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A photoluminescence study of nitrogen doping of gas-evaporated GaP microcrystals

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Abstract. In an attempt to produce GaP microcrystals doped with N atoms, gas evaporation was performed for a gas mixture composed of Ar and N_2. The microcrystals exhibited photoluminescence bands characteristic of N isoelectronic traps, thereby giving clear evidence of N doping. It was found that the doping level can be controlled by varying the partial pressure of N_2 gas. The PN molecules produced near a tungsten heater seem to play an important role in the doping process.

1. Introduction

During the past decade, optical properties of semiconductor nanocrystals prepared by various methods have been the subject of intensive research. The greatest interest centred around so-called quantum-size effects, which arise from the confinement of electrons and holes, or excitons in small volumes. For a variety of nanocrystals of II–VI and III–V compounds, a number of experimental and theoretical studies provided a detailed knowledge of the quantized electronic states [1, 2]. For microstructures made up of group-IV elements, such as Si, and Ge nanocrystals and porous Si, strong photoluminescence (PL) peaks in the visible region were reported [3, 4]. Although many authors stressed the quantum-size effects to explain the PL peaks, the origin of the PL is not yet clear.

Optical properties of semiconductor nanocrystals are expected to be greatly influenced by the presence of impurity atoms inside the nanocrystals. Although many theoretical studies [5, 6] were done on the electronic states associated with impurity atoms doped into semiconductor nanocrystals, only a few experimental studies have been performed so far. Very recently, Bhargava and Gallagher [7] produced ZnS semiconductor nanocrystals doped with Mn isoelectronic impurities by means of a chemical reaction. They reported large external luminescence efficiencies in doped nanocrystals accompanied by shortening of the lifetime of the transition associated with the impurities. From an experimental point of view, techniques for systematically doping semiconductor nanocrystals with impurity atoms, which may differ depending on the method of preparation of the semiconductor nanocrystals, are not yet well established. For further development of new physics and technology of semiconductor nanocrystals, the establishment of doping techniques and the characterization of doped nanocrystals might be of great importance.

In this paper, we report on the doping of N atoms into GaP microcrystals (μc-GaP). From our previous studies [8, 9], it is well known that μc-GaP of good crystallinity can be

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prepared relatively easily by a gas-evaporation technique. Although the gas evaporation is usually performed with pure Ar or He gas, we added N_2 to Ar in an attempt to dope μc-GaP with N atoms. In bulk GaP crystals, it is well known that the substitution for P atoms with N atoms produces isoelectronic traps and gives rise to characteristic PL bands in the yellow–green region due to the recombination of excitons bound to the traps [10–14]. In the present study, the N doping was monitored by observing these characteristic PL bands. Since the sizes of the microcrystals of μc-GaP currently prepared are rather large ($\sim$1000 Å), effects of quantum confinement on the impurity states are not expected. However, the present PL results give clear evidence of N doping of μc-GaP. The present results demonstrate also that the N concentration can be controlled by varying the partial pressure of N_2 gas and a N concentration as high as $\sim 10^{20}$ cm^{-3} can be achieved by evaporating GaP in pure N_2 gas.

2. Experimental procedure

μc-GaP was prepared by a gas-evaporation technique similar to that previously used by Hayashi and co-workers [8, 9]. Small pieces of bulk GaP crystals were evaporated from a tungsten basket in a gas mixture composed of Ar and N_2. The evaporated microcrystals were collected onto a Si substrate placed 5 cm above the heater. The temperature of the heater was set slightly above 1465 °C, which is the melting point of bulk GaP crystals. The substrate was kept at room temperature. In an attempt to vary the doping level, the partial pressure of N_2 was varied from 0 to 100 Torr, while the total pressure was kept constant at 100 Torr. The thicknesses of the μc-GaP layers were several tens of μm. Our gas-evaporated samples are soot-like deposits of μc-GaP in which microcrystals are only weakly bound to one another and to the substrate. In effect, the microcrystals can easily be scraped off from the substrate. Therefore, even at low temperatures, the strain due for instance to the different expansion coefficients of GaP and the Si substrate is negligible. Furthermore, there is no preferential orientation of the microcrystals (no epitaxy) [8, 9].

