

New Applications of Electrochemically Produced Porous Semiconductors and Nanowire Arrays

Malte Leisner · Ala Cojocararu · Emmanuel Ossei-Wusu ·
Jürgen Carstensen · Helmut Föll

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Abstract The growing demand for electro mobility together with advancing concepts for renewable energy as primary power sources requires sophisticated methods of energy storage. In this work, we present a Li ion battery based on Si nanowires, which can be produced reliable and cheaply and which shows superior properties, such as a largely increased capacity and cycle stability. Sophisticated methods based on electrochemical pore etching allow to produce optimized regular arrays of nanowires, which can be stabilized by intrinsic cross-links, which serve to avoid unwanted stiction effects and allow easy processing.

Keywords Li ion batteries · Porous Si · Nanowires

Introduction

The availability of cheap and reliable secondary batteries for energy storage is required in many fields of present and particular future technology. Demands include storage systems for renewable energy sources, batteries for portable devices like notebooks cell phones and the like, to affordable and powerful electric cars. In state-of-the-art battery concepts, a graphite anode is used together with a cathode based on Li-compounds like, e.g., LiCoO_2 . To

enhance the capacity of the battery, Si is a promising material for the use as anode. Si can incorporate very large amounts of Li, leading to a nominal capacity of about 4,200 mAh/g, about a factor 11 larger than the current state-of-the-art graphite anode [1]. The redox potential of this system is also suitable for the use as anode, i.e. only a small potential is needed to extract the Li from the Si. During the incorporation of Li, phases like $\text{Li}_{12}\text{Si}_7$, Li_7Si_3 , $\text{Li}_{13}\text{Si}_4$, and $\text{Li}_{22}\text{Si}_5$ are formed, and the corresponding phase transitions invariably lead to an expansion of the bulk Si of up to a factor of 4. In bulk Si, the resulting stress is so large that it fractures, preventing the use in a battery. A solution to this problem has been demonstrated by Chan et al. [2]. In this work, Si nanowires have been used as Li host material. The wires still have the superior Li incorporation properties of bulk Si, but also allow for the large volume expansion without fracture, since a free increase in their diameter is now possible. The nanowires in the work of Chan et al. have been grown by a vapor-liquid-solid (VLS) method, using Au droplets on a stainless steel substrate. It was possible to generate nanowires with a diameter around 90 nm, which were able to withstand 10 charging/discharging cycles.

Despite the success of this and follow-up [3] work, the production method of the nanowires has some drawbacks. Without substantial added process complexity, it is only possible to grow rather unordered arrays of nanowires in a small range of diameters. The optimal geometry of a nanowire array, and thus maximum capacity, might therefore not be achievable. The applicability of the VLS method to large-scale production has not yet been demonstrated and is doubtful. In this work, we therefore demonstrate a cheap and reliable method for the production of optimized nanowire arrays by easy available and fairly routine techniques.

M. Leisner (✉) · A. Cojocararu · E. Ossei-Wusu ·
J. Carstensen · H. Föll
Institute for Materials Science, Christian-Albrechts-University
of Kiel, Kaiserstrasse 2, 24143 Kiel, Germany
e-mail: ml@tf.uni-kiel.de
URL: <http://www.tf.uni-kiel.de/matwis/amat/>

Production of Nanowire Arrays

The production of nanowire array anodes has been facilitated in a three-step procedure. (1) Electrochemical etching of ordered macropore arrays into single-crystalline Si. (2) Chemical over-etching of the macropores until the pore diameters touch and only small wires remain between the pores. (3) Deposition of a Cu diffusion barrier and contact layer.

Figure 1 shows schematically the first two production steps. Figure 1a shows a top view of the electrochemically etched regular macropore array. The solid circles represent the pores, and the dashed circles indicate the effect of the subsequent chemical over-etch, which leads to the nanowires (top view) shown in Fig. 1b.

The third step is necessary to produce a working device. Since the production method yields nanowires that are directly attached to bulk Si, Li would be incorporated during the charging/discharging cycle not only into the nanowires, but also into the bulk Si, if no precautionary measures are taken. Hence, a Cu layer, acting as diffusion barrier, is galvanically deposited at the bottom of the nanowire, i.e. at the nanowire-bulk Si interface. Figure 1c shows this layer schematically.

Electrochemical Macropore Etching

The etching of macropores into n-type and p-type Si is by now an established technique that allows to produce highly ordered arrays of macropores with diameters in the range between 200 nm and 10 μm , and as deep as 500 μm . For detailed reviews of the technique, refer to [4–6].

