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# Indium phosphide nanocrystals formed in silica by sequential ion implantation

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**Abstract**

Fused silica substrates were implanted with: (1) phosphorus only, (2) indium only, and (3) phosphorus plus indium ions. Vibrational and electronic characterizations have been performed on the P only and In only samples to obtain an understanding of the thermal annealing behavior in order to obtain a meaningful guide for the fabrication of InP quantum dots (QDs) formed by sequential ion implantation of In and P in $SiO_2$. Thermal annealing procedures for InP synthesis have been established and InP quantum dots are confirmed by TEM, XRD and far infrared measurements. Far IR spectra show a single resonance at 323 $cm^{-1}$ rather than two absorption peaks in its counterpart of bulk InP crystals. The single band absorption is attributed to the surface phonon of InP quantum dots which will appear between transverse optical (TO) and longitudinal optical (LO) phonon modes of the bulk.


*Keywords:* InP quantum dot; Surface phonon; Ion implantation

## 1. Introduction

Research efforts devoted to the study of nanometer-sized semiconductor particles called quantum dots (QDs) are currently of great interest. In an effort to move toward the application of these materials to devices, initial research has focused on the properties of quantum dots and methods of synthesis. Many research groups have successfully fabricated quantum dots using a variety of methods in the solution phase [1] and in various host media. Such methods included inorganic synthesis, sol–gel synthesis [2], impregnation into porous dielectrics [3], self-assembly [4], vapor deposition [5] and ion implantation [6]. The interest in quantum dot research originates in part, from the dramatic changes in optical, structural and thermodynamic properties produced by particle size reduction and quantum confinement effects. However, future applications of these materials rest on producing new devices that make use of the modified properties of the QDs at nanoscale level.

One of the most intriguing characteristics of semiconductor nanocrystals is the change in optical properties as a function of size. As the size is reduced, electronic excitations shift to a higher energy. This originates from quantum confinement effects, which arises when excitons become spatially confined within the semiconductor particles. By comparing the physical size of the quantum dots $R$ with that of the exciton Bohr radius $a_b$, the degree of quantum confinement can be classified into three regimes [8,9]. (i) Weak confinement occurs when $R>a_b$. In this case, the Coulombic interaction between the electron and hole is dominant and the exciton experiences weak physical confinement. (ii) Intermediate confinement occurs when $R\sim a_b$. In this case, both Coulombic interaction and quantum confinement of the exciton are important. (iii) Strong

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confinement occurs when $R \ll a_b$. In this regime, the Coulombic interaction is negligible and the particle in the box concept can be readily applied. The dependence of the band gap shift on the particle size may be expressed as:

$$E = E_g + \frac{n^2 \hbar^2 \pi^2}{2\mu R^2} - \frac{1}{4\pi\varepsilon_0} \frac{1.8e^2}{\varepsilon^* R}, \qquad (1)$$

where $E_g$ is the band gap of a bulk semiconductor material, $n$ is the principal quantum number ($n$=1, 2, 3...), $\hbar$ is Planck's constant, and $\mu$ is the reduced mass of the electron and hole. The third term is due to Coulombic interaction, where $e$ is electronic charge and $\varepsilon^*$ is the static (relative) dielectric constant.

## 2. Experimental

### 2.1. Phosphorus only and Indium only

$P^+$ ions with an energy of 70 keV were implanted into Dow Corning 7940 optical grade silica substrates at room temperature. Nominal doses of 1, 3, 6 and $10\times10^{16}$ ions/cm$^2$ were chosen for implantation. Next, $In^+$ ions with an energy of 160 keV were implanted into additional silica substrates at the same nominal doses and experimental conditions.

The implanted substrates were annealed up to 1100 °C at 50 °C increments under a reducing atmosphere of 95% Ar and 5% $H_2$ for each set of samples. The initial annealing temperature was 200 °C with a typical annealing time of 15 min. The changes due to thermal annealing were monitored by measuring optical and vibrational spectra after each 15-min cycle.

