value of the critical current density. For vertically arranged silicon electrodes he observed a less sharp peak indicating that the switching from pore formation to electropolishing at first took place only in some regions of the silicon electrode and then spread to its entire surface.

Zhang et al. [76] also observed only one current peak on the current-voltage curves, after which pure electropolishing took place, meaning the second current peak j_{ox} . However, they also showed a transition region below this peak, where the exponential Tafel part changes to a slower linear increase. Additionally, Zhang et al. reported linear dependence of the critical current density at this peak on HF bulk concentration, and showed that there is only a weak dependence of the critical current density on the doping type and level (s. Fig. 2.17). The linear dependence of the critical current densities on HF concentration was also observed by Eddowes [81], Searson and Macaulay [90], Barret et al. [12], and others.

In contrast to the above references, non-linear dependencies of the critical current densities on HF concentration were also reported. The most cited

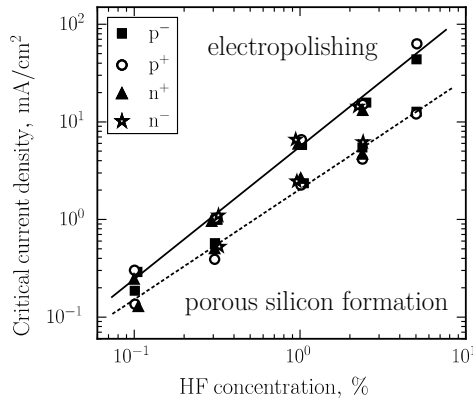


Figure 2.17.: Map of porous silicon formation and electropolishing modes for different values of current densities, HF concentrations in electrolyte, and doping level and type; the solid line shows j_{ox} , the region between the solid and the dotted lines is the transition region between pore formation and electropolishing; reproduced from Zhang et al. [76] by permission of The Electrochemical Society.

and applied is the dependence of order 1.5 found empirically for j_{PSL} by Lehmann [85]:

$$j_{PSL} = C w_{HF}^{1.5} \exp\left(-\frac{E_a}{k_b T}\right) \quad (2.37)$$

where $C = 3300 \text{ A}/(\text{cm}^2 \text{ m}\%^{1.5})$, activation energy $E_a = 0.345 \text{ eV}$, and w_{HF} is the HF mass fraction in percent. The measured valence values indicated that switching of the process from pore formation to electropolishing occurred in a wide region close to j_{PSL} (s. below in Fig. 2.18a, the switching appears to take place in a narrow region due to the logarithmic scale).

For the value of the second current peak j_{ox} , also different dependencies have been reported. For example, Eddowes [81] showed a second order dependence. Other orders of the dependence were summarized by Hassan et al. [291].

With addition of ethanol to the solution, remarkable change of the polarization curve with reduction almost to a half of current for both peaks and the

first plateau was reported [292]. For the electrolyte containing 1:1 volume parts of 50 m% HF and ethanol, used in this work, Lehmann et al. [268] reported $j_{\text{PSL}} \approx 600 \text{ mA/cm}^2$. However, the fit function proposed by Lehmann in his book [2] (Fig. 4.6) shows only a valence of approximately 2.6 at 1000 mA/cm^2 . No values of j_{ox} for the ethanoic electrolyte could be found in the literature.

Hassan et al. [291], and van den Meerakker and Mellier [243] emphasized the mixed effect of diffusional and kinetic aspects of the anodization process. Hassan et al. showed that at low HF concentration of 0.03 M the process is kinetically controlled at all current densities up to the oscillations after the second electropolishing plateau. At higher concentrations, diffusion control starts playing an important role.

To summarize, due to complexity of the anodization process, the peak current density values are not constant for a given electrolyte concentration, but depend on other parameters. The mass transport dependence means that geometrical factors (such as thickness of protective masking layer, anodization area dimensions, etc.) play an important role on the peak current density values, as known for diffusion-limited wet-etching processes [145]. Therefore, the values given in literature should be used with caution only as rough estimations.

2.5. Silicon anodization: influence of process parameters

Any process or system can be characterized in terms of input and output signals, or as applied action to the system and resulting reaction of the system. For the process of silicon anodization, input signals are the process parameters, and the output is the resulting structure of the anodized silicon surface with corresponding characteristic properties. Main process parameters and characteristic properties of the resulting etch structures in the anodization process for pore formation and electropolishing regimes are summarized in Tab. 2.3.

Table 2.3.: Silicon anodization process parameters and resulting properties

Process parameters (input)	Characteristic output properties
- current density j (or – more difficult to control – potential difference U) - etch time t_{etch} - illumination conditions - electrolyte composition, HF concentration, viscosity, additional agitation - temperature T - substrate doping type - substrate doping density N_a or substrate resistivity ρ_{el} - crystal orientation	- morphology (micro/meso/macro porous silicon, electropolished surface, or mixed) - etch rate R_{etch} - dissolution valence n_e - porosity of porous silicon $P_{\%}$ - quality of the electropolished surface or of the interface “porous silicon - bulk silicon”, e.g., in terms of average surface roughness R_a or root-mean-square (RMS) roughness R_q

Influences of the process parameters on the characteristic properties of the process are discussed in this section. The overview is emphasized on microporous and mesoporous sponge-like silicon, because macropores are less suitable for application of anodization as a structuring technique, and thus not studied in this work.^{xx} The doping type in this overview is limited to p-type for the same reasons, since micropores and mesopores are generated more readily in p-type silicon. For p-type silicon, illumination conditions do not play significant role, and are therefore not discussed.

^{xx}Macroporous silicon has a few specific applications as a structuring technique. Long vertical macropores can be used as is, for example, as channels with high aspect ratio in electrodes with high inner surface for capacitors or batteries [32]. Modulation of current during the process can result in quasi-3D structures used as photonic crystals [293]. Additionally, not only long channels, but also trenches can be formed with anodization process in macroporous regime [11, 39, 59]. This way, micromechanical structures for MEMS can be fabricated [294]. With increased current density, pore overlapping can be achieved, resulting in formation of nanowires [61]. Either way, the process with macropores is limited to these specific structures and is not applicable for fabrication of arbitrary 3D cavities, therefore it does not meet the goals of this work.

For this section, data from different references were collected and compared to each other in frames of this work. If multiple papers from the same authors were available, cross-checking of the data was performed. Where necessary, conversion of units and derivation of additional parameters were performed. References to all datasets are provided.

2.5.1. Current density

Current density is a very important parameter of the anodization process, because it defines the dissolution reaction pathway of the process (divalent pore formation vs. tetravalent electropolishing)^{xxi}. Thus, current density defines the dissolution valence n_e of the anodization process (s. Fig. 2.18a). Besides this fast change of the dissolution valence value at the critical current density, slow increase is observed in pore formation and electropolishing regimes. The effect of increasing dissolution valence with increasing current in pore formation regime is observed in both HF:water and HF:ethanol:water electrolytes (s. Fig. 2.18a,b).

Data published in several papers suggest that the porosity of micro/mesoporous silicon in general increases with increase of current density [87, 260, 295–298], although a short reduction at low current densities is also detectable, with minimum at 10–30 mA/cm² (s. datasets “0.1 Ω cm”, “1 Ω cm”, and “5 Ω cm” in Fig. 2.19a, and dataset “0.01 Ω cm” in Fig. 2.19b). According to Setzu et al. [299], the increasing part can be explained by considering electropolishing regime, where the porosity is 100 %. Then, by lowering the current, the process is moved away from the electropolishing regime, and the porosity decreases.

On the microscale, assuming that the dissolution valence n_e is known and the dissolution process is 100 % efficient, i.e., all charges are consumed for

^{xxi}To be more exact, the reaction pathway is defined with the applied potential difference (s. Fig. 2.14). In galvanostatic power supply, when current density near the first or the second peaks on the polarization curve is set, there are two corresponding possible values of overpotential, one smaller and one larger than the value of overpotential at the peak. However, one can expect that the electrochemical system tends to the minimal energy, therefore, in this case the smaller value of the overpotential is established. In general, galvanostatic control is preferred over the potentiostatic control, because values of overpotential are often not well defined and documented in electrochemical experiments, e.g., because reference electrodes are not used, therefore it is more convenient to use current-control in the experiments and make comparison of process parameters vs. current density.

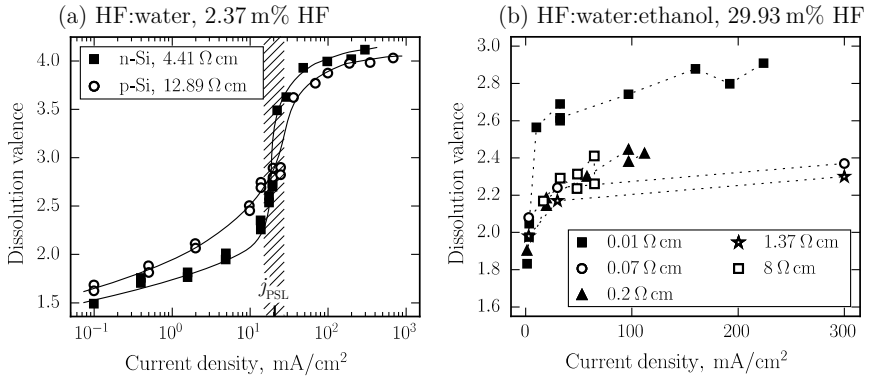


Figure 2.18.: (a) Dependence of the dissolution valence on applied anodic current density for a low-doped p-type and a strongly illuminated low-doped n-type silicon samples anodized in water:HF solution (2.37 m% HF) at RT (reproduced from Lehmann [85] by permission of The Electrochemical Society); (b) p-type silicon of different resistivity anodized in water:HF:ethanol solution (29.93 m% HF, 1:1 parts by volume of 50 m% HF and ethanol) at RT in pore formation regime (based on data from Frohnhoff et al. [273] and Lehmann et al. [268]); here and further in the chapter, points of each dataset are connected with lines for clarity.

the dissolution reactions, current density j defines the silicon dissolution rate R_{Si} according to the Faraday's law of electrolysis:

$$R_{Si} = \frac{j}{n_e e} \cdot \frac{M_{Si}}{\rho_{Si} N_A} \quad (2.38)$$

In the electropolishing regime, the dissolution of silicon runs through intermediate step of anodic oxidation. However, the reaction is considered to be fast enough, so that the main limitation is provided through the transport of the fluoride species to the oxide film. In turn, the transport of the ions in electrolyte is controlled by the applied electric field defining migration velocity. Therefore, the velocity of etch front in electropolishing regime R_{etch} (neglecting extreme case of porous silica growth at high potentials) is assumed to be equal to this dissolution rate, and thus to the applied current density:

$$R_{etch} = R_{Si} \quad (2.39)$$

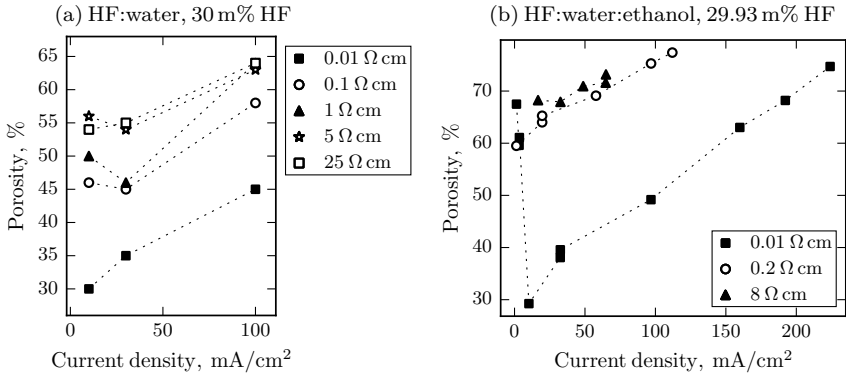


Figure 2.19.: Porosity of microporous silicon as a function of current density for p-type silicon anodized in (a) water:HF solution of 30 m% HF (based on data from Beale et al. [87]) and (b) 1:1, HF(50 m%):ethanol electrolyte (based on data from Frohnhoff et al. [273]).

In galvanostatic control, this means that for a defined charge flow, the electrochemical system is forced to provide enough ions to the reaction site by adjusting the electrical field.