In this work, macropores have been etched into (100)-oriented p-type Si single-crystalline wafers with specific resistivities in the range of (15–24) Ωcm . As electrolyte, 5 wt% HF diluted in DMF has been used. All experiments have been carried out at $T = 20^\circ\text{C}$, the current density was

$j = (3\text{--}23) \text{ mA/cm}^2$, following an optimized profile over time. The total etching time was in the range of 2 h, yielding pore depths of about 150 μm .

Chemical Over-Etching Yielding Nanowires

Increasing the pore diameter by chemical over-etching has been performed by using an acidic etchant consisting of a mixture of HF/HNO₃/HAc. Even though this generally isotropic etchant is well studied for “flat” structures, cf. e.g. [7], it is difficult to over-etch deep macropores homogeneously, since the concentration of the necessary species at the pore tips will always be different from the one at the top. It is only possible to etch the pores homogeneously, if the reactions are not diffusion controlled, necessitating very dilute acids. The drawback then is long etching times, which may take up to 12 h in our case. This might look like a severe obstacle for mass production on a first view, but the problem might easily be overcome by a batch process, i.e. many wafers are etched simultaneously in one (cheap) etching station, cutting down the effective production time.

Figure 2 shows an example of the nanowire array produced. At the bottom, the former pore tips can still be seen. The image also serves to demonstrate the flexibility of the nanowires, which do not break, even for heavy bending as shown.

Isolation by Galvanic Cu Deposition

The galvanic deposition of Cu onto Si is a standard process in IC technology. Nevertheless, as in the case of the over-etching of the pores, deposition of Cu on the bottom of a dense forest of nanowires is not easily achieved, but can be done, as has been demonstrated in [8–10]. As an electrolyte, a mixture of 300 ml H₂O, 70 ml H₂SO₄, 5 g CuSO₄, 0.1 g DTAC (1-dodecyl-trimethylammoniumchloride),

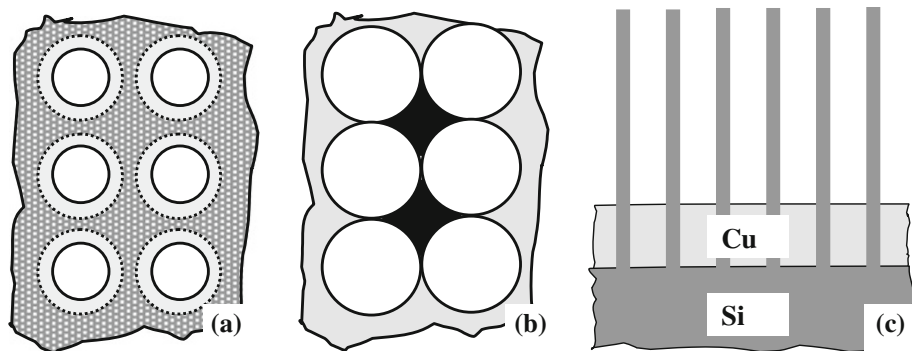


Fig. 1 Schematic illustration of the nanowire array production steps. **a** Top view of an electrochemically etched regular macropore array. The *dashed circles* indicate the effect of the chemical over-etching, which eventually yields the *(black)* nanowires shown in **(b)** (top

view). **c** The bulk Si has to be insulated from the Li by a Cu diffusion barrier layer to avoid the incorporation of Li into the bulk Si. The Cu layer also serves as electrical contact to the Si nanowires

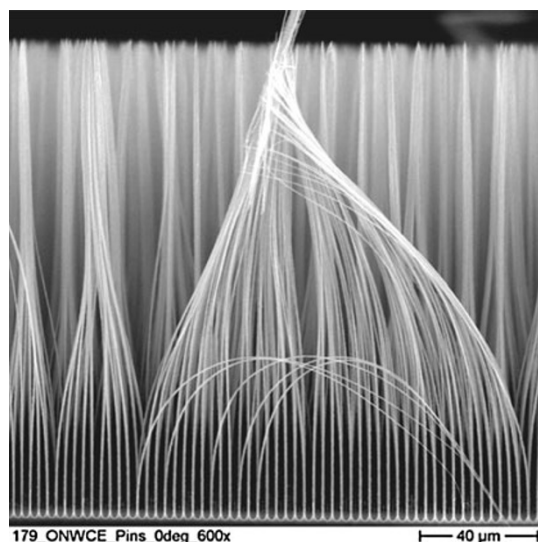


Fig. 2 Ordered nanowire array produced in p-type Si

0.1 g SPS (Bis-3-sodiumsulfo-propyl-disulfide, and 0.1 g PEG (Polyethylenglycol) has been used. Experiments have been carried out at $T = 20^\circ\text{C}$ under a constant potential of -0.5 V .

