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Optical properties of *p*-type porous GaAs

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Abstract. Samples of *p*-type porous GaAs was obtained by electrochemical anodization of (100) oriented *p*-type GaAs. The formation of porous structure has been confirmed by Raman spectroscopy and scanning electron microscopy investigations. The low-frequency Raman shift of the peaks conditioned by the main optical phonons was observed in the Raman spectra of the porous GaAs. Estimation of the size of nanocrystallites in porous GaAs both by Raman shift and scanning electron microscopy gives approximately the same values and was about 10-20 nm. Photoluminescence investigations of porous GaAs exhibit the presence of two infrared and one visible bands.

Keywords: porous GaAs, quantum confinement, electrochemical etching, photoluminescence, scanning electron microscopy.

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1. Introduction

At present time, sapphire (Al₂O₃) has been mainly used for epitaxial growth of GaN films. But GaN/Al₂O₃ structures are characterized by a high value of strains due to a significant difference in their thermal expansion coefficient and lattice mismatch between the substrates and epitaxial films. Strains lead to a high density of dislocations and significant worsening the optical and mechanical properties of GaN films. Recently, extensive scientific and technological researches were performed to diminish residual strains in GaN films on different foreign and “native” GaN substrates (SiC, Si, GaAs, GaN, etc.) [1-3]. Porous GaAs attracts attention in recent years as a promising substrate for GaN epitaxy, for the purpose of minimizing some negative effects due to large lattice mismatch and difference in the thermal expansion coefficient of GaAs and GaN, which usually leads to high strains and the high defect density in GaN/GaAs structures. Among the first attempts of using porous GaAs as a substrate for GaN epitaxy, it was reported in [4-6]. Earlier [7], we reports about properties of cubic GaN films obtained by nitridation of porous GaAs (001). Now formation of porous GaAs *p*-type attracts significant attention, hitherto there are few reports of obtaining the porous structure on a GaAs substrate of the *p*-type (for example, [8]). In this work, we reports on the optical properties of *p*-type porous GaAs by using Raman spectroscopy and photoluminescence (PL).

2. Experimental

Porous GaAs was produced by electrochemical anodization of (100)-oriented *p*-type GaAs substrate doped with Zn, having the carrier concentration approximately $6 \times 10^{17} \text{ cm}^{-3}$. The sample was electrochemically anodized in a HF-based solution under galvanostatic conditions. The electrochemical anodization conditions were: HF–EtOH (1:3) was used as the as electrolyte, the current density was set at $8 \text{ mA} \cdot \text{cm}^{-2}$ and the anodization time was 60 s. Prior to each experiment, the samples were degreased with acetone, propanol, methanol and extensively rinsed with deionized water and were then blown dry in N₂. Electric contact to the samples was established by smearing Ga-In eutectic onto the backside of cleaved samples. The samples were then pressed against an o-ring in Teflon electrochemical cell, with a platinum working electrode. The microstructure of the as-prepared porous GaAs layer was studied using scanning electron microscope (SEM), Raman spectroscopy and PL. Raman spectra were obtained using a double monochromator ДФС-24. The samples were excited with 488 nm line of an Ar⁺ laser with the power of 100 mW .

3. Results and discussion

3.1. Scanning electron microscopy

SEM was used to investigate the por-GaAs layers surface. From Fig. 1a, we observe pores having the form

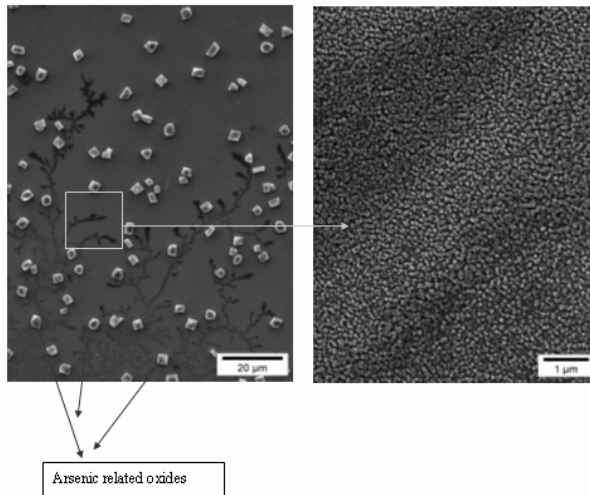


Fig. 1. SEM images of a) the top view of as-prepared porous GaAs, b) higher magnification view of the region inside the square of (a).

of the labyrinth, as well as crystallites of GaAs. On the surface of por-GaAs, diamondlike As_2O_3 crystallites were observed (Fig. 1a). Analysis of the SEM image (Fig. 1b) obviously demonstrates that the GaAs substrate was formed into the porous structure. From SEM investigations, the average size of GaAs nanocrystallites was estimated within the range 15-25 nm.

