

Local Transmittance Measurements as Large Area Diagnostic Tool for the Optimization of Porous Si Foils for Li-Ion Battery Anodes

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Silicon with its exceptionally high gravimetrical capacity of 4200 mAh/g has a great potential as anode material for Li-ion batteries. However, several critical problems have to be overcome to realize the up-scaling of the anodes from lab scale to mass production, especially with respect to long term cyclability and low cost fabrication techniques. In this paper, large area etched porous silicon foils are optically characterized with respect to local homogeneity in porosity and thickness and further prepared for a novel and promising type of anodes for Li-ion batteries. Since large areas (larger than 250 cm²) have to be analyzed locally with high spatial resolution (smaller than 50 μ m), a fast and contactless solar cell local characterization technique (CELLO [J. Carstensen, A. Schütt, G. Popkirov, and H. Föll, *Phys. Status Solidi C* 8(4), 1342 (2011)]) has been modified to measure the reflectance and transmittance of the porous silicon foils helps to modify the process parameters of the large area etching but more importantly allows a stable and cost effective new anode. This study illustrates the promising new battery concept based on a PorSi foil with adjustable porosities between 40 to 60 %.

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For many applications, batteries with high capacity and large cycling stability are obligatory. Silicon with an exceptionally high gravimetrical capacity of 4200 mAh/g is one of the prime candidates for Li-ion batteries meeting these requirements. However, due to the large volume expansion of over 400 % during lithiation, silicon has to be nano- or microstructured to avoid pulverization¹ during charging or discharging and to remove stresses to obtain mechanically stable longlife anodes. In addition, the strong volume expansion can lead to a delamination from the metal contacts as well as a disintegration of the whole anode. To overcome these problems several approaches exist. Often spherical silicon particles are mixed with either conductive additives like carbon black, graphite, graphene etc. or they are mixed with polymer binders.²⁻⁴ Such binders like cellulose (CMC) or polyvinyldifluoride (PVdF) mixed into silicon containing pastes enhance mechanical stability. In addition to an unfavorable increase of battery mass without adding active material, this approach has further drawbacks: First, after volume expansion the shrinking of the Si particles may form voids filled with electrolyte, which effectively leads to a demixing of the paste components by cycling. Second, the important solid electrolyte interphase (SEI) around these structures tends to form cracks which lead to undesired reactions with the exposed active material and to rearranged SEI growth in every cycle which drastically limits the battery performance.⁵⁻⁷ Third, the most critical point is the mechanical connection to the current collector, which has to sustain the periodic expansion and shrinking of the silicon. Thus, such anodes have to be cycled really slow in order to achieve high capacities.8,9

In contrast, highly ordered arrays of silicon microwires connected galvanically to a Cu foil show none of these disadvantages and allow stable cycling with high *C*-rates.^{10,11} Although large-scale production of silicon microwire anodes in principle is feasible, it is a quite expensive approach due to the precise structuring of the silicon microwires. The PorSi foils introduced here are designed to adopt many benefits of the silicon microwire array anodes but can be produced on large areas (larger than 250 cm²) in a very cost effective manner. This method is a scientifically new method and already exists. During this study, optimizations regarding the optimal parameters for possible applications in battery technology are shown. Therefore, process parameters like time, current and voltage of the large scale etching process need to be optimized in order to produce a homogeneously etched silicon wafer. Batteries from these foils benefit from their lightweight and high amount of active material. They are fabricated in a "top-down" approach with specifically tuned porosity and layer thickness by largescale ("in-line") electrochemical etching processes mainly controlled

by etching current time profiles. Cost-effective solar silicon material can be used. By etching a thin highly porous layer as the final formation step, an easy transfer of the PorSi foil without any kerf loss is possible, thus saving roughly 50 % of classical wafering costs. This etching technique is applicable to various fields of applications like, for example, solar cell industry, where fast and high local resolution "reaction" time is needed to optimize the homogeneity of a wafer surface. This approach is similar to the fabrication procedure for silicon solar cells, 12-14 but does not even involve a further CVD process. Compared to other techniques making porous semiconductor materials, the amount of remaining active material is very large (porosities of up to 70 % are achieved without using any other inactive material in this anode).^{6,15} Besides enhanced cycling stability, further principle advantages of porous materials for Li-ion batteries lie in an easier diffusion of the electrolyte into the pores by reducing diffusional paths.¹⁶ Therefore, there is the request to have a method to analyze porous Si foils on large scale i.e. the same size as they have at the end of the production line.

