Properties of 2D and 3D Dielectric Structures Fabricated by Electrochemical Dissolution of III-V Compounds

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ABSTRACT
Porous layers and membranes representing 2D and 3D dielectric structures were fabricated on different III-V compounds (GaAs, InP, GaP) by electrochemical etching techniques. Nonlithographically fabricated ordered nanopore arrays in InP are reported for the first time. We show that the reflectance from nanostructured InP is lower than from bulk InP in the spectral interval 1.5-2.2 eV. The artificial anisotropy induced by nanotexturization was studied in porous GaP membranes and the refractive indices for ordinary and extraordinary beams were evaluated.

INTRODUCTION

Electrochemistry proves to be a powerful tool for producing dielectric structures on solid-state materials. The fabrication of a 2D geometry, polycrystalline nanopore arrays with hexagonal ordering by self-organized anodization on aluminum has already been reported, e.g. [1]. The mechanical stress associated with the expansion of the aluminum during oxide formation was suggested to generate repulsive forces between neighboring pores during the oxidation process leading to self-organized formation of hexagonal pore arrays [2]. Ordered pore arrays on large areas can be prepared using prepattern-guided anodization of both aluminum and crystalline silicon [3,4]. Recently the electrochemical etching techniques were used to fabricate semiconductor sieves of gallium phosphide, i.e., two-dimensionally nanostructured membranes exhibiting a strongly-enhanced optical second harmonic generation in comparison with the bulk material [5]. Moreover, crossing pores were observed in GaAs indicating that anodic etching may be a suitable and unique tool for the production of 3D micro- and nanostructured III-V compounds [6]. In this work, we explore the possibility to produce quasi-periodic dielectric structures on III-V compounds by electrochemical etching techniques. Data concerning morphology studies and optical characterization of samples are presented.

EXPERIMENTAL

N-type (100) oriented InP, GaAs and (111)-oriented GaP wafers cut from Czochralski grown ingots were used in this work. The free carrier concentration was $n = 10^{18}$ cm^{-3} at 300 K. The anodization was carried out in an electrochemical double cell as described elsewhere [6] in HCl and H_2SO_4 aqueous electrolytes. The area of the sample exposed to the electrolyte was 0.2 cm^2. The supply of holes was due to the reverse bias applied to the semiconductor/electrolyte junction, which involves the avalanche breakdown effects accompanied by generation of electron-hole pairs.
A configuration with four electrodes was used: a Pt reference electrode in the electrolyte (REE), a Pt sense electrode on the sample (SES), a Pt counter electrode (CE), and a Pt working electrode (WE). The electrodes were connected to a specially designed potentiostat/galvanostat which can deliver currents and voltages up to 200 mA and ± 80V respectively. The temperature was kept constant at T = 20°C by means of a Julabo F25 thermostat. The electrolyte was pumped

continuously through both cells by means of peristaltic pumps. All the equipment used in the experiments was computer controlled. The morphology of the porous layers was analyzed with a scanning electron microscope (SEM).

RESULTS AND DISCUSSION

Study of Morphology

Fig. 1 illustrates SEM images taken from n-InP samples subjected to anodic etching in 7.5 % HCl solution at different applied voltages with subsequent removal of the nucleation layer (NL) by nonselective wet etching. One can easily see that the degree of porosity increases with the applied potential. Apart from that, in the voltage interval 5 to 9 V a self-organized ordering of pores is observed, the highest degree of order is observed at 7-8 V. As one can see from Fig. 1b, there are domains of micrometer size with nearly perfect hexagonal ordering. Two of such domains are marked in Fig. 1b by solid curves.

