JOURNAL OF Materials CHEMISTRY

On the synthesis and manipulation of InAs quantum dots

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Received 10th February 2000, Accepted 13th March 2000
Published on the Web 23rd June 2000

A novel metalorganic route to small (*ca.* 2 nm diameter) InAs nanocrystals has been developed. The nanocrystals were analysed by a number of methods including HRTEM, photoluminescence and electronic spectroscopy. Distinct quantum size effects were observed in the optical properties, attributable to the nanoparticles having dimensions smaller than the Bohr exciton diameter of InAs (*ca.* 740 Å). The nanoparticles were spin coated into a thin film, the morphology of which was investigated by atomic force microscopy (AFM).

Introduction

Quantum dots have recently been the subject of intense research, because of their novel optical, electronic and catalytical properties.[1–3] A particle of a semiconductor of a size below the excitonic diameter for the material exhibits quantum confinement effects and the electronic structure is altered. Notably, the band gap widens and the electronic states become discrete. Such particles are referred to as artificial atoms, quantum dots or nanocrystals.

Many methods now exist for the preparation of nanoscale semiconductors, many of which involve aqueous colloidal chemistry.[4] Other routes include restricting material growth inside a structured, porous medium, such as a zeolite or micelle.[5] One of the most useful methods of preparation was described by Murray *et al.* in which the thermolysis of dimethylcadmium and a chalcogen source in a Lewis base solvent such as tri-*n*-octylphosphine oxide (TOPO) resulted in high quality, crystalline, nearly monodispersed materials.[6] The physical chemistry of such passivated nanocrystals has been extensively investigated.[7–9] This method of preparation has since been adapted for the synthesis of III–V,[10–12] IV–VI[13,14] and II_3–V_2[15,16] materials by binary or single molecular precursor methods.

The excitonic diameters of II–VI compounds are small (*e.g.* 40 Å for CdS). In contrast, III–V materials have larger excitonic diameters (*e.g.* 740 Å for InAs) and will show confinement effects at larger diameters. There are problems associated with the preparation of III–V materials; these can in the main be attributed to the increased covalent nature as compared to the analogous II–VI compounds, and also to strong precursor–solvent interactions as exemplified by the ready hydrolysis of group 13 metal salts in an aqueous medium. Atoms or ions of group III metals are not chemically stable, so ill defined metalorganic precursors (*e.g.* '$InCl_3$–TOPO') are employed.[12] Nucleation and growth are high temperature processes and temporal separation of the two is difficult, resulting in polydispersed products.[10–12]

The work described here follows from our single-source preparation of InP nanoparticles in 4-ethylpyridine using a diorganophosphide precursor.[10] Diorganoarsenides have also been reported, but are harder to prepare.[17] An alternative arsenic source is needed, and a precursor previously employed in MOCVD, tris(dimethylamino)arsenic ($As(NMe_2)_3$) has been used in the present work.[18,19] A mixture of $InCl_3$ and $As(NMe_2)_3$ was thermolysed at 167 °C in 4-ethylpyridine to produce high quality nanodimensional InAs. In addition, $InCl_3$ was found to form a complex with 4-ethylpyridine, *mer*-[In(4-ethylpyridine)$_3$Cl$_3$], an air stable compound potentially useful in such syntheses.

Dimethylaminoarsenido compounds have previously been used as precursors in the low pressure MOCVD for As containing thin films.[18] Decomposition is suggested to involve the elimination of the cyclic compound aziridine as a major decomposition product.[19] It is reasonable to assume that a similar mechanism applies to solution phase decomposition.

Experimental

Indium chloride (99.99%, Aldrich), petroleum spirits bp 40–60 °C (BDH), pyridine (99%, Aldrich), tris(dimethylamino)arsenic (99%, Strem), bipyrimidine (96%, Lancaster) were used as received. 4-Ethylpyridine (99 %) was obtained from Aldrich, degassed and stored under nitrogen over 4 Å molecular sieves. GaAs wafers were a gift from EPI Ltd. Microscope slides (BDH) were used as glass substrates.

