Vapor phase synthesis of crystalline nanometer-scale GaAs clusters

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We report the synthesis of crystalline nanometer-scale GaAs clusters in the 5–10 nm size regime. The clusters are formed by the homogeneous nucleation of a nonequilibrium vapor created by the explosive vaporization of a bulk GaAs sample in an inert atmosphere. High resolution electron microscopy and diffraction show that the clusters have zincblende crystal structure and are faceted. Optical measurements on the particles are suggestive of quantum confinement effects.

Nanometer-scale clusters of semiconducting materials exhibit quantum size effects arising from the interaction of the electronic wave functions with the particle boundary.[1] As a result, clusters in the quantum size regime have a discrete electronic energy spectrum, in contrast to the continuous energy bands of the bulk, with the onset of optical absorption shifted to higher energy.[2] Due to their technological importance the direct band-gap III-V materials, such as GaAs, make attractive candidates for the study of quantum confinement effects.[3] However, because of difficulties in maintaining stoichiometry, the production of III-V clusters has proven challenging. We have developed a route to the synthesis of GaAs clusters by homogeneous nucleation from a nonequilibrium vapor produced by the explosive vaporization of a bulk "wire" of GaAs in an inert atmosphere. Transmission electron microscopy and diffraction reveal the clusters to be crystalline with a bulklike zincblende structure. Optical extinction measurements on a colloidal suspension of the clusters are indicative of quantum confinement effects.

Previously reported syntheses of nanometer scale GaAs clusters, though important steps forward, have not provided entirely satisfactory results. Alivisatos *et al.*[4] and Uchida *et al.*[5] have synthesized crystalline GaAs clusters in quinoline solution. However, elemental analysis reveals that particles produced in this manner incorporate significant impurities and, furthermore, have unequal Ga and As abundances.[4] Additionally, molecular species mask the optical properties of the GaAs clusters produced by this method.[5] In an alternate approach, Sandroff *et al.*,[6] using molecular beam epitaxy (MBE), have grown nanometer scale GaAs clusters on silica substrates. This method produces stoichiometric and crystalline particles. However, particle shapes and sizes are highly nonuniform, and they are in intimate contact with the substrate.

Vapor phase cluster synthesis has several advantages over other techniques, including controlled chemical purity and the generation of clusters with free surfaces. However, it also presents considerable technical challenges. At low growth temperatures, atomic mobilities are low in the solid phase, inhibiting formation of crystalline clusters. At high temperatures the partial pressures of Ga and As differ widely[7] leading to a loss of stoichiometry in the clusters.

Our apparatus for producing a nonequilibrium vapor of Ga and As is shown schematically in Fig. 1. The approach, adapted from techniques used to study the exploding wire phenomenon,[8] is easily adapted to a wide variety of materials. GaAs wires, typically $0.2\times0.2\times10$ mm^3, are etched from photolithographically patterned ⟨100⟩ oriented *n*-doped GaAs wafers or cleaved from wafers lapped to 0.1–0.2 mm thickness. A wire is soldered into a holder in a vacuum chamber backfilled with high purity gas (typically 99.999% Ar or He) to a pressure of approximately 1 atm. After charging the capacitor to 6–12 kV, the spark gap is triggered, completing the circuit and vaporizing the wire.

The details of aerosol formation by exploding wires are not completely understood.[9] However, our results indicate that the background gas quenches the vapor and induces cluster nucleation before vapor-solid equilibrium is established. The role of the background gas is confirmed by experiments with different gases. For instance, we find clusters produced in H_2 do not have a zincblende crystal structure. An analysis of clusters produced under typical conditions ($V = 6$ kV, $P = 1$ atm of Ar) shows that the size distribution is approximately log-normal with mean diameter $\bar{d} = 8.3$ nm and geometric standard deviation $\sigma_g = 1.4$. Taking reported aerosol recovery efficiencies of 80% as typical,[10] we estimate that each wire explosion produces approximately 10^{15} clusters.