Due to the strong volume expansion, any part of the PorSi foil with an insufficient porosity will be pulverized, leading possibly to a successive destruction of surrounding areas as well. Thickness variation of the PorSi foil contributes to ohmic losses on the Cu current collector as well as diffusion losses within the electrolyte. These two counterproductive scenarios demonstrate already the importance of a homogeneous etching process laterally as well as in depth of the PorSi foil. For battery applications, it is crucial to obtain a homogeneous pore distribution across the wafer surface during the large area etching. Differently sized pores or blocked pores on the PorSi foil lead to inhomogeneous Li diffusion. Surfaces with higher porosity show higher diffusion whereas there might be areas where the pores are blocked and the diffusion paths for the Li ions do not exist anymore. Furthermore, the correct active weight could not be determined for the subsequent battery application, which is crucial for cycling in the correct voltage corridor.

Thus, before fabricating battery anodes from PorSi foils, transmittance as well as reflectance measurements are performed with a spatial resolution of roughly 50 μ m on areas up to 250 cm² using a modified CELLO setup. The CELLO technique has been developed for the characterization of large area solar cells and allows fast local photo current measurements with high scanning rates, high spatial resolution, and large signal to noise ratio since a lock-in technique is employed. Accurate maps of the transmittance and reflectance data of the PorSi foil are made by placing a PorSi foil between the laser beam and reference solar cell and measuring the reflected light in addition. The interpretation of these data with respect to the local porosity and thickness variation of the PorSi foil and the resulting battery



Figure 1. Example of the as-prepared PorSi foil anodes. The process line is illustrated mostly by several SEM images. A shows an example of one PorSi foil still attached to the wafer. It illustrates on the far left the two layers (highly and low porous layer). The adjacent SEM images show the etched pores. Some parts of the pores is still blocked, the etching did not succeed. The schematic emphasizes further the different layer system. B shows the copper deposition of the current collector. The copper is directly deposited on top of the highly porous layer. At the interphase between the copper and the PorSi foil, the copper diffuses into the silicon and ensures a good contact. The fotograph shows the anode after removal from the wafer substrate.

anode performance in dependence of these parameters will be discussed below.

Experimental

Anode production and preparation.—The process to fabricate PorSi foil anodes consist of two important steps. The basic step is the large area electrochemical etching process in an "inline" process tool during a "top-down" process. The substrate material is p-doped solar cell silicon (100). The doping level is varied throughout the experiments to determine the influence on the pore diameter and growth; for the analyzed samples in this study, the doping level is constant at 10^{18} cm⁻³.

The etching is divided into two steps: a) first a low porous layer is etched; b) in a second step, a highly porous zip i.e. releasing layer is etched in a 50 wt% hydrofluoric acid (HF) solution. During the electrochemical etching process, parameter variation of voltage, current, and time lead to a variation in pore morphology, size and distribution. Mesopores with diameters from 9 - 15 nm could be obtained, as well as macropores with diameters between 50 to 200 nm. The thicknesses of the PorSi foil in total is influenced by the etching time. Thicknesses between 2 to 20 μ m are tested and evaluated for the designed application. Depending on the process variation, the etching of the silicon wafer can take only 5 minutes. For the here analyzed PorSi foils in Figure 4 the etching time is 30 minutes. This process is a very fast method to etch large-scale wafers.

For the designed application, the highly porous layer is very important for the subsequent layer-transfer process. Here, the PorSi foil is removed from the substrate with the current collector already on top. In this layer, the pores are first bigger and additionally the total free volume is larger in this layer. The copper can diffuse in-between the pores and enable a good contact between the PorSi foil and the current collector. Problems during the electrochemical etching process in this layer result in bad adhesion properties between both of them. This has drastic consequences on the battery performance later on.

Details for the copper deposition are already given in^{17,18} and not discussed here. The thickness of the current collector is 45 μ m. The good adhesion between the copper and the PorSi foil allows an easy detachment of both, electrode and PorSi foil, just by pulling on the Cu sheet and thus removing it from the silicon substrate. The silicon substrate can be re-used again in a new cycle for the anode preparation. The detachment does not work if the etched pores have a diameter smaller than 15 nm. The Cu cannot penetrate into the pores. Since a

strong mechanical interlocking between the Cu layer and the PorSi foil is essential, such porous layers can already be ruled out as PorSi foils for battery anodes as outlined above. Figure 1 shows exemplary SEM images of the process steps paying special attention to the two layers of the PorSi foil with different degree of porosities. Additionally, the SEM images taken after the copper deposition indicate the adhesion and the interphase between both materials. Schematically, it is shown how the layers are removed from the silicon substrate.

This study covers two sets of PorSi foils analyzed with CELLO: The first will be discussed in Figure 4 and shows an example for nonoptimal etching conditions that lead to a variety of defects, mainly to illustrate the strength of transmission measurements to identify various defect types. The second set of PorSi foils show homogeneous thickness and porosity produced with etching parameters after several optimization steps (see Figure 6c and 6d), well suitable as a mass producible and low cost high performance Li-ion battery anode. As indicated, the electrochemical etching process has a direct influence in the battery performance (i.e. adhesion between copper and highlyporous layer; thickness variation etc.). Therefore, it is highly important to monitor and optimize parameters like porosity differences and layer thickness to fabricate long life stable anodes.

