The effect of high non-hydrostatic pressure on III-V semiconductors: zinc blende to wurtzite structural phase transition and multiphase generation

P S Pizani¹ and R G Jasinevicius²

¹ Universidade Federal de São Carlos, Departamento de Física, C. P. 676 - 13565-905 São Carlos, SP, Brazil
² Departamento de Engenharia Mecânica, Escola de Engenharia de São Carlos, Universidade de São Paulo, C.P. 359, CEP 13566-590, São Carlos, São Paulo, Brazil

E-mail:pizani@df.ufscar.br

Abstract. Raman scattering was employed to study structural phase transitions of InSb, GaSb and GaAs induced by highly non-hydrostatic pressures applied by mechanical impact, in which high compression/decompression rates are imposed to the sample. The results showed that is possible to produce several structural phases localized in different micrometric regions of the same sample: the zinc blende to possibly wurtzite structural phase transition and the generation of a multiphase state.

1. Introduction

At normal atmospheric conditions, III-V semiconductors are cubic with zinc blende structure. Under hydrostatic pressure, several structural phase transitions were observed experimentally and most of these observations were corroborated theoretically by computational simulations [1-5]. Theoretical results using plane-wave pseudo potential calculations suggested that some III-V semiconductors, in particular InSb, InP and GaAs, could have a wurtzite structure [6,7]. This prediction was never observed experimentally for InSb, GaSb and InP in bulk form, in which wurtzite would be a metastable phase. Recently reported results from diamond anvil cell (DAC) experiments indicated the formation of hexagonal wurtzite phase of GaAs, but which could only be obtained from a high pressure cubic structure of GaAs (SC16) and requires thermal treatments [8]. On the other hand, in small particles of InSb, with dimensions of about few nanometers, this structure was identified by using high-resolution transmission electron microscopy [9]. Moreover, an unusual structure was observed also in nanorods of InSb, with diameters less than ~ 30 nm, with an unit-cell volume twelve times larger than that of the -tin phase of InSb, into which the zinc blende transforms under hydrostatic pressure above 2 GPa [10]. The effects of non-hydrostatic pressure on semiconductor materials have been much less reported in the literature. Raman spectrum of a possible wurtzite phase was reported for indented InSb, observed only at the center of the triangular face of the Vickers imprint [11,12]. A similar transformation produced by shock wave compression was reported, in which a cubic to hexagonal phase transformation of diamond was observed [13].

In this paper we report about the synergetic combination of the micro-Raman technique, which allows the analysis of small regions (~ 1 micron square) of a sample, and the application of non-hydrostatic pressures by mechanical impact to small samples. With our technique, it is possible to apply high pressures for some tens of milliseconds, potentially generating new multiphase states of materials, which may be not observed under minute or hour long static pressure application in a DAC.
Contrary to the cases where DAC is used, our mechanical impact method (MIM) is very simple; samples are prepared in few minutes at ambient conditions, and can be worked before pressure is applied. Here we report on the effects of applying high non-hydrostatic pressures to InSb, GaSb and GaAs by MIM.

In these three semiconductors small micrometer-sized regions were observed, whose Raman spectra indicate wurtzite structure, corroborating partially the theoretical predictions for InSb and GaAs. For GaSb, although not predicted theoretically, a similar behavior was also detected. Moreover, some small regions were also observed with very rich Raman spectra, indicative of multiphase state, never reported in the literature.

2. Experimental
To apply non-hydrostatic pressure with high shear components we have designed a mechanical device as depicted in figure 1. Small samples, measuring about 0.2 mm × 0.2 mm × 0.5 mm or less were placed in the sample chamber and an impact was applied to the piston resting on the sample by a metallic cylinder of 5.6 Kg hitting on the piston with velocities up to 10 m/s, producing nominal pressures up to 500 GPa for times about 50 to 100 ms. The resulting sample is a very thin sheet and powder composed by flat particles. Under optical microscope, there are several different small regions with flat, faceted, lamellar or porous aspect, to mention just a few. This diversity would be expected because under these experimental conditions there is a radial distribution of the hydrostatic component, which decreases with increasing distance from the center of the sample, combined of very high uniaxial pressure.

