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The Novel Synthesis of Silicon and Germanium Nanocrystallites

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ABSTRACT

Interest in the synthesis of semiconductor nanoparticles has been generated by their unusual optical and electronic properties arising from quantum confinement effects. We have synthesized silicon and germanium nanoclusters by reacting Zintl phase precursors with either silicon or germanium tetrachloride in various solvents. Strategies have been investigated to stabilize the surface, including reactions with RLi and MgBrR (R = alkyl). This synthetic method produces group IV nanocrystals with passivated surfaces. These nanoparticle emit over a very large range in the visible region. These particles have been characterized using HRTEM, FTIR, UV-Vis, solid state NMR, and fluorescence. The synthesis and characterization of these nanoclusters will be presented.

INTRODUCTION

There is currently a great deal of interest in exploring the synthesis and characterization of nanocrystalline Si and Ge. Visible emission has been observed from porous Si and Si nanocrystal produced by a variety of techniques including solution [1-6], gas phase decomposition of silanes [7-12], and thermal vaporization of silicon [13]. In all of the cases presented above, there is little size control during the synthesis step of any of the processes other than what can be achieved by changes in the initial reactant concentrations and the length of time over which agglomeration is allowed to take place. This results in a comparatively wide size distribution that can be greatly narrowed through the use of size-selective precipitation.

This group has been interested in exploring the solution chemistry route.[14-19] This work demonstrated that both silicon and germanium nanoclusters with functionalized surfaces can be formed in solution at low temperatures and ambient pressures. This approach to form nanocrystalline silicon or germanium utilizes the high reactivity of metal silicides with either silicon or germanium tetrachloride to form chloride capped group IV nanoclusters. Subsequent reaction of this product with either RLi or RMgCl (R = –methyl, –ethyl, –butyl, and –octyl) terminates the particles with alkyl groups forming R capped nanoclusters. This work provides the groundwork for an exciting new area of research, exploring the surface functionalization of Si and Ge nanoclusters, the next generation nanoparticles.

EXPERIMENTAL

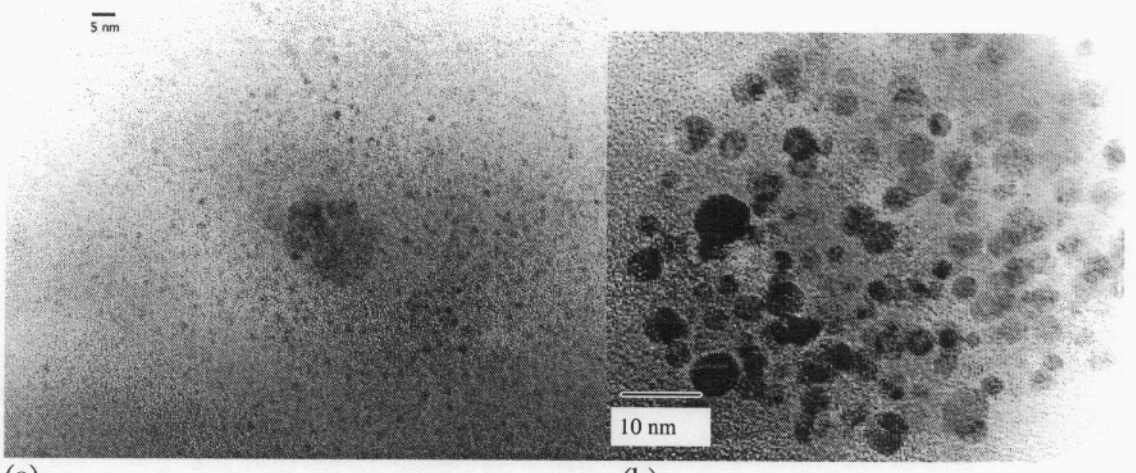
The synthesis of the nanoclusters from the starting reagents, KSi, Mg_2Si and Mg_2Ge has been published previously [14, 17, 19]. The nanoclusters were prepare by reacting the metal silicide or germanide with the respective tetrachloride in excess, in ethylene glycol dimethyl ether (glyme) or dimethylene glycol dimethyl ether (diglyme) solvent under anaerobic conditions. The reaction mixture was heated to reflux overnight and then cooled to room temperature. The solvent and any unreacted tetrachloride was removed *en vacuo*. Freshly distilled and dried glyme solvent was added along with an excess of n-butyllithium reagent. Other terminated alkyl groups were also investigated and were equally passivating, such as methyl, and octyl. The solution was stirred for 24 hours. The solvent was removed, HPLC grade hexane was added, and the solution washed with distilled water. The nanoclusters remain in the hexane phase and the salts are removed with the water phase.

