

InAs_xSb_{1-x} alloy nanocrystals for use in the near infrared†

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InAs_xSb_{1-x} alloy nanocrystals for the near-infrared, which have quite a monodisperse crystalline structure of 2.5–3.0 nm and are of a zinc blend structure, are developed.

Semiconductor nanocrystals (quantum dots, QDs) have attracted attention due to their potential use as tunable fluorescent markers in biological imaging, display devices, photovoltaics, and lasers.¹ QDs have physical properties that can be controlled by changing their composition, for example, photoluminescence can be fine tuned by composition changes in the homogeneous alloy, as explained by Vegard's law² and the compositions of alloy QDs can be controlled by changing the precursor concentration. In the case of alloy synthesis using the colloidal method, most studies have focused on II–VI family, which include CdZnS,³ CdSeTe⁴ and CdZnSe,⁵ because of the synthetic difficulties presented by the III–V QDs. Major advances in pure and alloy III–V QDs have been achieved using physical methods such as molecular beam epitaxy, and only a relatively limited number of reports on InAs and InP using colloidal methods have been published.⁶ However, QDs by physical method are useless in bio-applications because of water incompatibility. Alloy III–V QDs can emit tunable near-infrared fluorescence and are less toxic than II–VI QDs containing cadmium. Therefore, many researchers in biomedical areas are interested in the synthesis of solvent-soluble alloy III–V QDs and recently, Kim *et al.* reported the synthesis and application of InAsP alloy QDs using colloidal method.⁷

In this paper, we describe the synthesis of InAs_xSb_{1-x} alloy quantum dots using a colloidal method. InSb, a narrow bandgap semiconductor (0.18 eV) compared with InAs (0.38 eV), is an interesting mid-infrared emitting fluorophore and detector,⁸ however, it has not been prepared using a colloidal method. The synthetic procedure used in the present study, is similar to the method developed by Peng *et al.*⁶ for the production of InAs_xSb_{1-x} QDs, using indium acetate (In(OAc)₃), tris(trimethylsilyl)antimony ((TMS)₃Sb), and tris(trimethylsilyl)arsine ((TMS)₃As) as indium, antimony, and arsenic precursors, respectively. The antimony and arsenic precursors were synthesized as described in the literature,^{9†} and injected into a 1-octadecene solution containing In(OAc)₃ and oleic acid at 300 °C (for nucleation) and then maintained at 270 °C for 30 min (for growth). The detailed experimental procedures can be found in the Supporting Information.† Elemental analyses by wavelength dispersive X-ray spectroscopy (WDS) show that injected As : Sb ratios of 90 : 10, 66 : 33, and 50 : 50 resulted in

QD compositions with As : Sb ratios of 97 : 3, 90 : 10, and 86 : 14, respectively, which reflects the different reactivities of the arsenic and antimony precursors. As the antimony ratio was increased, much black aggregate was observed and stable alloy QDs could not be obtained. This is supposed to be due to the size difference (16%) between the arsenic and antimony atoms, which exceed the limit for homogeneous alloy formation (15%), as stated by the Hume-Rothery rule.¹⁰ The alloy QDs presented here were engineered to emit in the 770 to 870 nm range. Increasing the antimony composition led to a peak-shift of the first excitonic absorption and a photofluorescence change to the red due to the narrower bandgap of bulk InSb as compared with bulk InAs. In addition, such composition changes led to peak broadening of first excitonic absorption and wide emission FWHM (full width at half maximum; InAs: 84 nm, InAs_{0.97}Sb_{0.03}: 120 nm, InAs_{0.90}Sb_{0.10}: 151 nm, InAs_{0.86}Sb_{0.14}: 164 nm). These results were not caused by size distribution changes but rather by the characteristics of the ternary alloy.⁵ Fig. 1(c) shows the peak positions of the

