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Artificial birefringence introduced by porosity in GaP

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Abstract
Porosity-induced birefringence in a GaP membrane is studied using a method based on the analysis of beats in unpolarized and polarized transmittance spectra as well as in angular dependence of optical spectra. Birefringence as high as $n_e - n_o = 0.25$ was measured in a porous GaP membrane with the degree of porosity close to 40%. The measured values of n_e and n_o are compared with those calculated in the frame of effective medium theory for a GaP membrane with appropriate morphology.

1. Introduction

Over the past few years, increasing attention has been paid to porous GaP layers due to their strongly enhanced photoresponse, ability to support Fröhlich-type surface vibrations and enhanced nonlinear optical properties [1–4]. GaP is considered as prospective material for manufacturing photonic crystals for the visible spectral range [5, 6]. It is well known that III–V compounds possess second-order nonlinear optical coefficients several orders of magnitude higher than those of KDP, ADP and other materials used in frequency upconversion. However, the utilization of large nonlinear susceptibilities of III–V compounds has not been possible due to high dispersion and lack of birefringence necessary for phase matching [7, 8]. Electrochemistry proved to be a powerful tool for introducing the necessary optical anisotropy in Si [9]. In Si the pores grow predominantly in the [1 0 0] crystallographic directions. Therefore, the porous layers prepared on (1 0 0) substrates are optically isotropic at normal incidence and exhibit birefringence at oblique incidence. On the other hand, the mesoporous silicon layers prepared on low-symmetry (2 1 1) or (1 1 0) surfaces show strong birefringence at normal incidence, since the optical axis is located in the surface plane [10–12].

Anodization of (1 1 1)-oriented GaP substrates results in the formation of an array of pores stretching perpendicularly to the initial surface [2]. In this paper, we present results of a study of birefringence in porous GaP layers prepared on (1 1 1)-oriented substrates. Unpolarized and polarized optical transmittance spectra as well as angular dependence of optical spectra are analysed.

2. Experimental details

Free-standing membranes of porous GaP were fabricated by anodic etching of (1 1 1)-oriented wafers cut from n-GaP:Te Czochralski grown ingots. The free carrier concentration in as-grown samples was $n = 10^{18}$ cm^{-3} at 300 K. The anodic etching was carried out in H_2SO_4 aqueous electrolyte as described elsewhere [2]. A configuration with four electrodes was used: a Pt reference electrode in the electrolyte, a Pt sense electrode on the sample, a Pt counter electrode and a Pt working electrode. The electrodes were connected to a specially designed potentiostat/galvanostat. All the equipment used in the experiments were computer controlled. The morphology of the porous layers was analysed with a scanning electron microscope (SEM). SEM image taken from a porous GaP membrane is illustrated in figure 1. One can see that the transverse size of pores is between 50 and 100 nm.

The optical transmittance spectra were measured using a MDR-2 spectrometer equipped with a halogen lamp and a FEU-62 photomultiplier. The spectral resolution was better than 0.5 nm.

3. Results and discussion

Figure 2(a) shows the unpolarized transmittance spectrum of an 8 μm thick porous GaP layer measured at normal incidence.

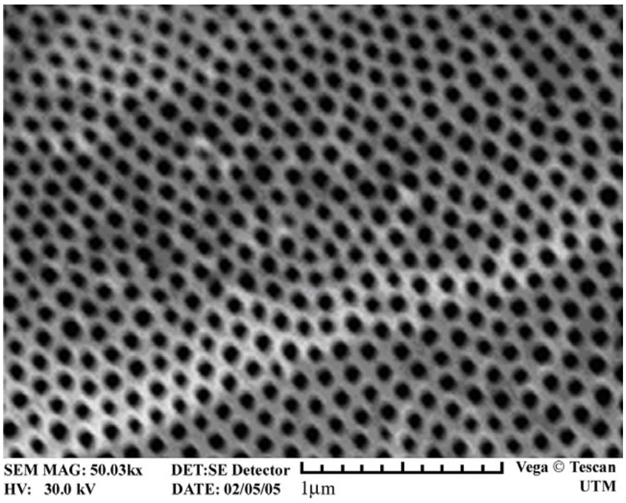

Figure 1. SEM image taken from a porous GaP membrane.