As described later, the present gas-evaporation conditions yield μc-GaP microcrystals as large as $\sim$1000 Å, which is too large to allow study of the effects of confinement on the impurity electronic states. In principle, it is possible to obtain smaller microcrystals by lowering the total gas pressure. However, as the gas pressure decreases, the number of microcrystals collected onto the substrate in one cycle of gas evaporation decreases and the optical measurement becomes more difficult. Therefore, in this study we contented ourselves with large microcrystals, and attempted to clarify whether or not the nitrogen doping is possible by the simple gas-evaporation technique.

Raman and PL spectra of the μc-GaP collected were obtained using a Spex Ramalog 5M spectrometer, equipped with a double monochromator, an R943-02 photomultiplier (Hamamatsu Photonics) and a photon-counting system. For the PL measurements, the samples were mounted on a cold finger in a He-gas-flow cryostat. The temperature was set to 10 K with the aid of a temperature controller. The Raman spectra were recorded in air at room temperature in a 90° scattering geometry. The 4880 Å line of an Ar-ion laser was used to excite the Raman and PL spectra. The incident laser beam was loosely focused on the sample surface by a cylindrical lens to form a line image with a width of $\sim$500 μm and length of $\sim$10 mm. The incident power density was kept less than $\sim$200 mW cm^{-2} to avoid local heating of the sample. For the PL spectra, the spectral response of the detection system was corrected with the aid of a reference spectrum of a standard tungsten lamp. After measurements of Raman and PL spectra, a portion of the microcrystalline deposit was scraped off from the substrate and put on electron microscopic grids covered with thin

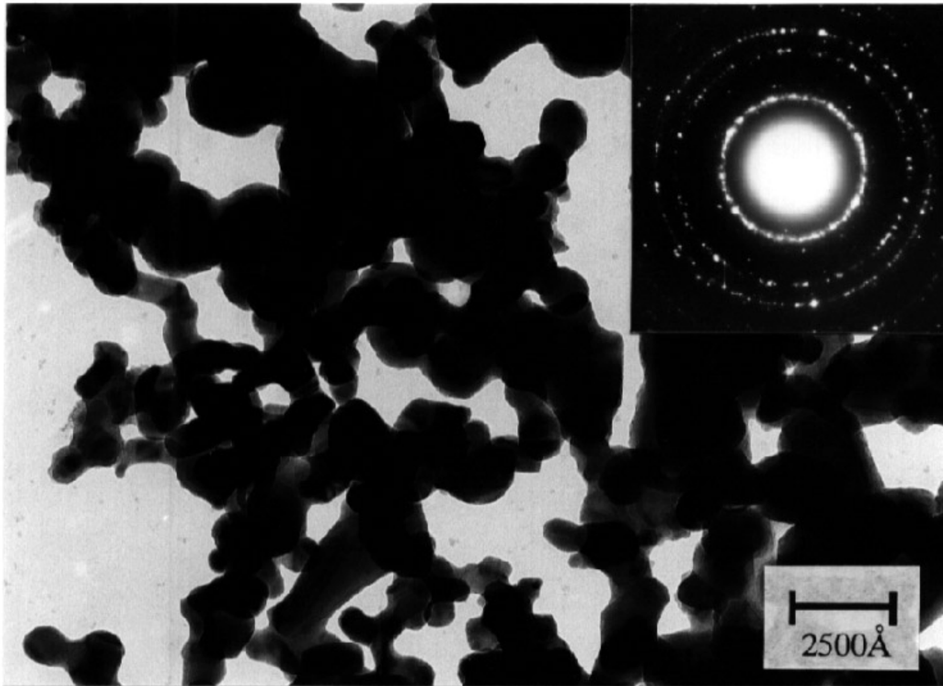

Figure 1. A TEM image and an ED pattern obtained for μc-GaP prepared with the pressure ratio of Ar:N_2 = 50 Torr:50 Torr.

carbon films. The samples were studied by means of a JEM-200CX electron microscope operated at 200 kV. A brief account of this work was given in a conference paper [15].

