

INFRARED REFLECTANCE OF GaP NANORODS

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The reflectance of GaP nanorods on GaP substrates was investigated in the frequency range of 300–500 cm^{-1} by Fourier transform infrared (FTIR) reflectance spectroscopy. GaP nanorods were fabricated by the anodic electrochemical etching technique. The structure of nanorods, formed by using galvanostatic and potentiostatic etching regimes was studied by the SEM technique. The correlation between particular features in the infrared reflection spectra in the reststrahlen region and the morphology of nanorods was analysed and discussed.

Keywords: III–V semiconductors, nanorods, infrared spectra

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1. Introduction

Recently, a large attention has been paid to porous semiconductors, which show potential applications in the development of optoelectronic devices [1]. A particular interest was due to enhanced photoluminescence [2] and nonlinear effects [3] in porous semiconductors, as compared to bulk samples. In particular, porous GaP (por-GaP) and GaP nanorods are considered as prospective materials for antireflection coatings [1] and as a pattern for organic cell deposition [4].

The optical studies of por-GaP in the infrared (IR) range have been carried out mainly by the Raman technique (see, e. g., [5–7]). The most interesting feature observed was due to Fröhlich modes in the spectral range between transverse optical (TO) and longitudinal optical (LO) excitations and their L–T splitting [5]. IR reflection was investigated in por-GaP formed in H_2SO_4 -based [5, 6] and HF-based [8] acid electrolytes.

The goal of the present work was to fabricate the GaP nanorods by using the electrochemical etching technique and to investigate the IR response of GaP nanorods.

2. Experiment

GaP nanorods were formed by electrochemical anodic etching of 300- μm -thick wafer of *n*-GaP with S-donor density $(5.0\text{--}5.3) \cdot 10^{17} \text{cm}^{-3}$. The wafers were cleaned in hot isopropyl/ethanol and washed in distilled water. Etching was carried out in dark by exposing the (111) face of *c*-GaP to electrolyte. The ethanol solution of 3M HNO_3 electrolyte was used. The backside contact was made by means of In–Ga eutectics and graphite electrode. The Pt-electrode was used as cathode in the electrolyte etching cell. The etching area of GaP was 6 mm in diameter. The galvanostatic etching conditions (sample 1) were realised by using potentiostat *Autolab PGSTAT 302* at constant current density $j = 80 \text{mA/cm}^2$. The potentiostatic etching conditions (sample 2) were realised by voltage source at $U = 23 \text{V}$. The etching time was 1 h. After the formation of por-GaP layer, the oxide layer on the top of the structure was removed in 30% KOH solution.

The surface and cross-section morphology of GaP nanorods were studied making use of a scanning electron microscope (SEM) *EVO 50 EP* (Carl Zeiss SMT). The IR reflectance spectra were meas-

ured in the region of $300\text{--}500\text{ cm}^{-1}$ using a Nicolet 8700 FTIR spectrometer equipped with a specular reflectance unit with the reflection angle 22° .

3. Results and discussion

The structural studies showed that under galvanostatic and potentiostatic etching conditions nanorods of $3\text{--}10\text{ }\mu\text{m}$ in height and $100\text{--}400\text{ nm}$ in width were formed (Fig. 1). For the first time, the GaP nanorods were formed by electrochemical etching.

In previous works [9, 10] it was noted that etching in the 3M HNO_3 aqueous solution led to the growth of the oxide layer only, and a porous layer did not form. However, using the 3M HNO_3 ethanol

solution, the nanorods were formed as discussed previously. It can be assumed that in this case ethanol acts as a stabiliser, preventing the formation of branches and favouring the increase of the pore diameter. When the pore walls become thin enough, resistance increases significantly, and the etching rate decreases. Nanorods originate from these thin walls during the further etching process. The height, diameter and concentration of nanorods depend on the etching conditions. By using different applied potentials, the nanorods of various height, width and concentration can be formed.

The typical IR reflection spectra of the investigated samples in the reststrahlen region are presented in Fig. 2(a). In the spectra of the normalised

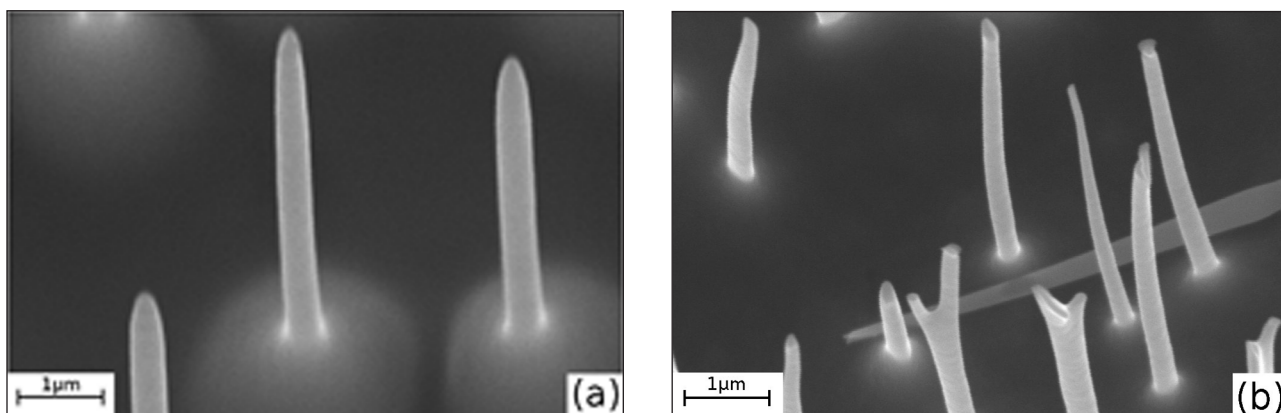


Fig. 1. SEM micrographs of GaP nanorods produced in (a) galvanostatic and (b) potentiostatic regime. Bars correspond to $1\text{ }\mu\text{m}$.

