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Photoluminescence and Raman Scattering of Porous GaP

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In this paper we report the first observation of a photoluminescence in GaP planar quantized structures. To produce this material we used an electrochemical etching of GaP:Te. The appearance of the intensive PL at 2.3 eV correlated well with a significant changing in Raman spectrum. After chemical etching of GaP wafer the Raman peak at 366 cm^{-1} corresponded to the "forbidden" in used scattering geometry TO-phonon was observed. The intensity of TO-phonon line as well as LO peak (403 cm^{-1}) was 4 times larger for porous GaP than for the untreated wafer. Our result shows that the observed photoluminescence of GaP is originated from the small microstructures.

1. INTRODUCTION

Nanocrystalline materials are interesting for the investigators due to their qualitatively new properties, differing them from the amorphous and crystalline phases of the same materials [1,2]. These properties are grounded on the great specific surface of a nanoscale material and on the contribution of the quantum dimensional effects, playing an essential role for the crystallites of few nanometers. By now one of the most known and intensively investigated materials of this type is porous silicon [3-5]. Side by side with the investigations of the porous silicon structure and the attempts to clarify the origin of its intensive photoluminescence (PL) the efforts are applied to produce the similar nanostructured (porous) materials on the base of another non-direct band gap semiconductors. The comparison of their properties seems to be promising for understanding the origin of PL. Moreover they are interesting by themselves as the new phases of the well-known materials. Nowadays the porous SiC [6,7] and SiGe [8] already have been produced and investigated.

This paper reports the first success in the synthesis of a porous GaP and in its optical properties investigating. The appearance of a narrow (FWHM of 35 nm) intensive PL band with a maximum at 540 nm has been registered. The Raman spectrum of a porous GaP demonstrates an additional low- frequency shoulder of the band, corresponding to LO-phonon of a substrate, and an intensive TO-phonon band, geometrically forbidden for a substrate. Porous GaP is going on the line of non-direct band gap semiconductors (porous Si, SiC, SiGe) possessing the intensive PL in visible. This material is a very convenient object for the investigations because its structure is very similar to silicon and the properties of the virgin GaP monocrystal are known very well [9].

2. EXPERIMENTAL DETAILS

For forming the porous GaP layers the process of an electrochemical anodization was used, completely identical to the process, utilizing for the porous silicon deposition (with the same HF electrolyte [10]). We have selected such process because of its simplicity and known good results for porous silicon, although we intend in the nearest future to look for the optimal regimes and electrolyte components namely for a porous GaP production.

We used n-GaP wafers (100), Te doped with the concentration $n=10^{17}$ cm^{-3} . Anodization was performed in a two-chambers cell with an electric current density 7-20 mA/cm^2 and the durations 10-20 min. Porous GaP layers were differed from the substrate because of their light - yellow colour. The intensive green photoluminescence of these layers were noticeable by eyes during the mercury lamp illumination.

Two types of the optical investigations of a porous GaP were performed: a Raman spectroscopy and a Photoluminescence registration.

Raman spectra were obtained in backscattering geometry with a triple monochromator with spectral slit width 2 cm^{-1}. The Ar-ion laser (488 nm) was used for the scattering excitation. To avoid the heating effects a cylindrical optics was utilized provided the spot sizes 1x0.02 mm^2 and corresponding intensity density not higher than 200 W/cm^2.

PL spectra were registered at room and liquid nitrogen temperatures. A beam of pulse nitrogen laser (diameter 2 mm, wavelength 337 nm, frequency 100 Hz, power density 5-10 mW) was used as an exciting irradiation.

3. RESULTS

Fig.1 demonstrates the Raman spectra of a virgin GaP wafer (curve 1) and a porous layer onto the same wafer (curve 2).

There is a single symmetrical peak at 403 cm^{-1} (LO-phonon) in the Raman spectrum of a wafer. It corresponds to the well-known shape of a spectrum for GaP monocrystal [11], where TO-phonon is forbidden. Nevertheless both of these peaks (LO and TO-phonons) present in the Raman spectrum of porous layer. Moreover the intensity of TO-peak becomes higher comparing with LO-peak, and an average scattering intensity in a porous layer is more higher, than in a virgin crystal. The peak maxima for both of lines correspond to their known values for GaP monocrystal but the LO-mode contour is asymmetrical because of an additional low-frequency shoulder. Such shape of the Raman spectrum already was observed for the sputtered polycrystalline GaP films, constituting of the grains with the sizes of 100 nm [11]. It should be mentioned that in the Raman spectrum of porous GaP (on the contrary to the sputtered films [12]) the wide band of an amorphous phase near 80-200 cm^{-1} is practically absent. So the structure of a porous layer may be supposed to be exceptionally monocrystalline.

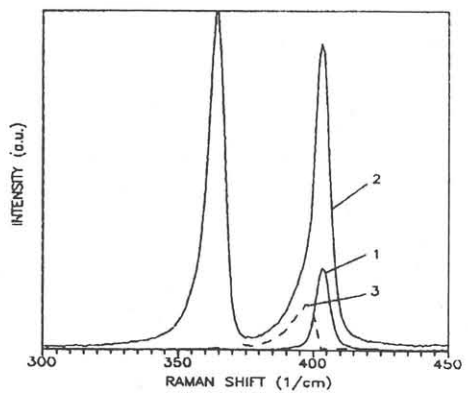

Fig.1 The Raman spectra of initial GaP wafer (1), and porous GaP layer (2). Dashed line (3) shows the result of computer decomposition of LO-phonon line.

