

Intense photoluminescence in porous gallium phosphide

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Nanopore gallium phosphide has been produced, and its optical characteristics have been studied. There is intense photoluminescence near the absorption edge. There are additional IR absorption bands. Measurements of the Raman scattering and IR reflection spectra reveal significant changes in the phonon spectrum. © 1994 American Institute of Physics.

Nanocrystal materials or nanocomposites are attracting research interest because of their qualitatively new properties, which are not seen in the corresponding substances in a purely amorphous or crystalline phase.^{1,2} These properties stem from the very large specific surface area of the interfaces between the nanocrystals and also from quantum size effects in the individual nanocrystals. A representative material of this class is porous silicon, whose properties have recently been the topic of very active research.^{3–5} In addition to more-detailed studies of the structure of porous silicon and attempts to unambiguously interpret its intense photoluminescence, efforts are being made to produce similar nanostructured (porous) nanocomposites on the basis of other semiconductors. In the first place, comparison and analysis of the properties of these nanocomposites may shed light on the photoluminescence mechanisms; second, the new nanocomposites would be of interest in their own right, as new materials based on known compounds. For example, porous SiC (Refs. 6 and 7) and porous SiGe (Ref. 8) have been produced, and their properties are being studied.

In this letter we are reporting the first production of porous gallium phosphide and a study of its optical properties. A narrow band (35 nm at half-maximum) of intense photoluminescence, peaking at 540 nm, has been detected. A substantial change in the phonon spectrum has also been detected. This change is manifested by significant changes in the IR reflection spectra in the region of LO and TO phonons, by the onset of a low-frequency edge in the line of Raman scattering by LO phonons, and by a significant intensification of the Raman line corresponding to the TO mode of the phonon spectrum, which is forbidden in the Raman spectrum of the original crystal. Additional absorption bands have been observed in IR transmission spectra.

Since intense luminescence has been observed in porous silicon, formed from the indirect-gap semiconductor Si, the indirect-gap compounds SiC and SiGe have been

selected as starting compounds for producing other porous semiconductors (Refs. 6–8). Gallium phosphide is very convenient from this standpoint, since it, too, is an indirect-gap compound, and its band structure is similar to that of silicon.⁹ The properties of bulk gallium phosphide have furthermore been studied in detail.

Layers of porous GaP were produced by electrochemical anodizing in a procedure completely identical to that used to produce porous silicon, with the same HF-based electrolyte. One might argue that the optimum electrolyte composition and the optimum values of other conditions would be quite different for producing porous GaP. However, the successful use of this electrolyte in the case of the compounds mentioned above, along with its simple chemical composition, persuaded us to use it. We produced porous gallium phosphide with the help of an *n*-GaP substrate in the (100) orientation, doped with tellurium to a carrier density $n = 3 \times 10^{17} \text{ cm}^{-3}$. The anodizing was carried out in a two-chamber cell at current densities of 7–20 mA/cm² at current durations of 10–20 min. The color of the layers of porous gallium phosphide (bright yellow, in the case at hand) differed from that of the substrate. During illumination with a mercury vapor lamp, a photoluminescence in the green part of the spectrum from the porous layer could be seen with the naked eye.

This study of the optical properties included Raman spectroscopy, photoluminescence measurements, and IR transmission and reflection Fourier spectroscopy. Raman spectra were recorded with the help of a triple monochromator with a slit with a spectral width $\sim 2 \text{ cm}^{-1}$ in a backscattering geometry. The Raman spectra were excited by the beam from an argon laser (the 488-nm line). Cylindrical optics was used to prevent effects of heating by the laser beam (the dimensions of the spot were $1.0 \times 0.02 \text{ mm}$, and the power density did not exceed 200 W/cm^2).

Photoluminescence spectra were recorded on an SDL-2 spectrometer. The pump was the unfocused beam, 2 mm in diameter, from an ILGI-503 pulsed nitrogen laser, with a wavelength of 337 nm (a photon energy $\hbar\omega = 3.68 \text{ eV}$), a pulse repetition frequency of 100 Hz, and a power of 5–10 mW. The IR transmission and reflection Fourier spectra were measured with the help of a Bruker IFS-113v spectrometer with a resolution better than 1 cm^{-1} over the range 20–15 000 cm^{-1} . The original substrate, without the porous layer, was used as a reference.