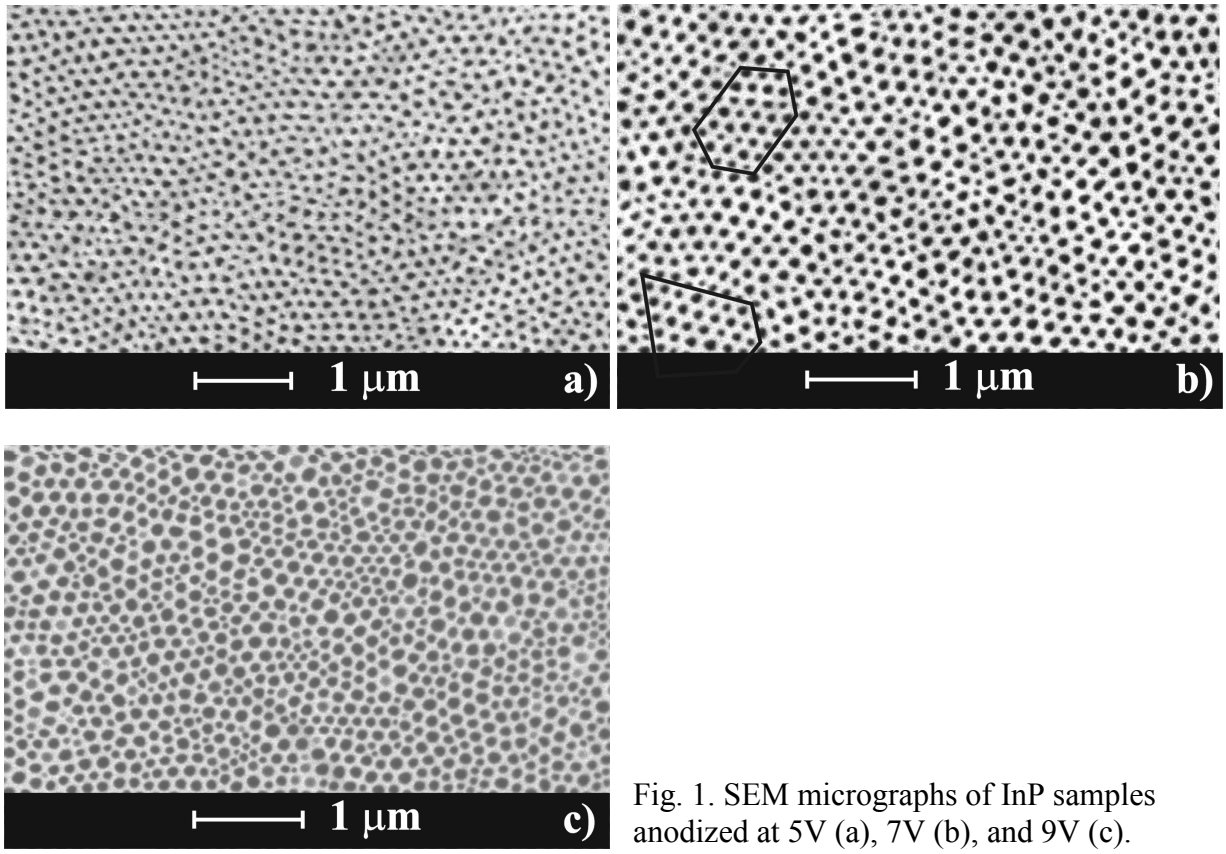

Fig. 1. SEM micrographs of InP samples anodized at 5V (a), 7V (b), and 9V (c).

When the samples are anodized in solution with 5 % HCl concentration, they exhibit the maximum degree of pore ordering at 9-10 V. Fig. 2a presents a cleavage of a porous layer produced by anodic etching of a n-InP substrate at 10 V for 1 minute. Note that the NL layer with the thickness 1.5 μm was removed by nonselective etching. One can see that the distribution of pores is highly uniform both along the top surface and in the depth of the porous layer. The pores grow perpendicularly to the initial surface. We believe that the interaction between pores by means of the space charge region as well as the high crystalline quality of our samples and computer-controlled accuracy of etching conditions are the primary factors leading to the observed uniformity in pore distribution. Moreover, as in the case of samples anodized in 7.5 % HCl electrolytes, the spatial distribution of pores proves to be ordered within domains of

