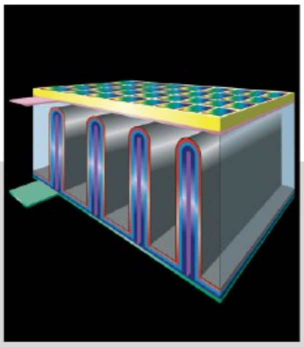
ADVANCED MATERIALS

DOI: 10.1002/adma.200702398

3-D Integrated All-Solid-State Rechargeable Batteries[**]

By *Peter H.L. Notten*[*], *Fred Roozeboom*, *Rogier A.H. Niessen* and *Loïc Baggetto*



Portable society urgently calls for integrated energy supplies. This holds for autonomous devices but even more so for future medical implants. Evidently, rechargeable integrated all-solid-state batteries will play a key role in these fields, enabling miniaturization, preventing electrode degradation upon cycling and electrolyte leakage. Planar solid-state thin film batteries are rapidly emerging but reveal several potential drawbacks, such as a relatively low energy density and the use of highly reactive lithium. Thin film Si-intercalation electrodes covered with a solid-state electrolyte are found to combine a high storage capacity of 3500 mAh g^{-1} with high cycle life, enabling to integrate batteries in Si. Based on the excellent intercalation chemistry of Si, a new 3D-integrated all-solid-state battery concept is proposed. High aspect ratio cavities and features, etched in silicon, will yield large surface area batteries with anticipated energy density of about 5 mWh μm^{-1} cm^{-2}, *i.e.* more than 3 orders of magnitude higher than that of integrated capacitors.

1. Introduction

Wireless electronics are becoming more and more important in our daily life. Examples of wide-spread electronic equipment are mobile phones, laptop computers and digital cameras but these are currently rapidly expanding into very large-scale applications, such as *hybrid (electrical) cars* and *micro power generating* systems, making transportation and energy generation much more efficient. Miniaturized *autonomous devices,* at the other outer end of the 'spectrum', are also becoming increasingly important. These devices induced a new electronic revolution, denoted as *ambient intelligence*.[1] This is generally considered as the next challenging development in the *knowledge age*.[2,3] Moreover, small medical devices and implants are expected to penetrate our society shortly, improving people's quality of life significantly. Obviously, these implants should also be small and preferably not contain any hazardous liquids, which might induce serious leakage problems.

Characteristic for small autonomous devices is that they have to operate independently, implying that on-board electricity is essential. When devices are becoming smaller and smaller it becomes, however, much more complicated to assemble these from their individual components and the contribution of inactive overhead mass and volume by, for example, the package will increase significantly. As the energy consumption will be small for autonomous devices this opens up the possibility to integrate electricity storage devices, making these highly efficient.

Electricity can be effectively stored in either capacitors or batteries. For capacitors, electrons are simply stored at the electrode/dielectric interfaces. As the energy to be stored in capacitors is proportional to the interface area it is obvious that an effective way to increase the amount of charge is to enlarge the effective surface area. This strategy has been suc-

---

[*] Prof. P. H. L. Notten, Dr. R. A. H. Niessen
Philips Research Laboratories
High Tech Campus 4, 5656 AE Eindhoven (The Netherlands)
E-mail: peter.notten@philips.com
Prof. F. Roozeboom
NXP Semiconductors Research
High Tech Campus 4, 5656 AE Eindhoven (The Netherlands)
Prof. F. Roozeboom
Department of Applied Physics
Eindhoven University of Technology (TU/e)
Den Dolech 2, 5600 MB Eindhoven (The Netherlands)
Prof. P. H. L. Notten, L. Baggetto
Department of Chemical Engineering and Chemistry
Eindhoven University of Technology (TU/e)
Den Dolech 2, 5600 MB Eindhoven (The Netherlands)

[**] This research has been financially supported by the Dutch Science Foundation, SenterNovem.

cessfully adopted in our laboratory, by making use of the fact that Si can be highly structured by either electrochemical,[4] or Reactive Ion Etching (RIE).[5] Figure 1 shows typical examples of RIE-etched trenches and holes, for which a surface area enhancement factor of 25 can be easily achieved. Using Low Pressure Chemical Vapor Deposition (LPCVD) the various active layers can be homogeneously deposited inside the deep trenches (Fig. 1c). This leads to capacitor values of 8 μF cm^{-2} geometric footprint.[6] Using a realistic voltage level of 10 V it can be calculated ($E=½CV^2$) that about 0.40 mJ cm^{-2} (~0.11 μWh cm^{-2}) of energy can be stored in these 3D-integrated capacitors, making these devices very attractive for low-loss decoupling to suppress cross-talk in high-frequency circuits.[7] To supply autonomous devices with electrical energy this is, however, orders of magnitude too low.

