Characterization of porous GaP by photoacoustic spectroscopy: The relation between band-gap widening and visible photoluminescence

K. Kuriyama, K. Ushiyama, K. Ohbora, Y. Miyamoto, and S. Takeda
College of Engineering and Research Center of Ion Beam Technology, Hosei University, Koganei, Tokyo 184, Japan
(Received 9 December 1997)

Photoacoustic and Raman spectroscopy as well as photoluminescence (PL) measurements have been used to investigate the effect of band-gap widening in porous GaP. A correlation between a blueshift of the absorption edge observed during photoacoustic measurements, accompanied by PL emissions in the blue and ultraviolet regions, and the occurance of a vibrational mode related to surface phonons is shown. Based on a simple scattering model, the structure of porous GaP is assumed to have a cylinderlike shape.
[S0163-1829(98)07727-3]

Porous semiconductors prepared using crystalline materials having an indirect band gap show visible photoluminescence (PL) emission beyond their band-gap energies.[1] Porous silicon (Si) is a promising material for the application as a visible light emitter, and has therefore been extensively studied during the last years.[1] Recently, similar research work has also been performed on the compound semiconductors GaP (Refs. 2–5), GaAs,[6] and SiC.[7] Porous GaP, prepared by electrochemical anodization of crystalline bulk material, exhibit PL in the blue and ultraviolet (UV) regions which has been explained by the confinement of charged carriers in crystalline quantum wires (of about 25 Å in diameter).[3] However, the reflectance recorded on porous GaP at energies less than 2.75 eV, corresponding to the direct optical transition for crystalline GaP, was found to be higher compared to that of a nonporous/virgin sample, which has been ascribed to the contribution of internal reflection.[4] Thus, the reflectance measured on a porous material is strongly affected by its structure. Therefore, a differentiated evaluation of the energy states above the bandgap of crystalline GaP is important for an understanding of radiative recombination mechanisms in porous semiconductors.

In this brief report, the band-gap widening in porous GaP is investigated by PL, Raman, and photoacoustic spectroscopy (PAS). It is shown that band-gap widening is accompanied by the occurence of PL emission.

The starting material was S-doped (111) oriented GaP (carrier concentration $n \sim 3.5 \times 10^{17}$ cm^{-3}) grown using the liquid-encapsulated Czochralski technique. Porous layers were obtained by anodic etching of the GaP crystals immersed in a 50% solution of HF in ethanol. The etching process was performed in darkness for 3 min using a current density of 10 mA/cm^2. PAS spectra were recorded at room temperature (RT) at energies between 2.0 and 3.5 eV employing a standard configuration.[8] The PAS technique was used to detect the appearance of energy gap using a xenon lamp as an excitation source. The photoacoustic (PA) signal was detected using a microphone and lock-in amplifier technique. Spectra were recorded at 20 Hz applying a scanning rate of 15 nm/min. Finally, all spectra were normalized against carbon black standard. Raman spectra were recorded at RT in backscattering geometry using 514.5-nm line of an Argon laser. PL spectra were obtained at RT using the 325.0-nm line of a He-Cd laser as an excitation source.

Raman spectra obtained from porous and crystalline GaP are shown in Fig. 1. In addition to the LO phonon at 406.2 cm^{-1} and the TO phonon at 368.2 cm^{-1} as observed in the spectrum from the crystalline material, a shoulder can be seen at about 399 cm^{-1} in the spectra obtained from porous GaP samples *A* and *B*. This shoulder has been attributed to a surface phonon mode observed in microcrystalline[9] and porous GaP,[10,11] indicating the existence of microcrystals within the porous layer. A second Raman spectrum was recorded on the porous GaP sample *A* after immersing it in anilin, i.e., a liquid with a higher dielectric constant ($\varepsilon_m = 2.56$) compared to air. As can be seen in Fig. 1, the increase in the dielectric constant of the surrounding medium caused a shift of this new peak to lower frequencies. In order to evaluate the shape of the quantum wire, the shape dependent depolarization factor *L* was calculated using the follow-

