International Edition: DOI: 10.1002/anie.201603040
German Edition: DOI: 10.1002/ange.201603040

# Silicon-Compatible Carbon-Based Micro-Supercapacitors

*Xiaodong Zhuang and Xinliang Feng**

carbon materials · elastic carbon films · micro-supercapacitor · power and energy density · silicon wafer

The development of on-chip energy devices, especially silicon-compatible on-chip energy devices, has become urgent because of the demand for modern, rapidly developed portable electronics of small size and minimal thickness. Planar micro-supercapacitors, which possess a controllable thickness down to the nanometer scale, have gained much attention because of their potential for high power density and areal capacitance in comparison with traditional electrochemical double-layer capacitors (EDLCs) and pseudocapacitors.[1] However, most micro-supercapacitors are prepared using wet processing methods, such as spin or spray coating of colloidal solutions or suspensions for the fabrication of electrodes, which are not fully compatible with modern silicon semiconductor devices.

The first patent on capacitors, by H. I. Becker,[2] was issued in 1957, more than a century after the discovery of electrode charging by Hermann von Helmholtz in 1853.[2] The first commercial capacitor for memory back-up was marketed by NEC in 1971, and since then various kinds of capacitors, such as hybrid capacitors and micro-supercapacitors, with different sizes and applications, have been developed. Among the large number of capacitive materials (e.g. transition-metal oxides, nitrides, carbides, sulfides, and conducting polymers), porous carbon materials including activated carbons, carbide-derived carbons (CDCs), carbon nanotubes, and graphenes, are the most promising candidates owing to their ultra-high specific surface areas, good electrical conductivity, and extremely small double-layer thickness of the order of a few Ångströms (0.3–0.8 nm).[1c] Significant advancements in carbon-based micro-supercapacitors have been made in the past decade because of their potential for modern electronics. However, research has mostly focused on developing new carbon materials with improved properties rather than on solving the incompatibility between newly developed carbon-based micro-supercapacitors and modern electronic devices. For instance, the CDC-based electrodes have achieved the best volumetric and areal capacitances of micro-supercapacitors among all carbon-based materials,[3] but it is very hard to avoid cracking and delamination[4] of CDC films from silicon wafers owing to the different volumetric thermal expansion coefficient of CDC and $SiO_2$.

Pioneering works by Gogotsi, Simon, Brunet, Kaner, Ajayan, Müllen, and Feng using TiC,[3] nanodiamond,[5] graphene oxide,[6] and polyimide[7] as precursors for the preparation of CDCs, onion-like carbons, and graphene films have been a major inspiration in the field of carbon-material-based on-chip micro-supercapacitors. Although most of these carbon-based electrodes exhibit excellent volumetric or areal capacitances, and some of them can deliver high power densities, all attempts to achieve comparable performances to those of pseudocapacitors based on traditional metal oxides (e.g. $RuO_2$ and $MnO_2$) have failed thus far as a result of the intrinsic bottleneck of carbon materials.[1a] Therefore, high-performance carbon materials that have not only good adhesion to silicon wafers but also high capacitance, and excellent power and energy densities need to be developed.

Simon and co-workers[8] have achieved, for the first time, silicon-wafer-supported CDC films without any delamination or cracks, by the partial chlorination of a TiC film ($T = 450\,°C$, $t_1 = 5$ min; Figure 1 a). This result was attributed to good adhesion between the residual 1 μm-thick TiC and $SiO_2$ (Figure 1 b) and ultra-tight occlusion between CDC and TiC needles (Figures 1 b,c). Additionally, the remaining metallic conducting TiC layer ($10^3\,S\,cm^{-1}$) under the CDC film can also act as a current collector in energy-storage devices. This method for the preparation of $SiO_2$-TiC-CDC layers has the potential for wide applications in the synthesis of carbon films, which have long been hampered by cracking and delamination problems on various substrates. Most importantly, such a dry processing method is fully compatible with modern silicon-semiconductor device manufacturing (Figures 1 d,e).

After completely removing Ti from the TiC film, the pore properties of the as-prepared CDCs were evaluated by Ar and $CO_2$ sorption measurement. The high specific surface area of up to $977 \pm 30\,m^2\,g^{-1}$, together with the ultra-narrow and uniform pore size (average pore size 0.59 nm, Figure 2 a) and the micropore volume of $0.47\,cm^3\,g^{-1}$ made the CDC film an outstanding candidate for the supercapacitors.

---

[*] Dr. X. Zhuang, Prof. X. Feng
Center for Advancing Electronics Dresden (cfaed)
and Department of Chemistry and Food Chemistry
Technische Universität Dresden
Mommsenstrasse 4, 01062 Dresden (Germany)
E-mail: xinliang.feng@tu-dresden.de

The ORCID identification number(s) for the author(s) of this article can be found under http://dx.doi.org/10.1002/anie.201603040.

