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Fourier-transform infrared reflection study of the morphology of porous semiconductor structures

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Abstract. Porous semiconductor films (GaAs and GaP) were studied by Fourier-transform infrared reflection spectroscopy, which was shown to enable one to determine their morphologies and such essential parameters for the porous structures as the filling factor.

Porous semiconductor structures possess specific electronic properties important in device applications. The most intriguing of these are the strong enhancement and the blue-shift of the fundamental photoluminescence (PL), which are explained by the quantum size effects accompanied by the transference of material from the indirect-gap bulk structure to the direct-gap porous one [1]. Bulk GaP belongs to the group of indirect-gap semiconductors and porous GaP exhibits a strong blue PL [2], which promises important practical applications. In contrast, bulk GaAs is a direct-gap semiconductor already widely used in electronics; therefore, the study of the optical properties of porous GaAs is of great interest, as one looks forward to increasing the effectivity of GaAs-based optoelectronic devices. Different methods for fabricating porous semiconductor structures have already been reported [3]. It is clear that the development of new technologies to produce porous semiconductor structures demands simple and rapid methods for their characterization. From this point of view, the optical characterization of the morphology of porous structures is an easy way to obtain their important characteristic parameters. In this paper we show that Fourier-transform infrared spectroscopy (FTIR), which to our knowledge has not yet been utilized to study porous structures, can be successfully used to extract the parameters characterizing their morphologies.

We studied porous structures prepared by electrochemical etching on (100)-oriented GaP and GaAs substrates with thicknesses around 300 nm. The initial semiconductor GaP wafers were doped with tellurium. The concentration of free carriers was found to be (2.7–5.0) $\times$ 10^{17} cm^{-3} at room temperature. The GaAs wafers were doped with Si to obtain an electron concentration of 3.0 $\times$ 10^{17} cm^{-3}. The porous layers were obtained by electrochemical reaction using a 50% liquid solution of HF in ethanol for GaP and the liquid solution HF:HCl:C_2H_5OH (5:1:10) for GaAs at a current density of 20 mA cm^{-2}. It is worth mentioning that in the case of GaP, after etching for 10 min, the colour of the surface changed from orange to yellow. All of the electrochemical experiments were performed in the dark. The details of the preparation of the porous GaP are described in [2]. TEM images showed the formation of vertically oriented porous structures with thicknesses varying from a few microns to some tens of microns. Prior to the spectroscopic measurements the samples were degreased by sonicating

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in methanol and de-ionized water and then they were dried in air. All the samples revealed an intense blue-shifted PL signal at room temperature, which, according to [4], attests to the presence of electron quantization due to the porosity. The PL peaks were found at 2.1–2.5 eV for the porous GaP and in the green and red spectral regions for the porous GaAs.

Reflection spectra taken at $T = 77$ K at an incidence close to normal (with the incidence angle close to 10°), were performed with a Fourier-transform spectrometer, Bruker IFS-113V.

The reflection spectra obtained are plotted in figures 1, 2. As is seen, the porous structures reveal both transverse optical (TO) and longitudinal optical (LO) phonons. The TO phonons are active in infrared spectra because of their direct coupling with light, while the LO phonons

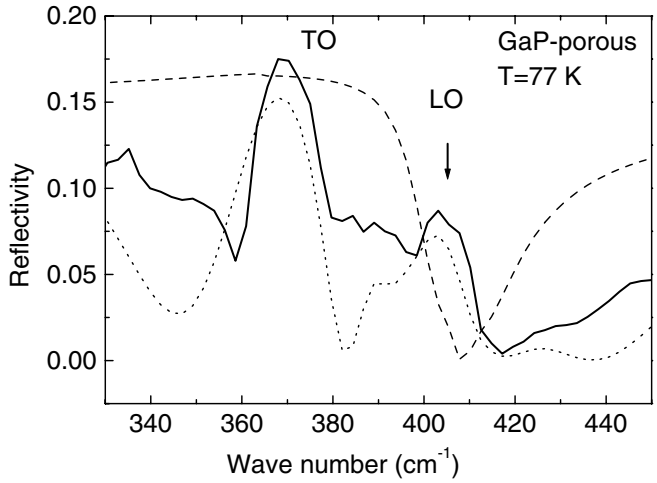

Figure 1. The reflection spectra of the porous GaP film measured at $T = 77$ K in the range of the optical lattice vibrations (solid line). The spectra given by the broken and dotted lines were calculated for the vacuum columns and for the GaP columns respectively.