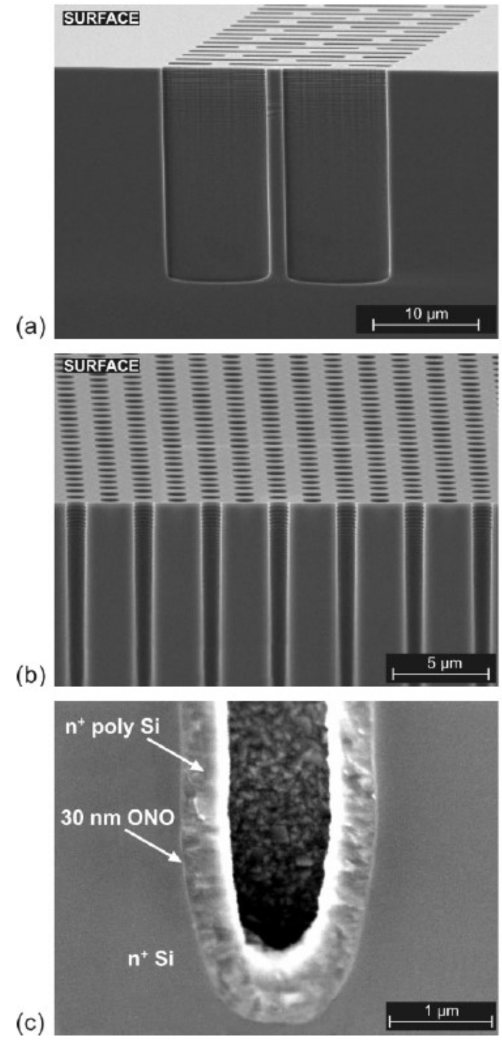


Figure 1. High aspect ratio trenches (a) and holes (b) etched in single-crystalline silicon substrate. 3D-integrated MOS-capacitor (c) visualizing the various indicated conducting and dielectric layers.

Electrical energy can be stored much more efficiently in batteries. In this case electrons are not only stored at the electrode/electrolyte interfaces but also converted into chemical energy, which can subsequently be stored inside the battery electrodes. Planar all-solid-state batteries already exist in the pilot production phase. These systems are almost all based on metallic Li as anode and LiPON as solid-state electrolyte.[8] In comparison to integrated capacitors the energy density of planar all-solid-state batteries is significantly higher. Yet, it is still not sufficient to power future autonomous devices. In addition, metallic Li is highly unfavorable in the processing and operation of electronics due to its extremely low boiling point of 181 °C. Therefore, it would be better to make use of more stable intercalation materials. Various integration concepts have been proposed.[9,10] An overview has been given by Long *et al.*[9] We adopt, however, a different approach, which copes well with state-of-the-art IC technologies.

2. Li-Intercalation in Si Thin Films

Si has been identified as promising high energy density intercalation material.[11] Interestingly, Si is the parent material for the electronic industry and therefore highly attractive as processing material for battery integration.[12] In order to increase the energy density of the proposed planar batteries the same strategy can be adopted as for integrated capacitors by increasing the surface area. By making use of advanced high-energy density electrode materials this will result in a new generation of highly efficient, 3D-integrated all-solid-state rechargeable batteries.[12,13]

For graphite these stages correspond to Li-storage between the various graphitic sheets. For Si it has been identified that the crystalline host material becomes amorphous already in the early stages of intercalation.[14] One of the most striking aspects of these Si-based results is the extremely high storage capacity of over 3500 mAh g^{-1} active Si-host material compared to 372 mAh g^{-1} reported for conventional graphite (Fig. 2a). Remarkably, at the end of the charging process the XRD-amorphous Si-material reverts into a crystalline form again with composition $Li_{15}Si_4$. The discharge curves reveal a high Coulomb efficiency, indicating high reversibility of the Si electrodes. Many researchers are currently trying to convert this interestingly high-energy density thin film configuration into the powder electrode concept so far, however, without much success. These disappointing results have been attributed to the extreme volume expansion induced by the Li-(de)intercalation process through which the mechanical integrity of bulk powders is violated and the electrodes deteriorate rapidly.

