

TEMPERATURE DEPENDENCE OF RAMAN SPECTRA OF POROUS GAP

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Abstract: *Nanostructure gallium phosphate was fabricated using laser-induced etching (LIE) process, and the characteristic dimensions were determined with phonon confinement model. The laser was also used for spectroscopic investigations. It was found that the surface phonon frequency depends on the nanocrystalline size, shape and dielectric constant of the surrounding medium, and the broadening Raman line was caused by the size distribution, which was dependent on the etching parameters. The temperature dependent Raman scattering of porous and bulk GaP were compared. The experimental and theoretical results indicated that there was a higher degree of anharmonicity existed in the porous than in the bulk. The anharmonic constants were found to be highly size dependent and increased with decreasing dimensions. The phonon lifetimes decreased with increasing temperatures independent, but both decreasing with decreasing of nanocrystals size.*

Keywords: temperature dependence, porous GaP, Raman

1. INTRODUCTION

In last ten years, researchers have been attracted to study porous semiconductors.¹ To study the properties of semiconductors requires a detailed investigation of the structure of the frame which remains after etching, of the initial bulk material and the state of its surface. The properties of GaP are interesting in the initial material, like Si, is an indirect-gap material (2.26 eV) and the band structure is similar to the Si. GaP is an inert material, oxidizes slightly in air and the expectation of the porous layers based on it will be more stable and is less subjected to the action of the surrounding medium. Porous GaP is promising for optical devices due to its large energy gap, intense blue and ultra violet (UV) luminescence as well as strong light scattering properties. The quantum confinement structure in the porous layer, the blue and UV emission is expected to be much stronger than the orange emission from bulk GaP.² The optical properties of the porous GaP are different from the properties of the original single crystal. The modification of the properties of GaP could be due to an intensification of the electron-phonon interaction in the submicron to nanometer

size structures of the porous layer.³ Quantum confinement also affects the excitonic properties of indirect-gap material, which is responsible for inducing an indirect to direct conversion for the character of optical transition. The blue shift of the exciton transition energy and exciton binding energy suggests strongly the importance of quantum confinement effects in the luminescence processes.⁴ The large width of the UV luminescence band can be regarded as an evidence of the size distribution of quantum structures in porous GaP layers. The characteristic dimension of nanocrystals can be ascertained by studying the change in the line shape of the first-order Raman spectrum.⁵⁻⁶ The vibrational properties, a shift in phonon frequency, and changes in the line-width and asymmetry are functions of the dimension of the nanocrystal. The increasing in temperature introduced perturbations in the harmonic potential term. The changes in the line-width of the phonon Raman can be used to estimate an indirect lifetime of strong interacting optical phonons.

The purpose of this paper is to examine the effects of confinement and temperature-induced charges on vibrational state of GaP nanostructure using Raman spectroscopy.

2. EXPERIMENTAL TECHNIQUE

The LIE processes had been used to treat the GaP sample and to synthesis nanostructures. The n-type GaP (sulfur-doped) wafers with carrier concentration of $3.7 \times 10^{17} \text{ cm}^{-3}$ with (100) surface orientation were used in our studies. The porous GaP samples were prepared by LIE process.

A simple experimental set-up was used for LIE, which consisted of a continuous wave (CW) argon-ion laser, reflecting mirror, focusing lens and plastic container, as shown in Figure 1. The laser beam 2.41 eV ($\lambda = 514.5 \text{ nm}$) was reflected by an aluminium coated highly reflecting mirror (99.5%) and focused onto a sample of 1.5 mm diameter by using a suitable quartz lens with focal length of 10 cm and 5 cm in diameter. This lens was mounted on a micrometer holder for the focusing adjustment. The laser beam power density required for the LIE process of GaP was varied up to 12 W/cm^2 .

