GaAs Nanocrystals via Hydrothermal Redox Reaction

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GaAs nanocrystals of 35 nm were synthesized via hydrothermal redox reaction of metal gallium with As_2O_3 and following annealing, which were characterized by X-ray diffraction, transmission electron microscopy, X-ray photoelectron spectra. The formation mechanism was discussed.

The quantum dots (QDs) of III–V group semiconductors have been studied intensively because of their potential application in photovoltaic cells, fluorescent biological labels, light-emitting diodes, and QD lasers. Compared with II–VI group and I–VII group semiconductors, III–V group semiconductors have a greater degree of covalent bonding, and larger exciton diameters due to a smaller effective mass for electron. Gallium arsenide (GaAs), as one of the most important direct band-gap III–V group semiconductor, has high electron mobility and an exciton diameter of 19 nm, which has been widely used for laser diodes, full-color flat-panel displays, high-speed transistors and is more likely to find applications in optical devices.[1,2]

In the past decade, many studies on the preparation and properties of GaAs nanocrystals (NCs) have been reported, including molecular beam epitaxy (MBE),[3] organometallic chemical vapor deposition (MOCVD), radio-frequency sputtering,[4] laser ablation method,[5] and solid-state metathesis reaction at elevated temperature.[6] Recently, organic-phase solution reactions become the most important route to GaAs NCs, which utilized the dehalosilylation reaction between $GaCl_3$ and $[(CH_3)_3Si]_3As$ in refluxing solvents including quinoline (240 °C),[7] decane (180 °C),[8] triglyme (216 °C, $Ga(acac)_3$ as gallium source).[9] GaAs NCs could also be obtained by solution metathesis reaction of $AsCl_3$ with $(Na/K)_3As$ in refluxing toluene, 1,4-dioxane, monoglyme or diglyme and vacuum anneals at 350 °C.[10] And crystalline GaAs could be prepared by organometallic reactions between $(t\text{-Bu})_3Ga$ and AsH_3 in 1,3-diisopropylbezene (203 °C), which was described as a solution–liquid–solid mechanism.[11] All of the above methods were based on metathesis reactions in organic solvents. Our previous work indicates that it is feasible to synthesize InP crystallites in aqueous solution.[12]

In this study, we report a hydrothermal route to 35 nm of GaAs NCs with spherical-like morphology. The products were characterized by X-ray diffractometry (XRD), transmission electron microscopy (TEM), and X-ray photoelectron spectroscopy (XPS). The formation mechanism and reaction conditions of GaAs NCs were discussed and attributed to the hydrothermal redox reaction between metal gallium and arsenous oxides in acidic condition.

In a typical hydrothermal preparation, As_2O_3 (0.495 g, 2.5 mmol) was dissolved into 50 mL of H_2SO_4 aqueous solution (1.8 $\text{mol}\cdot\text{L}^{-1}$) (or HCl aqueous solution, 1.4 $\text{mol}\cdot\text{L}^{-1}$), then metal gallium (99.99%, 0.600 g, 8.6 mmol) was added, the mixture was transferred into a 60 mL of Teflon-lined autoclave which was sealed and heated at 180–190 °C for 24 h, and cooled to room temperature on standing. (**CAUTION!** great carefulness should be taken when using toxic As_2O_3). The resulting suspension was vacuum filtered in air, and the black solid collected on the filter paper was washed with carbon bisulfide, distilled water, and anhydrous methanol, and then vacuum-dried at 70 °C. The resulting product was annealed at 400 °C in N_2 gas for 1 h to remove excess arsenic. The final products were collected for characterization.

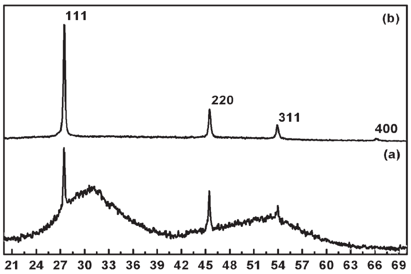

Figure 1. XRD of GaAs NCs, (a) the hydrothermal redox reaction product; (b) the product after annealing at 400 °C in N_2 gas.

XRD patterns were recorded on a Philips X'Pert X-ray diffractometer (Philips Co. Ltd.) with Cu Kα radiation ($\lambda = 1.54184\,\text{Å}$). Figure 1 shows the XRD pattern of the GaAs NCs, all the diffraction peaks could be indexed as the zinc-blende phase of GaAs with lattice constant $a = 5.6446\,\text{Å}$, which is close to the standard data.[13] As shown in Figure 1a, amorphous components coexisted with crystalline GaAs, which is similar to the product from metathetical reactions.[10] The thermal treatment at 400 °C removed amorphous component and according to the halfwidths of the major diffraction peaks (111, 220, and 311) of Figure 1b, the mean crystalline size was about 35 nm by using the Debye–Scherrer equation.[14]

The TEM images and selected area electron diffraction (SAED) patterns of the GaAs NCs were obtained using a Hitachi Model H-800 transmission electron microscope operated at 200 kV, and shown in Figures 2a and b, respectively. Aggregative spheric nanoparticles with 20–50 nm in diameter can be found in Figure 2a, and the concentric diffraction rings in Figure 2b can be indexed outwards as 111, 220, and 311 diffractions, which indicate the nanocrystalline nature of the GaAs product.