In order to proof that the observed changes in the transmittance map correspond to, for example, crystallinity changes, additionally X-ray diffraction (XRD) and SEM analysis were performed. Those measurements reveal etch (in-)homogeneities but can image crystallinity differences induced by the etching process as well. These XRD measurements are performed with the SEIFERT XRD 3000 PTS (1997). This very flexible XRD machine system allows with a four circle goniometer different tilting features. The measurements are performed in the same sample stack as for the CELLO measurements (Figure 3b) in an angular range between 10 and 80° for a 2 θ scattering geometry. The scan is performed with a step width of 0.2° and a scan time of 15 s.

CELLO transmittance measurements.—In a common CELLO measurement, designed for solar cell characterization, an intensity modulated laser beam is scanned with a piezoelectric mirror across an entire solar cell. Figure 2 illustrates the optical set-up. Four different laser wavelength (401 nm blue, 650 nm red, 830 nm IR, and 934 nm SIR) are applicable. The SIR laser has a penetration depth of around 40 μ m. The small-signal response of the solar cell is mapped using a lock-in routine. Here, the laser intensity modulation acts as perturbation signal and accordingly the mapped small-signal response



Figure 2. Optical set up of the CELLO system. Four different laser lights are led over semitransparent mirrors via a focus lens. The beam spotsize can be adjusted from 50 μ m to 2000 μ m and is scanned via a scangine scan mirror across the sample.

delivers an amplitude and a phase shift map. Although the phase shift map contains typically interesting information on solar cells,^{19–23} in this paper only amplitude maps are used.

For the characterization of the PorSi foils, the CELLO setup is slightly changed: a solar cell minimodule is used as reference instead of a solar cell. A minimodule is an encapsulated solar cell with front cover glass. The electrical contacts are the same as for the solar cells. This change is needed because the analyzed samples are not electrically connected as it is the case for standard solar cells. The principle of the CELLO is not affected due to the change in set-up.

In order to understand the measured signals and interpret them correctly, two amplitude maps of the photo current (potentiostatically, i.e. 0 V between reference (R)- and sense (S)-electrode) are required: first, a map with the sample on top of the minimodule; second, a reference map measured under the same conditions but without the sample. Finally each pixel of the map with the sample is divided by the same pixel of the reference map resulting in the final transmittance map in $\%_0$ (given in all of the histograms of the CELLO maps in this study). If necessary, a shift-routine is available that can shift the reference map in order to compensate lateral shifts of the minimod-

ule that might occur during mounting and demounting the sample. The differences between the modified and the standard, already existing CELLO method are clarified as follows: Normally, a solar cell is contacted according to the four electrodes shown in Figure 3; additional temperature control units and feedback loops are needed for this measurement technique as well. Instead of a solar cell, the modified set-up discussed in this study uses only a minimodule. The use of the minimodule has two advantages for the measurements developed for this study: the front glass is used as an internal sample table during measurement and in addition, the real minimodule acts as a reference large area detector in this set-up. The analyzed sample does not influence this working principle but changes only the transmittance of the laser. Since for transmission measurements no Cu layer is allowed, a PET tape with adhesive is used to separate the foils from the silicon wafer before deposition of the current collector. The changed set-up allows therefore to directly adhering the sample on the minimodule glass shown in Figure 3a. A schematic to illustrate the set-up and the measurement feedback loop is presented in Figure 3b. The polymer tape, which is used to separate the foil from the wafer is a specially designed foil with distinct thickness. The influence of this tape is evaluated beforehand with the same kind of transmission analysis, where no negative influence or artifacts are seen. The transmittance change at the foil or from possible gluing effects could be avoided upon optimization and no transmittance results are revealed due to interference of the foil with the laser lights. In order to evaluate the polymer transfer foil, different types of foils with different types of crystallinity were tested and compared. The function of the tape with or without adhesive is evaluated. For the layer transfer process, the adhesive has to fulfill additional requirements: The porous silicon foil which is still attached to the wafer after processing has to be removed. The local thickness differences can change about several orders of magnitude; but still the complete layer has to be removed. Therefore, the adhesive of the polymer foil has to be strong enough. Standard TESA or scotch tape is not very useful because the adhesive fails at the interphase between the silicon and the polymer. Therefore, the concerns about the artifacts of the polymer foils could be weakened. In addition, the influence of the polymer foil on the crystallinity was previously checked and normalized.

