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QUANTUM CONFINEMENT IN GaP NANOCCLUSERS

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ABSTRACT

We have prepared GaP and GaAs nanoclusters from organometallic condensation reactions of $E[\text{Si}(\text{CH}_3)_3]_3$ ($E = \text{P, As}$) and GaCl_3 . The size of the as synthesized clusters is 10 Å to 15 Å. Larger clusters of 20 Å to 30 Å size were obtained by thermal annealing of the as grown material. X-ray diffraction and transmission electron microscopy confirm the high crystalline quality. A lattice contraction of 6.7% could be seen for 10 Å sized GaAs clusters. The clusters are nearly spherical in shape. Optical absorption spectra show a distinct line which can be assigned to the fundamental transition of the quantum confined electronic state. The measured blue shift, with respect to the GaP bulk absorption edge is 0.53 eV. As the cluster is smaller than the exciton radius, we can calculate the cluster size from this blue shift and obtain 20.2 Å, consistent with the results from X-ray diffraction of 19.5 Å for the same sample.

INTRODUCTION

III-V semiconductor nanoclusters have attracted growing interest in recent years because of their structural, electronic, and optical properties.[1] Clusters in the size regime of a few nanometers show a crystalline structure, their electronic properties, however, are very different from those of bulk semiconductors.[2] The quantum confinement of the charge carriers leads to distinct electronic levels, having an energy higher than the bandgap of the bulk material (blue shift). Due to the long coherence length of the charge carriers in semiconductors, e.g. an excitonic Bohr radius of 12.4 nm in GaAs, the electronic and optical properties are strongly influenced by the cluster size.[3] The behaviour of quantum confined systems has been studied in semiconductor quantum wells, wires, and dots, fabricated by molecular beam epitaxy and electron beam lithography. Studies on nanoclusters, down to a few nanometers, have been done mostly with II-VI semiconductors.[4] There are few reports on the synthesis of III-V semiconductor clusters.[5-7] This study focuses on the synthesis, and the structural and optical properties of III-V semiconductor clusters in the 1 nm regime.

EXPERIMENT

We have fabricated GaP and GaAs nanoclusters using the organo-metallic condensation reaction:

Synthesis of GaP: GaCl₃ was dissolved in acetonitrile (MeCN) and P(SiMe₃)₃ was added, immediately producing a yellow solution. The reaction was heated to reflux for 16 hrs, producing an orange turbid solution. The solvent was removed to yield an orange solid, which can be redissolved in acetonitrile. **Synthesis of GaAs:** As(SiMe₃)₃ which was prepared via a published method,[8] was suspended in MeCN and GaCl₃ was added resulting in the immediate formation of a yellow-orange precipitate. The reaction mixture was heated to reflux and filtered to give a reddish solid. The alternate use of diethyl ether as solvent yielded a orange solid. Thermal annealing was performed under dynamic vacuum. Outgassing was observed and the samples darkened in colour proportionally to the annealing temperature. X-ray diffraction measurements were performed with a Siemens D 5000 diffractometer, using a curved germanium monochromator to obtain high resolution combined with the high intensity necessary for small powder samples. The samples were contained in a sealed cell with beryllium window.

RESULTS AND DISCUSSION

We have used X-ray diffraction to determine the lattice constant and the cluster size. III-V semiconductors have a face centered cubic structure. The strongest diffraction peaks are [111], [220], and [311]. The latter two strongly overlap if the linewidth exceeds a few degrees. Figure 1 shows a X-ray diffraction spectrum of a annealed GaP cluster sample with the [111], [220], and [311] reflections marked. The sharp lines are caused by the beryllium window and the sapphire plate which holds the powder in place. It should be noted that there are no diffraction peaks indicating other crystalline phases, e.g. of oxides. The effect of annealing the clusters is shown in figure 2, comparing as grown GaAs clusters with an annealed sample. Note the strong shift in the peak position. The as grown GaAs clusters of 9 Å size show a lattice contraction with a lattice constant 6.7% smaller than the bulk one, whereas the annealed, larger clusters of 32 Å size have the bulk lattice constant, similar to clusters grown by molecular beam epitaxy.[9] This shows the effect of surface tension. The cluster size was determined by a Warren-Averbach analysis and using the Scherrer formula. As shown in table 1, the values obtained by both methods agree. As synthesized material and samples annealed at lower temperatures (350 C or below) exhibit a Gaussian lineshape, a sign of

a narrow size distribution. Samples annealed at higher temperature, such as the GaAs annealed at 500 C a more Lorentz type lineshape.