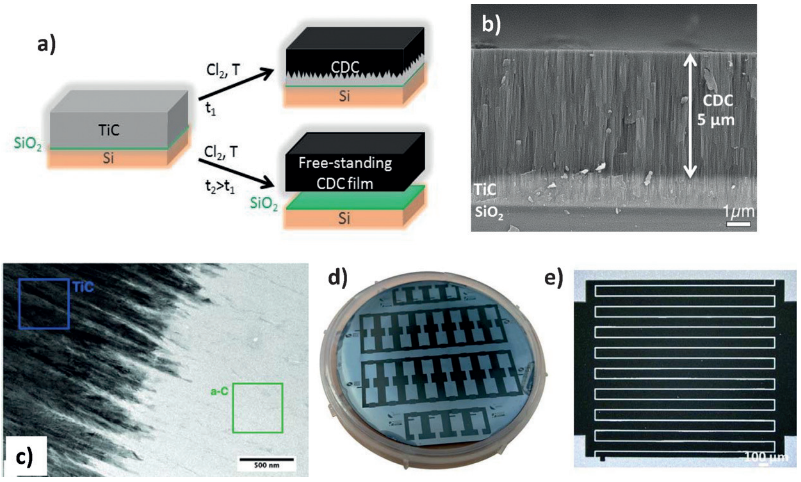

***Figure 1.*** a) Scheme for the chlorination process. b) Layer profile structure of the obtained $SiO_2$-TiC-CDC. c) Transmission electron microscope image of the TiC-CDC interface. d) A 7.62-cm wafer with 40 patterned CDC-based micro-supercapacitors. e) Optical image of one typical micro-supercapacitor with 18 interdigitated CDC electrodes. Reproduced by permission of AAAS.

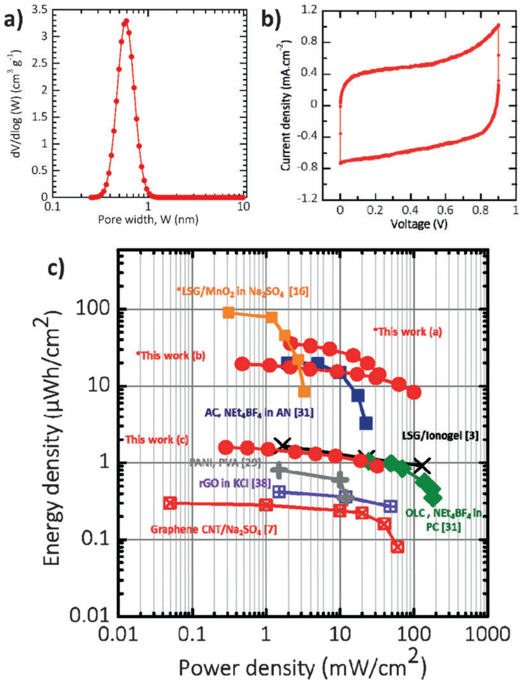

***Figure 2.*** a) Pore size distribution of the porous CDC film calculated by a reverse Monte Carlo model based on $CO_2$ gas sorption. b) Cyclic voltammetry analysis of a micro-supercapacitor in 1 M $H_2SO_4$ electrolyte recorded at 10 mV $s^{-1}$. The volumetric capacitance reached 350 F $cm^{-3}$. c) Areal-normalized Ragone plots of the CDC film in comparison with micro-supercapacitors based on reported carbon and pseudocapacitive materials. The CDC thicknesses for "This work (a), (b) and (c)" in Figure 2c are 4.1, 2.2, and 1.4 µm, respectively. Reproduced by permission of AAAS.

The CDC-TiC film obtained on the Si wafer was first annealed at 600 °C for 2 h under vacuum and then used as the electrodes in three-electrode cells. The volumetric and areal capacitances at 1 mV $s^{-1}$ in 1 M $H_2SO_4$ were determined as 410 F $cm^{-3}$ and 205 mF $cm^{-2}$, respectively. The CDC-TiC film was annealed at 600 °C under hydrogen to open the pores for an organic electrolyte (1-ethyl-3-methylimidazolium tetrafluoroborate), and then used as a single electrode in an electric double-layer capacitor. The CDC-TiC film exhibited a volumetric capacitance and a potential window of 170 F $cm^{-3}$ at 20 mV $s^{-1}$ and 2 V, respectively. For comparison, the CDC (2.2 µm)-TiC film based on partial chlorination at 700 °C demonstrated a potential window of up to 3 V and a volumetric capacitance of 160 F $cm^{-3}$ at 20 mV $s^{-1}$. A nine-fingered micro-supercapacitor (2 mm long, 100 µm wide, and 15 µm separation; Figure 1e) based on CDC (1.4 µm)-TiC (3.5 µm) films and 1 M $H_2SO_4$ electrolyte was finally studied, yielding a volumetric capacitance of 350 F $cm^{-3}$ at 10 mV $s^{-1}$ (Figure 2b). Remarkably, more than 50 % of the capacitance (180 F $cm^{-3}$) was retained at 10 V $s^{-1}$, which makes it a state-of-the-art micro-supercapacitor.

