



Electropolishing and passivation of silicon nanowires towards hybrid interfaces



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ABSTRACT

Surface defects on nanowire structured silicon (Si) surfaces prepared by metal assisted chemical etching generate trap states in the band gap and thus minimize the efficiency of the future device. Electropolishing treatment of Si surfaces results in a reduced surface defect density. Since the interband photoluminescence (PL) of Si is very sensitive towards changes of the surface defect density, electropolishing treatments have been monitored by in situ PL measurements. A strong enhancement in PL intensity during the electropolishing experiment was obtained, which correlates to a reduced amount of surface trap states. The subsequent electrochemical exchange of Si–H bonds by Si–C bonds via methylation preserved the low defect density of the surface and prevented the formation of a native silicon oxide layer. Additional PL measurements proved the long-term stability of the methyl passivated surfaces of the Si nanowires in ambient air.

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1. Introduction

Si nanowire arrays are of great interest for applications, e.g. field-effect transistors, field emitters, photovoltaic devices and chemical sensors [1]. Besides increased light trapping, nanowire-structured Si surfaces can reduce reflection losses due to decreased dielectric mismatch between the surface and air. Furthermore, the improved property of nanostructured surfaces of coupling light into the material more efficiently could open up additional cost saving advantages regarding the amount of material needed [2].

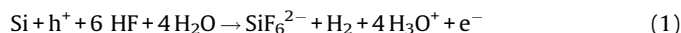
Nanowire-structured surfaces can be generated by different techniques. Several bottom-up and top-down techniques are available for Si, all having their specific inherent benefits and limits. The vapor–liquid–solid (VLS) method needs a metal catalyst like gold or copper and leads to power conversion efficiencies of up to 4% for 800 nm monochromatic light excitation [3]. Recently, a two-step methylation process has been applied to VLS-grown Si nanowires, leading to a suppression of SiO_x formation and to an enhancement in the power conversion efficiency of 1.2% for AM1.5 [4]. For our approach we used the metal assisted chemical etching (MACE) technique in combination with nanosphere lithography [5]. By selecting nanosphere diameter, time of reactive ion etching and time of the MACE process itself, wire length, diameter, and

periodicity can be easily controlled. Variations of these parameters lead to different nanowire morphologies [1,5,6].

Structuring of the Si surfaces provides additional trap states in the band gap what in turn enhances electron–hole recombination reactions [7]. Therefore, the increase in surface area by structuring techniques like MACE is inevitably combined with the creation of surface defects like dangling bonds, strains and kink sites. Thus, the increase in the density of surface defect states (D_{SS}) limits the efficiency of any future device and needs to be reduced. One possible procedure was recently published by Pudasini et al. by using a passivation layer of atomic layer deposited Al₂O₃, but they still used the as-etched rough surface of the Si nanowires [8]. In this paper, we focus on the electrochemical smoothing of the Si nanowire surface and its subsequent passivation by methyl groups.

Repetitive electrolytic growth and dissolution of oxide layers on Si surfaces, also referred to as electropolishing, can decrease D_{SS} by removing the defect states along with a thin layer of Si as observed for flat Si [9,10]. Oxide growth and dissolution are initiated and controlled by applying different potentials to the Si surface that is in contact with a fluoride containing solution [11]. Oxidation and etch-back potential regimes have been found out by determination of I–V-characteristics of the n-type Si [11,12].

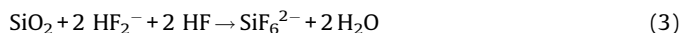
At low band bending, etching of the Si surface is induced as divalent dissolution of Si [13]:



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Whereas at higher band bending (more anodic potentials) oxide formation occurs followed by a tetravalent dissolution of Si in the HF containing electrolyte [14,15]:



The rate determining species for the oxidation of Si are holes, h^+ . Therefore, the oxidation rate of n-type Si can be increased by generating additional holes in the material using white light illumination of the sample [14]. During oxide formation, the rate determining species are HF/HF_2^- ions since the formed silicon oxide is an electrical passivation layer. Thus, Si oxide is preferably etched-back at hillocks and rough sites that stick out into the solution and are surrounded by etching HF/HF_2^- species. An equilibrium between both reactions, oxide formation and oxide removal, will be established, whereas the thickness of the oxide layer depends on the applied potential [16]. This equilibrium leads to smoothing of the surface [11,17,18]. Interruption of the electrochemical oxidation process leads to an etch-back of the oxide layer. At the SiO_2/Si interface are Si suboxide species with intermediate oxidation states (Si^+ , Si^{2+} , Si^{3+}). During the etch-back process, these suboxides are further oxidized leading to a charge injection into Si and finally to the observed dark-current transient [11,16,19–22]. The density of these suboxides species depends on the orientation of the crystalline Si surface [23]. Consequently, the flown charge during the dark-current transient depends on the amount the suboxides at the Si/SiO_2 interface [16,20,21] and is therefore a measure of the interface roughness (the rougher, the more suboxides at the interface). Finally the etch-back of the oxide layer in the dark ends in the H-termination of the Si surface [11,16,21,24,25]. Although the H-termination displays an excellent passivation of the Si surface, it is not stable under ambient conditions [26]. As a consequence, H-terminated Si surfaces oxidize in ambient air and the formed oxide generates recombination active defect states [27]. Grafting of small molecules, e.g. methyl groups, preserves the good passivation as obtained by H-termination and inhibits oxide formation on the Si surface due to the potentially complete coverage of the Si surface by CH_3 -groups that suppresses the attack of $\text{O}_2/\text{H}_2\text{O}$ at the Si—Si back bonds [28–30].

