A Straightforward, New Method for the Synthesis of Nanocrystalline GaAs and GaP

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A new, low-temperature method has been established for solution-phase synthesis of nanocrystalline III–V semiconductors, namely, gallium arsenide and gallium phosphide. This new approach consists of in situ synthesis of the pnictides, $(Na/K)_3E$ (E = P, As), in toluene and their subsequent metathetical reactions with gallium halide solutions in coordinating solvents such as monoglyme and diglyme. The effect of solvent on the particle size is clearly evident. The reactions in which gallium halides were dissolved in toluene, a noncoordinating solvent, and 1,4–dioxane, a coordinating solvent, produced larger crystallites while the use of gallium halide solutions in monoglyme and diglyme solvents, known to cause dissociation of gallium halides and form chelate complexes, led to reduction in particle size by a factor of 2 or more. The nature of the gallium halide employed also influenced the particle size of the resultant materials. The III–V semiconductor quantum particles have been characterized by XRD, TEM, XPS, UV–vis, and elemental analysis. The blue-shifted UV–vis absorption spectra are clear evidence of quantum confinement in these nanoparticles.

Introduction

Semiconductor nanocrystals have been intensely investigated in recent years due to their novel properties which are markedly different from those of the bulk solids.[1] For example, reduced melting temperatures of nanocrystals lead to the possibility of a new low-temperature route to thin-film formation.[1e,2] Previous work in our laboratories demonstrated the utility of silyl cleavage by reacting group III halides with $E(SiMe_3)_3$ (E = P, As) in hydrocarbon solvents to yield nanocrystalline III–V semiconductors or their precursors.[3] Recently, synthesis of GaAs nanocrystals in decane was reported,[4] and two other research groups have utilized the silyl cleavage to synthesize GaAs nanocrystals in quinoline.[5] In addition, Uchida et al. reported the synthesis of GaAs and InAs nanocrystals from $Ga(acac)_3$ and $In(acac)_3$, respectively, by reactions with $As(SiMe_3)_3$; however, formation of other byproducts or the fate of the acetylacetonate ligands was not reported.[6] Recently Kaner and co-workers[7] reported a general method involving solid state metathesis (SSM) to synthesize binary III–V semiconductors by reacting sodium pnictides with group III halides in either bombs or sealed glass ampules at high temperatures. These exothermic reactions generate enough heat to melt the sodium halide product and therefore, SSM reactions yield polycrystalline III–V semiconductors often contaminated with starting materials and byproducts. It has also been reported that the III–V materials produced by this method contain considerable amounts of nonremovable halide inclusions and the rapid exothermic SSM reactions introduce high defect concentration and lattice strain in resulting materials.[7d] However, an important aspect of Kaner's work involved controlling the particle size by adding inert materials, as heat sinks, to the SSM reaction mixtures. For example, the particle size of MoS_2 synthesized from SSM reaction between $MoCl_5$ and Na_2S was altered by the amount of NaCl added to the reactants. The larger the amount of NaCl, the smaller the particle size of MoS_2 obtained.[7e]

The SSM route involves rather severe reaction conditions and high temperatures; thus we investigated a fundamentally similar reaction to that described by Kaner but carrying out the reactions in organic solvents. Our reasoning was 3-fold: (1) solvents would be better heat sinks than inert solids; (2) solid state reactions are diffusion controlled, whereas the solution phase reactions can be stirred for proper mixing resulting in a better control; (3) the heat evolved in the exothermic reactions can be easily dissipated to the liquid reaction

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medium which would reflux rather than causing a meltdown of the reaction flux. Our results indicated that although use of solvents afforded reduced particle sizes, the more important criterion is the nature of the solvents employed. Thus, reactions carried out in coordinating and noncoordinating solvents yielded III–V materials with considerably smaller particles, but further reduction in the particle size was achieved by using glyme solvents known both to act as multidentate ligands and to cause dissociation of the gallium halide thereby forming ionic coordination complexes. Herein, we report the first detailed account[8] of the solution-phase synthesis of nanocrystalline GaAs and GaP which does not utilize substituted or unsubstituted arsines or phosphines (eqs 1 and 2).

$$3(\text{Na/K}) + \text{E} \xrightarrow[\text{toluene}]{\text{reflux}} (\text{Na/K})_3 \qquad (1)$$
$$\text{E} = \text{P, As}$$

$$\underset{\text{in toluene}}{(\text{Na/K})_3\text{E}} + \underset{\text{in glyme}}{\text{GaX}_3} \xrightarrow{\text{reflux}} \text{GaE} + 3(\text{Na/K})\text{X} \qquad (2)$$
$$\text{E} = \text{As, X} = \text{Cl, I; E} = \text{P, X} = \text{Cl}$$

