Micro-Raman-scattering study of surface-related phonon modes in porous GaP

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(Received 18 October 1996)

Porous GaP layers prepared by electrochemical dissolution of (100)-oriented bulk material have been studied by micro-Raman spectroscopy. The anodization causes a breakdown of the polarization selection rules, inherent to a (100) surface, accompanied by a downward shift of the LO-phonon frequency and by the appearance of a surface-related vibrational mode in the gap between the bulk optical phonons. The frequency of the surface-related mode was found to decrease from 398 to 394.3 cm^{-1} with increasing anodization current. A Raman line-shape analysis based on the light scattering due to the electro-optic and deformation potential mechanisms is presented. [S0163-1829(97)03312-2]

Like Si, compound semiconductors such as GaP and InP are currently investigated in the form of porous layers. The reduction of dimensions to nanometer sizes changes drastically the physical properties of the compounds under consideration and hence opens alternative possibilities for their applications. For instance, ultraviolet luminescence at energies as high as 3.3 eV was observed in porous gallium phosphide obtained by dissolution of crystalline substrates in a HF-based electrolyte.[1] This short-wavelength light emission was ascribed to charge-carrier confinement in crystalline quantum wires of about 25 Å in diameter, the quantum size effect having been supposed to transform the indirect-band-gap (E_g = 2.34 eV at 300 K) material into a direct-gap one. Recently, a strongly enhanced photoresponse was observed in *n*-GaP electrodes made porous by anodic etching in sulphuric acid solution.[2,3] It is to be noted that the photocurrent quantum yield was considerably increased for both $h\nu \geqslant E_g$ and $h\nu < E_g$.[3]

A subject of special interest is the extremely large surface inherent to porous layers. One expects, in this regard, porous layers to be suitable for the purpose of studying surface-related vibrational modes. A surface-related phonon mode at 397 cm^{-1} was recently observed in porous GaP fabricated by anodic etching of bulk material in a solution of HF in ethanol.[4] Since analogous phonon modes have not been found, for example, in extensively studied porous Si, the surface-related mode observed in porous GaP may be interpreted in terms of a Fröhlich mode, which should occur in small structures of heteropolar semiconductors in the region between the TO and the LO modes. The Fröhlich mode frequency depends on the shape of the microstructure as well as on the concentration and the dielectric constant of the surrounding material.[5–8] In this work we study the changes in micro-Raman spectra of GaP induced by electrochemical dissolution of bulk material at different anodic current densities in order to explore the properties of the surface-related mode. The influence of local heating caused by the absorption of the probing laser irradiation upon micro-Raman spectra is investigated as well.

The porous layers have been prepared by anodic etching of (100)-oriented n-GaP:S substrates in a solution of sulphuric acid. Prior to etching, the samples were subjected to 5 MeV of α-particle irradiation (^{238}Pu source) at a dose of 9×10^{11} cm^{-2}. The anodization process was carried out for 30 min with current densities in the inverval from 5 to 60 mA/cm^2 in a conventional electrochemical cell with a platinum working electrode. During dissolution the samples were kept in the dark. The porous layers obtained were 10–15 μm thick and exhibited light-yellow or light-green color, easily distinguishable from the dark-yellow one of the bulk substrates. According to images obtained by a scanning electron microscope, the GaP skeleton remaining after dissolution consists mainly of thin walls and isolated columns with transverse sizes up to tens of nanometers, their spatial distribution being rather uniform. Unlike in Ref. 1, no residual islands of bulk GaP were observed. Electron microprobe analysis evidenced the stoichiometric composition of porous GaP layers, while Raman-scattering (RS) data proved their crystallinity and the absence of an amorphous phase.

The micro-Raman spectra were excited with the 514-nm line of an Ar^+ laser. To avoid thermal effects, in typical experiments the laser beam power at the sample surface was 1 mW with the light spot diameter of about 2 μm. When studying heating effects caused by the absorption of the laser irradiation, the beam power was changed within the interval from 1 to 15 mW. The scattered light, in a nearly backscattering geometry, was analyzed by a triple monochromator (Jobin-Yvon, T64000) with a spectral resolution 0.5 cm^{-1}.