Instrumentation

^1H NMR spectra were obtained using a JEOL ESX 270 NMR machine, using deuterated pyridine. IR spectra were carried out on samples as pressed discs (1% in CsI) on a Perkin Elmer 1720X machine. Photoluminescence spectra of 4-ethylpyridine solutions were recorded on a Spex fluorimeter spectrophotometer at room temperature, and optical spectra were recorded using a Philips PU 8710 spectrophotometer. Electron microscopy experiments were carried out using either a JEOL-JEM 1200 EX II scanning and transmission electron microscope operating at 100 kV (TEM) or a JEOL J535CM (SEM) on samples deposited on carbon coated copper grids. XRD patterns were obtained using a Guinier camera and a Philips 1130 X-ray generator (Cu-K$_\alpha$ radiation). Samples were

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DOI: 10.1039/b001354o

prepared by drying a solution onto a glass substrate. AFM experiments were carried out using a Topometrix Explorer in non-contact mode. Single crystal analysis was carried out using a Siemens P4/PC diffractometer with Mo-K$_\alpha$ radiation. The structure was refined using the SHELXTL PC program system.[20]

Synthesis

All manipulations were carried out in an inert atmosphere using Schlenk line techniques. The addition of $InCl_3$ to 4-ethylpyridine resulted in the formation of *mer*-[In(4-ethylpyridine)$_3$Cl$_3$]. Crystallization could be effected by placing the flask in a refrigerator overnight. The air stable crystals were isolated by filtration.

***mer*-[In(4-ethylpyridine)$_3$Cl$_3$].** ^{1}H NMR (C_5D_5N, 25 °C, 400 MHz) δ 1.06 ppm (t, CH_3, 3H), 2.44 ppm (q, CH_2, 2H), 7.21 ppm (s, aromatic CH, 2H), 8.73 ppm (s, aromatic CH, 2H); Elemental analysis (calculated): 46.6% C (46.5), 5.0% H (5.0), 7.9% N (7.7).

The thermolysis of $InCl_3$ and $As(NMe_2)_3$ in 4-ethylpyridine produced an optically clear deep red solution of nanocrystals. Addition of further precursors to the reaction vessel results in epitaxial growth.

In a typical experiment 0.5 g (2.23 mmol) of dry anhydrous $InCl_3$ was dissolved in 20 ml dry 4-ethylpyridine whilst under nitrogen. Once fully dissolved, 0.48 g (2.23 mmol) $As(NMe_2)_3$ was added and allowed to stir in. The temperature was then slowly raised to 167 °C over 2 hours and left for up to 6 days. To obtain slightly larger dots, 0.28 g (1.26 mmol) dry $InCl_3$ was mixed with 0.26 g (1.26 mmol) $As(NMe_2)_3$ and 10 ml dry 4-ethylpyridine in a separate flask then injected into the original flask at 167 °C. After refluxing for a further 3 hours, the solution was allowed to cool to room temperature and 60 ml dry light petroleum added, causing the nanocrystals to precipitate. The quantum dots were isolated by centrifugation, re-dispersed in 4-ethylpyridine and centrifuged further to remove solid waste products.

Single crystal X-ray diffraction study of *mer*-[In(4-ethylpyridine)$_3$Cl$_3$]

Crystal data. $C_{21}H_{27}Cl_3InN_3$, $M=542.63$, Triclinic, $a=9.733(1)$, $b=20.826(2)$, $c=25.311(3)$ Å, $\alpha=74.97(1)$, $\beta=83.31(2)$, $\gamma=89.26(2)°$, $U=4921.0(9)$ Å^3, $T=293$ K, space group $P\bar{1}$, $Z=8$, λ(Mo-Kα)$=0.71069$ Å, 18468 reflections collected, 17345 unique ($R_{int}=0.097$) which were used in calculations. The final $wR(F2)$ was 0.2874. $R1$ was 0.0953.