In case of pore formation, etch rate is defined with the movement velocity of the interface between bulk silicon and porous silicon. Due to selective etching of pores into silicon, the dissolution rate R_{Si} defined with current density has to be corrected for the porosity $P_{\%}$ of the formed porous layer:

$$R_{\text{etch}} = \frac{R_{Si}}{P_{\%}} \cdot 100 \quad (2.40)$$

i.e., a highly porous layer will grow slower than a less porous layer at the same dissolution rate. In eq. (2.40) it is assumed that the dissolution process runs always at the interface “porous silicon - bulk silicon”, that is confirmed with the fabrication of 1D photonic crystals, where porosity (and therefore the refractive index) at each moment of anodization, i.e., at each depth of the interface “porous silicon - bulk silicon”, is defined by the applied current density, and the already generated modulation of the porosity remains unchanged during further anodization.

Measured growth rates as a function of current density in HF:water and in HF:water:ethanol electrolytes reveal nearly linear dependence (s. Fig. 2.20).

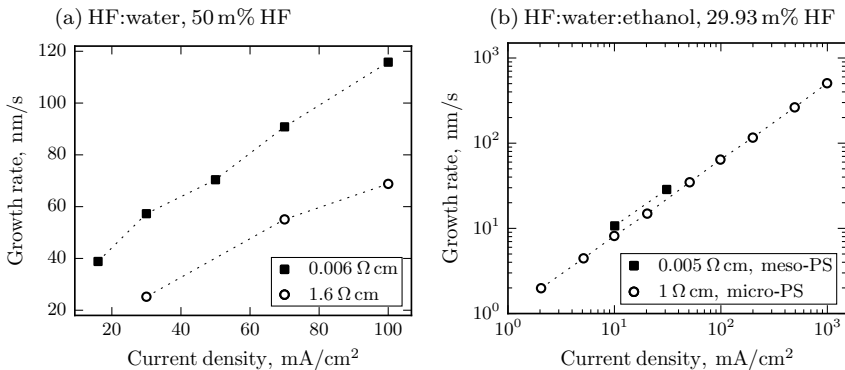


Figure 2.20.: Dependence of growth rate on current density for p-type silicon of different resistivity in (a) aqueous HF solution with 50 m% HF (based on data from Arita and Sunohara [295]) and (b) 1:1, HF(50 m%):ethanol electrolyte (based on data from Lehmann and Rönnebeck [86]).

Surface quality after electropolishing or after removal of porous silicon (interface roughness) can be characterized in terms of surface roughness, which gives information about height variations, and fractal dimension, which characterizes also the surface morphology^{xxii}. Léronel et al. [300] have found that the root-mean-square (RMS) roughness of the interface “porous silicon - bulk silicon” decreases with increase of current density (s. Fig. 2.21). Similar effect was observed by Ha et al. [23]. This increase can be explained from the point of electropolishing regime, where roughness decreases to atomic scale. The further the process is moved away from the electropolishing regime by decreasing current density, the rougher the etch front is achieved [299].

It is worth noting that the quality of the surface under porous silicon depends also on the process of porous silicon removal, as will be discussed in sec. 2.6.2.

^{xxii}More information on surface characterization is given in sec. 3.2.3.

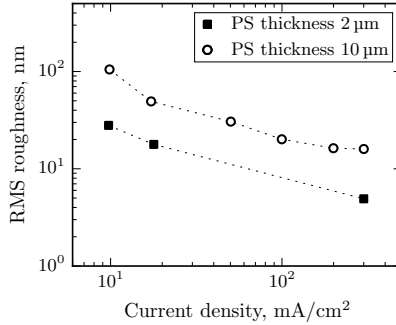


Figure 2.21.: Influence of current density on interface surface roughness for 4–6 Ω cm p-type silicon with thickness of the removed porous silicon 2 μ m and 10 μ m, based on data from L  rondel et al. [300].

Electropolishing can provide surface of superior quality. Tjerkstra [47] has reported roughness of lower than ± 5 nm (estimated from SEM micrographs) after electropolishing at potentials corresponding to the first and second plateaus in electrolytes with HF concentration in the range from 0.5 % to 10 % for lightly-doped (5–10 Ω cm) and heavily-doped (0.01–0.018 Ω cm) (100) p-type silicon. Comparable results have been reported by Rappich et al. for (111) n-type silicon substrates [301]. In contrast, Artmann and Frey have reported roughness of up to 200 nm for 15 Ω cm p-type silicon in 5 % HF electrolyte with ethanol and current density between 10 mA/cm² and 75 mA/cm² [10]. However, they used electropolishing to undercut a lateral oscillating structure of a gyroscope, thus additional roughness could be induced by the underetched elements.

2.5.2. Etch time

In HF:water electrolytes, dissolution valence shows strong dependence on etch time (s. Fig. 2.22a), with almost no difference between the values of dissolution valence for a given etch time for various current densities in pore formation regime. As shown above, current density defines the growth rate (s. Fig. 2.20) and, consequently, the thickness of the porous layer. Since porous silicon layers of different thickness, but formed with the same etch time, reveal almost the same dissolution valence, there is no diffusion limitation induced by already formed porous layer in this case. Because almost

no dependence on current density is visible, dependence of the dissolution valence on etch time can be explained with chemical dissolution, running simultaneously with the electrochemical dissolution [75,77,258]. Then, less electrons are consumed per a dissolved silicon atom, and the dissolution valence decreases. Chemical dissolution was reported to be higher for low concentrated HF solutions [302–305], which is attributed to the increased OH^- concentration (increased pH value) in the low concentrated HF solution [4].

In contrast, Hedrich et al. reported almost no effect of the etch time on the dissolution valence in HF:water:ethanol electrolyte (s. Fig. 2.22b) [24], thus it can be concluded, that there is no/little chemical etching running in the HF:water:ethanol electrolyte. However, this statement should be used with caution, because only one value of porosity, from which the dissolution valence is calculated, is provided for each current density in [24].^{xxiii}

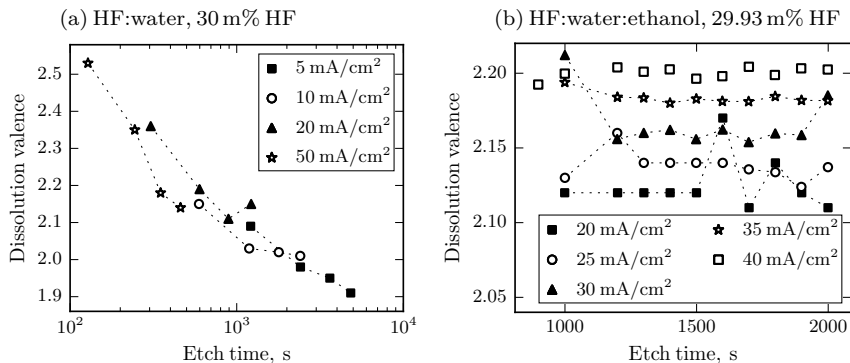


Figure 2.22.: Dissolution valence as a function of etch time for low-doped p-type silicon in pore formation regime with (a) resistivity $1.5 \Omega \text{ cm}$ in 30 m% HF electrolyte (HF:water) (based on data from Unno et al. [302]); (b) resistivity $2\text{--}9 \Omega \text{ cm}$ in 29.93 m% HF electrolyte (1:1 of HF(50 m%):ethanol) (based on data from Hedrich et al. [24]).

^{xxiii}There are real data on thickness and etch time for each data point, though. The calculation of the dissolution valence was done according to eq. (A.60) in Appendix.

Porosity was reported to depend strongly on etch time in HF:water electrolytes, as shown in Fig. 2.23a for 30 m% HF. The effect is more pronounced for higher current densities. The dependence versus porous layer thickness is similar for different current densities (s. Fig. 2.23b). Increase of porosity with duration of contact of porous silicon with HF electrolyte can be also explained with chemical dissolution. Halimaoui [303] showed that keeping an already formed $1\text{ }\mu\text{m}$ thick porous silicon layer in ethanoic solution of 5 % HF without electrical supply resulted in increase of porosity from 51 % to over 95 % after 30 minutes.

Similarly, Hamm et al. [305] have studied dependence of porosity of porous silicon of p-type samples with resistivity $10\text{--}20\text{ }\Omega\text{cm}$ on etch time till 200 minutes in different mixtures of HF(47 m%) and ethanol at 2 mA/cm^2 . They found an increase of porosity with etch time for high concentrated electrolytes (28 m% HF and 35 m% HF), and a decrease of porosity with etch time for lower concentrated electrolytes (14 m% HF and 22 m% HF). In contrast, for 29.93 m% HF electrolyte (1:1 of HF(50 m%):ethanol), Hedrich et al. [24] reported that porosity is independent of the porous layer thickness in the range up to about $66\text{ }\mu\text{m}$.

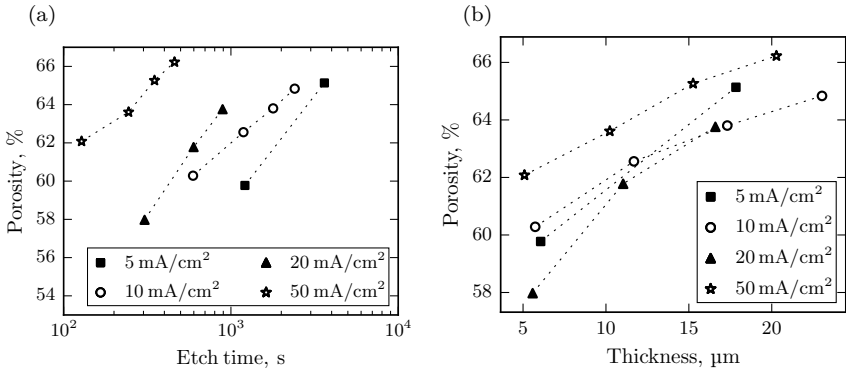


Figure 2.23.: Porosity vs. (a) etch time and (b) porous layer thickness for low-doped p-type silicon with resistivity $1.5\text{ }\Omega\text{cm}$ in 30 m% HF electrolyte (HF:water) (based on data from Unno et al. [302]).

Assuming constant porosity, the growth rate of porous silicon does not depend on the etch time for a given current density, in both HF:water and

HF:water:ethanol electrolytes, as demonstrated by Unno et al. [302] for current densities in the range 10–200 mA/cm² for thicknesses up to about 16 μm (Fig. 2.24a) and by Hedrich et al. [24] for current densities in the range 20–40 mA/cm² for thicknesses up to about 66 μm (s. Fig. 2.24b). However, mass transport limitation can be expected for higher current densities and thicker porous layers, which can change local HF concentration near the interface between bulk silicon and porous silicon. As a consequence, porosity and growth rate might change in depth. According to Korotcenkov and Cho [77], for very thick porous layers (150 μm), 20 % difference in HF concentration between that at the etch front and that in the bulk solution was reported.

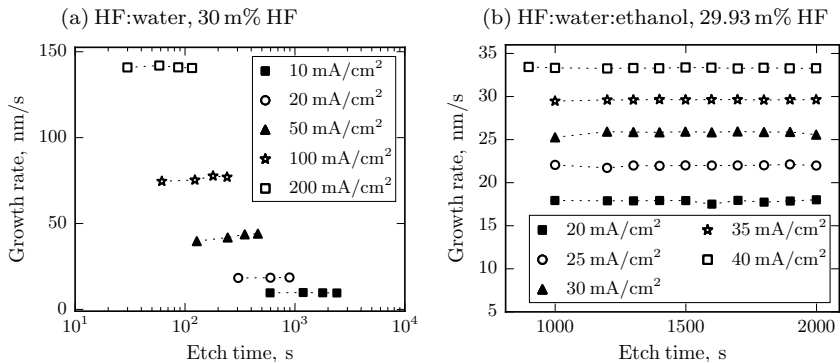


Figure 2.24.: Growth rate vs. etch time for low-doped p-type silicon with (a) resistivity 1.5 Ωcm in 30 m% HF electrolyte (HF:water) (based on data from Unno et al. [302]); (b) resistivity 2–9 Ωcm in 29.93 m% HF electrolyte (1:1 HF(50 m%):ethanol) (based on data from Hedrich et al. [24]).