3.2. Raman spectroscopy

Treatment of porous GaAs in H_2 ambient was used to remove residual chemical reaction products formed on the GaAs surface during electrochemical processing. The estimation of the average diameter of GaAs nanocrystallites was made using the shift value of the Raman peak, the shift is due to longitudinal optical (LO) phonons of GaAs. Fig. 2 shows Raman spectra for the

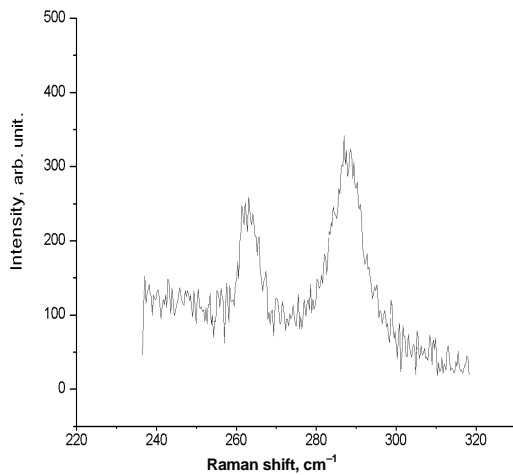


Fig. 2. Raman spectra of porous GaAs (sample with the maximum value of the peak shift).

sample of por-GaAs with the maximum shift value. From the obtained data, we estimated the average size of GaAs nanocrystallites, as described in [9], its value is about 8 nm.

3.3. Photoluminescence measurements

Fig. 3.1 shows PL spectra (at 77 K) of initial GaAs (a) and por-GaAs (b). There are no shift to the shorter wavelengths for the peak at 833 nm (1.49 eV) of por-GaAs, as it was reported for the similar peak in [10]. We associated this peak with quasi-interband transition in the initial mono-GaAs substrate. Also, the peak at 903 nm (1.37 eV) was observed, its presence is scarcely noted for porous GaAs of the *p*-type except for [8], where this peak (with a much less intensity) was also observed. We associate it with significant fluctuations of conduction and valence band extrema due to layer porosity.

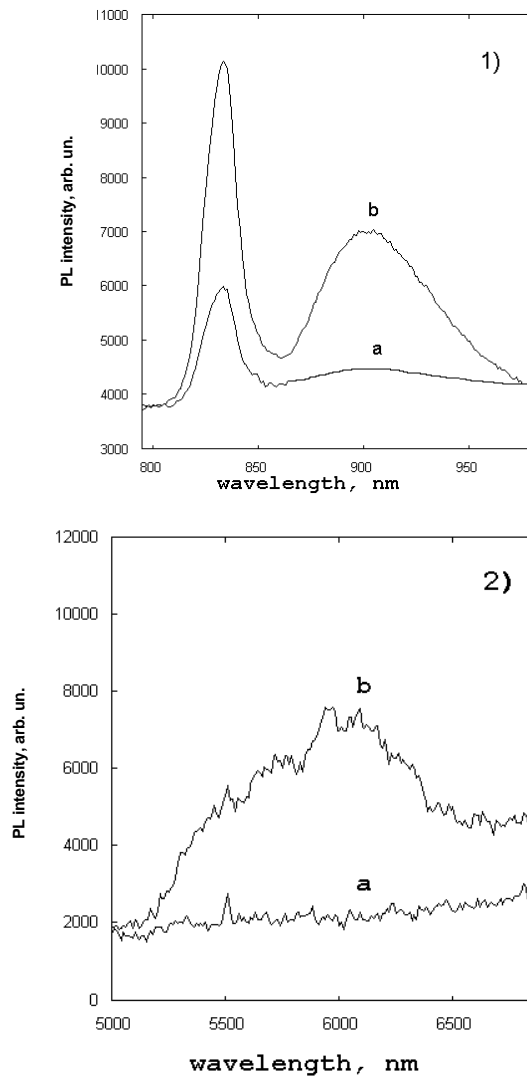


Fig. 3. 77 K Photoluminescence spectra of : a) initial GaAs, b) porous GaAs.

Beside peaks at 833 and 903 nm, the broad line in the visible region (peaking approximately at 600 nm) was observed for por-GaAs, the so-called yellow PL (Fig. 3.2), which indicates formation of GaAs different-sized cluster at electrochemical etching, a) - initial GaAs, b) - por-GaAs. The similar data for visible PL were presented in [11]. There are two basic assumption of the origin of visible PL in por-GaAs. The first explanation implies that the band in the visible region of photoluminescence is caused by residual products of the chemical reaction in the cause of etching (oxides Ga₂O₃, As₂O₃) [7]. The second assumption associates visible PL with quantum confinement effects due to nano-sized GaAs crystallites [12]. The average size of GaAs nanocrystallites was calculated from PL measurements, its value was about 10 nm.

We suppose that oxides has no considerable contribution to the origin of visible PL in porous GaAs inasmuch as after electrochemical etching the samples were treated in H₂ ambient. XPS measurements show that such treatments lead to a significantly decreasing intensity of the oxides signal, as was reported earlier [10]. On the other hand, comparison of the position of PL peak in the visible spectral range (for porous GaAs) and that of GaAs nanocrystal [13] let us consider that quantum confinement effects prevail in origin of the band in visible PL.

4. Conclusion

From PL measurements of por-GaAs, the average size of GaAs nanocrystallites was determined, its value is about 10 nm. The distinctive features of presented PL spectra is the broad intensive band with the peak at 903 nm, which is typical for *p*-type por-GaAs. The broad PL band in the visible range indicates the presence of GaAs nanocrystallites on por-GaAs. From Raman spectroscopy, the average value for GaAs nanocrystallites was estimated, it was about 8 nm. PL and Raman investigation are in a good agreement in a view of calculations for GaAs nanocrystallites. Morphology of por-GaAs surface was investigated by scanning electron microscopy, calculation of the size of GaAs nanocrystallites gave the value of 15-25 nm. The difference in values of nanocrystallite sizes obtained from PL, Raman, on the one hand, and SEM investigations, on the other hand, can be explained as the presence of oxide layers on por-GaAs surface that in its turn led to the increasing visible size of GaAs nanocrystallites.

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