CCDC reference number 1145/215. See http://www.rsc.org/suppdata/jm/b0/b001354o/ for crystallographic files in .cif format.

Preparation of InAs quantum dot films

0.05 g of InAs quantum dots was mixed with 1 ml of 4-ethylpyridine and 0.01 g bipyrimidine. Thin films of InAs were prepared by spin coating the solution onto either a clean glass substrate or a GaAs substrate. (Solution dropped on substrate at 100 rpm and spread evenly with a pipette. Speed was then ramped up to 2000 rpm for 15 seconds and dried at 6000 rpm for 10 seconds.)

Results and discussion

mer-[In(4-ethylpyridine)$_3$Cl$_3$]

Crystals of *mer*-[In(4-ethylpyridine)$_3$Cl$_3$] were serendipitously obtained during initial experiments on the preparation of InAs nanoparticles. The compound was prepared by dissolving $InCl_3$ in excess 4-ethylpyridine and isolated as crystals. The complex has potential use as an air stable indium source for solution synthesis. The complex has an approximately octahedral arrangement with meridional stereochemistry (Fig. 1). Similar compounds *mer*-[In(pyridine)$_3$X$_3$]·pyridine (X = Br, Cl) are known.[21,22] Carty and Tuck calculated steric angles for $InCl_3$·3N systems and predicted a facial geometry to be preferred.[23] Strong repulsive interactions between bulky ligands in [In(pyridine)$_3$X$_3$]·pyridine systems have subsequently been suggested to lead to the meridional geometry.[22] The bond angle between the two *trans* Cl atoms is 172.04° hence the complex is only approximately octahedral. A similar distortion in bond angles is observed in [In(pyridine)$_3$X$_3$]·pyridine (X = Br, Cl).[21,22] The In–N bond lengths (2.31 Å average) are comparable to [In(pyridine)$_3$Cl$_3$]·pyridine (2.33 Å average), indicating that the electron donation strengths of 4-ethylpyridine and pyridine are similar.[21] In–Cl(*trans*) bond lengths (2.46 Å average) are similar to those observed in [In(pyridine)$_3$Cl$_3$]·pyridine (2.47 Å average), but the *cis* In–Cl bond length is slightly shorter (2.41 Å). The shortening of the *cis* In–Cl bond was not observed in the simple pyridine complex.[21]

Optical properties and growth of InAs nanoparticles

The thermolysis of $InCl_3$ and $As(NMe_2)_3$ in 4-ethylpyridine (167 °C, up to 6 days) produced an optically clear deep red solution of nanocrystals. Optical absorption spectra taken at different stages of growth at 167 °C are shown in Fig. 2. Electronic spectroscopy of an aliquot taken after 30 min showed a band edge at 2.96 eV (418 nm). Samples left for 6 days gave a band edge at 2.63 eV (471 nm), consistent with further growth of particulate material. The predicted diameters of such particles are 5.19 nm and 5.55 nm respectively, as calculated using an effective mass approximation as suggested by Brus.[24]

The estimation of the particle size using the effective mass approximation suggests little growth of the particles over the 6 days after the initial reaction. This observation is consistent with those of TOPO capped III–V materials[11,12] where the majority of growth is achieved in around one hour and prolonged heating is used principally for annealing. Further growth could be achieved by the injection of more $InCl_3$ and $As(NMe_2)_3$ (1 : 1 ratio, dissolved in 4-ethylpyridine) and refluxing for 3 more hours. Optical spectra of the sample obtained from further application of precursor showed absorption consistent with larger particles (Fig. 2). An excitonic peak was clearly visible at 451 nm (2.75 eV). The electronic spectrum of the sample suggested some growth of the