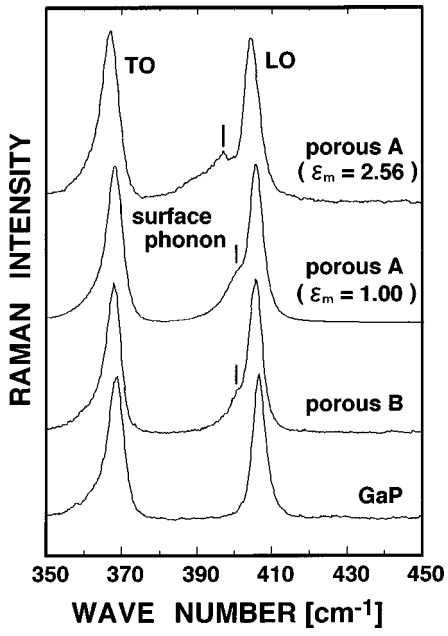

FIG. 1. Raman spectra recorded on porous and crystalline GaP. Spectra from sample *A* were measured before and after immersing the porous sample in aniline ($\varepsilon_m = 2.56$).

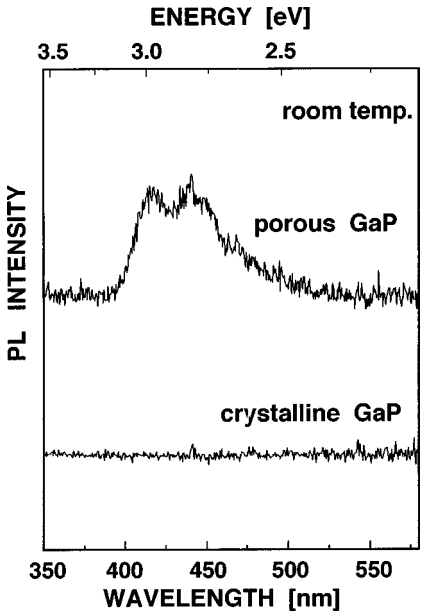

FIG. 2. RT PL spectrum recorded on porous GaP (sample *A*). A spectrum from crystalline GaP is shown for comparison.

ing expression for the surface phonon frequency ω_S (Ref. 12):

$$(\omega_S^2/\omega_T^2)=[\varepsilon_0+\varepsilon_m(1/L-1)]/[\varepsilon_\infty+\varepsilon_m(1/L-1)], \quad (1)$$

where ω_T is the frequency of the TO-phonon mode, ε_0 $(=12.85)$ and ε_∞ $(=10.89)$ are the static and high-frequency dielectric constants, respectively. A factor of $L=0.57$ is obtained using $\omega_S=396.0\,\mathrm{cm}^{-1}$ and $\omega_T=368.2\,\mathrm{cm}^{-1}$ as determined from our measurements. This value is close to 0.5, which was calculated considering a cylindrical shaped wire and a polarization perpendicular to the rotational axis of this cylinder.[12] Thus, based on the Raman scattering model for small samples,[12] the porous structure is assumed to be of cylinderlike shape.

The PL emission recorded at RT from a porous layer (sample *A*) is shown in Fig. 2 together with a spectrum from a GaP crystal. Blue and UV emissions bands were observed at energies between 2.5 and 3.25 eV from samples exhibiting a strong surface phonon mode, i.e., a cylinderlike-shaped structure. On the other hand, in samples showing a relatively weak surface phonon mode (see for example porous *B* in Fig. 1), efficient PL emissions in this energy region could not be observed. The presence of surface phonon modes in the Raman spectra correlates with the occurance of blue and UV PL emissions.

