1. Award: DE-FG02-07ER46476; PI: Slavi C. Sevov, University of Notre Dame
2. Title: “Nanorods of Silicon and Germanium with Well-Defined Shapes and Sizes”
3. Period: September 1, 2007 – August 31, 2011
4. Findings:

We have made number of important discoveries along the major goals of the project, namely i) electrodeposition of germanium thin films from clusters, ii) synthesis of cluster-based surfactants with long hydrocarbon chains and micelles made of them, iii) grafting of Ge₉-clusters onto self assembled films of siloxanes attached to glass substrates, iv) doping of Ge₉-clusters, and v) expanding the clusters to ten-atom cages of Ge₁₀²⁻. These achievements are important steps towards practical devices for various catalytic, electronic, optoelectronic, and photochemical applications.

i) Electrodeposited germanium films. Low dimensional structures of Group IV semiconductors like Ge are of great interest because of their applications in novel optoelectronic as well as energy conversion devices. There are several well established techniques devoted to their fabrication and include chemical vapor deposition, electron beam evaporation, pulsed laser deposition, ion implantation, molecular beam epitaxy, and sputtering. Literature reports related to electrodeposition of Ge (a relatively simple and cost effective technique), particularly on metallic and semiconductor substrates, are few and far in-between. The reason is due to the low hydrogen overpotential on germanium surfaces in aqueous solutions. Once a limited amount of Ge has formed on the electrode surface, all the subsequent current is used for the proton reduction. In approaches wherein non-aqueous solutions are used, e.g. pure glycol or ionic liquid solvents, the free proton concentration in solution is considerably reduced and this eliminates the side reaction of hydrogen formation. However, such approaches involve the disadvantages of high viscosity media or high cost of solvent materials. There has been only one literature report of electrodeposition of Ge on silicon substrates, and it describes the growth of cathodically electroplated amorphous Ge thin films on *n*- and *p*-doped Si substrates using germanium tetrachloride solution in 1,3-propandiol at temperatures of 60-80°C.

Figure 1. a) The electrolytic cell in which germanium films are plated onto the Si(100) anode from Ge_9 -clusters dissolved in ethylenediamine. b) The resulting uniform film of germanium on Si(100) surface. c) MALDI-TOF mass-spectrum of the germanium film showing only purely Ge_n species which indicates that the films are free of impurities and are not oxidized.

In the light of the scenario aforementioned, there is an ongoing effort to develop cost-effective new synthetic pathways for fabrication of thin films of metals and semiconductors that can exhibit improved efficiency and selectivity towards light energy conversion and semiconductor optoelectronics. In this context, the field of anionic Zintl ions is rich, vast, and largely unexplored from the point of view of their *anodic* electrodeposition. There is a two-fold advantage in using them for such plating, namely a) they are very soluble in polar organic solvents like ethylene diamine and hence the problem with hydrogen overpotentials associated with aqueous media is eliminated, and b) high viscosity and costs associated with non-aqueous media currently reported in the literature are also not there. We have now achieved for the first time anodic electrodeposition of germanium on *p*-doped Si(100) substrates. The deposition was carried out at ambient conditions in an electrolytic cell (Figure 1a) from an electrolyte of Ge_9 clusters in ethylenediamine. This produced very uniform and well adhering films of germanium on the

Figure 2. Powder X-ray diffraction of Ge-films electrodeposited anodically on Si(100) from ethylenediamine solutions of Ge_9^{4-} : a) as deposited, b) after heating at 500 °C.

silicon surface (Figure 1b). Subsequent MALDI-TOF mass spectrometry showed only Ge_n peaks (Figure 1c) which indicates that the films are made of pure germanium and without organic impurities.

The resulting, as-deposited, films on *p*-doped Si(100) substrates are amorphous (Figure 2a) but become crystalline upon annealing at 500 °C (Figure 2b). All prior work pertaining to electrodeposition of germanium on metal and semiconductor substrates concerned deposition at the cathode. Those deposition baths contained germanium halides or, in a few instances, germanium oxides either as melts or dissolved in aqueous media, glycols, diols, or ionic liquids. There is a three-fold advantage in using anionic Ge_9^{4-} clusters for the electrodeposition. First, the current efficiencies are high as no side reactions occur at the anode.²⁶ Second, the usage of polar organic solvents like ethylenediamine eliminates the large hydrogen overpotentials associated with aqueous media. And third, the disadvantages of high viscosities associated with non-aqueous media such as propylene glycol or the high costs pertaining to ionic liquid solvents are also circumvented.