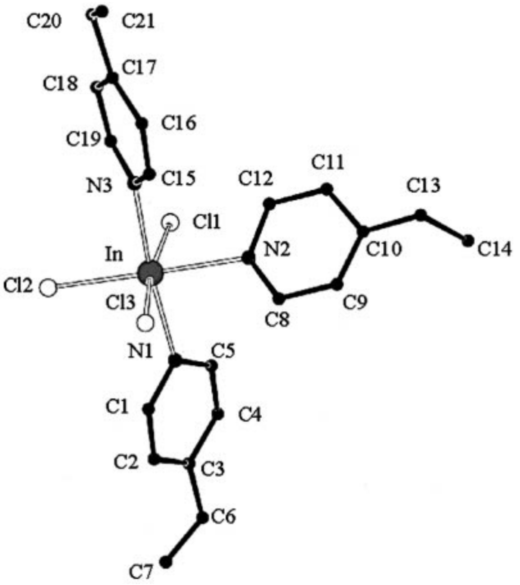

Fig. 1 Crystal structure of *mer*-[In(4-ethylpyridine)$_3$Cl$_3$].

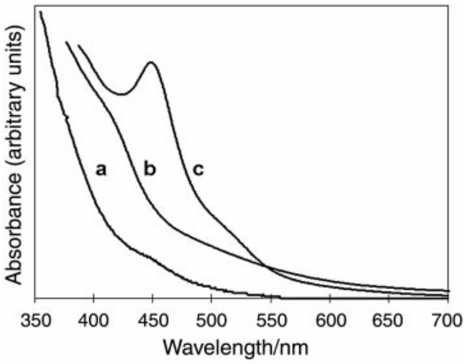

Fig. 2 Optical absorption spectra of Q-InAs synthesised under different conditions; $a = 30$ minutes growth, $b = 6$ days growth, $c =$ addition of further precursor.

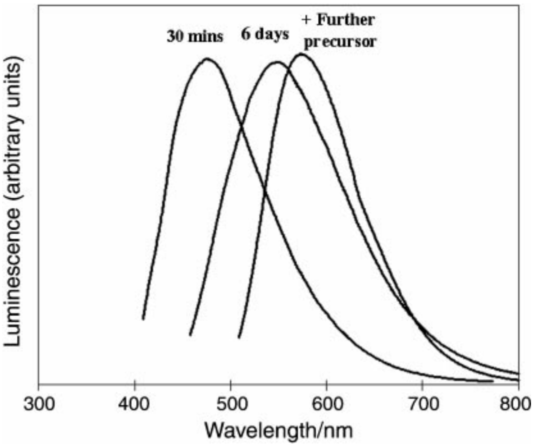

Fig. 3 Emission spectra from 3 samples of Q-InAs. $\lambda_{\mathrm{exc.}} = 400$ nm.

sample with a band edge at 2.43 eV (510 nm) (predicted diameter of 5.81 nm using the effective mass approximation).

Addition of a further aliquot of precursor appeared to result in further growth of the nanoparticles and the electronic spectrum shifted to lower energy. An increase in monodispersity may also occur as a clear excitonic feature emerges in the optical spectra. An increase in size, coupled with monodispersity upon addition of precursor to a reaction mixture, has been previously observed in the growth of II–VI and III–V nanoparticles.[25] Size fractionation did not result in any significant separation of different sizes of nanoparticles. Addition of light petroleum to a 4-ethylpyridine sol until flocculation did result in fractions, but comparison of the electronic spectra of the first 20 fractions showed little discrimination in size. The ineffectiveness of size selective precipitation has been reported for TOPO capped InP and been attributed to a stable oxide layer forming on the quantum dot which inhibits the effect of the non-solvent.[26] In contrast, II–VI materials are not reported to form stable oxide species, causing nanocrystal surface degradation. The absence of a stable oxide layer allows size fractionation procedures.[27]

Photoluminescence spectra for selected samples are summarised in Fig. 3 and Table 1. The observed emission is broad, consistent with a wide size distribution of III–V materials. Comparison of the breadth of emission profiles provides evidence of what has recently been referred to as growth focusing after addition of further precursor.[25] The emission from the sample obtained after 30 minutes had a FWHM of 0.36 eV which increased with shell growth up to 0.62 eV (3 days). Addition of further precursor resulted in samples with emission profiles with a FWHM of 0.41 eV, possibly indicating a reduction in the size distribution.

