

Built To Disappear

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ABSTRACT Microelectronics dominates the technological and commercial landscape of today's electronics industry; ultrahigh density integrated circuits on rigid silicon provide the computing power for smart appliances that help us organize our daily lives. Integrated circuits function flawlessly for decades, yet we like to replace smart phones and tablet computers every year. Disposable electronics, built to disappear in a controlled fashion after the intended lifespan, may be one of the potential applications of transient single-crystalline silicon nanomembranes, reported by Hwang *et al.* in this issue of *ACS Nano*. We briefly outline the development of this latest branch of electronics research, and we present some prospects for future developments. Electronics is steadily evolving, and 20 years from now we may find it perfectly normal for smart appliances to be embedded everywhere, on textiles, on our skin, and even in our body.



Roughly 20 years ago, mobile phones first entered the market, yet no one could have anticipated the roles such devices play today. Smart phones, tablet computers, and the like accompany us in our daily lives, and we replace them frequently, usually far in advance of the products' operational lifetimes, which are measured in years or even in decades. This causes severe environmental problems, with faster than exponentially increasing amounts of electronic waste.¹ There are two strategies to overcome this problem: either designing devices for full recyclability or building a form of electronics that completely disappears in a controlled fashion after fulfilling its duty. The latter form of electronic devices may not only be applicable for throwaway disposables but also paves the way for electronics everywhere, including on the skin or even within our bodies.

Biodegradable and Edible Forms of Electronics.

In initial work on disposable or implantable electronic devices, resorbable biopolymers were employed as substrates. Kim *et al.*² deposited 260 nm thick silicon nanomembrane circuits onto silk, and Bettinger *et al.*³ fabricated organic electronic components on poly(L-lactide-co-glycolide). Large parts of the devices resorbed in aqueous solutions or in the body over time—important steps toward electronics that completely disappear after use. Following these initial steps, Irimia-Vladu *et al.*⁴ realized the potential of organic electronics for the development of fully biodegradable, biocompatible, bioresorbable, or even metabolizable electronic circuits. Fabrication from natural or

commodity materials was suggested as an ideal pathway for such ingestible devices (Figure 1a). Resorbable dielectrics and semiconductors were identified; ecoflex, a polymer made from potato and starch, hard gelatin capsules, and even caramelized glucose were employed as substrates; glucose and sucrose formed the dielectrics for the field-effect transistors; and beta-carotene, indanthrene yellow G, and brilliant orange RF turned out to be suitable organic semiconductors. The gold used was not resorbable, although it is classified as an edible material.

This new class of “edible” electronics inspired recent developments of sensors for food monitoring⁵ (Figure 1b) and batteries that are compatible with non-invasive deployment strategies⁶ (Figure 1c). Food safety is critically important for public health, but current analytical techniques are often time-consuming and too expensive for daily use. The passive antennas described by Tao *et al.*⁵ were ideal sensors to probe the evolving properties of food items, where a resonant frequency shift was observed as eggs aged, fruits ripened, and dairy products spoiled. Being edible, no harm is done when the sensors are ingested; being biodegradable, they can be disposed of in an eco-friendly manner. Capsule endoscopy is a powerful imaging tool for the gastrointestinal tract. Actively powered edible and bioresorbable electronic devices are the logical next steps toward non-invasive diagnostic and post-operative therapy systems without the need for extraction surgery. Self-deployable edible batteries with activated

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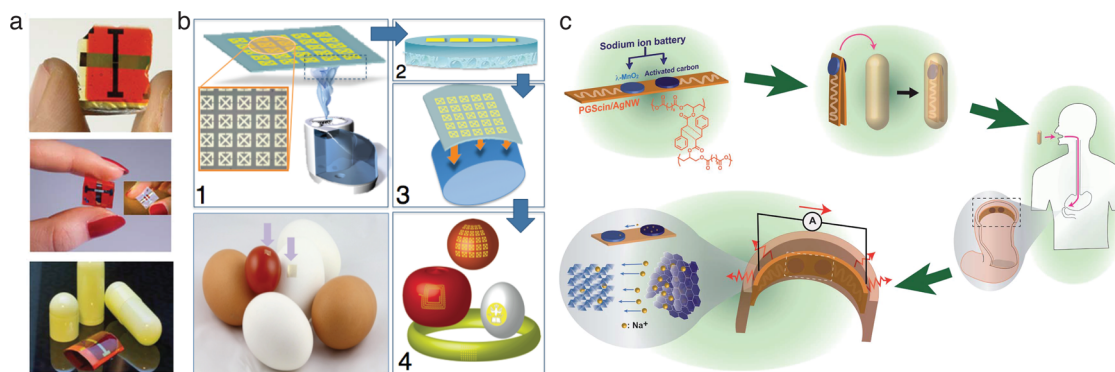


Figure 1. (a) Edible bio-organic field-effect transistors on ecoflex, caramelized glucose, and a gelatin capsule. Reproduced with permission from ref 4. Copyright 2010 Wiley. (b) Silk-based radio frequency antennas for food quality monitoring. The sensors are transferred to curved food item surfaces following the functionalization of the silk film with water vapor. Reproduced with permission from ref 5. Copyright 2012 Wiley. (c) Self-deployable edible batteries based on sodium-ion-activated carbon–manganese dioxide chemistry. When ingested, the capsule dissolves and activates the battery in the sodium-rich gastrointestinal environment. Reproduced with permission from ref 6. Copyright 2013 The Royal Society of Chemistry.

