



DIPLOMARBEIT

FIB Generated Nanowires for CMOS Compatible pH Sensor

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Abstract

Over the past decade, one-dimensional nanostructures have been proven as powerful building blocks in active nanometer-scale devices. Aside from carbon nanotubes, nanowires (NWs) are one of the most promising approaches considered for scaling down optic-, electronic-, magnetic- and sensor devices.

Nanowires are usually fabricated using either a top down or a bottom up strategy. The former technique is extremely flexible, but suffers from limitations in minimum feature size and uniformity. The latter one, utilizing spontaneous self-ordering effects, is limited by the broad size distribution and the lack of control of the positioning of the self-organized nanostructures. In particular resist-less focused ion beam (FIB) techniques are most suited for the combination of top-down structuring with selective bottom-up self-assembling techniques. One of the most recent topics in FIB-solid interaction is the evolution of self-organized nanoscale pattern on solid surfaces. The diameters of these nanostructures are comparable to the sizes of biological and chemical species, and thus intuitively represent excellent primary transducers for producing signals that ultimately interface with macroscopic instruments.

The FIB based approach for synthesis of nanowires, based on a model similar to VLS with gallium (Ga) acting as catalyst, on germanium (Ge), on gallium antimonide (GaSb) and on pure antimony (Sb) substrates is discussed. The influence of the ion beam-substrate incidence angle on the surface evolution in the case of Ge and GaSb is shown. The surface evolves from the sponge-like into the wire-like form according to an incidence angle change.

Additionally, the Sb surface response on FIB is investigated in detail. Energy-dispersive X-ray spectroscopy (EDX), Transmission electron microscopy TEM (HRTEM) and Raman investigations were performed to gain information about the chemical compound, crystal structure and the composition of the Sb nanowires. The Raman investigation showed that the FIB assisted grown Sb nanowires consist of Sb with a thin oxide shell. TEM and HRTEM analysis showed that the as-grown nanowires are amorphous.

FIB generated nanowires which are annealed for 30 minutes at 180°C in air are recrystallized and can be used as a chemically stable electrode for a pH measurement device.

The application of a FIB generated Sb nanowire network as a microscale pH sensing electrode is explored. The CMOS compatible fabrication method and the pH measurement is shown. The measurements showed linear relationship between electromotive force (e.m.f.) and the pH scale (pH 2 to pH 10).

Kurzfassung

In den letzten Jahrzehnten haben sich eindimensionale Nanostrukturen als leistungsfähige Bauelemente in aktiven Nanobauteilen erwiesen. Gemeinsam mit Nanotubes bieten Nanowires (NW) die vielversprechendsten Ansätze für Miniaturisierung von optischen, elektrischen, magnetischen und Sensorbauteilen.

Nanowires werden üblicherweise durch das "Top-Down" oder das "Bottom-Up" Verfahren hergestellt. Erstere Methode zeichnet sich durch extreme Flexibilität aus, stößt aber bei Miniaturisierung und Uniformität schnell an ihre Grenzen. Die zweite Methode hingegen bedient sich spontaner Selbstordnungsprozesse, ist allerdings in Hinblick auf gezieltes Wachstum (Position, Dicke, etc.) eingeschränkt. Resist-less Focused Ion Beam (FIB) Techniken sind besonders für die Kombination von „Top-Down“ Strukturen mit selektiven, selbstordnenden „Bottom-Up“ Methoden geeignet. Die Entwicklung von selbstorganisierenden Strukturen im Nanobereich auf Festkörperoberflächen ist daher ein aktuelles Forschungsgebiet der FIB-Oberflächen-Wechselwirkungen. Da sich die Durchmesser dieser Nanostrukturen in der Größenordnung von biologischen und chemischen Proben befinden, stellen Nanowires hervorragende Bindeglieder zwischen mikroskopischen Strukturen und makroskopischen Messgeräten dar.

Im Rahmen der vorliegenden Diplomarbeit wird die auf FIB basierende Synthese von Nanowires auf Germanium (Ge), Gallium Antimonid (GaSb) sowie auf reinen Antimon (Sb) Substraten untersucht. Dabei kommt ein VLS (vapour-liquid-solid)-ähnliches Modell mit Gallium (Ga) als Katalysator zur Anwendung. Es wird gezeigt, dass die Beschaffenheit der Oberfläche bei Ge und GaSb maßgeblich vom Einfallswinkel des Ionenstrahls abhängt, wobei sich die Oberfläche von einer schwammartigen in eine Nanowire-artige Struktur umwandelt.

Zusätzlich wird die Reaktion der Sb-Oberfläche auf die Einwirkung des Ionenstrahls untersucht. Um Informationen über chemische Zusammensetzung, Kristallstruktur und Aufbau der Sb-Nanowires zu erhalten, werden Energie-dispersive Röntgenspektroskopie (EDX), Transmissionselektronenmikroskopie TEM (HRTEM) und Raman Spektroskopie verwendet.

Durch Annealen an Luft für 30 Minuten bei 180°C rekristallisieren die mit der FIB Methode hergestellten Nanowires, welche als chemisch stabile Elektroden für pH-Messungen eingesetzt werden können. Die Anwendung von einem Netzwerk von FIB-generierten Sb-Nanowires als eine Elektrode für pH-Wert-Messungen im Mikrobereich sowie die CMOS Kompatibilität dieser Fabrikationsmethode wird im Folgenden gezeigt. Wie die Messungen beweisen, besteht zwischen der elektromotorischen Kraft und der pH-Wert-Skala (für pH-Werte von 2 bis 10) ein linearer Zusammenhang.

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Hvala mama i tata, bez vase vjere u mene, vase beskrajne ljubavi i podrške nista ovo ne bi bilo moguće.

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1 Introduction

The fabrication and characterization of one-dimensional nanostructured materials such as nanowires, nanorods, nanobelts, and nanotubes has attracted much interest due to their novel physical properties (quantum size effects) which differ from those of bulk materials. These nanostructures, and in particular the nanowires, have found the application as interconnect and functional units in electronic, optoelectronic, electrochemical, thermoelectric, and electro-mechanical nanodevices.

The nanowires were discovered decades ago and many different approaches for their fabrication have been proposed. Since the conventional *Top-Down* approach suffers from limitations in minimum feature size and uniformity, the development of new methods for nanowire fabrication became the main subject of interest for the researchers.

The *Bottom-Up* approach, in particular the Vapor-Liquid-Solid (VLS) method, became a widely used mechanism for the fabrication of the nanowires, although it is limited by the broad size distribution, the lack of control of the positioning of the self-organized nanostructures and high temperatures. Nanowire growth based on VLS mechanism utilizes various metals as catalysts for nanowire growth. The liquid alloy cluster serves thereby as a preferential site for the adsorption of reactant from the vapor phase and, when supersaturated, as the nucleation site for crystallization¹.

A FIB based approach for nanowire growth, that is most suited for the combination of top-down structuring with selective bottom-up self assembling techniques, is presented in this thesis. In contrast to the VLS approach, FIB induced growth of nanowires requires no additional material source, and the growth is initiated at room temperatures.

As nanowires show up a high surface-to-volume ratio the impact of the ambient atmosphere on the conducting behavior is extreme. The diameters of these nanostructures are comparable to the sizes of biological and chemical species being sensed, and thus intuitively represent excellent primary transducers for producing signals that ultimately interface with macroscopic instruments. Additionally, nanostructure based sensors exhibit a fast response with a substantially higher sensitivity and selectivity than polycrystalline

and crystalline bulk film based sensors. Therefore they are ideal functional modules for all kinds of sensors.

FIB induced Sb nanowires are therefore ideal candidate for sensor applications. Antimony has a remarkable linear response to the H^+ concentration in a solution and it is applied for commercial pH electrodes^{2,3}. Unlike conventional glass tube-based pH electrode, the solid-state Sb electrode represents a good candidate for an integrated pH sensor with a fabrication process that is compatible to the silicon-based complementary metal oxide semiconductor (CMOS) process. In addition, due to its high resistance to corrosion, macroscopic Sb-based pH electrode has been used in a wide range of applications. For instance, the Sb electrode withstands hydrofluoric (HF) acid and allows reliable determination of the proton concentration in HF-containing solution in which a glass electrode normally cannot be used. Moreover, the Sb electrode has demonstrated effectiveness in clinical operations. It has been utilized to determine the intramyocardial pH during open-heart surgery⁴, the ambulatory esophageal pH⁵, and dental plaque pH⁶. In addition, by coating with suitable enzymes, the Sb electrode functions as a potentiometric enzyme electrode that can be used to determine the concentration of urea⁷. Because of its versatile sensing applications, a Sb probe on a size scale compatible to cells has great potential for meeting the demands of biomedical research⁸. The *in vivo* and *in vitro* intracellular real time monitoring of pH⁹, Na^+ , K^+ - a key subject in cell biology and physiology - may require nanoscale electrodes in close contact with cells.

2 Fundamentals

2.1 Focused Ion Beam System

The focused ion beam (FIB) systems have gained wide spread use in fundamental materials studies and technological applications offering both high-resolution imaging and flexible micromachining in a single platform.

The FIB instrument is similar to a scanning electron microscope (SEM), except that the beam that is rastered over the sample is an ion beam rather than an electron beam. Secondary electrons are generated by the interaction of the ion beam with the sample surface and can be used to obtain high-spatial-resolution images.¹⁰

In conjunction with SEM as well as a variety of add-on tools (micromanipulators, gas-injection systems, spectroscopic and crystallographic analysis tools), the FIB can be used for prototyping of devices, failure analysis and debugging, *in situ* characterization, or as a sample preparation tool for other analyses.¹¹

The typical FIB consists of a high vacuum system, an ion column with a liquid metal ion source, a sample stage, a secondary electron detector, a gas delivery system and the respective controller unit.¹² (see Figure 1)

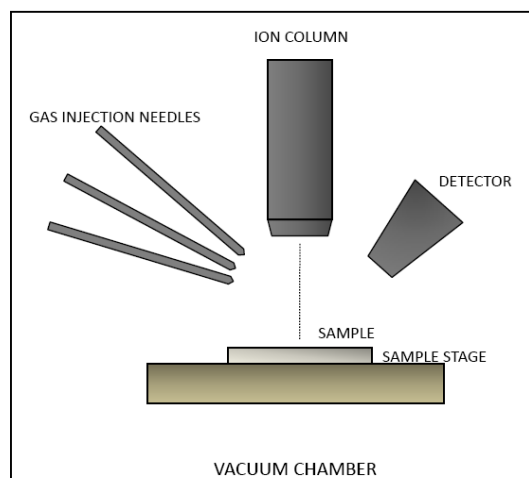


Figure 1. Schematic diagram of a basic FIB system.

2.1.1 Vacuum System

The vacuum system is required to ensure a safe and reliable operation of the instrument. Since the instrument used for experiments presented in this thesis (CrossBeam Neon40) combines a high resolution SEM, and a FIB the vacuum system of the instrument has to satisfy the following requirements:

1. The pumping system must be free of vibrations to ensure the high-resolution capability in the sub nm range of the SEM.
2. The vacuum system must be oil free to avoid sample contamination during SEM or FIB processing.
3. The vacuum system must be able to handle aggressive gases for gas assisted etching or deposition processing.

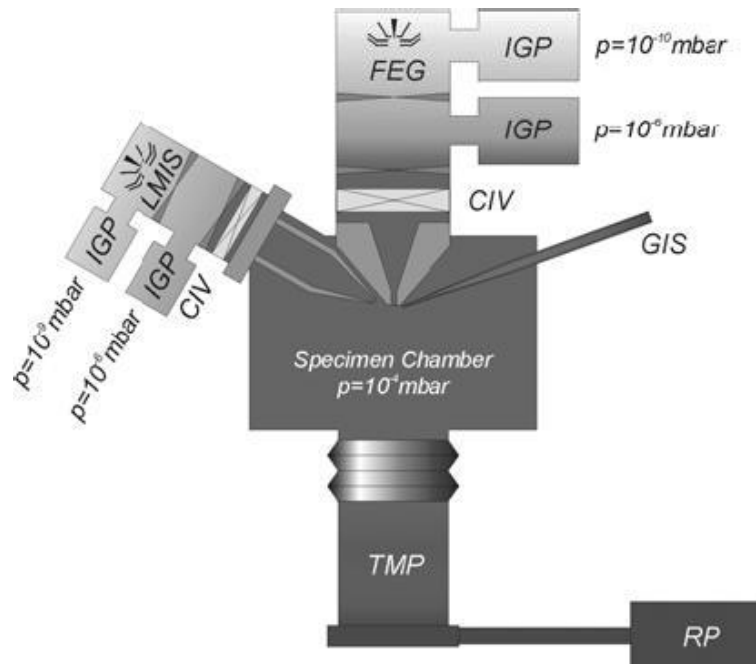


Figure 2. The vacuum system of the CrossBeam® (taken from Ref.13).

Figure 2 shows the schematic of the vacuum system of a CrossBeam® system. The SEM column and the FIB column consist of three pressure regions that are separated by two pressure limiting apertures. The vacuum in the range of about 10^{-10} mbar in the field emission gun/liquid metal ion source (FEG / LMIS) area and the upper part of each column

are maintained by two ion getter pumps. The lower part of the column is pumped by a turbo-molecular pump (TMP) in the pressure range of about 10^{-4} mbar. Each column can be separated from specimen chamber by an automated column-isolation-valve (CIV). A gas injection system (GIS) is provided for enhanced etching, metal deposition and insulator deposition etc.¹³

2.1.2 Liquid Metal Ion Source

Within the different types of ion sources, the liquid metal ion source LMIS provides the brightest and most focused beam. There are a number of different types of LMIS sources but currently the most commonly used is a Ga-based needle source.¹⁰ Ga as the source material has advantages over other LMIS metals such as In, Bi, Sn, and Au because of its low melting point ($\sim 30^\circ\text{C}$), low volatility and low vapor pressure.

The ion source consists of a tungsten needle with a sharp tip (radius of approx. $10\mu\text{m}$) and a Ga reservoir (see Figure 3). During operation, the Ga flows from the reservoir to the needle tip. A large negative potential between the needle and an extraction electrode generates an electric field of magnitude 10^{10} V/m which leads to a deformation of the Ga film forming the so-called “Taylor cone”. For typical emission currents used in FIB microscopes (~ 2 mA), a cusp forms at the tip of the Taylor cone with a tip radius of approximately 5 nm. Because of the small dimensions of the tip, when force balance is achieved, extraction voltage can pull Ga from the tungsten tip and ionize it by field evaporation of the metal at the end of the Taylor cone. Figure 3 shows a schematic diagram of a typical LMIS.

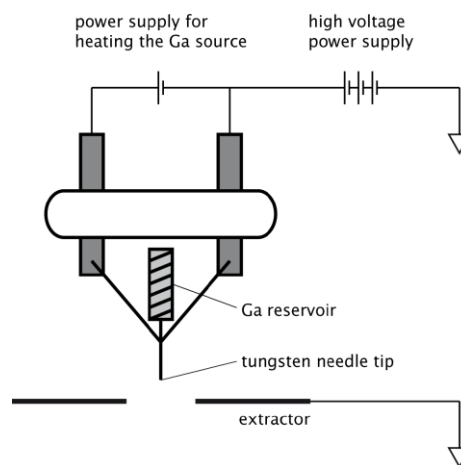


Figure 3. Schematic of a liquid metal ion source (taken from Ref.14).

2.1.3 Ion Column

The Ga^+ ions extracted from a LMIS form a divergent beam. The beam passes further the aperture of various diameters (10-400 μm) which defines the beam size and provides a range of ion currents that may be used for different applications. For the CrossBeam Neon40, ion beam currents can be varied from 1 pA to 50 nA. After the aperture the beam enters an electrostatic lens system for the creation of finely formed ion beam. Optimizing the beam shape is obtained by centering each aperture, tuning the column lenses, and fine tuning the beam with the use of stigmators that ensure spherical beam profile. The size and shape of the beam intensity profile on the sample determines the basic imaging resolution and micromachining precision.

Figure 4 shows the schematic of the FIB column of Neon[®] 40EsB.

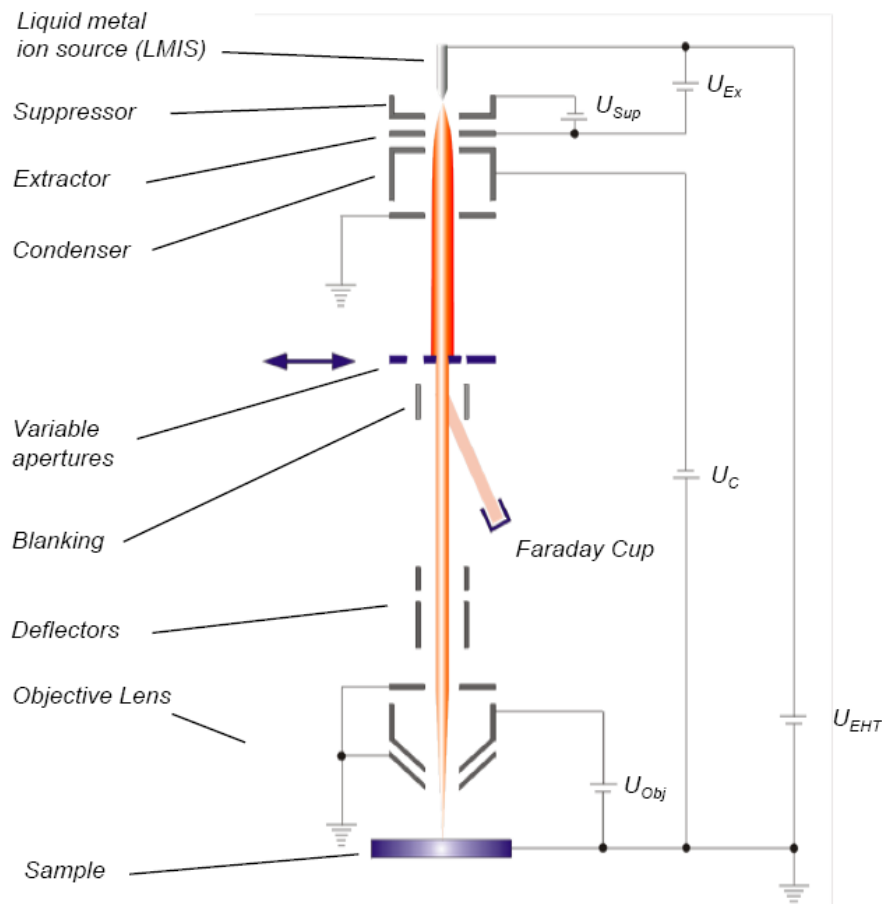


Figure 4. Schematic illustration of the ion column of the Neon[®] 40EsB (taken from Ref.15).

