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Raman-active modes of porous gallium phosphide at high pressures and low temperatures

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Abstract

Porous gallium phosphide (GaP) with a honeycomb-like morphology and a skeleton relative volume concentration $c = 0.7$ was investigated by Raman spectroscopy under pressure up to 10 GPa at $T = 5$ K. The porous samples were prepared by electrochemical etching. The transverse optical (TO) and longitudinal optical (LO) mode frequencies were found to shift with pressure similarly to those of bulk GaP. As in bulk GaP, the TO feature of the porous GaP exhibits a pressure-induced narrowing which is interpreted in terms of a Fermi resonance. The scattering intensity observed on the low-frequency side of the LO mode is attributed to surface-related Fröhlich mode scattering. The latter results are interpreted on the basis of an effective medium expression for the dielectric function. The Raman spectra indicate that both the morphology and degree of porosity are unaffected by pressure in the range investigated.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

Porous III–V compounds have recently attracted interest [1–5] due to their potential applications in electronics and photonics [6]. By changing the morphology and characteristic dimensions of the porous skeleton entities, the material properties can be modified in a controlled manner. When the characteristic dimensions are smaller than the exciton Bohr

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radius, the quantum size effects cause an increase of the band gap and strong modifications of the optical and electrical properties. Considerable changes in the optical properties of porous materials are also expected if the characteristic dimensions are much larger than the exciton Bohr radius. For instance, when electromagnetic radiation with a wavelength larger than the pore dimensions propagates through a porous structure of a polar material, the electric-field-induced polarization of the skeleton entities results in the excitation of electric dipoles vibrating at specific frequencies. These vibrations, not present in the bulk material, give rise to optical modes in Raman scattering, located in the frequency gap between the bulk transverse optical (TO) and longitudinal optical (LO) phonons of the binary compound. The surface-related optical modes, predicted by Fröhlich [7], have been calculated for small ionic crystals of different morphology by Fuchs and Kliewer [8, 9] and have been observed in infrared (IR) spectra of powders by many authors.

Fröhlich-type surface modes in mesoporous samples can be measured more easily in IR absorption and reflectance spectra than in Raman scattering because typical wavelengths in the IR experiments are much larger than the laser wavelengths commonly used in Raman spectroscopy. According to Ruppin [10], only porous gallium phosphide (GaP) samples with a crystallite size smaller than 100 nm are candidates for use in the study of the Fröhlich modes by Raman spectroscopy. Under such conditions, the scattering efficiency of the lowest-energy Fröhlich mode ($l = 0$) is comparable with those of bulk LO and TO phonons, the contributions of Fröhlich modes with $l > 0$ being negligible.

Porous GaP layers and free-standing membranes, in addition to powders, were used in investigations of Fröhlich mode behaviour [11–15]. Several theoretical calculations of these modes have dealt with the case of isolated particles [7–10]. In porous layers and free-standing membranes, a suitable effective medium expression for the dielectric function needs to be taken into account. Effective medium calculations [15–18] predict a longitudinal–transverse splitting of the Fröhlich mode. This splitting in a porous polar material was first observed by Danishevskii *et al* [19] and by Macmillan *et al* [20] in the IR reflectance spectra of porous 6H-SiC layers.

The study of porous materials under hydrostatic pressure is expected to provide additional insight into the properties of the skeleton entities. In a recent pressure Raman study [12] of porous GaP at 300 K, a rather broad feature located between the TO and LO modes was observed and attributed to Fröhlich surface scattering. A longitudinal–transverse splitting of the Fröhlich mode could not be detected in that work, but was observed in low-temperature Raman measurements at ambient pressure [21].

In this work we report Raman spectra for porous GaP measured at low temperature and under high hydrostatic pressures. We have obtained the pressure dependences of the bulk-like TO and LO mode frequencies and the corresponding Raman line as well as the frequencies of surface-related modes. Our results for the bulk-like phonons are compared with recently reported experimental and theoretical results for bulk GaP, and our results for the Fröhlich modes are compared with previous experimental results on porous samples and with a simulation based on an effective medium expression for the dielectric function.

2. Experimental details

The 30 μm thick porous membranes used in the present study were prepared on (100)-oriented Te-doped liquid-encapsulation-Czochralski-grown GaP substrates with a free electron concentration $n = 5 \times 10^{17}$ cm^{-3} at 300 K. The porosity was introduced by etching the samples for 30 min in a 0.5 molar aqueous solution of sulfuric acid at a current density 5 mA cm^{-2} using a conventional electrochemical cell with a Pt working electrode. According