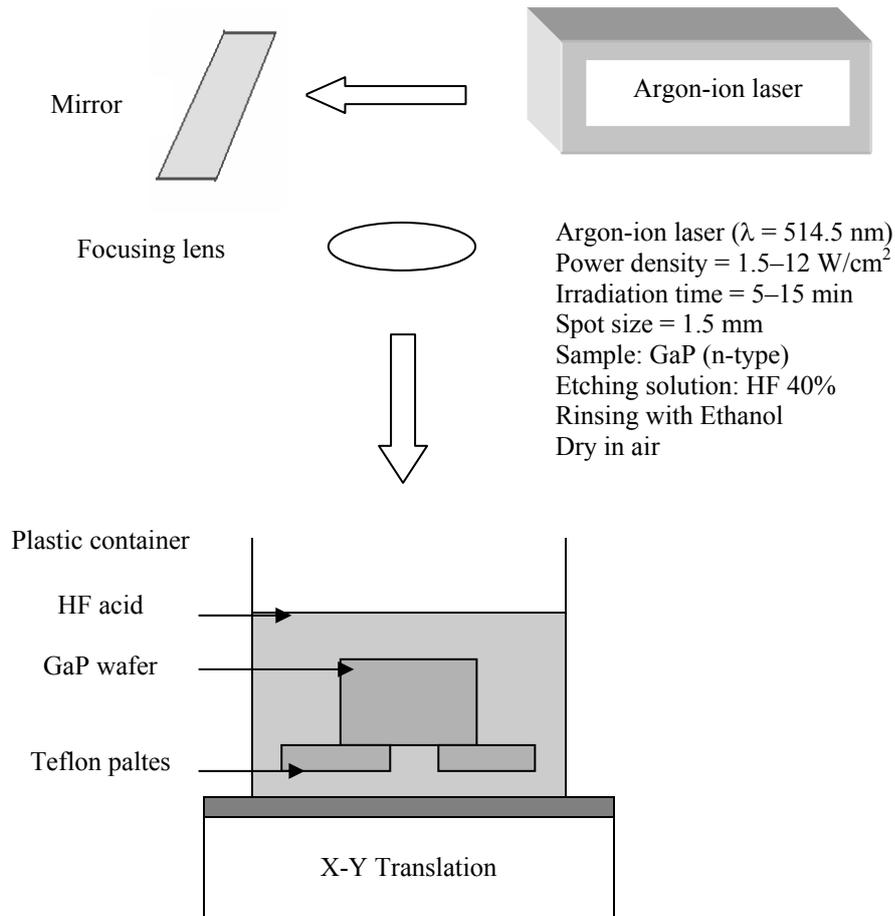


Figure 1: The LIE set-up.

The GaP wafers (n-type) were rinsed with ethanol for 10 min to clean the surface and then immersed in aqueous 40% wt. HF acid. The immersed wafer was mounted on two Teflon plates in order to allow the current that could pass from bottom to top area (irradiation area) through electrolyte, with suitable power density and irradiation time (IT), as shown in Figure 2. The etching was carried out at a laser power density of 12 W/cm^2 and 15 min IT. An argon-ion laser beam of energy (514.5 nm) was used for recording the Raman spectrum. A special thermodynamic cell was used for the temperature dependence studies.

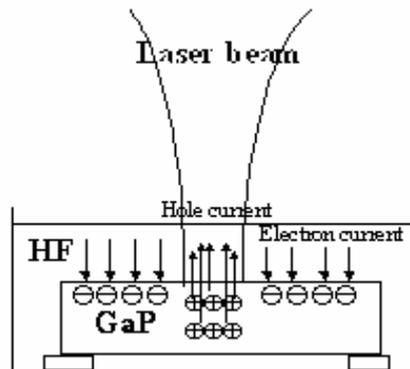


Figure 2: Schematic diagram of LIE process.

3. RESULTS AND DISCUSSION

3.1. Raman Spectrum of Porous GaP

The Raman spectrum of porous GaP sample prepared using the LIE technique is shown in Figure 3. The Raman peak position shifted to a lower frequency of 398 cm^{-1} after etching.

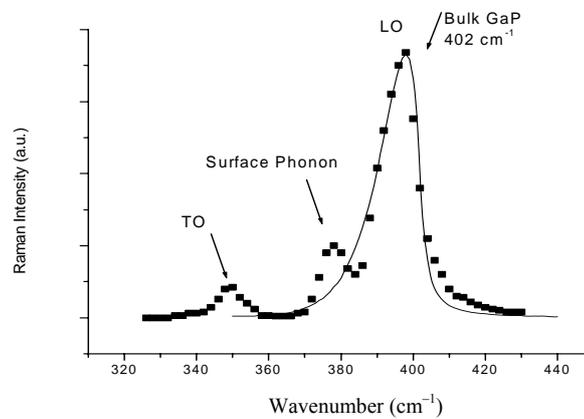


Figure 3: Raman spectrum of GaP nanostructure prepared by LIE.