### 2.2. Sequentially implanted phosphorus and indium

The III–V elemental pairs, P and In, were sequentially implanted into fused silica substrates (Dow Corning 7940) with $P^+$ implanted first to minimize the possible well-known bimodal distribution in the substrate. The substrate temperature and implantation energies were chosen to allow for maximum overlapping of the P and In implantation profiles. Phosphorous ions, with an energy of 70 keV, were implanted into silica substrates at the nominal doses of 1, 3, 6, and $10\times10^{16}$ ions/cm$^2$. During the $P^+$ ion implantation, the substrate temperature was maintained at 600 °C to facilitate nanoparticles formation. While $In^+$ ions were implanted at 160 keV into the same set of silica substrates at room temperature and the same nominal doses as the $P^+$ ions in order to produce a 1:1 ratio.

Rutherford backscattering spectrometry (RBS) together with Stopping Range In Matter (SRIM) simulations indicate that the highest peaks of the implantation concentration profiles for these samples are located at ~0.05 μm below the surface and could be approximated by a Gaussian distribution.

Under a reducing atmosphere of 5% $H_2$ and 95% Ar, the sample substrates were annealed at 750 °C for 30 min to promote the growth of InP nanocrystals. Before and after annealing, a set UV–Vis, NIR, and FIR spectra were collected to examine changes in electronic and vibrational spectra of the samples.

Optical transmission measurements were collected in the region of 3200–185 nm with a UV–Vis–NIR spectrophotometer (Hitachi 3501). All infrared reflectance and Raman spectra were collected with an FTIR and FT-Raman spectrometer (Bomem DA3 interferometer) at room temperature under a vacuum of ~1 Torr.

## 3. Results

### 3.1. Phosphorus only and indium only samples

RBS measurements for both In (only) and P (only) have been carried out (not shown). The implantation concen-

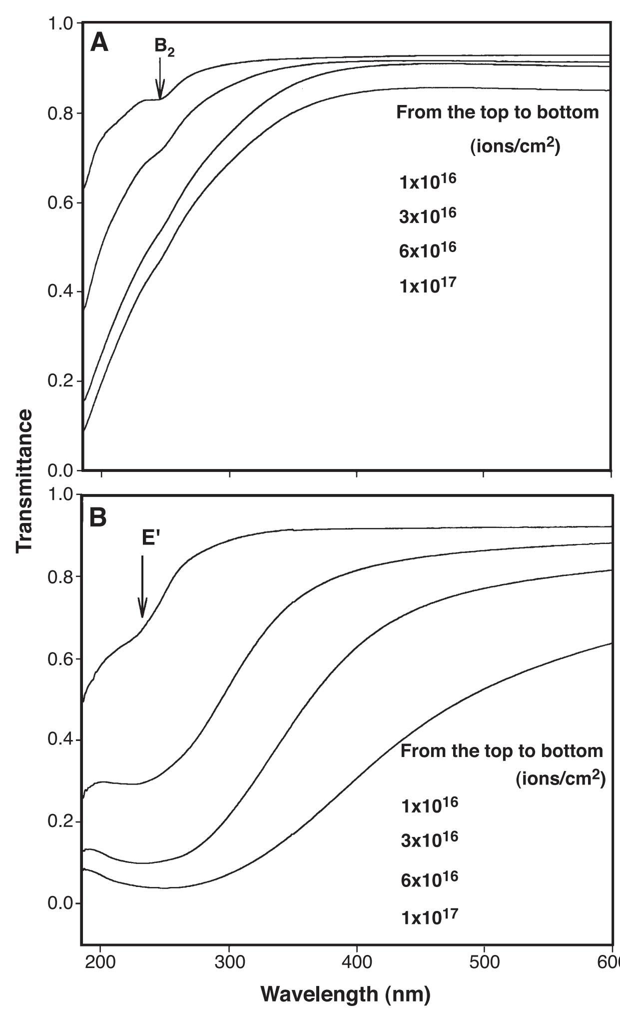


Fig. 1. Optical transmission spectra of as-implanted $P^+$ and $In^+$ ions implanted in silica substrates with nominal doses of 1, 3, 6 and $10\times10^{16}$ ions/cm$^2$. (A) P ion implanted only; (B) In ion implanted only.