Battery preparation and testing.—In order to demonstrate how CELLO measurements enable knowledge gain and thus give the possibility to adopt and optimize electrochemical etching processes – the



Figure 3. a) Modified CELLO setup with additional schematic of the cross-sectional sample stack on top of the minimodule; b) measurement feedback loop. The CELLO software controls the laser intensity modulation and the scanning across the sample. The small-signal response (here potentiostatically the amplitude of short circuit photocurrent) is collected via the four electrodes (working (W); sense (S), reference (R), and counter (C)) by the data-acquisition-board of the CELLO-unit, in our measurement mode basically a potentiostat, and then analyzed using a lock-in routine. The transmittance change at the foil or from possible gluing effects could be avoided upon optimization and no transmittance results are revealed due to interference of the foil with the laser lights. Several test measurements with different air gaps between foil and minimodule are performed, but they did not indicate that such a gap had any difference on the transmission maps.

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Figure 4. Transmittance map of a sample stack of PorSi foil using the SIR laser. Four positions with different patterns are marked and analyzed in detail in the following (cf. Figure 5). The attached histogram shows the dependency of the relative number of pixels in the map on the transmission. The transmission is given in %. The x-axis has a minimum and a maximum value and is scaled in that way that is has everywhere the same distance. The map is analyzed according the pixel distribution which is color coded. It gives an indication of the dimension of the pixel in the map. The red color indicates the highest transmission, wheras dark blue indicates almost no transmission with the lowest value. The patterns visible represent areas of different porosities. The offset between these areas is due to different film thicknesses. The thickness differences lie around 15 to 18 μ m at the highest point. The total thickness of the PorSi foil is 30 μ m. The detailed thickness changes are displayed in Figure S2 in the Supplementary Informations.

base for the battery testing – first examples for battery tests are shown in this study. After galvanic deposition and complete detachment of the anodes, they are tested in half-cells for their cycling stability.

The PorSi foil anodes are tested in half-cells with metallic lithium as counter and reference electrodes. The standard battery anode electrolyte LP30 provided by BASF is used with lithiumhexafluorophosphate (LiPF₆) as Li salt. This salt has a medium conductivity of 15 mS/cm. In combination with two solvents (DMC/EC in a 1:1 ratio), it provides a stable electrolyte for these types of electrodes.²⁴

Cyclic voltammetry measurements are performed to analyze the phase transformations during lithiation and delithiation of such foils. The lithiation and delithiation behavior is analyzed by the shape of the peaks (representation for phase transformations) and the position of the peaks as well. In order to measure under steady-state conditions, the voltage sweep rate is reduced to 0.1 mV/s. Higher sweep rates lead to shifts of the equilibrium conditions and the lithiation and delithiation process is too fast for the Li_xSi_y alloys to form. These measurements are performed between 1 V and 20 mV (and vice versa) for five cycles. During the first five cycles, the most important information could be gained due to the formation of the solid electrolyte interphase. This passivation layer is formed due to the dissociation of the electrolyte products as a result of the application of voltage.²⁴ During this process, the (non-faradaic) current is larger due to the byproducts, which are formed. Once this layer or process is stabilized, the current reduces and the phase transformations are stable. Another important parameter could be identified during cycling.²⁵

Cycling is performed with potentiostatic and galvanostatic steps under capacity limitations of up to 75 % state of charge of the maximal silicon capacity with different *C*-rates. The *C*-rate is commonly calculated in such a way that a full charging or discharging takes for example for *C*/10 takes 10 hours. The PorSi foils are charged with two different *C*-rates: from experience of making silicon microwire arrays,^{10,18} the first cycles have to be charged slowly in order to allow the SEI to form homogeneously and to allow the volume expansion to be more stable. After this passivation layer is formed, the anode is charged with *C*/2.

Results and Discussion

Transmittance Analysis of PorSi-Foils by the CELLO Technique.—For the battery application, the electrochemical etching of the PorSi foils has to be homogeneous in terms of pore sizes (pore differences) and as well thickness differences. If the pore distribution and, consequently, the porosities are different on one large area sample, the cycling parameters are far off from the true values and capacities will be low. Like discussed above, the complete large $(15*15 \text{ cm}^2)$ area sample size should be scanned simultaneously in order to have a quality control directly after the large area fabrication process. With standard tools, this requirement cannot be fulfilled in an imaging technique where additionally local information about surface defects could be generated. For this study, samples with different pore sizes, thicknesses, and porosities are fabricated in order to develop and design this transmittance analysis. Commercially available methods have severe disadvantages. With thicknesses of about 20 μ m and locally up to 50 to 60 μ m, the ellipsometry is the wrong method to compare the transmittance results. It is designed for only nm sized or single-digit µm regions. For larger thicknesses, the refractive indexes are only fitted and approximated independently of the thickness. Those results contain many errors and cannot be trusted. The performed ellipsometry measurements gave a refractive index of 2.54 to 3.2; depending on the different thicknesses. The here discussed technique is an image based lock-in technique, which gives clear and easy correlation to the surface defects.