Experimental Section

General Techniques. All the manipulations were performed in an argon-filled Vacuum Atmospheres Dri-Lab HE-493 or using standard high vacuum/Schlenk line techniques.[9] Solvents were dried over and distilled from sodium benzophenyl ketyl prior to use. Anhydrous $GaCl_3$ (99.999%) and Na-K alloy (44 wt % Na, 56 wt % K) were purchased from Strem Chemicals and used as received. Ultra dry GaI_3 (99.999%) was purchased from Johnson Matthey (Aesar) and used without further purification. White phosphorus was purchased as the yellow allotrope and purified by vacuum sublimation. Oxygen depleted arsenic powder (99.9995%) was purchased from Atomergic Chemetals and used as received. XRD data were collected on a Phillips XRG 3000 diffractometer using Cu Kα radiation. The diffractometer was equipped with a single crystal graphite monochromator. XPS analyses were performed at the XPS facility of the University of North Carolina at Chapel Hill with data collected on a Perkin-Elmer PHI 5400 system using Mg Kα radiation. High-resolution transmission electron micrographs (HRTEM) were recorded on a Topcon 002B microscope using 200 kV accelerating voltage at the Analytical Instrumentation Facility of North Carolina State University. UV–vis absorption spectra were measured on a Hewlett-Packard 8452A diode array spectrophotometer. For UV–vis studies, methanol dispersions of the semiconductor quantum particles were employed. Solvent was used as blank and the methanol spectrum was subtracted from the sample spectra. The instrumental cutoff was 190 nm and the spectra were recorded between 210 and 820 nm. Elemental analyses were performed by E+R Microanalytical Laboratory, Corona, NY.

Synthesis of GaAs Nanocrystals. In the drybox, 1.05 g of $GaCl_3$ (5.98 mmol, 5% excess) was dissolved in 90 mL of diglyme by stirring in a flask equipped with a magnetic stir bar. Immediately a dark, opaque solution resulted. This solution was quantitatively transferred to the 100 mL addition bulb of a two-bulb 300 mL flask equipped with a stir bar, Teflon valves, a greaseless Rodaviss ground-glass joint and a sidearm with a ground glass joint. After the $GaCl_3$ solution was transformed, the Teflon valve to the addition bulb was closed and 0.58 g of arsenic powder (7.74 mmol, 36% excess) was added to the 300 mL reaction flask followed by 80 mL of toluene and 0.55 g of Na–K alloy (17.04 mmol). [**Caution:** Sodium–potassium alloy is pyrophoric and should be handled with great care. The use of sodium metal should yield similar results, however, due to Na–K being a liquid and the ease of manipulating it in the drybox, it was chosen.] A condenser equipped with RODAVISS joints was connected to the flask and an adapter was connected to the condenser. The whole apparatus was then transferred to the Schlenk line and was heated to reflux in an oil bath while being stirred under dry argon atmosphere. When the temperature was about 100 °C, a greenish coloration was noticed in the reaction mixture with simultaneous appearance of a black solid. Within 2 h, the greenish tint disappeared and only the black solid [$(\text{Na/K})_3\text{As}$] remained in the reaction flask. The reflux was continued for 2 days; the reaction flask was slowly cooled to room temperature and then jacketed with an ice-water bath for 30 min with stirring. $GaCl_3$ solution in diglyme was added to the $(\text{Na/K})_3\text{As}$ in toluene. The reaction was stirred at 0 °C for 30 min and then slowly warmed to room temperature. The reaction mixture was again heated to reflux (boiling point of toluene 111 °C) in an oil bath with stirring for 2 days. After refluxing for 2 days, the flask was allowed to cool to room temperature and approximately 100–130 mL of deionized water (ethanol or methanol can also be used; however, due to low solubilities of alkali metal halides in these solvents, water was chosen) was added under inert atmosphere to dissolve the alkali halide byproducts and to destroy trace amounts of the remaining arsenide, if any. [**Caution:** If sufficient time is not allowed for the completion of the reaction, unreacted arsenide may react with added alcohol or water, leading to generation of toxic arsine.] The resulting suspension was stirred for 15 min under inert atmosphere followed by opening the flask to air and stirring for additional 15 min. The dark gray-brown suspension was then vaccum filtered in air, and the solid collected on the filter paper was washed with copious amounts of deionized water followed by washing with acetone. The resulting solid was air-dried overnight and then heated to 350 °C in a sublimer under dynamic vacuum for 2–3 h to remove excess arsenic. The elemental analysis of a typical GaAs sample showed a slight excess of gallium (Ga:As ratio 5.1:4.0); however, halogen-containing impurities were typically less than 0.01%. The elemental analysis also showed presence of small amounts of carbon (2–5%) and hydrogen (less than 0.5%). The XRD pattern indicated that the sample consisted of small crystallites of GaAs, and the average particle size was calculated to be approximately 10 nm using the Scherrer equation.[10] A similar procedure was used when $GaCl_3$ was substituted with GaI_3. However, the XRD pattern indicated that the particle size was reduced to approximately 6 nm. For studying the effect of toluene, 1,4-dioxane, and monoglyme on the GaAs particle size, $GaCl_3$ was dissolved in the respective solvent and a similar procedure was followed.

