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ns or fs pulsed laser ablation of a bulk InSb target in liquids for nanoparticles synthesis

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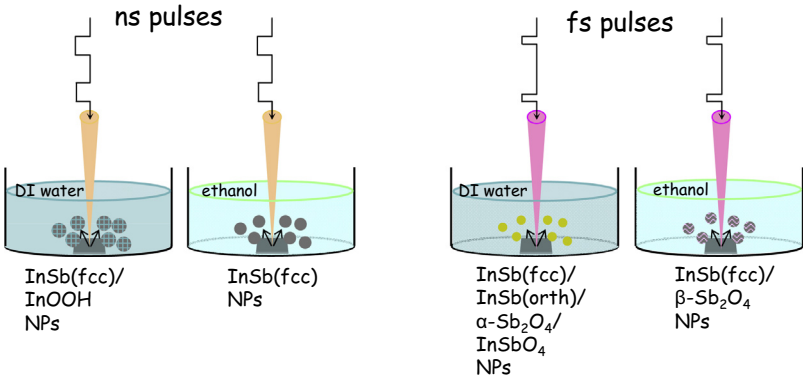
GRAPHICAL ABSTRACT



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ABSTRACT

Laser ablation of bulk target materials in liquids has been established as an alternative method for the synthesis of nanoparticles colloidal solutions mainly due to the fact that the synthesized nanoparticles have bare, ligand-free surfaces since no chemical precursors are used for their synthesis. InSb is a narrow band gap semiconductor which has the highest carrier mobility of any known semiconductor and nanoparticles of this material are useful in optoelectronic device fabrication. In this paper a bulk InSb target was ablated in deionized (DI) water or ethanol using a nanosecond (20 ns) or a femtosecond (90 fs) pulsed laser source, for nanoparticles synthesis. In all four cases the largest percentage of the nanoparticles are of InSb in the zincblende crystal structure with fcc lattice. Oxides of either In or Sb are also formed in the nanoparticles ensembles in the case of ns or fs ablation, respectively. Formation of an oxide of either element from the two elements of the binary bulk alloy is explained based on the difference in the ablation mechanism of the material in the case of ns or fs pulsed laser irradiation in which the slow or fast deposition of energy into the material results to mainly melting or vaporization, respectively under the present conditions of ablation, in combination with the lower melting point but higher vaporization enthalpy of In as compared to Sb. InSb in the metastable phase with orthorhombic lattice is also formed

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in the nanoparticles ensembles in the case of fs ablation in DI water (as well as oxide of InSb) which indicates that the synthesized nanoparticles exhibit polymorphism controlled by the type of the laser source used for their synthesis. The nanoparticles exhibit absorption which is observed to be extended in the infrared region of the spectrum.

1. Introduction

As it is well known, InSb is a narrow band gap semiconductor (E_g = 0.17 eV at 300 K) which has the highest room temperature electron mobility (~78,000 cm^2/Vs) of any known semiconductor. It is widely used in infrared detectors, ultrafast electronic circuits, thermal imaging cameras, terahertz radiation generation and other applications [1]. It also has the largest exciton Bohr radius (~60 nm) due to the extremely small electron effective mass ($m_e^* = 0.014\ m_0$) and the smallest exciton binding energy (0.5 meV) among all semiconductors. As a result, extremely strong quantum confinement is observed in even relatively large quantum dots (QDs) as compared to the other semiconductors [2].

Wet chemical synthesis of III–V QDs in general, is challenging mainly due to the fact that because of the strong covalent character of the two elements in the corresponding tetrahedrally bonded semiconductor, high temperatures or long reaction times are required for a slow crystallization which results in difficulties in controlling the nanoparticles size distribution [3]. The lack of reactive and/or stable enough antimony-based chemical precursors (trimethylsilyl derivatives) contrary to the phosphorous or arsenic-based ones has lead to difficulties in the synthesis of InSb nanoparticles in particular (as well as of GaSb nanoparticles) as compared to InP or InAs nanoparticles [4–6]. Only recently, monodisperse InSb QDs with size tunable absorption and emission have been synthesized by using alkylamides of antimony (Sb $[NMe_2]_3$) as the antimony source and reacting them with indium tris[bis(trimethylsilyl)-amide] (In$[N(SiMe_3)_2]_3$) [3] or reacting (Sb $[N(Si\text{-}(Me)_3]_2]_3$) with $InCl_3$ in oleylamine in the presence of lithium triethylborohydride ($LiEt_3BH$) [7]. Initial work on the synthesis of InSb QDs was focused on the growth of the dots on substrates by molecular beam epitaxy [8,9] or metalorganic vapor phase deposition [10], formation of InSb nanoparticles inside a SiO_2 matrix by RF co-sputtering deposition [11], low-energy cluster beam deposition of first indium particles on amorphous carbon films followed by the deposition of antimony molecules on the indium aggregates and subsequent dissolution into them [12] or solvothermal reduction synthesis by reacting $SbCl_3$ directly with In in benzene at 180 °C [13].