3. Results and discussion

Figure 1 shows a transmission electron microscopic (TEM) image and an electron diffraction (ED) pattern for μc-GaP prepared with a pressure ratio of Ar:N_2 = 50 Torr:50 Torr. The average particle size obtained from the TEM image is about 1000 Å. An analysis of the ED pattern revealed that the particles have the zincblende structure. Typical Raman spectra of μc-GaP are shown in figure 2. The upper spectrum corresponds to the sample prepared with a pressure ratio of Ar:N_2 = 50 Torr:50 Torr and the lower spectrum to that prepared with 100 Torr of N_2. We see that the two spectra are almost the same. The spectra exhibit a peak at around 398 cm^{-1} between the transverse optical (TO, 367 cm^{-1}) and longitudinal optical (LO, 402 cm^{-1}) modes. The peak is due to a surface phonon (SP) mode [8, 9]. TEM and Raman results for other samples prepared under different conditions were very similar to those presented in figures 1 and 2. The present TEM and Raman results demonstrate that the GaP microcrystals have good crystallinity, though they were produced in an Ar and N_2 gas mixture.

PL spectra obtained for μc-GaP prepared with N_2 partial pressures of 0, 20, 50 and 100 Torr are presented in figures 3(a)–3(d), respectively. A PL spectrum of a piece of bulk GaP crystal used in this work is also presented in figure 3(a), as a broken line. Our bulk GaP exhibits a relatively sharp PL peak at around 2.21 eV and weak peaks at around 2.16 and

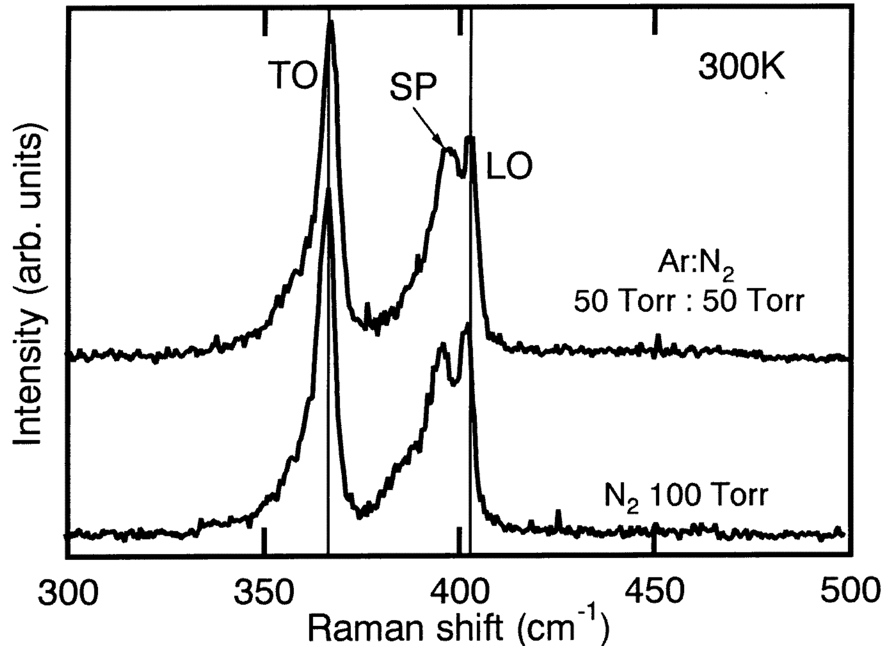

Figure 2. Raman spectra obtained for μc-GaP prepared with the pressure ratio of Ar:N_2 = 50 Torr:50 Torr and 100 Torr of N_2.

2.11 eV, and also a broad peak at around 1.9 eV. The PL spectra of bulk GaP crystals have been studied extensively [16, 17]. Referring to the literature, the peak at around 2.21 eV and those at around 2.16 and 2.11 eV seem to be due to a shallow-donor–acceptor transition and its optical phonon replica. Possible candidates for the shallow-donor atoms are Te or S, while the acceptor atom is believed to be Zn. The broad peak at around 1.9 eV is attributable to the deep-donor–acceptor transitions. The donor and acceptor are believed to be O and Zn, respectively [17]. Unfortunately, it is rather difficult to exactly identify the impurity atoms from the PL data alone. The donor and acceptor atoms contained in our bulk GaP remain uncertain.

As can be seen in figure 3(a), when the bulk GaP is evaporated in 100 Torr of Ar, the resulting μc-GaP shows a PL spectrum quite different from that of the bulk GaP. For μc-GaP, the PL peaks between 2.1 and 2.3 eV become extremely weak, and a broad peak appears at around 1.95 eV. The broad peak seems to arise from the deep-donor–acceptor transitions, which is similar to what is observed for bulk GaP. The changes in the PL spectrum imply that some kinds of impurity atom are lost, while other kinds are reincorporated into the microcrystals after the gas-evaporation processes. The behaviour of impurity atoms initially contained in the bulk GaP during the gas evaporation is not well known at present and deserves further study.