The Raman line is broad and asymmetric in comparison to the Raman line for crystalline GaP, which has a narrow and symmetric shape centered at 402 cm^{-1} at room temperature. The weak structure near 349 cm^{-1} is a forbidden transverse optical (TO) phonon, which arises due to structural disorder in the material. The peak that appears near 378 cm^{-1} is attributed to a surface phonon mode.

The downward shift of the longitudinal optical (LO) phonon frequency and an increase broadening is apparent. The theoretical fit to the experimental curve is obtained using a three-dimensional quantum confinement model incorporating appropriate size distribution.

3.1.1. The crystallite size distribution in porous GaP

The observed broad Raman line shape is a consequence of the crystallite size distribution around a mean value L_0 as well as the confining geometry. The size distribution function that we have used is a Gaussian:⁷

$$\Phi(L) = \frac{1}{\sqrt{2 \cdot \pi}} \cdot \frac{1}{\sigma} \cdot \exp \left[\frac{-(L - L_0)}{2 \cdot \sigma^2} \right]$$

where, L_0 and σ are the mean and standard deviation of the crystallite size distribution, respectively. The Gaussian functions for the crystallite size distribution in the phonon confinement model have been used for the total Raman intensity, which may be written as:

$$I(\omega, L) = \int_{L_1}^{L_2} \Phi(L) \cdot I(\omega, L) dL$$

The peak position for the Raman mode is determined by L_0 . L_1 and L_2 are the minimum and maximum contributing nanocrystallites sizes (1 and 10 nm, respectively). In this work, these are taken as fitting parameters in Figure 3, as shown in Table 1. A change in the mean nanocrystallite size, L_0 leads to the shift in Raman peak position, and variations of L_1 and L_2 values lead to changes in the Raman line shape broadening without changing the peak position.

Table 1: Fitting parameters of Figure 3.

Excitation photon energy (eV)	L_0 (nm)	L_1 (nm)	L_2 (nm)	σ (nm)	FWHM (cm^{-1})	Raman peak position (cm^{-1})
2.41	3	1	10	5	6.5	398

The average size estimated from the fitting procedure is 3 nm. The broadening of Raman line is caused by the size distribution, which is dependent on etching parameters. We have observed another two weak Raman lines besides the intense LO phonon line at 398 cm^{-1} .

The weak structure near 349 cm^{-1} is a forbidden TO phonon, which arises due to structural disorder in the material. The peak at 378 cm^{-1} is attributed to a surface phonon mode. The surface phonon frequency critically depends on the nanocrystalline size, shape and dielectric constant of the surrounding medium. We have calculated the surface phonon frequency (ω_s) by considering a shape using:⁸

$$\frac{\omega_s^2}{\omega_T^2} = \left[\epsilon_0 + \epsilon_m \left(\frac{1}{L} - 1 \right) \right] / \left[\epsilon_\infty + \epsilon_m \left(\frac{1}{L} - 1 \right) \right]$$

where ω_T is the frequency of the TO phonon, $\epsilon_0 = 11.01$ and $\epsilon_\infty = 9.09$ are the static and high frequency dielectric constant, respectively $\epsilon_m = 1.00$ and L is the depolarizing factor.

The calculated value of surface phonon frequency in air for cylindrical shape is in good agreement with the observed value, as shown in Table 2.

Table 2: Surface phonon frequency in air.

Surface phonon Peak (cm^{-1})	TO phonon Peak (cm^{-1})	Dielectric constant			Depolarizing Factor L
		ϵ_0	ϵ_∞	ϵ_m	
378	349	11.01	9.09	1.00	0.3

3.2 Temperature Dependence of Raman Spectra

3.2.1 Crystalline and nanocrystalline GaP

Theoretical calculations were performed for the temperature dependence of the line-center and line-width of the first-order LO-phonon mode in GaP crystal. The variations in the line-center and line-width with temperature are shown in Figures 4 and 5, respectively. A decrease in the line-width and a shift in the line-center toward higher frequencies are indicated as the temperature is lowered.⁹ ω_0 and the constants A, C for GaP at 0 K are listed in Table 3.

The constants A and C at 0 K used in the calculation of phonon shift ω_0 and broadening for GaP nanocrystals are listed in Table 4.