The product has been characterized by HRTEM, electron diffraction, FTIR, UV-Vis, solid state NMR, and fluorescence. HRTEM samples were prepared by evaporation of colloids on lacy carbon-coated electron microscope grids. The electron microscope is a JEOL 200CX or a Topcon 002B HRTEM operating with a 200 KV accelerating voltage at the National Center for Electron Microscopy (NCEM) at Lawrence Berkeley Laboratory. Fourier Transform Infrared (FTIR) spectra for the nanoclusters were obtained at room temperature by pipetting the hexane colloid on a CsI plate and allowing the solvent to evaporate. The spectra were collected on a Mattson Galaxy series FTIR 3000 spectrophotometer. Optical absorption spectra of the hexane colloid in a quartz cell were obtained with a Hewlett-Packard 8452A diode-array spectrophotometer. Photoluminescence (PL) spectra were obtained with a Perkin Elmer LS 50B luminescence spectrophotometer.

DISCUSSION

Although Zintl compounds have been explored as potential precursors in the synthesis of novel compounds [20-23] and ASi (A = Na, K) compounds have been known for some time [24]. there are few examples of their use as synthetic reagents [25]. The ASi and AGe (A = Na, K) compounds consist of covalently bonded T_4^{4-} (T=Si, Ge) anionic clusters separated by 4 A^+ (A=Na, K) cations [24]. The anionic clusters are isostructural and isoelectronic with those of white phosphorous. These clusters are suspended in an appropriate coordinating solvent and are reacted with the (formally) cationic Si^{4+} or Ge^{4+} of $SiCl_4$ or $GeCl_4$ respectively. Mg_2Si crystallizes as an anti-fluorite structure. We have had the most success with polyether solvents, such as ethylene glycol methyl ether (glyme), digylme, and triglyme. In all cases, the reaction mixture is initially heterogeneous. In the higher boiling point solvents the Zintl salt completely dissolves upon addition of the tetrachloride reagent. Figure 1 shows Si nanoclusters prepared from KSi and Mg_2Si. It is clear that the nanoclusters produced from KSi are much smaller and have a narrower size distribution that those prepared from Mg_2Si. KSi is much more reactive than Mg_2Si, producing amorphous silicon along with

the nanocrystalline silicon. The average diameter of the nanoparticles from KSi is 2(1) nm whereas for the product from Mg_2Si it is 3(2) nm, based on several TEM images.



(a) (b)

Figure 1. The micrograph (a) shows Si nanoparticles prepared from KSi + $SiCl_4$ (b) Si nanoparticles prepared from Mg_2Si + $SiCl_4$.

The HRTEM data, along with the selected area electron diffraction and powder x-ray diffraction obtained in these experiments shows diamond-structured particles for both the silicon and germanium nanoclusters. During the past year, we have investigated Mg_2Si as a reagent. Since this phase is less reactive with oxygen, it is easier to handle and it is expected that we would be able to obtain Si nanoclusters. The reaction with $SiCl_4$ apparently produces a surface terminated with -Cl. Although we have yet to prove this point, it is consistent with subsequent chemical reactivity. The reaction with methyllithium or Grignard reagents produces a solid that is hydrophobic. This is consistent with a surface that is terminated with the alkyl group. It has been shown that this type of reaction on Si surfaces provides an alkyl surface that does not oxidize [26].

Figure 2 shows the FTIR of the nanoclusters produced from Mg_2Si. The FTIR

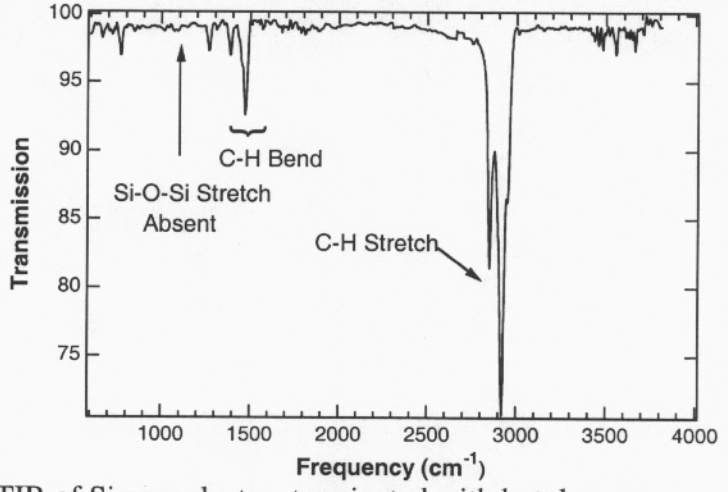


Figure 2. FTIR of Si nanoclusters terminated with butyl groups.

shows C-H stretches and bends consistent with butyl termination of silicon nanoclusters

regardless of the identity of the starting metal silicide. FTIR spectra of the nanoclusters terminated with alkyl groups basically show no evidence for a peak at 1100-1000 cm^{-1}, which could be attributed to Si-O stretching.