Figures 3(b)–3(d) demonstrate that the PL spectrum of μc-GaP changes drastically depending on the N_2 partial pressure. As the N_2 gas is introduced, several sharp lines appear at between 2.1 and 2.2 eV (figure 3(b)). As the partial pressure increases, the sharp lines become stronger and the broad peak at around 1.95 eV merges into the strong band (figure 3(c)). The spectrum obtained for μc-GaP prepared with only N_2 gas shows another broad peak at around 2.08 eV (figure 3(d)). It should be noted that the PL intensity tends to

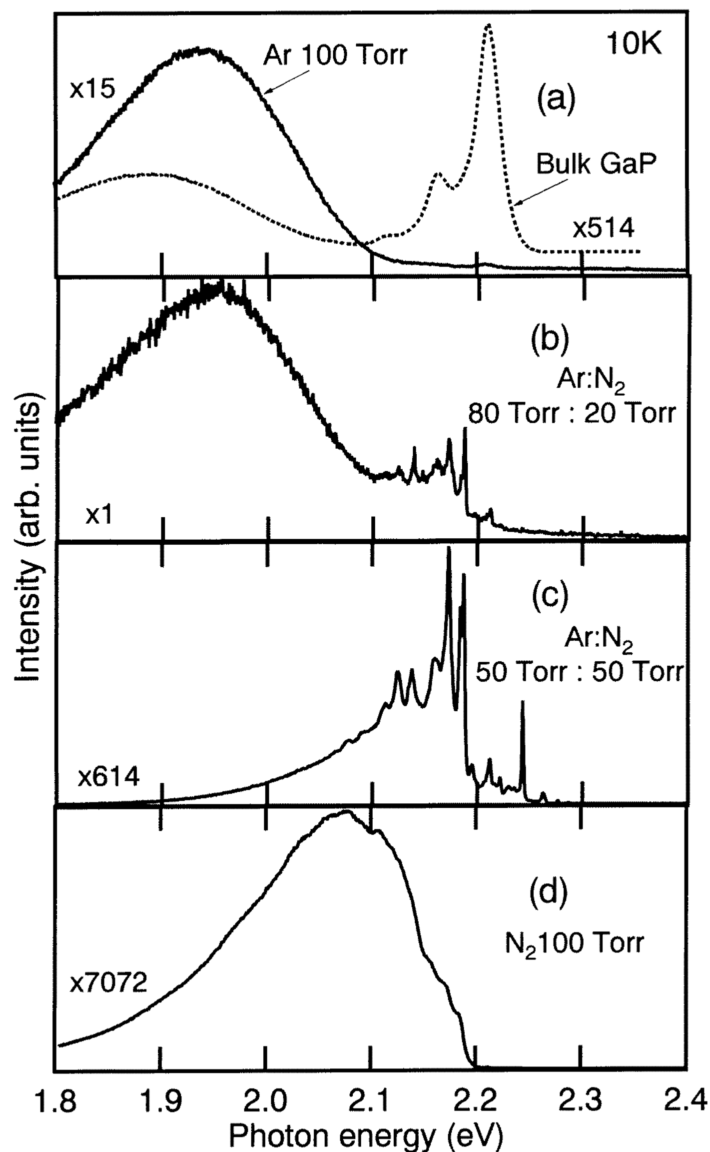

Figure 3. Typical PL spectra of μc-GaP prepared with various partial pressures of N_2 gas. The spectra were measured at 10 K. The μc-GaP samples were produced for 100 Torr of Ar (a); Ar:N_2 = 80 Torr:20 Torr (b); Ar:N_2 = 50 Torr:50 Torr (c); and 100 Torr of N_2 (d). In (a), a PL spectrum of a bulk GaP crystal used for evaporation is also shown.

increase as the N_2 partial pressure increases (the multiplication factors given in the figure refer to the scale, i.e., the PL intensity increases as the factor increases). Since the PL spectrum changes drastically with the N_2 partial pressure, it is very likely that N atoms are incorporated in μc-GaP.