The emission spectra have Stokes shifts of up to 90 nm, with the larger particles having the largest shift (Table 1). The change in Stokes shift with change in particle size has previously been observed with TOPO capped InP.[12] No evidence of surface traps was present, suggesting that the luminescence is near-band edge due to surface states being filled by the capping ligand 4-ethylpyridine.

Structural characterisation of Q-InAs

InAs usually exists as the cubic (zinc blende) phase.[28] The particle diameter predicted from the optical data suggests quantum dots around 2 nm, much smaller than those reported by Alivisatos *et al.*[11] and Micic *et al.*[12] and are therefore expected to show an XRD pattern consistent with particles of a small crystalline domain. The low temperature of synthesis (167 °C) also limits the crystallization of the particles. EDAX analysis shows the presence of both In and As. The signal from silicon was due to the sample being supported on a silicon wafer (Fig. 4). The XRD pattern of samples prepared at 167 °C for 6 days showed a strong reflection from the 111 plane but weak reflections from the 311 and 220 planes, consistent with poorly crystalline/amorphous material. XRD data were not collected for samples with a shorter growth time. The width of the reflection from the 111 plane is consistent with particles with a diameter of *ca.* 0.98 nm (Scherrer equation), half the diameter predicted by the Brus equation. The TEM micrographs of samples synthesised over 6 days of growth show the presence of small particles with an average diameter of 2.32 nm $\pm$ 0.56 nm (24%) (Fig. 5). HRTEM analysis of the nanoparticles revealed no discernible lattice fringes, suggesting that the particles were amorphous. It may be that the particles are only partially crystalline, with a crystalline core of *ca.* 1 nm^3 and an amorphous surface shell. The validity of the effective mass approximation for amorphous particles is unsure, so the utiility of the Brus equation in this case may be questioned. The InAs nanocrystals obtained in this work are smaller than those prepared by other organometallic routes, for which the smallest particles were reported to be 2.5 nm.

^{1}H NMR shows the presence of the capping group, however the resonances are not clear which is attributed to the inhomogenous distribution of magnetic environments on the nanoparticle surface. Infra-red spectroscopy also shows the presence of the capping group band (Table 2). The indium nitrogen stretch has been tentatively identified (ν(In–N)) at 459 cm^{-1} inferring that binding to the nanoparticulate surface occurs through the heterocyclic nitrogen. This assignment was made by reference to the work of Goldstein *et al.*, who stated that ν(M–N) vibrations are predominantly found between 200 and 300 cm^{-1}, but can be found up to 600 cm^{-1}.[29]

Manipulation of Q-InAs

One of the advantages of using a liquid capping agent is that the sample can be redispersed in the solvent used to cap them. In contrast TOPO capped dots are dispersed in hydrocarbons (TOPO is a solid at room temperature). TOPO capped dots can

Table 1 Selected information on optical properties of Q-InAs

Reaction conditions	Band edge/eV (nm)	Emission $\lambda_{\mathrm{max.}}$/eV (nm)	Stokes shift/eV (nm)	Predicted diameter/nm
30 min growth	2.96 (418)	2.59 (478)	0.37 (60)	5.19
6 days growth	2.63 (471)	2.25 (550)	0.38 (79)	5.55
6 days growth + further precursor	2.43 (510)	2.14 (577)	0.29 (67)	5.81

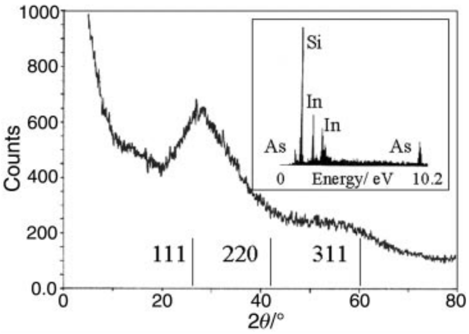

Fig. 4 XRD pattern for Q-InAs, showing the major Miller indices expected for InAs. Inset; EDAX analysis of InAs nanocrystals.