The X-ray photoelectron spectra (XPS) were employed to characterize the component of the as-prepared GaAs NCs, which were recorded on a VGESCALAB MKII X-ray photoelectron spectrometer (Al Kα, 1486.6 eV, C1s, 284.7 eV as internal standard). Figure 3 shows the narrow-scan XPS of the as-prepared GaAs NCs. The Ga 3d core spectrum (Figure 3a) shows an unresolved spin-orbit doublet peak at 19.3 eV with a half width of 0.6 eV which is characteristic of GaAs,[15] neither peak

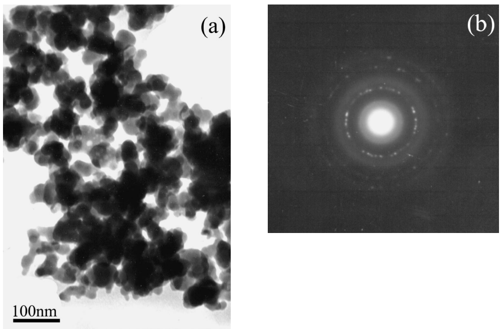

Figure 2. TEM image and SAED of the GaAs NCs.

of metal gallium (18.7 eV) nor gallium oxides (20.2 eV for Ga_2O_3) could be observed in this region. The Ga LMM Auger line (not shown) found at 1066.0 eV also corresponds to the reference value of GaAs.[16] The As 3d core spectrum (Figure 3b) shows an unresolved spin-orbit doublet peak centered at 41.1 eV with a half width of 2.05 eV, which is characteristic of GaAs (40.6–41.5 eV[17]), no peak was found between 44 and 46 eV, showing that the NCs surfaces did not contain As_2O_3 or As_2O_5. Both Ga 3d and As 3d peaks have asymmetrical broadening on high energy side due to the overlapping of $3d_{5/2}$ and $3d_{3/2}$ peaks with doublet separation of 0.6 eV for As 3d,[18] and 0.45 eV for Ga 3d,[19] respectively. The molar ratio of Ga:As was 1.16:1 according to the area ratio of the Ga 3d to As 3d peaks. Therefore, the product is pure GaAs NCs without obvious oxidation or hydrolysis occurring at their surfaces.

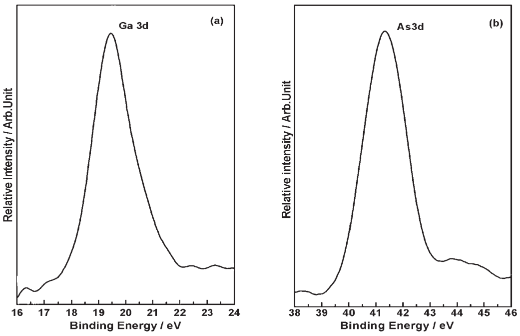

Figure 3. XPS of the GaAs NCs, (a) Ga 3d region, and (b) As 3d region.

As one typical method of determining arsenic, the Marsh reaction is suitable for most arsenides:

$$3Zn + 9H^+ + AsO_3{}^{3-} \rightarrow 3Zn^{2+} + AsH_3 + 3H_2O$$

That is, in acidic aqueous solution, metal zinc has a standard electrode potential of $\varphi^\circ(Zn^{2+}/Zn) = -0.76\,V$ and could reduce $AsO_3{}^{3-}$ to AsH_3. Metal gallium also has a negative standard electrode potential of $\varphi^\circ(Ga^{3+}/Ga) = -0.56\,V$. Is it possible to replace zinc with gallium to reduce $AsO_3{}^{3-}$ and form GaAs under acidic hydrothermal condition? Our study indicates that this is only feasible at certain acidity of aqueous solution and reaction temperature where crystalline GaAs nanocrystals could survive against hydrolysis. Hence, the hydrothermal formation mechanism can be speculated as follows,

$$2Ga + 9H^+ + AsO_3{}^{3-} \rightarrow 2Ga^{3+} + AsH_3 + 3H_2O$$
$$Ga^{3+} + AsH_3 \rightarrow GaAs + 3H^+$$

In this process, metal gallium is not only the Ga^{3+} source but also the reductant of arsenic source, and this coupling could be realized only at certain acidity (<2 M HCl) condition. Higher acidity will promote the hydrolysis of product; on the contrary, lower acidity will result in the incompleteness of reaction. And lower temperature (e.g. 150 °C) or shorter reaction time (e.g. 12 h) will also lead to the incompleteness of reaction.

In summary, GaAs NCs of 35 nm were synthesized via hydrothermal redox reaction. Since most of preparation methods for GaAs NCs and QDs were carried out in organic solvents, our results indicate that hydrothermal synthesis is another practical method for preparing GaAs NCs. And it is possible to obtain other arsenides NCs in hydrothermal systems. Further researches are underway to obtain monodispersed morphology.

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