For bulk GaP crystals, it is well known that nitrogen is an isoelectronic substituent for phosphorus [10–14]. The isoelectronic substitution of nitrogen for phosphorus is a strong perturbation because of the large difference between the cores of nitrogen and phosphorus

atoms. This strong short-range perturbation introduces new electronic bound states into the forbidden gap. The green or yellow luminescence of bulk GaP crystals doped with N atoms is due to the recombination of excitons bound to the isoelectronic centres. In weakly doped bulk GaP crystals ($N \sim 10^{15} - 10^{17}$ cm^{-3}), the emission spectrum is dominated by so-called A and B lines near 2.317 eV, which are attributed to an exciton bound to an isoelectronic nitrogen atom [11, 12, 14]. In relatively heavily doped GaP crystals ($N \sim 10^{18}$ cm^{-3}), the emission is dominated by so-called NN lines which are located on the low-energy side of the A and B lines and attributed to excitons bound to pairs of nitrogen atoms.

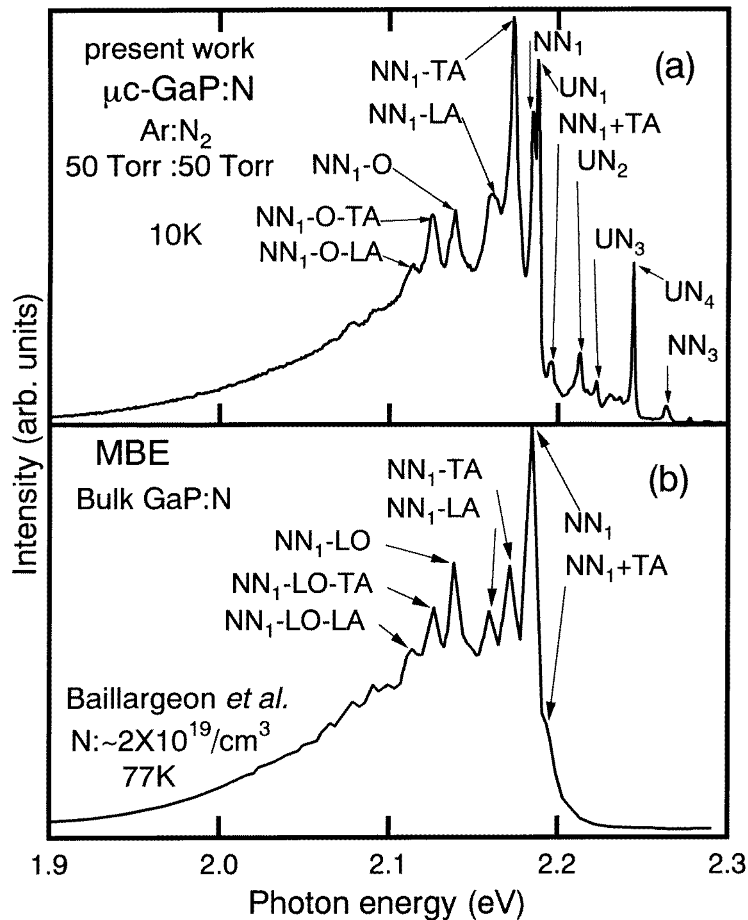

Figure 4. A comparison of the PL spectrum of μc-GaP prepared for Ar:N_2 = 50 Torr:50 Torr, (a), with that of the GaP film reported by Baillargeon and Cheng [18], (b). The GaP film was grown by MBE and contained N atoms with a concentration of 2×10^{19} cm^{-3}.

Here we clarify the origins of the sharp lines observed in the PL spectrum of μc-GaP prepared with the pressure ratio Ar:N_2 = 50 Torr:50 Torr (shown in figure 3(c)). By comparing the spectrum of the μc-GaP with various spectra of GaP crystals containing N atoms [18–21], we find that the PL spectrum in figure 3(c) is very similar to those observed for GaP crystals containing N atoms with relatively high concentrations. In figure 4, our spectrum is compared with that of a GaP film reported by Baillargeon and

Cheng [18]. The GaP film was grown by molecular beam epitaxy (MBE) and contained N atoms with a concentration of $\sim 2 \times 10^{19}$ cm^{-3}. Baillargeon and Cheng assigned the sharp lines appearing in their spectrum to the NN_1 pair transition and TA-, LA-, and LO-phonon-assisted transitions, as indicated in the figure. Here, NN_1 represents a pair of N atoms occupying the nearest-neighbour sites of the GaP lattice. Since the NN_1 line is known to be located at 2.185 eV at 4.2 K [11] and Baillargeon and Cheng reported only the spectrum measured at 77 K, the original spectrum of Baillargeon and Cheng was slightly shifted to locate the NN_1 line at 2.185 eV and compared with our spectrum measured at 10 K. We can see that our spectrum of μc-GaP is very similar to that obtained by Baillargeon and co-workers and major sharp lines correlate fairly well with those of Baillargeon and Cheng. The good correlation of our spectrum with that of Baillargeon and Cheng suggests that doping of N atoms into μc-GaP with a relatively high N concentration of $\sim 10^{19}$ cm^{-3} was successfully achieved.

