185a Control of Germanium Nanocrystal Morphology and Surface Functionalization

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We have developed a simple synthesis route for Ge nanocrystals (Ge NCs) via reduction of Ge(II) precursor at 300 □C and 1 atm. The synthesis does not require strong reducing agents and does not produce salts or undesirable byproducts. Literature reports on Ge NC syntheses have focused mainly on direct reduction of Ge(IV) to Ge(0), which requires a combination of high temperature (>400 □C), high pressure (>1 atm), and strong reduction agents. $Ge[N(SiMe_3)_2]_2$ is chosen as the Ge(II) precursor due to the ease of its synthesis in high yield, the absence of potential halide contamination, and the labile amido ligand sets. The synthesis involves the injection of $Ge[N(SiMe_3)_2]_2$ dissolved in oleylamine into non-coordinating solvent 1-octadecene at 300 □C and 1 atm Ar. The resulting Ge NCs form quickly and show a high degree of crystallinity with no oxide formation. These NCs are mostly spherical in shape. The Ge(II) precursor's ligands can be tailored to form $Ge[TMPP]_2$ (TMPP = 2,2,6,6 tetramethyl piperidine) and using identical reaction conditions, cuboid Ge NCs are formed. Another alternative Ge(II) precursor, $Ge[DBP]_2$ (DBP = 2, 6-ditert-butylphenoxide) can be isolated from an amide alcohol metathesis reaction between $Ge[N(SiMe_3)_2]_2$ and 2 equivalents of DBP-H. The use of $Ge[DBP]_2$ under identical reaction conditions as discussed above yields Ge nanowires (Ge NWs) instead of Ge NCs. These results suggest that the Ge(II)-ligand bond strength, the steric orientation of ligands, and the subsequent surfactants formed upon decomposition of the various precursors dictate the size and morphology of Ge NCs by controlling the surface kinetics during crystal growth. We will further discuss optical and electrical characterization of Ge nanocrystals and functionalizing Ge NC surface to incorporate them into a silica matrix.