Cycling Test of the Anode

To test the potential anode, a half-cell has been built with a Li reference electrode and a standard glass fiber separator. As an electrolyte, 0.5 ml of LP-30 (Merck) has been used, which essentially consists of dimethylcarbonate and ethylencarbonate (1:1) with 1 mol/l of LiPF_6 as conducting salt. All components have been mounted under Ar atmosphere into a cylindrical Ti housing after previous removal of residual water from the components. The half-cell has been charged to $C/10$ (C : nominal capacity) for the first 10 cycles, and to $C/5$ for the remaining cycles. Figure 3 shows the measured efficiency in percent, which is defined as charge to discharge percentage.

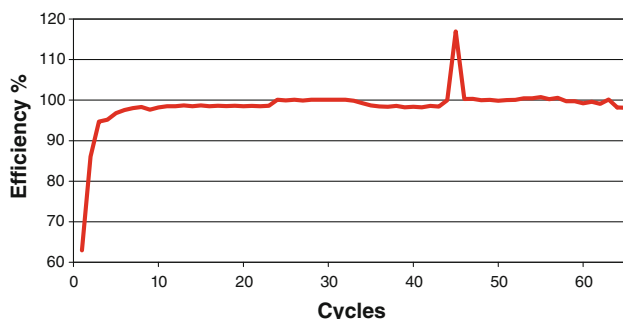


Fig. 3 Charge/discharge efficiency of the nanowire anode mounted into a half-cell. The peak at cycle 44 is an artifact caused by a failure in the temperature control

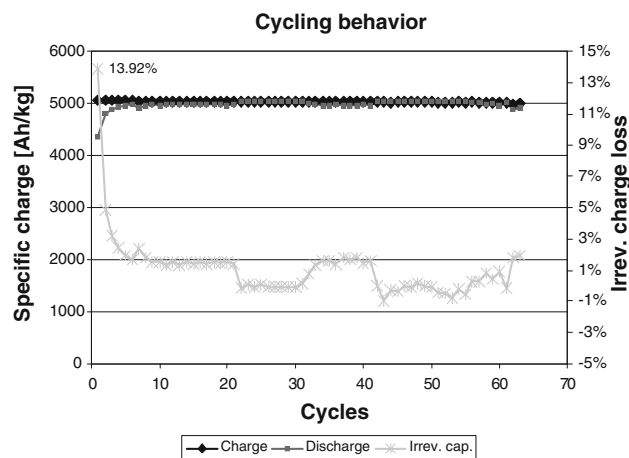


Fig. 4 Charge/discharge efficiency of a battery made of the nanowire anode. Their reversible losses are small, a good cycle stability is observed

Initially the efficiency is low, which is due to conditioning the Si (the initiation of the first phase transformation from Si to Si-Li) and also to the formation of the so-called silicon–electrolyte interface (SEI). The irreversible losses are about 18.8%.

The cycle stability of the anode is very good and always close to 100%. This indicates that the anode is mechanically stable and no nanowires are detached during the cycling. The cell has also been demounted after cycling and inspected by SEM. The structural investigation into the anode (not shown here) validates this statement; the anode is mechanically still intact.

Test batteries have been assembled in a similar way, by using a standard NCM ($\text{LiNi}_x\text{Co}_y\text{Mn}_z\text{O}_2$) cathode. The battery was charged/discharged 65 times with a capacity $C/5$, Fig. 4 shows the result.

The results are similar to the results obtained for the half-cell set-up. The irreversible losses are small in comparison with other Si anodes, and a good cycle stability is obtained.

Process Improvements

A big improvement of the production process can be obtained if in a first step some small but sophisticated changes to the macropore etching part are made that result in a specific pore profile with depth. The pore profile in Fig. 5 gives a schematic illustration of this optimization of the pore form.

Most important are the constrictions, which can be produced by lowering the etching current, which will result in a decreased pore diameter. After the subsequent chemical over-etching, nanowires will form everywhere except

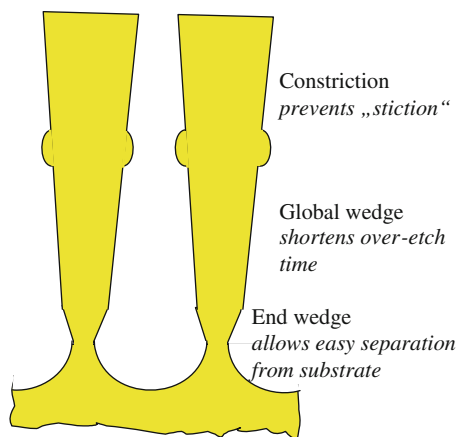


Fig. 5 An improved pore form produced by macropore etching yielding several advantages to the battery production process. For details, see the text

at the constriction places. There the pore walls are not yet touching, which means that the nanowires are connected by Si “bridges”. These bridges provide a stabilizing layer between the nanowires and prevent stiction, Fig. 6 illustrates this point.