Figure 4 demonstrates the strength of the transmittance analysis with a PorSi foil that contains four different surface defects recorded with the SIR laser. Here, only small parts of a complete 15*15 cm² wafer is analyzed. The reason for that is the reduced spot and sample size for comparable commercial, analytical techniques. SIR laser maps are selected for this overview, because they show the best contrast and the best local resolution. Not presented here are the blue, red, and IR laser maps. In general, blue maps show no influence of the porosity and film thickness and are typically used for analyzing selective emitter structures. The local information of the SIR is comparable to the red and IR lasers. The foil shows different porosities and pores with a diameter of 30 nm. Different regions of interest are marked from 1 to 4 in Figure 4 which are analyzed in detail within this paper. For comparison, Figure 4 shows additionally an optical photograph of the sample in order to distinguish the appearance of the regions in the transmittance map. The benefit of the color coding is to give direct feedback if the etching worked or not.

The CELLO records the transmission that means the light, which is transferred through the PorSi foil sample. Each histogram column next to the transmittance map gives the integral measure of how much light is transmitted and how often this sort of transmittance occurs on the PorSi foil. The range between the upper and lower limit of the transmittance values is divided in equal distances to subranges,



Figure 5. Transmittance-zoom maps of marked positions 1–4 of Figure 4 recorded with the SIR laser: a) transmittance map of position 1, b) corresponding XRD pattern of position 1; c) transmittance map of position 2, d) corresponding XRD pattern of position 3, f) corresponding XRD pattern of position 3, g) transmittance map of position 4, h) corresponding XRD pattern of position 4. Different thicknesses (thickness changes marked in the diagram) at the positions are reflected in the different peak heights of the XRD pattern.

representing the different colors of the color-coding. The height of each column of the color-coding is proportional to the frequency. Thus, red areas indicate high transmittance values; black areas on the other hand indicate hardly any transmittance.

The minimodule in the background of the sample shows the highest transmission next to the transparent PET tape, which is lightly lower in the transmittance values (Figure 4, orange surroundings of the sample) because the tape absorbs the laser light to some extent. These areas are red in the image. The offset in the colors between position 2 and 3 (also called terraces) is due to different foil thicknesses.

The transmittance measurements are compared with XRD measurements obtained at exactly the same spots on the foil as discussed above. The XRD measurements act as reference analysis to support the statement that the extracted transmittance differences are porosity, thickness, or even crystallinity differences.

The different regions are discussed in additional transmittance zoom maps with the XRD diffraction pattern in Figure 5. The scaling of the zoom maps is optimized to make the local fluctuations in the porosities visible.

Figure 5a shows the transmittance map and Fig. 5b the corresponding XRD pattern for position one. The areas are marked according to the numbers in Figure 4. In this area, narrow stripe-like structures could be seen in the transmission map. Those stripes are so-called striations, which are local doping concentration differences in the PorSi foil. Those striations are common for silicon wafers and occur usually during the growth of bulk silicon (during CZ growth). The same sample with the same sample stack was measured with the XRD.

In the corresponding XRD pattern, two peaks are distinguishable at 25.86° and at 68.8°. In comparison to the literature,^{26–28} the first peak corresponds to the crystalline behavior of the PET tape. By converting the peak into {hkl}-planes, this corresponds to the (200) plane. In the following XRD patterns, this peak will be neglected because it is not of interest for this study. The peak at 68.8° corresponds to the PorSi foil in the (400) plane. This orientation is typically seen for solar cell industry wafers, which are grown in this direction. Due to the fluctuations in the porsit, the peak intensity is rather low. The variation in the PorSi foil thickness can be matched nicely with the XRD peak height and thus is nicely correlated to the CELLO transmittance intensity.

Figures 5c and 5d correspond to position 2 in Figure 4. Here again parts of concentric rings are visible. From their distance and width as well as the etching process it could be determined that they are clearly no striations (i.e. intrinsic variation of silicon properties). Several possible explanations can be found, which are all related to the non-linear behavior of silicon pore etching. Pore etching especially at high current densities for fast and large area formation, as used in these experiments, tends to cause self-organization phenomena.²⁹ The tendency to form periodic changes in the porous layers is even enhanced by the transport of the wafers on a conveyer belt system used in fabrication, leading to short interruptions of the etching process. This explains variations of the porosity through the depth of the porous layer, which can lead to the delamination of whole flakes as visible in Figure 5e. This can explain as well the lateral porosity variations as visible in Figure 5c, e.g. by a successive increased partial delamination of porous layers enabling fresh nucleation of pores at the interface. A new design of the etching process can overcome these problems but obviously only with the help of reliable and adopted tools for identifying such defect types that might never occur in miniaturized lab experiments as discussed in this section.