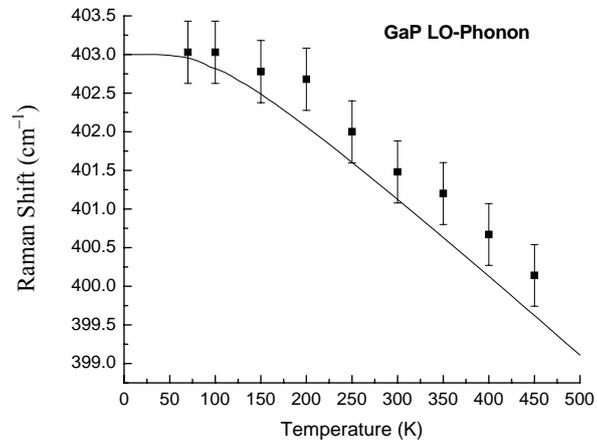


Figure 4: Temperature dependence of line-center of LO phonon.

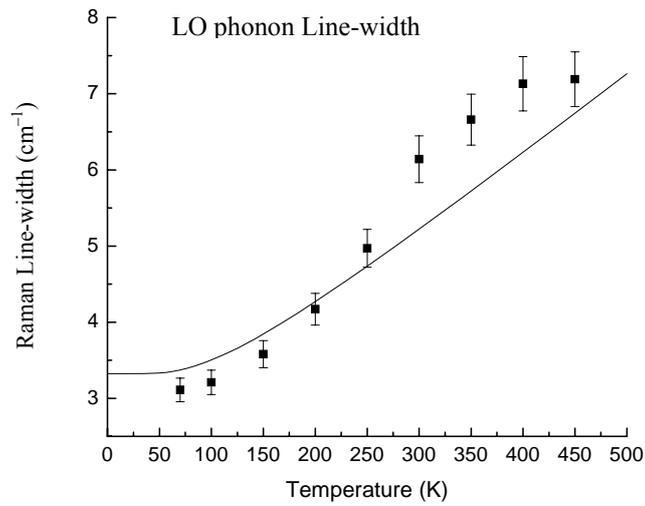


Figure 5: Temperature dependence of line-width of LO phonon.

Table 3: Parameters used for temperature dependence on crystalline GaP.

C (cm ⁻¹)	A (cm ⁻¹)	Γ (cm ⁻¹)	ω_0 (cm ⁻¹) at 0 K
-2.457	1.266	3.3	403

Table 4: Parameters used for temperature dependence on GaP nanocrystalline.

C (cm ⁻¹)	A (cm ⁻¹)	Γ (cm ⁻¹)	ω_0 (cm ⁻¹) at 0 K
-3.668	2.558	3.3	395

4. CONCLUSION

The charge transfer occurs at the semiconductor-electrolyte interface when a semiconductor is immersed in aqueous solution, which contains the electron acceptor species. The employment of modulated photocurrent produces the photo-generated holes that are directly transferred to the electrolyte solution, which surrounds the pores material.

High surface quality along with a slight blue shifted emission, due to the quantum-size effect, indicates that the anodization method is promising for the fabrication of high-quality quantum wire structures. The softening and broadening of the optical phonon line in the Raman spectrum also explains the reduction of the coherence length of phonons. The Raman studies of nanocrystals provide information on the behavior of the fundamental optical and vibrational properties. Since Raman scattering is very sensitive to the lattice microstructure, a phonon confinement model is employed to explain the Raman shift of phonon modes of a nanocrystal and describes the size confinement effect on lattice vibration wave functions.

The Raman scattering spectrum of porous GaP has a number of characteristic features. Both LO and TO phonons are always simultaneously present in the porous GaP spectra. The surface phonon frequency critically depends on the nanocrystalline size, shape and dielectric constant of the surrounding medium.

The line-center as well as line-width varies with temperature in bulk materials, and this temperature dependence has been attributed to the anharmonic terms in the vibrational potential energy. It is observed that the line-width decreased and the line-center shifted toward higher frequencies at low

temperature. It indicates that the phonon lifetime decrease with increasing temperature.

The exact determination of the positions and line-width of these microscopic gap modes open a new field of application in studying surface bonding, anharmonicity effects and coupling to other excitations.

5. REFERENCES

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