

## Recent Advances and Techniques for Ge Nanomaterials

Elizabeth Miller

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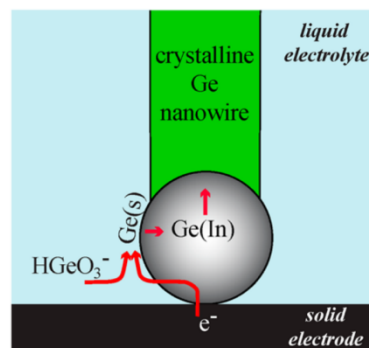
Ge nanomaterials have attracted much attention recently due to their potential applications in semiconductor technologies and energy-related fields.<sup>1,2</sup> While Ge has been largely incorporated in optoelectronics due to its low refractive index, current research additionally seeks to utilize the high electron and hole mobilities of Ge ( $3900 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$  and  $1900 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ ), which are twice and four times that of Si.<sup>3</sup> These properties make Ge a good candidate for complementary metal-oxide semiconductor transistors.<sup>4</sup> Additionally Ge shows promise for Li-ion battery anodes because it has a much higher theoretical capacity ( $1620 \text{ mAhg}^{-1}$ ) than the commercial graphite electrode ( $330 \text{ mAhg}^{-1}$ ).<sup>5</sup> Like Si, however, Ge anodes suffer from large volume changes leading to anode deterioration and capacity fade.<sup>6</sup>

Despite these attractive properties, the high price of Ge, the limitations of fabrication techniques, and the instability of the Ge interface hinder the implementation of Ge technologies.<sup>4,7-10</sup> A shift toward nano-scale materials and new techniques, incorporating aqueous electrodeposition and a more stable interface, addresses these challenges.

The electrodeposition of crystalline Ge nanowires and thin films from aqueous solutions has been demonstrated in the past 5 years, using electrochemical atomic layer deposition (e-ALD) and electrochemical liquid-liquid-solid growth (ec-LLS). The Maldonado group discovered that liquid metal electrodes could be used to dissolve deposited Ge and act as a seed for crystallization (Figure 1).<sup>11</sup> By altering the size of the liquid nanodroplets (In, Ga, Hg) and the flux into the electrode and substrate, Ge nanowires could be grown with various sizes and crystallinity.<sup>12</sup> Because this technique utilizes the alloying process between Ge and liquid metals, the nanowires retain some of the liquid metal as impurities. The Switzer group found that the doping ( $0.14 \pm 0.04 \text{ atom } \%$ ) of In in Ge nanowires was too high to be useful for conventional electronic applications.<sup>3</sup>

Alternatively, nanowires formed using the ec-LLS technique could be possible Li-ion anode materials. While the electrodeposited Ge nanowires showed impressive discharge capacities ( $973 \text{ mAhg}^{-1}$ ), the Coulombic efficiencies plateaued around 94%, indicating that these materials still required significant optimization.<sup>6</sup>

Similar to nanowires, thin films have been electrodeposited from aqueous solutions. In water, hydrogen evolution occurs at potentials more positive than bulk Ge electrodeposition.<sup>13</sup> To circumvent this decomposition, a monolayer of Ge can be deposited at potentials more thermodynamically favored than bulk Ge deposition, a process called underpotential deposition (UPD). UPD results from a stabilization of a monolayer through a bonding or alloy with the



**Figure 1.** Schematic of the ec-LLS process for aqueous Ge electrodeposition at an In nanoparticle.<sup>k</sup>

substrate. Stickney et al. demonstrated that thin films of Ge could be grown through an electrochemical analog of atomic layer deposition using UPD.<sup>14</sup> To grow thin films, the Stickney group deposited alternating layers of Ge with Te. The Te was then reductively stripped to  $\text{Te}^{2-}$ , leaving only Ge layers. This method, coined the *bait and switch*, allowed crystalline layers of Ge to form on Au and Cu at room temperature. While this method is less expensive than high vacuum, high temperature techniques, the authors did not address the stability effects in air or the ability to transfer these thin films to more useful substrates like Si.