2.1.4 Gas Delivery System

By using a FIB together with a gas injection system (Figure 5.), it is possible to remove materials (etching) using aggressive gases such as XeF_2 , Cl_2 or to deposit materials such as tungsten. At the Neon[®] 40EsB there are 5 injection needles available for the gas injection system. The injection needles are motorized enabling operator to position the needle opening as close as possible to the reaction surface.

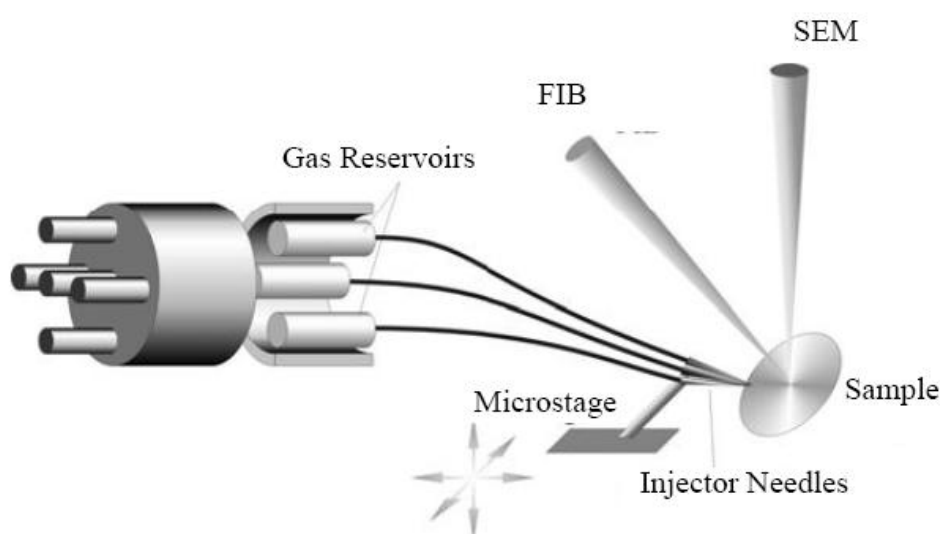


Figure 5. Schematic of the gas injection system of the Neon[®] 40EsB (taken from Ref.13).

2.1.5 Imaging Properties of the CrossBeam[®] System

Specific feature of a CrossBeam[®] system is the combination of a SEM and FIB. Thereby it is possible to use both beams simultaneously enabling SEM observation while milling. Schematic of this instrument is given in Figure 6.

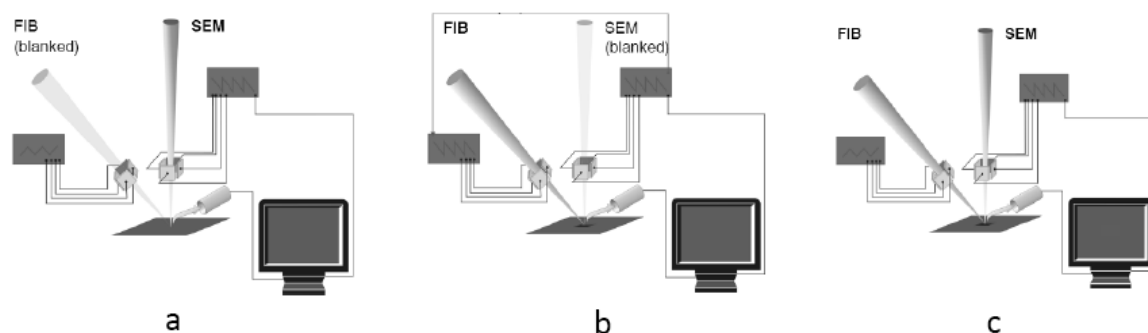


Figure 6. Imaging modes of the CrossBeam[®] system. a) SEM imaging: The ion beam is blanked and the secondary electron (SE) - signal is synchronized to the SEM scan. b) FIB imaging: The electron beam is blanked and the SE - signal is synchronized to the FIB scan. c) CrossBeam[®] operation: Both beams are scanned completely independent from each other and the SE Signal is synchronised to the SEM scan. This results in the CrossBeam[®] operation feature: The ion milling process can be imaged using the SEM in real-time (taken from Ref.13).

CrossBeam[®] system can operate at three different imaging modes¹⁶:

- SEM imaging mode (Figure 6a)

By blanking the ion beam and only using the electron beam, the system operates as high resolution field emission SEM.

- FIB imaging mode (Figure 6b)

The second imaging mode uses the ion beam while the electron beam is blanked. The FIB imaging mode can be used for grain analysis, voltage contrast imaging and for a very precise defining of the milling areas.

Typically, 1–10 electrons with energies below 10 eV are generated per incoming 5–30 keV Ga ion¹¹. Imaging resolution and the contrast depends on crystal orientation of specimen, the surface orientation, the atomic mass and on how well is ion beam focused.

On the other hand, SEM imaging strongly depends on surface conductivity. For insulating surfaces it is hard for SEM to image properly even for low acceleration voltages. For FIB imaging Ga implantation creates thin conducting layer which is suitable for imaging of non coated samples.

During FIB imaging process the destruction of sample due to sputtering and Ga implantation is inevitable (Figure 7). Intensity of these consequences depends of material being inspected and of imaging current.

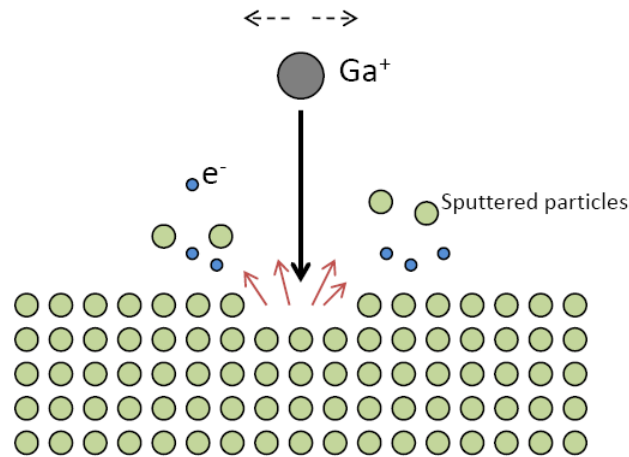


Figure 7. Schematic of the FIB imaging process.

- CrossBeam operating mode (Figure 6c)

In the CrossBeam Operation mode, both beams are turned on and while the ion beam is milling, the SEM is used to image the milling process in real time. This enables the operator to control the milling process on a nanometre scale and to perform extremely accurate cross sections and device modifications.

2.1.6 FIB Processing

For the purpose of structuring the FIB is scanned over a pre-defined area (milling box) in discrete steps with well defined step size (pixel spacing) and dwell time, i.e. the time the beam rests in each position (Figure 8). In other words, ion beam moves in discrete steps in one direction with defined step size until one end of the milling box. Then it moves one level up to the next line, scans in another direction and so further on until the whole box is scanned. Each scan across the selected area deposits a certain ion fluence which is correlated to the above mentioned parameters.

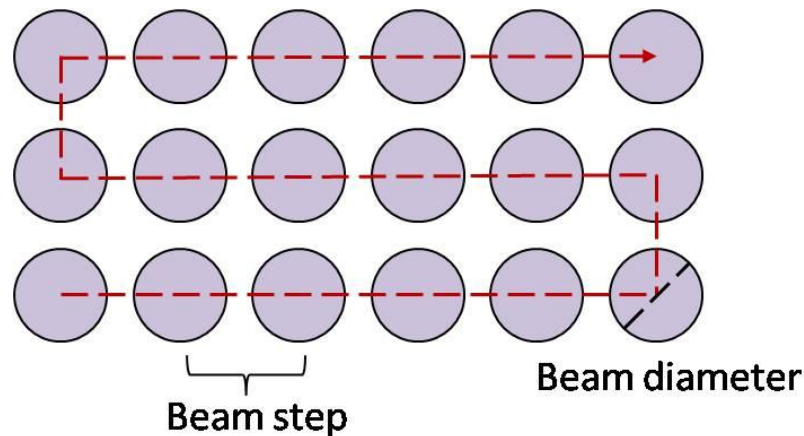


Figure 8. Schematic illustration of the FIB scanning strategy. The dashed line shows the path of the FIB in the single-pass mode (in serpentine).

In the following, single pass milling denotes a scanning strategy where the whole fluence is deposited within one single scan. For multi pass milling, the beam is scanned several times across the predefined area and the number of scan repetitions determines the total ion fluence.

When solid state body is exposed to ions with high kinetic energy these ions interact with the surface. Implantation leads to destruction of specimen, or in other words to displacement of atoms in specimen, which also depends on energy transfer mechanism in the specimen. If more than 50% of atoms in specimen are dislocated from their origin the initial crystalline structure becomes amorphous.

FIB processing with CrossBeam Neon40 makes it possible to observe FIB milling in SEM. The sample has to be moved in the position where both beams are crossed, the coincidence point, since only at this location live imaging during milling is possible. Stage has to be tilted to 54° and positioned 5mm (working distance) below the objective lens SEM. These parameters are for FIB processing under angle of 90° to a specimen. Obligatory condition for two beams to coincidence is the distance of 5mm below SEM but the stage can be tilted between -15° and 60° to vary FIB-specimen incidence angle (Figure 9).

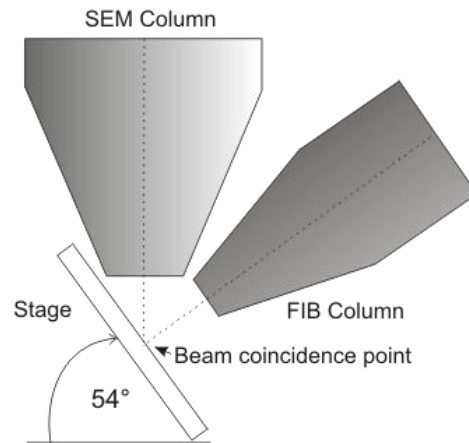


Figure 9. Geometrical layout of the CrossBeam Neon[®] 40EsB system. The electron and the ion beam coincide at a crossover point 5mm below the objective lens of the SEM. Stage tilt of 54° means FIB-specimen incidence angle of 90°.

Since FIB sputters material, one should be careful by choosing mill direction because of sputtered material redeposition on already scanned surface. This is also important by etching of deep narrow holes where the probability of the sputtered material re-depositing onto the sidewalls increases. If a line or hole is milled 10 to 15 times deeper than its width, redeposition results in V-shaped cross sections¹⁷.

Although this property seems undesired it will be of a great importance for forming of nanowires or nanowire-like structures which will be described later in this work.

2.2 Nanowire Growth Techniques

Low-dimensional nanostructures are usually fabricated using either a Top-Down or a Bottom-Up strategy. The former technique is extremely flexible, but suffers from limitations in minimum feature size and uniformity. The latter one, utilizing spontaneous self-ordering effects, is limited by the broad size distribution and the lack of control of the positioning of the self-organized nanostructures. Both ease and reproducibility of the processes involved are key factors for its practical use¹⁸.

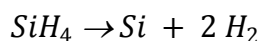
In the Top-Down approach, material is cut down to small dimensions through different means such as reactive ion etching or laser ablation of powder targets¹⁹.

With Bottom-Up approach nanostructures are grown from the bottom up on substrate.

2.2.1 The Vapor-Liquid-Solid (VLS) Nanowire Synthesis

The VLS mechanism will exemplarily be shown for the synthesis of Si nanowires.

As schematically shown in Figure 10, silicon wires grown with the help of gold usually exhibit a Au/Si alloy particle at their tip, and it is this Au/Si alloy particle that plays the central part in the vapour-liquid-solid growth of nanowires. At temperatures above the eutectic temperature the Au/Si alloy particle transforms into a liquid droplet. During growth, silicon is supplied via the gaseous silicon precursor, silane. The silane molecules from the vapor phase are adsorbed on the droplet surface and cracked into silicon and hydrogen



After the incorporation of the silicon atoms, resulting from the chemical reaction at the droplet surface, the silicon atoms diffuse through the droplet to the liquid-solid interface, separating the metal alloy droplet from the silicon wire. Under growth conditions, the silicon concentration in the droplet is higher than the equilibrium concentration at this temperature, which is equivalent to a silicon chemical potential in the liquid that exceeds the chemical potential of the silicon nanowires. The droplet is then said to be supersaturated. The supersaturation of the Au/Si alloy droplet represents the driving force for the growth of the silicon wire. Thus the vapor-liquid-solid mechanism of silicon wire growth basically consists of three steps: 1) the adsorption and cracking of the gaseous silicon precursor, providing atomic silicon for the growth, followed by the incorporation of silicon atoms into the droplet; 2) the diffusion of the silicon atoms through the droplet; and 3) the condensation of silicon onto the silicon wire at the liquid-solid interface. The question, which of these three steps effectively determines the silicon wire growth rate was controversially discussed. Concerning this discussion, it must however be clear that under steady state growth conditions the incorporation rate has to equal the condensation rate, which requires some kind of interaction between both processes.

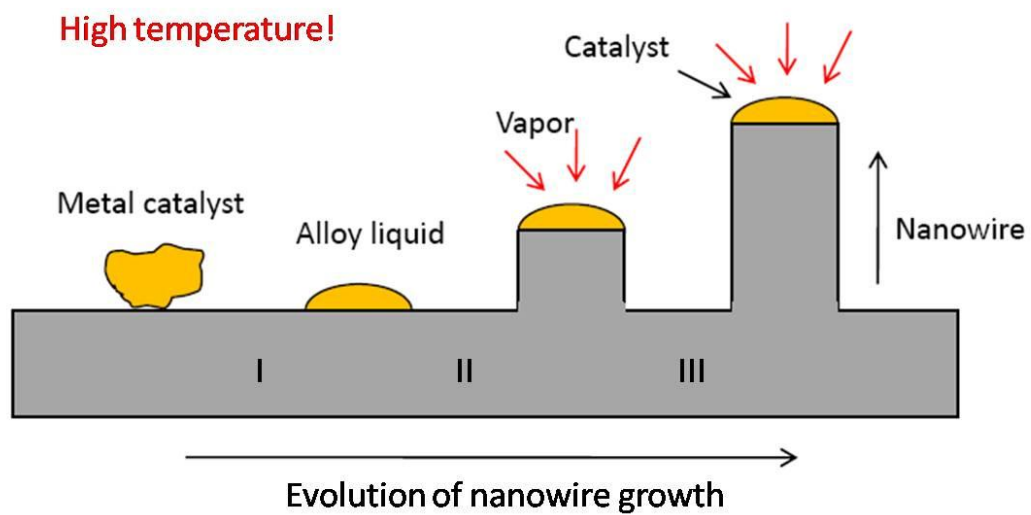


Figure 10. Schematic representation of the nanowire growth. In the first step metal catalyst forms alloy, in the second step comes to nucleation followed by axial nanowire growth.

The TEM image in Figure 11 shows a single Si nanowire grown with standard VLS process. At the top of the nanowire the catalytic gold nano-particle can be seen, which is characteristic for the VLS mechanism.

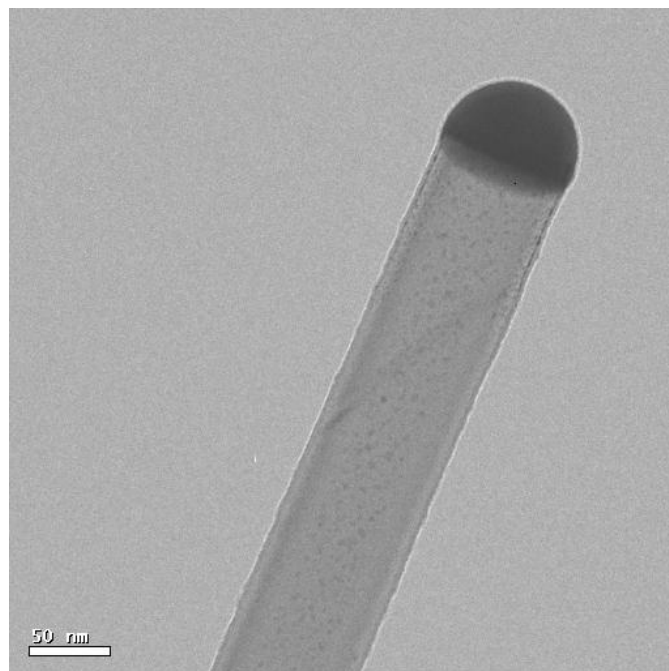


Figure 11. TEM image of a single Si nanowire with a gold catalyst at the top.