A close examination of our spectrum of μc-GaP reveals that the line appearing at around 2.185 eV is a doublet consisting of two lines separated by 3 meV. We assign the lower-energy line to the NN_1 transition, since with this assignment we can consistently assign the sharp lines appearing at lower and higher energies to phonon replicas of the NN_1 line in a way very similar to what was done by Baillargeon and Cheng. Our assignment of the lines is indicated in the figure. The energies of related phonons are about 12, 23 and 45 meV. These energies correspond to those of the transverse acoustic (TA), longitudinal acoustic (LA) and optical (O) phonons at the X point in the Brillouin zone [22], respectively.

In our PL spectrum in figure 4(a) we see that the NN_1–TA replica is stronger than that of the NN_1 line. Since the intensity of a phonon replica is usually lower than that of a no-phonon line, it is possible that another line caused by another transition is superposed on the NN_1–TA line. It is also possible that the electron–phonon interaction is large in the present microcrystalline samples [23]. However, why the line is so strong is not well understood at present.

The appearance of the doublet at around 2.185 eV seems not to be due to the contributions of two excitonic states with different total angular momenta $J = 1$ and 2, which are known to be separated by 0.87 meV for bulk GaP crystals [11, 14]. It is well known that the NN_1 line is split into a doublet under stress [24], but the splitting due to the stress can be excluded for our μc-GaP, since our microcrystals are only weakly bound to one another and to the substrate as mentioned before. At present the origin of the high-energy line of the doublet is unknown and this peak is denoted as UN_1 in the figure.

Besides the NN_1 line and its phonon replicas, a relatively strong line at 2.245 eV and weak lines at 2.264, 2.223 and 2.218 eV are also clearly seen in figure 4(a). The weak line at 2.264 eV can be assigned to NN_3 from its position [11], where NN_3 represents pairs of N atoms occupying the third-nearest-neighbour sites. In the literature, we could not find any peak which coincides in position with the strong line at 2.245 eV and weak lines at 2.223 and 2.218 eV. At present, the origins of these lines are not known. These lines are denoted as UN_2, UN_3 and UN_4 in the figure.

In contrast to the spectrum shown in figure 3(c) the spectrum shown in figure 3(d) exhibits only a featureless broad peak at around 2.08 eV. Recently, efforts have been made to grow heavily N-doped GaP crystals, which can be regarded as P-rich $GaP_{1-x}N_x$ alloy crystals [20, 21, 25]. The PL studies of these alloy crystals demonstrated that as the N concentration exceeds $\sim 2 \times 10^{20}$ cm^{-3}, the PL spectrum exhibits a very broad peak, instead of sharp lines, which shifts to lower energies as the N concentration increases. In figure 5 our spectrum of μc-GaP (identical to that shown in figure 3(d)) is compared with that of an alloy reported by Liu *et al* [21]. The sample of Liu *et al* was grown by MBE and contained

