Germanium Nanocrystals Synthesized in High-Boiling-Point Organic Solvents

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Ge nanoparticles with sizes from 1 to 15 nm were synthesized by thermal decomposition of the germane precursors trichlorogermane, tetraethylgermane, and tetrabutylgermane. Experiments were performed in the organic solvents trioctylamine, squalene, and octacosane, which have boiling points in the temperature range from 380 to 429 °C. The use of high-boiling-point solvents extended the temperature range of the reactions, thus enabling the experiments to be conducted with organogermane precursors which have high decomposition points above 400 °C. Characterization by X-ray diffraction and transmission electron microscopy showed that, depending on the reaction temperature, the final decomposition products consist of amorphous Ge nanoparticles, nanocrystals, or nanowires that grow only in the ⟨110⟩ direction.

Introduction

Intensive studies of quantum confinement effects in semiconductors have stimulated rapid development of synthesis techniques to produce nanoscale materials, among which Si and Ge have specific importance because of their possible integration into Si-based light-emitting devices. Different methods to produce colloidal Ge nanocrystals (NCs) include metathesis reactions using Zintl salt,[1,2] reduction of germanium halides with various reducing agents,[3−7] and thermal decomposition of organogermanes.[8−11] Recent synthetic developments are in the direction of producing NCs in large quantities,[7,10,12] which are needed for comprehensive studies of their structural and optical properties. In this respect, synthesis in temperature−pressure reactors[8−10,13] operating at elevated temperatures seemed to be the most promising approach to obtain macroscopic amounts of Ge NCs. The possibility of reaching high temperatures above 400 °C needed for decomposition of organogermanes and formation of highly crystalline Ge is an advantage of these methods. At the same time, formation of precursor and solvent decomposition byproducts, which remain inside the closed pressure reactors, often produces difficulties in complete separation and purification of the final NC product.[10] Identification of new precursors that readily decompose at lower temperatures[12] enables this problem to be overcome through the use of classical wet-chemistry methods. Additional benefits in the synthesis of colloidal nanoparticles can be introduced by the use of more appropriate solvents with higher boiling points. Among the most widely used coordinating solvents, such as TOPO (tri-*n*-octylphosphine oxide), TOP (tri-*n*-octylphosphine), and TBP (tri-*n*-butylphosphine), TOPO has the highest boiling point, 360 °C, which limits the use of broader varieties of precursors known to produce elemental Ge upon their decomposition at higher temperatures. Here we report the results of experiments done with alternative solvents, tri-*n*-octylamine (TOA, $C_{24}H_{51}N$), squalene ($C_{30}H_{50}$), and octacosane ($C_{28}H_{58}$), which have high boiling points in the range of 380−429 °C. The goal of this work was to study conditions of Ge NC formation by decomposition of a previously unused precursor trichlorogermane (TCG) along with the more traditional germanoalkyls tetraethylgermane (TEG) and tetrabutylgermane (TBG).

Experimental Section

Syntheses were conducted in a standard 100 mL, three-neck, heavy-wall Pyrex flask connected to a vacuum/inert gas (Schlenk) line. In a typical experiment, 15 g of TOA (Aldrich, 98%), squalene (Aldrich, 98%), or octacosane (Aldrich, 99%) was introduced into the flask at room temperature and evacuated to a level below 100 mTorr. To remove any trace of water, evacuation continued at 110 °C for 30 min, and then the flask was heated to the experimental temperature of 380−429 °C under continuous Ar flow. The basic precursors were prepared in an Ar-filled glovebox as mixtures of TCG (Gelest), TEG (Aldrich), or TBG (Aldrich) in a 1:1 weight ratio with squalene vacuum-dried prior to the introduction into the glovebox. The precursors were injected into the flask through a septum lid using a syringe with a long needle immersed into the boiling solvent. The size of the final NCs was controlled by the amount of the precursor injected, which was varied from 0.1 to 1 mL, and by the reaction time, which was changed from a few seconds to 35 min in different experiments. Syntheses were terminated by the removal of heat. After being cooled to room

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temperature, the reaction flasks were open in air and the final solid fraction was separated by centrifugation and washed at least three times with ethanol (for synthesis in TOA), ethyl acetate (syntheses in squalene), or toluene (syntheses in octacosane). The final powders were dispersed in toluene (99.8%), diethyl ether (99.5%), or dimethylformamide (DMF) for further analysis. All solvents were purchased from Aldrich.