micrometer sizes (Fig. 2b). The transverse sizes of pores and InP wall thicknesses equal 200 and 120 nm respectively, leading to a degree of porosity of about 55 %. An autocorrelation analysis of the pores position shows an ordering of up to the sixth neighbor. A corresponding analysis of the radial distribution of the pore position shows a 60° angle between the neighbors of one pore. Combining these data a medium range ordering of pores in a closed packet arrangement is found.

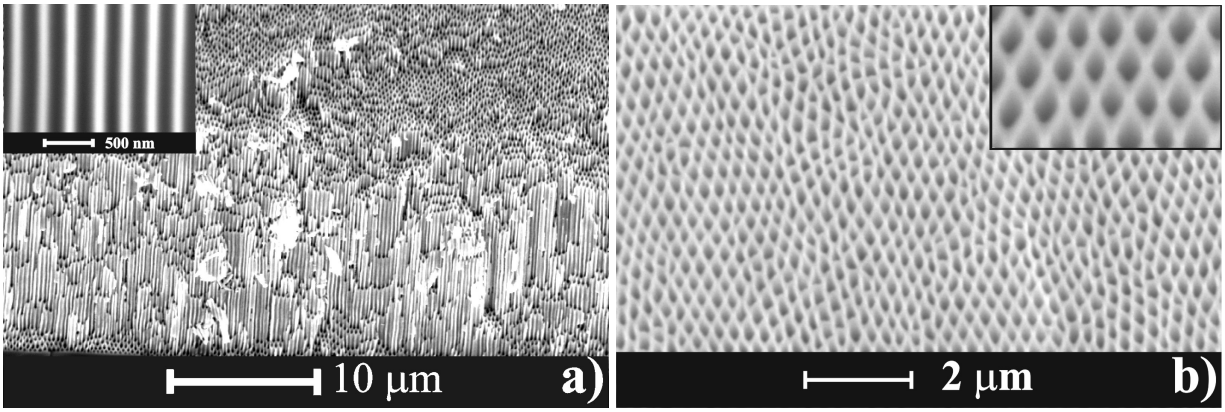

Fig. 2. SEM micrographs taken from an InP sample anodized at 10V: a) random cleavage, overview; b) top view.

The direction of pore growth in InP strongly depends upon the anodic current density [7]. In GaAs the pores grow usually along the <111> crystallographic direction regardless the value of the anodic current. Moreover, <111> oriented pores in GaAs intersect each other without changing their direction of growth or shape [6], which is essential for producing 3D dielectric structures by intersecting quadruples of <111> pores starting from a common nucleus. We explored the possibility to fabricate three-dimensional photonic structures with pitting occurring on (100) surface and pores propagating along <111> crystallographic directions (the so-called "Moldavite" structures). Being mechanically stable for low degrees of porosity, such structures were evidenced to easily collapse at high degrees of porosity. For instance, when the pits are arranged in a two-dimensional square lattice with the lattice constant a, the material percolation proves to be broken at pore radius $r = 0.35a$. For the percolation limit, the volume of pores in the dielectric structures was found to be as high as 74 %.

We found that four <111>-directions of pore growth are not equivalent from the chemical/electrochemical point of view. Two of them, the so-called <111>B directions, have a lower dissolution rate than the other two <111>A directions. When the <111>A oriented pores are distributed close to each other, the nucleation of <111>B pores is strongly inhibited. An example of high density <111>A oriented pores in GaAs is shown in Fig. 3. Note that the triangles result from the intersection of pores oriented along <111>A directions. The insert shows the nucleation of two <111>A oriented pores at the initial surface of the GaAs substrate.