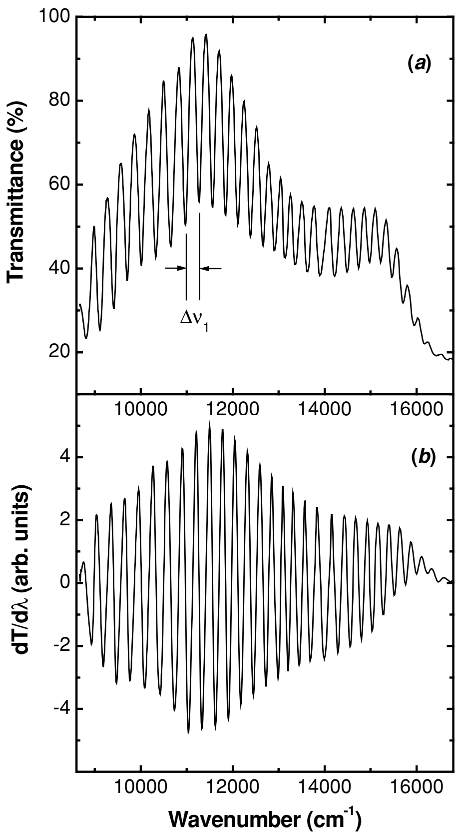

Figure 2. Unpolarized transmittance spectrum (*a*) and wavelength derivative spectrum (*b*) measured at normal incidence for an 8 μm thick GaP porous membrane.

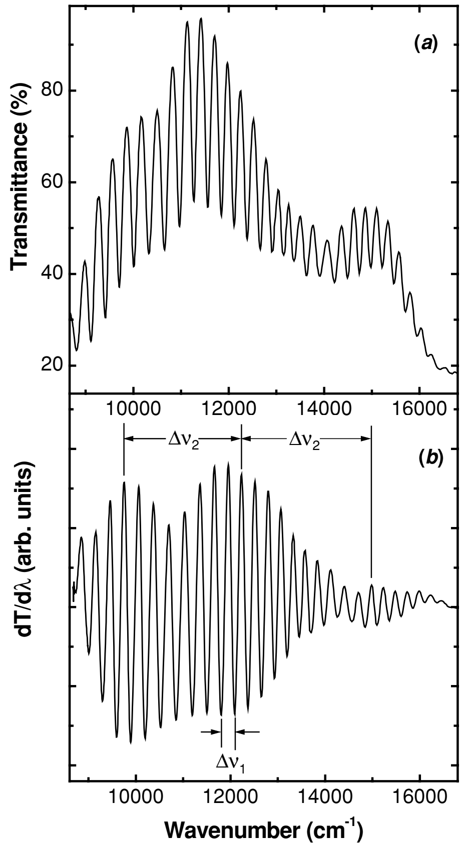

Figure 3. Same as figure 2 but for an angle of incidence of 25°.

Oscillations characteristic for interference in a thin layer are clearly seen in the spectrum. We have calculated the average refractive index of our layer by using the simple formula

$$n_{\mathrm{eff}} = \frac{1}{2d(\Delta\nu)}, \tag{1}$$

where n_{eff} is the effective refractive index, d is the film thickness, and $\Delta\nu$ is the difference between the wavenumbers ($\nu = 1/\lambda$) corresponding to two neighbouring maxima (minima) of the spectrum. The resulting average value of $n_{\mathrm{eff}} = 2.30$ is interpreted in terms of an effective medium expression for the dielectric function. According to the effective medium theory [13, 14], in the case of pores stretching perpendicular to the initial surface, the dielectric function of the porous membrane can be written as

$$\varepsilon_{\mathrm{eff}}(\omega) = \varepsilon_1(\omega)\frac{(2-c)\varepsilon_2 + c\varepsilon_1(\omega)}{c\varepsilon_2 + (2-c)\varepsilon_1(\omega)}, \tag{2}$$

where c is the skeleton relative volume concentration $c = V_1/(V_1 + V_2)$, $\varepsilon_1(\omega)$ is the dielectric function of the GaP, ε_2 is the dielectric constant of air inside the pores, V_1 is the relative volume occupied by GaP and V_2 is the relative volume occupied by the air.

By using the reported value of the refractive index for the bulk GaP $n = 3.2$ [15], and the value of $n_{\mathrm{eff}} = 2.3$ obtained from the interference spectra, one can calculate the value of $c = 0.61$, according to formula (2). This value is in good agreement with the value of 0.62 measured by gravimetry.