Samples for transmission electron microscopy (TEM) were prepared using Cu grids with an amorphous carbon support film dipped into the solvents or dispersions. TEM analysis was done at the University of California, Berkeley, using a Tecnai-12 transmission electron microscope with an accelerating voltage of 100 kV. High-resolution TEM (HRTEM) and elemental analysis were done using a Philips CM300FEG with an accelerating voltage of 300 kV. X-ray diffraction (XRD) was acquired using a CPS 120 INEL curved, position-sensitive detector system utilizing Cu Kα radiation. Raman scattering data were collected on powdered Ge nanoparticle samples on a Jobin Yvon Horriba LabRam spectrograph with a liquid nitrogen cooled CCD detector. The 632.8 nm line from a 35 mW HeNe laser was used as the excitation source with the laser intensity controlled by neutral density filters and typically kept to $\leq$1 mW. Fourier transform infrared (FTIR) spectroscopy was performed using a Nicolet 850 FTIR spectrometer with pellet samples of Ge nanoparticles mixed with KBr. Photoluminescence (PL) spectra were measured using a Fluoromax-2 spectrometer.

Results and Discussion

The boiling points of the solvents used, which are typically listed only for low pressures, were estimated prior to the experiments by measuring the highest temperatures that could be reached in the boiling liquids under Ar flow at ambient pressure. The measured temperatures were 384 °C for TOA, 412 °C for squalene, and 429 °C for octacosane. Additional experiments were done to verify the decomposition temperatures and formation of elemental Ge for each precursor. In these experiments, 1 mL of a precursor was injected at room temperature into an evacuated 250 mL glass flask and heated to the temperature of decomposition, as indicated by formation of a dark solid. The decomposition of precursors with the yield of elemental Ge occurred at temperatures of about 140 °C for TCG, 390 °C for TBG, and 420 °C for TEG. One more germanoalkyl, tetramethylgermane, was also tested in preliminary experiments, but was eliminated from further experiments due to its high decomposition temperature of 450 °C. Among those precursors tested, TCG had the lowest decomposition temperature, showing good agreement with previous data,[14] according to which the decomposition of TCG above 140 °C proceeds with formation of elemental Ge in the following reaction:

$$2HGeCl_3 \rightarrow Ge + GeCl_4 + 2HCl \qquad (1)$$

Taking into account that gaseous HCl and $GeCl_4$ can be easily removed from the reaction at the decomposition temperature, TCG presents special interest as a precursor for solution synthesis of Ge NCs without the formation of any solid byproducts. Test experiments done in the temperature range of 140−300 °C showed that elemental Ge was formed with a yield of about 90% relative to that expected from eq 1. When decomposition of TCG was carried out in the absence of any solvents in an evacuated glass flask, black powder consisting of fully crystalline Ge formed heterogeneously on the walls of the flask. However, first attempts to synthesize Ge NCs by homogeneous nucleation from solution in the temperature range of 300−360 °C were not successful. Reaction in TOPO did not result in any solid product, while decomposition in TOP yielded mainly amorphous, easily oxidized Ge. The use of TOA enabled better control over the synthesis, resulting in the formation of nanoparticles highly resistant to oxidation (Figure 1). In a typical experiment with TOA, 0.2 mL of the precursor mixture was injected into the boiling solvent between 380 and 384 °C. The decomposition of TCG started in 1−2 min after injection, producing Ge particles, which could be collected in the amount of 20−24 mg as a final dry powder. The particles were freely soluble in DMF and diethyl ether, also having partial solubility in toluene and chloroform. When the reaction was terminated a few seconds after TCG decomposition, the final solid powder consisted mainly of amorphous Ge (XRD spectrum 1 in Figure 2A). Increasing the reaction time to 30 min resulted in formation of a crystalline fraction, as indicated by the appearance of sharper peaks of crystalline Ge in XRD pattern 2 of Figure 2A. Electron diffraction analysis (inset in Figure 1A) done with these powders showed diffuse rings with maximum intensities corresponding to *d* spacings of 3.26, 1.97, and 1.80 Å