2.2.2 FIB Induced Nanowire Synthesis

Particular resist-less FIB techniques are most suited for the combination of top-down structuring with selective bottom-up self-assembling techniques. The appearance of nanostructures on surfaces induced by ion bombardment has attracted growing interest. One of the most recent topics in FIB-solid interaction is, as erosion proceeds, the evolution of nanowires on solid surfaces. The diameters of these nanowires are comparable to the sizes of biological and chemical species, and thus intuitively represent excellent primary transducers for producing signals that ultimately interface with macroscopic instruments.

Up to now FIB induced nanowire synthesis was observed on Ge, GaSb, Sb and In substrates.

In accordance with the catalytic VLS approach it is supposed that the formation of FIB induced nanowires synthesis necessitates a catalytic particle, mostly a eutectic alloy, with a low melting point. In this approach it is supposed that Ga droplets are formed in situ during FIB exposure (Figure 12, process step 1).

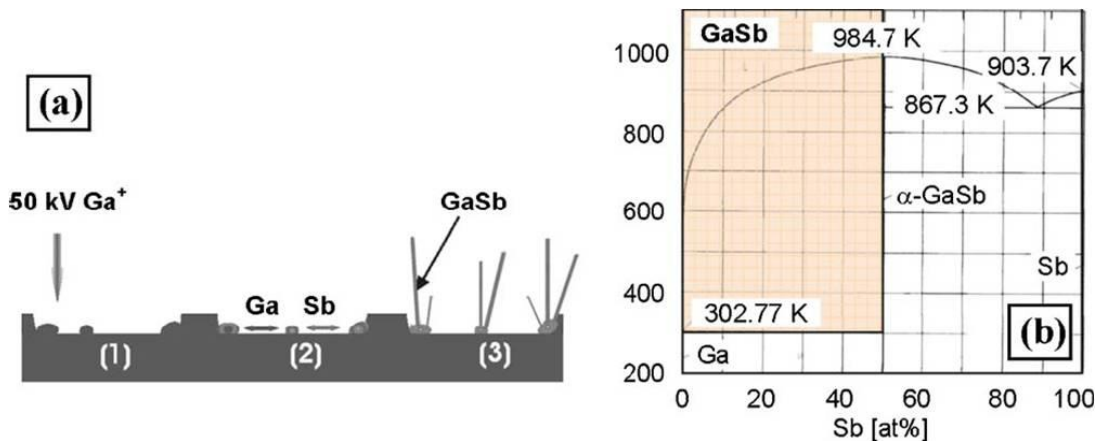


Figure 12. (a) The proposed growth model and **(b)** The phase diagram of the binary Ga-Sb system illustrates the thermodynamics of the nanowire growth. (step 1) FIB exposure leads to material decomposition due to physical sputtering. The excess Ga atoms because of enhanced diffusion, agglomerate into Ga-rich precipitations. (2) Due to the low melting point of Ga and high energy injection during FIB milling these precipitations behave like a liquid under milling conditions and decomposed material – diffusing on the surface - is absorbed and dissolved by the Ga containing clusters. (3) when the concentration of the solved materials exceeds supersaturation, nucleation sites will be formed and initiate the growth of the coexisting phase.

As it was recently reported, FIB milling of GaAs leads to the formation of Ga droplets on the surface²⁰. For FIB exposure with the 30 keV beam it was also observed in-situ migration of Ga precipitations on the GaSb surface. Due to the high energy injection during FIB milling and the low melting point of Ga ($T_{\text{Melt}} = 302,9 \text{ K}$) these precipitations behave like a liquid. Further the idea of conventional VLS growth mechanism is not applicable to this method as the concentration of Ga and Sb in the vapor phase is negligible. The only available source for the sustained growth of the nanowires is the substrate. It is assumed that exposing the substrate to the 30 keV Ga^+ ion beam leads to material decomposition due to physical sputtering. The excess Ga atoms because of enhanced diffusion agglomerate into Ga-rich precipitations (Figure 12, process step 1). Due to the low melting point of Ga and high energy injection during FIB milling with the 30 keV beam, these precipitations behave like a liquid. Decomposed material from the substrate - diffusing on the surface - is adsorbed and dissolved by the Ga containing clusters (Figure 12, process step 2). Finally, when the concentration of the solved materials exceeds supersaturation, nucleation sites will be formed and initiate the growth of the coexisting solid GaSb phase (Figure 12, process step 3). In accordance with the phase diagram shown in Figure 12b (Ref.21) precipitation of GaSb nanowires continues at the liquid-solid as long as the catalytic particle remains in a liquid state and reactant is available.

The formation of pure Sb nanowires could be discussed straightforward by examining the Sb rich part of the binary Ga-Sb phase diagram (Figure 12b). Within the framework of this approach, FIB processing of the Sb substrate produces mobile Ga and Sb species on the surface that rapidly agglomerate forming Sb-rich nanoclusters. In case of the Sb substrate Ga is introduced only by the FIB and the concentration of these clusters is somewhere in the right-most part i.e the Sb-rich region of the phase diagram. Again due to supersaturation of the nanocluster, the coexisting pure Sb phase precipitates as nanowires. Ga droplets could simultaneously catalyze the growth of hundreds of thousands of nanowires. In contrast to the conventional VLS mechanism the growth rate for this approach is extremely high. As the whole FIB processing of 2 μm long nanowires takes only a few seconds, growth rate must be in the range of a few 100 nm/s.

According to the experimental results, it is assumed that at least two key parameters are required to induce nanowire formation by an intense FIB. One should use an equilibrium phase diagram to choose a substrate that can form a liquid alloy with Ga. Even when FIB-induced nanowire growth occurs far-off the thermodynamic equilibrium, known phase diagrams can be used to choose a specific composition (catalyst - nanowire material) so that there is coexistence of liquid alloy and solid material. Second, sufficiently high beam energy is necessary, to ensure that the liquid alloy is formed during the FIB processing.

This FIB based approach requires no additional material source and the growth is initiated at room temperatures. This approach should not be limited solely to the materials discussed here – other substrates or sources of the ion beam should extend this method to other materials.

2.3 pH Measurement

Measuring pH is of a great importance in a wide range of industries, particularly in the field of medical diagnostics and a biological research. There is a variety of methods and of devices for pH measurements, like bulky, fragile glass bulb electrodes, antimony electrodes, ion-sensitive field-effect transistors (ISFET-s)²² or a pH indicator that changes color around a particular pH value which one is an easy but not very precise method for pH measurement.

2.3.1 pH-Value Definition

pH is a quantitative unit of measure which describes the degree of acidity or alkalinity of a substance on a scale from 0 to 14 (Figure 13).

The term pH (Pondus Hydrogeni) was first introduced by Søren Peder Lauritz Sørensen in 1909.

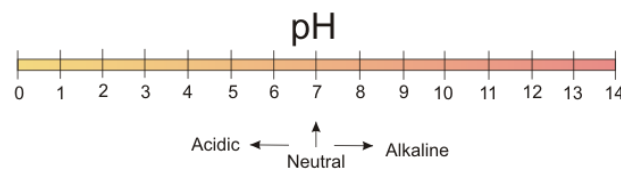


Figure 13. pH scale in the range from 0 to 14. A pH of 7 is neutral, a pH less than 7 is acidic and a pH greater than 7 is alkaline.

The formal definition of *pH* is the negative logarithm of the hydrogen ion concentration,

$$pH_c = -\log_{10}[H]^+ \quad (1)$$

The logarithmic pH scale means that a solution with 10^{-n} moles of H^+ ions per liter has a pH value of n for $n \in \{0,1 \dots 14\}$.

In practice it is the hydrogen ion activity which is measured rather than its concentration. Ion activity is the product of the concentration and an activity coefficient. The single-ion

activity coefficient of the hydrogen ion is a quantity which cannot be measured experimentally. In that case it has to be determined conventional *pH*-scale where each value is determined with measurement of standard solutions²³.

2.3.2 Electrode Potential

The chemical potential μ_i is defined by²³:

$$\mu_i = \mu_i^0 + RT \ln \frac{a_i}{a_i^0} \quad (2)$$

where μ_i^0 is standard chemical potential of the standard state with the standard activity a_i^0 ; R is the gas constant per mole and T is the absolute temperature. The activity a_i is defined as:

$$a_i = f_i c_i \quad (3)$$

where f_i is the activity coefficient that gives aberration from ideal behaviour ($a_i = c_i$) and c_i ion concentration.

When two different phases are in direct contact the system strives to reach chemical equilibrium. A universal criterion for equilibrium within a system is that the chemical potential μ_i of any component i have a uniform value in all parts of the system.

$$\mu_i(I) = \mu_i(II) \quad (4)$$

If, for instance, the metal Cu and the corresponding solution $CuSO_4$ are brought together than it can be written:

$$\mu_{Cu^{++}}(Metal) = \mu_{Cu^{++}}(Solvent) \quad (5)$$

System will try to reach equilibrium but, due to the electrical potential difference that builds up between two phases that are brought together, this would not be the case.

If one mole of a z -fold charged component is brought into a mix phase that has certain potential φ , there is certain work $z_i F \varphi$ (F is Faraday constant and z is the electrical charge carried by a single charge carrier - unity for electrons) that has to be included in equilibrium equation, where $z_i F$ is the charge per mole and φ is the inner electrical potential. In that case Eq. 5 can be written in form:

$$\mu_i(I) + z_i F \varphi(I) = \mu_i(II) + z_i F \varphi(II) \quad (6)$$

where:

$$\mu_i^* = \mu_i + z_i F \varphi = \mu_i^0 + RT \ln a_i + z_i F \varphi \quad (7)$$

represents the electrochemical potential μ_i^* of charged component i with the chemical potential μ_i .

The electric potential difference between two points in the bulk of two phases ($\varphi(I)$ and $\varphi(II)$) is called Galvani potential $\Delta\varphi$. Combining equations 6 and 2 the $\Delta\varphi$ is given by:

$$\Delta\varphi = \varphi(II) - \varphi(I) = \underbrace{\frac{\mu_i^0(I) - \mu_i^0(II)}{zF}}_{\Delta\varphi_{00}} + \frac{RT}{zF} \ln \frac{a_I}{a_{II}} \quad (8)$$

The difference of the inner potentials of the electrode and the solution ($\Delta\varphi_{00}$) at the activity $a_I = 1$ is called Galvani potential. Equilibrium Galvani potential of a metal electrode $\Delta\varphi$ changes with the variation of solution for one decade and this change has a value of $0.05915/z$ V. Based on Eq. 8 the equilibrium potential φ of a metal ion electrode can be calculated with the equation:

$$\varphi = \Delta\varphi_{00} + \frac{RT}{zF} \ln a_{Me^{z+}} \quad (9)$$

This so called Nernst equation expresses dependency of equilibrium potential of ion concentration.

However, the potential of a single electrode cannot be measured alone. To be able to determine its potential one more electrode has to be introduced. The cell is then divided into two contributory electrode potentials; one as the function of ion activity and the other (reference electrode) is only sensitive on, for instance, chlorine ion concentration. Electromotive force (e.m.f.) E_0 of the cell in that case is given as the potential difference of the two electrodes:

$$E_0 = \varphi^{M1} - \varphi^{M2} \quad (10)$$

2.3.3 pH-Sensitive Electrodes

Electrodes with their potential, directly related to the hydrogen ion concentration of the solution, are called pH-sensitive electrodes.

2.3.3.1 Standard Glass Electrode

The standard glass electrode is the most popular pH electrode because it has a low electrical resistance, stable potentials and low electrode errors²⁴. It is also not influenced by oxidizing and reducing agents and is almost not limited in its applications to aqueous solutions. The potential between the surface of the glass membrane and the electrolytic solution in which the electrode is immersed is usually dependable only on the hydrogen ion concentration. A schematic representation of pH probe, combining glass electrode and reference electrode in one body is given in Figure 14.

The bottom of a pH electrode balloons out into a round thin glass bulb. The pH electrode is best thought of as a tube within a tube. The inside most tube (the inner tube) contains an unchanging saturated KCl and a 0.1M HCl solution. Also inside the inner tube is the cathode terminus of the reference probe. The anodic terminus wraps itself around the outside of the inner tube and ends with the same sort of reference probe as was on the inside of the inner tube. Both the inner tube and the outer tube contain a reference solution but only the outer tube has contact with the solution on the outside of the pH probe by way of a porous plug that serves as a salt bridge.

This device is essentially a galvanic cell. The reference end is essentially the inner tube of the pH meter, which for obvious reasons cannot lose ions to the surrounding environment (as a reference is good only so long as it stays static through the duration of the measurement). The outer tube contains the medium, which is allowed to mix with the outside environment (and as a consequence this tube must be replenished with a solution of KCl due to ion loss and evaporation).

The measuring part of the electrode, the glass bulb on the bottom, is coated both inside and out with a ~10 nm layer of a hydrated gel. These two layers are separated by a layer of dry glass. The silica glass structure (that is, the conformation of its atomic structure) is shaped in such a way that it allows Na^+ ions some mobility. The metal cations (Na^+) in the hydrated gel diffuse out of the glass and into solution while H^+ from solution can diffuse into the hydrated gel. It is the hydrated gel, which makes the pH electrode an ion selective electrode.

H^+ does not cross through the glass membrane of the pH electrode, it is the Na^+ which crosses and allows for a change in free energy. When an ion diffuses from a region of activity to another region of activity, there is a free energy change and this is what the pH meter actually measures.²⁵

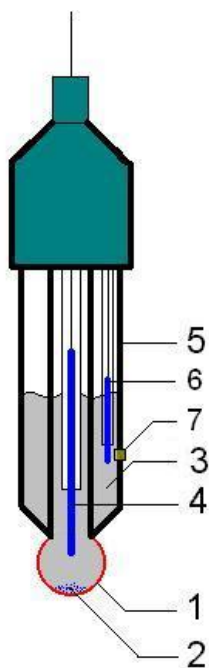


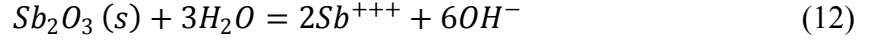
Figure 14. Schematic of the standard glass electrode. 1. a sensing part of electrode, a bulb made from specific glass; 2. small amount of AgCl precipitate inside the glass electrode; 3. internal solution, usually 0.1 M HCl for pH electrodes; 4. Internal electrode, usually silver chloride electrode or calomel electrode; 5. body of electrode, made from non-conductive glass or plastics; 6. reference electrode, usually the same type as 4.; 7. junction with studied solution, usually made from ceramics or capillary with asbestos or quartz fiber (taken from Ref.26).

2.3.3.2 The Sb Electrode

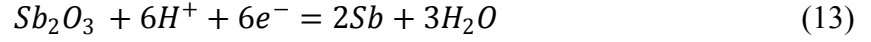
With the ever growing need for evaluation of smaller and smaller aspects of organisms in biologic research or for miniaturization in non invasive diagnostic and intervention in a medicine (e.g. determination of pH in blood, gastric research), glass electrode became unsuitable due to the difficulty of its miniaturization. To overcome this problem, metallic pH-sensitive electrodes became a matter of interest. The most popular metallic pH-electrode is the antimony electrode. The reaction of antimony in solutions is given by equations 11 and 12²⁷:



and



Therefore the potential of Sb in aqueous solutions is controlled by the equilibrium²⁸:



From equations 9, 11, 12 and 13 the equation for the potential of the Sb electrode can be written:

$$E = E_0 + 0.05915 \left(pH - \frac{1}{6} \log Sb_2O_3 + \frac{1}{2} \log H_2O \right) \quad (14)$$

If the last two terms are ignored, E_0 can be calculated from difference in potential between the antimony-antimony trioxide electrode and the hydrogen electrode, immersed in the same solution.

Experimentally, E_0 shows large variations due to different crystallographic orientation of Sb resulting from different approaches of electrode synthesis. The electrical potential of Sb electrodes is also sensitive to the oxygen content of the solution or precisely it is sensitive on solutions containing oxidizing or reducing agents²⁷. Therefore the electrode has to be calibrated under controlled conditions.

Over years, different manufacture methods of Sb electrode have been developed such as pulsed electrodeposition²⁹ or micro-wave-assisted growth³⁰. In experimental part of this thesis the FIB induced synthesis of a novel Sb sensing electrode and its properties will be described.

In Table 1 are listed some results of measured e.m.f. over pH which have been reported and that shows the linear relationship of the type $E = a + b \text{ pH}$. This relationship is equivalent with the equation 14 where a is standard potential of the electrode; b is the parameter that governs the change of Galvani potential of an electrode for one decade with variation of solution. The theoretical value for b is $0.05915/z \text{ V}$.