The same approach can be used to prepared butyl terminated Ge nanoclusters [18, 19] and a typical TEM is shown in Figure 3.

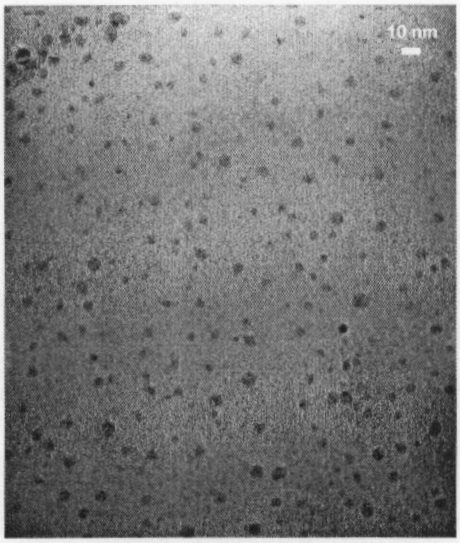


Figure 3. TEM of butyl terminated Ge nanoclusters.

These nanoclusters show photoluminescence consistent with the quantum confinement model. Figure 4 shows the photoluminescence of methyl terminated silicon

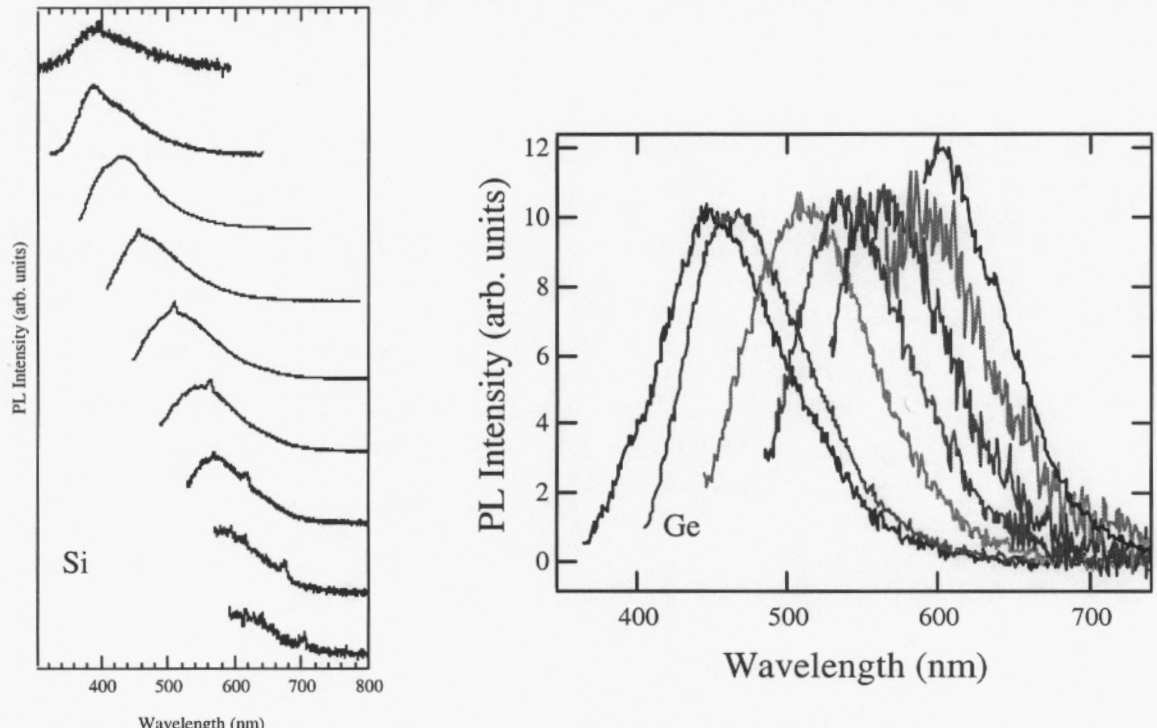


Figure 4. Photoluminescence of Si and Ge nanoclusters with alkyl termination.

nanocluster sample that was prepared from Mg_2Si and photoluminescence of methyl terminated germanium nanoclusters prepared from NaGe. It emits over a broad range in the visible region of the spectrum.

The shift in the spectrum results from the excitation of specific sizes of Si nanocrystals and indicate size-dependent energy levels consistent with a quantum confinement model. This is also observed for the Ge nanoparticles where the spectra have been normalized so that the shifting in the emission spectra is clearly seen.

CONCLUSIONS

Tunable photoemission is demonstrated from samples containing a size distribution of Si or Ge nanoclusters terminated with alkyl groups. There is no evidence for oxidation of the surface of these particles. This group is now concentrating on approaches that will produce monodispersed nanoparticles utilizing solution methods, including inverse-micelles.

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