Reports

GaAs Clusters in the Quantum Size Regime: Growth on High Surface Area Silica by Molecular Beam Epitaxy

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Molecular beam epitaxy has been used to grow microcrystalline clusters of gallium arsenide (GaAs) in the size range from 2.5 to 60 nanometers on high-purity, amorphous silica supports. High-resolution transmission electron microscopy reveals that clusters as small as 3.5 nanometers have good crystalline order with a lattice constant equal to that of bulk GaAs. Study of the microcrystallite surfaces by x-ray photoelectron spectroscopy shows that they are covered with a shell (1.0 to 1.5 nanometers thick) of native oxides of gallium and arsenic (Ga_2O_3 and As_2O_3), whose presence could explain the low luminescence efficiency of the clusters. Optical absorption spectra of the supported GaAs are consistent with the blue-shifted band edge expected for semiconductor microcrystallites in the quantum size regime.

THE STRUCTURAL, OPTICAL, AND electronic properties of clusters are attracting ever more attention because they represent an intermediate physical regime where neither molecular nor solid-state descriptions are totally adequate. Semiconductors are particularly interesting in this regard because the relatively long coherence lengths characteristic of charge carriers in these materials cause their electronic properties to be very sensitive to physical size. Indeed, much current research on electronic materials is devoted to exploiting the effects of reduced dimensionality to create artificial semiconductor systems with unique electronic and optical properties (*1*). Most work in this area has focused on the properties of semiconductors in two dimensions, where sophisticated epitaxial techniques are used to prepare multilayered structures whose thicknesses can be controlled down to atomic dimensions. But increasing experimental (*2–16*) and theoretical (*17–19*) attention is being paid to the fabrication and behavior of semiconductor microstructures—quantum wires, dots, and boxes—in which electrons or holes are confined in two or even all three spatial dimensions.

Experimentalists have adopted two basic strategies for making microstructures in the quantum size regime. The first relies on adding a degree of lateral confinement to carriers already confined in one spatial dimension within a layered quantum well. This can be accomplished by microlithography (*2–6*), strain (*7*), or controlled growth on stepped substrates (*8, 9*). The second method exploits synthetic chemical techniques to grow and stabilize very small semiconductor microcrystallites, often as particles suspended in solution or in solid matrices (*10–16*).

We report on the use of high surface area silica (SiO_2) as an inert, refractory support for the deposition of GaAs clusters grown by molecular beam epitaxy (MBE). This growth procedure combines several of the favorable attributes of the physical and chemical approaches outlined above: microcrystalline semiconductor structures with extremely small dimensions can be prepared in high concentration in a well-characterized environment. The supported microcrystallites, which vary in size from 2.5 to 60 nm, can be quantitatively identified as stoichiometric GaAs, and high-resolution transmission electron microscopy reveals that their lattice constant is equal to that of bulk GaAs. The high coverage of the silica support by microcrystalline GaAs has also allowed us to study the surface composition of a semiconductor cluster. Using x-ray photoelectron spectroscopy (XPS), we detected a 1.5-nm skin of native oxides (Ga_2O_3 and As_2O_3) on the GaAs microcrystallites, whose presence is consistent with the low luminescence efficiency of the supported clusters. Optical absorption spectra indicate a blue-shifted band edge characteristic of semiconductors in the quantum size regime.

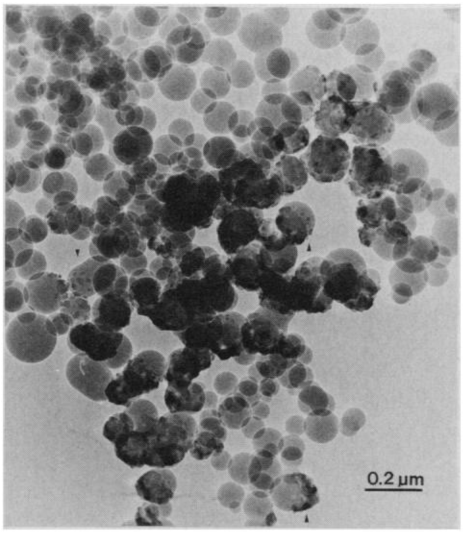

Fig. 1. Transmission electron micrograph of GaAs clusters grown on spherical SiO_2 particles by molecular beam epitaxy. Arrowheads mark SiO_2 spheres with small isolated GaAs clusters and regions where a large fraction of the silica is covered with GaAs. Growth of GaAs took place at 580°C for 5 min at a rate of 0.5 μm/hour.