Lérondel et al. [300] studied roughness of the interface between bulk silicon and porous silicon, and reported increase of RMS roughness with thickness for p-type silicon samples anodized in HF:water:ethanol electrolyte (s. Fig. 2.25). The increase is more pronounced for lower current densities (s. also Fig. 2.21): for 20 mA/cm², an increase from about 1 nm up to about 52 nm was measured for the thickness of about 60 μm . For thicker porous layers, roughness comes to saturated values. These results match those reported by Setzu et al. [299].

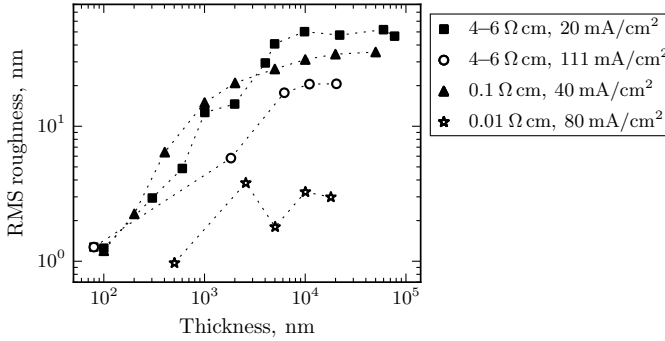


Figure 2.25.: Dependence of the root mean square roughness of the interface between bulk silicon and porous silicon on thickness of porous layer for p-type silicon samples anodized in HF:water:ethanol electrolyte (based on data from L  rondel et al. [300]).

2.5.3. Electrolyte mixture and concentration

As shown in Fig.2.17, HF concentration in electrolyte defines the critical current densities between pore formation and electropolishing regimes [89]. Therefore it influences the corresponding dependence of the dissolution valence on the current density (s. Fig.2.18a). The effect of HF concentration on the dissolution valence for p-type silicon in pore formation regime is shown in Fig.2.26. The effect is more pronounced for lower-doped silicon. Similar dependence was reported by Kordas et al. [236] and Unno et al. [302]. In electropolishing regime, the dissolution valence is reported to have no dependence on electrolyte concentration [2].

Porosity of the micro/meso porous layer decreases with increase of HF concentration for highly-doped p-type silicon anodized in HF:water and HF:water:ethanol electrolytes as shown in Fig.2.27. According to Kordas et al. [236], with decrease of HF concentration, the porosity is raised until there is enough HF serving F^- -ions in the electrolyte in the pores providing charge carriers. Therefore, at lower HF concentration higher porosity is observed. Similar dependence was also reported in HF:water electrolyte for low-doped silicon (s. Fig. 2.28, datasets from Beale et al. and Unno et al.). However, at low concentrations below 12 m% HF, Irajizad et al. [306] have measured increase of porosity with increase of current density (s. Fig.2.28).

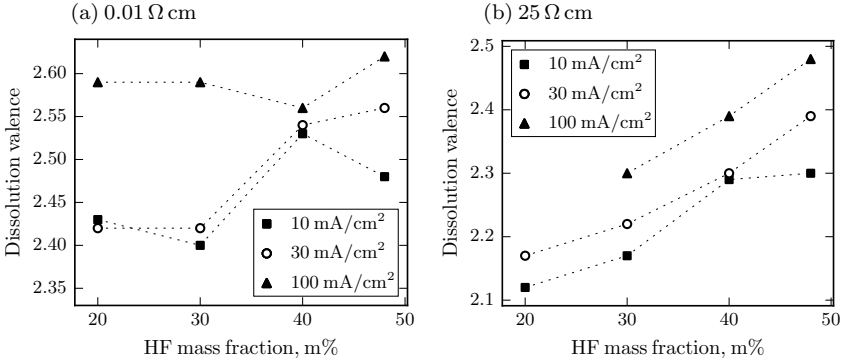


Figure 2.26.: Dissolution valence vs. HF mass fraction at various applied current densities for p-type silicon of resistivity (a) 0.01 Ω cm and (b) 25 Ω cm in pore formation regime, based on data from Beale et al. [87].

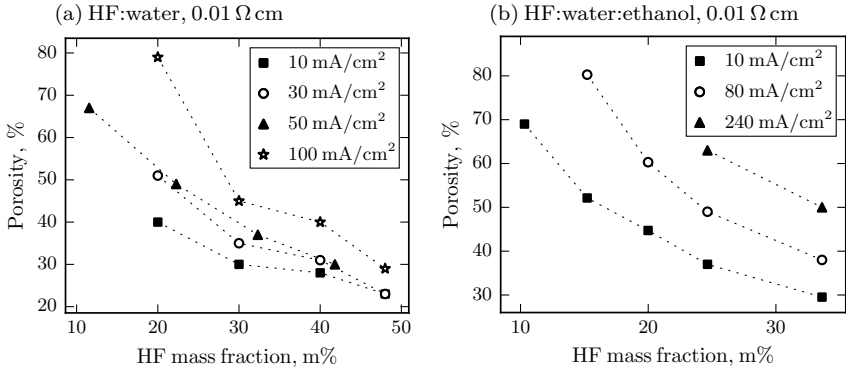


Figure 2.27.: Porosity of microporous silicon as a function of HF concentration for p-type silicon of resistivity 0.01 Ω cm anodized in (a) HF:water electrolyte (datasets for 10 mA/cm², 30 mA/cm², and 100 mA/cm² are from Beale et al., and the dataset for 50 mA/cm² is from Kor-das et al. [87, 236]) and in (b) HF:water:ethanol electrolyte (based on data from Herino et al. [296]).

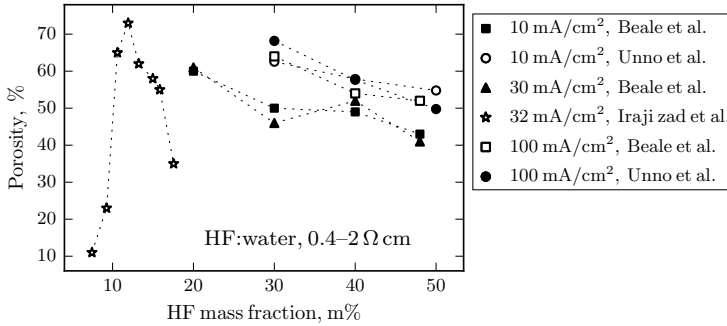


Figure 2.28.: Porosity of microporous silicon as a function of HF concentration in HF:water electrolyte for p-type silicon of resistivity 0.4–2 Ω cm (dataset from Irajizad et al. [306]) and 1–1.5 Ω cm (datasets from Beale et al. [87, 302]).

For a given HF concentration in the range $10 \text{ M} < c_{\text{mol HF}} < 29 \text{ M}$, no significant effect of ethanol concentration in the electrolyte on porosity has been found [236].

Decrease of porosity with increase of HF concentration can explain observed increase of growth rate with increase of HF concentration (s. Fig. 2.29). There is almost no difference between the growth rate for low- and highly-doped p-type silicon at low current densities. With increase of current density, the curves get steeper. This effect is more pronounced for highly-doped silicon.

2.5.4. Temperature

For p-type silicon, Turner [71] reported linear dependence of the critical current density for electropolishing on temperature in 5 m% HF, with slope change at ca. 30 $^{\circ}\text{C}$ (s. Fig. 2.30a). According to Turner, electropolishing is favored when a viscous layer near the reaction site causes mass transport limitation. Therefore, the critical current density is dependent on both the diffusion coefficient and viscosity of the HF electrolyte, and both parameters are temperature-dependent, resulting in the temperature dependence of the critical current density. The change of the slope at ca. 30 $^{\circ}\text{C}$ is due to start of convection stirring caused by thermal effects. Temperature dependence is

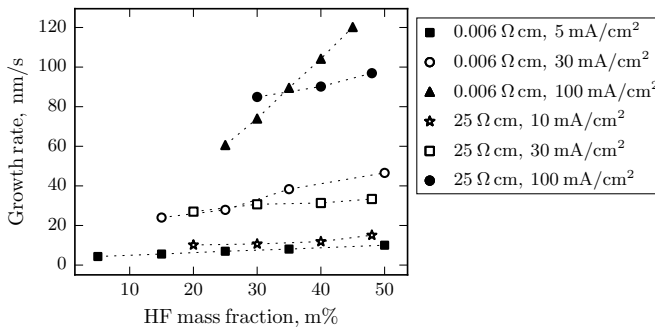


Figure 2.29.: Dependence of growth rate of porous layer on HF concentration in HF:water electrolyte for p-type silicon of resistivities $0.006 \Omega \text{ cm}$ (based on data from Arita and Sunohara [295]) and $25 \Omega \text{ cm}$ (based on data from Beale et al. [87]).

also included in the Lehmann's empirical dependence of the critical current density on HF concentration (s. eq. (2.37)).

Balagurov et al. [259] have shown that increase of temperature in the range from about 18°C to 65°C decreases the dissolution valence from 2.23 to 1.58 for p-type silicon of resistivity $10 \Omega \text{ cm}$ anodized in 5:1 parts per volume of 41 % HF and 95 % ethanol at 10 mA/cm^2 (s. Fig. 2.30b). The etch time was 8.5 minutes for all data points. The authors demonstrated that the dependence was due to temperature-dependent chemical dissolution of silicon which is significant at elevated temperatures even in this rather high-concentrated electrolyte: chemical dissolution rate increases exponentially from $4.71 \times 10^{-5} \text{ nm/s}$ at 18°C to $9.62 \times 10^{-4} \text{ nm/s}$ at 65°C .

For temperatures in the range from -35°C to 37°C , Setzu et al. [299] and Blackwood et al. [307] reported decrease of porosity with increase of temperature (s. Fig. 2.31). According to Setzu et al. [299], this temperature dependence of porosity can be explained by considering the temperature dependence of the critical current density as was shown by Turner (s. Fig. 2.30a): with increase of temperature the critical current density increases, therefore by increasing the temperature at a given applied current density the process is moved away from the electropolishing regime (where porosity is 100 %), so the porosity decreases (s. also Fig. 2.19).

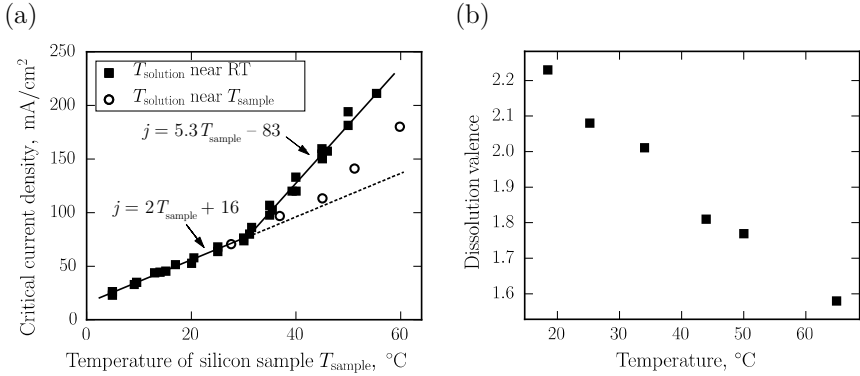


Figure 2.30.: (a) Critical current density for electropolishing vs. temperature for $3.5 \Omega \text{ cm}$ p-type silicon, where the silicon sample was heated and its temperature measured, and the temperature of the solution was near room temperature or near the temperature of the sample (reproduced from Turner [71] by permission of The Electrochemical Society); (b) dissolution valence as a function of temperature in pore formation regime for p-type silicon of resistivity $10 \Omega \text{ cm}$ anodized for 8.5 minutes in 5:1 parts per volume of 41 % HF and 95 % ethanol at $10 \text{ mA}/\text{cm}^2$ (based on data from Balagurov et al. [259]).

For higher temperatures in the range from 18°C to 65°C , Balagurov et al. [259] have shown increase of porosity with temperature (s. Fig. 2.31, dataset “ $10 \text{ mA}/\text{cm}^2$, 32 m% HF, Balagurov et al.”). The effect was explained again with chemical dissolution, as for the dissolution dependence in Fig. 2.30b.