Figure 1, curve 1 illustrates the micro-Raman spectrum from a bulk *n*-GaP crystal; curves 2 and 3 were obtained from the samples anodized at current densities of 5 and 15 mA/cm^2. The as-grown crystal exhibits only one RS band

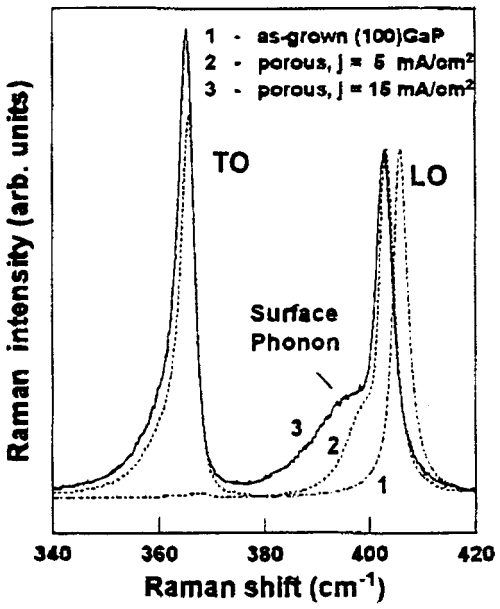

FIG. 1. Unpolarized micro-Raman spectra of bulk GaP and porous layers. The curves are normalized to the intensity of the LO peak.

centered at 404 cm^{-1}, which corresponds to the Brillouin-zone-center LO phonon. The $\mathbf{q} = 0$ TO phonon is forbidden in (100) geometry and therefore it is absent in the bulk GaP spectrum. The anodization process leads to a small downward frequency shift and broadening by 15–20 % of the LO-phonon band accompanied by a significant RS signal intensification (up to 5–6 times). A complete breakdown of the polarization selection rules was observed in our experiments, which is reflected in Fig. 1 by the appearance of a strong TO-phonon band. Like the LO phonon, the TO phonon also exhibits a downward frequency shift with increasing the anodization current.

TABLE I. Numerical results of the deconvolution of micro-Raman spectra: shift (ω), full width at half height (b), and ratio (A_S/A_{LO}) of the areas of Raman bands corresponding to surface and LO phonons.

	LO-phonon		Surface phonon		
Anodic current (mA/cm^2)	ω (cm^{-1})	b (cm^{-1})	ω (cm^{-1})	b (cm^{-1})	$\frac{A_S}{A_{LO}}$
5	403.3	3.2	398.0	6.7	0.35
15	402.9	3.6	394.3	15.0	1.11

Another important feature caused by anodic etching is the emergence of a RS peak positioned in the frequency gap between the TO and LO phonons. As seen from Fig. 1, this peak appears as a well-defined shoulder on the low-energy side of the LO band. According to the results of a spectral deconvolution (Fig. 2), the peak under consideration broadens and shifts to lower frequencies with increasing anodization current density corresponding to decreasing GaP concentration. The maximum of the peak corresponds to 398 cm^{-1} for $j=5$ mA/cm^2 and to 394.3 cm^{-1} for $j=15$ mA/cm^2, respectively (Table I).

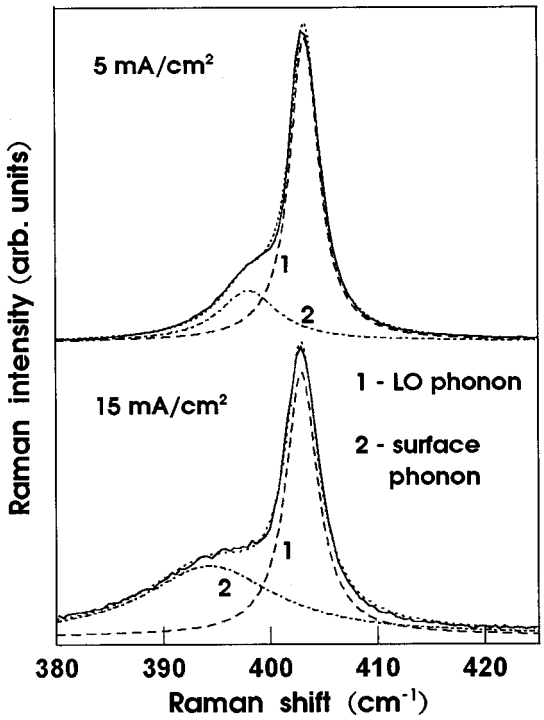

FIG. 2. Deconvolution of micro-Raman spectra of porous GaP layers prepared at different anodization current densities.