A high resolution transmission electron micrograph of an agglomerate of the GaAs clusters, collected on a holey carbon substrate, is shown in Fig. 2. Within several clusters, atomic rows are easily recognized. In addition, hexagonal features, indicative of faceting, are apparent. The clusters appear to have random relative orientations, which suggests that cluster nucleation occurs on a much shorter time scale than does agglomeration. An absence of lattice fringes which extend to the particle boundaries is due to a native oxide layer, approximately 1.5 nm thick, which surrounds each particle. This is attributed to the oxidation of collected particles during sample preparation for electron

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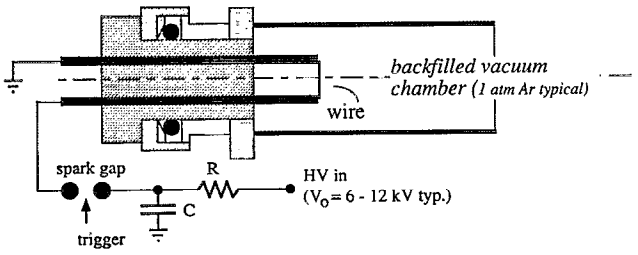

FIG. 1. A schematic diagram of the exploding wire apparatus. By discharging the capacitor through the GaAs wire, a stoichiometric vapor of Ga and As is produced which subsequently nucleates to form crystalline GaAs clusters. Typically V is 6–12 kV and $C = 1\ \mu$F. The stored energy corresponds to approximately 100 eV/atom.

microscopy. Energy-dispersive x-ray analysis and electron energy loss spectroscopy both give results which are consistent with the clusters having a stoichiometric elemental composition. The diffraction pattern, shown as an inset of Fig. 2, confirms that the clusters have a zincblende crystal structure.

Optical extinction (the sum of absorption and scattering) measurements on clusters produced by this method

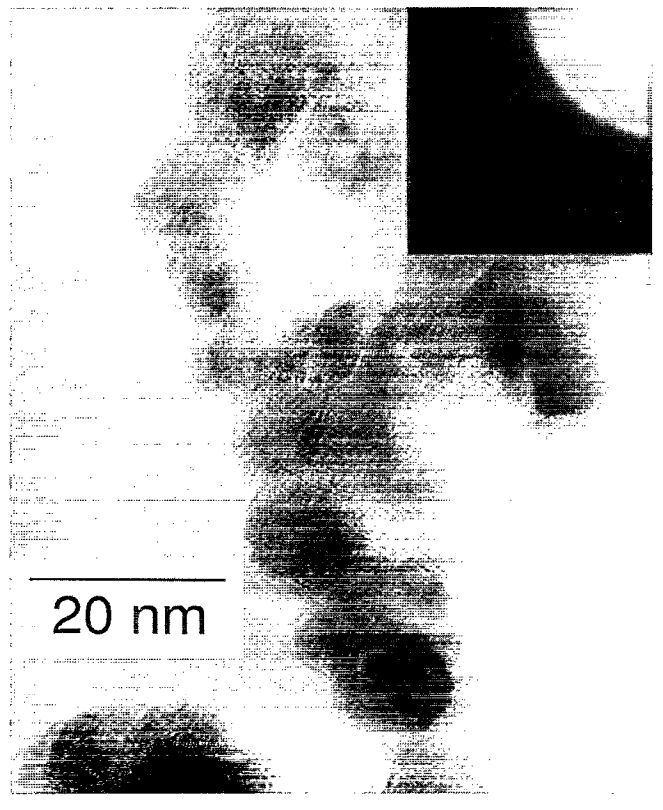

FIG. 2. A high resolution transmission electron micrograph of GaAs clusters. Due to a high cluster density and small volume of the experimental apparatus, the clusters agglomerate into micron length chains. This has the advantage that the agglomerates may span holes in the carbon film, permitting measurements without interference from the carbon background. Lattice fringes and hexagonal features, suggesting faceting, are apparent. Inset: electron diffraction pattern which indexes to the zincblende structure.