Fig. 2. High-resolution transmission electron micrograph of GaAs-covered SiO_2. Lattice fringes correspond to (111) spacings in GaAs. The large cluster at the top of the micrograph is composed of several microcrystallite grains with random orientations. The arrowheads mark lattice fringes in single GaAs microcrystals, the smallest of which is 3.5 nm.

The high-purity silica used as the support in our experiments was made by the hydrolysis of $SiCl_4$ vapor in an oxyhydrogen flame (*20*). A similar process has been used to make silicon particles as a substrate for the deposition of microcrystallites of gold (*21*). For the growth of GaAs, the ~100-nm SiO_2 particles were collected on a quartz substrate that was indium-mounted in a Riber 1000 MBE system. The silica was preheated at 400°C in a beam of As_4 (3×10^{-6} torr) for 1 hour, allowing ample time to remove adsorbed contaminants. The subsequent deposition of GaAs took place at a rate of ~0.5 μm/hour at 580°C under conditions typical-

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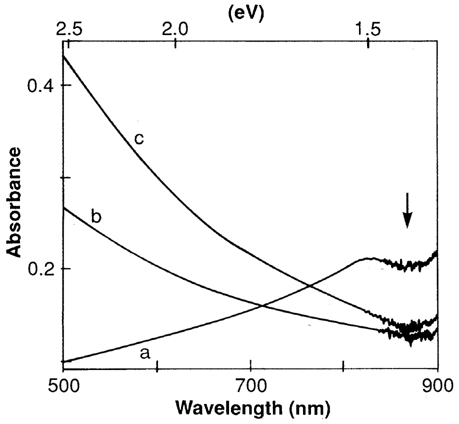
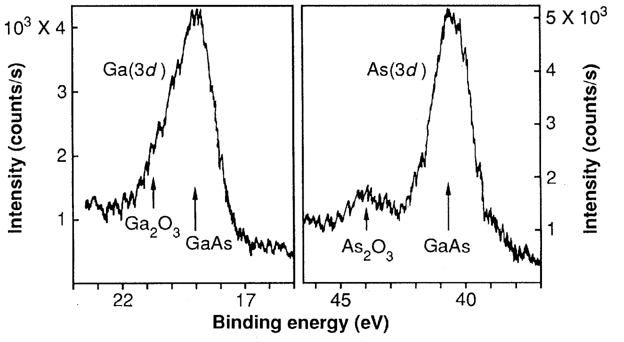


Fig. 3. Absorption spectra of the GaAs-coated silica particles. Curve a: bare SiO_2; curve b: after GaAs growth for 2 min; curve c: after GaAs growth for 5 min. The GaAs clusters begin to absorb at wavelengths to the blue of the bulk band gap position (marked by the arrow), consistent with quantum size effects. The spectra were taken in a diffuse reflectance mode.

Fig. 4. X-ray photoelectron spectra of GaAs clusters on silica. The Ga(3*d*) and As(3*d*) regions reveal that the native oxides, Ga_2O_3 and As_2O_3, are formed on the cluster surface after exposure to air.



ly used for the growth of high-quality epitaxial material. We were able to vary the microcrystallite dimensions by depositing GaAs for 2.5 or 5 min, which would correspond to ~20 nm and ~40 nm, respectively, of epitaxial GaAs grown on a flat GaAs substrate.

Figure 1 shows a typical transmission electron micrograph of the SiO_2 spheres decorated with MBE-grown GaAs clusters. The micrograph was obtained with a JEOL 4000 FX transmission electron microscope (TEM) capable of 0.26-nm point-to-point resolution. We prepared the TEM samples by wetting carbon-coated copper grids with acetone and placing them on top of the silica substrate, allowing the liftoff of a thin layer composed largely of GaAs-covered particles. A wide distribution in cluster size and shape is evident, with cluster dimensions varying from 2.5 to 60 nm. Energy-dispersive x-ray microanalysis performed in the TEM confirmed the presence of both gallium and arsenic, and the x-ray intensity ratio of the elements was consistent with the formation of stoichiometric GaAs.