Slow increase of the growth rate with temperature was reported by Arita and Sunohara [295] for highly-doped p-type silicon anodized in HF:water electrolyte at temperatures in the range from about 4°C to 66°C and $100 \text{ mA}/\text{cm}^2$ (s. Fig. 2.32a). Setzu et al. [299] showed stronger increase of the growth rate for low-doped p-type silicon anodized in HF:water:ethanol electrolyte at temperatures in the range from -35°C to 25°C for higher current densities (s. Fig. 2.32a).

Setzu et al. [299] measured surface roughness of the interface between the porous silicon and bulk silicon for different temperatures and current densities. They showed that for thicknesses of the porous layer in the satu-

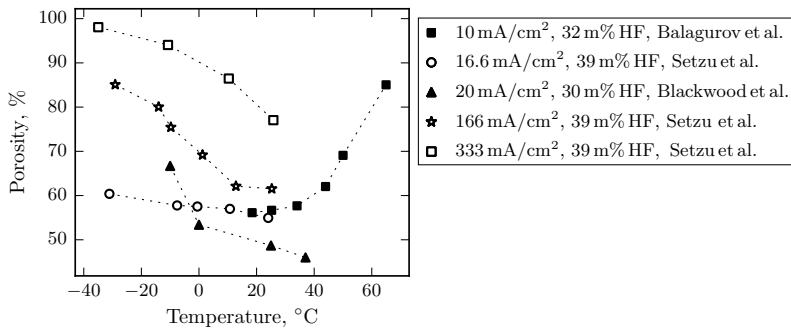


Figure 2.31.: Porosity vs. temperature for low-doped p-type silicon in HF:water:ethanol electrolytes ($5\ \Omega\text{ cm}$ in 29.93 m% HF, $8\text{--}9\ \Omega\text{ cm}$ in 39 m% HF and $10\ \Omega\text{ cm}$ in 32 m% HF) for different current densities (based on data from Balagurov et al., Setzu et al., and Blackwood and Zhang [259, 299, 307]).

ration range (more than few micrometers, s. Fig. 2.25 in sec. 2.5.2), roughness increases with increase of temperature from $-35\ ^\circ\text{C}$ to $25\ ^\circ\text{C}$, with the effect being more pronounced for smaller current densities (s. Fig. 2.32b). Setzu et al. explained this dependence in the same way as for porosity by considering electropolishing regime and the temperature dependence of the critical current density from Turner (s. Fig. 2.30a): in the electropolishing regime, surface roughness decreases to atomic scale; therefore, when the process is moved further away from electropolishing regime at constant current by increasing temperature, the roughness increases.

Wehrspohn et al. [103] proposed that additional temperature dependent effect on morphology of porous silicon and growth front can be due to temperature dependent resistivities of silicon and electrolyte. In case resistivity of electrolyte is higher than that of p-type silicon substrate, there is stabilizing mechanism of nanopore formation. In the opposite case, unstable macropore formation process is observed.

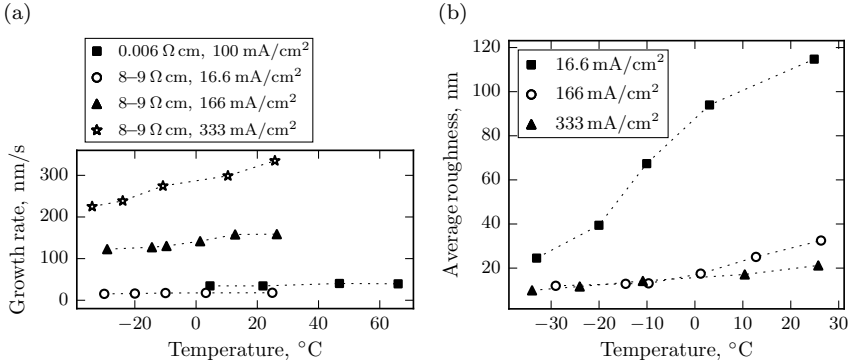


Figure 2.32.: (a) Growth rate as a function of temperature for p-type silicon of resistivity 0.006 Ω cm in 50 m% HF (HF:water electrolyte) (based on data from Arita and Sunohara [295]) and p-type silicon of resistivity 8–9 Ω cm in 38.84 m% HF (HF:water:ethanol electrolyte) (based on data from Setzu et al. [299]); (b) average roughness of the interface between the porous silicon and bulk silicon vs. temperature for p-type silicon of resistivity 8–9 Ω cm in 38.84 m% HF (HF:water:ethanol electrolyte) (based on data from Setzu et al. [299]).

2.5.5. Substrate doping density

Dissolution valence increases with increase of doping density^{xxiv} in pore formation regime in HF:water electrolyte (Fig. 2.33a). In HF:water:ethanol electrolyte, similar curves, although, slightly lower, have been reported (Fig. 2.33b). In electropolishing regime, dissolution valence does not depend on doping density [2, 91].

Growth rate decreases with decrease of doping density in pore formation regime in HF:water electrolyte in the range of high doping density (s. Fig. 2.34a). At low doping densities, this decrease slows down or even switches to increase. In contrast, in HF:water:ethanol electrolyte, increasing growth rates for low resistivities and decreasing growth rate for higher resistivities have been reported by Lehmann et al. [268], with maximum in the range 0.01–0.1 Ω cm (s. Fig. 2.34b). The data from Berger et al. in [258] also follow the decreasing trend in Fig. 2.34b.

^{xxiv}Conversions between resistivity and doping density, considering doping density dependent mobility, is performed with data from Sze [106].

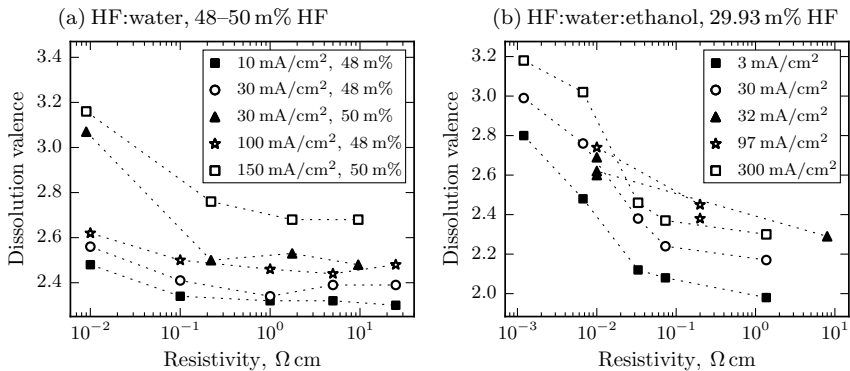


Figure 2.33.: Dissolution valence as a function of substrate resistivity for p-type silicon anodized in (a) HF:water electrolyte (the datasets for 48 m% HF are from Beale et al. [87], the datasets for 50 m% HF are from Arita and Sunohara [295]) and (b) 1:1 volume ratio of HF(50 m%) and ethanol (the datasets for 3 mA/cm², 30 mA/cm², and 300 mA/cm² are from Lehmann et al. [268], the datasets for 32 mA/cm², and 97 mA/cm² are from Frohnhoff et al. [273]).

Dependence of growth rate on doping density can explain waviness (also called macroroughness) in form of concentric rings with a spacing in the order of millimeters, often observed after removal of porous layer: during the crystal growth process, striations (resistivity oscillations in silicon substrates) are introduced into silicon crystal [300].

According to Zhang [308], doping density of p-type silicon influences strongly the size and shape of pores. The porous silicon formed in moderately-doped p-type silicon (10^{15} – 10^{18} cm⁻³) has very small pores from 1 nm to 10 nm. In heavily-doped p-type silicon ($> 10^{19}$ cm⁻³) pores are typically 10 nm to 100 nm wide. In low-doped p-type silicon ($< 10^{15}$ cm⁻³), depending on electrolyte, macropores of diameters in the order of micrometers or micropores with diameters in the order of nanometers are formed.

Porosity for p-type silicon in HF:water electrolyte of 48–50 m% HF increases with increase of resistivity up to about 1 Ωcm , and then comes to saturation or starts to decrease (s. Fig. 2.35a). In contrast, in the 1:1 mixture of HF(50 m%):ethanol, porosity decreases with increasing resistivity in the

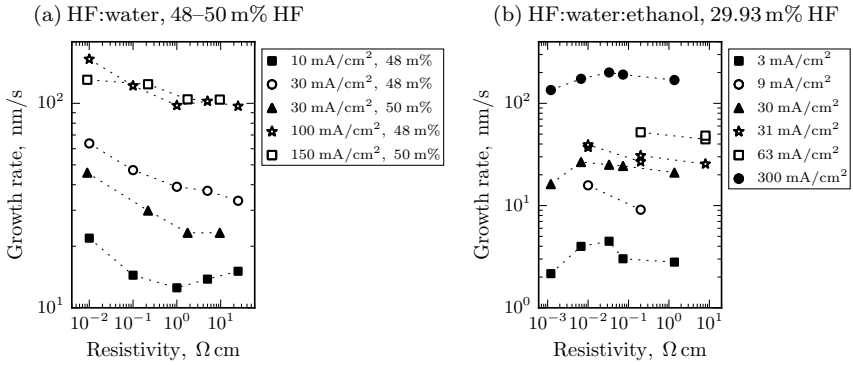


Figure 2.34.: Growth rate as a function of substrate resistivity for p-type silicon anodized in (a) HF:water electrolyte (the datasets for 48 m% HF are from Beale et al. [87], the datasets for 50 m% HF are from Arita and Sunohara [295]) and (b) 1:1 volume ratio of HF(50 m%) and ethanol (the datasets for 3 mA/cm², 30 mA/cm², and 300 mA/cm² are from Lehmann et al. [268], the datasets for 9 mA/cm², 31 mA/cm², and 63 mA/cm² are from Berger et al. in [258]).

range 10^{-3} – 10^{-2} $\Omega \text{ cm}$, and then increases again (s. Fig. 2.35b), as also confirmed with the datasets for 31 mA/cm² and 63 mA/cm² from Berger et al.

According to Léron del et al. [2, 300], the roughness frequency shows no strong dependence on doping density. The amplitude of surface height and, therefore, roughness increase from few nanometers for degenerately-doped material to several tens of nanometers for low-doped silicon (s. Fig. 2.25). However, the current density for these data was changed with doping density (higher-doped samples anodized at higher current density), therefore the effect of doping density on roughness cannot be separated from the effect of current density (s. Fig. 2.21), where decrease of roughness is observed with increase of current density.

Wehrspohn et al. [103] proposed with their stability analysis of pore formation mechanism, that any source of noise, such as poor stirring in electrolyte near the bottoms of the pores, ionized impurities in the space charge region, etc., is more effectively damped for highly conductive substrates, resulting in low interface roughness.

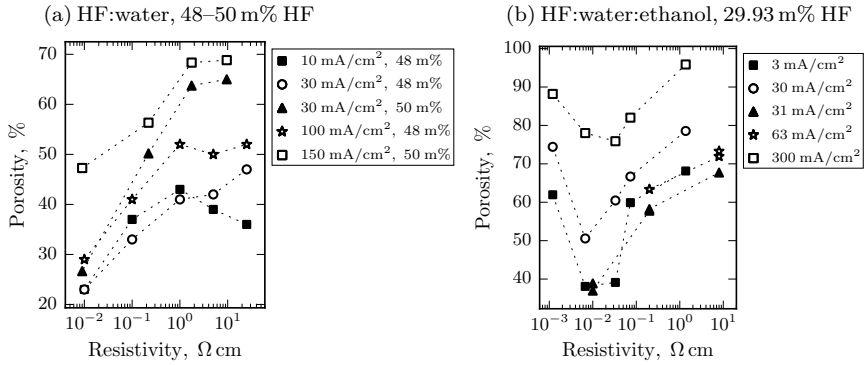


Figure 2.35.: Porosity as a function of substrate resistivity for p-type silicon anodized in (a) HF:water electrolyte (the datasets for 48 m% HF are from Beale et al. [87], the datasets for 50 m% HF are from Arita and Sunohara [295]) and (b) 1:1 volume ratio of HF(50 m%) and ethanol (the datasets for 3 mA/cm², 30 mA/cm², and 300 mA/cm² are from Lehmann et al. [268], the datasets for 31 mA/cm² are from Berger et al. in [258]).