Electrode Type	a [V]	b [V]	Temperature °C	pH Range
Stick	0.0415 0.009	0.0485 0.0536	14 14	1-5 >9
Stick	0.050	0.054	25	0-12
Powder	0.1445	0.05915	25	2.2-10
Stick	0.052	0.057	26-29	2-12
Plated	0.118	0.043	18	Neutral
Plated	0.009	0.053	14	3-9
Stick	0.0234	0.0498	30	-
Stick	0.018	0.0534	14	-
Plated	0.009	0.0531	14	3-9
Stick	0.030	0.05915	25	2-7
Stick	0.019	0.0575	24	3-12
Stick	0.022	0.0567	20	2-12
Stick	0.249	0.0538	10-25	1-9
Stick	-0.0293	0.0591	25	2.5-8.5
Stick	0.005	0.059	25	5-11
Stick	-0.020	0.0580	20	2-7
Plated	0.022 -0.0558	0.0560 0.0453	18 18	5-7 7-9
Stick	-0.008 0.050	0.059 0.051	25 25	3-7 7-11
Stick	0.2552	0.05893	25	2.2-8
Stick	0.224	0.0586	30	1.9-7.25
Plated	0.220	0.0647	30	1.9-7.00
Stick	0.00	0.055	25	2-12
Stick	-	0.0536	25	2-12

Table 1. Relationships between the e.m.f. and pH value with antimony-antimony oxide electrode measured with different Sb electrodes (taken from Ref.27).

2.3.4 Reference Electrodes

The study of the properties of an ionic solution comprises a comparison between unknown and known standard states of the system. The standard state may, as expected, vary according to the nature of the system and must be calibrated for that purpose. Generally speaking, all electrodes that have standard behavior for standard conditions can be referred to as reference electrodes. In case of a pH measurement only electrodes that are indifferent to a hydrogen ion concentration/activity can be used as reference electrodes. The most used

reference electrodes for pH measurements are the Silver-Silver Chloride (Ag/AgCl) and Mercury/Calomel (Hg_2Cl_2) electrode.

The most important advantage of this electrodes is that they are small, compact and stable not to contaminate any medium in which they are immersed.

The silver-silver chloride electrode consists of solid silver chloride on silver. Solution of chloride, when it is in contact with the AgCl electrode, becomes saturated with AgCl and provides thus the constant activity of silver chloride. The potential of the Ag/AgCl electrode therefore depends on the activity of the chloride ions:

$$E_{Ag,AgCl}^0 = E_{Ag,Ag^+}^0 + \frac{RT}{F} \ln K_s \quad (15)$$

$$K_s = a_{Ag^+} \cdot a_{Cl^-} \quad (16)$$

The typical methods of forming AgCl on Ag include anodization in chloride containing solutions, chemical oxidation and thermal or plasma treatment in chlorine containing atmospheres^{31, 32, 33, 34, 35, 36, 37}. One special method, also used in this work, is the treatment with ferric chloride³⁸ (FeCl_3) and will be described in the experimental part of thesis.

Measurement of *pH* value comprises two electrodes - sensing and reference electrode, and voltage measurements instrument that measures potential difference between these two electrodes (Figure 15).

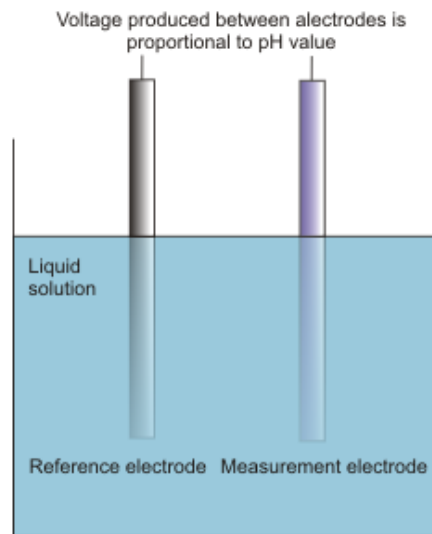


Figure 15. Schematic of the pH dependable potential read-out setup.

3 Experimental

3.1 FIB Milling and Surface Response

In this work special attention is paid to the surface evolution of three semiconductor materials namely Germanium (Ge), Antimony (Sb) and Gallium antimonide (GaSb). It has been already reported that these materials when exposed to FIB form sponge- and nanowire-like structures^{39, 40, 41, 42}. The sponge like structures formed on Sb will be used as a pH value sensitive element as shown in section 3.2.

In general, milling of surfaces at sufficient high ion fluences and energies leads at first to a crystal-to-amorphous transformation. Additionally, it also leads to net material removal by sputtering. When all parameters- predefined area, step size, dwell time and ion fluence (current over time) are matched for a given material, different nanoscale structures such as nanodots, nanocrystals and nanofibers may be formed.

3.1.1 Ge Surface Response on FIB Irradiation

The SEM image in Figure 16 shows the influence of the angle of FIB incidence. All four (10x10) μm^2 boxes were exposed to the same ion dose of $4,5 \times 10^{16}$ ions/cm² with a beam current of 20 pA.

In the Figure 16a the FIB impinges perpendicular to the surface and the formation of the sponge like structure can be observed. As the incidence angle changes (Figure 17b-d) it can be observed how the structure arises and takes nanowire-like shape.

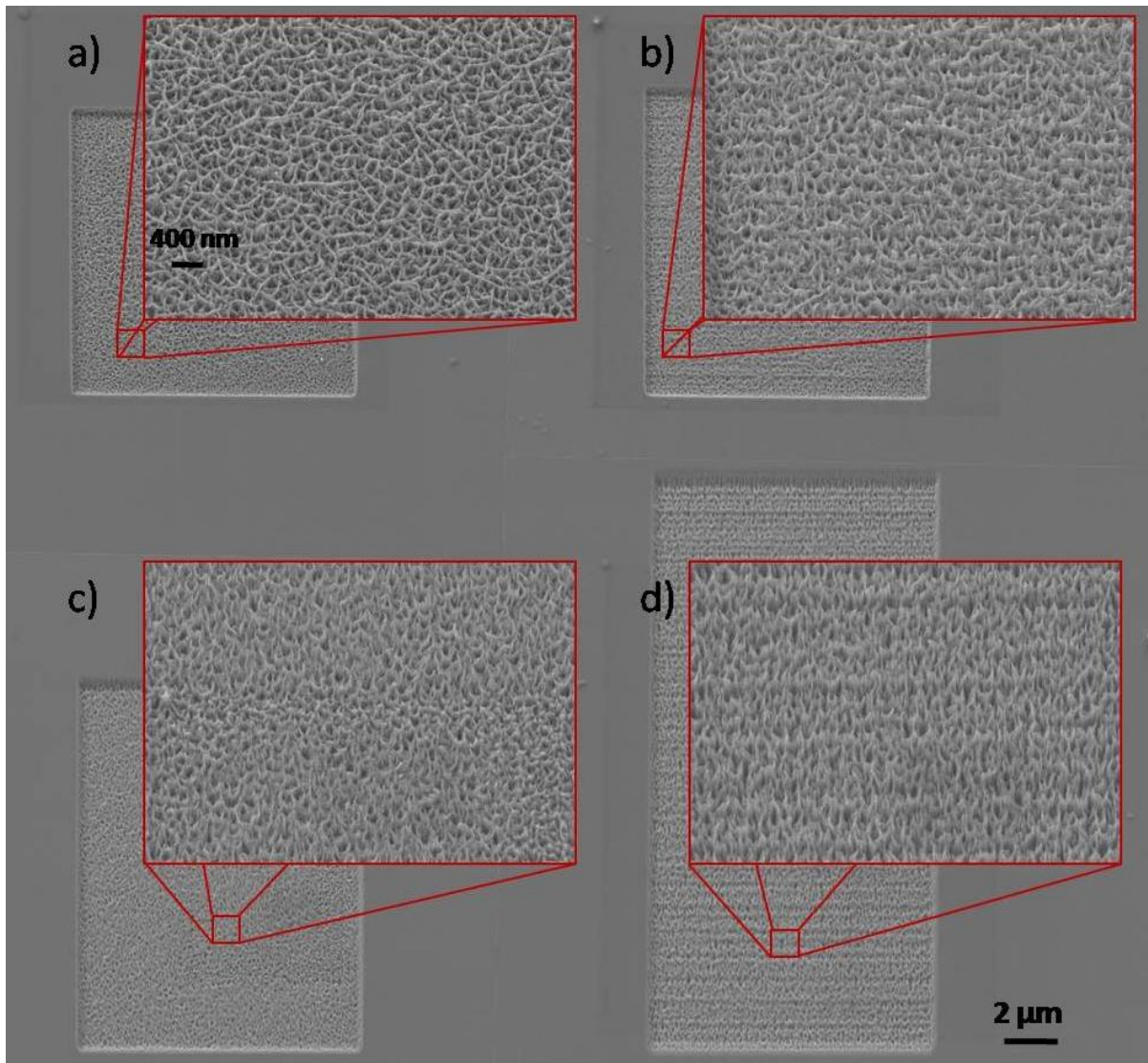


Figure 16. SEM image of the Ge boxes ($10 \times 10 \mu\text{m}^2$) milled with ion fluence of $4,5 \times 10^{16}$ ions/ cm^2 under different angles of FIB incidence. a) 90° incidence angle, surface forms sponge-like structure b) 70° incidence angle, less dense sponge-like structure. c) 50° incidence angle, it can be observed how the sponge-like arises and takes shape of nanowires at the tips. d) 30° incidence angle, formation of the nanowire-like structure.

3.1.1 GaSb Surface Response on FIB Irradiation

The SEM image in Figure 17 shows the influence of the angle of FIB incidence on the surface evolution of a GaSb substrate. All four (10×10) μm^2 boxes were exposed to the same ion dose of 1×10^{16} ions/ cm^2 with a beam current of 10 pA.

In the Figure 17a the FIB impinges perpendicular to the surface and the formation of the sponge like structure can be observed. As the incidence angle changes (Figure 17b-d) it can be observed how the structure arises and takes nanowire-like shape.

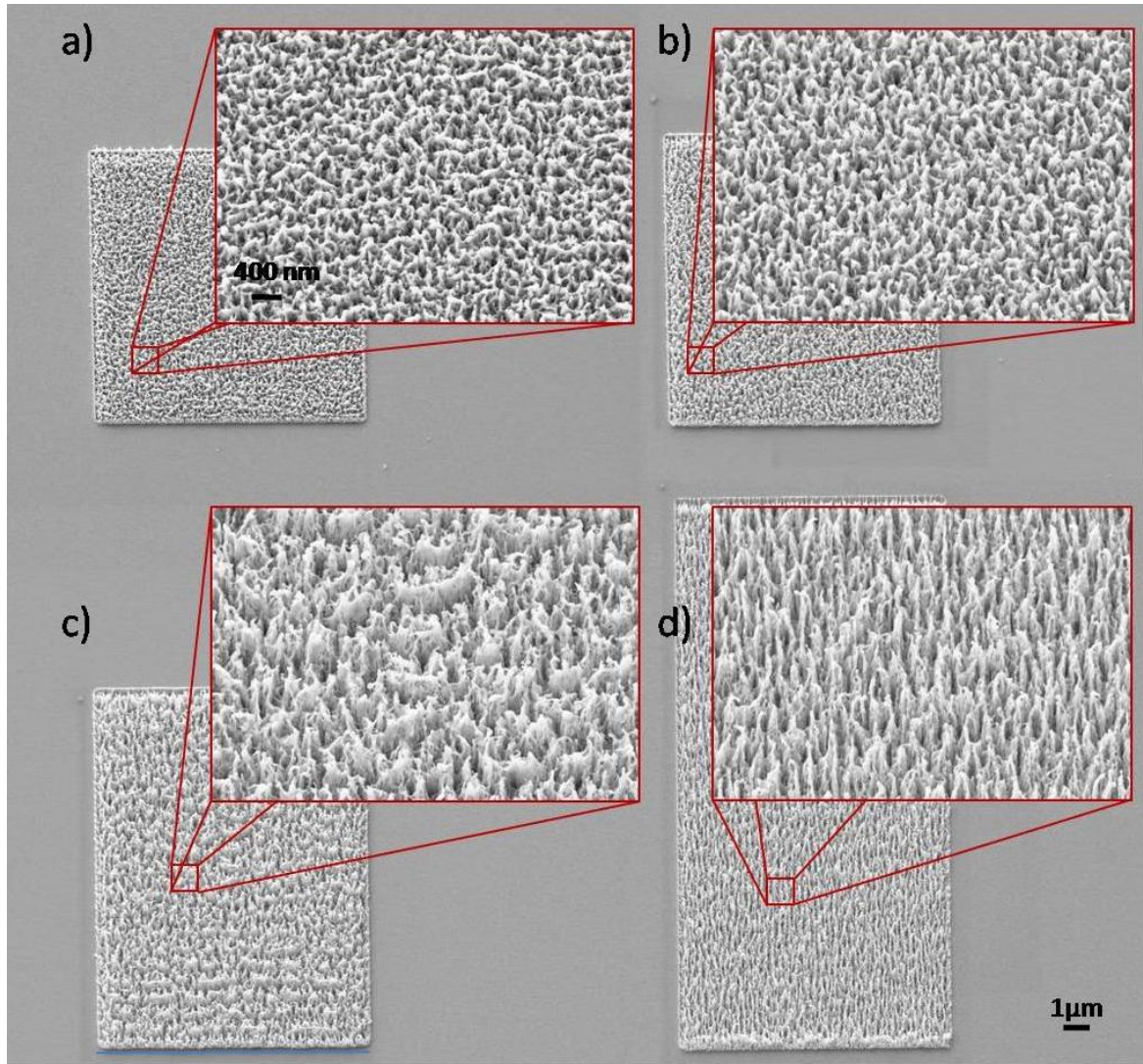


Figure 17. SEM image of four GaSb boxes ($10 \times 10 \mu\text{m}^2$) milled with ion fluence of 1×10^{16} ions/ cm^2 under different incidence angles. a) 90° incidence angle, surface forms sponge-like structure b) 70° incidence angle, less dense sponge-like structure. c) 50° incidence angle, it can be observed how the sponge-like structure arises and takes shape of nanowires at the tips. d) 30° incidence angle, formation of the nanowire-like structure.

3.1.2 Sb Surface Response on FIB Irradiation

Figure 18 shows the SEM image of the Sb surface after FIB exposure with a ion dose of $6,2 \times 10^{16}$ ions/cm². Dot-like features are observed with a density of about 200 dots/μm². Ongoing FIB exposure leads further to the formation wires as shown in Figure 19.

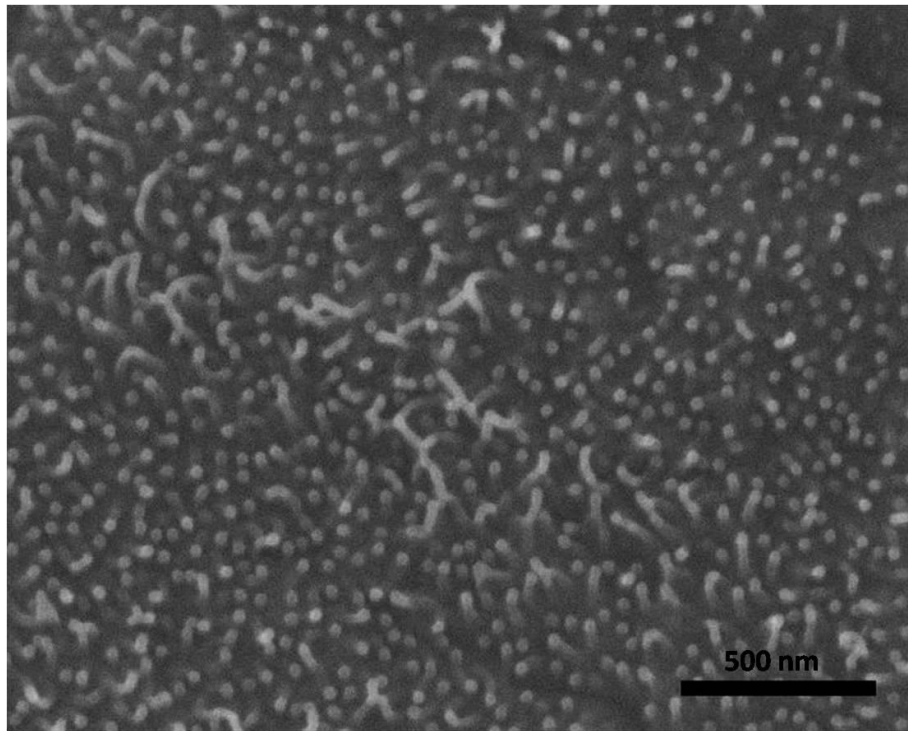


Figure 18. SEM image of the Sb surface after FIB exposure with an ion fluence of $6,2 \times 10^{16}$ ions/cm² (after Lugstein et al.).

Four $(5 \times 5) \mu\text{m}^2$ wide boxes were exposed to the FIB with a beam current of 50 pA for different exposure times as indicated in figure caption. Each field has been milled with only two passes but each pass with different duration. The first layer of the first field (Figure 19a) is milled for 2 minutes ($1,5 \times 10^{17}$ ions/cm²) and the second layer for 8 minutes (6×10^{17} ions/cm²). The first layer of the second box (Figure 19b) is milled for 4 minutes (3×10^{17} ions/cm²) and the second layer for 8 minutes. The first layer of the third box (Figure 19b) is milled for 4 minutes and the second layer for 6 minutes ($4,5 \times 10^{17}$ ions/cm²). The first layer of the fourth box (Figure 19b) is milled for 6 minutes and the second layer for 10 minutes ($7,5 \times 10^{17}$ ions/cm²). From the SEM images it can be seen that the density of the nanowires is the highest there where the highest ion fluence is deposited

during the first layer. Therefore it can be said that with the first FIB pass the Sb surface can be considered as “prepared” for nanowire growth.