To determine the crystalline quality of the GaAs clusters, we obtained high-resolution lattice images of the decorated silica particles. A typical cross-fringed lattice image of the supported GaAs clusters is shown in Fig. 2. The large cluster at the top of the figure is composed of several randomly oriented grains. Each of these microcrystalline grains contains well-resolved lattice planes, which become discernible one or two monolayers above the amorphous silica substrate. Measurements of the lattice fringe period show that the planes correspond to (111) spacings (0.326 nm) in GaAs.

Although the larger GaAs clusters are generally composed of several microcrystallites, clusters with dimensions smaller than ~10 nm grow as single crystals. Several of these single microcrystalline clusters, some as small as 3.5 nm, can be identified in Fig. 2 by the (111) lattice fringes that appear on the surface of the silica particle. Because the silica is amorphous, the high degree of crystallinity in the GaAs cannot be attributed to an epitaxial process. Instead, we believe that the formation of high-quality GaAs microcrystallites is the result of the high growth temperature used in our MBE process and the large surface-to-volume ratio of the clusters. Both factors would aid in annealing out structural defects in the microcrystallite, once cluster growth had been nucleated on the silica support.

Because the typical dimensions of the GaAs clusters are smaller than the exciton diameter in the bulk material (~15 nm), we expect electrons and holes to be confined in all three spatial dimensions within the microcrystallites. This extra confinement energy manifests itself as an increase in the effective band gap, *E*, of the microcrystalline semiconductor. Considering only the confinement of the more mobile electrons, it has been shown that, in the ground state,

$$E = Eg + h^2/8m_eR^2 \qquad (1)$$

where *Eg* is the bulk band gap of the semiconductor, *h* is Planck's constant, m_e is the effective mass of the electron, and *R* is the cluster radius (*11, 17*). For the smallest GaAs clusters in Fig. 1 (2.5 nm) Eq. 1 would predict a band gap shifted to the blue by 0.9 eV, to 2.3 eV. Figure 3 shows the absorption spectra of the supported microcrystallite as obtained by diffuse reflectance measurements. The wide distribution in cluster size makes it difficult to specify the location of the distinct absorption edge necessary to quantitatively test Eq. 1. However, both GaAs spectra indicate an absorption onset that is shifted to the blue of the bulk GaAs band gap, consistent with the physical confinement of charge carriers in a finite microcrystalline volume.

One of the most vivid contrasts between materials in the quantum size regime and their bulk analogs lies in the overriding electronic influence exerted by atoms at the microcrystallite surface. The smallest GaAs cluster shown in Fig. 2 contains about 2500 atoms, one-third of which reside on the cluster surface. Two features of our deposition process have made it possible to study the surface composition of the microcrystalline GaAs with XPS. First, our clusters are prepared on high surface area supports, which increases the amount of microcrystalline GaAs by five to ten times over what would be available on a flat substrate. Second, with the well-controlled growth conditions characteristic of MBE, it is possible to deposit chemically pure microcrystallites without using the surface binding agents needed to stabilize clusters in condensed-phase syntheses (*10*).

For the XPS investigation of the chemical composition of the microcrystallite surface, we mounted the as-grown, supported GaAs clusters in a Kratos x-ray photoelectron spectrometer and examined the Ga(3*d*) and As(3*d*) core level regions, using unmonochromatized Mg Kα x-rays as the excitation source. Figure 4 shows the XPS spectra obtained from the sample in Fig. 1. The two strongest peaks at 19.1 and 40.5 eV correspond to the Ga(3*d*) and As(3*d*) binding energies, respectively, for GaAs. Their ratio agrees well with the value for air-exposed GaAs single crystals, providing additional confirmation for the formation of stoichiometric GaAs microcrystallites. Besides these characteristic signatures for bulk GaAs, there are two higher binding energy peaks at 20.5 and 44.5 eV, which are readily identified as Ga_2O_3 and As_2O_3 (*22*), respectively. These native oxides are common products on air-exposed GaAs surfaces, and we estimate their thickness on the GaAs cluster surface to be 1.0 to 1.5 nm.

The presence of terminating oxide phases has important ramifications in understanding the optical behavior of the GaAs clusters. We tried unsuccessfully, using photoluminescence and cathodoluminescence, to measure light emission from microcrystallites cooled to 10 K. It is well known that air-exposed GaAs surfaces are characterized by a high density of surface states localized near the middle of the GaAs band gap (*23*). These states are extremely efficient at capturing mobile charge carriers generated in the bulk of the semiconductor and severely limit the luminescent quantum efficiency of the crystal. The presence of surface oxides would be even more deleterious in our microstructures, where surface-to-volume ratios are orders of magnitude larger than in bulk crystals.