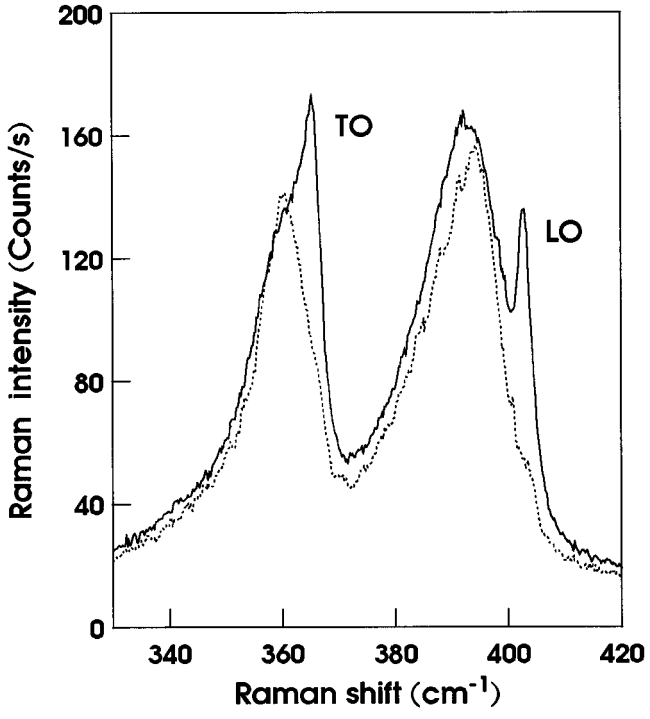

FIG. 3. Micro-Raman spectra from especially selected regions of a porous GaP layer prepared at a current density of 60 mA/cm^2.

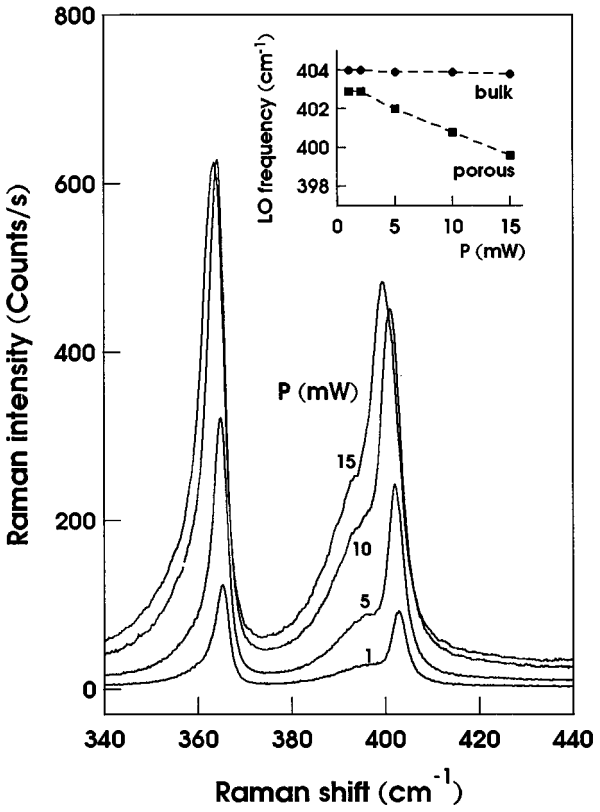

FIG. 4. Dependence of micro-Raman spectra upon the power P of the exciting laser beam. The porous layer was prepared at a current density of 15 mA/cm^2. The inset shows the shift of the LO band position of the porous layer in comparison with that of bulk n-GaP.

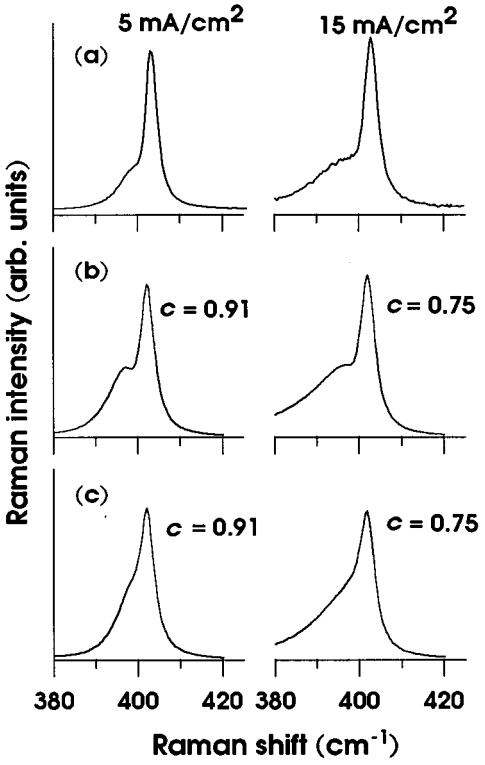

FIG. 5. Comparison of (a) experimental spectra with theoretical curves obtained in a (b) column and (c) sphere approximation.