Binary semiconducting nanoparticles in general, synthesized in solution by chemical methods utilizing organometallic precursors bear on their surfaces insulating organic ligands and passivation layers such as oleic acid or oleylamine, chloride or trioctylphosphine oxide (TOPO) [3,7] which on one side renders them soluble in common organic solvents, a property important for the processing of the nanoparticles from solution but on the other side are detrimental for the operation of devices which are based on the use of nanoparticles. A well established alternative method for the synthesis of nanoparticles in solution involves laser ablation of a bulk target material while the material is immersed in a liquid [14]. The nanoparticles are formed by the debris which is generated as a result of the material's ablation and a nanoparticles colloidal solution is formed. Since no chemical precursors are utilized for nanoparticles synthesis, colloidal solutions with reduced reaction by-products, and most importantly nanoparticles with bare (ligand-free) surfaces are produced. This characteristic makes the laser ablation-based synthesis of semiconducting nanoparticles particularly attractive for the synthesis of nanoparticles which are to be used in the fabrication of nanoparticles-based devices since the charge transport in such devices is largely determined by the state of the nanoparticles surfaces. Throughout the years, nanoparticles out of a number of different materials have been synthesized using this method [14]. Laser ablation (20 ps, 1060 nm, 1 MHz, 1.6 μJ) of Si-doped GaAs in water or ethanol gives nearly stoichiometric nanoparticles which are surface passivated by a Ga-rich oxidized amorphous compound [15]. GaAs QDs with a narrow size distribution were synthesized by laser ablation (10 ns, 532 nm, 5 kHz, 4–14 J/cm^2) of GaAs in methanol or ethanol [16]. Laser ablation (10 ns, 337 nm, 10 Hz, 7 mJ) of InP in DI water produces nanoparticles with sizes in the 100 nm range which consist of InP but also of In oxides [17]. The laser ablation (5 ns, 10 Hz, 12 mJ) products of InP in ethanol consist of InP and In_2O_3 (4–10 nm nanoparticles size range) or P and In_2O_3 (2–3 nm nanoparticles size range) in the case of 532 or 266 nm ablation, respectively [18]. The nanoparticles synthesized using 266 nm were also found to be disordered or amorphous and P-rich while the ones synthesized using the 532 nm radiation were found to be In-rich [18].

This paper involves the synthesis of InSb nanoparticles in solution by using the method of laser ablation of a bulk InSb target material in deionized (DI) water or ethanol.

2. Experimental details

Laser ablation for nanoparticles generation in this work was carried out using two different laser sources: (i) a Q-switched Nd:YAG pulsed laser (pulse width = 20 ns) at beam wavelength of 1064 nm and pulse repetition rate of 1 kHz using a pulse energy of 380 μJ (~50 J/cm^2, beam radius ≈ 15 μm), and (ii) a femtosecond pulsed laser (pulse width = 90 fs) at beam wavelength of 800 nm and pulse repetition rate of 1 kHz using a pulse energy of 110 μJ (~11 J/cm^2, beam radius ≈ 18 μm). The target was a bulk piece of n-type InSb, ⟨1 1 1⟩ orientation, resistivity = 0.14–0.19 Ω cm and carrier concentration = (3.9–5.2) × 10^{13} cm^{-3} (at 77 K) with dimensions of 10 × 10 × 5 mm. Ablation was carried out with the target lying at the bottom of a beaker filled with 5 ml of either DI water or absolute ethanol. The height of the liquid above the target surface was ~10 mm. The beam was impinging vertically onto the horizontally lying target at the bottom of the beaker, scanning the target surface in a meander fashion (5 mm length, pitch 0.01 mm, scanning speed of 1 mm/s, 400 overscans) and ablation was carried out for ~15 or 35 min each time, for the ns or the fs case, respectively, resulting to ~1.8 mg or 1.35 mg and 1.1 mg or 0.9 mg of nanoparticles in the 5 ml of DI water or ethanol in the ns and fs case, respectively. Formation of the nanoparticles resulted in the initial solvents becoming from transparent to brownish (Fig. 1). The nanoparticles colloidal solutions were characterized by UV–vis spectrophotometry. The synthesized nanoparticles, from solution droplets dried out onto carbon coated copper grids, were characterized by Transmission Electron Microscopy (TEM) and High Resolution TEM (HRTEM) and from droplets dried out onto clean glass substrates by X-ray Diffraction (XRD) using a diffractometer with a Cu Kα source (λ = 1.5406 Å) and FT-IR reflectance spectroscopy. Crystal structures were determined from the