Areal capacitance is an important parameter that determines the possible applications of micro-supercapacitors in silicon-based electronics. As indicated in areal-normalized Ragone plots (Figure 2c), the CDC films show the best areal power and energy densities among the reported carbon-based electrodes. This result is even comparable with thick pseudocapacitive laser-scribed graphene-$MnO_2$ composite electrodes (800 mF $cm^{-2}$).

To understand the difference between the as-developed CDC films and cracked CDC films as well as other carbon-based electrodes, the mechanical properties of the CDC films were further studied. The hardness and Young's modulus of the as-developed 5 µm-thick CDC film (Figure 1b) reached 1.6 and 14.5 GPa, respectively. Delamination of the CDC-TiC film typically occurred at 130 mN, indicating an adhesion of 18 J $m^{-2}$. As a proof-of-concept, a CDC film (3.5 µm thick) was transferred to a polyethylene terephthalate substrate. The resulting flexible micro-supercapacitor delivered an areal capacitance of 240 mF $cm^{-2}$ (300 F $cm^{-3}$) in 1 M $H_2SO_4$.

This method for the preparation wafer supported CDC films may suffer from difficulty for the controlled fabrication of CDC films with the thickness from several nm to a few hundreds of nm because of the formation of 0.5–1 µm TiC needles after partial chlorination (Figure 1c). Nevertheless, the formation of CDC films on silicon wafers without any cracks and delamination is already highly encouraging, and it is an important milestone for the silicon-compatible on-chip micro-supercapacitors. We believe that this work represents a new start for on-chip energy devices given that the reported CDC film fabrication technique can be readily extended to the development of different substrate-supported porous carbon films as well as silicon-wafer-supported heteroatom-doped porous carbon films and hybrid material films with versatile applications in the field of—but not limited to—energy storage.

## Acknowledgments

This work was financially supported by ERC Grant on 2DMATER and EU Graphene Flagship.

**How to cite:** *Angew. Chem. Int. Ed.* **2016**, *55*, 6136–6138
*Angew. Chem.* **2016**, *128*, 6244–6246

---

[1] a) M. Beidaghi, Y. Gogotsi, *Energy Environ. Sci.* **2014**, *7*, 867–884; b) P. Simon, Y. Gogotsi, *Nat. Mater.* **2008**, *7*, 845–854; c) B. E. Conway, *Electrochemical Supercapacitors: Scientific Fundamentals and Technological Applications*, Springer, New York, **1999**.

[2] a) H. Helmholtz, *Ann. Phys.* **1853**, *165*, 211–233; b) H. I. Becker, US 2800616, USA, **1957**.

[3] J. Chmiola, C. Largeot, P.-L. Taberna, P. Simon, Y. Gogotsi, *Science* **2010**, *328*, 480–483.

[4] a) P. Huang, M. Heon, D. Pech, M. Brunet, P.-L. Taberna, Y. Gogotsi, S. Lofland, J. D. Hettinger, P. Simon, *J. Power Sources* **2013**, *225*, 240–244; b) P. Huang, D. Pech, R. Lin, J. K. McDonough, M. Brunet, P.-L. Taberna, Y. Gogotsi, P. Simon, *Electrochem. Commun.* **2013**, *36*, 53–56.

[5] D. Pech, M. Brunet, H. Durou, P. Huang, V. Mochalin, Y. Gogotsi, P.-L. Taberna, P. Simon, *Nat. Nanotechnol.* **2010**, *5*, 651–654.

[6] a) W. Gao, N. Singh, L. Song, Z. Liu, A. L. M. Reddy, L. Ci, R. Vajtai, Q. Zhang, B. Wei, P. M. Ajayan, *Nat. Nanotechnol.* **2011**, *6*, 496–500; b) M. F. El-Kady, V. Strong, S. Dubin, R. B. Kaner, *Science* **2012**, *335*, 1326–1330; c) M. F. El-Kady, R. B. Kaner, *Nat. Commun.* **2013**, *4*, 1475; d) Z. S. Wu, K. Parvez, X. Feng, K. Müllen, *Nat. Commun.* **2013**, *4*, 2487.

[7] J. Lin, Z. Peng, Y. Liu, F. Ruiz-Zepeda, R. Ye, E. L. G. Samuel, M. J. Yacaman, B. I. Yakobson, J. M. Tour, *Nat. Commun.* **2014**, *5*, 5714.

[8] P. Huang, C. Lethien, S. Pinaud, K. Brousse, R. Laloo, V. Turq, M. Respaud, A. Demortière, B. Daffos, P. L. Taberna, B. Chaudret, Y. Gogotsi, P. Simon, *Science* **2016**, *351*, 691–695.

Received: March 28, 2016