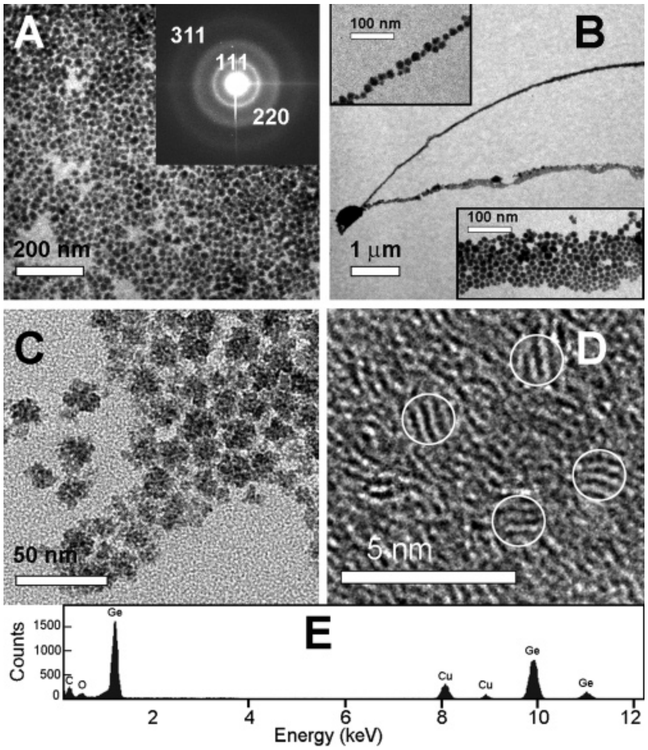

Figure 1. Bright-field TEM images of Ge nanoclusters formed by decomposition of TCG in TOA at 380 °C. (A) Nanoclusters obtained from DMF solution. The maximum intensity of the broad diffraction rings (inset) corresponds to *d* spacings of 3.26, 1.97, and 1.80 Å close to those of diamond cubic Ge. (B) Long chains obtained from ether solution. The insets show arrays of nanoparticles in the chains probably formed due to peculiarities of ether drying on a carbon support film. (C) Higher magnification images of the clusters with nonuniform contrast of smaller nanoparticles. (D) HRTEM image showing an amorphous structure with inclusions of small nanocrystals (some are circled). The average distance between clearly distinguished planes (3.3 Å) is close to that of the (111) *d* spacing of diamond Ge. (E) EDS pattern showing Ge as the main component of the nanoclusters with small traces of residual oxygen. Carbon and copper signals are from the TEM grid.

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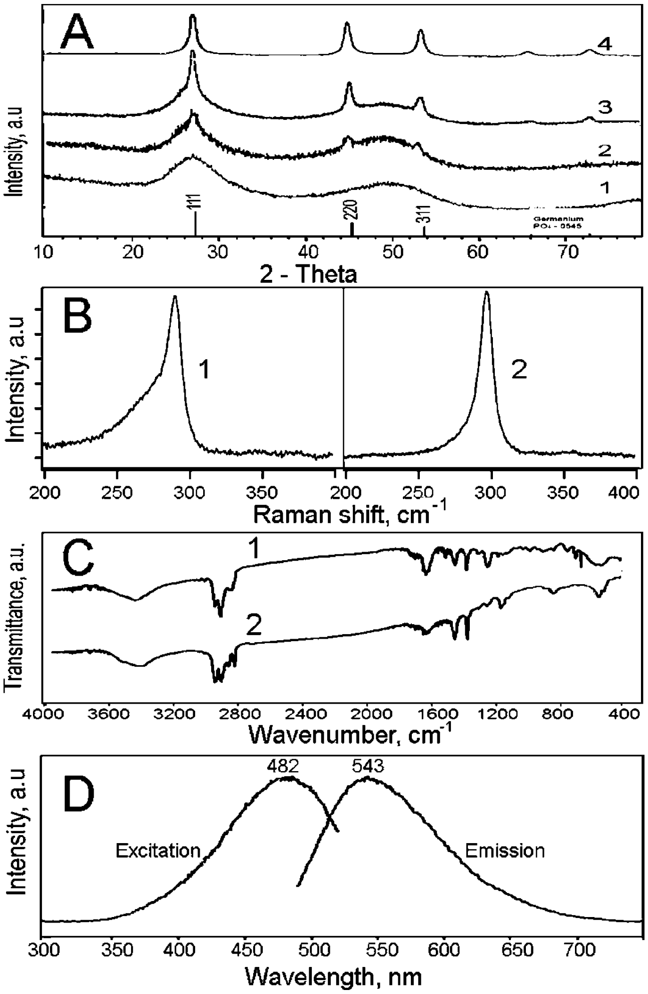