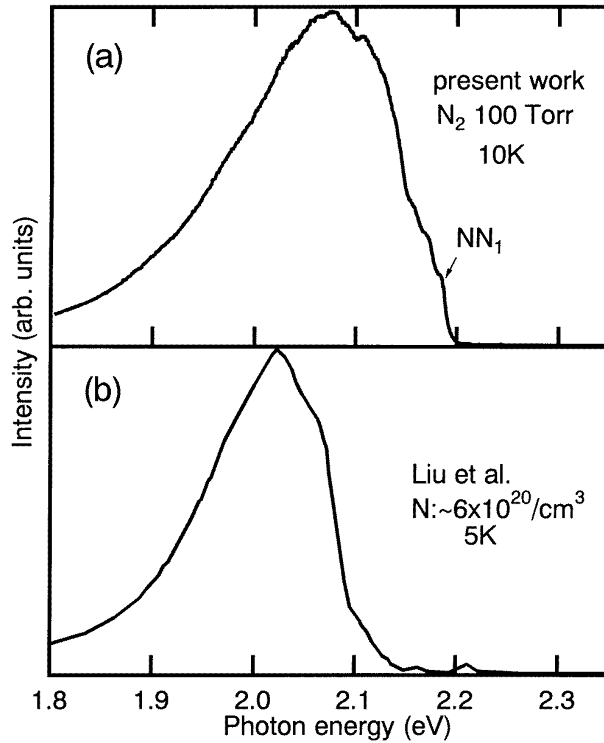

Figure 5. A comparison of the PL spectrum of μc-GaP prepared with 100 Torr of N_2, (a), with that of an $GaP_{1-x}N_x$ alloy reported by Liu *et al* [21], (b). The $GaP_{1-x}N_x$ alloy was grown by MBE and contained N atoms with a concentration of $\sim 6 \times 10^{20}$ cm^{-3}.

$\sim 6 \times 10^{20}$ cm^{-3} N atoms [21]. Their PL spectrum was measured at 5 K. By comparing the two spectra in figures 5(a) and (b), we find that the spectrum of μc-GaP prepared with 100 Torr of N_2 gas is very similar to that of the $GaP_{1-x}N_x$ alloy, except for as regards some features. For our μc-GaP, we can still see a broadened NN_1 line and its phonon replicas on the high-energy side of the peak, while the spectrum of Liu *et al* shows a relatively sharp cut-off on the high-energy side of the peak. The peak in the spectrum of Liu *et al* is located at an energy about 0.4 eV lower than that of our μc-GaP. Since the PL peak of the P-rich $GaP_{1-x}N_x$ alloy crystals is known to shift to lower energies as the composition x increases, the value of x is thought to be smaller in our μc-GaP. Nevertheless, the similarity of our spectrum of μc-GaP to that of the $GaP_{1-x}N_x$ alloy allows us to conclude that μc-GaP prepared with 100 Torr of N_2 gas contains N atoms with a concentration as high as 10^{20} cm-3, which is higher than that of μc-GaP prepared with a mixture of 50 Torr of Ar and 50 Torr of N_2.

For our μc-GaP prepared with 100 Torr of N_2 gas the composition x can be estimated to be $\sim$0.01 from the position of the PL peak. However, this alloy composition is still too low to affect the Raman spectrum. Usually, significant changes in Raman spectra of alloys are observable for $x \gtrsim 0.1$, an order of magnitude larger than the composition currently achieved. Therefore, the Raman spectrum remains unchanged even for μc-GaP prepared with 100 Torr of N_2 as seen in figure 2.

From the PL results presented in figure 3 together with those in figures 4 and 5, we

can finally conclude that the N doping into μc-GaP could successfully be achieved by the gas-evaporation technique using the gas mixture composed of Ar and N_2. Figure 3 clearly demonstrates that the N concentration in μc-GaP can be controlled by varying the partial pressure of N_2 gas. The N concentration currently attained is rather high and reaches the order of 10^{20} cm^{-3}, as judged from the comparison with the PL data for MBE-grown films. The gas-evaporation technique appears to be extremely effective for the N doping of μc-GaP.

Here, a question arises as to why the gas evaporation is so effective for the N doping of μc-GaP. Bulk GaP crystals, grown by liquid-phase epitaxy, are usually doped by an addition of GaN to GaP solution at high temperatures [11]. However, it was reported that treatments of bulk crystals with N_2 gas produced no strong effects because of the stability of the N_2 molecule [11]. In vapour-phase epitaxy or MBE, the N doping of GaP crystals is usually achieved by adding NH_3 gas to a vapour stream [19, 26]. Baillargeon *et al* [19] have stressed the importance of PN molecules as effective doping sources, which are produced by co-injection of PH_3 and NH_3 gas. In our gas-evaporation processes, PN molecules again seem to play an important role. It is known that PN molecules are produced by heating a tungsten wire in a nitrogen and phosphorus gas mixture at $\simeq$1500–1800 °C [27]. In the first stage of our gas-evaporation processes, the GaP crystals are heated in a tungsten heater to well above their melting point (1465 °C) and the decomposition of GaP crystals into Ga and P vapour is thought to take place. It is likely that N atoms are first adsorbed on the surface of the hot W heater and then react with evaporated P atoms to form PN molecules. The PN molecules can then be incorporated into μc-GaP during the well-known processes of crystal growth in gas evaporation, namely, (1) formation of nuclei by condensation of evaporated atoms, (2) vapour growth of the nuclei and (3) coalescence growth in which two or more microcrystals join to form a single microcrystal. Details of the mechanism of nitrogen doping still remain unclear and deserve further study.