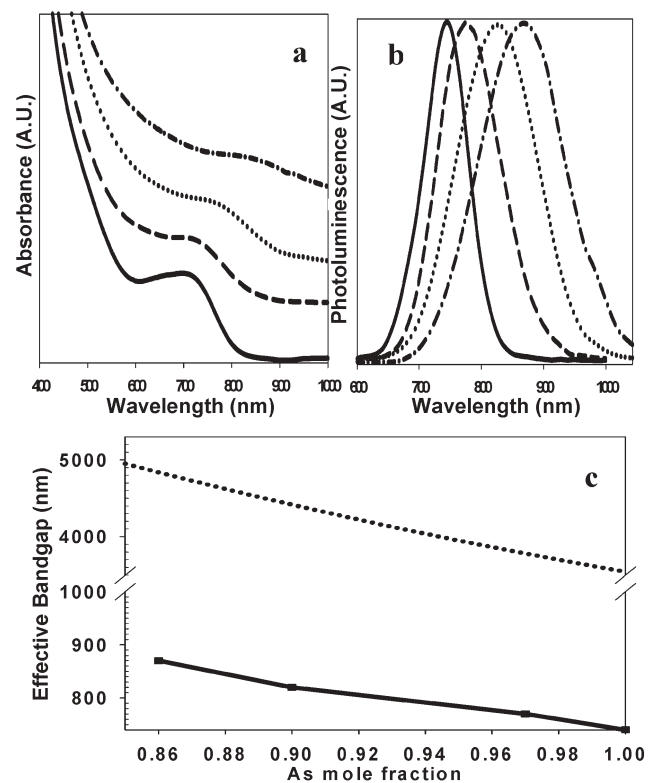


Fig. 1 Absorbance (a) and photoluminescence (b) of InAs (solid line), InAs_{0.97}Sb_{0.03} (dashed line), InAs_{0.90}Sb_{0.10} (dotted line), InAs_{0.86}Sb_{0.14} (dash-dotted line). (c) Plot of band gap of bulk materials (dashed line, ref. 10) and the emission peak wavelength as a function of arsenic content (solid line).

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† Electronic supplementary information (ESI) available: TEM image of InAs_{0.97}Sb_{0.03} and experimental details. See DOI: 10.1039/b611099a

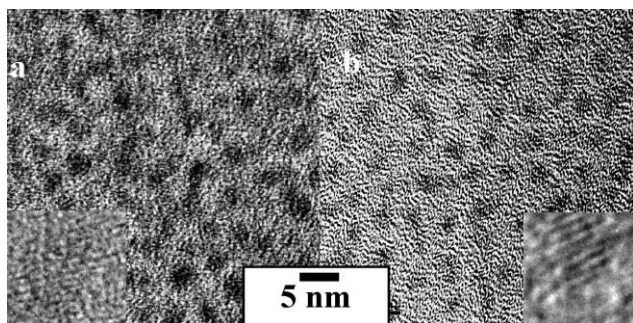


Fig. 2 TEM images InAs_{0.86}Sb_{0.14} (a), InAs_{0.90}Sb_{0.10} (b).

photoluminescences from alloy QDs (solid line) and the bandgaps of the bulk alloy (dotted line) as a function of arsenic mole ratio, which have a similar shape. The alloy QDs showed weak fluorescence due to the oxidative properties of III-V QDs (QY < 1%).

TEM images showed that the dots have roughly similar sizes by different composition (Fig. 2a: InAs_{0.86}Sb_{0.14} ($d_{ave} = 3.01$ nm, $\sigma = 0.40$ nm), Fig. 2b: InAs_{0.90}Sb_{0.10} ($d_{ave} = 2.73$ nm, $\sigma = 0.28$ nm), InAs_{0.97}Sb_{0.03} (Supporting Information, $d_{ave} = 2.50$ nm, $\sigma = 0.35$ nm†)). The inset image in Fig. 2a and 2b shows that alloy QDs produced have a single crystalline structure. Pure InAs QDs synthesized using this method have sizes of about 2 nm.

To confirm the existence of antimony, X-ray photoelectron spectroscopy (XPS) analysis was performed on InAs_{0.97}Sb_{0.03} alloy QDs with the lowest antimony composition and showed distinct indium, arsenic and antimony peaks (Fig. 3). Though powder X-ray diffraction (XRD) patterns showed complex peaks due to indium oxide of the (222) reflection at 31°, the (400) reflection at 35°, and the (440) reflection at 51°, the zinc blend structure of the alloy QDs was evident, which was indexed to the scattering from the (111), (220), and (311) planes of the alloy dots (Fig. 4). The possibility of a homogeneous alloy is not convincing because no continuous peak shift was obvious.