These findings are supported by the XRD measurements in Figure 5d. The peak intensity increases about one order of magnitude. Thicker PorSi foil is darker (more blue) in the transmittance map and nicely corresponds to the intensity peaks. The intensity of the diffraction peak is higher with the thickness of the material. The porosity fluctuations are typically observed in Si pore etching and depend on the local doping concentration and on the etching parameters like voltage, current, and time of the etching. The different terraces are possibly the result of inhomogeneous etching with high porosities.

Figures 5e and 5f correspond to a third position of interest in the transmittance maps. The dark blue color reveals low transmittance and the PorSi foil thickness increases. The thickness change could be supported by the XRD measurement. The peak intensity increases again about two orders of magnitude corresponding to higher thicknesses. Looking back at Figure 4 (the overall CELLO transmittance map) the dark blue regions are regions with higher thicknesses because the laser light could not easily penetrate through the material. From this transmittance map, the adhesion or difference between the two etched layers could be distinguished. In the surroundings of this third position, the thickness is lower. Here, the etching of the highly porous layer is inhomogeneous leading to thickness and porosity differences. As indicated, this thickness layer difference should be avoided because it directly effects the layer-transfer process. As indicated in Figure 1, the electrode is detached from the substrate after depositing the current collector on the PorSi foil (partially in between the pores). The current collector is deposited on top of the PorSi foil, covering thickness terraces. When detaching the foil from the wafer, exactly those terraces are translated and stick to the current collector, leaving an inhomogeneous anode surface behind where an incomplete PorSi foil is released.

The last position looks similar to region two and has the wave-like structure as well, which corresponds to porosity differences. Region two and four show the same thicknesses which is supported by the same intensity peak.

Figure 5h shows the XRD pattern for the fourth position in more detail. In all the XRD data for the silicon peak, a splitting of the peak is observed. These findings are in good agreement with those at Bisi et al.³⁰ who analyzed porous silicon. There as well, the splitting of the peaks is considered to be from contributions of the porous silicon and from the crystalline silicon itself.^{30–32} The multi-author edition of 32 demonstrated that porous silicon behaves like a single crystal having similar peaks as bulk silicon. The splitting into the two peaks can be attributed to the increase of the lattice constants of the two layers.³² The conditions and the sample thickness and material is the same and comparable. The (relative) peak intensities depend on several parameters like "operational" parameters of the X-ray source (e.g. current, voltage, wavelengths, slit width, etc.). The most important structural parameters are the structure, Lorentz-, polarization-, and temperature factor. All the measurements are performed under the same conditions at room temperature. Therefore, most of the parameters do not have to be taken into account except the structure factor, which takes all the scattering of all the atoms in one unit cell into account. The position of the XRD peaks depends on the crystal structure like the shape and sizes.^{28,33–35} The direct comparison between position two and four is depicted in Figure 5h. The thickness of the positions on the foil is nearly the same because the peak intensity is in the same order of magnitude (nearly the same values). The peak positions in the XRD pattern shift indicating different porosities or pore sizes. If the peak position directly correlates to the crystal structure and sizes, it also means that the volume that is filled with pores influences the crystallinity of the sample position. Figure 6 demonstrates the power of the transmittance measurement. The thickness of the different positions indicated in Figure 5 is verified by confocal microscopy (see Supplementary Information). The black part in position 3 has the largest thickness difference of 18 μ m (the total thickness of that part would be around 30 μ m). As indicated, the black part shows almost no transmittance. In order to correlate it, Figure 6 shows the graphical representation, where the average value for each region of interest is calculated.

Regions with the highest thickness show only about 20 % (200 %), those with a very low thickness over 500 % (50 %) transmittance. The representation supports that the transmittance could show thickness dependencies. To emphasize that the XRD diffraction pattern support that information the peak intensities are correlated with the thickness. Both representations show a quite linear behavior and emphasize the described tendencies.

The thickness differences in the different regions of interest are determined by AFM measurements and confocal microscopy measurements (for further information see the supplementary information). Those techniques are only applicable for small areas and used for this study to support the resulting transmittance analysis. They may give local characterization of the thickness, like thickness vs. position in a graphical representation, but they are not image-based. The graphical representation gives no easy correlation about the position on the wafer, where the thickness variation is located. However, exactly this is very important in order to react fast and improve the etching process by process and hardware optimization of the etching tool.