During the milling process the FIB passes over the milling area in serpentine. With each line that passes over defined area material is being removed by sputtering. In the forefront, the nanowires that are already grown are removed by sputtering but those nanowires “behind” the scanning line stay unaffected. The last scan line can be seen at the end of each milled area in Figure 19.

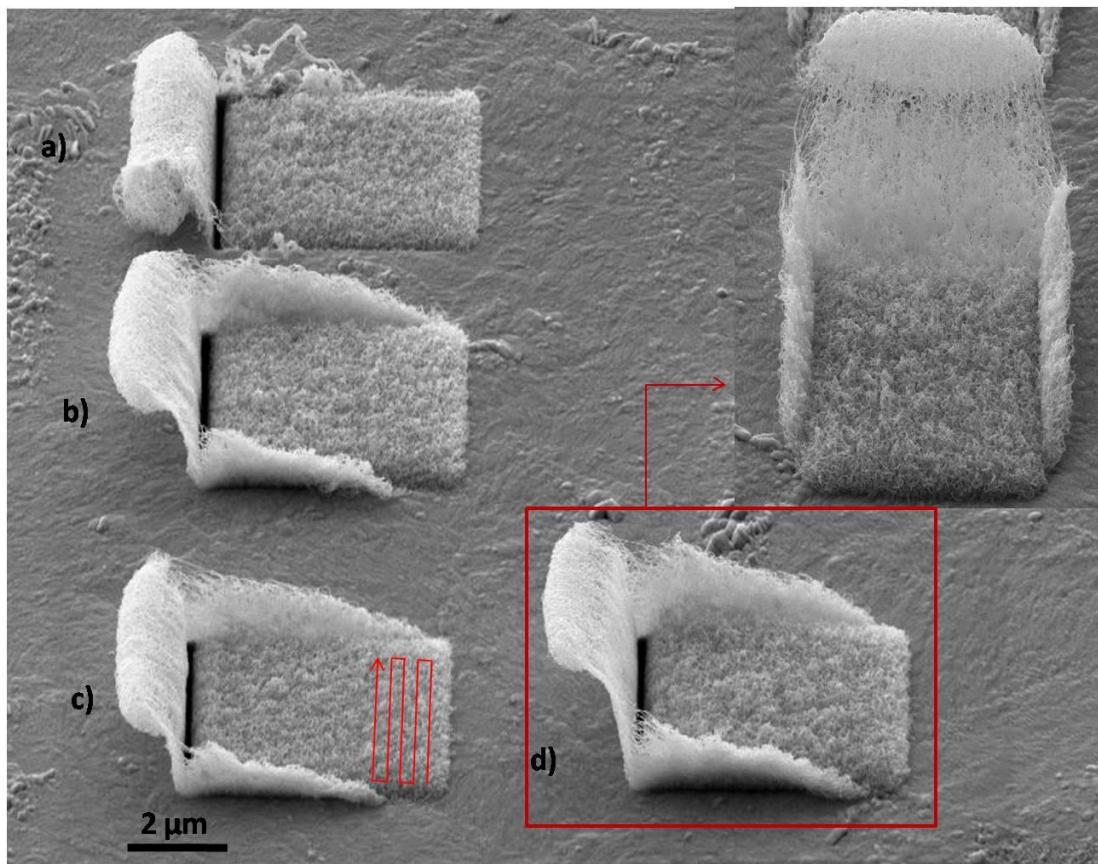


Figure 19. Sb boxes milled with 50pA, increment style 5nm. a) First layer 2 minutes, second layer 8 minutes. b) First layer 4 minutes, second layer 8 minutes. c) First layer 4 minutes, second layer 6 minutes. d) First layer 6 minutes, second layer 10 minutes.

With FIB multipassing over the same area, Sb is sputtered and redeposited, and the nanowire network is densified. Therewith will be also the angle, under which the sputtered material leaves substrate, reduced. As a consequence, the sputtered Sb will be picked up by the network which leads to an uprising of structures. Also the sidewalls, where the beam changes the scanning direction, can be explained with escape angle reduction.

Figure 20 shows the SEM image of the cross-section of the Sb nanowire network ($10 \times 10 \mu\text{m}^2$) synthesised with an ion fluence of $3,1 \times 10^{18}$ ions/ cm^2 . The surface is covered with the porous Sb nanowire network and it also can be seen that the network reaches about $3 \mu\text{m}$ underneath the surface.

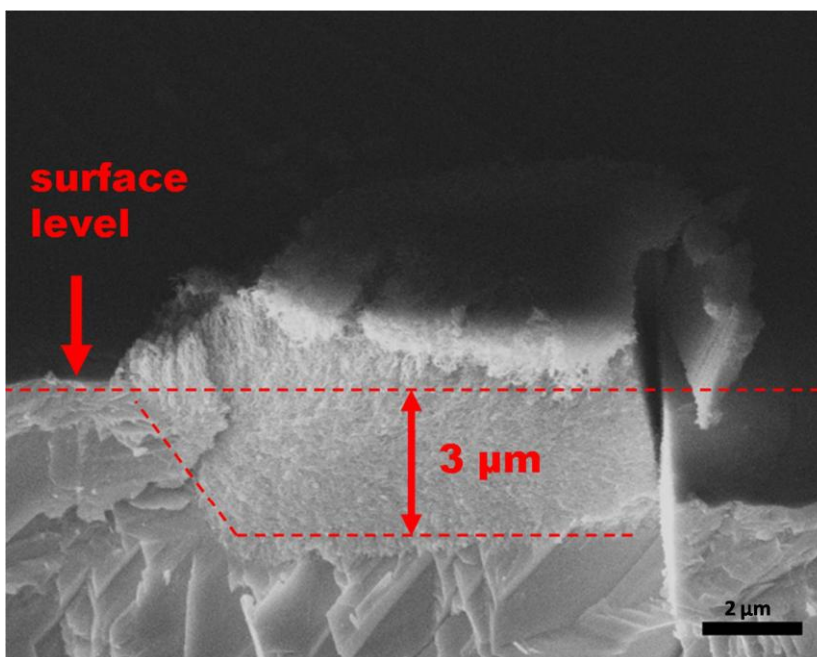


Figure 20. Cross-section of the box milled with an ion fluence of $3,1 \times 10^{18}$ ions/ cm^2 . The nanowire network reaches about $3 \mu\text{m}$ under the surface, into the substrate (taken from Ref.43).

3.1.3 EDX, Raman and TEM Analysis of Sb Nanowires

3.1.3.1 Energy-Dispersive X-Ray Spectroscopy of Sb Nanowires (EDX)

EDX is a type of spectroscopy mostly combined with SEM or TEM that is used for characterization of chemical compound of the sample. The EDX technique detects x-rays emitted from the sample during bombardment by an electron beam. X-ray signals are typically produced when a primary beam of electrons causes the ejection of an inner shell electron from the sample. An outer shell electron makes the transition to fill this vacancy and gives off an x-ray whose energy can be related to the difference in energies of the two electron orbitals involved characteristic for the element⁴⁴.

Examination of a single Sb nanowire reveals that the nanowire consists of Sb with traces of oxygen resulting from the thin oxide layer surrounding the nanowire (see Figure 21). The

Cu signal in the EDX spectrum in Figure 21 is an artifact arising from the TEM sample holder.

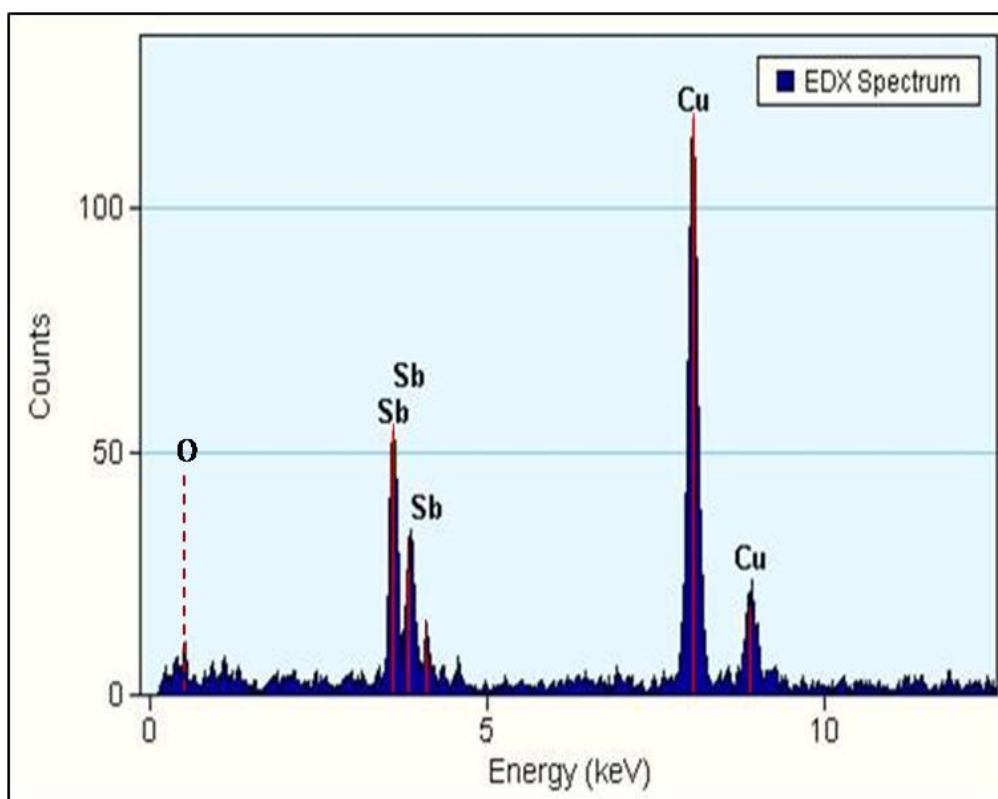


Figure 21. EDX Spectrum of a single Sb nanowire reveals also the presence of the Copper signal that is the artifact that comes from the TEM sample holder (after Lugstein et al.).

3.1.3.1 Transmission Electron Microscopy (TEM) and High Resolution TEM (HRTEM)

In a TEM with EDX detector, a beam of focused electrons is transmitted through a thin sample to reveal information about its morphology, crystallography, particle size distribution, and its elemental composition. It is capable of providing atomic-resolution lattice images, as well as giving chemical information at a spatial resolution of 1 nm or better.

Crystal structures can also be investigated by HRTEM where the images are formed due to differences in phase of electron waves scattered through a thin specimen. HRTEM allows

the direct reconstruction of Bragg differential electron beams to create interference patterns, which can give a representation of the underlying crystallographic diffraction grating⁴⁶.

3.1.3.1.1 TEM Investigation of as-grown Sb Nanowires

For purposes of TEM analysis, a small piece of Sb was mounted on a TEM sample holder before FIB processing. The nanowires were grown with standard FIB milling procedure (see 3.1.2). This setup enables the investigation of individual nanowires without any further preparation. Figure 22 shows the inverted dark field TEM image of such-grown Sb nanowires. It can be seen that the diameters of the nanowires are about of 20-30 nm and very homogenous over the entire length of several micrometers.

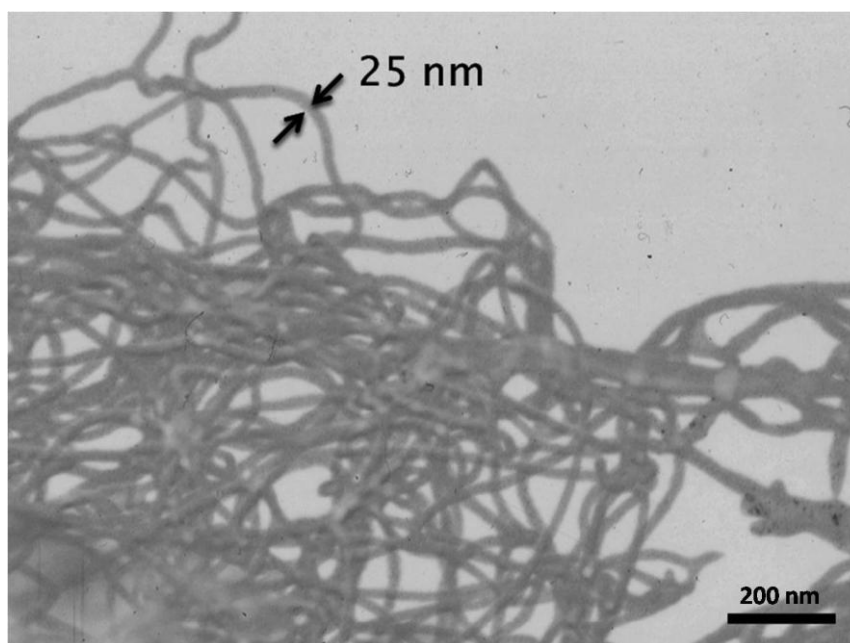


Figure 22. Inverted dark field TEM image of as-grown Sb nanowires (after Lugstein et al.).

The HRTEM image in Figure 23 shows the enlarged view of a single 25 nm thick Sb nanowire. The Sb nanowires appear to be fully amorphous as proven by the selected area electron diffraction (SAED) pattern in the inset of Figure 23.

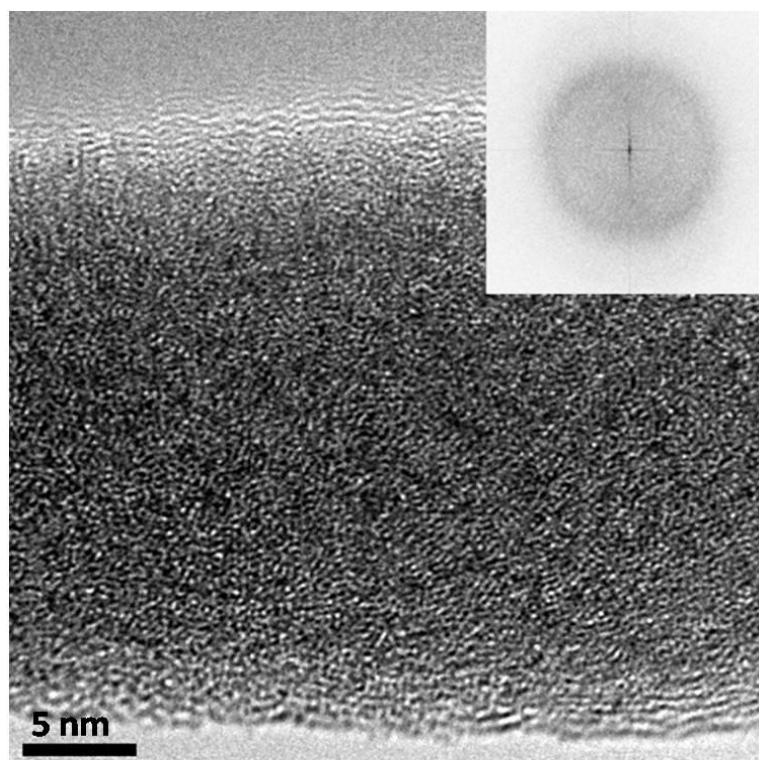


Figure 23. HRTEM image of as-grown Sb nanowire and the respective SAED pattern in the inset (after Lugstein et al.).

3.1.3.1.2 TEM Investigation of Sb Nanowires After Thermal Annealing

Figure 24 shows the TEM image of Sb nanowires after annealing at 180°C for 30 minutes in air. The comparison of the Figure 22 and the Figure 24 shows that the diameter and the shape remain unaffected. The black dots that can be seen in Figure 24 are the crystallites with common crystallographic orientation with the diameter usually in the range of that of the nanowire. The HRTEM image in Figure 25 shows the Sb nanowire after the annealing process. One can see clearly well ordered crystallites. Diffraction pattern in the inset shows (110) and (120) reflections for Sb with its trigonal crystal structure. The lattice parameter is 0,354 nm which fits well with the tabulated value for bulk Sb⁴⁵.

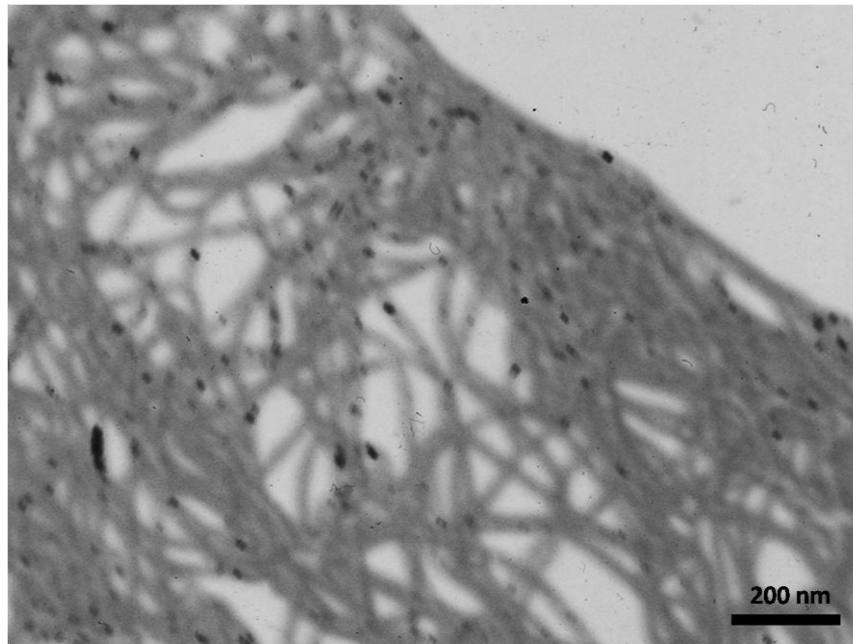


Figure 24. Inverted dark field TEM image of Sb nanowires after annealing at 180 °C for 30 min in air.