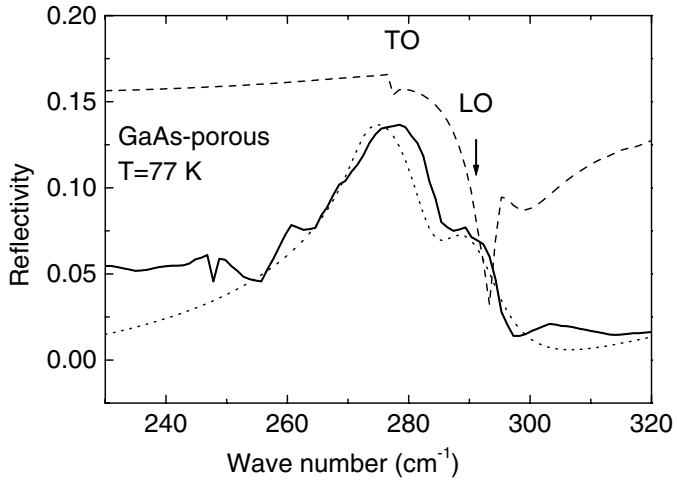

Figure 2. The reflection spectra of the porous GaAs film measured at $T = 77$ K in the range of the optical lattice vibrations (solid line). The spectra given by the broken and dotted lines were calculated for the vacuum columns and for the GaAs columns respectively.

contribute because of the Berreman effect [5] known to occur due to the finite-size effects, when $r_0 < \lambda$ (where r_0 is the characteristic size and λ is the wavelength of light).

In order to calculate the reflection spectra of the porous semiconductor structures studied here, we used the dielectric function tensor of quasi-two-dimensional composite media calculated in [6] where two cases have been considered. In the case of crystal columns of radii r_0 in vacuum, the components of the dielectric function tensor are

$$\epsilon_{xx} = \epsilon_{yy} = \frac{\epsilon + 1 + C(\epsilon - 1)}{\epsilon + 1 - C(\epsilon - 1)} \tag{1}$$

while for vacuum columns in a dielectric matrix they are

$$\epsilon_{xx} = \epsilon_{yy} = \epsilon \frac{2 + C(\epsilon - 1)}{2\epsilon - C(\epsilon - 1)}. \tag{2}$$

In both cases

$$\epsilon_{zz} = 1 + C(\epsilon - 1) \tag{3}$$

where C is the bulk material concentration (filling factor); in the case of the crystal columns, $C = \pi r_0^2 N$, where N is the surface concentration of the vertical columns.

$$\epsilon(\omega) = \epsilon_\infty \frac{\omega^2 - \omega_L^2}{\omega^2 - \omega_T^2}$$

is the frequency-dependent dielectric function of the dielectric matrix, with ω_L and ω_T being the frequencies of the LO and TO phonons respectively. As follows from TEM measurements, the columns are preferentially oriented normal to the surface, along the z-axis. Each column is supposed to be sufficiently large to produce macroscopic dielectric permittivity, but small as compared with λ.

The dielectric function tensor determined in such a way was utilized to calculate the reflectivities of the samples under investigation according to the formulae for the reflectivity of a uniaxial film deposited on an isotropic thick substrate, given in [7].

The results of the numerical calculations carried out for both types of porous structure, as determined by (1)–(3), are shown in figures 1, 2. All the parameters of bulk GaAs and GaP indispensable for the calculations were taken from [8]; they were the same for both of the types of porosity analysed, as determined by (1), (2). The filling factor C and the thickness of the film, together with the phonon damping constants, were used as adjusting parameters during the fittings of the calculated spectra to the experimental ones.

As is seen, the morphology of the porous systems crucially influences the reflection. The change of the morphology from vacuum columns to material columns causes a drastic alteration in the reflection spectra. A good fitting was obtained for the columns in vacuum with the filling factor $C = 0.5$ (0.75) and with the total thickness of the porous film $H = 30$ μm (6 μm) obtained for the porous GaP (GaAs) respectively. Consequently, the model used to analyse the reflection spectra is able to reproduce essential features of the experimental reflection spectra of the porous structures.

To conclude, the reflection spectroscopy allowed us to determine the morphologies of porous structures and permitted us to obtain their structural parameters, such as the thicknesses and the material concentrations.

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