To this end, the Goldberger group synthesized hydrogen-terminated Ge sheets from the deintercalation of  $\text{CaGe}_2$ .<sup>15</sup> These corrugated honeycomb sheets called germanane (GeH) were stable up to  $75^\circ\text{C}$  before dehydrogenation would occur. At room temperature, the surface layer slowly oxidized over the course of 5 months, while the underlying layers were not oxidized. Interestingly, like other layered materials (graphite), individual sheets of GeH could be exfoliated and transferred onto other substrates, like  $\text{SiO}_2/\text{Si}$ . These properties make GeH an exciting new material for semiconductor and optoelectronic devices.<sup>16</sup>

While several new cost-effective techniques have been developed to synthesize nano-scale Ge materials, additional research is necessary to understand and improve their properties. Future studies need to address the stability of these nanowires and thin films as well as work toward integration with current Si-based technologies.

1. Pillarisetty, R. Academic and Industry Research Progress in Germanium Nanodevices. *Nature*, **2011**, *479*, 324.
2. Gomez, L.; Chleirigh, C.; Hashemi, P.; Hoyt, J. Enhanced hole mobility in high Ge content asymmetrically strained-SiGe p-MOSFETs. *IEEE Electron Device Lett.*, **2010**, *31*, 782.
3. Mahenderkar, N.; Liu, Y.; Koza, J.; Switzer, J. Electrodeposited Germanium Nanowires. *ACS Nano*, **2014**, *8*, 9524.
4. Goley, P.; Hudait, M. Germanium based Field Effect Transistors, Challenges and Opportunities. *Materials*, **2014**, *7*, 2301.
5. Kennedy, T.; Mullane, E.; Geaney, H.; Osiak, M.; O'Dwyer, C.; Ryan, K. High-Performance Germanium Nanowire-Based Lithium-Ion Battery Anodes Extending over 1000 Cycles Through in Situ Formation of a Continuous Porous Network. *ACS Nano*, **2014**, *14*, 716.
6. Gu, J.; Collins, S.; Carim, A.; Hao, X.; Bartlett, B.; Maldonado, S. Template-Free Preparation of Crystalline Ge Nanowire Film Electrodes via an Electrochemical Liquid-Liquid-Solid Process in Water at Ambient Pressure and Temperature for Energy Storage. *ACS Nano*, **2012**, *12*, 4617.
7. Yang, M.; Wu, R.; Chen, Q.; Deng, S.; Feng, Y.; Chai, J.; Pan, J.; Wang, S.; Impact of Oxide Defects on Band Offset at GeO<sub>2</sub>/Ge Interface. *Appl. Phys. Lett.*, **2009**, *94*, 142903.
8. USGS Mineral Information **2014**
9. Endres, F. Electrodeposition of a Thin Germanium Film on Gold from a Room Temperature Ionic Liquid. *Phys. Chem. Chem. Phys.*, **2001**, *3*, 3165.
10. Huang, Q.; Bedell, S.; Saenger, K.; Copel, M.; Deligianni, H.; Romankiw, L. Single-Crystalline Germanium Thin Films by Electrodeposition and Solid-Phase Epitaxy *Electrochem. Solid-State Lett.*, **2007**, *10*, D124.
11. Carim, A.; Collins, S.; Foley, J.; Maldonado, S. Benchtop Electrochemical Liquid-Liquid-Solid Growth of Nanostructured Crystalline Germanium. *JACS*, **2011**, *133*, 13292.
12. Fahrenkrug, E.; Gu, J.; Jeon, S.; Veneman, A.; Goldman, R.; Maldonado, S. Room-Temperature Epitaxial Electrodeposition of Single-Crystalline Germanium Nanowires at the Wafer Scale from an Aqueous Solution. *Nano Lett.*, **2014**, *14*, 847.
13. Liang, X.; Kim, Y.; Gebergziabihier, D.; Stickney, J. Aqueous Electrodeposition of Ge Monolayers. *Langmuir*, **2010**, *26*, 2877.
14. Liang, X.; Zhang, Q.; Lay, M.; Stickney, J. Growth of Ge Nanofilms Using Electrochemical Atomic Layer Deposition with a "Bait and Switch" Surface-Limited Reaction. *JACS*, **2011**, *133*, 8199.
15. Bianco, E.; Butler, S.; Jiang, S.; Restrepo, O.; Wolfgang, W.; Goldberger, J. Stability and Exfoliation of Germanane: A Germanium Graphene Analogue. *ACS Nano*, **2013**, *7*, 4414.

16. Vogg, G.; Brandt, M.; Stutzmann, M. Polygermyne – A Prototype System for Layered Germanium Polymers. *Adv. Mater.*, **2000**, *12*, 1278.