Figure 1a shows Raman spectra of the original substrate (curve 1) and of the porous layer (2). The spectrum of the original substrate has a single, symmetric peak at 403 cm^{-1} (this is scattering involving an LO phonon). This spectrum corresponds to the well-known results for single-crystal gallium phosphide in the given geometry, in which scattering involving a TO phonon is forbidden. In the spectrum of the Raman scattering of the porous layer we see both lines. The intensity of the scattering involving the TO phonon is higher than that of the scattering involving the LO phonon, and the total intensity of the Raman scattering is higher than that for the original material. The positions of the peaks correspond, within the resolution, to the frequencies of LO and TO phonons of bulk gallium phosphide, but it can be seen that the line of the LO mode is asymmetric and has a low-frequency knee. These features are characteristic of sputtered polycrystalline gallium phosphide film with nanocrystal dimensions $\sim 100 \text{ nm}$ (Ref. 10). The Raman spectrum of the porous gallium phosphide is essentially free of the band of amorphous GaP at $80\text{--}200 \text{ cm}^{-1}$, which is characteristic of sputtered films.¹¹

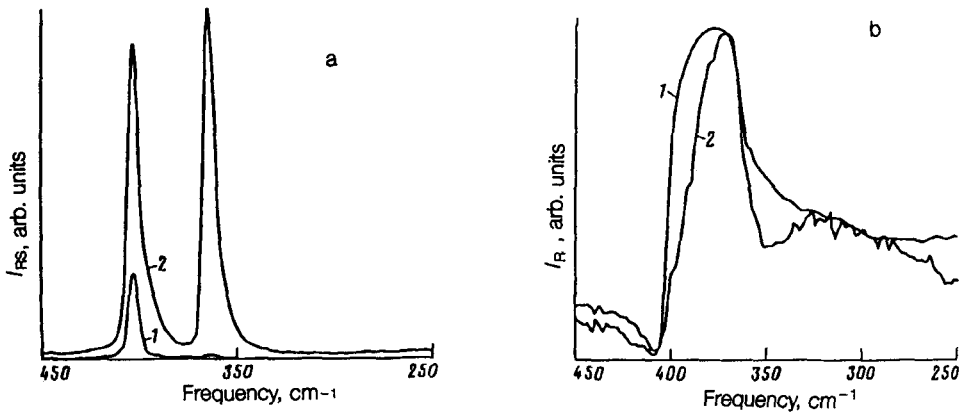


FIG. 1. a: Raman-scattering spectra I_{RS} of the original substrate (curve 1) and of the porous GaP layer (2). b: Reflection spectra I_R of the original substrate and of the porous GaP layer (curves 1 and 2, respectively), in arbitrary units, at different scales.

It can thus be asserted that the layer of porous gallium phosphide consists primarily of nanocrystals. If we assume that the asymmetric LO line is the superposition of at least two peaks (curves 2 and 3 in Fig. 2), then the second peak (curve 3 in Fig. 2) has a frequency of 397 cm^{-1} and corresponds to the frequency of surface vibrations.¹¹ This interpretation is supported by the IR reflection spectra in the region of phonon frequencies in Fig. 1b (curve 2). It follows from these spectra that the phonon spectrum of porous GaP is quite different from that of the original substrate (curve 1). Specifically, in the interval between the TO and LO frequencies there are several vibrations, rather than just one. This result apparently is evidence of variations in the size and shape of the nanocrystals making up the film of porous gallium phosphide. In connection with the orientation and dimensions of these crystals we should point out the following: While the orientation in nanocrystals tends to preserve the original orientation, as in porous silicon,

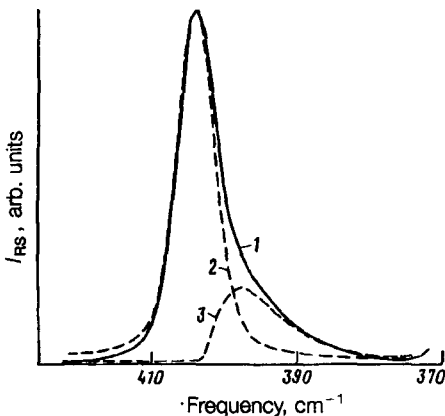


FIG. 2. Line of the LO Raman line (curve 1) and its decomposition into two components (curves 2 and 3).

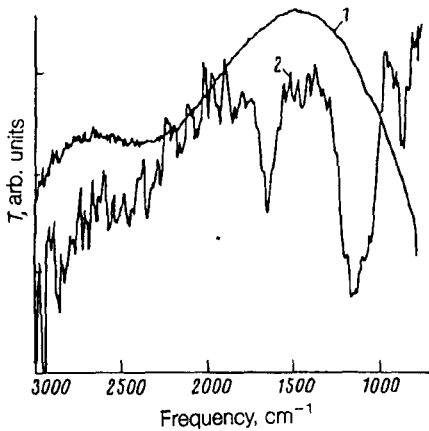


FIG. 3. Fourier spectra of the IR transmission of the original substrate and of the porous layer (after subtraction of the substrate contribution) of GaP (curves 1 and 2, respectively).

the onset of the TO line is due primarily to spatial confinement of phonons in the nanocrystals.¹² Determining the dimensions of the nanocrystals and the variations of these dimensions, however, will require either direct measurements or more-detailed measurements of Raman scattering and a detailed analysis of the scattering lineshapes. If, on the other hand, the line of a TO phonon arises in the Raman spectra because of a disorder of the crystallites which arises during the electrochemical etching, then we would have to assume that the crystallographic orientation of these crystallites is essentially unrelated to the original orientation of the substrate and that, furthermore, we are seeing some excess of the number of crystallites whose orientation corresponds to a rotation of the crystallite through 90° with respect to the substrate (Fig. 1a).

