VNU Journal of Science: Natural Sciences and Technology

Journal homepage: https://js.vnu.edu.vn/NST

Study on Photoluminescence Properties of Porous GaP Material

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Received 06 April 2018
Revised 30 May 2018; Accepted 28 June 2018

Abstract: This paper reports on the photoluminescence of porous GaP prepared by electrochemical anodization of (111)-oriented bulk material. Porous and bulk GaP exhibits green and red photoluminescences, respectively when excited by a 355-nm laser. The photoluminescence intensity of porous GaP is much stronger than that of the bulk sample. Temperature-dependent time-resolved photoluminescence shows that the green emission gradually decreases when the temperature increases and the photoluminescence full width at haft maximum (FWHM) slightly narrows with decreasing temperature. These results are assigned to the contribution of lattice vibrations. Raman scattering measurement is carried out to confirm the size decrease of the porous GaP material.

Keywords: PorousGaP, photoluminescence, time-resolved photoluminescence, electrochemical etching.

1. Introduction

The discovery in 1990 by Canham of the observation of visible room-temperature luminescence in etched silicon [1] has led to a renewed interest in porous semiconductors. Si presents an indirect band gap semiconductor of 1.1eV at 300 K, which makes it useful for optical applications in near- infrared range. However, Si emits strong luminescence in the visible spectral range in the form of porous structure. Due to its unique optical properties compared to bulk Si [2-3], porous silicon has attracted much attention of technologists recently for developing optical, photonic and electronic devices [4,5,10], sensors [6,7,8] and (bio) chemical reactors [9]. Similar to silicon, III-V semiconductor such as GaP has an indirect band gap (2.27eV at room temperature) and its band structure is similar to that of silicon. These make porous GaP a very promising photonic material for the visible spectral range. Porous GaP is of considerable interest for both fundamental research and technological application [11-21]. However, the temperature-dependent time-resolved photoluminescence study has not been much mentioned.

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https://doi.org/10.25073/2588-1140/vnunst.4703

In the present work, the optical characteristics of porous GaP were investigated by means of steady-state and time-resolved photoluminescence spectroscopies. The overall photoluminescence (PL) spectra of porous GaP shows two spectral components peaking at 550 nm (2.25eV) in the near-band-edge region of GaP and 770 nm (1.65 eV) at room temperature. The intense and narrow green luminescence band may be attributed to radiative combination of excitons related to bulk GaP [11] while the red luminescence band is assigned to radiative recombination via donor acceptor pairs in the band gap [12,13]. These emission bands have been also typically observed in bulk GaP. However, the intensity is much lower than that in porous GaP [12, 14-16]. In the temperature-dependent time-resolved photoluminescence (TRPL) spectroscopies, we did not observe the emission at 770 nm. Intensity of the green emission gradually decreases when the temperature increases in the temperature range from 25K to 210K.

2. Experimental

The sample used in this study was produced with the help of an n-GaP substrate in the (111) orientation, doped with tellurium to a carrier density n = $3x10^{17}cm^{-3}$. Porous GaP was formed by anodic etching GaP in an electrochemical cell at current density of 20 mA/cm^2 for 15 min. A mixture solvent of HF and methanol (25% HF) is used as an electrolyte. The color of layers of porous GaP is bright yellow and differ from that of the substrate. All etching experiments were done at room temperature.

In the PL measurements, the 355-nm laser line, which is above the GaP transition energy was used as the excitation source. The PL signals were dispersed by using a 0.55-m grating monochromator (Horiba iHR550) and then detected by a thermoelectrically cooled Si-CCD camera (Synapse). The TRPL signals were dispersed by using a 0.6-m grating monochromator (Jobin-Yvon HRD1) and then detected using a fast photomultiplier (Hamamatsu model H733, with the rise time of 700 ps). Averaging the multi-pulses at each spectral point using 1.5 GHz digital oscilloscope (LeCroy 3962) strongly improved the signal-to-noise ratio. The Raman excitation was provided by the 632.8 nm line of He-Ne laser. To deconvolute the Raman scattering spectra into reasonable components, the best curve fits were performed based on the assumption that each band is a Gaussian band-shape.

3. Results and discussion

The Raman spectra of bulk GaP and porous GaP was showed in Figure 1. The spectrum of original substrate and porous GaP has both peak at 404.2 cm^{-1} corresponding to LO phonon and peak at ~ 365 cm^{-1}corresponding to TO phonon. The intensity of the scattering involving LO phonon in porous GaP is higher than that of original material. The electrochemical anodization leads to a more complex Raman spectrum, where the LO-phonon peaks is shifted to lower frequency (0.5 cm^{-1}) and broadened with a low-frequency shoulder. Such transformations of the Raman scattering have been previously attributed to the manifestation of quantum size phenomenon [17,18]. It is to be noted here that the Raman spectrum of porous GaP is free of the band of amorphous GaP at 80 – 200 cm^{-1}. It can thus be asserted that porous GaP consists primarily of nanocrystals [11,12]. A detailed analysis of the porous GaP spectrum has shown that the asymmetric LO line consists of two Gaussian components peaked at 403.7 cm^{-1} and 397 cm^{-1}. The first one is ascribed to LO phonon, while the second one corresponds to the frequency of surface vibrations[11,12]. The intensity of the latter band increases with surface-to-volume ratio [11]. This result proves significant contribution of surface to the formation of porous GaP properties.