2.5.6. Crystal orientation

Lehmann [85] showed that the critical current density for both (110) and (111) oriented samples was up to 30 % less than for (100) oriented samples, depending on the HF concentration.

Christophersen et al. [309] reported almost no dependence of the dissolution valence for p-Si samples on the studied orientations, namely, (100), (5 1 1), (5 5 12), and (111).

Beale et al. [87] reported that growth of individual pores is determined by stochastic nature of the initiation of protrusions, i.e., it is of a random nature and, therefore, not crystal orientation dependent. The overall trend in the growth direction is determined by the general direction of current flow.

According to Lehmann [2], effect of crystal orientation on the growth rate of porous silicon R_{PS} is not observed for microporous silicon layers etched into

a moderately-doped p-type substrate. Guendouz et al. [310,311] observed a certain dependence for highly-doped silicon, with the growth rate for $\langle 100 \rangle$ direction being higher than for $\langle 111 \rangle$ (s. Fig. 2.36a). The orientation dependence results in more flat walls of the shape of the porous volume for (100) oriented substrates anodized through a mask, and with sufficient anodization duration a sharp bottom is evolved (Fig. 2.36b). Guendouz et al. named this kind of shape a “pseudo V-shape”. Tjerkstra [47] also reported on similar kind of shapes in (100) p-type silicon substrates of resistivities $0.01\text{--}0.018\ \Omega\text{ cm}$ and $5\text{--}10\ \Omega\text{ cm}$ anodized in electropolishing regime through a mask in electrolytes with HF concentrations in the range from 0.5% to 10%. He showed that the effect is more pronounced for anodization potentials corresponding to the first plateau of electropolishing than for the second plateau. In contrast, Baranov et al. [70] reported on isotropic, i.e., independent of the crystallographic orientation, electropolishing of silicon.

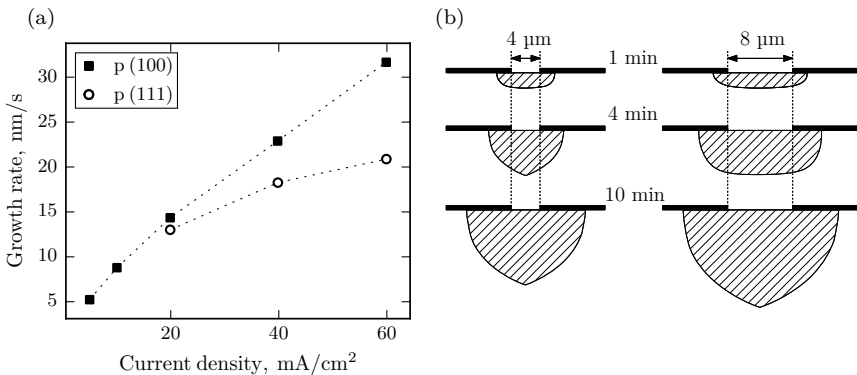


Figure 2.36.: (a) Orientation dependence of growth rate for p-type silicon of resistivity $0.007\text{--}0.008\ \Omega\text{ cm}$ anodized in HF:water:ethanol mixture with HF concentration 14.78 m%; (b) resulting etch form evolution for n-Si, with a “pseudo V-shape” formed at longer etching time (for p-Si, the result is to some extent similar); reproduced from Guendouz et al. [310] © 2000 with permission from Elsevier.

2.5.7. Conclusions

In this section, general dependencies of anodization parameters on process conditions have been reviewed. By comparing results from various studies, some differences could be observed. This means, the process of silicon anodization is so sensitive, that even when considering same process conditions, some deviations exist between the results reported from different research groups. Therefore, not only the process conditions, such as current density and electrolyte concentration, but also general process flow can influence results, as, for example, influence of porosity on how quick a sample is taken from anodization cell after anodization (increase of porosity due to chemical dissolution).

Therefore, establishing a reliable process with expected results cannot be done by only relying on the literature, and requires preliminary experiments with sweeping the main parameters, in order to get the reference data for own experiments. This was also one of the reasons to perform systematic study of substrate resistivity and current density dependencies on porosity, growth rate, and dissolution valence of p-type silicon in pore formation regime in this work (s. chapter 4) in order to have reliable data for the model development in chapter 5.

2.6. Application of silicon anodization for structuring

2.6.1. Fabrication aspects

Working with HF requires strict following the safety precautions, since even minor contact with high concentrated HF can be lethal for human [2]. Chemically resistant safety gloves, full face protection, and, preferably, overall coat represent a typical “dress-code” for working with concentrated HF (s. Fig. 2.37). Additionally, good ventilation in the work place is prerequisite for handling HF. Environmental aspects for disposal of used electrolytes have to be also strictly fulfilled.

Additional safety concerns arise from using high currents during the process, since even for a relatively small current density of 100 mA/cm^2 , the total current for a full area of a 4-inch wafer is about 6 A. Application of ethanol requires additional precautions against electric spark formation in order to avoid fire. On industrial scale, to improve safety and process reproducibility, fully-automated systems are introduced [312].



Figure 2.37.: “Dress-code” for working with concentrated HF (photograph B. Müller, model A. Ivanov).

Anodization process is conducted in HF-stable electrochemical cell typically fabricated from PTFE [75]. An example of double tank cell with vertical placement of a silicon wafer is shown in Fig. 2.38, where the silicon wafer separates the two tanks (one with anode and another with cathode) of the cell. There are also setups with horizontal placement of the wafer. Optionally, circulation of electrolyte with cooling/heating might be integrated into the setup. At least two electrodes must be present in the cell. As was explained above, the anodization process runs on the side of silicon substrate that is facing the cathode. This side of the substrate – frontside – plays the role of secondary anode, therefore the name anodization is used for the process. Electrical supply from anode to the opposite side of the substrate (backside) can be either also through electrolyte (“wet” backside contact), as shown in Fig. 2.38, or directly to the wafer (“dry” backside contact). For low-doped wafers, a highly-doped surface layer formed by ion implantation of boron (for p-type) or phosphorus (for n-type) is necessary in order to provide good uniform electrical contact of the substrate backside to the electrolyte or metal electrode. Electrodes immersed in HF are typically made of platinum (stable in HF), or silicon (sacrificial, consumed) for metal-free electrochemical cells. In case of high resistive n-type silicon, illumination of back- or frontside of the substrate is required in order to generate holes for the process. For this purpose, PMMA for low concentrated HF-electrolytes

till 15 % HF or sintered clear Al_2O_3 (sapphire) windows which are stable even for higher concentrated HF-electrolytes are integrated into the cell [77].

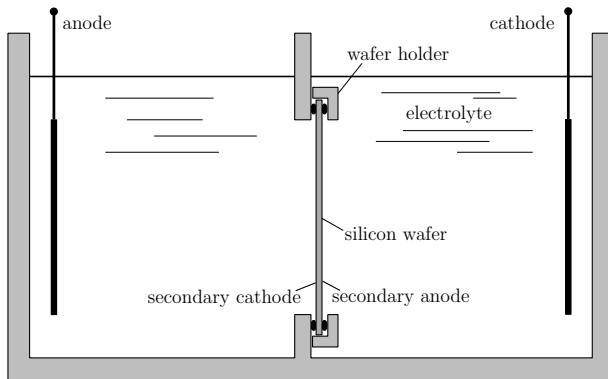


Figure 2.38.: Double-tank anodization cell setup with two electrodes (schematic view).

Anodization process is performed under current or voltage control, i.e., in galvanostatic or potentiostatic regime, respectively. Galvanostatic regime provides better control of the process, since etch rate is typically proportional to the applied current density according to the Faraday's law of electrolysis, assuming that leakage current (i.e., current flowing not through the substrate, but through other parts of the electrochemical cell) is negligible. In galvanostatic regime, it is important to remember that the active area (anodized area) of the process increases during the process [30, 313]. For formation of all types of pores and especially for macropores, it might be not quite correct to talk about average current density calculated based on the area of silicon surface exposed to the electrolyte, because the actual current density on tips of the pores is always larger and not well defined [77]. Additionally, for etching of macropores, adjustment of current during the process is performed for compensation of mass transport limitation in the pores for reactants and products in order to provide formation of straight pores with constant pore diameters [22, 85].

In potentiostatic regime, one has to take into account the voltage drop in the electrolyte, cables and other parts of the electrochemical circuit. For analytical purposes, in order to compensate for such unwanted voltage

drops and non-linear current-voltage dependence of Pt/HF, and to know the potential difference applied to the interface silicon-electrolyte, reference electrodes (e.g., Ag/AgCl) placed close to the reaction site are used. These reference electrodes must be HF-stable, therefore glass reference electrodes are only applicable for low concentrated HF solutions [226].

Same as for other electrochemical processes [314,315], oscillating or pulsed voltage/current supply might be applied for enhancement of the process uniformity and etch rate by accelerating transport of reactants and products in the electrolyte [316], and can lead to more efficient photo-luminescence from the porous silicon fabricated this way [317].

In order to further enhance uniformity or etch rate of the process, additional physical impacts typically applied in electrochemical processes, such as magnetic field [318] or ultrasound [319–321], can be employed during the anodization process. Ultrasonic waves provide better transport of reactants and products from the pores and promote vertical etching [37,38,322]. Application of strong magnetic field can enhance uniformity or direction of pore growth and improve photoluminescence of porous silicon fabricated this way [2,97].

Drying of porous silicon layers after anodization and rinsing in water is a crucial step. Since porous layer of silicon may be very fragile, drying with a nitrogen gun or in a spinner can break the structure of porous silicon. Natural drying in air by water evaporation is also risky, because large capillary stress associated with the evaporation process often induces cracks or total collapse in porous silicon [1, 2, 30, 77]. In order to reduce surface tension, water-replacing liquids with lower surface tension can be applied. For example, porous silicon samples can be immersed in alcoholic solution (typically methanol or 2-propanol) subsequently after rinsing in DI-water, and then naturally dried in air. Even lower surface tension is provided by pentane, but in this case intermediate step of rinsing in, e.g., methanol is still necessary, because pentane is not miscible in water [77,323]. Other drying techniques include supercritical drying or freeze drying [297, 324–326]. Stability of porous silicon depends also on its thickness, with thicker porous layers, in general, being more susceptible to damages during drying process or further processing, e.g., oxidation.

2.6.2. Process flow for structuring with anodization process

The basic process flow of application of the silicon anodization for structuring is presented in Fig. 2.39. The process can proceed in three ways:

- at low current density, silicon is transformed into porous silicon; this sacrificial porous silicon layer is then removed, e.g., in 1 m% KOH (s. Fig. 2.39a);
- when higher current density is applied, silicon is dissolved in electropolishing regime (s. Fig. 2.39b);
- porous silicon formation and electropolishing regimes can be combined: first, porous silicon volume is formed at low current density, then the process is switched to electropolishing by increasing current density to release the porous volume; after this, removal of remaining porous silicon in KOH still might be necessary.

When the process shown in Fig. 2.39a is used, it is necessary to remove sacrificial porous silicon volume. One of the advantages of porous silicon as a sacrificial layer is that it is very reactive due to its high inner surface. Thus, weak silicon etch solutions at room temperature can be used to remove it very quickly. Typically, dilute (0.1–1 m%) anisotropic silicon etch solutions (hydroxide solutions) such as KOH, NaOH or CMOS-compatible TMAH, also in form of photoresist developers, are applied. By dissolving some silicon in TMAH solution, reduction of etch rate of aluminum can be achieved [152], which is especially useful for substrates with aluminum elements. Silicon stain etch solution of hydrofluoric acid and nitric acid in water [150] has been also used for removal of porous silicon [327]. Another approach for removal of porous silicon is to convert it to porous oxide by thermal oxidation, and then remove it in some oxide etch process [24].

After fabrication of porous silicon layer and during further processing, porous silicon layer gets natively oxidized. To remove such oxidized porous silicon with alkaline solutions, an intermediate HF-dip can be necessary.

During the etching of porous silicon, hydrogen bubbles are formed and can hinder further reaction. Addition of ethanol helps to solve this problem [38].