Curves 1 and 2 in Fig. 3 show IR transmission spectra of the original substrate and of the film (after the substrate contribution has been subtracted), respectively. We see that some additional absorption lines at 1660 , 1160 , and 886 cm^{-1} arise in the porous gallium phosphide. An interpretation of these lines will require a more detailed study.

Apparently more interesting are the luminescence properties of the layers of porous gallium phosphide. Figure 4 shows photoluminescence spectra of the original substrate (curve 1) and of a layer of porous gallium phosphide (curve 2) during excitation by the beam from an argon laser ($\hbar\omega = 3.68\text{ eV}$). In the original crystalline GaP there is a broad photoluminescence band (200 nm at half-maximum) only in the red region (the peak is at 740 nm), which is due to recombination between levels in the band gap.⁹ The same photoluminescence spectrum is observed during excitation by an argon laser (the lines at 457.9 and 488 nm). In the case of the layer of porous gallium phosphide, excitation by the beam from the nitrogen laser gives rise to, in addition to the red photoluminescence band, an intense and narrower (35 nm at half-maximum) photoluminescence band in the green part of the spectrum, peaking at 540 nm ($\hbar\omega = 2.3\text{ eV}$). This energy is just slightly above the indirect width of the band gap of crystalline GaP at room temperature (2.27 eV), but it is below the energy of the direct transition (2.78 eV). For a pump with a smaller photon energy, e.g., the beam from an argon laser (the 457.9-nm line with $\hbar\omega = 2.71\text{ eV}$), the green photoluminescence line can still be seen, but its intensity is 5% of that of the red band, and its peak has shifted to 550 nm. During excitation by the

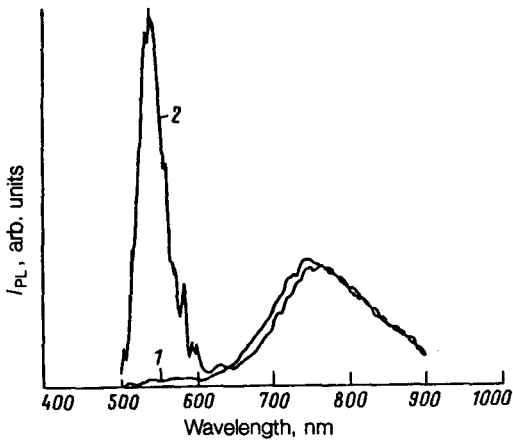


FIG. 4. Photoluminescence spectra of the original GaP substrate (curve 1) and that of the porous layer (2) during excitation by the beam from a nitrogen laser (wavelength of 337 nm, $\hbar\omega = 3.68$ eV).

488-nm line (2.54 eV), the green photoluminescence is essentially absent. In the latter cases, the energies of the pump photons are below the energy of the direct transition, although above the peak of the green photoluminescence and the width of the band gap of crystalline GaP.

Measurements of the photoluminescence spectra at room temperature and at liquid-nitrogen temperature (with pumping by a nitrogen laser) showed that the intensity and spectral position of the photoluminescence lines are essentially independent of the temperature over the specified range. In view of experience gained in research on the nature of the photoluminescence of porous silicon, it would have been rash to conclude on the basis of this preliminary study that the intense photoluminescence in porous gallium phosphide is the result of exclusively quantum size effects in the GaP nanocrystals, since it is difficult to overestimate the role of the surface. The state of the surface may completely suppress the photoluminescence, even if quantum size effects are occurring, and it may add some new radiative transitions to recombination from size-effect levels. Accordingly, further research will be necessary to identify the radiative transitions in porous gallium phosphide and to determine the nature of its photoluminescence.

In summary, porous gallium phosphide has been produced for the first time, and its optical properties have been studied. A narrow band (35 nm at half-maximum) of intense photoluminescence has been observed. This band has its peak at 540 nm. It has been found that there is a substantial change in the phonon spectrum, which is manifested by a significant change in the IR reflection spectra in the region of LO and TO phonons, by the onset of a low-frequency wing in the line of Raman scattering by LO phonons, and by the onset of an intense Raman line corresponding to the TO mode of the phonon spectrum, which is forbidden in the Raman spectrum of the original crystal. Additional absorption bands at 1660, 1160, and 886 cm^{-1} have been observed in the IR transmission spectra. It is suggested on the basis of the experimental data that a layer of porous gallium phosphide consists of GaP nanocrystals and that the changes in the phonon spectrum may be due to a spatial confinement of phonons and the onset of surface phonon excitations.

Further research will be required to determine the nature of the photoluminescence and the IR absorption bands.

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