To confirm the formation of nanocrystalline GaAs simply by refluxing the reaction mixture containing $GaCl_3$ in diglyme and $(\text{Na/K})_3\text{As}$ in toluene, the reaction mixture was quenched and washed with methanol instead of water. Stoichimetric amount of arsenic powder was used for synthesis of this sample. This as-prepared sample was not heated to 350 °C. The elemental analysis of this sample indicated Ga:As present in 3:4 ratio. Impurities such as Cl (0.26%), H (1.24%) and C (7.36%) were also present.

Synthesis of GaP Nanocrystals. For the synthesis of GaP nanocrystals, similar procedures were used for the reaction and workup as those described for the GaAs syntheses except white phosphorus was substituted for arsenic powder. [**Caution:** White phosphorus is toxic and flammable. It should be handled accordingly.] Synthesis of $(\text{Na/K})_3\text{P}$ was adapted

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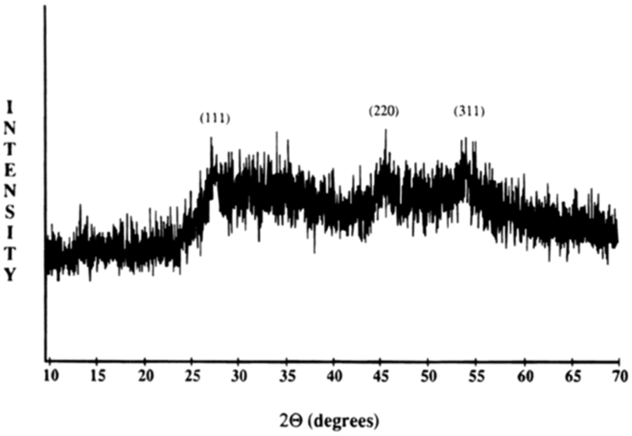

Figure 1. XRD pattern of as-prepared GaAs nanocrystals synthesized by refluxing a mixture of $GaCl_3$ in diglyme and $(Na/K)_3As$ in toluene. The *y* axis shows relative intensity.

from the reported synthesis of Na_3P.[11] At least 30% excess white phosphorus was found to be essential for the synthesis of $(Na/K)_3P$ to go to completion. The excess phosphorus was removed by vacuum sublimation at 350 °C for 3 h. The elemental analysis of a typical GaP sample indicated the Ga:P ratio to be 1.1:1.0, and it contained a negligible amount (less than 0.01%) of halogen impurities. The average particle size obtained from the XRD pattern was found to be approximately 11 nm.

Results and Discussion

Synthesis of $(Na/K)_3P$ and $(Na/K)_3As$ was adapted from a similar procedure described by Peterson et al. for the synthesis of Na_3P in benzene.[11] It was essential to prepare the pnictides in an aromatic solvent and toluene was chosen due to its higher boiling point. As discussed elsewhere,[12] a minimum 30% excess of white phosphorus seemed to be critical for synthesizing $(Na/K)_3P$; otherwise, undesirable results were obtained. At present, it is not known if a similar excess of arsenic powder was essential, however, excess arsenic was used to ensure completion of the $(Na/K)_3As$ synthesis. Since white phosphorus and arsenic easily sublime, the excess used can be easily removed from the final products. It was observed that nanocrystalline GaAs was formed in these reactions simply by reflux. The as-prepared GaAs nanocrystals were characterized by XRD, TEM, and elemental analysis. The small amount of chlorine observed may be due to residual alkali halide left after washing with methanol, and the carbon and hydrogen may be originating from the solvents used in synthesis and workup procedure. The XRD pattern of the as-prepared GaAs at reflux is shown in Figure 1. It clearly shows the (111), (220), and (311) reflections of GaAs. Meaningful particle size calculations of the as-prepared materials were not possible from the XRD data due to a high level of noise. The broadness of the XRD pattern is likely to be due to extremely small nanocrystals (less than 3 nm) or presence of amorphous material. The high-resolution transmission electron micrographs of the as-prepared materials are shown in Figure 2. Several extremely small crystallites are seen in Figure 2A whose sizes can be estimated by counting the lattice fringes evident in the micrograph. The *d* spacing for (111) planes in GaAs is 3.26 Å;[13a] thus, a crystallite showing five planes in the TEM image can be estimated to be approximately 16 Å wide. Some crystallite appear to be as small as 1 nm. The arrow in Figure 2A points to a nanocrystal exhibiting as few as three lattice fringes from GaAs (111) planes, this crystallite is approximately 1 nm wide. Although this is a crude way of measuring the size as there are no visible sharp boundaries, it should enable one to visualize the infinitely small size of such crystallites. Wang and Herron have reported synthesis of monodisperse 10 Å CdS particles.[14a] However, it is extremely difficult to observe and photograph the lattice fringe patterns of such small particles, and they are rarely seen. Duff et al. have recently reported observation of lattice fringes of gold clusters as small as 15 Å .[14b] Figures 2B–D clearly show lattice fringe patterns of (111) planes from larger GaAs nanocrystals ranging from 3 to 12 nm. Extremely small crystallites are also present in these micrographs. Figure 2D shows a GaAs nanocrystal less than 3 nm wide and numerous smaller crystallites similar to those shown in Figure 2A. These particles are too small to produce any measurable diffraction pattern, and hence, electron diffraction experiments were unsuccessful. Such crystallites, along with the amorphous material, would also increase the