Figure 1. Stainless steel device, used to apply high non-hydrostatic pressure via mechanical impact, composed by a piston a), guide/stopper b), and base c).

The samples used in this study were wafers of commercial InSb, GaSb and GaAs single crystals grown on the [001] surface. This direction was chosen because in the backscattering configuration with the incident and scattered light along [001] direction, the Raman spectrum has only a single peak, due to the light scattering by the longitudinal optical (LO) phonon, predicted by the Raman selection rules for the zinc blende structure of these three III-V semiconductors: at 190 cm⁻¹ for InSb, at 234 cm⁻¹ for GaSb and at 291 cm⁻¹ for GaAs. The presence of the peak at 179, 224 and 268 cm⁻¹ for InSb, GaSb and GaAs, respectively, due to the light scattering by the disorder-activated transverse optical phonon (DATO) and the broadening of the Raman peaks indicate structural disorder. So, the intensity ratio between the TO to LO Raman peaks can be used to probe the structural disorder.

The Raman scattering measurements were performed using a micro-Raman spectrometer with a triple monochromator and a CCD detector. An Ar⁺-Kr⁺ ion laser provided the excitation wavelengths, with the beam focused on the sample as a spot of about 1 micron square by a microscope with a 100X objective. Finally, all measurements were performed at room temperature, with the laser power kept at below 1 mW at the entrance of the microscope to avoid thermal effects on the spectra.

3. Results and Discussion
The Raman spectrum of the samples submitted to mechanical impact depends essentially on the region of the surface where the measurement is performed. Over most of the surface, whose visual
aspect is flat, the well-known spectra were found, with peaks due to highly disordered zinc blende structure (broadened Raman peaks of the disorder-active transverse optical (DATO) and longitudinal optical modes). Figure 2 displays, for reference, the Raman spectra of crystalline GaAs, GaSb and InSb in the zinc blende phase taken in backscattering geometry along the [100] direction, where it can be observed the LO modes only for the three materials. Into the regions where the surface seems clear under the optical microscope, the Raman spectra present three peaks attributed to the hexagonal wurtzite phase of GaAs, GaSb and InSb, as shown in figure 3.

![Figure 2. Raman spectra of crystalline [100]-oriented GaAs, GaSb and InSb, in the zinc blende structure, in backscattering configuration, showing the characteristic LO peak.](image)

![Figure 3. Raman spectra of GaAs, GaSb and InSb after mechanical impact. The Raman peaks are possibly characteristic of the hexagonal wurtzite phase.](image)

In this structural phase, group theory predicts one $A_1$, one $E_1$, two $E_2$ and two $B_2$ Raman-active modes, not all of them observed easily in a depolarized spectrum [14]. However, since the wurtzite structure, with four atoms in the primitive cell, is very similar to the zinc blende, with two atoms per primitive cell, the dispersion curves for wurtzite can be partially predicted from that of zinc blende by folding the Brillouin zone along the [111] direction. So it is expected that all frequencies of the wurtzite phase are lower than those of the zinc blende. For example, the $E_2$ modes in the wurtzite phase come from the TO(L) at about 230, 200 and 180 cm$^{-1}$ and TA(L) at about 70, 50 and 40 cm$^{-1}$ for GaAs, GaSb and InSb respectively, of the zinc blende phase [15]. The low-frequency modes were not observed in our experiments. It is also worth mentioning that, as expected, the atomic masses effect on the phonon frequencies can be seen in figure 2, with increasing frequencies decreasing the reduced mass: the reduced mass are about 36, 44 and 59 (from the atomic weight) for GaAs, GaSb and InSb, respectively.