When the thickness of a thin film Si electrode is limited to about 50 nm the electrodes remains mechanically intact as is evidenced by the long cycle life in Figure 2b. Cycling a Si-electrode in a conventional Li^+-salt containing organic battery electrolyte, the storage capacity is stable up to about 30 cycles but starts to decline due to the formation of a so-called Solid

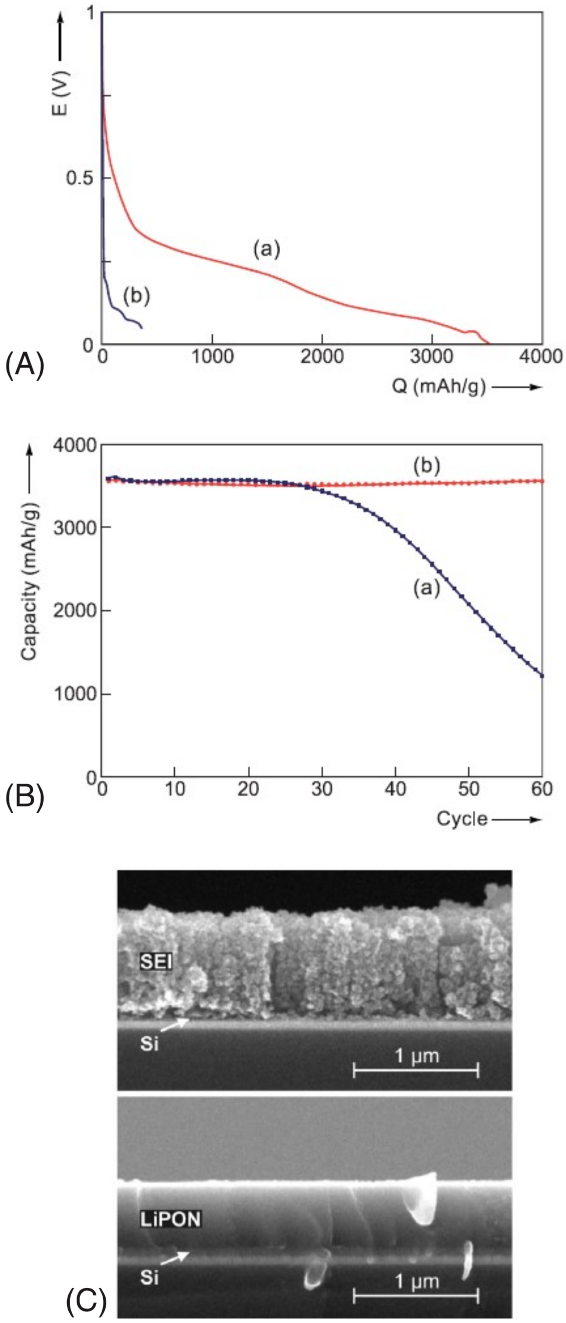


Figure 2. A) Constant-current charging of a thin film silicon electrode (3579 mA g^{-1} = 1C), deposited on a barrier layer, protecting Si substrate (a), and a conventional graphite electrode (372 mA g^{-1} = 1C) (b). The electrode potential is measured with respect to a metallic lithium reference electrode. B) Cycle-life of a thin film silicon electrode in a conventional organic Li-ion battery electrolyte (a) and of the same electrode covered with a solid-state LiPON electrolyte (b).C) Cross-section of the Si/liquid electrolyte interface (upper photograph) and Si/LiPON interface (lower photograph) after electrochemical cycling, corresponding to Fig.2B, curve (a) and (b), respectively.

Electrolyte Interface (SEI) at the electrode surface (curve (a)). In the case of graphite the formation of such SEI layer is well known and has been attributed to decomposition of the liquid electrolyte.[15] A similar process takes place at the Si/organic electrolyte interface.