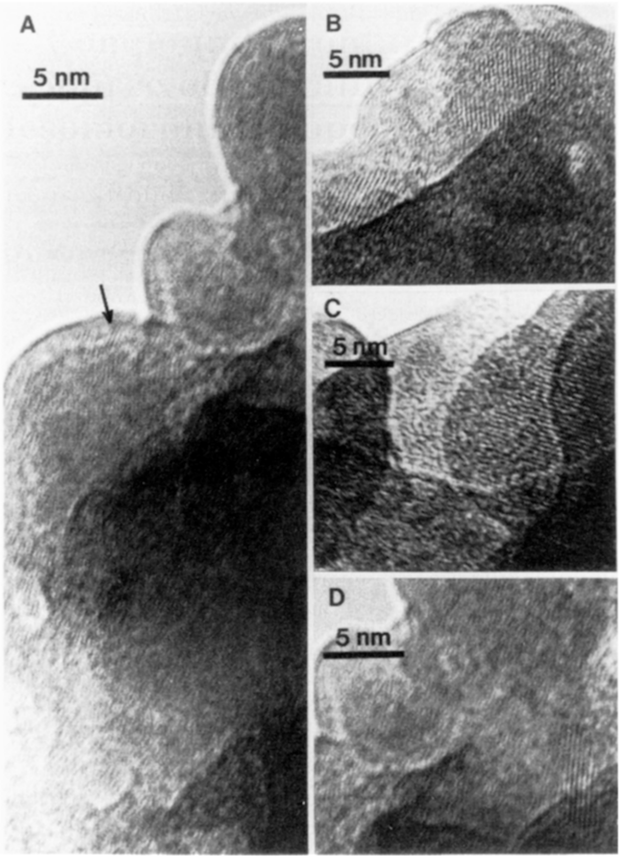

Figure 2. Transmission electron micrographs of the as-synthesized GaAs quantum particles. The marker in the top left corner in each figure represents the scale. (A) Lattice planes of several extremely small nanocrystallites are seen. The arrow points to a 1 nm crystallite. (B)–(D) Various crystallites with sizes ranging from less than 3 nm to as large as 12 nm.

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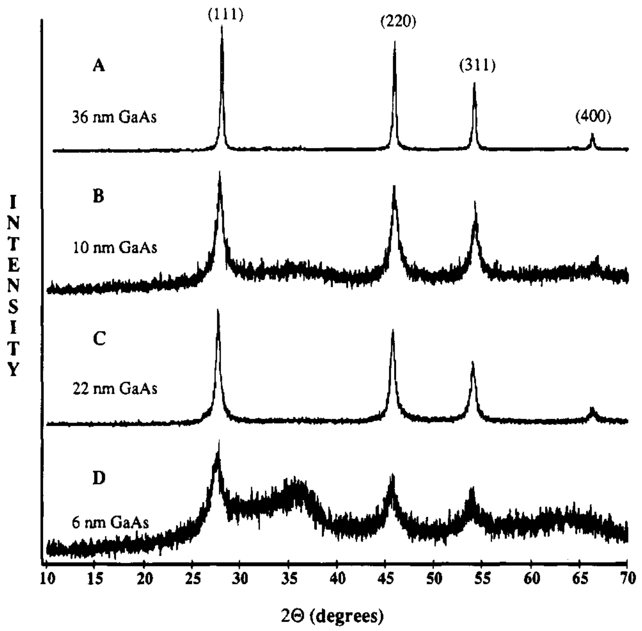

Figure 3. Effect of solvent, concentration, and the nature of gallium halide on the GaAs particle size as calculated from the XRD patterns. The *y* axis indicates relative intensity. In all the reactions $GaCl_3$ solutions were added to $(Na/K)_3As$ in toluene. (A) 36 nm GaAs formed on adding $GaCl_3$ solution in toluene and refluxing. (B) 10 nm GaAs resulted on adding $GaCl_3$ dissolved in diglyme and refluxing. (C) 22 nm crystallites formed on doubling the amount of reactants as in Figure B while using the same amounts of solvents. (D) 6 nm GaAs obtained on using GaI_3 solution in diglyme and refluxing.