After the computer decomposition of the asymmetrical contour of LO-mode onto the sum of two bands the position of an additional low-frequency band (Fig.1 curve 3) was determined (397 cm^{-1}). This value corresponds to the frequency of a surface mode [12].

A contribution of the surface vibrations was also revealed in IR reflection spectra [14].

As for an appearance of a geometrically forbidden TO-phonon mode, it seems reasonable to consider two reasons: phonon confinement in the small crystallites, constituting the porous layer [13], or a sufficient misorientation of these crystallites comparing to the substrate. Indeed, if the preferable crystallographic orientation of thenanocrystallites coincides with the substrate's one (as it was observed for a porous silicon [10]) then a spatial restriction of phonons could be considered as a main reason of TO-mode appearance. In this case it is possible to estimate the sizes of crystallites using the position and width of an observed band. But for the calibration it is necessary to perform a few direct measurements (HREM) of their sizes and dispersion.

In case of a disorder-induced appearance of TO-line in the Raman spectrum of a porous GaP it is necessary to suppose that the electrochemical anodization led to the crystallographic orientation of the crystallites completely independent on the initial orientation of a substrate. Moreover the orientation along the axis, turned on 90 with respect to the initial orientation can be considered as a preferable one.

The new peculiarities in luminescence spectrum are, evidently, the most interesting. Fig.2 shows PL spectra of GaP substrate (curve 1) and of the porous layer (curve 2).

For excitation a radiation of a nitrogen laser (hw=3.68 eV) was used. There was the only wide (FWHM=200 nm) band of PL in a red spectral area (maximum at 740 nm) in PL spectrum of a substrate. This band is connected with the recombination of the levels inside band gap [10].

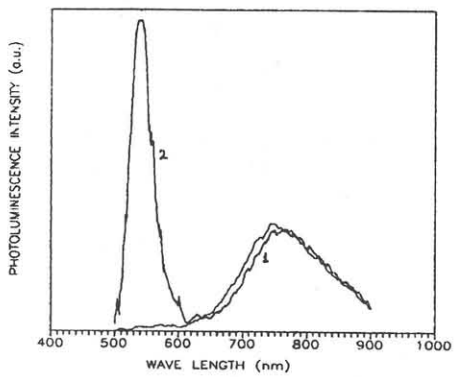

Fig.2 Photoluminescence spectra of initial GaP wafer (1) and porous GaP layer (2).

The same PL spectrum was observed for GaP crystal excited by the radiation of Ar-ion laser (wavelengths 458 and 488 nm). For porous GaP layer in case of a nitrogen - laser excitation side by side with a "red" PL

an intensive and narrow PL band appears in a "green" spectral area (maximum at 540 nm, hw=2.3 eV). This energy is some higher than the indirect width of a crystalline GaP band gap at room temperature (2.27 eV), but lower than the direct transition energy (2.78 eV). In case of an excitation with a lower photon energy (Ar-ion laser with 458 nm (2.71 eV)), a "green" PL line was still noticeable, but its intensity was just 5% from the "red" band intensity, and its maximum shifts to 550 nm. In case of an excitation with 488 nm (2.54 eV) a "green" PL line was practically absent in the spectrum. It should be noticed that in the last two cases the pump photon energies were lower than the direct transition energy, although they were higher than the position of a "green" PL maximum and a band gap width of a a crystalline GaP.

We have performed the measurements of PL spectra of a porous GaP (with excitation by a nitrogen-laser) at room temperature and at a liquid nitrogen temperature. No changes in the intensity and in the spectral positions of the lines have been revealed. Taking into account an experience of the porous silicon studing, we couldn't ascribe an intensive luminescence in a porous GaP only to the action of the quantum effects. The role of the surface is difficult to overestimate. Even in the case of the quantum dimensional effects an intensive PL may be completely quenched by the surface, and on the contrary the surface may add the new radiation transitions to the recombination from the quantum levels. So the additional investigations are required to clarify the origin of PL in porous GaAs and to identify its radiation transitions.

4. CONCLUSIONS

Thus, this paper reports about a first experience of synthesizing a porous GaP and investigating its optical properties. A new narrow (FWHM=35 nm) band of an intensive PL was revealed in a "green" spectral range (band maximum position 540 nm). The Raman spectra of a porous GaP have demonstrated an additional low-frequency tail of the band, corresponding to LO-mode of the crystalline GaP; and an appearance of an intensive line, corresponding to TO-mode, geometrically restricted in a virgin (100) GaP wafer. On the base of the observed data the porous GaP layer was supposed to be continued from the nanocrystals of GaP, and the observed changes in the Raman spectra were ascribed to the contributions of the phonon confinement effects and the surface modes. The origin of a photoluminescence is questionable now and requires the additional investigations.

5. REFERENCES

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