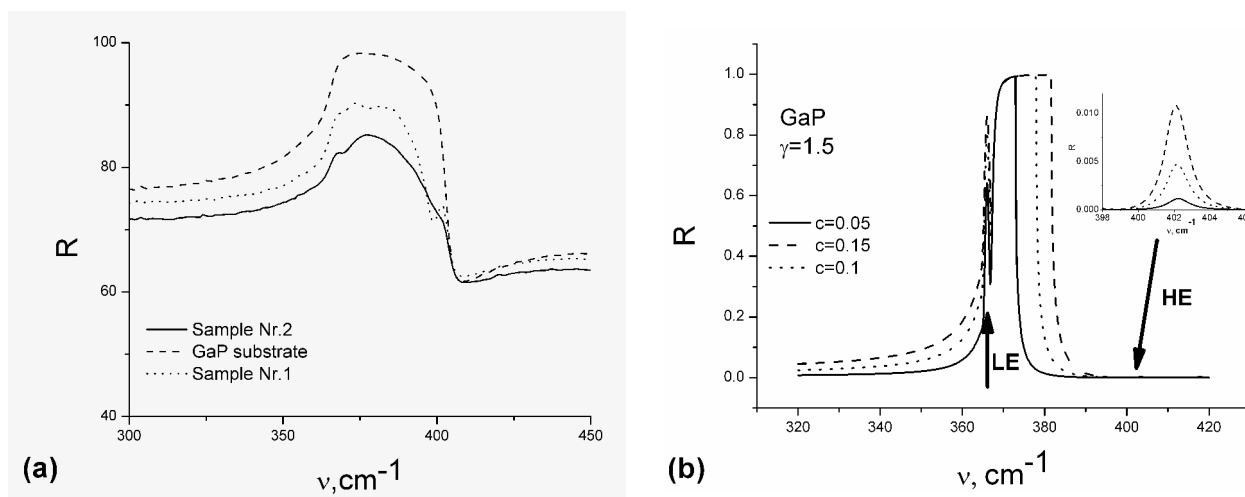


Fig. 2. (a) Reflectance spectra of c-GaP and por-GaP with nanorods. (b) Modelled reflectance spectra.

reflection coefficient $R_{\text{norm}}(\omega)$, two bands, low-energy (LE) and high-energy (HE), appeared for nanorods formed using both etching conditions. The origin of the fine structure in the reflection spectra follows from model calculations (Fig. 2(b)). The reflection spectra have been calculated in the model developed in [5] with electronic dielectric function $\varepsilon_{\infty} = 9.036$ [11] and the energies of TO- and LO-modes equal to 366 and 402.3 cm^{-1} [5], respectively:

$$\varepsilon(\omega) = \varepsilon_{\infty} \left(1 + \frac{\omega_{\text{LO}}^2 - \omega_{\text{TO}}^2}{\omega_{\text{TO}}^2 - \omega^2 - i\omega\gamma} \right). \quad (1)$$

The relative volume concentration $c = V_{\text{GaP}} / V_{\text{air}}$ and damping γ were treated as free parameters. The LE band in reflection spectra originates from GaP TO phonon whereas the HE band is related to GaP LO phonon and to Fröhlich TO- and LO-modes.

On the basis of the model calculations (Fig. 2(b)), the correlation between the reflection spectra and morphology of the samples under consideration were revealed. It should be emphasized that a decrease of the volume concentration of GaP (c -parameter) results in the decrease of the HE-side of the reststrahlen band. Therefore, the difference in the spectra for samples 1 and 2 is caused by the volume concentration of nanorods. From the structure investigations, the estimated c -value was 0.1 and 0.08 for samples 1 and 2, respectively. Also, the HE band was masked in the spectrum of sample 2. This feature can be due to irregularities in the nanorod shape in this sample which results in the increase of the damping parameter γ and broadening of the HE-band.

As follows from model calculations (Fig. 2(b)), the intensity of the LE band decreases when the volume concentration of GaP (c -parameter) is decreased. This also explains differences in sample 1 and sample 2 spectra. The c -parameter of sample 2 is smaller, so the intensity of the LE band is smaller.

4. Conclusions

GaP nanorods were made by electrochemical etching for the first time. The nanorods of 3–10 μm in height and 100–400 nm in width were more regular in por-GaP sample fabricated in galvanostatic regime as compared to that formed in potentiostatic regime.

GaP nanorods were characterised by the FTIR technique. A complex structure due to LO, TO and Fröhlich modes were seen in IR spectra. The particular features in IR reflection spectra correlate with the morphology of samples and are well interpreted by the modelled spectra.

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GaP NANOSTRYPELIŲ INFRARAUDONASIS ATSPINDYS

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Santrauka

Aprašyta n -GaP (S) nanostryelių formavimo elektrocheminio ėsdinimo būdu 3M HNO₃ etanolio elektrolite technologija. Šiuo būdu pirmą kartą suformuoti 3–10 μm aukščio ir (100–400) nm skersmens n -GaP nanostryeliai. Aptarti darinių, gautų ėsdinant

galvanostatiniame ir potenciostatiniame režime, morfologijos skirtumai. GaP dariniai su nanostryeliais buvo tiriami nuskaitančio elektroninio mikroskopo ir atspindžio IR (300–500) cm^{-1} spektro ruože metodais. Išanalizuoti IR spektrų ypatumai bei jų koreliacija su nanostryelių morfologija.