Summarizing these results, it can be stated that the CELLO transmittance maps reveal porosity and thickness changes along the sample surface by only recording the transmitted signal. The electrochemical etching process with the large area etching tool delivers large amounts of PorSi foils. In order to have a fast quality control about the success of the etching, the modified CELLO set-up showed that it is a good alternative to commercially available analytical techniques. It is a qualitative measure to analyze the surface differences on the different PorSi foils. The benefit is the imaging i.e. on large surface areas, the surface differences are illustrated by a color-coding. As shown, the color coding reveals locally thickness and porosity differences; expressed differently, it reveals if the etching was homogeneous. It is not the intention to show the total porosity of the PorSi foil, but very importantly, the differences in both thickness and porosity as shown in the discussion. Only the difference in those parameters call for parameter optimization during the electrochemical etching process.



Figure 6. Correlation between the thickness change of the PorSi foil and the transmittance measured results by the CELLO method. The image shows how the thickness is related to the peak intensity in the XRD. This supports the measured transmittance signal in the maps. For that, the average transmittance value is calculated. The thickness changes are determined by confocal microcsopy measurements. For more details, consider the Supplementary Information.

These measurement results (together with here not presented additional data) could be used to calibrate CELLO maps. Calibrating CELLO maps means that transmittance could be referred to thickness and porosity differences in order to have a direct correlation between those properties. The additional data from those maps mean more efficient characterization routines, which allow for a direct feedback for the fabrication processes (with only one characterization technique that combines several techniques).

Transmittance analysis of different PorSi foils after process optimization.—Figure 7 shows the second example of analyzed samples recorded with the 830 nm SIR laser after the first parameter optimizations during the electrochemical etching process. As a comparison, Figures 7a and 7b show again a PorSi foil before the optimization. The PorSi foil shows holes or round terraces, which is a consequence from an unsuccessful layer-transfer process on the PET foil, resulting from an inhomogeneous etching process of the highly porous zip layer.

Figures 7c and 7d show transmittance maps after parameter optimizations. They show striations, which are intrinsic material properties of the silicon itself. They are no process related parameters and could not be optimized at this point without changing doping level or resistance of the used silicon. The same is visible in Figure 7d. Here, a clear correlation between the success of the etching and the layer-transfer is possible. These types of PorSi foils could be used for battery application because the etching is homogeneous.

Battery cycling tests of PorSi foils.—In order to show how promising the here discussed approach of the PorSi foils is, first electrochemical analysis of the resulting anodes is shown in this section. These investigations are still ongoing, finding the optimal parameters of thickness as well as porosity. Nevertheless, they should indicate that it is possible and very promising to produce large area anodes by this etching technique, which are characterized with this large area diagnostic tool. From the first PorSi foils, no anodes and no battery performance or electroanalytical tests could be performed. There, the thickness differences on the PorSi foils was too large so that parts of the foil already delaminated from the wafer directly after etching. Like discussed in Figure 4 the CELLO map shows the surface defects in more detail and etching inhomogeneities. Starting from the first optimization steps and the CELLO measurements, the first battery experiments are performed. As discussed above, the first optimizations regarding the process parameters lead to homogeneous transmittance maps.

Typical porosities between 40 to 60 % are produced. The following cycling tests show the promising new application resulting from the PorSi foils.

Striations like those in Figure 5a are only internal properties of the silicon material and not influenced by the electrochemical etching process. If the CELLO analysis only reveals striations, the PorSi foil is prepared as anodes for Li-ion batteries, whereas thickness differences on the PorSi foil anode, as one of the discussed defects on the analyzed sample in Figure 5e, lead to diffusion losses during cycling. If the adhesion among those islands with higher thickness is weak, it will lead to delamination and destruction of the anode during cycling. These thickness differences as well as the porosity differences discussed in Figure 5c and 5g have to be optimized in order to have a stable cycling performance.

Figures 8a and 8b show SEM images with thickness differences between the highly porous and its underlying low porous layer. The pores are homogeneously oriented over the sample and the pore wall thickness is very small of about 10 nm compared to the pore diameter of about 150 nm and sometimes 200 nm. This sample is tested during cycling performance tests due to the homogeneous pore size distribution. This sample does not show any striations, tree-rings, or other porosity artefacts and is therefore chosen for the electrochemical characterization as battery anode. The corresponding transmittance map of this sort of sample is shown in Figure 7d. Figure 8b shows another SEM image from the copper contacted electrode.



Figure 7. SIR laser transmittance maps of different PorSi samples. The contrast of the transmittance maps illustrates different PorSi foil thicknesses a), and different grades of porosity, c) and d). The pore sizes vary from 50 nm (c) to 200 nm (d). An example of a homogeneous PorSi sample is shown in c).