Photoluminescence (PL) measurements are a valuable tool to evaluate the electronic quality of Si surfaces. The interband PL efficiency of c-Si is determined by radiative recombination processes of electron–hole pairs [31]. Assuming that the bulk recombination of charge carriers is not influenced by modification of the surface states, changes in PL intensity are due to changes in the surface recombination velocity only [32]. Therefore, a high D_{SS} will ultimately result in a low PL signal intensity. A surface with low D_{SS} will give intense PL signal because generated charge carriers will contribute to the bulk related PL signal with less non-radiative recombination loss. After electropolishing, the surface will have less defect concentration and will therefore exhibit an improved PL intensity.

For the present paper an electropolishing setup was combined with a PL setup to monitor changes of the surface defect density during electropolishing experiments on nanowire-structured Si surfaces. It reveals that the PL intensity increased strongly by the repetitive oxide growth and dissolution process (electropolishing). The comparison of PL spectra of treated and untreated Si nanowire surfaces confirms the reduction of surface defects by electropolishing experiments and the possibility to preserve this condition by passivation with methyl groups. Additionally, the long-term stability in ambient air of the H- and CH_3 -terminated

nanowire-structured surfaces was investigated by PL measurements.

2. Experimental

2.1. Fabrication of silicon nanowires by metal assisted chemical etching

Experiments have been conducted using (100) oriented Si wafers (electron concentration of 10^{16}cm^{-3} , resistivity of 0.6–1.1 Ωcm). The Si wafers were cleaned by the RCA treatment [33] followed by an implementation of a back-surface-field by deposition of 5 nm a-Si:H(i) and 20 nm a-Si:H(n^+) layers on the back side.

To fabricate Si nanowires, polystyrene spheres (e.g. $\sim 600 \text{nm}$ diameter, commercially available at Microparticles GmbH) were deposited on the Si surface using a Langmuir Blodgett trough [34]. This technique leads to densely packed hexagonal monolayer array structures of the polystyrene spheres on the surface. Afterwards, the spheres were reduced in diameter by reactive ion etching using oxygen plasma (60 sccm, 30 W, 3 or 5 min). Subsequently, a 60 nm thick Ag layer was deposited by thermal evaporation. The spheres were removed by sonification in toluene for 10 min. The Ag patterned Si surface was etched by dipping the sample into a solution consisting of 5.65 M HF and 0.1 M H_2O_2 for 3 or 4 min (see SEM images of the obtained nanowires in Fig. 1). The etching process was stopped by dipping the sample in deionized water. Finally, the silver pattern was removed by immersion of the sample

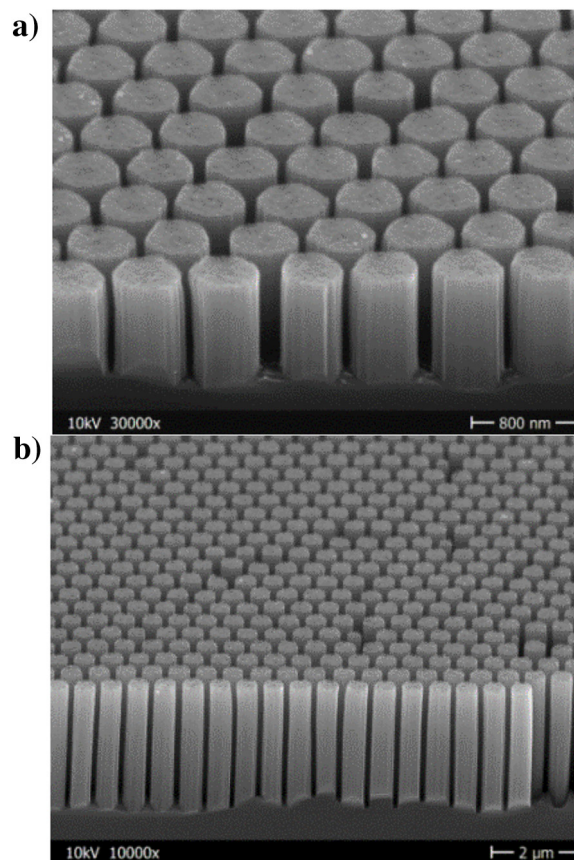


Fig. 1. Different morphologies of Si nanowires obtained by choosing different parameters for nanosphere diameter etching by time used for the RIE process (60 sccm, 30 W) and the time for the metal assisted chemical etching. RIE and MACE process times: a) each 3 min, length and diameter of the nanowires: $\sim 900 \text{nm}$ and $\sim 500 \text{nm}$; b) 5 and 4 min, length and diameter of the nanowires: $\sim 3.15 \mu\text{m}$ and $\sim 440 \text{nm}$, respectively.

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