Figure 2. (A) X-ray diffraction patterns of Ge powders obtained by decomposition of TCG: (1) amorphous with a partial crystallographic order at 380 °C, 1 min after TCG decomposition; (2) amorphous with a fraction of Ge NCs at 380 °C, 30 min after TCG decomposition; (3) amorphous with a fraction of Ge NCs at 395 °C; (4) crystalline diamond cubic Ge at 410 °C. The Scherrer diameter of 6.9 nm calculated from the full width at half-maximum of the (111) reflection is consistent with TEM measurements of 6.6 nm (Figure 3B). (B) Raman spectra of Ge nanoclusters: (1) amorphous with a fraction of Ge NCs; (2) 6.6 nm Ge NCs. (C) FTIR patterns of Ge nanoparticles produced by decomposition of TCG in TOA (1) and squalene (2). (D) Photoluminescence excitation and emission spectra obtained from DMF solution of a sample shown in Figure 3A.

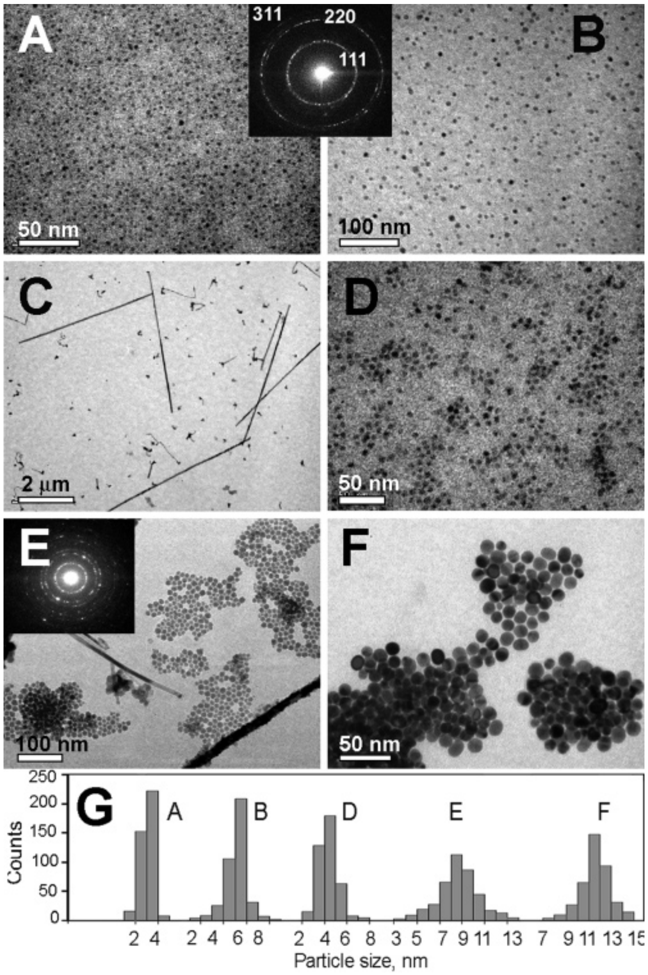

Figure 3. TEM images of Ge NCs obtained by variation of precursors, solvents, and reaction times: (A) 0.1 mL of TCG precursor in squalene at 410 °C, 1 min; (B) 0.5 mL of TCG precursor in squalene at 410 °C, 20 min; (C) 0.5 mL of TEG precursor in squalene at 410 °C, 35 min; (D) 1 mL of TEG precursor in octacosane at 425 °C, 10 min; (E, F) 0.6 mL of TBG in squalene at 410 °C, 35 min; (F) 0.05 weight fraction of dichlorobenzene added to the TBG−squalene precursor mixture. (G) Corresponding histograms of Ge NC sizes each based on measurements of 400 particles from different regions of the TEM grids.