The existence of such passivation layer can beautifully be visualized by making use of Si wafers, easily facilitating to make cross-sections. Figure 2c indeed reveals that a thick SEI layer has been formed after cycling (upper photograph). Strikingly, when in addition a ~500 nm thick inorganic solid electrolyte is used to cover Si, electrolyte reduction does not take place (lower photograph). The SEI layer is completely absent and, consequently, the cycle life of the Si electrode is not negatively affected at all (Fig. 2b, curve (b)). Obviously, the excellent cycle-life performance of an all-solid-state system is highly beneficial and nicely copes with the lifetime of autonomous devices. Interestingly, the (dis)charge rates in our experiments were found to be extremely high due to the limited diffusion length of lithium inside the thin film electrodes and the very fast charge transfer kinetics, *i.e.* about 90% of the rated capacity can be (dis)charged within 30 seconds![13]

3. Integrated Battery Concept

Based on the remarkable Li-intercalation properties of thin film Si electrodes, a new all-solid-state 3D-integrated battery concept is proposed. The basic principles of this concept are schematically represented in Figure 3a.[12,13] Starting with a thin-film current collector (a) covering a highly doped, well conducting, Si-substrate (b), a large surface area is obtained by anisotropic etching of the Si-substrate. Subsequently, the active battery layers are coherently deposited inside this highly structured substrate, starting with an effective barrier layer (c), preferably TiN or TaN,[13] to protect the substrate from Li penetration, followed by a ~50 nm Si thin film anode (d), a solid-state electrolyte, *e.g.* Li_3PO_4-based (e) and a thin film, transition metal oxide, cathode material, in this example, ~1 µm $LiCoO_2$ (f). Deposition of a second current collector (g) completes the 3-D integrated battery.[12,13] During charging, lithium ions are withdrawn from the $LiCoO_2$ electrode, transported via the solid-state electrolyte to the silicon anode where they are intercalated. Obviously, the opposite processes take place during discharging. The thickness of the $LiCoO_2$ in the given example matches quite well with the huge intercalation potential of Si.

Based on a surface enhancement factor of 25 the predicted energy 3D-integrated batteries can deliver will amount to about 20 J cm^{-2} geometric footprint, using a 1 µm thick $LiCoO_2$ electrode, implying in battery terms ~5 mWh µm^{-1} cm^{-2}. This amount of charge is over 3 orders of magnitude higher than that can be stored in 3D-integrated capacitors. This complies not only well with the predicted requirements of many autonomous devices and medical implants but also with the energy required to power System-in-Package devices, like real time clocks and electronic back-up systems, such as

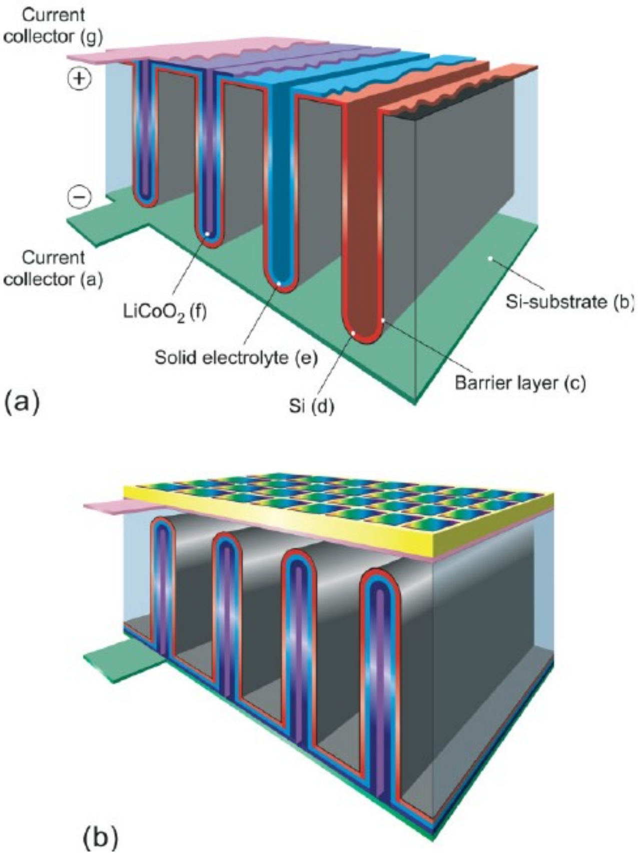


Figure 3. 3-D integrated all-solid-state Li-ion battery for which surface enlargement has been accomplished by electrochemical or Reactive Ion Etching (RIE) of a silicon substrate (a). Autonomous energy-generating and storage device, combining a Si-solar cell with an integrated all-solid-state battery (b).