Recent experiments, however, have shown that simple chemical treatments are capable of removing the native oxides from GaAs and replacing them with covalently bound phases that considerably reduce the density of nonradiative surface states (*24*). Because the GaAs clusters are chemically bound to the silica substrate, we believe it should be possible to perform similar modifications on the microcrystallite surface, which would render these extreme quantum systems more attractive candidates for potential opto-electronic applications.

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Experiments on Hydraulic Jumps in Turbidity Currents Near a Canyon-Fan Transition

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The point at which a submarine canyon debouches on its associated abyssal fan is generally characterized by a drop in channel slope. Turbidity currents of the kind responsible for the genesis of the canyon and fan should display an internal hydraulic jump near the slope transition. No direct field observations of any such jump appear, however, to have been made. Experiments on the nature of the jump and the resulting sedimentary deposits indicate that the thickness of the deposits just downstream of the jump tends to increase as the ratio of bed shear velocity immediately behind the jump to particle fall velocity decreases.

TURBIDITY CURRENTS ARE CURRENTS of water laden with suspended sediment that move down slopes of otherwise still bodies of water. Their driving force is obtained from the sediment, which renders the flowing turbid water heavier than the clear water above. Turbidity currents occur in the ocean, lakes, and reservoirs. They constitute an important mechanism for moving sediment brought in by rivers or littoral drift to the ocean floor. In the process of doing so, turbidity currents are widely assumed to be responsible for the excavation of many submarine canyons. Below the mouth of the canyon, such a current deposits an abyssal fan that parallels in many ways its subaerial cousin (*1*). The sedimentary rocks deposited by turbidity currents (known as turbidites) constitute a major part of the geological record. The mechanics of turbidite formation also influence the development and location of possible petroleum traps in submarine fans (*2*).

The change in down-channel slope observed at the canyon-fan transition is indicative of a transition from an overall erosive environment upstream (*3*) to an overall depositional environment downstream (*2*). This transition appears to be driven at least in part by a change in flow regime of major turbidity currents from high-velocity supercritical flow to low-velocity subcritical flow (*4*). Studies of subaerial open-channel flows and density flows have indicated that this change in flow regime is accomplished via a hydraulic jump. A bulk Richardson number Ri describing the flow possesses a critical value Ri_c near unity, such that the range $Ri < Ri_c$ corresponds to the high-velocity regime upstream of the jump, and the range $Ri > Ri_c$ corresponds to the low-velocity regime downstream.

The nature of the submerged hydraulic jump and the resultant sedimentary deposits have been the subject of speculation. Menard (*5*) argued that the development of levees bordering deep-sea channels was caused by the thickening of a turbidity current after a hydraulic jump. Van Andel and Komar (*6*) posited the occurrence of hydraulic jumps in order to interpret the characteristics of sediment deposits in enclosed basins. Ravenne and Beghin (*7*) observed that certain characteristics in the sedimentary record of debris flows, for example, strong local deposition, may indicate the location of a jump. Although recent field observations of turbidity currents (*8*) have contributed greatly to their understanding, the hydraulic jump itself remains unobserved in the field, in part because it is inferred to occur at great depths (>1000 m). Likewise, experimental studies conducted on depositional turbidity currents (*9*) did not include the change in slope necessary to induce a hydraulic jump. Internal hydraulic jumps associated with salinity or temperature-induced stratification have been studied extensively (*10*), whereas jumps in sediment-driven flows have received little attention.

Recently Parker, Fukushima, and Pantin (*11*) have presented a theory of eroding and depositing turbidity currents. The theoretical framework accounts for the attainment of high velocities in submarine canyons and the consequent excavation of the canyons themselves. The model has been used to predict the development of turbidity currents in Scripps Submarine Canyon (*12*). Attempts to apply the model to the vicinity of the slope change between canyon and fan motivated our experiments described below. For simplicity, we modeled the slope change as a slope discontinuity.

We conducted flume experiments to elucidate: (i) the degree of similarity between internal hydraulic jumps in the vicinity of a slope discontinuity in underflows driven by salt and sediment; (ii) the nature of the deposits of sediment from suspension upstream and downstream of the hydraulic jump; and (iii) the conditions under which the slope discontinuity is clearly reflected in the depositional record.

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