Figure 4 shows the Raman spectra of the multiphase state of the three semiconductors, performed on regions that look like small faceted mountains, with a dark visual aspect under the optical microscope. An interesting point to emphasize is the inelastic light scattering efficiency, at least one order of magnitude greater than that of the zinc blende phase. A complex Raman spectrum is not easy to interpret, as it may result from the superposition of several different structural phases or from a single structural phase with low symmetry or with several atoms in the unit cell. A real possibility is that such a Raman spectrum could be attributed to a structural phase such as that reported in reference 9, since in this case there are several atoms in the primitive cell. To determine exactly the structures generated by the mechanical impact, it is important to employ suitable techniques for this purpose. Our preliminary attempts to determine this multiphase or new structural phase by conventional x-ray diffraction were unsuccessful, probably due to the fact that the crystallites occupy a very small volume relative to the disordered zinc blende-like phases. However, our findings are partially corroborated by Kishimura et al. [16], that reported X-ray diffraction analysis of InSb single crystals...
submitted to shock compression up to 24 GPa by using flyer plate impact. In addition to the zinc blend structure, peaks corresponding to \textit{Cmcm} or \textit{Immm} phases were observed. Furthermore, they found also some different and unidentified X-ray diffraction peaks not yet reported in the literature.

\textbf{Figure 4}. Raman spectra of GaAs, GaSb and InSb after mechanical impact, showing a multiphase phase generated by highly non-hydrostatic pressure.

\textbf{4. Conclusions}

The results of the present Raman scattering study of structural phase transitions of InSb, GaSb and GaAs induced by highly non-hydrostatic pressures applied by mechanical impact opened the possibility to produce several structural phases localized in different regions of the same sample. The mechanical impact method, which is very simple and direct, may lead to phase transformations that are not obtained by conventional methods such as applying hydrostatic pressures in diamond anvil cells. The main difference between these methods is that, in mechanical impact, very high shear components are present, and the pressure is applied in short periods of time. Furthermore, the samples can be worked before submitted to high pressures. For the three semiconductors studied, our method leads to the formation of a possible wurtzite phase and a new structural phase, whose Raman spectrum presents several peaks. The wurtzite phase of InSb, InP and GaAs was predicted by theoretical calculations. Our result showed also that GaSb may also have wurtzite structure, not predicted theoretically. The possibility of generating a wurtzite phase in GaAs at room conditions, for example, may be very interesting from the technological point of view, since in general in this phase the electronic band gap is greater than that in the zinc blende one, with optical emission in the blue or ultraviolet spectral range. Furthermore, the very different and new Raman spectra observed in some regions of the samples are indicative of a new and/or multiphase state of these three semiconductors. Finally, these results show that this subject is completely open to further contributions, mainly by using techniques suited to structural analysis.

\textbf{Acknowledgements}

This work was supported by the Brazilian agencies FAPESP, CNPq and CAPES.

\textbf{References}

[1] Mujica A, Rubio A, Munoz A and Needs RJ 2003 \textit{Rev. Mod. Phys.} 75 863
[2] Nelmes R J et al 1993 \textit{Phys. Rev.} B 47 35
[3] Nelmes R J and McMahon M I 1996 \textit{Phys. Rev. Lett.} 77 663
[4] Ackland G J 2001 \textit{Phys. Stat. Sol (b)} 223 361
[5] Costa S C, Pizani P S and Rino, J P 2002 \textit{Phys. Rev.} B 66 214111
[6] Wang S Q and Ye H Q 2002 \textit{J. Phys.: Condens. Matter} 14 9579
[7] Wang S Q and Ye H Q 2003 \textit{Phys. Stat. Sol (b)} 240 45
[8] McMahon M I and Nelmes R J 2005 Phys. Rev. Lett. 95 215505
[9] Besson D, Treilleux M, Hoareau A and Esnouf C 2000 Phil. Mag. 80 1139
[10] Yousuf M, Qadri S B and Skelton E F 2003 Appl. Phys. A 76 133
[11] Pizani P S et al. 2005 Proceedings of the First International Conference on Diffusion in Solids and Liquids (Aveiro, Portugal) 551
[12] Kailer A, Nickel K G and Gogotsi Y G 1999 J. Raman Spectrosc. 30 939
[13] He H et al 2002 Appl. Phys. Lett. 81 610
[14] Arguello C A, Rouseau D L and Porto S P S 1969 Phys. Rev. 181 1351
[15] Perlin P et al. 1992 Phys. Rev. B 45 83
[16] Kishimura H and Matsumoto H 2013 AIP Conf. Proc. 58 54