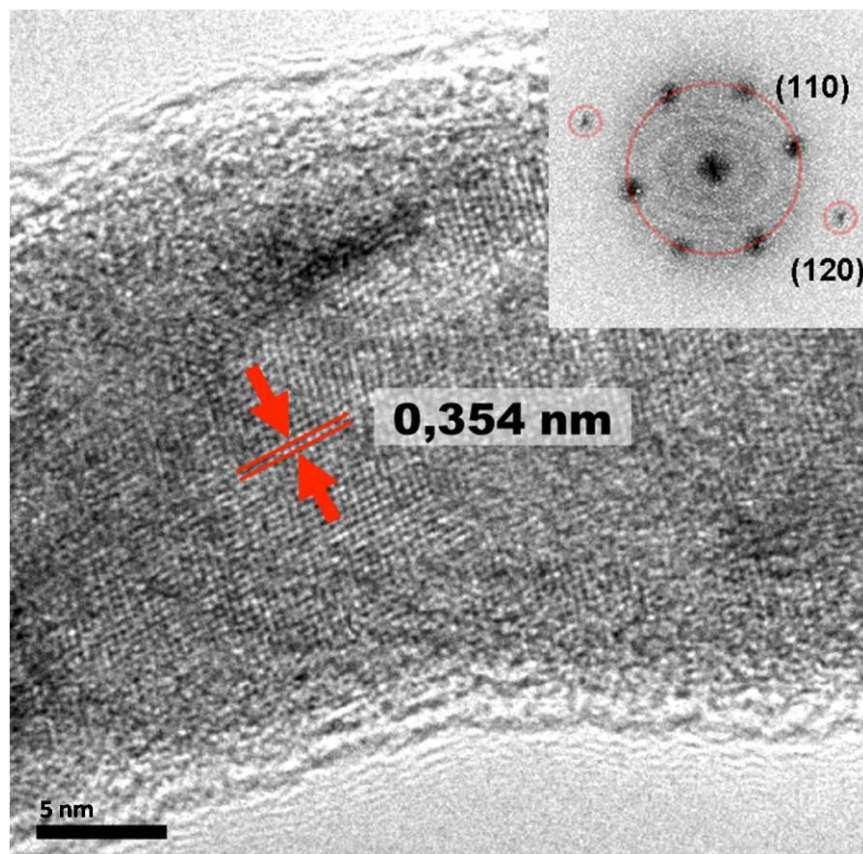


Figure 25. HRTEM image of a Sb nanowire after thermal annealing at 180 °C for 30 min in air. The lattice planes show a distance of 0,354 nm which corresponds to the Sb (110) direction. The inserted SAED pattern shows the crystalline nature ((110) and (120) reflections) of the nanowires after the post growth annealing (after Lugstein et al.).

3.1.3.1 Raman Spectroscopy of Sb Nanowires

Raman spectroscopy is an analytical tool for the qualitatively and quantitatively analyzing of the composition of materials. The principle of Raman spectroscopy is that the sample is irradiated with light of known polarization and wavelength (generally in the visible or infrared ranges). Inelastic (or Raman) scattering from molecules or crystals occurs and the scattered light is wavelength-shifted with respect to the incident light. The spectrum of the scattered light is then analyzed to determine the changes in its wavelength. In a Raman spectrum, the wavenumbers of the Raman shifts are plotted against their respective intensities, which originate from the interaction photons with molecular vibrations (phonons in a crystal)⁴⁶.

Figure 26 shows the Raman image of the Sb surface after FIB exposure with ion dose of $3,1 \times 10^{18}$ ions/cm² and after annealing at 180°C for 30 minutes in air.

The green color surrounding the milled box is untreated Sb. The appropriate spectrum (green line Figure 26b) is in good coincidence with the Raman spectrum of pure Sb. The irradiated area is marked by the dashed rectangle and colored blue and red in the image. The corresponding spectra (blue and red line in Figure 26) shows additional Raman peaks at 192 cm⁻¹, 257 cm⁻¹, 375 cm⁻¹, and 453 cm⁻¹ which are characteristic for antimony oxide. The variation of the peak intensities results from differences in the morphological structure of the antimony oxide. By this method, the existence of an oxide species on the nanowires is clearly verified.

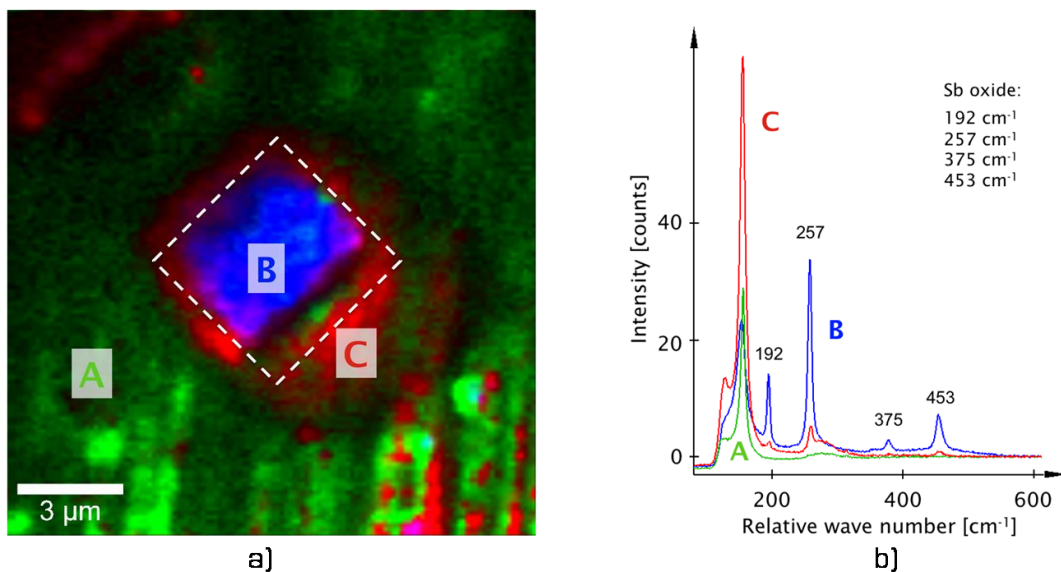


Figure 26. Raman image of the (5x5) μm² box (ion dose $3,1 \times 10^{18}$ ions/cm², annealed at 180°C for 30 minutes in air). Green coloured surface in a) and green spectrum in b) show untreated Sb. Red and blue color are FIB milled box that shows presence of oxide (after Lugstein et al.).

3.2 CMOS compatible pH Sensor with Sb Electrode

Following the trend of miniaturization and the increasing demand of portable biomedical sensing devices we explored a microscale and CMOS compatible sensors for precise pH determination.

Sb as material for pH electrodes has practical properties, such as linear response to the H^+ concentration in solutions, chemical resistance, biocompatibility, and availability in pure form^{27,47}. It also withstands hydrofluoric (HF) acid and allows reliable determination of the proton concentration in HF-containing solution in which a glass electrode normally cannot be used. These properties in combination with the large surface area to volume ratio, make them a suitable material for novel pH electrodes.

The FIB induced synthesis of a dense Sb nanowire network discussed within this thesis will be applied for fabrication of such microscale sensing electrode for CMOS compatible pH sensor.

3.2.1 Processing of the CMOS compatible pH Sensor

3.2.1.1 Layer Formation

The CMOS compatible pH sensor was formed combining well known semiconductor processing techniques with a FIB based method for nanowire formation (Figure 27). Highly doped Si substrate covered by a 6 μm thick Sb layer was provided by Institute of Photonic Technologies Jena. After that, the Sb layer was covered with a 3 μm thick insulating SiO_2 layer deposited via plasma enhanced chemical vapor deposition (PECVD). Deposition time was 70 minutes at the temperature of 300°C using 425 sccm of silane (SiH_4) and 710 sccm of nitrous oxide (N_2O). Finally a 1 μm thick Ag layer was deposited via a thermal deposition (shadow mask) which finally form the Ag/AgCl reference electrode.

The mask has three openings and thus three reference electrodes are fabricated on each device. The layered structure is shown in Figure 27a.

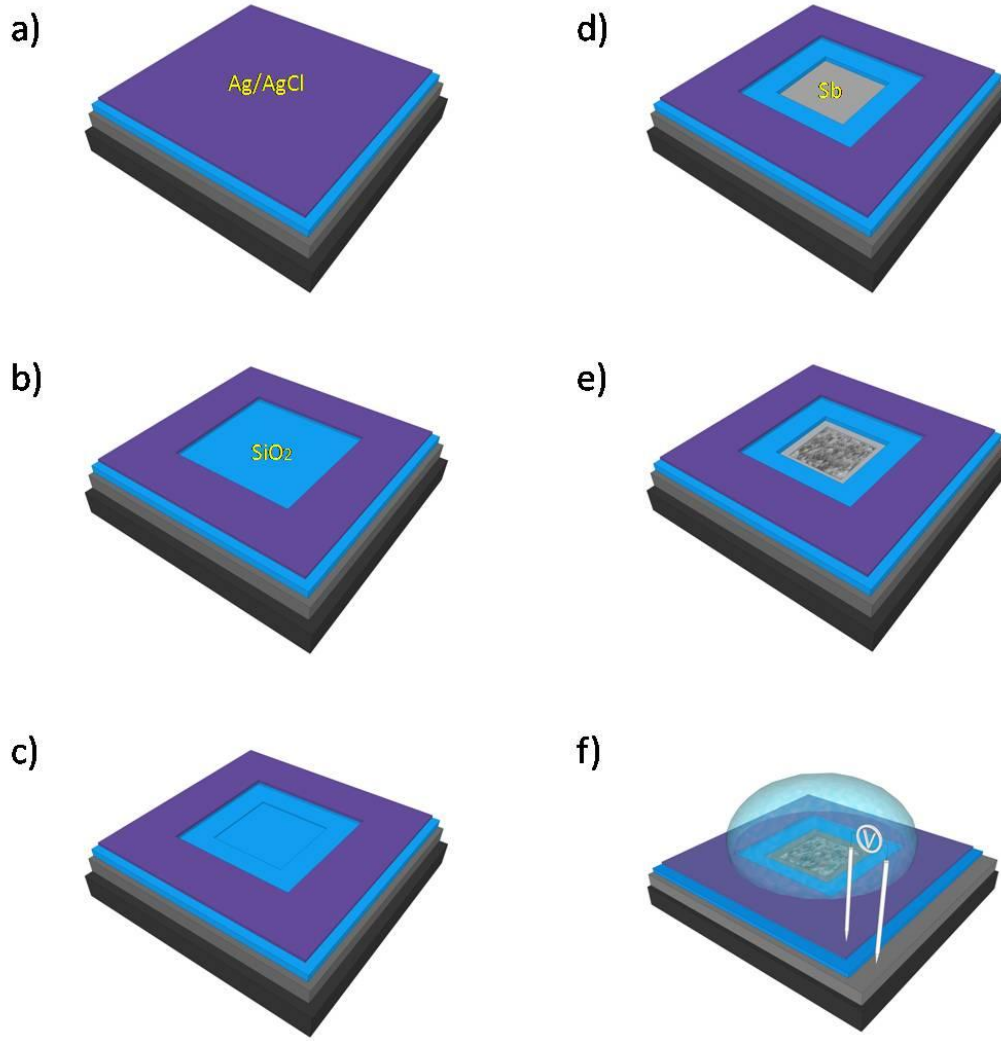


Figure 27. Schematic process flow for microscale pH sensor fabrication. a) Si wafer with 6 μm thick sputter deposited Sb layer covered by 3 μm thick layer of SiO_2 (PECVD) and a 1 μm thick Ag layer for reference electrode. b) FIB removal of reference electrode and one third of the SiO_2 insulating layer. c,d) FIB removal of the rest of SiO_2 . e) FIB induced synthesis of Sb nanowire network. f) fabricated sensor with pH measuring setup.

3.2.1.2 Formation of Reference Electrode

To form a reliable reference electrode on the device, the Ag electrode was converted to Ag/AgCl. Typical methods of forming AgCl are anodization of Ag in chloride containing solutions, or thermal or plasma treatment in chlorine containing atmospheres. As oxidation method for Ag in order to produce AgCl layer as the reference electrode, we choose a treatment with aqueous ferric chloride (FeCl_3). This treatment is fast and electrode stability is the same as electrochemical anodization with HCl ³⁸.

The Ag surface was treated with 50 mM solution of FeCl_3 for 50 sec at room temperature, followed by rinsing with deionized water. Figure 28 shows SEM image and EDX analysis of the silver electrode before (a) and after treatment with FeCl_3 (b). The AgCl layer appeared to be fine granular with a Cl content of about 25% (at).

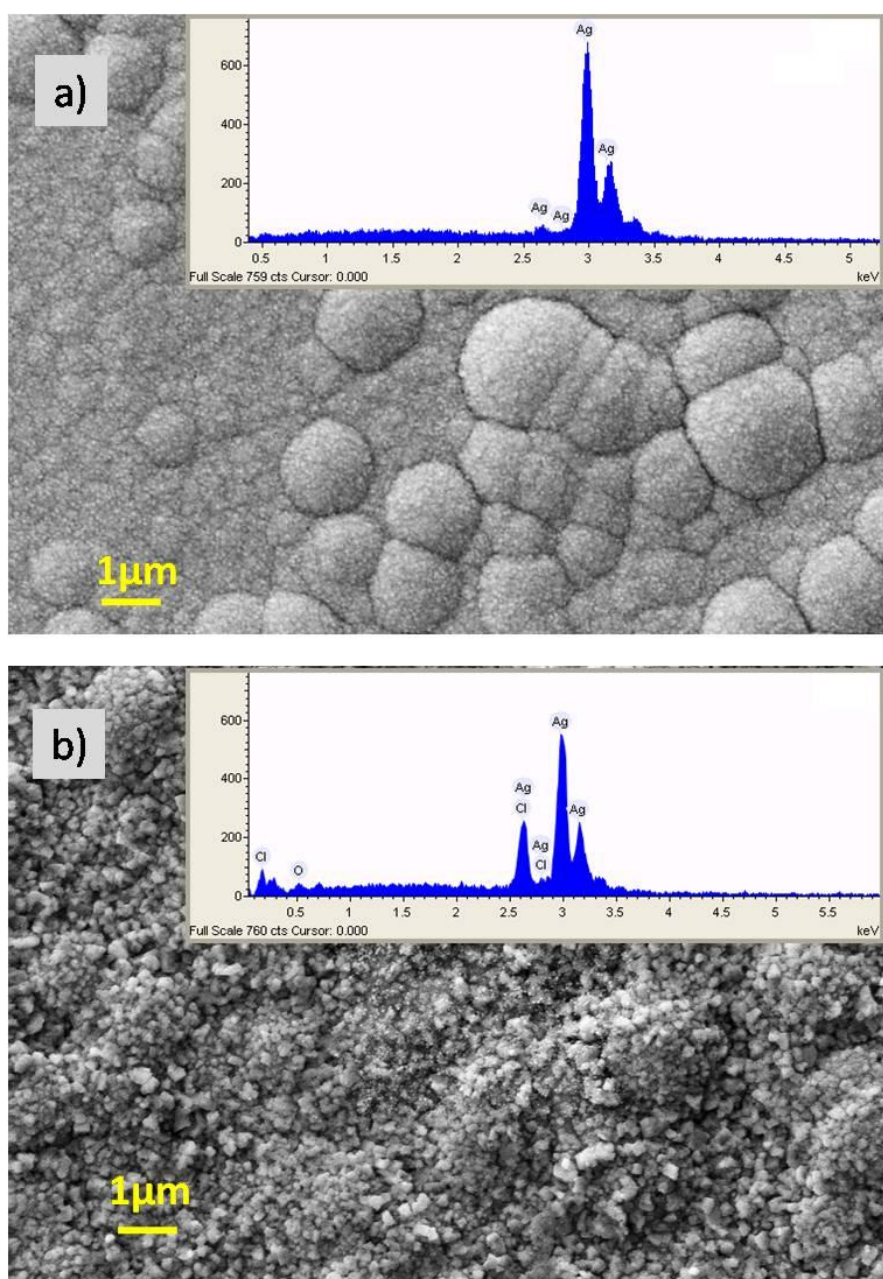


Figure 28. a) SEM image of the untreated silver electrode with corresponding EDX spectrum. b) SEM image of the Ag/AgCl electrode treated with FeCl_3 for 50 seconds at room temperature with the corresponding EDX spectrum.

After electrode fabrication, short-circuit measurements were carried out between each of the three Ag/AgCl electrodes and Sb. Figure 29 shows the final microscale pH sensor with 2 Ag pads transferred to Ag/AgCl reference electrode. It was shown that sometimes there exists a contact between Sb and Ag/AgCl, may be due to pinholes in the PECVD deposited SiO_2 layer. This fields were excluded from investigation and testing.