noise level and produce broad diffraction patterns as seen in Figure 1. The as-prepared materials contained the initially used excess arsenic powder. This necessitated the sublimation procedure to remove arsenic. It was observed that these nanocrystals underwent annealing process during the sublimation and the XRD patterns (Figure 3B) showed stronger reflections possibly due to grain growth and crystallization. However, the XRD patterns still showed line broadening due to small particles. The approximate average particle sizes calculated from the XRD patterns of GaAs after sumblimation were still within the limits of the sizes required for quantum confinement effects. The subsequent discussion deals with materials from which excess arsenic or phosphorus was sublimed away unless mentioned otherwise. The literature survey indicated wide use of XRD line broadening as a measure of average particle size, hence, the synthesized nanocrystallites were primarily characterized by XRD for identification of the crystalline phase and determination of approximate average particle size from the line broadening caused by small crystallites. The XRD patterns of the samples matched well with the literature data for GaAs and GaP.[13a,b] Due to the symmetry of the (220) reflection, it was used for calculating the particle sizes for GaAs and GaP. However, for some of the samples, there seemed to be a broad hump in the XRD patterns near the 36° 2θ angle. The origin of this feature is not clear but is likely to be due to presence of very small crystallites or amorphous materials as well as surface oxidation which was evident in our XPS studies described later. The observed location of this broad hump agreed well with the *d*-spacing expected for the most intense (400) reflection of Ga_2O_3.[13c] The elemental analysis of GaAs powders indicated that there was a slight excess of gallium in the samples giving the Ga:As ratio of 5.1:4.0. Fitzmaurice and co-workers[4] and Alivisatos and co-workers[5a] have observed a similar excess of gallium (Ga:As ratio 5:4) in nanocrystalline GaAs prepared from $GaCl_3$ and $As(SiMe_3)_3$. Sandroff et al. reported surface oxidation of nanocrystalline GaAs exposed to air resulted in 1−1.5 nm layers of Ga_2O_3 and As_2O_3.[15] The depth of these oxide layers may be quite significant with decreasing particle size of gallium arsenide. As_2O_3 is known to sublime at 193 °C[16] and would do so during the vacuum sublimation carried out at 350 °C to remove excess arsenic. This would effectively increase the amount of gallium in the specimen relative to arsenic. Stickle et al. observed similar depletion of arsenic from the air-oxidized GaAs surfaces due to evaporation of As_2O_3 at ordinary temperatures.[17]

The effect of diglyme on the particle size is evident from Figure 3. When $GaCl_3$ was dissolved in toluene and allowed to react with $(Na/K)_3As$ in toluene, GaAs was formed with an average particle size of 36 nm (Figure 3A). However, on dissolving $GaCl_3$ in diglyme and carrying out the reaction under similar conditions, approximately 10 nm crystallites of GaAs were obtained (Figure 3B). The effect of concentration on the particle size is shown in Figure 3C. On When doubling the amounts of reactants for the same amounts of solvents were doubled, a larger average particle size of 22 nm resulted. This effect (Figure 3B vs Figure 3C) is probably similar to that observed by Kaner on addition of incremental amounts of NaCl, namely, reduced particle size of MoS_2. The larger amount of solvent should effectively cause better heat dissipation from the reacting species. The reaction temperature seemed to alter the particle size of the resultant semiconductor powders. The nature of the halide used also seemed to play an important role in determining the particle size. As shown in Figure 3D, when GaI_3 dissolved in diglyme was used as the gallium source, 6 nm GaAs particles resulted. On comparison of parts A−D of Figure 3, the higher relative intensity of the broad hump in the XRD pattern of GaAs with a smaller average particle size is noticeable. Due to the larger surface area, the smaller crystallites may be prone to considerable surface oxidation. When monoglyme was substituted for diglyme in the GaAs synthesis, the XRD pattern of the resultant material indicated average particle size of approximately 17 nm, still within the limits of predicted quantum confinement (19 nm).[18] Approximately 36 nm GaAs crystallites were produced on dissolving $GaCl_3$ in dioxane and then carrying out the reaction. The effect of solvent on the resultant particle size (Figure 4) was also observed during GaP synthesis. Figure 4A shows the XRD pattern of approximately 21 nm GaP particles produced when $GaCl_3$ solution in toluene was used, but the particle size of GaP dropped to 11 nm on using $GaCl_3$ solution in diglyme (Figure 4B). The average particle size produced in diglyme is comparable to the Bohr radius of exciton reported to be 55 Å (hence, 11 nm diameter) in GaP.[18] GaI_3 was not used for synthe-

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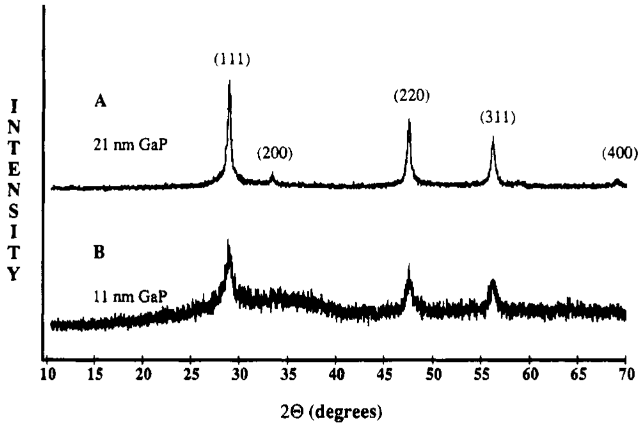

Figure 4. Effect of solvent on the particle size of GaP as calculated from the XRD patterns. The *y* axis represents relative intensity. In all the experiments, $GaCl_3$ solution was added to $(Na/K)_3P$ in toluene. (A) 21 nm GaP formed on adding $GaCl_3$ solution in toluene followed by refluxing. (B) 11 nm GaP resulted when $GaCl_3$ solution in diglyme was added followed by refluxing the reaction mixture.