When the process with sacrificial porous silicon (s. Fig. 2.39a) is used, the roughness of the surface remaining after the process is influenced, on the one hand, by the process parameters (e.g., current density, s. Fig. 2.21, or etch depth, s. Fig. 2.25). On the other hand, the process of porous silicon

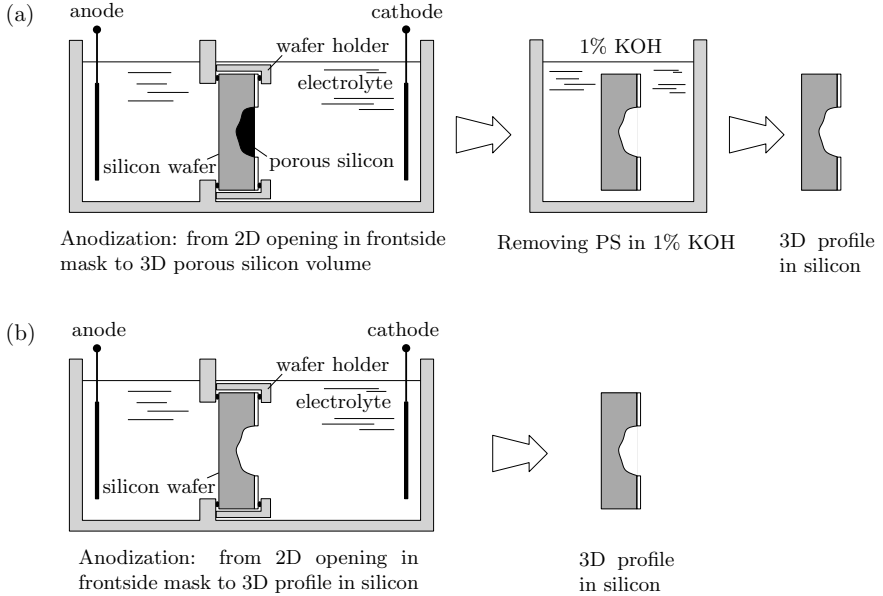


Figure 2.39.: Process flow of structuring silicon wafer by anodization: (a) with sacrificial porous silicon; (b) in electropolishing regime; backside doping of the substrate is not shown.

removal in weak KOH or other etchant can induce additional roughness [4]. The effect is more pronounced for concentrated KOH with concentration over 30 %. Such concentrated etchants, although rarely used for removal of porous silicon, might be necessary for etching porous silicon with low porosity [328].

2.6.3. Shape control in anodization process

The principle of shape control during the anodization process is based on localization of electrical and chemical access to the silicon substrate (s. Fig. 2.40). Chemical and electrical localization of the anodization process is achieved with such techniques as surface masking films, surface and volume doping, etc. Typical localization techniques are reviewed in this section.

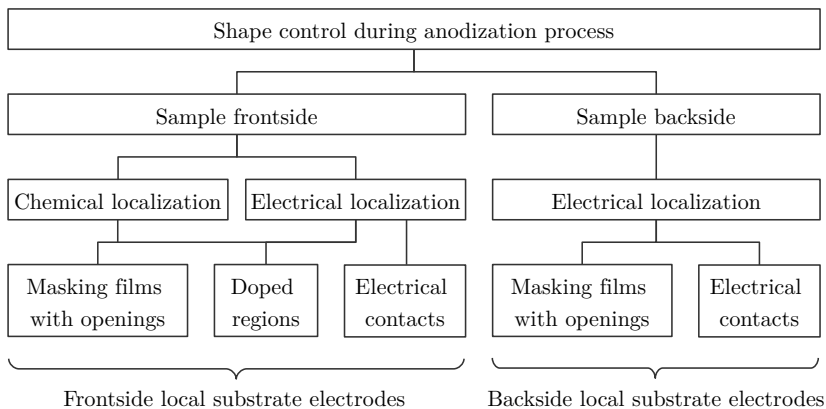


Figure 2.40.: Shape control in anodization process by chemical and electrical localization techniques.

2.6.3.1. Localization by surface coating (masking)

Localization by protective thin films on sample is the common technique that is used for etch processes in microelectronics technology. Openings in such films on the frontside of the substrate define a 2D layout that is transferred into – slightly bigger due to underetching – 3D form under influence of mass transport phenomena in electrolyte and electrical current distribution in the substrate. In case of electrochemical etch process, such as silicon anodization, electrical properties of a film must be taken into account as they define the current flow through the substrate, thus influencing local reaction rate of a surface electrochemical reaction that is proportional to the local current density according to the Faraday’s law of electrolysis.

There are several materials which are stable in hydrofluoric acid and can be used as protective masking during silicon anodization. Silicon nitride can be used for relatively short processes (< 1 hour depending on the silicon nitride properties, electrolyte concentration and temperature) [45, 93, 329]. Photoresist has shown to have weak adhesion to silicon during anodization process and can be used only for very short processes (< 10 min) [45, 96]. Etch rate of silicon dioxide in hydrofluoric acid is very high, so that it is hardly applicable for the anodization process [93]. As very stable protective layers carbon films, amorphous silicon carbide and, more recently, fluoropolymer films with etch rates below few ångströms per hour have

been reported [45, 329–332]. Films of noble metals such as platinum or gold are also very stable in hydrofluoric acid. However, they require some intermediate layer of, for example, NiCr to improve adhesion to silicon [5]. There are also other material stacks reported, such as polycrystalline silicon on oxide, where the poly-silicon layer remains stable to hydrofluoric acid as it is electrically isolated from the silicon substrate by the oxide layer [27]. The drawback of this solution is that the oxide layer is attacked from side by hydrofluoric acid, so that underetching of the poly-silicon film occurs. Ammonium fluoride etch mixture (AFEM, pad etch), consisting of 13.5–14.5 m% of ammonium fluoride, 32.6–33.8 m% of acetic acid, and water, has lower aluminum etch rates compared to that of hydrofluoric acid and was proposed as alternative electrolyte for anodization of wafers with aluminum structures [325].

Depending on the material used as patterned protective layer, electrical structures such as metal-insulator-semiconductor (MIS) or metal-semiconductor Schottky diode are formed and define the shape of the porous silicon volume (Fig. 2.41a-c) [45]. Insulating layers typically result in pronounced etch rate near the mask edges due to current crowding resulting in convex shapes^{xxv}, although concave shapes have been also reported [333, 334]. In some cases, conductive films have shown to solve the problem of current crowding near the mask edges and produce concave shapes as well [45].

Dimensions of the anodized regions also influence local reaction rates: smaller regions are anodized faster than the larger ones [24, 335]. This effect was applied by Mescheder and Kovacs to form 3D volumes with micro-features by 2D complex patterns of openings in a protective masking layer (s. Fig. 2.42) [224, 334, 336].

2.6.3.2. Localization by doping

The process of silicon anodization in fluoride containing electrolytes requires positive charges coming from silicon due to applied potential difference, photo-generation, thermo-generation, and tunneling. Therefore, without illumination only p-type silicon and moderately- or highly-doped n-type silicon can be anodized [13, 337], and p-type silicon in wide range of doping

^{xxv}Here the terms *concave* and *convex* refer to the shape of the silicon surface remaining after removal of porous silicon.

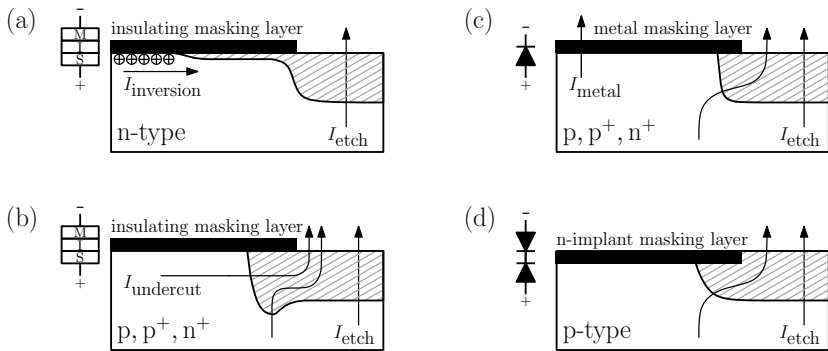


Figure 2.41.: Porous silicon shape depending on the masking material and the substrate doping: (a) insulating masking for n-type silicon; (b) insulating masking for p, p^+ , and n^+ -type silicon; (c) metal masking for p, p^+ , and n^+ -type silicon; (d) n-implant masking for p-type silicon; reproduced from Steiner and Lang [45] © 1995 with permission from Elsevier.

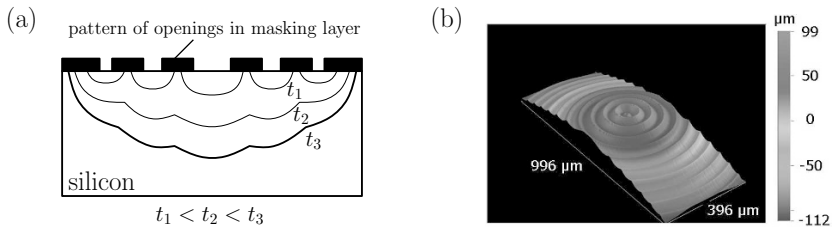


Figure 2.42.: 3D shape control by 2D complex patterns of openings in a protective masking layer: (a) principle of the technique, cross-section of silicon substrate, the lines within the silicon substrate show etch front movement during the process (reproduced from Mescheder and Kovacs [224]); (b) example of structure obtained with the technique, topographical scan (reprinted from Ivanov et al. [334] © 2011 with permission from John Wiley and Sons).

level from low-doped to highly-doped is anodized faster than moderately-doped n-type silicon [338]. Additionally, n-type and p-type regions formed in surface layers or in depth of silicon substrate create pn-junctions which can be used to block current flow (s. Fig. 2.41d) [45].

With this technique, doped regions which are anodized selectively to the substrate or doped regions working as protective layer or etch stop can be defined. Typical combinations are highly-doped p-type regions which are etched selectively to low-doped p-type regions, or p-type regions etched selectively to n-type regions. Surface n-type doped layers in p-type substrate are used the same way as protective masking layers discussed above (s. Fig. 2.41d) [12, 89, 339–343].

Doping regions can be also formed in depth by high energy ion implantation [344] or epitaxial growth of another silicon layer on top of a doped layer as shown in Fig. 2.43 [14, 63, 344].

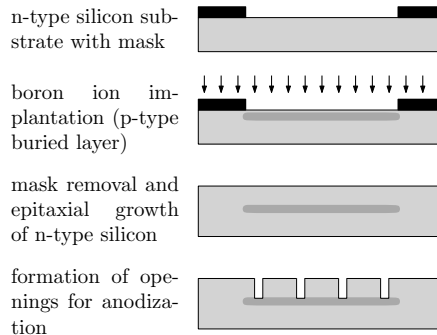


Figure 2.43.: Process flow to form a buried p-type silicon region in n-type substrate.

2.6.3.3. Other localization techniques

Similarly to the localization by doping, resistivity of silicon can be increased a few orders of magnitude with hydrogen ion implantation (HI-PS) and subsequent annealing [92, 345–349].

Additional shape control can be achieved by defining local electrical contacts on the backside or frontside of the substrate without chemical access (electrical backside/frontside localization). The idea is that porous silicon formation front is following the current lines. Then, with the help of local backside contacts, a current focusing can be achieved [62]. This way high

lateral porous silicon formation rates are possible for underetching the functional structures (s. Fig. 2.44). In a case of wet backside contact, when electrical contact to the backside is provided through electrolyte, local backside contacts can be defined with formation of local highly-doped p-Si regions on the backside of a highly resistive p-Si substrate [75]. With these highly-doped regions, local electrical contacts between electrolyte and the backside of the substrate are achieved, whereas remaining low-doped regions of the substrate form reversed biased Schottky contact to the electrolyte [89].