close to those of diamond cubic Ge, thus indicating the presence of amorphous Ge with partial crystallographic order. HRTEM analysis (Figure 1D) confirmed that the XRD peaks were determined by the presence of small NCs with sizes of 1−2 nm formed in the initial amorphous matrix. The amount of the final product could be increased up to about 100−110 mg by injection of the larger amount of the initial precursor from 0.2 to 1 mL. However, this increase did not noticeably affect the size of the crystalline islands without increasing the reaction temperature limited by the boiling point of TOA. EDS (energy dispersive spectroscopy) performed with multiple grids showed Ge as the main component of the nanoparticles, which contained only small traces of residual oxygen (Figure 1E) not detected by XRD or Raman analysis in the macroscopic samples. Figure 2B shows a Raman spectrum (1) consisting of a sharp peak with a broad component, located below 300 cm^{-1}. Both Raman scattering features are consistent with the small size of the Ge NCs[15] and with a large fraction of amorphous Ge. The FTIR spectrum of the same sample (Figure 2C, pattern 1) reveals peaks at 2960, 2924, and 2873 cm^{-1}, which are characteristic of C−H stretching modes for CH_2 and CH_3 groups, and at 1462 and 1384 cm^{-1}, which correspond to CH_3 bending vibrations. The peak at 1625 cm^{-1} is characteristic for C=C stretching vibrations. Since double bonds are absent in the structure of TOA, this peak is an indication that squalene, which was introduced into the initial precursor mixture to decrease the decomposition rate of TCG, also participates in the formation of hydrocarbon layers that determine the solubility of the clusters and their resistance to oxidation.

A substantially higher fraction of crystalline Ge was obtained when TOA was replaced by squalene used as a solvent. In some syntheses conducted below 400 °C, XRD analysis still showed an amorphous fraction that essentially disappeared at the boiling temperature of squalene (Figure 2A, patterns 3 and 4). Figure 3A,B shows TEM images of

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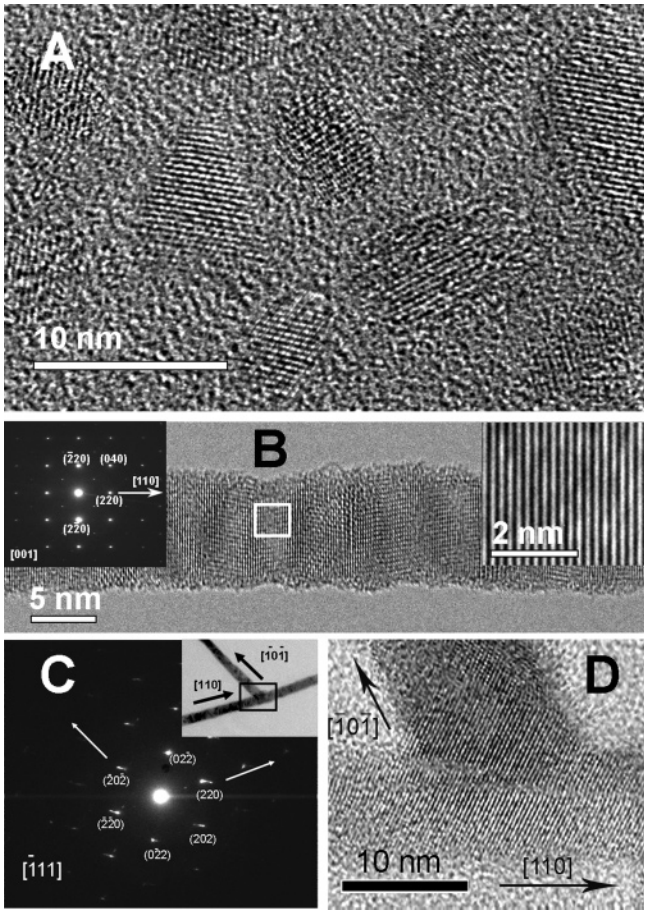

Figure 4. HRTEM images of Ge nanocrystals and nanowires formed in squalane at 410 °C: (A) Ge NCs obtained by decomposition of TCG; (B) a single Ge nanowire obtained by decomposition of TEG. The right inset shows a magnified area squared on the image. The diffraction patterns in (B) and (C) show only ⟨110⟩ directions of growth for both straight and branched rods. (D) HRTEM image of a single-crystal branched nanowire corresponding to the squared area of the inset of (C).