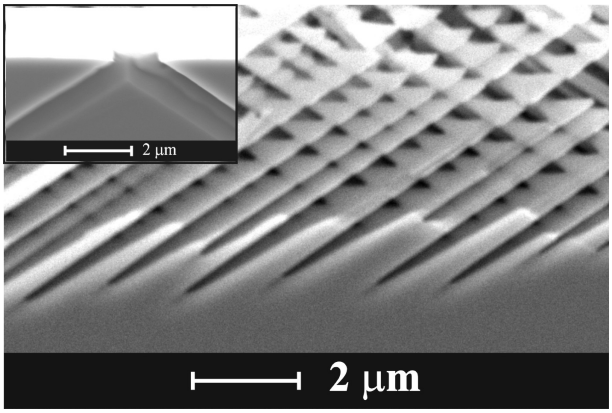

Fig. 3. Cross-sectional SEM image taken from a GaAs sample anodized at a constant current density j = 200 mA/cm^2. The insert illustrates the ramification of pores starting from a common nucleus.

Optical Properties

Taking into account the strongly enhanced second harmonic generation in porous GaP [5], we have studied the linear optical properties of porous membranes to evaluate the material transparency and optical anisotropy.
Fig. 4 shows the transmission spectrum of a porous GaP membrane fabricated on a (111) oriented crystalline substrate as described in Ref. 5. According to SEM analysis (see Fig. 1 in [5]), the membrane exhibits triangular-prism like pores with lateral average dimensions of about 50 nm. The pores are uniformly distributed and no pronounced fluctuations in their sizes exists. As one can see in Fig. 4, the optical transmission spectrum of the porous membrane shows pronounced interference fringes in the spectral interval corresponding to quantum energies lower than the indirect band gap of bulk GaP ($h\nu < E_g$ = 2.24 eV).

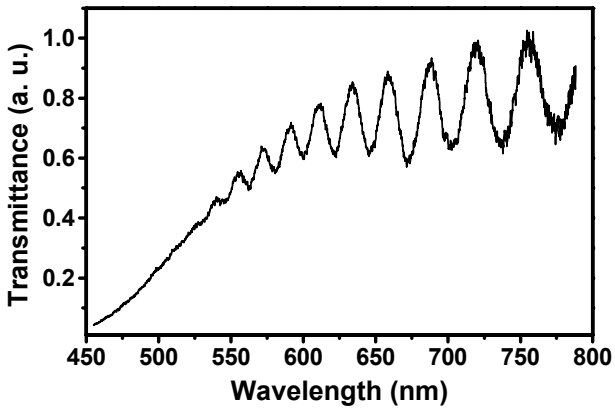

Fig. 4. Optical transmission spectrum of a porous GaP membrane.

The observation of interference fringes is indicative of the optical homogeneity of the porous medium. Due to the relatively small dimensions of both pores and skeleton entities, the porous medium proves to be optically homogeneous and, therefore, the light propagates through it without pronounced scattering. The degree of porosity defines the value of the refractive index of the membrane and the optical anisotropy caused by the preferential orientation of pores along <111> crystallographic directions. According to the effective medium theory [8], in the case of pores stretching perpendicular to the initial surface, the components of the dielectric tensor of the porous membrane can be written as follows:

$$\varepsilon_{//}(\omega) = (1-c)\cdot\varepsilon_1 + c\cdot\varepsilon(\omega) \quad (1)$$

$$\varepsilon_{\perp}(\omega) = \varepsilon(\omega)\cdot\frac{\varepsilon_1\cdot(2-c)+c\cdot\varepsilon(\omega)}{\varepsilon_1\cdot c+\varepsilon(\omega)\cdot(2-c)} \quad (2)$$

where c is the concentration of GaP, $\varepsilon(\omega)$ is the dielectric function of GaP, and ε is the dielectric constant of air. Due to $\varepsilon_{\perp}(\omega) < \varepsilon_{//}(\omega)$ for all c, porous GaP is a positive uniaxial material.