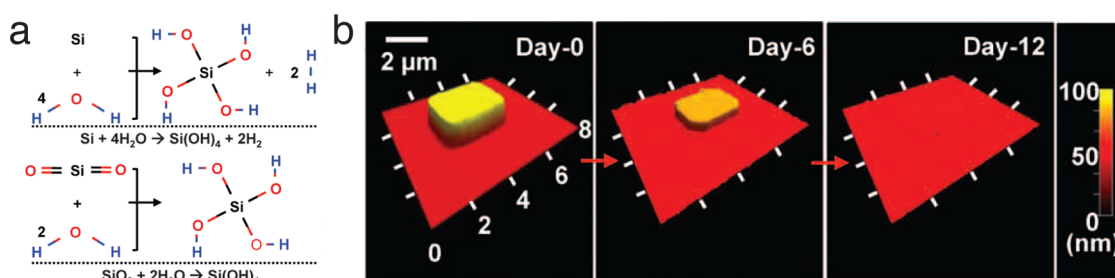


Figure 2. (a) Hydrolysis of Si in water. (b) Topographical images of a Si nanomembrane at various stages of hydrolysis under physiological conditions. Reproduced with permission from ref 9. Copyright 2013 American Academy for the Advancement of Science.

carbon as the anode and sodium-enriched manganese dioxide as the cathode were demonstrated by Kim *et al.*⁶ and could deliver output powers between 3 and 12 μW , levels that are already relevant for practical use. The innovative work on edible electronics inspired Glowacki *et al.*⁷ to introduce a new class of hydrogen-bonded organic semiconductors, where the tight stacking of the molecules significantly improves the stability under standard environmental conditions. Organic semiconductors that stack tightly enabled Knopfmacher *et al.*⁸ to develop sensors that are operable in fresh water and even under harsh seawater conditions for extended periods of time.

Transient Silicon Electronics. Until recently, only organic electronic materials were believed to be fully biodegradable, whereas conventional silicon semiconductors were

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considered to be extremely stable. This is, however, only true for the bulk material. The observation of a physically transient form of silicon electronics by Hwang *et al.*⁹ was a major breakthrough that made the high performance of an inorganic semiconductor accessible to the biological world and its temporally limited lifespans. In this issue of *ACS*

Nano, Hwang *et al.*¹⁰ report on the kinetics of hydrolysis of silicon nanomembranes in biofluids as well as their biocompatibility *in vitro* and *in vivo*. Water reacts with silicon and with silicon dioxide to orthosilicic acid (Figure 2a), causing thin nanomembranes of silicon to disappear completely in a controlled fashion (Figure 2b). The nanoscale thickness of the silicon membranes is critically important for use in devices built to disappear, by reducing the time scales for dissolution to well-defined, relatively short time frames. *In vitro* cell culture evaluations of degradation and cytotoxicity (Figure 5 in ref 10) showed clear evidence of biocompatibility of the silicon nanomembranes. Test structures implanted in the subdermal region of Balb/c mice demonstrated complete bioresorption without affecting the health conditions of the

animals (Figure 6 in ref 10). Metals like Mg and some of its alloys, Zn, Fe, W, and Mo associate silicon nanomembranes, which are useful as contacts and interconnects in transient electronic circuits.¹¹

Merging the fields of edible, transient, and imperceptible electronics promises a class of products that meet practical engineering requirements and scalable manufacturing on large areas.

Outlook and Future Challenges. Although several essential ideas evolved in the design of disposable, edible, and implantable electronic devices, many opportunities remain for future research. Efforts are needed to demonstrate further functionalities that are required for autonomous systems-level applications, such as bioresorbable energy harvesters and energy-storage elements. The large variety of physically transient metals and their oxides provide opportunities for challenging research on fully biocompatible and bioresorbable supercapacitors and electrochemical batteries. Expanding the options in both passive and active materials for substrates, sensors, and actuators provides new avenues in studying the chemistry and mechanics of transience in a wide range of materials. The electronics of tomorrow will permeate ever more domains of our surroundings, requiring imperceptible devices that camouflage their presence.^{12,13} In the design of next-generation smart appliances for sports and healthcare that assess our physiological conditions, flexibility, compliance, weight, softness, and transience will turn out to be key metrics. Merging the fields of edible, transient, and imperceptible

electronics promises a class of products that meet practical engineering requirements and scalable manufacturing on large areas. Twenty years from now, we will likely be comfortable with electronics virtually everywhere, much as we are now familiar with smartphones and tablet computers.