ii) Cluster-based surfactants and micelles. Our extensive and systematic studies of the reactivity of Ge_9 and Sn_9 clusters towards various organic functional groups have shown that reactions with alkynes $\text{R}-\text{C}\equiv\text{C}-\text{R}'$ lead to alkenylation of the clusters, i.e. to $[\text{Ge}_9-\text{C}(\text{R})=\text{CHR}']^{3-}$ and $[\text{Ge}_9(-\text{C}(\text{R})=\text{CHR}')_2]^{2-}$. A cluster can add up to two organic molecules and in the process the triple bond is reduced to a double bond. We have now used this knowledge to attach long-chain alkynes with terminal tripple bonds to the cluster and form assemblies with negatively-charged and polar cluster heads and nonpolar long tails such as $[\text{Ge}_9-\text{CH}=\text{CH}-(\text{CH}_2)_n\text{CH}_3]^{3-}$ and $[\text{Ge}_9(-\text{CH}=\text{CH}-(\text{CH}_2)_n\text{CH}_3)_2]^{2-}$ (Figure 3). The resulting organo-Zintl ions have two very different regions, namely charged polar cluster-heads with localized charge and long hydrophobic (nonpolar)

Figure 3. We have shown that Ge_9^{4-} clusters react with alkynes and add up to two of the latter as alkenes. This has now been used to attach long-chain alkynes in order to produce surfactant-like species with polar cluster “head” and two nonpolar hydrocarbon “tails”.

hydrocarbon tails. These characteristics make the ions very similar to surfactant molecules and, as such, we can expect similar behavior, for example micelle or reversed-micelle formation for the double-tail species in polar and nonpolar solvents. Furthermore, our discovery that substituted clusters (independent of the substituents) are stable even in the presence of water, makes this type of research possible even in aqueous solutions.

iii) *Germanium clusters grafted onto self-assembled films of siloxanes.* Covering glass slides with siloxanes, $(\text{RO})_3\text{Si-R}$, to form films of cross-linked siloxane groups and protruding organic tails is a straightforward and well known process. Furthermore, the organic tails can be terminated with a variety of functional groups. The fact that the Ge_9 -clusters react with alkynes and add them as alkenes was used also for grafting the clusters on preformed layers of siloxanes with triple bonds self-assembled on glass surfaces. Thus, molecules such as $(\text{EtO})_3\text{Si}-(\text{CH}_2)_n\text{C}\equiv\text{CH}$ are first attached to the glass surface as shown in top left of Figure 4. The self-assembled surface now has multiple sites with triple bonds which can react with the clusters. This film is then immersed in an ethylenediamine solution of Ge_9^{4-} clusters. The whitish surface quickly becomes red due to the red color of the germanium clusters attached to the ends of the chains (Figure 4a). In this process the triple bond is hydrogenated to a double bond.

Figure 4. Treatment of self-assembled layers of alkynylated siloxanes with Ge_9^{4-} clusters leads to the covalently-bonded clusters to the ends of the chains where the triple bonds are hydrogenated to double bonds in the process (top). Similar treatment of protonated ammonium tail-ends of the self-assembled siloxane layers with already di-functionalized clusters leads to electrostatically attached clusters on the surface (bottom).

In a similar process clusters are grafted on similarly assembled siloxane layers but this time with protonated amino groups at the tail end (Figure 4, bottom). The clusters in this case must be difunctionalized and with charge 2-, i.e. $[\text{R-Ge}_9\text{-R}]^{2-}$, because the naked clusters are too reducing and reduce the $-\text{NH}_4^+$ groups to amines and alkenes. Disubstituted clusters, on the other hand, do not react with the ammonium cations but are rather simply attracted electrostatically by them. Thus the grafting in this case is not via covalent bonds but via simple electrostatic interactions (Figure 4, bottom).

iv) Doping of Ge_9 -clusters. Our early work with Ge_9 clusters focused on their functionalization with main-group organometallic fragments. Thus, substitution reactions with Ph_3Sb , Ph_3Bi , Ph_4Sn , Me_3SnCl , Ph_3GeBr , etc., resulted in the corresponding mono- and di-functionalized species $[\text{Ge}_9\text{-SbPh}_2]^{3-}$, $[\text{Ge}_9\text{-SbPh}_2]^{2-}$, $[\text{Ge}_9\text{-SnPh}_3]^{3-}$, $[\text{Ge}_9\text{-SnPh}_3]^{2-}$, etc. However, it turns out that the same reactions, but carried out for longer times (6-20 hours) and at somewhat elevated temperatures (60-80 °C), lead to substitution of Ge-atoms within the clusters. For example, synthesized and characterized were species such as $[(\text{SbGe}_8)\text{-SbPh}_2]^{2-}$, $[(\text{BiGe}_8)\text{-(Ge}_8\text{Bi)}]^{4-}$, and $(\text{Sb}_2\text{Ge}_7)^{2-}$ (Figure 5). Although the mechanism of these dramatic exchanges are not known at this stage, the products are quite important. These clusters are of lower charges, i.e. Ge_9^{4-} vs. $(\text{Sb}_2\text{Ge}_7)^{2-}$, because each Sb and Bi atom brings one extra electron compared to Ge. It is known that the lower the charges of such negatively-charged clusters of main-group metals and semimetals, the more stable they are in ambient conditions, i.e. they may not need protection from moisture and air. Furthermore, they potentially give us direct access to *n*-doped bulk germanium semiconductors and/or similarly doped nanoparticles. It is important to note that Ge and Bi as well as Ge and Sb are immiscible in the bulk, and using such pre-made small clusters may potentially lead to metastable and very beneficial bulk phases.