It is important to note that the micro-Raman spectra were the same when taken from different areas of the porous layers prepared at current densities of 5 and 15 mA/cm^2. Only samples subjected to dissolution at $j>40$ mA/cm^2 were found to exhibit rather different spectra when scanned by the laser beam (Fig. 3). Apart from that, the broad RS band in the region 80–200 cm^{-1}, inherent to amorphous GaP,[9] was not observed in the porous layers studied. This proves the crystallinity of GaP skeleton remaining after dissolution.

Since the GaP skeleton consists of nanometer-size structures, a reduced thermal conductivity may be expected for porous layers in comparison with the bulk material leading to an enlarged temperature enhancement with increasing excitation power. In order to throw light upon this matter, the micro-Raman spectra have been measured at different powers of the exciting laser beam. A RS signal intensification occurs with increasing the excitation power. No changes in the frequency position and full width at half maximum of RS peaks were observed at $P\leqslant 2$ mW. At the same time a pronounced broadening and low-frequency shift of RS bands occur in porous layers with a further increase of the excitation power (Fig. 4). For the purpose of comparison Fig. 4 presents the dependence of the Raman peak position upon the excitation power for both the as-grown crystals and porous layers fabricated at $j=15$ mA/cm^2. We have estimated the local temperature in porous GaP layers under laser-beam excitation using the value of the temperature shift gradient for optical phonon frequencies in GaP.[10] For $P=15$ mW it equals about 160 °C.

Taking into account the nearly symmetric shape of the LO-phonon bands as from the LO mode (Fig. 3), we propose the surface-related mode to be a Fröhlich mode as first observed by Raman measurements in GaP microcrystals.[5] On the basis of a one-pole approximation for the calculation of an effective dielectric constant[8] we obtain for a system of oriented columnlike pores in GaP interpolated to a system of GaP columns in air

$$\varepsilon_{\text{eff}}=\varepsilon_1\left(1-\frac{c-\beta}{s}-\frac{\beta}{s-s_0}\right), \tag{1}$$

with $s=\varepsilon_1/(\varepsilon_1-\varepsilon_2)$, $\beta=(1/2s_0)c(1-c)$, and $s_0=\frac{1}{2}-c/2+\frac{3}{2}c^2-c^3$. Here c denotes the GaP concentration, $\varepsilon_1=1$, and $\varepsilon_2=\varepsilon_2(\omega)$ is the dielectric function of bulk GaP in the phonon region. From the poles and zeros of $\varepsilon_{\text{eff}}(\omega)$ one can deduce an unchanged (compared with the bulk value) TO phonon, a downward shift of the LO phonon with decreasing c, and a Fröhlich mode, degenerate at $c\sim 0$ and $c\sim 1$, which splits into TO-like and LO-like surface-related modes for $c\neq 0$ or 1 as in the case of spherical microcrystals and voids.[7]

In Fig. 5 the measured spectra are compared with calculations assuming $c=0.91$ and $c=0.75$. A column size distribution was taken into account by a Gaussian distribution of the GaP concentration centered at these c values with a standard deviation of 0.1. Because the porous GaP is not ideally

columnlike shaped, calculations for spheres are enclosed in Fig. 5 too. The good agreement between the experimental and theoretical results supports the interpretation of the surface-related mode as a Fröhlich mode. The observed frequency shift of the bulk TO phonon, however, cannot be obtained on the basis of an effective-medium approach taking into account only $\varepsilon_2(\omega,\mathbf{k}=\mathbf{0})$. This shift may be due to additional confinement effect[11] and/or internal strain.

In conclusion, the surface-related Raman band observed in porous GaP in the gap between the bulk optical phonons was found to shift to low frequencies and to broaden with increasing anodic current. Taking into account the results of a Raman line-shape analysis based on the effective dielectric function of a composite, we interpret the surface-related vibrational mode as a Fröhlich mode. A reduced thermal conductivity was evidenced for porous GaP layers.

I.M.T. gratefully acknowledges the support of the Alexander von Humboldt Foundation.

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