Ge NCs obtained by decomposition of TCG in squalene at 410 °C. HRTEM analysis (Figure 4A) confirmed the highly crystalline diamond cubic structure of the nanoparticles. Very small NCs, with diameters of 2−3 nm, were formed in some syntheses that were continued only for a few seconds after decomposition of TCG injected into 0.1 mL of the precursor mixture. Larger NCs were obtained by increasing the amount of injected precursor to 0.5 mL and the reaction time to 20 min. The average size of the NCs calculated from TEM images (histogram B in Figure 3G) is consistent with the results of XRD (pattern 4 in Figure 2) and Raman analysis (spectrum 2 in Figure 2B). Both XRD and Raman scattering did not show any oxidation of Ge NCs. Room-temperature photoluminescence was typically observed in samples containing particles smaller than 4 nm (Figure 2D). However, our preliminary results did not reveal consistency in the size dependence of the peak energy that could vary in a range up to 50 nm for particles of about the same size and size distribution. This phenomenon, which is a subject of separate, more detailed studies, indicates that the observed photoluminescence not only relates to the quantum confinement effects, but can be largely influenced by the composition of the NC surface layers. As in the case of TOA-synthesized particles, the FTIR spectrum obtained from the NCs synthesized in squalene (Figure 2C, spectrum 2) shows the presence of organic species. The similarity of the spectrum below 1000 cm^{-1} to that of squalene[16] suggests the presence of squalene as a stabilizing ligand. Comparison of the two spectra of Figure 2C shows that, although squalene takes part in formation of organic species in both cases, the resulting composition of the surface layer is different depending on the synthesis procedure.

The complication in the syntheses conducted using squalene as a solvent was connected with the strong tendency of Ge to crystallize heterogeneously on the walls of the glass flasks. Ge NCs similar to those shown in the image of Figure 3A,B could be collected by separation of the soluble part of the final product from the larger particles of insoluble polycrystalline Ge that could be as large as 50% of the total mass of the final product. This phenomenon most likely relates to the high rate of precursor decomposition exceeding the rate of Ge attachment to the surface of the crystallizing particles. The fact that it does not occur in the synthesis with TOA shows that the decomposition rate of TCG not only is a function of temperature, but also depends on the chemical environment. The addition of a small amount of TOA to the initial TCG−squalene mixture, in combination with the injection through a long needle immersed into the solvent, could decrease the fraction of the heterogeneously formed Ge. However, more experimental studies are needed to eliminate the problem completely.

The high boiling temperature of squalene enabled experiments with other Ge precursors, such as TEG and TBG, which have higher decomposition temperatures than TCG. Since the decomposition temperature of TEG (420 °C) is above the boiling point of squalene, the total yield of Ge with this precursor was relatively low, about 20% of that expected from the full decomposition, with the final product consisting largely of nanowires (NWs). Similarly to reported studies,[13,17,18] formation of the NWs occurred without any added metal catalysts, but as described previously could proceed according to a vapor−liquid−solid (VLS) mechanism on the drops of the boiling solvent condensed on the walls of the flask.[17] The uniqueness of these NWs is that they form in the absence of any crystalline substrate which may influence the direction of their growth as occurs with the traditional VLS mechanism. Electron diffraction analysis performed with 26 single NWs in the present work confirmed an earlier observation that all straight NWs formed in solution syntheses grew only along the ⟨110⟩ direction (Figure 4B). Additional analysis of kinked and branched NWs (Figure 4C,D) showed that the set of ⟨110⟩ orientations was actually the only direction of growth for all Ge NWs formed spontaneously in the absence of crystalline substrates or metal catalysts. Formation of nanostructured Ge of different shapes most likely relates to the difference in the decomposition rates of TCG and TEG at the temperatures of the syntheses. It has been well-known that formation of wirelike crystals by VLS growth proceeds at temperatures much lower than those needed for the nucleation and formation of regular