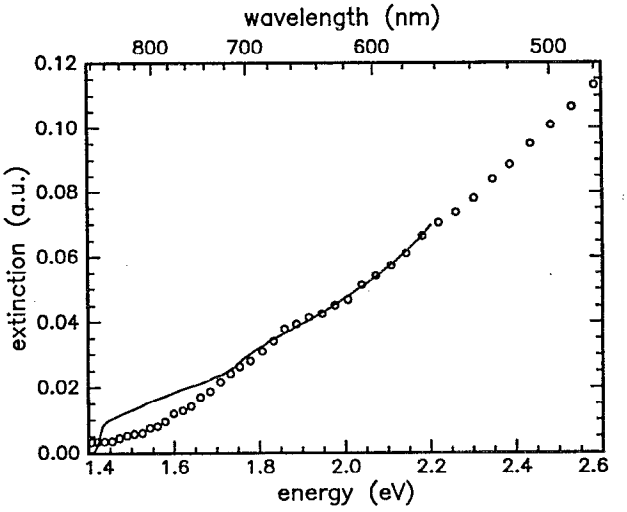

FIG. 3. The measured optical extinction of a colloidal suspension of GaAs particles produced by the exploding wire technique (○). The absorption efficiency of bulk GaAs (-), showing the rise in optical absorption at the band gap at 1.42 eV, is included for comparison. The absorption of the GaAs clusters rises slowly, with no measurable feature at the bulk band gap, and is suggestive of quantum confinement effects. A slight feature in the cluster absorption curve is apparent at 1.9 eV.

are strongly suggestive of quantum size effects. By producing the clusters in a flow of Ar saturated with isopropanol vapor, a colloid suitable for measurements with a commercial spectrophotometer can be produced by condensation on a cold finger. The measured extinction for the colloid is shown in Fig. 3 along with the absorption coefficient of bulk GaAs. The curves are adjusted to agree at high energy. The extinction of the clusters rises gradually with increasing photon energy with a broad rise in absorption near 1.9 eV, whereas the bulk absorption efficiency shows a sharp feature, indicating the bulk band edge at 1.42 eV. Spectra taken over a period of time show that the 1.9 eV feature progressively weakens and disappears altogether in about half an hour. This suggests that cluster coagulation may continue in the colloid phase.

For clusters whose radius, $R \ll \lambda$, where λ is the wavelength of light, Q_{ext}, the optical extinction efficiency,[11] is given by

$$Q_{\text{ext}} = -8\pi R/\lambda\ \text{Im}[(m^2-1)/(m^2+2)]$$
$$\cong 12\alpha n R/(n^2+2)^2 \qquad (1)$$

where $\alpha = 4\pi k/\lambda$ is the bulk absorption coefficient, and n and k are the real and imaginary parts of the complex refractive index, $m = n - ik$. Here, it is assumed that $k \ll n$. For GaAs, $m = 3.64$–$0.079i$ (Ref. 12) for $\lambda = 827$ nm (1.5 eV). Since n varies by less than 5% over the range of Fig. 3, to a good approximation Q_{ext} should be proportional to α, provided the cluster and bulk dielectric response are identical. Conversely, the observed difference between the cluster and bulk data of Fig. 3, notably the absence of an abrupt step at the bulk band edge, implies that the cluster and bulk dielectric response are not the same. This suggests that the absorption edge in the clusters is shifted to higher energy, consistent with a quantum size effect. Indeed, an

absorption feature at 1.9 eV is consistent with the predicted response of particles in the 5–10 nm size range.[2,13]

The spectrum of Fig. 3 shares some features with the absorption spectrum reported by Sandroff *et al.*,[6] who noted a smooth increase in absorption without a sharp onset at the bulk band gap, though without any significant features. On the other hand, it differs significantly from the absorption measurements of Alivisatos *et al.*[4]and Uchida *et al.*[5] whose spectra are dominated by the presence of molecular species in the colloid rather than by the GaAs clusters themselves.[5]

In summary, we have demonstrated the vapor phase synthesis of crystalline nanometer-scale GaAs clusters. The method relies on the rapid condensation of a nonequilibrium vapor produced by the explosion of a GaAs wire in an inert atmosphere. Electron microscopy and diffraction show that the cluster sizes fall well within the quantum size regime and that they have a bulklike zincblende crystal structure. These results, combined with optical measurements which suggest quantum confinement, are an encouraging first step toward the gas-phase synthesis of quantum dots.

Two significant advantages of this method are its economy and the ease with which it can be adapted to other materials. We have performed preliminary studies with InAs and produced clusters in the 40 nm size range. In this range, clusters appear mostly monocrystalline, though we have also observed twinned structures. We are presently characterizing source parameters with regard to cluster size and crystallinity, and are exploring methods to reduce cluster agglomeration.

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