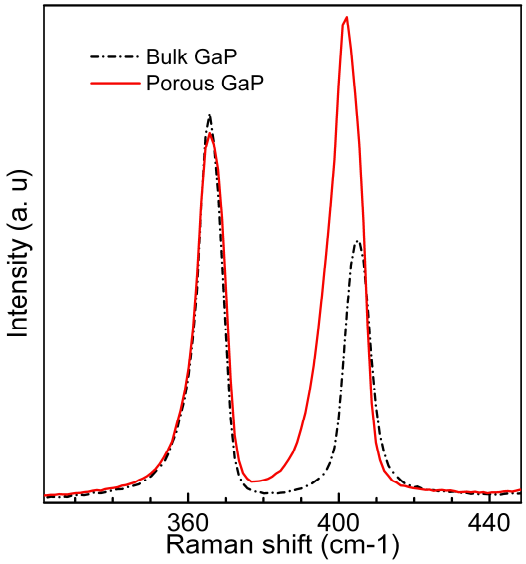

Figure 1. Raman scattering spectra of bulk and Porous GaP at 300 K

Figure 2 shows the PL spectra of bulk and porous GaP under 355-nm excitation. In the PL spectra of both samples, we observed not only the peak in the near-band-edge region of GaP at 550 nm (2.25 eV) but also that in red region at 770 nm (1.65 eV). The energy at 2.25eV 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). The intense and narrow (35 nm at haft-maximum) green luminescence band may be attributed to radiative recombination of excitons related to bulk GaP [11]. In addition to the green PL band, a broad red photoluminescence (140 nm at haft-maximum) is assigned to the molecular complexes Zn_{Ga} - O_P and/or Cd_{Ga} - O_P, in the result of radiative combination via donor acceptor pairs in the band gap [12,13]. The photoluminescence intensity of porous GaP is much stronger than that of the original sample [12, 14-16]. However, the enhancement of intensity of porous GaP is still a mystery, probably caused by surface states.

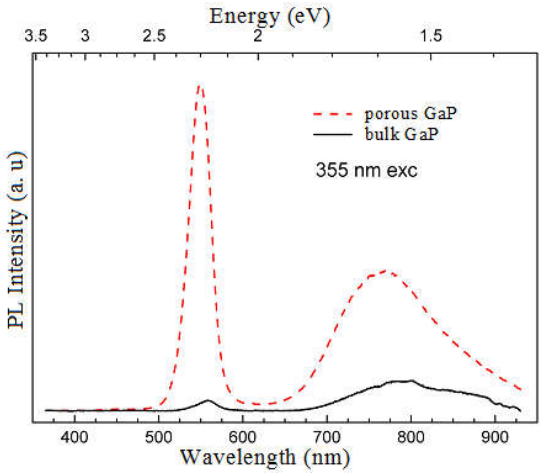

Figure 2. PL spectra of bulk and porous GaP under 355-nm excitation.

In the TRPL spectra, we only observed the green emission band at 550 nm (2.25eV) but did not observe the red emission band at 770 nm (1.65 eV). The absence of the emission band resulting from radiative recombination via donor- acceptor pairs possibly due to that the life time of two bands is very different (1 ns with the green emission and hundreds of nanoseconds with the red emission) and the instant PL intensity of the green emission band at a certain time interval after the pulsed excitation is hundreds of times greater than that of the red emission band. Figure 3 presents the TRPL spectra of the green band at 2.25eV of porous GaP under the 355-nm laser line excitation at various temperatures from 15 K to 275 K. It is clearly seen that the green emission intensity increases and PL full width at haft maximum (FWHM) narrows gradually with decreasing temperature. This reveals a contribution of lattice vibrations. To study in more clear about the evolution of green band with temperature, we analyze the data from the temperature-dependent PL. Figure 4 shows TRPL intensity of the green emission band from porous GaP as a function of temperature under 355-nm excitation. The experiment shows that intensity of the green emission gradually decreases when the temperature increases in the temperature range from 25K to

210K. This means that even with a very small assemble of atoms to form nanocrystals of porous GaP the temperature-dependence of PL intensity takes place the same as in the bulk, meaning the contribution of the microfield induced by lattice vibrations.