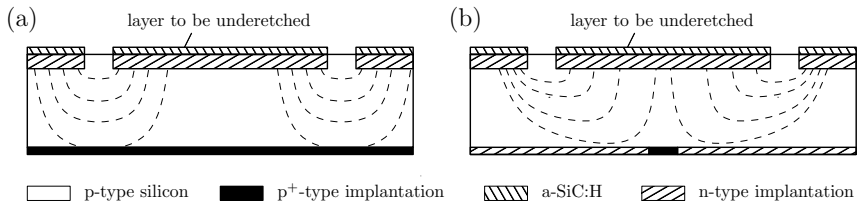


Figure 2.44.: Current focusing: (a) wafer cross-section with full area backside contact (no current focusing); (b) wafer cross-section with local backside contact for current focusing; thin lines show the equipotential lines (etch fronts); reproduced from Zeitschel et al. [62] © 1999 with permission from Elsevier.

2.6.3.4. Conclusions

The above listed shape control techniques can be also combined. According to the diagram (s. Fig. 2.40), all these localization techniques include an electrical component. Localized regions on the substrate with electrical contact to the substrate, such as the local backside contact in Fig. 2.44b, will be denoted in the work as *local substrate electrodes* (further in text: *local electrodes*). To make an overview of shape control techniques by process localization in electrochemical etching of silicon complete, there are also *local electrolyte electrodes* used in ECM or EDM as tool-electrodes (s. sec. 2.2.3.2). As a rule, in this work electrodes are called *local* if they directly define the shape of the etch form, e.g., have dimensions comparable to the dimensions of the etch form.

In contrast to *local substrate electrodes*, there might be also undefined electrical contacts of electrolyte and the substrate covering entire area which is

much bigger than the resulting etch form. Such electrodes will be denoted as *global substrate electrodes*. An example of backside *global substrate electrode* is wet contact of substrate backside with electrolyte, when the full backside of the highly resistive substrate is highly doped or highly-conductive substrate is used, and there are no masking films on the backside (s. Fig. 2.44a). To complete the classification of global and local electrodes, platinum electrodes typically used to provide electrical supply in case of double-tank anodization cell for anodization of full wafers will be called *global electrolyte electrodes* (s. Fig. 2.38).

2.6.4. Structuring by pore formation (*sacrificial porous silicon*)

Typically, microporous or mesoporous silicon with sponge-like morphology and pore size not exceeding few tens nanometers is used as sacrificial layer. Thick layers of such material can be quickly formed (in comparison to other typical sacrificial layers, such as silicon dioxide) and removed (due to very high reactivity provided with large inner surface). Additionally, the surface remaining after removal of porous silicon has a roughness in the order of pore size, thus allowing fabrication of optical and fluidic microcomponents with high surface quality. Main applications of porous silicon as sacrificial layer are described in this section.

One of the basic applications of sacrificial porous silicon is for etching cavities of different shapes in silicon substrate. Porous silicon in this case is just a by-product of the etch process. Various applications of sacrificial porous silicon for structuring have been proposed. Lang et al. [5] used sacrificial porous silicon to form flow channels. Undercutting of the mask was reduced by using heavily-doped p-type or n-type substrates with resistivities of $0.2 \Omega \text{ cm}$ and $0.01 \Omega \text{ cm}$, respectively, and a metal mask. Joubert et al. [311] applied sacrificial silicon to form $75 \mu\text{m}$ deep pseudo-V-shaped grooves used for positioning of optical fibers in silicon integrated optical circuits. Vitantov et al. [327] reported on application of sacrificial porous silicon to form channels in silicon substrates for buried-contact silicon solar cells.

Another useful application of sacrificial porous silicon is to fabricate free standing mechanical elements. In this case cavity, remaining after removal of the sacrificial layer, provides mechanical isolation of free standing elements from the substrate. This way, suspended beams or masses for various MEMS devices, such as force sensors, accelerometers, and gyroscopes, are fabricated [8, 10, 13, 350–353].

Deep cavities are also necessary to isolate functional free-standing elements thermally or electrically. Thermal isolation is an important issue for temperature-sensitive sensors or sensors working at elevated temperatures, such as bolometers, gas sensors or mass flow sensors [21, 24, 45, 354–357]. Electrical isolation with sacrificial porous silicon layer is applied for fabrication of RF semiconductor devices [358–360].

Some applications of sacrificial porous silicon in microelectronics were reviewed by the author elsewhere [361] (to be published).

2.6.5. Structuring by electropolishing

Advantage of using electropolishing regime for structuring of 3D forms in silicon substrate is that the resulting cavities have very good surface quality which is sufficient for optical and fluidic applications.

Kleimann et al. [29] applied electropolishing to create quasi-3D microstructures in form of protrusions such as needles, columns or tubes (s. Fig. 2.45a). The process localization is based on the SCR pore formation mechanism: with pre-structuring of a silicon substrate surface, a space charge region depleted from holes is formed, thus blocking the anodization there (s. Fig. 2.45b).

Another approach to use anodization for structuring is to switch between pore formation and electropolishing regimes. This way, a sacrificial porous volume can be removed from the cavity, or left as an intermediate layer. Tjerkstra et al. have used such combined process to create multi-walled microchannels with intermediate porous silicon wall for micro total analysis systems (μ TAS) and gas chromatographs [47, 362]. Similar approach was used by Kaltsas et al. to form buried microchannels, where a top porous silicon layer formed at the beginning of the process was used to seal the channel [363].

Lammel et al. [30, 31, 364] used pore formation with subsequent electropolishing to fabricate a free-standing tunable interference filter for a microspectrometer. First, a 1D photonic crystal was formed in pore formation mode by modulating current density (s. Fig. 2.46a). Then, the formed photonic crystal was released from the substrate with electropolishing and subsequent removal of the masking material. For support arms of the structure, anodization was done through a perforated mask, which resulted in non-uniform porosity in depth in these regions. During oxidation of the

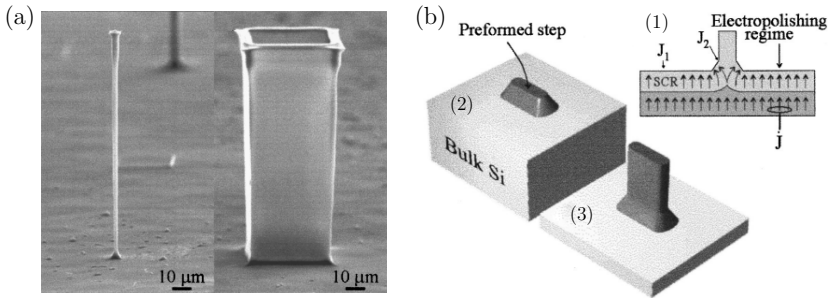


Figure 2.45.: Microstructures formed in electropolishing mode: (a) SEM micrographs; (b) schematic illustration of the principle, where (1) is the cross-sectional view showing etching current line bending due to the electrical field in the SCR and the conditions for stable microstructure formation (with J_1 in the electropolishing range and $J_2 = 0$), (2) is the starting structure (n-type silicon with preformed step), and (3) is the vertical structure formation by electropolishing flat parts; reprinted from Kleimann et al. [29] © 2001 with permission from AIP Publishing LLC.

structure in the final steps, this non-uniformity caused desired lift-up of the whole structure (s. Fig. 2.46b).

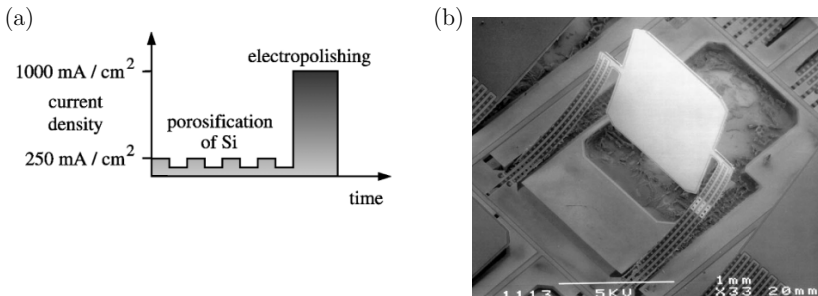


Figure 2.46.: Free-standing tunable interference filter for microspectrometer [364]: (a) schematic diagram of current density during the phases of porosification and electropolishing of silicon; (b) SEM micrograph of a resulting structure; reprinted from Lammel et al. [364] © 2001 with permission from Elsevier.

2.7. Macroscale models of silicon anodization for structuring

In order to use a process for structuring, i.e., formation of cavities of a specific 3D shape, it is important to be able to predict behavior of the process. For this, knowledge about the process, such as design rules, description of definite cases or models describing etch front movement, etc., are necessary.

As was shown above in this chapter, the process of electrochemical etching of silicon is a rather complicated process featuring:

- two regimes of reactions, resulting in pore formation and electropolishing;
- mass transport of reactants and reaction products in electrolyte;
- mixed polarization dependence resulting in tertiary current distribution;
- additional influence of porous layer on mass transport phenomena in pore formation regime;
- complex dependence of results on the process parameters.

There are multiple models describing the process of silicon anodization on the microscale, which to some extent manage to explain formation of pores of various size and shape, predict their influence on the process parameters and explain polarization curves and oscillation mechanisms (s. sec. 2.4.2.5). In contrast, little effort was done so far to describe the macroscopic behavior of the process needed for practical 3D structuring.

2.7.1. Charge flow models - primary and secondary current distribution

One of the basic ideas to describe the etch front movement (i.e., etch rate) in this electrochemical process is based on consideration of charge flow through the anodization cell with electrolyte and silicon substrate. In this case, only resistivities of the electrolyte and substrate are taken into account for calculation of charge flow at the applied potential, and etch front velocity is considered to be proportional to the local current density according to the Faraday's law. This way, the current crowding induced with insulating frontside mask [333,365] and the current-focusing technique to enhance lateral etching were explained qualitatively [62] as reviewed briefly below.

Kim et al. [333] studied shape of etch forms anodized with an insulating silicon nitride mask. In the resulting semi-spherical shapes, they observed

“primary undercutting”, that is lateral widening of a structure under the mask edge, and “secondary undercutting”, that is etching of the substrate in the surface layers under the mask, causing the mask to pile-off. Both effects have been explained with the current crowding. The primary undercutting was due to general flow of holes from big-area backside to small-area opening in the mask. The secondary undercutting was explained with the field-effect causing charges to accumulate near the interface between the mask and the substrate on the frontside, resulting in the promoted etching there. The model of current density distribution of holes in the substrate was calculated in the device simulator SILVACO (modules Athena and Atlas). Based on both the modeling and experimental results, Kim et al. concluded that the current crowding is significantly less for low-resistive p-type substrates. The model described by the authors showed only potential distribution in silicon substrate for the beginning of the process, i.e., for a flat initial etch front at etching time $t_{\text{etch}} = 0$, thus it could not be applied to simulate real 3D etch forms resulting from anodization.

Mescheder et al. [335,365] have used a similar approach to simulate the current density distribution of holes with another semiconductor device simulator TMA Medici for 2D cases and TMA Da Vinci for 3D cases. In their model the resistivity of electrolyte was not taken into account, and the model consisted of a low-doped silicon substrate with two metal electrodes connected to its frontside and backside (s. Fig. 2.47b), where the frontside electrode represented the contact silicon-electrolyte (s. Fig. 2.47a). This frontside contact was defined as Schottky contact [89]. The simulations showed that the current crowding is responsible for the experimentally observed convex shapes (s. Fig. 2.47c). Effect of local backside contacts on etch form could be also shown qualitatively. Again, the models simulated only the current density distribution for the initial state of the process, thus no etch form development was shown with the model.