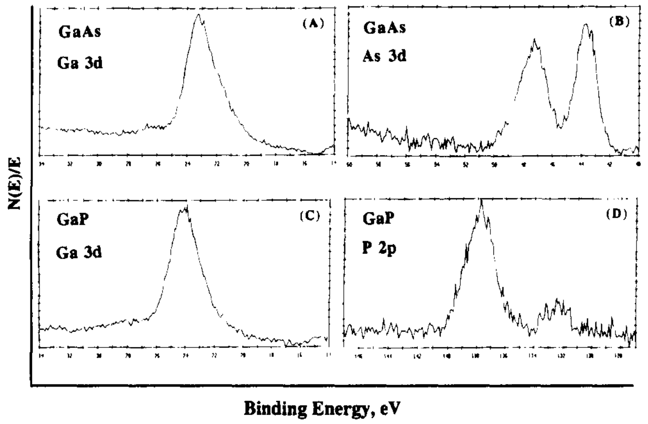

Figure 5. X-ray photoelectron spectra of nanocrystalline GaAs and GaP. The spectra show surface oxidation as both samples had been exposed to atmosphere for several months. (A) Ga 3d spectrum of 10 nm GaAs, (B) As 3d spectrum of 10 nm GaAs, (C) Ga 3d spectrum of 11 nm GaP, (D) P 2p spectrum of 11 nm GaP.

sizing GaP but it may have a similar effect to that observed on GaAs particle size.

To further investigate the origin of the broad hump near 36° 2θ angle in the XRD patterns, XPS studies were performed on the nanocrystalline GaAs and GaP samples. The binding energies obtained in the XPS analyses were corrected for specimen charging by referencing the carbon 1s signal to 284.8 eV, however, the spectra in Figure 5 show signals at uncorrected binding energies. Figure 5a shows the Ga 3d spectrum of the 10 nm GaAs sample. Curve-fitting analysis of the asymmetrical gallium peak showed the existence of two signals due to gallium-containing species, one from gallium (at 18.9 eV) in GaAs and the other from gallium (at 20.4 eV) in Ga_2O_3. Due to the small differences in the binding energies in these two different gallium environments, the two signals were unresolvable. As can be seen in the As 3d spectrum in Figure 5B, clearly two arsenic signals were observed. The signal from arsenic in GaAs was observed at 40.8 eV while the other signal was due to arsenic oxides. Curve-fitting analysis of the signal due to oxidized arsenic species indicated two kinds of arsenic environments, As_2O_3 at 44.3 eV accounted for over 80% of the arsenic oxides whereas the other signal at 45.5 eV was due to other oxidized arsenic species which are likely to be primarily As_2O_5. The XPS analysis of GaP also showed evidence of surface oxidation. Figure 5c shows the Ga 3d spectrum from the 11 nm GaP sample. Once again, the gallium signal consisted of two gallium environments, namely, gallium from the phosphide (at 19.3 eV) and the oxide (at 21.2 eV). The phosphorus spectrum shown in Figure 5d indicated two distinct phosphorus environments, one signal from GaP (at 129.4 eV) and the other originating from phosphorus containing oxidized species (at 134.7 eV). In addition to gallium, arsenic, and phosphorus signals, the XPS analysis indicated presence of carbon and oxygen impurities, however, in contrast to the III−V materials produced by the SSM method, halogen or alkali metal impurities were not detected. The oxidation of our samples was not surprising for two reasons: first, the semiconductor powders had been exposed to air for several months prior to analysis and second, in the synthesis of analyzed samples, the reactions were quenched with water rather than methanol or ethanol. As mentioned earlier, surface oxidation of III−V materials due to atmospheric exposure is known to occur. Liliental-Weber and co-workers reported that the water-induced oxidation of GaAs also results in gallium and arsenic oxides.[19] This is consistent with our results. However, they also reported that oxidation of GaAs was not observed in methanol which suggests that oxidation due to water can be avoided by employing methanol in the workup procedure. The possibility of oxygen incorporation from polyether solvents cannot be completely eliminated; however, the small amounts of carbon and hydrogen detected in the elemental analyses suggest that solvent may not be a major source of observed oxidation. The preceding discussion suggests the extent of oxidation in our samples to be primarily a function of particle size (or surface area) rather than exposure to either air or water. This is consistent with the XRD patterns which show reduction in the relative intensities of the broad humps with increasing particle size. The GaAs samples whose XRD patterns are shown in Figure 3 were all prepared in a similar manner in reactions which were quenched with water and all the samples had been exposed to air for similar lengths of time. Similar arguments can be made for GaP from the XRD data shown in Figure 4.