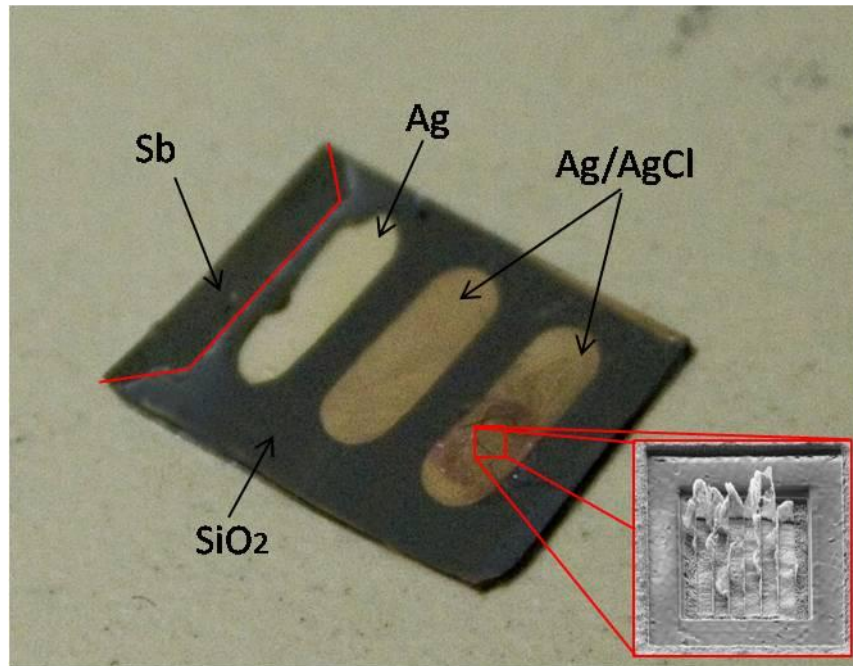


Figure 29. Optical image of the fabricated sensor ($1 \times 0,7$) cm^2 with two reference Ag/AgCl electrodes insulated from each other with SiO_2 . At the left side of device wet etching with HF was utilized to remove an oxide and expose a Sb surface making a contact for the back electrode (Sb). Inset in figure shows the $(60 \times 60) \mu\text{m}^2$ FIB processed microscale sensor part.

3.2.1.3 Formation of the Active Sensor Element (Sb Nanofibers) by FIB Exposure

After the chemical oxidation with FeCl_3 , wet etching with HF (Hydrofluoric acid) was utilized to remove an oxide and expose a Sb surface on one side of device (Figure 29) making a contact for the back electrode (Sb).

In a second sensor fabrication step a $(60 \times 60) \mu\text{m}^2$ area of the Ag/AgCl layer as well as one third of SiO_2 layer was removed by FIB sputtering (Figure 27b). The whole SiO_2 layer was

not completely removed in the first step in order to ensure better isolation between Ag/AgCl and Sb electrode. In the next step, sputter area on SiO₂ layer was reduced to (40x40) μm^2 and the rest of SiO₂ was removed (Figure 27c-d).

Finally on a (30x30) μm^2 area a dense Sb nanowire network was formed by FIB in the center of the SiO₂ opening. The whole area (30x30) μm^2 could not be processed in one fabrication step. The reason why it was not possible to obtain satisfactory nanowire network in one step for large processing areas is that the Ga droplets, that build up after the ion beam passes, lose their temperature by the time the ion beam gets to the next parallel line and sputters Sb. In that case there will be no adequate conditions for VLS process to occur and no nanowires can be grown.

As an alternative, six boxes with dimensions (5x30) μm^2 were processed next to each other to create the required nanowire network on the full (30x30) μm^2 area (Figure 30).

As shown in Figure 27e the final microscale pH sensor comprise two electrically insulated electrodes (Ag/AgCl and Sb nanowire network). When one drop of solution (Figure 27f) is placed on the active sensor element, the electrochemical potential of electrodes builds up and the potential difference between them can be measured.

The SEM image in Figure 30 shows the enlarged view of the active pH sensor element.

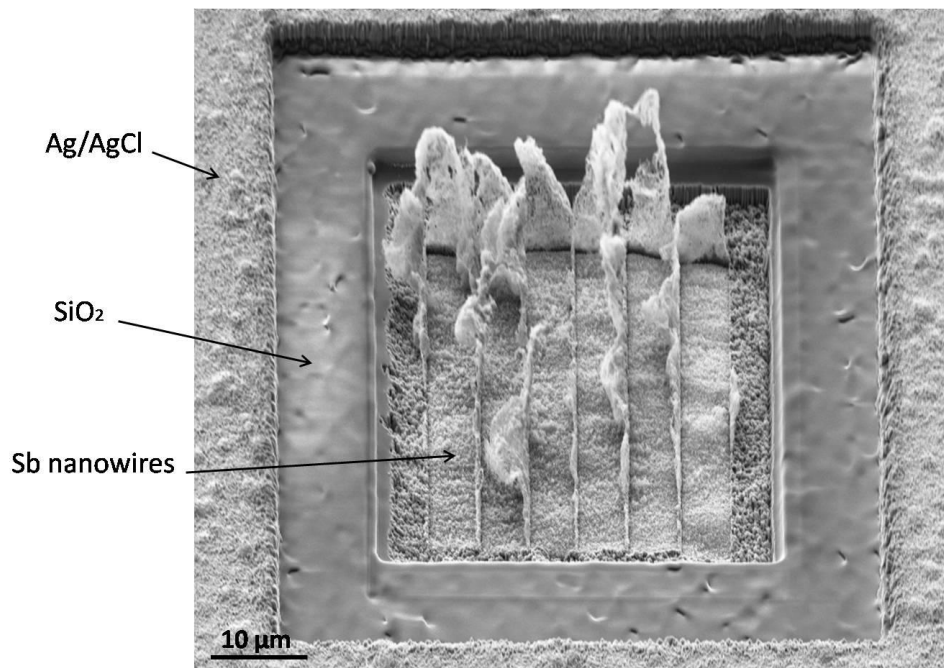


Figure 30. SEM image of the microscale pH sensor fabricated in course of this work.

3.2.2 pH Sensor Testing and Calibration

For purposes of device testing and calibration, a needle prober (Analytical Probe System PSM6, Karl Süss MicroTec AG) and standard buffered solutions, provided by Acros Organics, were used. The chemical compound of the buffer solutions and concentration is listed in Table 2.

pH	Chemical compound	[at] %
2	Glycine	0.39
	Mercuric chloride	0.001
	Hydrogen chloride	0.18
	Sodium chloride	0.031
	Water	99.119
4	Potassium hydrogen phthalate	1.02
	Fuchsin acid	0.0005
	Mercuric chloride	0.001
	Water	98.9785
6	Sodium hydroxide	0.023
	Mercuric chloride	0.01
	Water	Balance
	Potassium dihydrogen phthalate	0.69
8	Sodium hydroxide	0.016
	Potassium chloride	0.38
	Water	Balance
	Boric acid	0.316
10	Sodium hydroxide	0.175
	Potassium chloride	0.373
	Water	Balance
	Boric acid	0.309

Table 2. Buffer solutions used for pH sensor testing and their chemical compound in [at] %.

Needle prober comprises precise manageable probe needles connected to a semiconductor parameter analyzer (Agilent/HP 4156B), a moveable stage in x, y and z direction and a microscope for probe alignment (Figure 31-c and d) .

Manual manipulators allow precise placing of probe needles at the surface without damaging it, which is controlled by microscope.

The measurements of the potential difference, which builds up between the Ag/AgCl and Sb nanowire network, when the solution is measured, have to be conducted without current source in order to avoid voltage drops across sensor electrodes and ensure an actual measuring of potentials. This requirement is very important since the expected voltages are in mV range (ideally 59.16 mV per pH unit at room temperature). Therefore the measurement unit used must have an extremely high input resistance. Semiconductor parameter analyzer fulfills these requirements and enables measurements with simply choosing current $I = 0$ within measurement parameter configuration.

Figure 31 shows the measurement setup. One needle probe is placed on the Ag/AgCl (Figure 31-a) electrode and the other on the Sb common/back electrode at one side of device (Figure 31-b). The reference electrode is set to be ground and the potential over time was measured on Sb nanowire network.

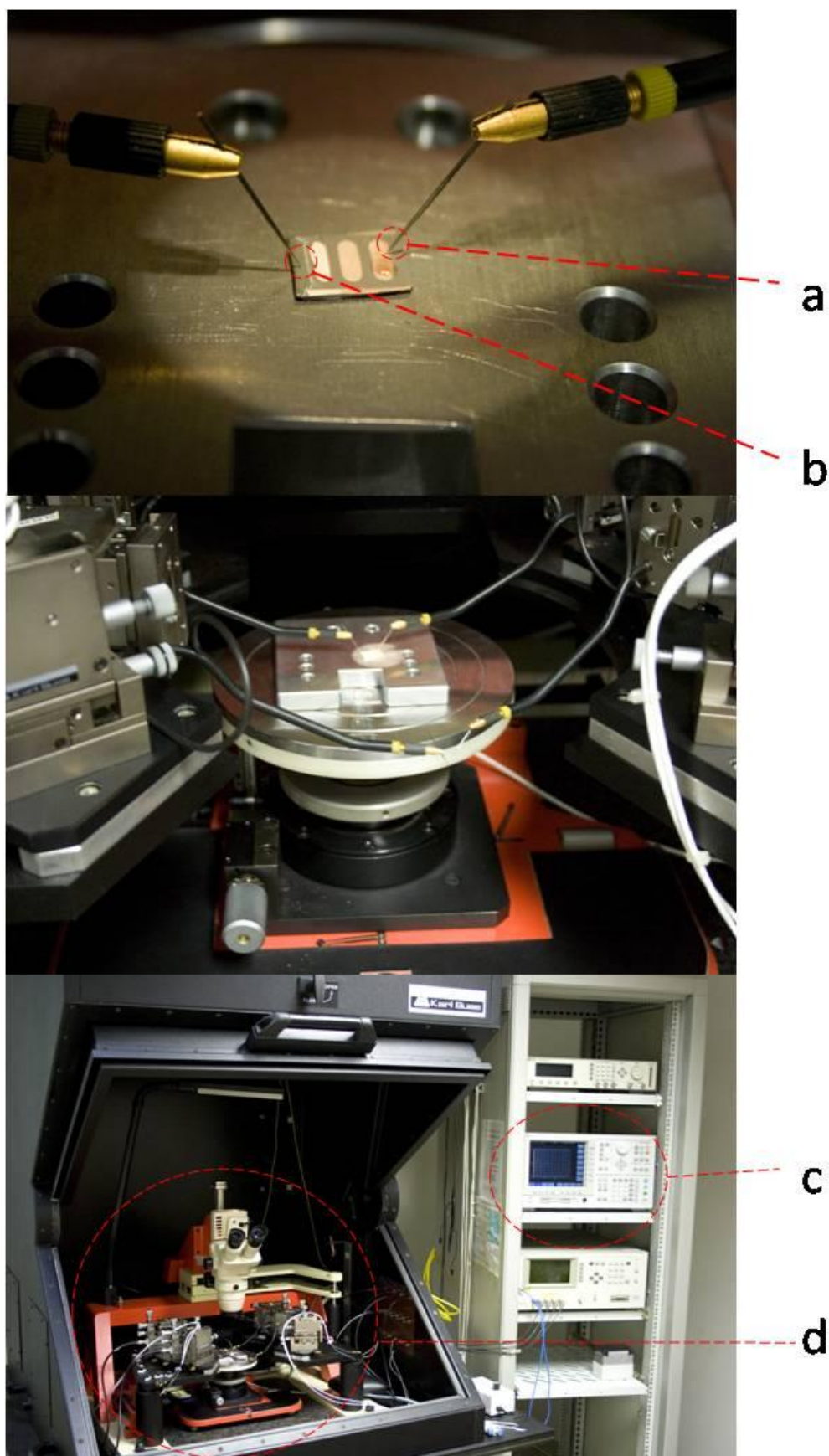


Figure 31. Optical image of the measurement setup. a) needle probe placed on Ag/AgCl electrode. b) needle probe placed on back Sb electrode. c) semiconductor parameter analyzer (Agilent/HP 4156B). d) a needle prober (Analytical Probe System PSM6, Karl Süss MicroTec AG).

3.2.2.1 pH Measurements of as-fabricated pH Sensor

Figure 32 shows the e.m.f. response of three individual pH sensors for the buffer solution pH 4.

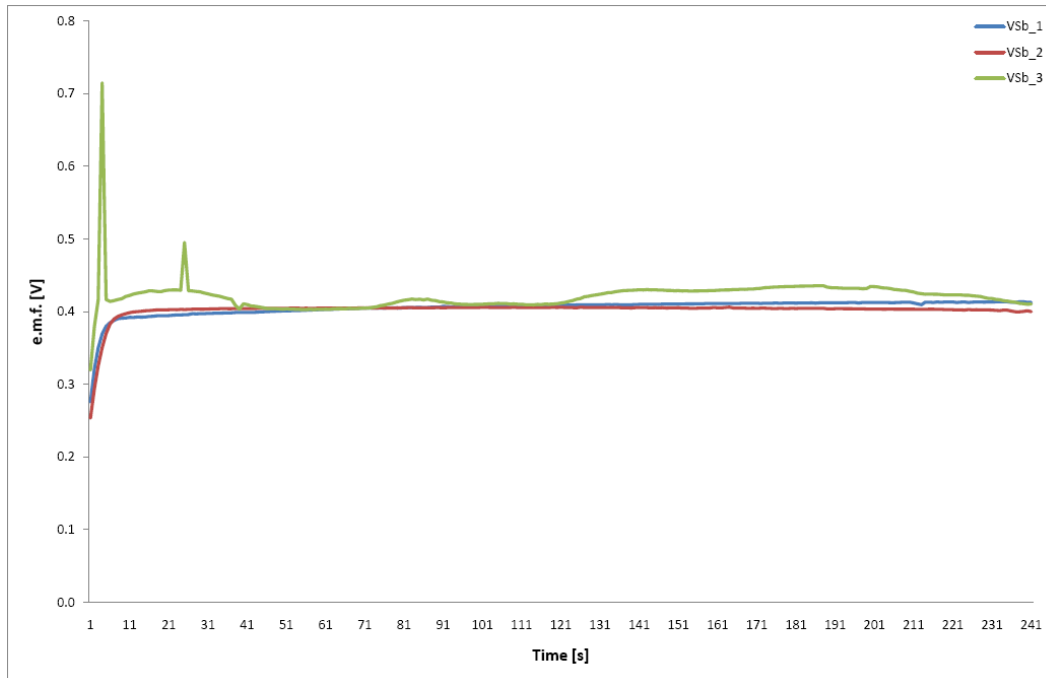


Figure 32. e.m.f of the sensor measured with 3 sensors, fabricated with the same parameters. The curve shows potential response on a pH 4 buffer solution for 4 minutes.

The response time is very short (less than 10 s) and the potential shows good stability over time. The e.m.f. is in the expected range of about 400 mV.

Influence of the Cl concentration in solution on as-grown NW

One of the problems that occurred during measurements of as-fabricated pH sensor is that the potential stability appeared to be dependable on the chlorine concentration in the solution. We made this assumption since only two buffer solutions (pH 4 and 6) show stable potential response and these buffer solutions have unnoticeable chlorine concentration (see Table 2). To make sure if chlorine concentration influences measurements, we mixed 0,38M calcium chloride (CaCl_2) with pH4 buffer and the measurement showed that chlorine concentration has unfavorable influence on sensor (Figure 33). The blue curve in Figure 33 represents the measurement of the pure pH 4 buffer solution. As it can be seen it stays in region of 400mV as it was measured

previously. After that the chloride has been added and the curve became unstable (red curve). The measurement taken afterwards, without chlorine, is stable again (green curve). It is evident that the potential measured afterwards is slightly shifted. The reason for that is the partially destruction of the nanowires.

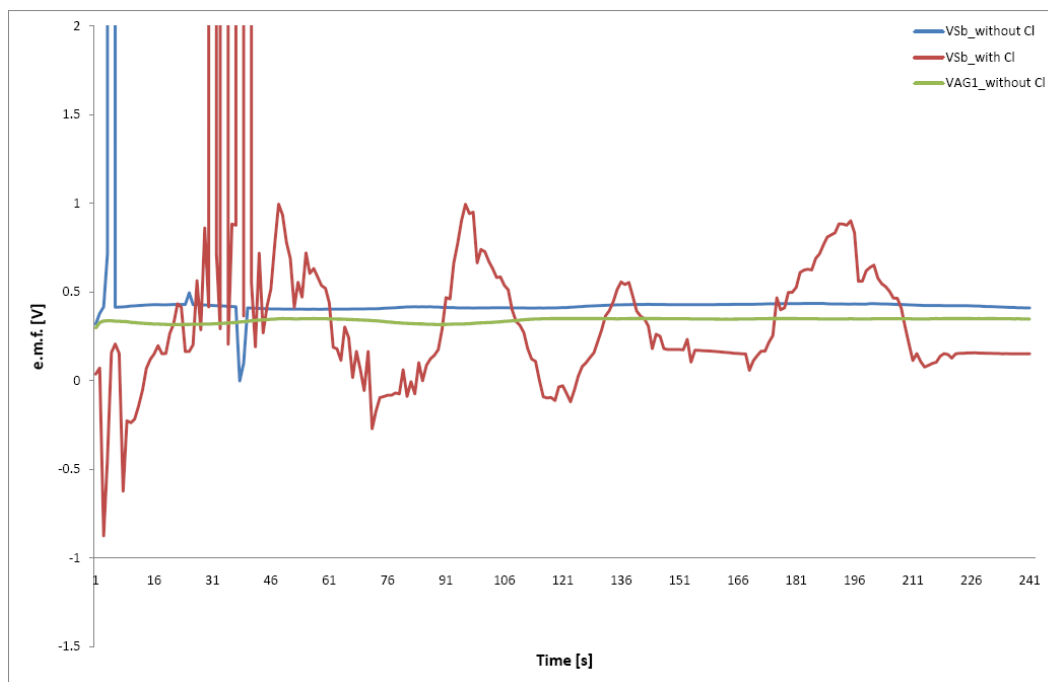


Figure 33. Chloride influence on the potential response of as-formed nanowires.