Without stabilizing layer(s), the nanowires tend to show stiction, i.e. they stick together at the tips like wet hair. The surface is thus no longer well defined and cannot be easily processed in follow-up processes. With the stabilizing layers, this is different and the now well-defined surface of the nanowires can be used to reduce the overall cost since now the copper layer can be placed on top of the nanowires. Figure 7 shows the Cu layer on top of the nanowires.

In order to obtain a working anode, the nanowires need then to be detached from the substrate. To allow easy

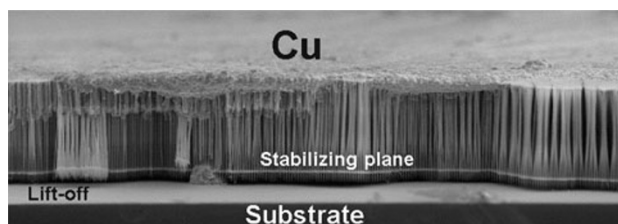


Fig. 7 Cu layer deposited by sputtering on top of the stabilized nanowire array

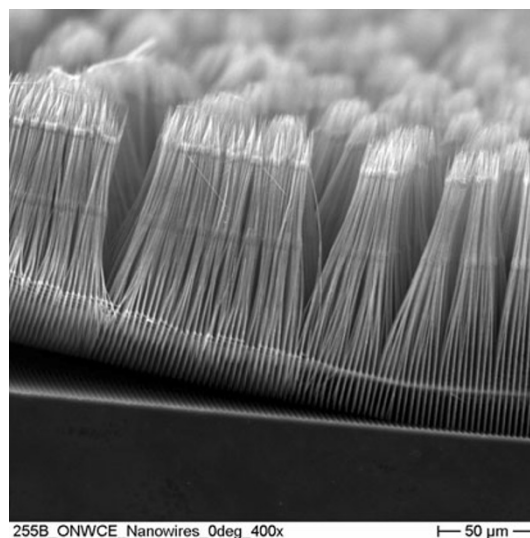


Fig. 8 The nanowire layer can be easily detached from the substrate

detachment of the nanowires, the end wedge shown in Fig. 5 is included in the pore shape, producing very thin nanowires at the point of contact to the Si substrate. The nanowire layer now can be easily “zipped off” from the

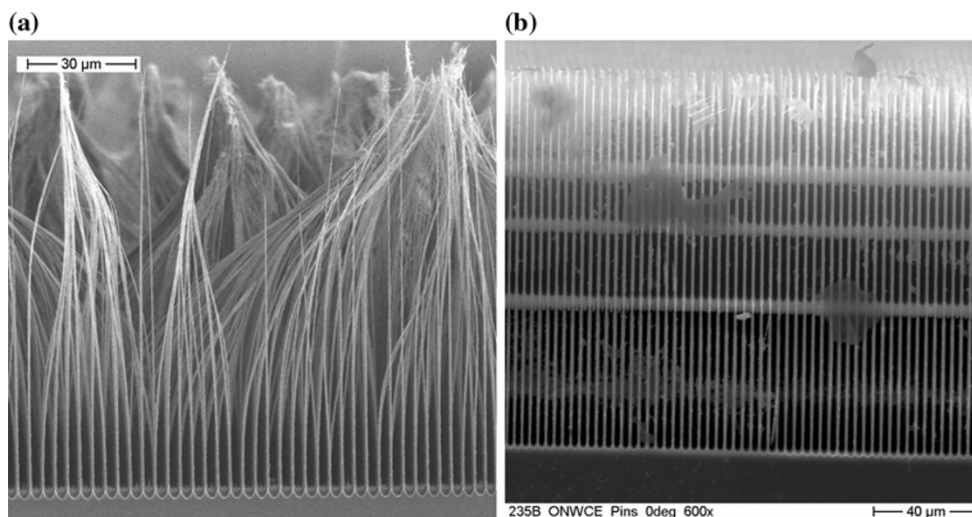


Fig. 6 Nanowire arrays. **a** Without stabilizing layer, the wires show stiction, i.e. stick together at the tips. **b** With three stabilizing layers, no stiction occurs

substrate. Figure 8 shows this easy detachment of the nanowire layer.

The last feature shown in Fig. 5 is the global wedge, which makes the pore slightly bigger with increasing pore depth. This is done to counter the aforementioned diffusion limitation of the chemical over-etching speed at different pore depths since now less material needs to be removed deep down in the pores. Higher concentrations of the etchant are now possible, significantly reducing the etching time and thus production costs.

Conclusion

It has been demonstrated that optimized Si nanowire anodes can be produced by cheap and reliable standard techniques. The resulting structures are suitable for the use as anodes in Li ion batteries of the future. First tests have shown a substantially increased capacity and full cycle stability.

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