Our UV−vis spectroscopic investigations provided insight into the quantum confinement in GaAs and GaP nanoparticles. Figure 6A shows the blue-shifted UV−vis absorption spectrum of GaAs dispersed in methanol. This dispersion was prepared from an as-synthesized GaAs sample which was not subjected to the 350 °C sublimation process to remove excess arsenic. The particle size giving rise to the absorption onset at 330 nm was estimated to be approximately 3 nm using the effective mass approximation (EMA).[20] Methanol dispersion of GaP nanocrystals also exhibited blue-shifted UV−vis spectrum (Figure 6b) as evidence of pronounced quantum confinement. The slow rise in the absorbance at 350 nm corresponds to approximately 4 nm GaP

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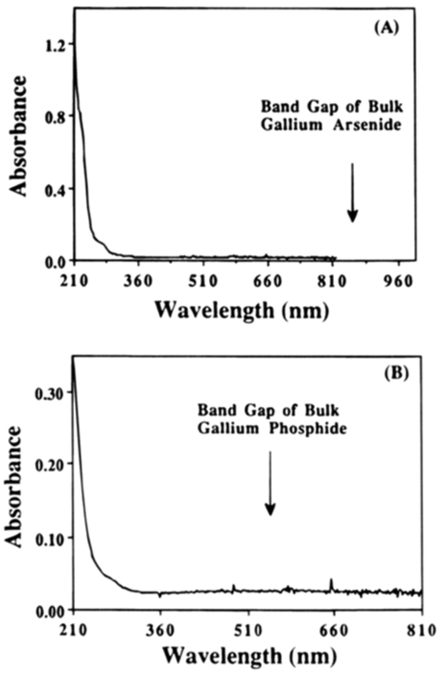

Figure 6. UV–vis absorption spectra of GaAs and GaP dispersions in methanol. For both semiconductors, the pronounced blue-shifts in the absorption onsets indicate quantum confinement (A) Spectrum of as-prepared GaAs crystallites. (B) Spectrum of GaP nanocrystals.

crystallites. These are estimated values and by no means accurate as the EMA is known to fail for small nanocrystallites and several workers have suggested alternative theoretical approaches.[18,21] It should be noted that there are no prior reported studies of isolated nanocrystalline III–V semiconductors. All of the previous UV–vis studies on GaAs nanocrystals were performed on the reaction mixtures in which GaAs was synthesized, without isolating any solid product or washing off the initial reactant species.[4,5,6a] 2However, Fitzmaurice and co-workers[4] synthesized GaAs nanocrystals in a noncoordinating solvent, and our UV–vis data on isolated washed materials compare well with their report for similar sized GaAs crystallites. Although XRD data suggested larger average particle sizes, this could not be verified by our UV–vis studies. Due to agglomeration of smaller crystallites into larger clusters, it was not possible to disperse larger particles/aggregates as these easily settled down. Deagglomeration of the sample was not attempted.

Although as-prepared nanocrystalline materials underwent grain growth and crystallization during the sublimation step, these materials still consisted of crystallites small enough to be within the limits required for quantum confinement. Definitive evidence of the nanoscale dimensions and crystallinity of GaAs and GaP (Figure 7) quantum particles was obtained in our HRTEM studies. Lattice fringe pattern resulting from a 10 nm GaAs particle is shown in Figure 7A. Three other crystallites with particle sizes ranging from 3 to 5 nm are also seen in the photomicrograph. Figure 7 shows GaAs crystallites in 3–6 nm range. The images of lattice planes of 12 nm GaP particles are shown in Figures 7C,D, respectively. A 4 nm crystallite is also seen in Figure 7d. Several lattice fringe patterns resulting from 2–12 nm GaP crystallites are shown in Figure 7e. Although lattice plane images originating from crystallites as small as approximately 1.5 nm (not shown in Figure 7) were observed, they were not as numerous as seen in the as-prepared materials (Figure 2A,D). The TEM studies also indicated the presence of some amorphous material, likely to be oxides, giving broad humps in the XRD patterns. The observed dimensions of the crystallites in the TEM studies were consistent with calculated average particle sizes from the XRD patterns. The XPS and TEM findings were consistent in that both the studies suggested, despite surface oxidation, the cores of these particles still consisted of nanocrystalline GaAs and GaP.