Solubility of nanowires

The very small diameter of the Sb nanowires makes them more sensitive to corrosion than the bulk material.^{48,49} After certain time (ca. 20 min) for which the sensor has been in use (that the nanowires were in buffer solution) an abrupt potential drop has been observed. Figure 34 shows the e.m.f. response after long term measurement. The blue curve shows the e.m.f. drop after about 20 minutes long measurement. Afterwards one more measurement has been taken for 15 minutes (red curve in Figure 34) to show that the e.m.f. drop remains. After this voltage drop the sensor could not be recovered anymore. The sensor was examined in SEM revealing that the structure was damaged beyond repair (Figure 35).

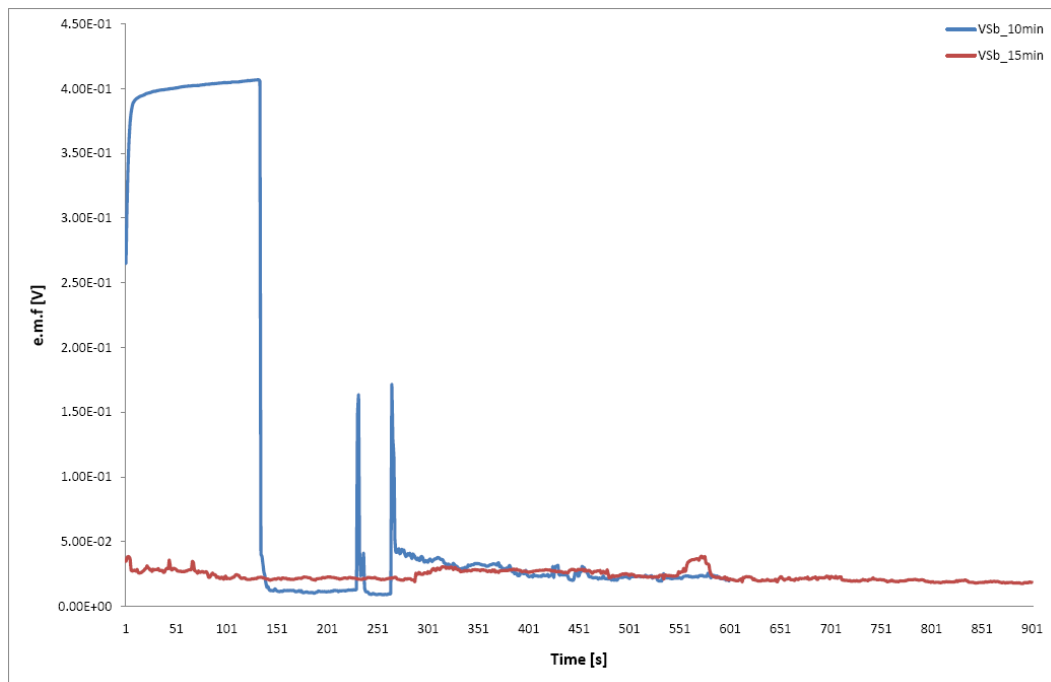


Figure 34. Voltage drop after a long-term measurement shows that the nanowire network is defective and therefore the sensor is not functioning properly. The blue curve shows the e.m.f. drop after an about 20 minutes long measurement. The red curve was taken after this voltage drop to show that it remains unchanged over time.

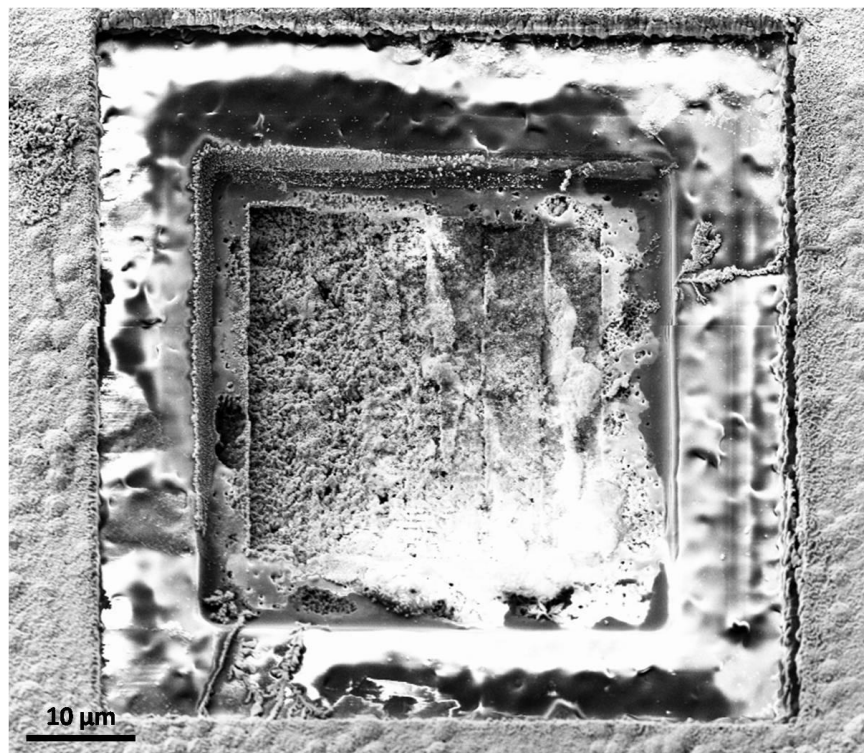


Figure 35. SEM image of the microscale pH-sensor after long term measurement of pH 4 solution. The nanowire network is damaged.

It has been also observed that after measurements of other buffer solutions (pH 2 to pH 10) this problem occurred even faster.

In order to determine how the buffer solutions affect the nanowires, $(10 \times 10) \mu\text{m}^2$ wide boxes were processed and exposed to the buffered solutions.

Figure 36. shows the SEM image of four samples that have been held in the buffer solutions with pH 2, 4, 8 and 10 for 10 minutes. First and second sample (Figure 36. a and b) were immersed in solutions with pH value 2 and 4 respectively. In comparison with the SEM images in Figure 36. c and d, where the samples were immersed in buffer solutions with pH value 8 and 10 respectively, a conclusion can be drawn that the Sb nanowires are more soluble in alkaline solutions than in acidic. However that doesn't mean that the Sb nanowires are not soluble in acidic solutions, rather that this process is somewhat slower.

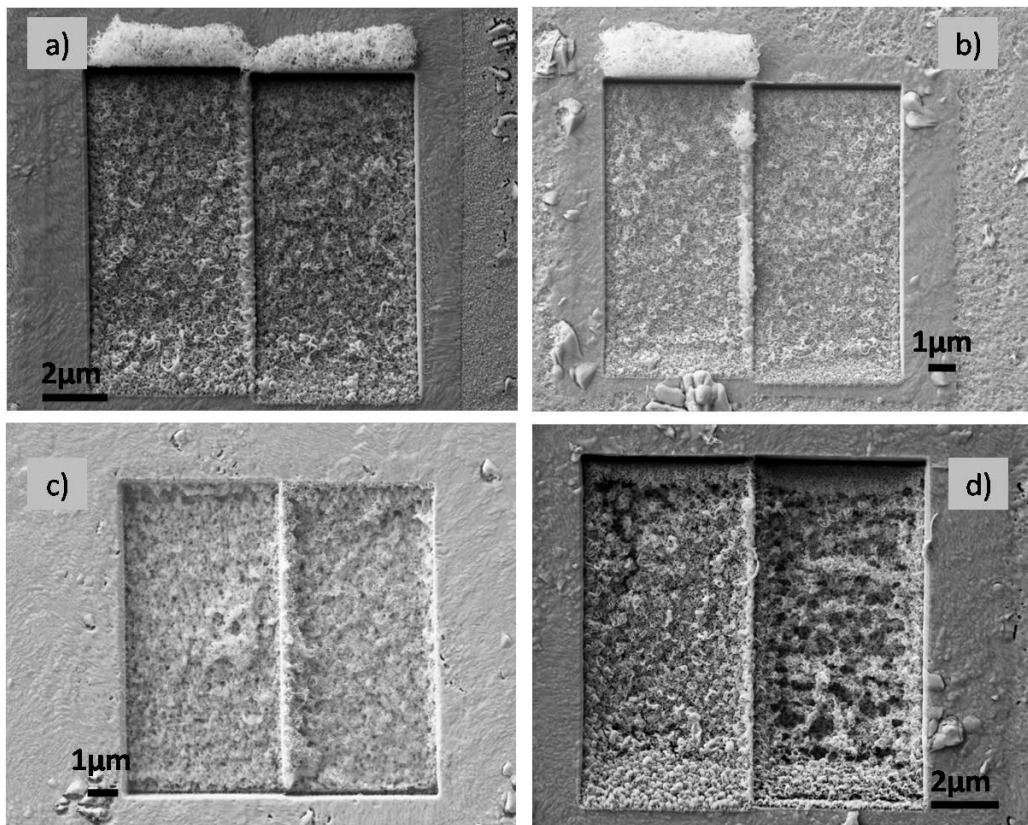


Figure 36. SEM image Sb nanowire network $(10 \times 10) \mu\text{m}^2$ after the solubility test on buffer solutions. a) sample after 10 minutes in pH2 buffer solution, b) sample after 10 minutes in pH4 buffer solution, c) sample after 10 minutes in pH8 buffer solution, d) sample after 10 minutes in pH10 buffer solution.

3.2.2.2 pH Measurements of pH Sensor After Thermal Annealing

In the previous section we have shown how the measuring procedure affects the active sensing element of the device. The solubility of the nanowires can be improved by a postprocess annealing leading to recrystallization of the Sb nanowires.

In order to re-crystallize Sb nanowires, they were annealed for 30 minutes on 150°C in air. After the anneal process the sensor enabled stable measurements even in buffer solutions with chlorine.

Since it was possible to conduct measurements even in the alkaline regime (pH2, 4, 6, 8, 10), the e.m.f. over pH was plotted (Figure 37.).

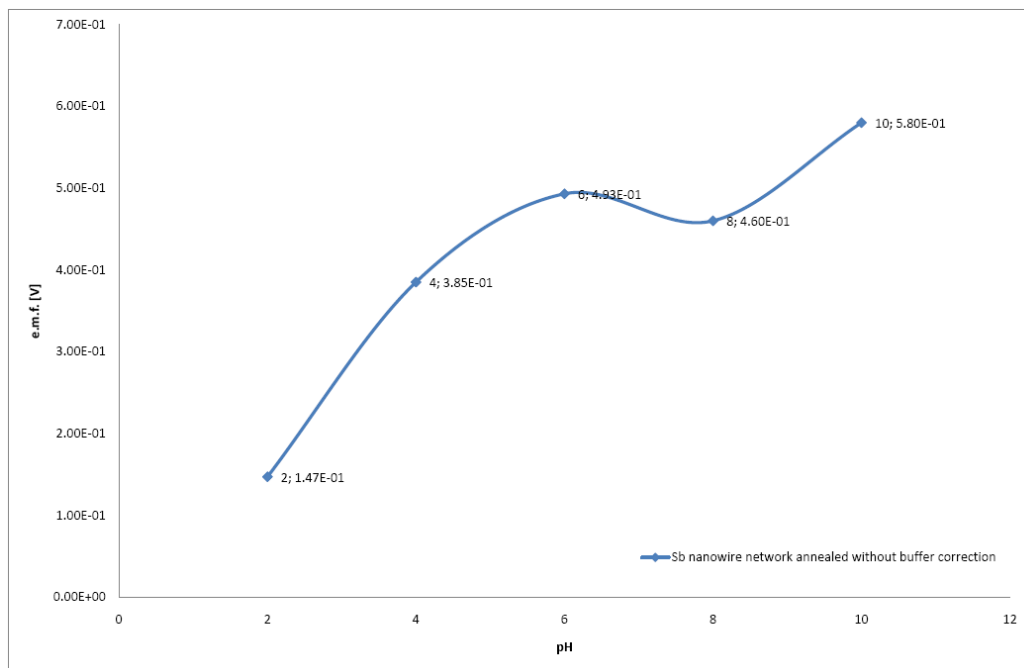


Figure 37. e.m.f plotted over pH scale. pH 4 and pH6 contain no chloride and their measurements can not be considered as a correct sensor read out.

The relationship is not linear. The e.m.f. measured for solution with pH 4 and pH 6 appeared to be higher than expected. If we exclude values for pH4 and pH6 we will have a linear ascending e.m.f. response over pH values that can be described with the relationship $e.m.f. = a + b * pH$.

To ensure exact measurements over the full pH scale, the same amount of the chlorine, as it is in the other solutions, was added to pH 4 and pH 6 solutions. The pH value of the new

solutions has been measured with a standard glass pH meter. The pH values were slightly shifted which was taken in account by plotting of e.m.f over pH scale (see Figure 38).

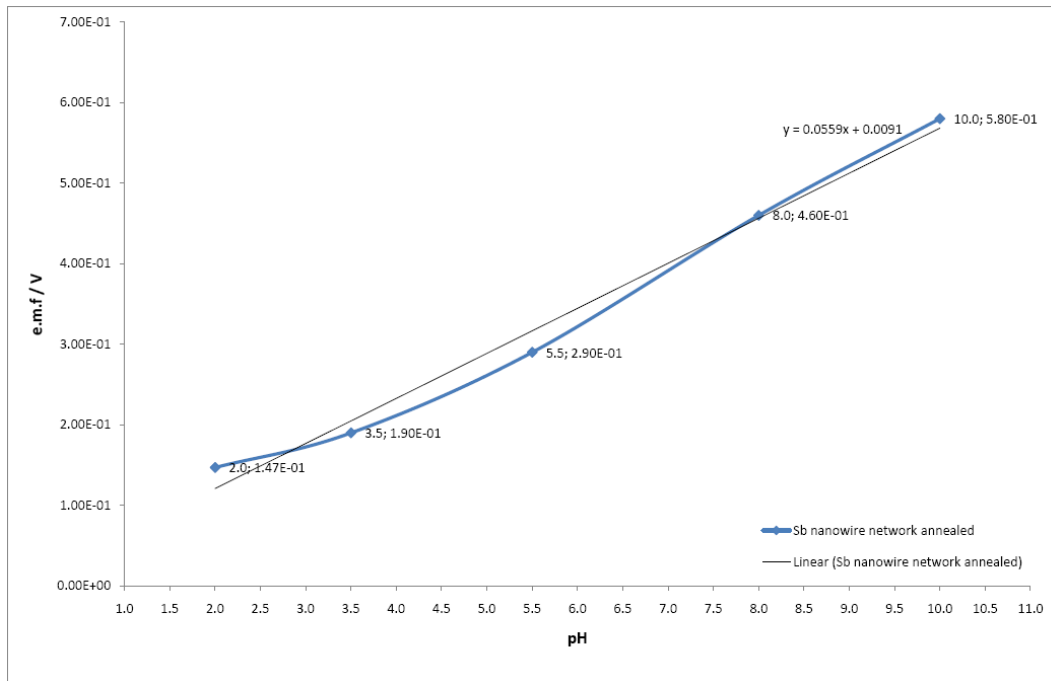


Figure 38. e.m.f. plot over pH scale. pH value of pH 4 and pH 6 was shifted to a pH 3,5 and pH 5,5 respectively and was considered in plot.

After the buffer solutions had been matched, the relation between e.m.f and the pH scale can be described with the equation $y = 0.009 + 0.055x$ which is in good agreement with the theoretical value of $E = E_0 + 0.05915 \text{ pH}$.

4 Summary and Conclusion

In this work the FIB induced synthesis of nanowires on different substrates (Ge, GaSb and Sb) and the application of the Sb nanowire network as microscale CMOS compatible pH sensor was explored.

In chapter 2 an overview of the FIB instrument and the FIB processing as well as the theoretical background on pH sensing and measuring system and nanowire growth techniques was given.

In the first part of chapter 3 the influence of the FIB incidence angle on the surface evolution behavior for Ge and GaSb substrates was shown. At first the FIB impinges perpendicular to the surface and the formation of the sponge like structure can be observed. As the incidence angle changes the nanowire-like structure appears.

In the case of the Sb, the influence of the ion dose, and scanning strategy on the Sb nanowire network density was investigated. The Raman proved that the FIB assisted grown Sb nanowires consist of Sb with a thin oxide shell. TEM and HRTEM analysis showed that the as-grown nanowires are amorphous, but after thermal annealing for 30 minutes at 180°C in air they regain the crystalline structure.

In the second part of chapter 3, the microscale pH sensor was discussed. Because of the fabrication method and the construction showed, it can be said that it is CMOS compatible.

The measurements of the e.m.f over pH scale (pH2, pH4, pH6, pH8 and pH10) showed the linear response in good agreement with the theoretical value of $E = E_0 + 0.05915 \text{ pH}$. Experimentally E_0 has large variation due to different crystallographic orientation of Sb resulting from different approaches of electrode synthesis.

In our case additionally this value can be altered due the fact that the reference electrode is not insulated from the measured solution as realized by standard glass bulb pH sensor. Because of that it is also important to point out that the e.m.f. response of the sensor depends also on chlorine concentration in solution. That means that the calibration curve made with buffer solutions with the same concentration of chlorine can be used only for pH measuring of species with the same chlorine concentration as it is in the buffer calibration solutions.

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