be manipulated into thin films by controlled crystallisation from solution or by deposition onto Langmuir–Blodgett films.[30]

A sol of 4-ethylpyridine-passivated InAs dispersed in 4-ethylpyridine could be spin coated onto various substrates. AFM showed the particles deposited onto glass with no evidence of close packing (Fig. 6) with a top layer depth profile of *ca.* 7 nm. The film thickness was found to be approx. 10 microns (Fig. 7). The SEM image shows vertical columns typical of spin coated films due to the quick drying procedure and relatively high forces experienced during processing.

Determination of nanoparticle diameter by AFM is unreliable due to microscopic enlargement, often overestimating particle dimensions.[31] However, if the AFM image is inspected carefully, it can be seen that the surface consists of spherical particles approx. 15–25 nm in diameter, an unusually large increase in diameter from *ca.* 2.5 nm. It is therefore suggested that the bridging ligand bipyrimidine binds the dots in an agglomerate. We estimated an average of 65 particles per agglomeration.

AFM images of InAs on GaAs show islands of agglomeration similar to those observed for TOPO capped CdSe encapsulated in a polymer host (Fig. 8).[32,33] Earlier studies have shown that nanocrystals of InP capped with 4-ethylpyridine form a framework, presumably of an organic, polymeric nature.[10] The cross linking of pyridine capped particles is well documented, however this behaviour is poorly understood.[34,35]

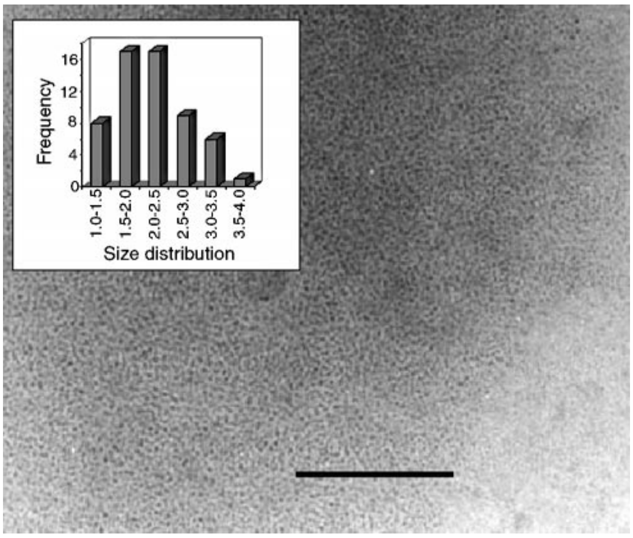

Fig. 5 TEM image of Q-InAs synthesised at 167 °C for 6 days, bar = 100 nm.

Table 2 Selected infrared spectroscopic data for Q-InAs and 4-ethylpyridine

Q-InAs–4-ethylpyridine/cm^{-1}	Free ligand/cm^{-1}	Assignment
1606	1608	ν(C–C)
1417	1394	ν(C–C)
—	1135	ν(C–H)
1066	1062	ν(C–H)
777	773	ν(C–H)
459	—	ν(In–N)

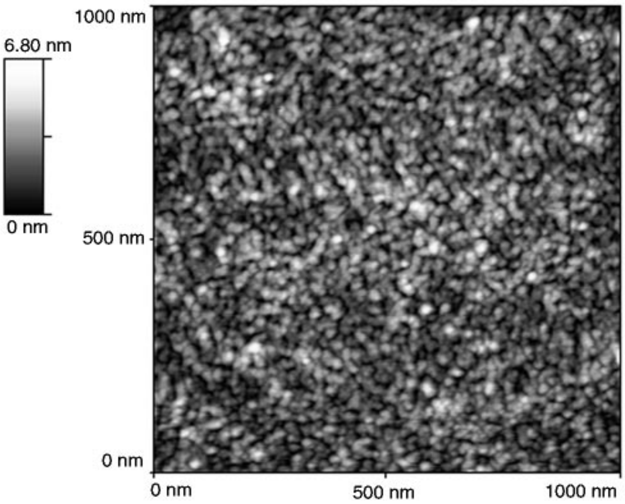

Fig. 6 AFM image of Q-InAs spin coated glass.