With the deviation from the normal incidence, the amplitude of oscillations in the transmittance spectrum is modulated by beats as illustrated in figure 3 for an angle of incidence of 25°. The beats are better observed in the wavelength derivative spectrum (figure 3(*b*)), due to the removal of the background inherent to the transmittance spectrum. The period of the beats is labelled as $\Delta\nu_2$, while the period of the short-period oscillations is labelled as $\Delta\nu_1$. Similar beats were revealed in optical spectra of porous Si layers [12]. The presence of short-period and long-period

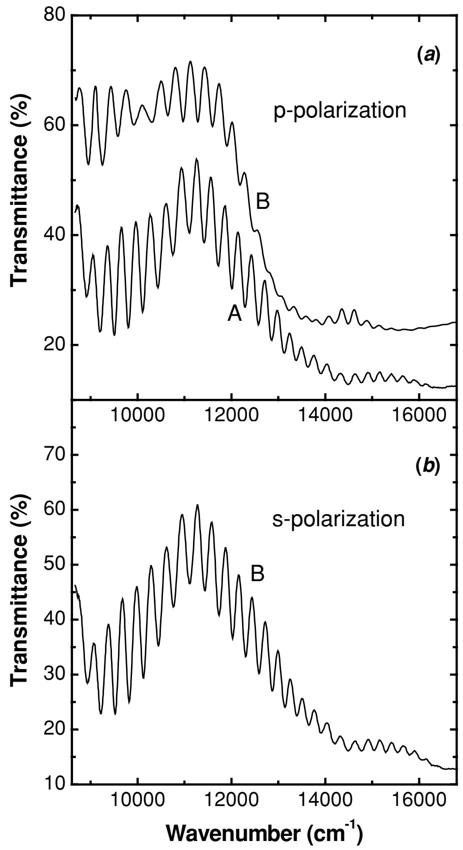

Figure 4. Transmittance spectra measured with p-polarized light (*a*) and s-polarized light (*b*) at an angle of incidence of 10° (curve A), and 55° (curve B).

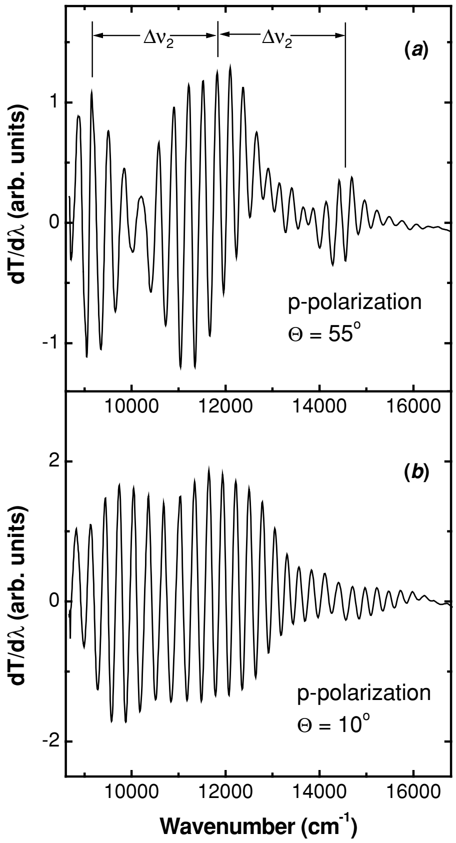

Figure 5. Wavelength derivative spectra measured with p-polarized light at an angle of incidence of 10° (*a*), and 55° (*b*).

oscillations in the optical spectra is due to the propagation of ordinary and extraordinary waves in the layer. Since the pores are aligned in our layer in the direction perpendicular to the membrane surface, evidently, the optical axis coincides with the normal to the surface. Therefore, at normal incidence, the light rays impact the membrane in a direction that is parallel to the optical axis and they behave as ordinary rays, i.e. there is no component of the electric field vector parallel to the optical axis. With the deviation from the normal incidence, there are both components of the electric field vector parallel and perpendicular to the optical axis, and the interference of ordinary and extraordinary waves results in beats.

It is easy to measure birefringence in a membrane with the optical axis in the surface plane, since in such a case at normal incidence the components of the electric field vector parallel and perpendicular to the optical axis have nearly the same magnitude. In order to have an identical situation with a membrane with the optical axis perpendicular to the surface, it is necessary to direct the light beam towards the edge of the sample. Special equipment including polarization preserving lensed fibres and micro-adjustment apparatus are needed for focusing the beam and collecting the light with a sample thinner than 10 μm. This makes difficult to observe the interference fringes.