Conflict of Interest: The authors declare no competing financial interest.

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REFERENCES AND NOTES

- Irimia-Vladu, M. "Green Electronics"—Biodegradable and Biocompatible Materials and Devices for Sustainable Future. *Chem. Soc. Rev.* **2014**, *43*, 588–610.
- Kim, D.-H.; Kim, Y.-S.; Amsden, J.; Panilaitis, B.; Kaplan, D. L.; Omenetto, F. G.; Zakin, M. R.; Rogers, J. A. Silicon Electronics on Silk as a Path to Bioresorbable, Implantable Devices. *Appl. Phys. Lett.* **2009**, *95*, 133701.
- Bettinger, C. J.; Bao, Z. Organic Thin-Film Transistors Fabricated on Resorbable Biomaterial Substrates. *Adv. Mater.* **2010**, *22*, 651–655.
- Irimia-Vladu, M.; Troshin, P. A.; Reisinger, M.; Shmygleva, L.; Kanbur, Y.; Schwabegger, G.; Bodea, M.; Schwödiauer, R.; Mumyatov, A.; Fergus, J. W.; et al. Biocompatible and Biodegradable Materials for Organic Field-Effect Transistors. *Adv. Funct. Mater.* **2010**, *20*, 4069–4076.
- Tao, H.; Brenckle, M. A.; Yang, M.; Zhang, J.; Liu, M.; Siebert, S. M.; Averitt, R. D.; Manno, M. S.; McAlpine, M. C.; Rogers, J. A.; et al. Silk-Based Conformal, Adhesive, Edible Food Sensors. *Adv. Mater.* **2012**, *24*, 1067–1072.
- Kim, Y. J.; Chun, S.-E.; Whitacre, J.; Bettinger, J. Self-Deployable Current Sources Fabricated from Edible Materials. *J. Mater. Chem. B* **2013**, *1*, 3781–3788.
- Głowacki, E. D.; Irimia-Vladu, M.; Kaltenbrunner, M.; Gasiorowski, J.; White, M. S.; Monkowius, U.; Romanazzi, G.; Suranna, G. P.; Mastroianni, P.; Sekitani, T.; et al. Hydrogen-Bonded Semiconducting Pigments for Air-Stable Field-Effect Transistors. *Adv. Mater.* **2013**, *25*, 1563–1569.
- Knopfmacher, O.; Hammock, M. L.; Appleton, A. L.; Schwartz, G.; Mei, J.; Lei, T.; Pei, J.; Bao, Z. Highly Stable Organic Polymer Field-Effect Transistor Sensor for Selective Detection in the Marine Environment. *Nat. Commun.* **2014**, *5*, 2954.
- Hwang, S.-W.; Tao, H.; Kim, D.-H.; Cheng, H.; Song, J.-K.; Rill, E.; Brenckle, M. A.; Panilaitis, B.; Won, S. M.; Kim, Y. S.; et al. A Physically Transient Form of Silicon Electronics. *Science* **2012**, *337*, 1640–1644.
- Hwang, S.-K.; Park, G.; Edwards, C.; Corbin, E. A.; Kang, S.-K.; Cheng, H.; Song, J.-K.; Kim, J.-H.; Yu, S.; Ng, J.; et al. Dissolution Chemistry and Biocompatibility of Single-Crystalline Silicon Nanomembranes and Associated Materials for Transient Electronics. *ACS Nano* **2014**, *8*, DOI: 10.1021/nn500847g.
- Yin, L.; Cheng, H.; Mao, S.; Haasch, R.; Liu, Y.; Xie, X.; Hwang, S.-W.; Jain, H.; Kang, S.-K.; Su, Y.; et al. Dissolvable Metals for Transient Electronics. *Adv. Funct. Mater.* **2014**, *24*, 645–658.
- Kim, D.-H.; Lu, N.; Ma, R.; Kim, Y.-S.; Kim, R.-H.; Wang, S.; Wu, J.; Won, S. M.; Tao, H.; Islam, A.; et al. Epidermal Electronics. *Science* **2011**, *333*, 838–843.
- Kaltenbrunner, M.; Sekitani, T.; Reeder, J.; Yokota, T.; Kuribara, K.; Tokuhara, T.; Drack, M.; Schwödiauer, R.; Graz, I.; Bauer-Gogonea, S.; et al. An Ultralightweight Design for Imperceptible Plastic Electronics. *Nature* **2013**, *499*, 458–465.