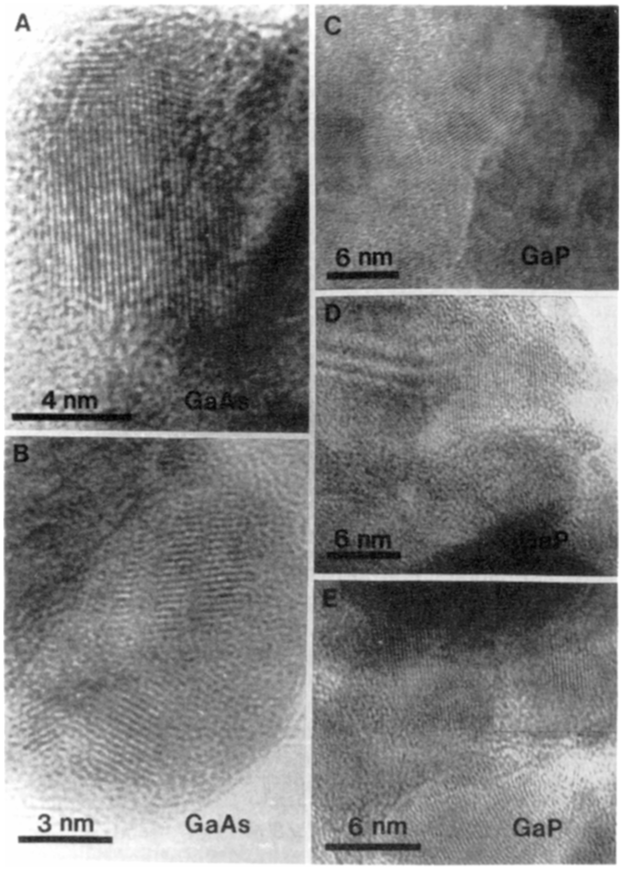

Figure 7. Transmission electron micrographs of GaAs and GaP quantum particles. The marker in the lower left corner in each figure represents scale. (A) and (B) Lattice fringe patterns resulting from GaAs crystallites, (C)–(E) Images of lattice planes of GaP crystallites.

Formation of ionic complexes of the group III halides and the polyether solvents, prior to synthesis, seemed to be critical for reduced particle sizes of the resultant material. The role of glyme solvents is not yet clear, although the fact that ether solvents form adducts with group III compounds is well known.[22] In general, group III halides exist as dimers due to the Lewis acidity of the group III metal atom, however, Nöth and co-workers reported that the glyme solvents tend to break up the dimeric structures of these halides and form ionic coordination complexes by expanding the coordination

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sphere of the metal center.[23] They have crystallographically established the structure of the ionic compound formed from $GaCl_3$ and monoglyme as $[Cl_2Ga(monoglyme)_2]GaCl_4$.[23a] From NMR studies, they suggested complex equilibria in solutions of $GaCl_3$ in monoglyme and diglyme. It was reported that various species can exist in glyme solvents of group III halides. Monoglyme and diglyme are open chain polyethers and can act as bidentate or tridentate ligands, respectively. This should facilitate formation of chelate complexes with group III halides. However, from ^{71}Ga NMR studies and conductivity measurements they also concluded that such dissociation of $GaCl_3$ and formation of ionic complexes does not occur in dioxane, as this ether formed only a simple adduct. Boardman et al. have reported the crystal structure of $GaCl_3$·1,4-dioxane which is a molecular addition compound.[24] Dioxane is a cyclic ether and, due to steric rigidity, may not form a chelate type complex with gallium(III) chloride. In light of these earlier reports, the average particle sizes of GaAs obtained in toluene (36 nm), dioxane (36 nm), monoglyme (17 nm), and diglyme (10 nm) may be indicative of a trend. It was not surprising that larger size crystallites were obtained in toluene which is a noncoordinating solvent. However, dioxane contains two oxygen donor sites and the reported crystal structure suggests that dioxane leads to the dissociation of dimeric $GaCl_3$ into two monomeric units and subsequently resulting into molecular adduct. The particle sizes of GaAs crystallites obtained in dioxane reactions are similar to those obtained in toluene solutions and may suggest that merely adduct formation may not be a sufficient requirement of the donor solvent if reduced particle size is desired. On the other hand, monoglyme and diglyme, both known to cause dissociation of $GaCl_3$ and formation of ionic chelate complexes, indeed gave particle sizes reduced by a factor of 2 or more. The smaller particle size produced in diglyme compared to monoglyme may be due to the former being a longer chain polyether as well as a tridentate ligand. Our observations are consistent with the reported behavior of ether solutions of $GaCl_3$. It seems reasonable to suggest that these ionic chelate complexes may play an important role in the mechanism to limit the growth of particles/clusters beyond a certain size due to expected steric restraint on chelation.

Conclusions

Due to the ease in synthesis of CdS and other II–VI semiconductors, these have been the most widely studied nanomaterials. Synthesis of III–V materials is quite challenging due to various safety hazards and extreme reactivity of the starting materials. We have presented a new synthetic approach for the preparation of III–V nanocrystals. Although rigorous handling precautions are necessary, this method is relatively safer as isolation of any group V compounds is not necessary. The complex solution chemistry of gallium(III) halides in glyme solvents proved to be crucial for synthesizing nanocrystalline GaAs and GaP. It seems that either dissociation of $GaCl_3$ or chelating effect of the polyether may be responsible for the observed reduction in particle sizes. Alternatively, both the properties of the polyether solvents may be essential for the synthesis of nanoparticles. Undoubtedly, this aspect merits further investigation as it may be applicable to synthesis of other nanocrystalline materials. Our initial results indicate that it is possible to prepare more than 1 g quantities of the nanocrystals using this new procedure and it is also possible to extend this methodology to other III–V systems.[12] The observed oxidation may be prevented by rigorous exclusion of air and by substitution of water by methanol in the workup procedure. Our straightforward approach should make these materials more accessible to a wider research community and further our understanding of the observed behavior of quantum particles.

We believe that a wide particle size distribution results from our syntheses, however, this was not investigated. Possibility of separating various particle sizes is currently under investigation. Particle size analysis is not a straightforward task as each analytical technique probes a different property of the investigated material. Considering this, it is difficult to precisely measure a particle size of a sample. However, our XRD, TEM and UV–vis studies are consistent in that they all provide the evidence of nanoscale dimensions of GaAs and GaP.

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