We also tried to synthesize InP_xSb_{1-x} alloy quantum dots using colloidal method. The PL peak positions of the InP_xSb_{1-x} alloys were similar to those of InAs_xSb_{1-x} alloys, however, the large size difference (28%) between the sizes of the phosphine and antimony atoms resulted in very weak emission.

In summary, we have developed alloy QDs composed of InAs_xSb_{1-x}, which show tunable emission from 770 to 870 nm. They are quite monodisperse crystalline of 2.5–3.0 nm and are of a zinc blend structure.

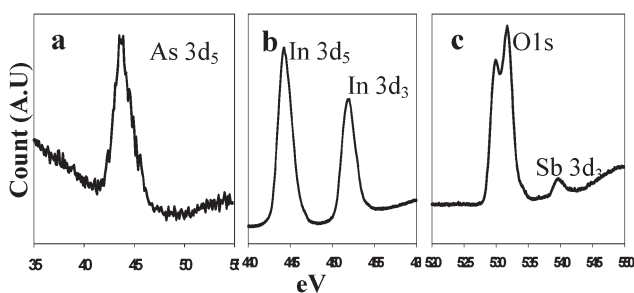


Fig. 3 XPS spectra of As (a), In (b), Sb (c) for InAs_{0.97}Sb_{0.03}.

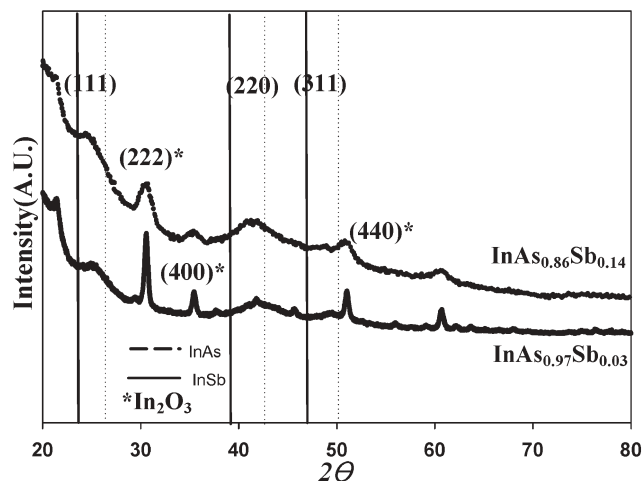


Fig. 4 Powder XRD patterns of InAs_{1-x}Sb_x alloyed QDs; Solid line (bulk InSb) and dotted line (bulk InAs); InAs_{0.86}Sb_{0.14} (dot), InAs_{0.97}Sb_{0.03} (solid).

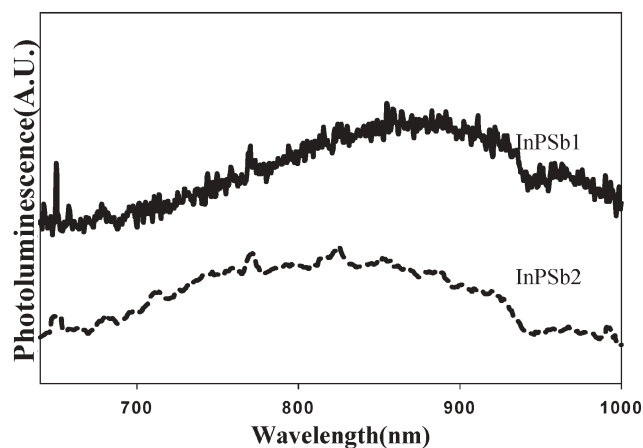


Fig. 5 Photoluminescence of InPSb1 (solid line: precursor ratio of P and Sb = 1 : 1) and InPSb2 (dashed line: precursor ratio of P and Sb = 2 : 1).

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