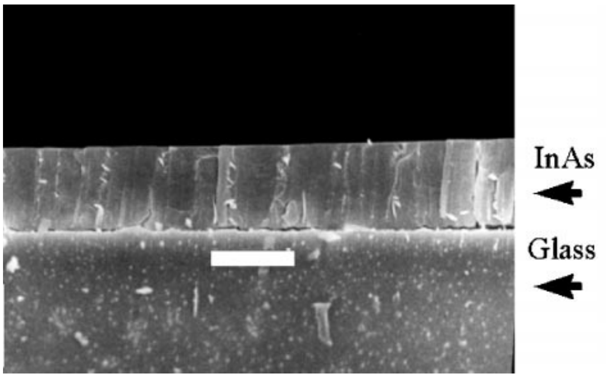

Fig. 7 SEM side profile of InAs film on a glass substrate, bar = 10 microns.

Murray *et al.* have produced superlattices of TOPO capped CdSe by evaporation of an octane–octanol solution under reduced pressure, inducing crystallisation into an ordered close packed array of particles.[36] The application of a gentle vacuum (*ca.* 0.05 Torr) to a 4-ethylpyridine solution of Q-InAs at room temperature resulted in the formation of a glass, which was then washed with light petroleum. The glass had an XRD pattern consistent with the nanoparticles used to produce it and

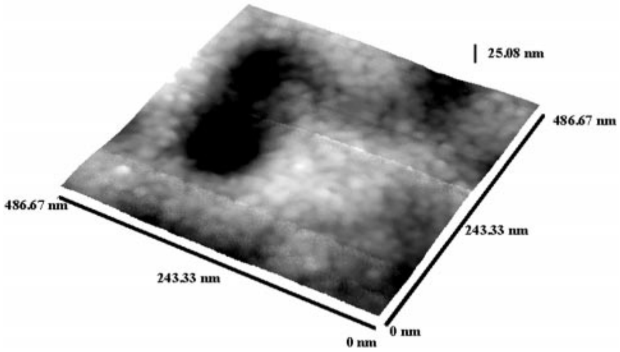

Fig. 8 AFM image of Q-InAs (6 days growth) spin coated onto GaAs substrate.

exhibited no evidence for a superlattice.[36] The reason for glass formation rather than a superlattice is attributed to the relatively large size distribution when compared to analogous II–VI superlattices. The nanoparticulate CdSe prepared by Murray *et al.* had a size distribution of *ca.* 5%. Prior to manipulation into a superlattice, the CdSe was size fractionated, decreasing the size distribution further. InAs used in this study was found to be unaffected by size fractionation and therefore probably had too large a size distribution for effective crystallisation into a lattice. However, that 4-ethylpyridine capped InAs was found to be easily manipulated into a glass under such mild conditions is surprising.

Conclusions

Nanoparticles of InAs, *ca.* 2.5 nm in diameter and capped with 4-ethylpyridine, have been prepared from metalorganic precursors. The optical and structural properties have been investigated and the quantum size effects clearly demonstrated. The manipulation of a 4-ethylpyridine solution into films and glass have been achieved, and the surface of such films has been investigated by AFM.

Acknowledgements

We thank Keith Pell (Basic Medical Science, QMW College) for SEM and EDAX, Graeme Briers (Dept. Materials, IC) for TEM and Richard Sweeney (Dept. Materials, IC) for XRD. We also acknowledge British Telecom and EPSRC for Funding *via* a CASE award (MG). POB was the Sumitomo/STS Professor of Materials Chemistry at Imperial College and acknowledges the support of the Royal Society as the Amersham International Research Fellow during the period this work was carried out (1997–1998).

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