Later, application of the Medici program described in [335] was further extended by the author of this PhD in his master thesis work [366]. There, qualitative results for conducting masks under consideration of various work function values for the masking material and the electrolyte have been obtained [367]. It was demonstrated that the ratio between the work function values of the electrolyte and the masking material, i.e., the electrical properties of the contacts mask-silicon and electrolyte-silicon, define the resulting shape (convex or concave) (s. Fig. 2.48a). Additionally, an attempt to simulate the process for $t_{\text{etch}} > 0$ with another static model has been performed. It was shown that even if the etch form develops concave in the beginning

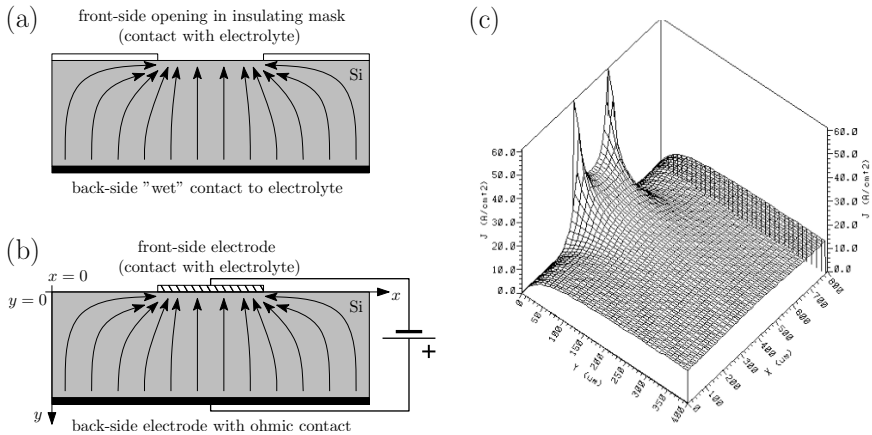


Figure 2.47.: Secondary current distribution model of the etch form in the anodization process: (a) cross-sectional view of experimental setup - substrate with insulating masking layer on its frontside with opening; (b) the 2D model; (c) typical resulting hole current density distribution as surface for the 2D model (Ivanov 2005, unpublished).

of the anodization process, later it converts to a convex form (s. Fig. 2.48b). The disadvantage of the used approach was that the models for both cases ($t_{\text{etch}} = 0$ and $t_{\text{etch}} > 0$) were still static models, and no real etch front movement could be simulated. Therefore, the results could only be taken with caution, although to the moment of that work, these qualitative results confirmed experimental results, where only convex shapes could be obtained for insulating and metal masks.

Kröner et al. [368] have developed a dynamic electrical finite element model (FEM) in ANSYS. Development of anodization forms through simple openings with axial symmetry, such as circles and rings, was shown and fitted to experiments. Growth of convex etch forms, transformation of convex forms to concave, influence of neighboring openings on each other and development of etch forms for local backside contact configurations could be demonstrated. However, the chosen resistivity values for the substrate and electrolyte were rather controversial. Current density dependent porosity and valence in pore formation regime have been also not considered. Additionally, application of general ANSYS software required great effort of

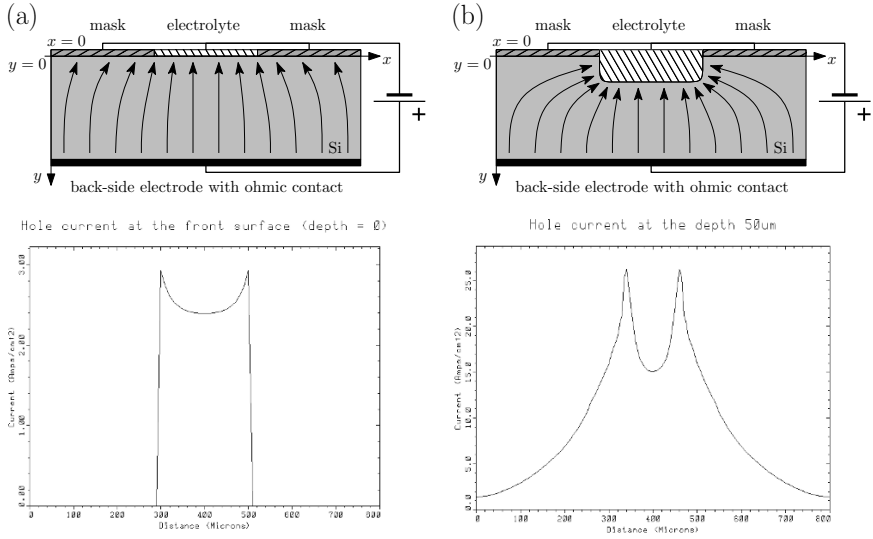


Figure 2.48.: Secondary current distribution model of the etch form in the anodization process with conductive mask for (a) $t_{\text{etch}} = 0$ and (b) $t_{\text{etch}} > 0$ (concave etch form with depth 50 μm), reproduced from Ivanov [366].

scripting to describe the etch front movement, which seems to be not practical.

To conclude on primary and secondary current distribution models, although they neglect mass transport limitation mechanisms in the electrolyte and the porous media, they can show quite good (at least, qualitative) results for etch form development for the anodization process in pore formation regime, where the process is considered to be limited by the charge transfer at the interface silicon-electrolyte, and not by the transport of ions in electrolyte. Additionally, in secondary current distribution models, activation polarization provides a stabilizing effect for the current distribution, therefore more smooth shapes are achieved than with primary current distribution models [254].

2.7.2. Mass transport and tertiary current distribution models

For the process of silicon anodization, especially in electropolishing regime, mass transport phenomena are proposed to play an important role (s. sec. 2.4). Therefore, it can be expected that in this case a tertiary current distribution model is necessary in order to describe etch front movement. To the best of our knowledge, there are no such macro-scale models, so far, which could show etch form evolution during the anodization process. However, some ideas can be taken from models available for other (electro-)chemical processes and microscale models of the anodization process as described below.

2.7.2.1. Models of chemical etching

Mass transport phenomena have been considered in macroscale models of chemical dissolution in diffusion-controlled regime [144, 145, 369–371]. The transport of species is described there according to the Fick's law of diffusion (s. Nernst-Planck equation (2.12) in sec. 2.3.2.3 in the absence of electric field). This way, a typical etch form development for etching through a mask could be demonstrated (s. Fig. 2.2b,c): In a diffusion-limited process, in the beginning, there is a higher supply of reactants to the reaction site near the mask edges, that results in higher etch rate near the mask edges (convex shape). Later in the process, when the etch form gets deep enough, the shape transforms to a concave.

Chemical polishing of silicon in a mixture of an oxidizing agent (nitric acid) and an oxide-etching acid (hydrofluoric acid) was analyzed and modeled by Kulkarni et al. [372, 373]. Two-phase model was proposed, where reagents diffuse through a liquid film in the interface of electrolyte-silicon. This layer is called “exhausted layer” and is also known as the concentration boundary layer of the mass transport film. Optimal conditions for polishing and influence of extrinsic bubbles (introduced to the solution during the process) and intrinsic bubbles (formed in the dissolution reactions) have been worked out.

2.7.2.2. Microscale models of silicon anodization

As was partly covered in sec. 2.4.2.5, there are multiple microscale models of silicon anodization process aimed on simulation of surface roughness, pore

morphology or polarization curves. Some aspects of these models can be as well applied for a macroscale model of interest.

Cattarin et al. [284] have discussed the steady-state electrodisolution current density (the plateau current density) in electropolishing regime. In this regime, the anodic oxide dissolution rate is in equilibrium with the anodic oxide formation rate, which is directly proportional to the applied current density. Three paths of silicon dioxide dissolution were considered, involving either HF or HF_2^- separately, or a combination of both, with a second order kinetics. It was assumed that fast equilibrium exists for the dissociation reactions (s. sec. 2.3.2.2) both in the diffusion layer near the reaction site and in the bulk solution. For simplification, the concentration of hydrogen ions H^+ was assumed to be constant everywhere, because the model referred to buffered solution. Equal diffusion constants for F^- , HF, and HF_2^- were assumed. The total current was the sum of the currents of the three proposed dissolution reactions. Then, with experimentally found value of the dissolution valence of 3.6, a dependence of the steady-state current density in electropolishing regime on total fluoride concentration, pH, and mass transfer rate were derived and found to be in good agreement with experiments. In their later work, Cattarin and Musiani [292] have extended their study to HF:water:ethanol electrolytes. Addition of ethanol was shown to change anodization current in the whole anodic range (pore formation and electropolishing). It was proposed that this change could be due to the changed dissociation equilibria in the solution with ethanol (s. sec. 2.3.2.2) and (for the electropolishing region) due to change in the kinetic constants for the process of anodic oxide dissolution.

Liu and Blackwood [227] have analyzed the electropolishing regime of silicon anodization in the first plateau for p-type silicon of various resistivities in HF electrolytes of concentration in the range 0.01–15 m%. As in the work of Cattarin et al. [284], direct dependence of current density on dissolution rate of anodic oxide was assumed. However, the anodic oxide was considered to be hydrated oxide ($\text{SiO}(\text{OH})_2$) which dissolution involved only the undissociated HF molecules. The dissolution valence of 3.5 was applied. As a result, an expression of anodic oxide dissolution rate as a function of amount concentration of undissociated HF molecules was derived.

2.7.2.3. Macroscale models of other electrochemical processes

Electrochemical dissolution of metals was modeled for various applications, such as dissolution through a mask [374–377], replication with ECM [378],

ECM for drilling [166,379], micro-machining with electrolytic jet [380], electrochemical formation of micropins [381], wire-ECM [382], ECM with ultra-short pulses [383], general considerations on electrochemical forming [384], etc.

In the COMSOL MultiphysicsTM software applied in the work for calculation of FEM models of the anodization process, there is a module specifically designed to simulate electrodeposition problems (electrodeposition module), and recently introduced a module for electrochemical dissolution problems (corrosion module)^{xxvi}. In the electrodeposition module, there is an example of a model of copper electrodeposition in a trench, which can be as well used to model the opposite process of copper dissolution. However, application of the model to silicon anodization requires complete revision of the parameters, equations, and reactions.^{xxvii}

To conclude, first attempts on building charge-flow models have been made. However, to the best of our knowledge, no systematic analysis and comparison to experiments were done. In this work, among other goals, primary and secondary current distribution models for silicon anodization through an opening in a frontside mask are developed and compared to experiments.

2.8. Conclusions on state of the art

In this chapter, state of the art on silicon anodization process, with emphasis on its application as a structuring technique, has been given. Overview of other structuring techniques for silicon has been also done, and theory and technology of silicon anodization process were discussed in detail.

Based on this literature research, the following conclusions could be drawn:

^{xxvi}As confirmed by the representatives of the software, the modules do not differ from each other in theoretical backgrounds. In the work the electrodeposition module was used as the one available to the author.

^{xxvii}It is important to note that in general, although such software, as COMSOL MultiphysicsTM, includes all typically used equations for mass and charge transfer phenomena, all reactions and parameters for specific process have to be defined by a user. Thus, the role of the software in this case is only to minimize low-level programming for calculations and coupling of various differential equations in the time dependent environment of deforming mesh. This way, more attention can be paid to underlying theory.

- There are multiple structuring techniques for silicon to form 3D shapes. However, every technique has its own limitations and drawbacks. Thus, with further advancement, silicon anodization can deserve its place among other structuring techniques.
- Various applications of silicon anodization as a structuring technique have been published. However, only few of them could develop themselves from laboratory-scale to industrial implementation, presumably due to low reproducibility of the result. Development of a macroscale model of the anodization process could simplify application of the process for specific application-oriented structures.
- The multitude of parameters significantly influencing the process on the microscale makes comparison of experimental results from different research groups difficult, revealing some inconsistencies between the results. Therefore, it seems to be unavoidable to verify the data with own experiments.
- Although there were some attempts to simulate partially the process on the macroscale, no systematic and quantitative comparison to experiments was done so far.

These conclusions, together with the research goals dictated by the research projects, in which the author was employed, with their specific technical and economical limitations, defined the goals and set the limits of this work:

- study of the influence of current density, electrolyte composition, and wafer doping level on the etch rate, porosity, dissolution valence, and interface roughness; this study is limited due to the following considerations:
 - only p-type silicon is studied, as the one readily providing etching of microporous/mesoporous silicon that was applied (out of the scope of this work) for fabrication of 1D photonic crystals, and is more suitable for application as a structuring technique;
 - in the pore formation regime, only one electrolyte (1:1 (50 m% HF):ethanol) was applied, because this electrolyte has already proved (with external and internal studies) to be very suitable for generation of uniform micro- and mesopores;
 - in general, the number of data points, i.e., single anodization experiments, studied was limited from the point of financial and time resources available to specific projects.

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- investigation of etch front movement in anodization process for various localization techniques; as the main test structure, silicon substrate with a frontside insulating masking with a circular opening was selected as rather simple, but not yet studied in detail for silicon anodization process;
 - simulation of the etch front movement in a macroscale time-dependent models with primary and secondary current distributions, using the experimentally obtained parameters for porosity and dissolution valence, and comparison of the results to experiments.

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