SRAMs and MEMS. The combination with an integrated Si-solar cell and integrated battery finally fulfils the ultimate dream to power future autonomous devices (Fig. 3b).

4. Summary and Outlook

The combination of thin film Si-electrodes and solid-state electrolytes reveals an ultrahigh Li-intercalation storage capacity with a high cycle life, without any significant degradation upon cycling. This combination forms the basis of the newly proposed *3D-integrated all-solid-state battery* concept, which opens the possibility to integrate rechargeable batteries with other electronic parts either in monolithic Si-wafer or as System-in-Package. The predicted energy storage capability of integrated batteries is over 3 orders of magnitude higher than that of integrated capacitors currently in production.

Once this concept has proven its viability, many other materials than those presented here can be successfully applied in the future. For example more flexible substrates, such as porous Al-foils and porous electronic conducting membranes, can be used, making it possible to fold up the 3D-structure into an even higher-order geometry. In addition, there are many possible high-energy density materials, including both intercalation and oxidic materials, which can be combined with a variety of solid-state inorganic and (hybrid) organic electrolytes. Thus, the combination of integrated batteries and capacitors offers interesting future applications.

---

[1] E. Aarts, R. Collier, E. van Loenen, in *Ambient Intelligence* (Ed.: B. de Ruyter), Springer-Verlag, New York 2003.

[2] A. Toffler, in *Future Shock* (Ed.: A. Toffler), Bantam books, New York 1970.

[3] W. Verhaegh, E.H.L. Aarts, J. Korst, in *Algorithms in Ambient Intelligence* (Eds: W. Verhaegh, E. H. L. Aarts, J. Korst), Kluwer Academic Publishers, Dordrecht, The Netherlands 2003.

[4] J.E.A.M. van den Meerakker, R.J.G. Elfrink, F. Roozeboom, J.F.C.M. Verhoeven, *J. Electrochem. Soc.* **2000**, *147*, 2757.

[5] F. Lärmer, A. Schilp, *US Patent 5501893*, 1996.

[6] F. Murray, F. LeCornec, S. Bardy, C. Bunel, J. Verhoeven, E. van den Heuvel, J. Klootwijk, F. Roozeboom, *Mater. Res. Soc. Symp. Proc.* **2007**, *96*, 27.

[7] F. Roozeboom, A.L.A.M. Kemmeren, J.F.C. Verhoeven, F.C. van den Heuvel, J. Klootwijk, H. Kretschman, T. Fric, E. C. E. van Grunsven, S. Bardy, C. Bunel, D. Chevrie, F. LeCornec, S. Ledain, F. Murray, P. Philippe, *Thin Solid Films* **2006**, *504*, 391.

[8] J.B. Bates, N.J. Dudney, D.C. Lubben, G.R. Gruzalski, B. S. Kwak, X. Yu, R. A. Zuhr, *J. Power Sources* **1995**, *54*, 58.

[9] J.W. Long, B. Dunn, D. R. Rolison, H. S. White, *Chem. Rev.* **2004**, *104*, 4463.

[10] D. Golodnitsky, M. Nathan, V. Yufit, E. Strauss, K. Freedman, L. Burstein, A. Gladkich, E. Peled, *Solid State Ionics* **2006**, *177*, 2811.

[11] T. Takamura, S. Ohara, M. Uehara, J. Suzuki, K. Sekine, *J. Power Sources* **2004**, *129*, 96.

[12] P. H. L. Notten, F. Roozeboom, L. Baggetto, presented at the Materials Research Society (MRS) Fall Meeting, Boston, MA, November 2004.

[13] L. Baggetto, R.A.H. Niessen, F. Roozeboom, P. H. L. Notten, unpublished.

[14] T. D. Hatchard, J. R. Dahn, *J. Electrochem. Soc.* **2004**, *151*, A838.

[15] D. Aurbach, *J. Power Sources* **2000**, *89*, 206.