Since the intensity of the PA signal depends only on the absorption properties of the material, the influence of light

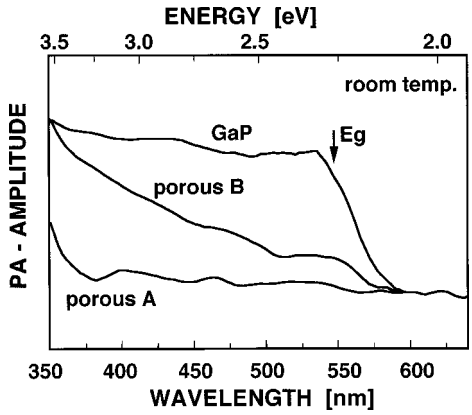

FIG. 3. PAS spectra for recorded on crystalline and porous GaP (samples *A* and *B*).

scattering effects is greatly reduced.[13] The PAS spectra for porous and crystalline GaP are shown in Fig. 3. As can be seen, there is an abrupt increase at a photon energy of about 2.25 eV in the PA signal of the crystalline material, which corresponds to the indirect band gap. This means that nonradiative processes of excited carriers arising from the absorption of photons are dominant above this energy. Furthermore, the porous samples *A* and *B* have different absorption properties in comparison to that of crystalline GaP, i.e., the energy position of the absorption edge differs from sample to sample. In the case of the porous sample *B*, the PA signal increased gradually from 2.25 to 3.5 eV, whereas the signal from sample *A* is almost constant in the energy region 2.25–3.25 eV, but strongly increased at about 3.5 eV. This means that the absorption edge of the porous sample *A* was shifted to about 3.25 eV, i.e., beyond the edge of crystalline GaP. This band-gap widening correlates with the occurrence of the surface phonon mode in the Raman spectrum as well as with the presence of PL emission in the blue and UV regions. In contrast, at energies between 2.25 and 3.25 eV nonradiative relaxation processes are dominant in sample *B*, which did not show PL emission in the energy region. A similar situation has been observed in a recent study[14] on porous Si. Thus, the effect of band-gap widening is supposed to be caused by a quantum confinement of carriers in the porous sample *A*.

In conclusion, a correlation between band-gap widening in porous GaP observed by PAS, and PL emission in the blue and UV regions as well as the occurence of a vibrational mode related to surface phonons has been found. In particular, a blueshift of the absorption edge of about 1 eV compared to crystalline GaP was obtained by PAS in the porous material. This effect of band-gap widening is attributed to a quantum confinement of charged carriers.

[1] L. T. Canham, Appl. Phys. Lett. **57**, 1046 (1990).

[2] A. I. Belogorokhov, V. A. Karavanskii, A. N. Obraztsov, and V. Yu Timoshenko, Pis'ma Zh. Eksp. Teor. Fiz. **60**, 262 (1994) [JETP Lett. **60**, 274 (1994)].

[3] A. Anedda, A. Serpl, V. A. Karavanskii, and V. M. Ichizli, Appl. Phys. Lett. **67**, 3316 (1995).

[4] B. E. Erne, D. Vanmaekelbergh, and J. J. Kelly, J. Electrochem. Soc. **143**, 305 (1996).

[5] F. I. Marin, M. A. Hamstra, and D. Vanmaekelbergh, J. Electrochem. Soc. **143**, 113 (1996).

[6] M. M. Faktor, D. G. Fiddyment, and M. R. Taylor, J. Electrochem. Soc. **122**, 1566 (1975).

[7] J. S. Shor, I. Grimberg, B. Z. Weiss, and A. D. Kurtz, Appl. Phys. Lett. **62**, 2836 (1993).
[8] K. Kuriyama, Takashi Kato, S. Tajima, Tomoharu Kato, and S. Takeda, Appl. Phys. Lett. **66**, 2995 (1995).
[9] S. Hayashi and H. Kanamori, Phys. Rev. B **26**, 7079 (1982).
[10] I. M. Tiginyanu, G. Irmer, J. Monecke, and H. L. Hartnagel, Phys. Rev. B **55**, 6739 (1997).
[11] I. M. Tiginyanu, V. V. Ursaki, V. A. Karavanskii, V. N. Sokolov, Y. S. Rapits, and E. Anastassakis, Solid State Commun. **97**, 675 (1996).
[12] R. Ruppin and R. Englman, Rep. Prog. Phys. **33**, 144 (1970).
[13] G. Amato, Jpn. J. Appl. Phys., Part 1 **34**, 1716 (1995).
[14] M. Ohmukai and Y. Tsutumi, Thin Solid Films **302**, 51 (1997).