Another way to enhance the beats is through the use of polarized light. In the case of s-polarized incident light, the orientation of the electric field vector is always perpendicular to the optical axis, independently of the angle of incidence. Therefore, no beats are observed in the transmittance spectra with s-polarized incident light at any angle of incidence, as illustrated in figure 4(*b*) for an angle of incidence equal to 55°. In contrast to that, with p-polarized incident light, the orientation of the electric field vector in a medium with refractive index close to unity changes from the direction perpendicular to the optical axis at normal incidence to the direction parallel to the optical axis at an angle of incidence close to 90°. Therefore, the character of the incident ray in a medium with refractive index close to unity would change from ordinary to extraordinary when the angle of incidence changes from 0 to 90°, i.e. only ordinary waves would propagate in such a material at normal incidence, and only extraordinary waves would propagate at an angle of incidence close to 90°. In such a case, no beats would be observed at normal incidence as well as at an angle of incidence close to 90°, while maximum beats would be inherent to an angle of incidence close to 45°, at which the components of the electric field vector parallel and perpendicular to the optical axis have nearly the same magnitude. In our sample, the value of the effective refractive index is more than 2. Consequently, the angle of refraction cannot exceed 30°, and the electric field vector component perpendicular to the optical axis is always bigger than the parallel component, but the ratio of the parallel to the perpendicular component continuously increases with the increase of the incident angle. As one can see from figure 4(*a*), the beats are hardly observed at an angle of incidence of the p-polarized light equal to 10°, while strong beats are evidenced

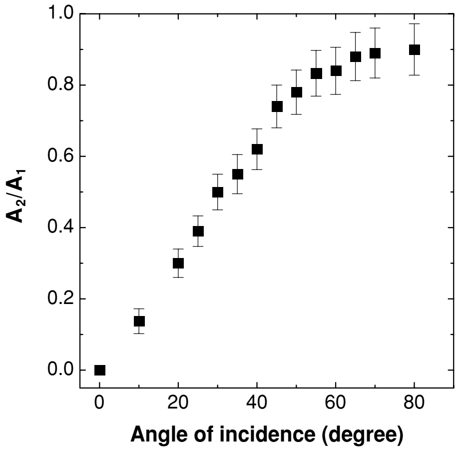

Figure 6. Dependence of the magnitude of beats in the transmittance spectrum (see the text for explanation) on the angle of incidence.

at an angle of incidence of 55°. This observation is better illustrated in the wavelength derivative spectrum shown in figure 5. The ratio of the amplitude of beats (i.e. the amplitude of the long-period oscillations) to the amplitude of the short-period oscillations in the transmittance spectrum A_2/A_1, as a function of the angle of incidence of the p-polarized light is presented in figure 6. One can see a monotonic increase of this ratio with the increase of the incident angle.

The values of the ordinary n_o and extraordinary n_e refractive indices for the ordinary and extraordinary waves can be calculated from the measured period of the long-period and short-period oscillations in the transmittance spectrum [12]:

$$\Delta\nu_1 = \frac{1}{d(n_0 + n_e)\cos\theta'} \quad \text{and} \quad \Delta\nu_2 = \frac{1}{2d(n_e - n_0)\cos\theta'} \tag{3}$$

where θ' is the angle of refraction.

The average values of $n_o = 2.30$ and $n_e = 2.55$ were calculated in the measured wavelength range. According to the effective medium theory [13, 14], in the case of pores stretching perpendicular to the initial surface, the dielectric function of a porous membrane for ordinary waves (at normal incidence) is given by relation (2), while the dielectric function for extraordinary waves (for electric fields parallel to the pore direction) can be written as follows:

$$\varepsilon_e(\omega) = (1 - c)\varepsilon_2 + c\varepsilon_1(\omega). \tag{4}$$

The value of the refractive index calculated according to this relation for a porous GaP membrane with $c = 0.61$ equals 2.57. Note the good correlation of this value with the experimentally determined one.

4. Conclusion

The results of this study demonstrate the possibility of employing a simple method based on the analysis of beats in the polarized transmittance spectra for measuring the birefringence in a thin porous membrane with the optical axis perpendicular to the surface of the membrane. Birefringence as high as $n_e - n_o = 0.25$ was measured in a porous GaP membrane with the degree of porosity close to 40%. The measured values of $n_e = 2.55$ and $n_o = 2.30$ are in good agreement with the results of calculations based on the concept of effective medium theory for a GaP membrane with pores stretching perpendicular to the initial surface.

Acknowledgments

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