Figure 8. Overview of the battery results. a-b) SEM images of the PorSi foil contacted with copper. The SEM images show a terrace with the transition between the highly porous and low porous layer. The pore sizes vary from 150 to 200 nm in diameter. c) Cyclic voltammetry measurements support the two-step lithiation and delithiation process. d) First cycling tests show a constant capacity of 600 mAh/g with a current density of 2000 mA/g.

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Figure 8c shows the results of the cyclic voltammetry measurements. The voltammograms show the lithiation and delithiation behavior for the first five cycles. In the first cycle, no lithiation peaks exist because the formation of crystalline LixSiy alloys takes some time. The formation of the solid electrolyte interphase (SEI) could be seen at 0.65 V as a small peak. This layer protects the anode from unwanted dissociation products.^{10,24} The peak below 20 mV is associated to lithium plating which could be ignored for the ongoing discussion. The lithiation and delithiation is a two-step process also here in the PorSi foil although the partial lithiation peak is not very pronounced.

From the peak shape, ^{10,25,36} it could be deduced that the diffusional process into the PorSi foil is slow. This could be explained by two factors: the low conductivity of the PorSi foil is slowing down the diffusional process because it then takes time for the Li ions to diffuse into the anode. Another factor is the ohmic resistance for the connection of the PorSi foil to the current collector. The copper ions have to diffuse into the small pores. If this resistance is high, not only the influence will be seen in the voltammograms but also in the cycling experiments. These cycling experiments are performed with various galvanostatic and potentiostatic steps limiting the maximal silicon capacity to 75 % to allow stable stress reduced cycling (Figure 8d). It shows a stable capacity of 750 mAh/g thus being a promising candidate for long time stable anodes. Although the cycle number is not very high, the essential understanding of this PorSi foil anode is still given. The first five cycles are the most important ones, during which the most information about the inside processes could be gained.^{10,37} It is essential to understand the physics and kinetics during the first cycles in order to perform long-term cycling tests. It is not advised to perform long-term tests before understanding the fundamental processes. The first thing is the formation of the SEI layer. This passivation layer forms due to the dissociation of the electrolyte during which the electrochemical and thermodynamical equilibrium is disturbed. This has severe consequences on the irreversible losses and therefore on the capacity. This is shown in addition by the cyclic voltammetry measurements. In the first cycles, the non-faradaic currents are higher due to this dissoziation. They reduce after the SEI layer stabilizes. We performed additional Fast Fourier Transform Impedance Spectroscopy (FFT-IS) measurement on these PorSi foil anodes (which are not shown in this paper) during the first five cycles. In-situ FFT-IS reveals how the kinetical and diffusional processes depend on the lithiation processes. Those results indicate how the adhesion between the copper current collector and the PorSi foil influence the battery performance. A loss of this adhesion will impose series resistance losses on the anode, reducing capacities. In addition, it shows the charge transfer processes during the first cycles.

In comparison to the here presented PorSi foil performance, other porous silicon anodes have a reduced areal capacity. At the same Crate, they show lower capacities,⁹ compared to this study.⁸ The rapid capacity fading in the first cycles could be explained by the formation of the SEI and the fast C-rate. In order for thin films to accommodate the volume expansions, it is evident to reduce the C-rate for not impeding too high stresses on the sample.

This battery analysis is the starting point for ongoing investigations. Scaling up the electrochemical etching from small areas to a diameter of 15 cm needs the understanding of how the processes change. Diffusion-related processes as well as a temperature increase during etching leads to a change in pore size and distribution.

Conclusions

This study presents a novel diagnostic tool developed to analyze large area PorSi foils on a silicon wafer. The PorSi foils are etched in a two-step electrochemical process where a low porous layer is etched and a highly porous layer is etched on top. This highly porous layer is important to detach the PorSi foils in a self-engineered highly efficient layer-transfer process from the wafer. The here-presented CELLO transmittance analysis is developed to be a large area diagnostic tool in order to analyze and characterize porosity differences,

(etching) inhomogeneities in the highly porous layer, and thickness differences of silicon foils. Unlike SEM or other microscopy methods, the CELLO can scan large samples of up to 250 cm² size with a spatial resolution of 50 µm suitable to identify the typical and relevant defects using a large scale in-line production tool for the electrochemical formation of the PorSi foils. Especially the transmission intensity maps at a wavelength of 934 nm allowed to identify all kinds of defects like doping variations within p-type Si wafers, delamination problems due to porosity changes, and thickness variations within the PorSi foil. The advantage of such a transmittance measurement is the fast and non-destructive way of measuring with high local resolution. This allows for a quick feedback or quality control to influence the electrochemical etching process to have a homogeneous pore distribution and a homogeneous thickness.

This study demonstrated after first optimization steps a successful, novel type of battery anode for Li-ion batteries. This anode benefits from the mechanically stable current collector, the lack of any conductive additive, which reduces the amount of active material, but more importantly could be operated at high current densities.

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