Figure 1: X-ray diffraction spectrum of annealed GaP nanoclusters with a size of 19.5 Å.

Figure 2: X-ray diffraction spectra of as synthesized 9 Å GaAs nanoclusters (bottom) and 32 Å GaAs clusters annealed at 500C (top).

	a (Å)	$\Delta \frac{a_{\text{cluster}}}{a_{\text{bulk}}}$	L(Å)		Line shape
			Scherrer / Warren-Averbach		
<u>GaP</u> as grown	5.26	-3.5%	11.5	-	Gauß
annealed (350°C, 20h)	5.40	-1%	19.5	18.5	Gauß
<u>GaAs</u> as grown	5.275 5.51	-6.7% -2.5%	9.0 12.0	10 -	Gauß
annealed (500°C)	5.68		32	30	Pseudo-Voigt

Table 1: Lattice constant and cluster sizes of GaP and GaAs nanocrystallites

In order to obtain a verification of the crystallinity and the size of the clusters we performed transmission electron microscopy. Figure 3 shows a cluster of annealed GaP. The lattice planes can be clearly seen.

Figure 3: TEM image of a GaP nanocluster with a size of 19 Å.

Measuring a number of clusters, we obtain a typical size of 19 Å, like the cluster shown in the TEM image, a maximum size of 23 Å and a minimum size of 15 Å, confirming the narrow size distribution suggested by the Gaussian X-ray lineshape. The clusters have a nearly spherical shape, and they appear to be only weakly faceted. A thin shell covering the crystalline cluster can be seen in figure 3. As the clusters were prepared by a chemical reaction in a solution, the residual reaction products, Cl and $\text{Si}(\text{CH}_3)_3$, can chemically bond to the surface, saturating the dangling bonds which a bare surface would have. This surface layer seems to prevent the oxidation of the clusters. This effect is similar to efforts to coat II-VI semiconductor clusters.[10]

We have performed optical absorption measurements using an UV-visible absorption spectrometer. The as grown material, GaP and GaAs, showed an absorption edge blue shifted with respect to the bulk, but without distinct structure. The annealed GaP exhibits a distinct line in the absorption spectrum, that can be assigned to the lowest electronic level caused by the quantum confinement of the charge carriers; see figure 4.

Figure 4: Optical absorption spectrum of GaP nanoclusters (same material as in figures 1 and 3).

This spectrum is similar to absorption spectra reported for II-VI semiconductor clusters.[11] We measured the position of the absorption line as 2.80 eV, resulting in a blue shift of 0.53 eV with respect to the bulk absorption edge at 2.27 eV. As the cluster size is smaller than the excitonic Bohr radius, we can use the following equation for 3- dimensional charge carrier confinement:[6,12]

$$\Delta E(\text{eV}) \approx \frac{\hbar(J_s) \hbar(\text{eVs}) \pi^2}{2 R^2(\text{nm}^2)} \left(\frac{1}{m_c} + \frac{1}{m_v} \right)$$

This results in a cluster size of 20.2 Å, in good agreement with the X-ray diffraction and the TEM results. Note that the blue shift is a sensitive function of the cluster size. From the width of the absorption line we can estimate a cluster size distribution from 17 Å to 23 Å, consistent with the crystallite sizes obtained by TEM.

CONCLUSION

We have shown, that GaP and GaAs nanoclusters can be fabricated by organometallic synthesis with high crystalline quality in the size regime of 10 Å to 30 Å. They seem to be coated with a chemically bonded shell of the residual reaction products, inhibiting oxidation. Calculating the particle size from the measured blue shift of 0.53 eV using the function for 3-dimensional charge carrier confinement gives 20.2 Å, consistent with the structural measurements. This gives clear experimental evidence for a quantum confinement of carriers in these GaP nanoparticles.

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