6.3 All Other Research

6.3.1 Putting an End to It

Here are the points from the introduction that I still need to cover:

2. Investigating pore etching in Si, Ge, GaAs, InP, ...,

3. Inventing and developing the "current burst" theory to understand self-organizations phenomenae at semiconductor electrodes

4. Looking at various applications of pore etching in semiconductors; in particularity the Si anode for the Li ion battery.5. Miscellaneous.

Well - I won't. This archive was supposed to preserve photographs that would be lost as the printed versions decay and crumble. But most of the publications relating to the research mentioned above have long since been digitized and thus are preseved for eterity, however long that will last.

True, the quality of these pictures may not be as good as that of the originals. The originals, however, usually consist of digitized and relatively small **SEM** pictures and do not offer much more than the prints in journals. Thus I will only supply a few pictures here.

All I'm doing here is to give a very brief summary of what we have achieved. It is of course biased but so what.

Pore Etching in Semiconductors

The easy thing to do. There is an almost unlimited amount of experimental work that students can do working for a Bachelor, Master or Ph.D. thesis It takes a bit of learning the tricks of the trade (in particular not to klll yourself with the dangerous chemicals involved) but productive work starts quickly. The parameter field is huge and it is unavoidable to come up with new kinds of pores that nobody has seen before.

A large number of publications bears witness to that. Here I will present just a few plus some presentations. That should be sufficient to give a taste treat.

135 <u>Föll, M. Christophersen, J. Carstensen, G. Hasse</u>: Formation and application of porous silicon (invited review) Mat. Sci. Eng. R 39 (4) (2002) 93-141. (1063 citations)

This paper reviews **pores in silicon**. It appeared 2002 and thus does not include a wealth of "new" pores found later.

150 <u>FÖLL, H., LANGA, S., CARSTENSEN, J., CHRISTOPHERSEN, M., TIGINYANU, I.M.</u> Review: Pores in III-V semiconductors. (invited review) Advanced Materials, 15(3) (2003) 183 - 198 (315 citations) Here we review pore formation in III-V semiconductors, Again, after 2003, more new results came to light.

191 <u>C. Fang, H. Föll, and J. Carstensen</u>, "Electrochemical pore etching in Germanium", J. Electroanal. Chem. 589, 259 (2006) (103 citatipons)

Not an actual review but a "work report". However, it contains most of what was then known about **pores in** germanium since this knowledge came from this work.

A brief review can be found here:

216 <u>C. Fang, H. Föll, J. Carstensen, and S. Langa</u>, "Electrochemical pore etching in Ge - An overview", Phys. stat. sol. (a) 204(5), 1292 (2007) (16 citatipons)

241 J. Carstensen, E. Foca, S. Keipert, H. Föll, M. Leisner, and A. Cojocaru, "New modes of FFT impedance spectroscopy applied to semiconductor pore etching and materials characterization", Phys. Stat. Sol. (a) 205(11), 2485 (2008). (31 citations)
An in depth account of our unique EET impedance technique applicable to CELLO and nore etching. A major

An in-depth account of our unique FFT Impedance technique applicable to <u>CELLO</u> and pore etching! A major papereven so it has not yet been fully appreciated by the community.

280 <u>H. Föll, M. Leisner, A. Cojocaru, and J. Carstensen</u>, "Macroporous semiconductors", Materials 3, 3006 (2010). (81 citations)

A voluminous review, the last word of pore formation and modelling same in 2010 and possibly still today

293 <u>H. Föll, M. Leisner, and J. Carstensen</u>, "Modeling some 'meta' aspects of pore growth in semiconductors", ECS Trans. 35(8), 49 (2011). (3 citations)

Looking at the into "meta" level of pore formation mechanisms. The still one and only basic explanations of all aspects of pore formation in semiconductors

Föll et al. Potsdame 2007
 Föll et al. S. Francisco 2009
 Presentations regarding self-organization of pores and the "meta" theory.
 Lots of good pictures can be found

I'm sure that pore etching in semiconductors will remain an active research area for many years to come. There is a simple reason for that. Pore formation, in ways becoming clear to us but not to the community at large, express self-organization features that are based on the stochastic nature of the elementary processes leading to the dissolution of a semiconductor - see below.

To say it bluntly: The current burst theory introduced a new paradigm into electrochemistry. The community at large has not yet noticed this but time will tell.

Self Organization Phenomenae

Volker Lehmannand I had spent a lot of time looking into the topic of self-induced current or voltage oscillations at the Si electrode. We conducted many specific experiments and went down many dead end roads in the pursuit of a clear understanding. In Kiel, J. Carstensen and I finally solved the problem by inventing the "current burst" (CB) theory. As far as I'm concerned, the CB theory quantitatively explains these oscillations and all the ones not known at this time.

Current or voltage oscillations are just on specific expression of self-organization phenomena at the dissolving anode. We soon found far more self-organization events and in particular that many pore structures must be interpreted as *current oscillations in space*. The CB model provides the base for these phenomenae, too. Fully developed macroscopic oscillations demand the synchronization of many small events occurring at the dissolving electrode, and this requires not only very homogeneous conditions in the electrolyte but extremely homogeneous electrodes, too. Single crystalline and almost defect-free semiconductor provide for this, while polycrystalline metals full of dislocations and precipitates will not be capable of sustaining the long coherence lengths required for macroscopic self-organization expressions.

There are many publications to self-organization phenomenae, the following links will suffice to give a taste treat:

- 217 E. Foca, J. Carstensen, and H. Föll, "Modelling electrochemical current and potential oscillations at the Si electrode", J. Electroanal. Chem. 603, 175 (2007) (review) (59 citatipons)
- 269 <u>H. Föll, M. Leisner, A. Cojocaru, and J. Carstensen</u>, "Self-organization phenomena at semiconductor electrodes", Electrochim. Acta 55(2), 327 (2009). (32 citations)

Looking at Various Applications of Pore Etching in Semiconductors

Pore etching in semiconductors was always done with an eye on applications. Quite a few projects dedicated to some specific applications were started in Kiel and elsewhere. Not much success, however, as far as commercial products are concerned.

- I won't go into details here but only give one example: The silicon microwire anode for Li ion batteries. Here is a publications and a presentation:
- 294 E. Quiroga-González, E. Ossei-Wusu, J. Carstensen, and H. Föll, "How to make optimized arrays of Si nanowires suitable as superior anode for Li-ion batteries", J. Electrochem. Soc 158(11), E119 (2011). (57 citations)
- Helmut Föll, Dr. Enrique Quiroga-González, Sandra Nöhren, Dr. Jürgen Carstensen, Optimizing Silicon Anodes for Li-Ion Batteries

A presentation given during a small conference in Mexico organized by Enrique Quiroga-González, who had returned from his post-doc position in Kiel to his native land.

There might be a commercially used Si anode for the Li ion battery yet. Work on this topic continues and there is always hope.

Miscellaneous

As far as publications are concerned, the <u>preceding module</u> covered it all. However, if we look at output not formally counted among publications, there is a lot to say, In particular since these "non-publicartions" had and have a far larger impact then the "real" publications. More to that in the next chapter.

As stated before, there is no large need to immortalize pictures here. In fact, most pictures were already obtained in an electronic format (e.g. from SEM's or directly computer generated like ELYMAT and CELLO pictures),. SEM pictures are typically not of large size anyway.

So here I just present a rather random selection of a few pictures :