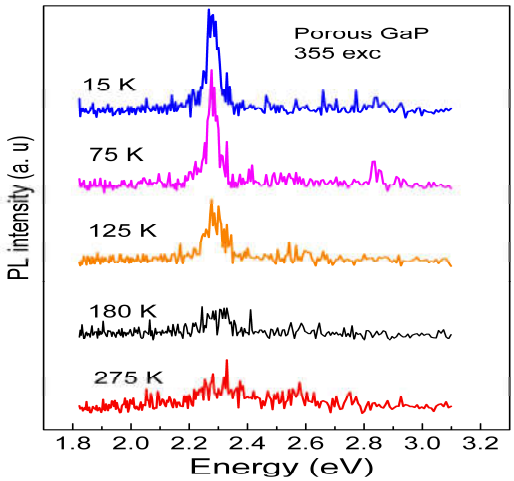

Figure 3. TRPL spectra of porous GaP as a function of temperatureunder 355-nm excitation.

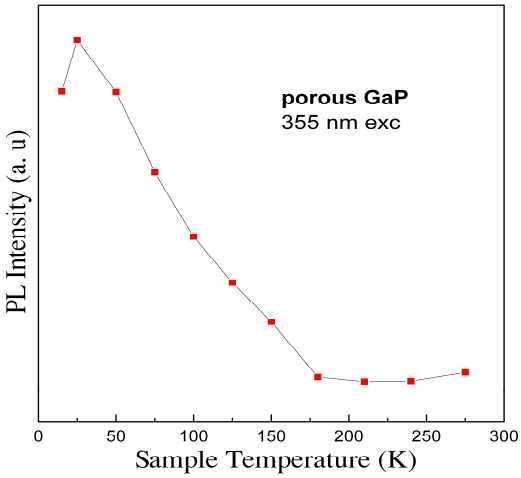

Figure 4. TRPL intensity of porous GaP as a function of temperature under 355-nm excitation.

Generally, almost electronic transitions could contribute more or less to the lattice vibrations. In the bulk crystal, themicrofields (originated from lattice vibration) induced the PL intensity decreasing. In a very small assemble of atoms to form nanocrystals the contribution of the microfield induced by lattice vibrations is also taking place, giving a rise in intensity with decreasing temperature. Thus, some characteristics taken place in bulk materials could happen even in the very small assemble of atoms in nanocrystals as porous structure, e.g. the PL intensity decreasing with temperature and donor-acceptor pairs recombination [22].

4. Conclusion

Porous GaP was studied using PL and TRPL techniques and the 355-nm light as the excitation source. In PL spectra of bulk and porous GaP, we observed two peaks. The first peak is in the near-band-edge region of GaP at around 550 nm (2.25eV) originating from radiative recombination of excitons related to bulk GaP. The second peak is in the red region at about 770 nm (1.65eV) resulting from radiative recombination via donor-acceptor pairs. The photoluminescence intensity of bulk GaP is much lower than that of porous GaP. Additionally, TRPL of porous GaP shows that the intensity from green emission gradually decreases when the temperature increases in a range from 25K to 210K. These obtained results demonstrate that the temperature-PL intensity dependence of porous GaP takes place the same as in the bulk, meaning the contribution of the microfield induced by lattice vibrations. The observed changes in RS spectrum caused by anodization give an evidence for the increased surface-to-volume ratio in porous GaP compared to that of bulk GaP.

Acknowledgment

The authors acknowledge financial support from Sai Gon University. I would like to thank to Prof. Nguyen Quang Liem and Dr. Bui Huy

for allowing me the great opportunity to carry out my research work in their lab in Institute of Materials Science and for their valuable help through fruitful discussions.

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Nghiên cứu tính chất phát quang của vật liệu xốp GaP

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Tóm tắt: Bài báo trình bày về tính chất phát quang của vật liệu xốp GaP tổng hợp bằng phương pháp anod điện hóa định hướng cấu trúc (111). Vật liệu GaP dạng xốp và dạng khối lần lượt phát ra các ánh sáng phát quang màu xanh và màu đỏ khi chúng được kích thích bởi tia laser ở bước sóng 355 nm. Vật liệu GaP dạng xốp có cường độ phát quang mạnh hơn nhiều so với dạng khối. Nghiên cứu sự phụ thuộc của nhiệt độ vào thời gian phân giải cho thấy hiện tượng phát ánh sáng màu xanh giảm khi nhiệt độ tăng và bề rộng bán cực đại của phổ hẹp dần khi giảm nhiệt độ. Kết quả này tương ứng với những dao động mạng lưới trong cấu trúc vật liệu tổng hợp. Phổ tán xạ Raman khẳng định sự giảm về kích thước của vật liệu GaP xốp.

Từ khóa: GaP xốp, sự phát quang, thời gian phân giải quang hóa, khắc điện hóa.