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isometric crystals.[19] The phenomenon is explained by the catalytic effect of the liquid drop surface on the kinetics of the precursor decomposition. The high decomposition temperature of TEG (420 °C) inhibits decomposition and the supply of Ge atoms needed for homogeneous formation of regular crystals at the boiling temperature of squalene (410 °C). At the same time, increased kinetics of TEG decomposition on the surface of liquid drops allows faster nucleation and growth of NWs according to the VLS mechanism. In the case of TCG, the much lower decomposition temperature leads to almost instant decomposition of the precursor. NWs do not form because the high rate of supply of the Ge atoms benefits homogeneous nucleation and regular crystal growth.

A few experiments done with TEG at higher temperatures using octacosane as a solvent showed that decomposition of this precursor can also result in homogeneous nucleation and formation of isometric Ge NCs at temperatures higher than 420 °C (Figure 3D). the size distribution in this case could be controlled by the duration of the reaction, from a few seconds to 10 min. The final yield however was also low (5−10%), probably due to the still slow decomposition rate of TEG at the temperature of the reaction.[20] In addition, syntheses in octacosane were complicated because of the difficulties in final NC purification. Octacosane, which is solid at room temperature, is not soluble in ethanol or ethyl acetate, which were used for separation of NCs in syntheses with TOA or squalene. The only solvents found to dissolve octacosane were toluene and chloroform, which also partially dissolved small NCs, a fraction of which could be lost during the purification procedure due to this mutual solubility.

As mentioned above, TBG has a decomposition temperature of 390 °C, suggesting its potential use as a Ge precursor for decomposition in squalene. Figure 3E presents TEM images of Ge NCs obtained in the TBG decomposition experiments when the TBG precursor was injected into squalene at 410 °C. Sudden decomposition of TBG started only 30 min after the injection, producing isometric NCs with some fraction of NWs. Homogeneous formation of NCs in the syntheses with TBG was also accompanied by crystallization of bigger Ge particles on the glass walls. As shown by the image and electron diffraction pattern of Figure 3E, final separated and purified samples still had inclusions of NWs and bigger NCs. Addition of a small amount of dichlorobenzene to the initial mixture of TBG and squalene led to the formation of NCs with a slightly narrower size distribution for the same duration of time (Figure 3F). This result indicates the possibility to better tune the size and structure of Ge NCs by variations of the surfactants and precursor mixtures, which may be achieved in further studies.

In conclusion, Ge NCs were synthesized by decomposition of trichlorogermane, tetraethylgermane, and tetrabutylgermane. The temperature range of Ge NC colloidal synthesis was extended up to 429 °C by use of the high-boiling-point solvents trioctylamine, squalene, and octacosane. Trichlorogermane was introduced as a new precursor, decomposing at relatively low temperatures above 140 °C, with a high yield of elemental Ge in the absence of any solid byproducts. The results of the experiments showed that homogeneous formation of Ge nanoparticles depends on the temperature of TCG decomposition. Purely amorphous structures were obtained below 360 °C. Uniform nanoparticles, with inclusions of small Ge NCs having sizes of 1−2 nm, formed at 380 °C in boiling trioctylamine. Highly crystalline Ge NCs with sizes from 2 to 7 nm were synthesized in squalene at increasing temperatures. The high-boiling-point solvents studied here enabled the use of Ge precursors previously uninvestigated in colloidal synthesis because of high decomposition temperatures above 390 °C. Uniform Ge NCs with sizes from 4 to 15 nm were obtained by decomposition of tetrabutylgermane in squalene. Formation of isometric NCs by decomposition of tetraethylgermane requires higher temperatures, up to 429 °C, reached in boiling octacosane. At temperatures below 429 °C, decomposition of tetraethylgermane proceeds with formation of nanowires that were found to grow only in the ⟨110⟩ crystallographic direction.

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