Figure 5. The structures of $[(\text{SbGe}_8)\text{-SbPh}_2]^{2-}$ (left), $[(\text{BiGe}_8)\text{-(Ge}_8\text{Bi)}]^{4-}$ (middle), and $(\text{Sb}_2\text{Ge}_7)^{2-}$ (right). These clusters are made by controlled “doping” of Ge_9^{4-} clusters with Sb or Bi in reactions with SbPh_3 and BiPh_3 , respectively, where the level of doping depends on the reaction temperature and duration.

v) *Synthesis and characterization of Ge_{10}^{2-} .* The 9-atom *nido*-clusters of Ge, Sn, and Pb have been known for more than a century and have been structurally characterized tens of times and with different charges, i.e. E_9^{4-} and E_9^{3-} . Also known, for quite some time, have been the five atom species E_5^{2-} of the same elements. Five years ago we added to this collection the corresponding 9- and 5-atom silicon clusters Si_9^{3-} , Si_9^{2-} , and Si_5^{2-} . At the same time, until very recently, nothing was known about eventual 10-atom *closo* species that would form by adding the missing tenth vertex to the *nido* 9-atom deltahedra. The first such *closo* deltahedron was reported four years ago. The cluster, Pb_{10}^{2-} , was made by soft oxidation of Pb_9^{4-} with Au(I) but the yields were relatively low and large amounts of precipitation of metallic lead was observed. Meanwhile, while working on organic functionalization of Ge_9 deltahedral clusters by reactions with alkyl halides and alkynes, we briefly surveyed many other organic functional groups for their reactivity towards the clusters. To our surprise, the electrospray mass spectra of the reactions with ketons, aldehydes, and esters in DMF were dominated by Ge_{10} -species while the amounts of nine-atom clusters were almost negligible. However, numerous attempts to crystallize the clusters failed, and it was unclear if they were real or artifacts of the mass spectrometry experiment. The crystallization was finally achieved by using the clusters as two-electron ligands to transition metals. Thus, Ge_{10}^{2-} was structurally characterized in the complex anion $[\text{Ge}_{10}\text{-Mn}(\text{CO})_4]^{3-}$ (Figure 6) where the cluster is coordinated to Mn via the lone pair of one of the capping germanium atoms. The Mn-center achieves 18-electron configuration by an additional negative charge, i.e. $[\text{LMn}(\text{CO})_4]^-$ where $\text{L} = \text{Ge}_{10}^{2-}$. Similarly, Sn_{10}^{2-} was later crystallized as coordinated to two Co-centers via both capping tin atoms in $[(\text{CO})_3\text{Co-Sn}_{10}\text{-Co}(\text{CO})_3]^{4-}$ (Figure 6). These structures confirm that the large amounts of 10-atom clusters observed in the mass spectra are real. This provides us with the opportunity to study the chemistry of these *closo* species the same way as we have studied the nine-atom clusters before.

Figure 6. Ten-atom deltahedral clusters coordinated as ligands to transition metals: $[\text{Ge}_{10}\text{-Mn}(\text{CO})_4]^{3-}$ (left) and $[(\text{CO})_3\text{Co-Sn}_{10}\text{-Co}(\text{CO})_3]^{4-}$ (right).

5. Publications (the DOE support has been acknowledged):

- 1) "Anodic Electrodeposition of Germanium Films from Ethylenediamine Solutions of Deltahedral Ge_9^{4-} Zintl Ions", N. Chandrasekharan and S. C. Sevov, *J. Electrochem. Soc.* **2010**, *157*, C140.
- 2) "The Elusive *closo*- Ge_{10}^{2-} Zintl Ion: Finally "Captured" as a Ligand in the Complex $[\text{Ge}_{10}\text{Mn}(\text{CO})_4]^{3-}$ ", D. Rios and S. C. Sevov, *Inorg. Chem.* **2010**, *49*, 6396.
- 3) Structural, Vibrational, and Optical Characterization of Anodically Electroplated Germanium Thin Films, N. Chandrasekharan and S. C. Sevov, *J. Electrochem. Soc.* **2010**, *157*, C419.

6. Co-workers on the project:

Dr. Nirmala Chandrasekharan - Nirmala spent two years in the group, from June 1, 2008 to May 31, 2010. She had very extensive experience in synthesis and characterization of nanoparticles and her expertise was very valuable for the initial rapid progress of the project. She worked mainly on the anodic deposition of germanium thin films from solutions of clusters and produced two publications.

Dr. Daniel Rios - Dr. Rios joined the group on January 1, 2009 and left in April, 2011, to join the Lawrence Berkeley National Lab. He acquired very good training in synthesis and handling of air-sensitive main-group organometallic compounds. His work focused on making larger nano-formations of the Ge-clusters and produced one publication.

Dr. Mahesh Karunaratne - Mahesh was in the group for a very short time. He started on October 1, 2010 and left in April of the following year to join the chemistry faculty at the University of Sri Lanka.