Fig. 5 shows the transmission of light with λ = 1064 nm by a porous membrane with the thickness 8.2 μm as a function of the incident angle of the laser beam. The position of the maxima displayed by the interference patterns depends upon the direction of light polarization. For the ordinary beam, the maxima occurs at the incident angles 17° and 43°, while for the extraordinary beam the maxima occurs at 21° and 49°. The analysis of the interference conditions for the two beams taking into account Eqs. (1) and (2) allowed to calculate the refractive indices: n_o = 2.43 and n_e = 2.67. So, the porous membranes exhibit pronounced birefringence necessary for phase matching in the optical second harmonic generation [5].

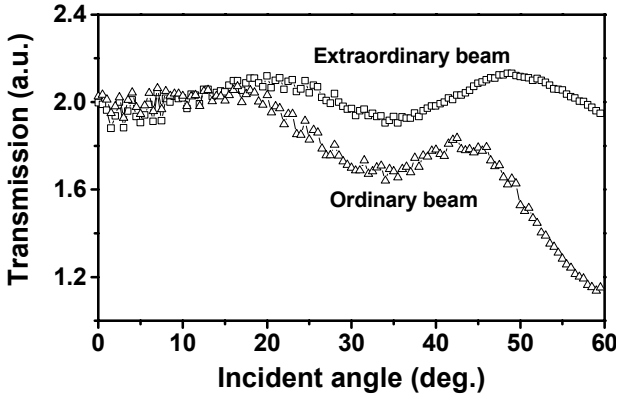

Fig. 5. Transmission of light with λ = 1064 nm by a porous GaP membrane as a function of the incident angle of the laser beam.

The possibility to fabricate ordered nanopore arrays on indium phosphide looks promising for photonic crystal applications. We carried out a comparative study of reflectance spectra taken from bulk and porous InP samples (Fig. 6). The samples were cleaved and the non-polarized reflectance was measured from the side. Interestingly, the porous specimen exhibits a pronounced decrease in reflection when approaching the infrared region. The reason of the reduced reflectance is not clear yet and further investigations are needed to throw light upon the nature of this effect.

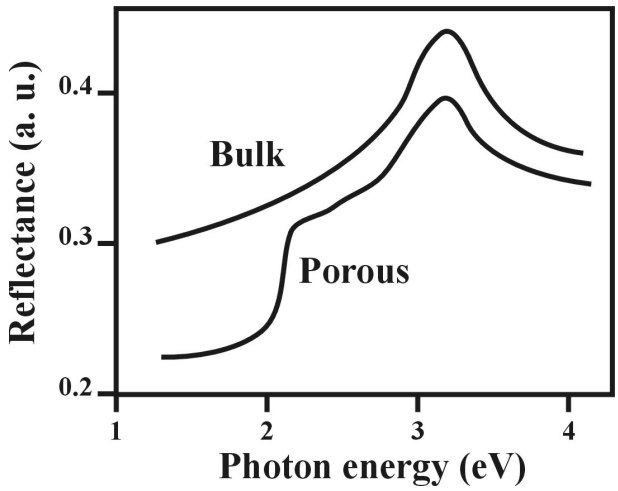

Fig. 6. Reflection spectra taken from bulk and porous InP with self-organized ordering of pores.

CONCLUSIONS

Both 2D and 3D dielectric structures can be produced on III-V compounds by electrochemical etching. Under certain etching conditions self-arrangement of submicrometer parallel pores in two-dimensional hexagonal lattices occurs in InP crystalline substrates. Anodic etching of (100)-oriented GaAs results in the formation of 3D dielectric structures due to the preferential orientation of pores along <111> crystallographic directions. The material percolation should be taken into account when designing and producing 3D dielectric structures. 2D structures exhibit porosity-induced optical anisotropy that makes anodically etched GaP and InP perspective for advanced nonlinear optical applications.

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