4. Conclusion

In an attempt to produce N-doped μc-GaP, small pieces of GaP crystals were evaporated from a tungsten heater in a gas mixture composed of Ar and N_2. The total gas pressure was kept constant at 100 Torr, while the partial pressure of N_2 was varied from 0 to 100 Torr. From Raman spectroscopy and TEM observation, it was shown that the currently obtained μc-GaP microcrystals have good crystallinity. The average size found was about 1000 Å. The PL spectra measured for the samples prepared with relatively low N_2 partial pressures showed clearly the peaks attributable to the recombination of excitons bound to pairs of N atoms and their phonon replicas. The samples prepared with high N_2 partial pressure or pure N_2 gas showed broad PL peaks, which is very similar to what is observed for P-rich $GaP_{1-x}N_x$ alloy crystals. These results clearly demonstrate that the gas evaporation with the addition of N_2 gas to Ar gas is very effective for producing N-doped μc-GaP and that the N concentration can be controlled very easily by varying the partial pressure of N_2 gas. It is very likely that N doping is achieved by the formation of the PN species near the tungsten heater and its incorporation into μc-GaP during the gas-evaporation processes.

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References

[1] Ekimov A I, Éfros A L and Onuschchenko A A 1985 *Solid State Commun.* **56** 921
[2] Brus L 1986 *IEEE J. Quantum Electron.* **QE-22** 1909
[3] Vial J-C, Canham L T and Lang W (ed) 1994 *Light Emission From Silicon* (New York: North-Holland)
[4] Kamimura H, Kanemitsu Y, Kondo M and Takeda K (ed) 1994 *Light Emission from Novel Silicon Materials; J. Phys. Soc. Japan Suppl.* B **63**
[5] Einevoil G T and Chang Y-C 1989 *Phys. Rev.* B **40** 9683
[6] Zhu J-L, Xiong J J and Gu B L 1990 *Phys. Rev.* B **41** 6001
[7] Bhargava R N and Gallagher D 1994 *Phys. Rev. Lett.* **72** 416
[8] Hayashi S and Kanamori S 1982 *Phys. Rev.* B **26** 7079
[9] Hayashi S and Ruppin R 1985 *J. Phys. C: Solid State Phys.* **18** 2583
[10] Thomas D G, Hopfield J J and Frosch C J 1965 *Phys. Rev. Lett.* **15** 857
[11] Thomas D G and Hopfield J J 1966 *Phys. Rev.* **150** 680
[12] Merz J L, Sadowski E A and Rodgers J W 1971 *Solid State Commun.* **9** 1037
[13] Migliorate P, Margaritondo G, Perfetti P and Margadonna D 1974 *Solid State Commun.* **14** 893
[14] Brocklesby W S, Harley R T and Plaut A S 1987 *Phys. Rev.* B **36** 7941
[15] Kim H-M, Hayashi S and Yamamoto K 1995 *Proc. Int. Conf. on Optical Properties of Microstructures; Japan. J. Appl. Phys. Suppl.* 1 **34** 40
[16] Dean P J 1977 *Electroluminescence* ed J I Pankove (Berlin: Spinger) p 63
[17] Dean P J 1973 *Progress in Solid State Chemistry* vol 8, ed J O McCaldin and G Somorjai (Oxford: Pergamon) p 1
[18] Baillargeon J N and Cheng K Y 1991 *J. Appl. Phys.* **70** 1841
[19] Baillargeon J N, Cheng K Y, Jacskson S L and Stillman G E 1991 *J. Appl. Phys.* **69** 8025
[20] Baillargeon J N, Cheng K Y, Hofler G E, Pearah P J and Hsieh K C 1992 *Appl. Phys. Lett.* **60** 2540
[21] Liu X, Bishop S G, Baillargeon J N and Cheng K Y 1993 *Appl. Phys. Lett.* **63** 208
[22] Hobden M V and Russell J P 1964 *Phys. Lett.* **13** 39
[23] Morgan T N 1970 *J. Lumin.* **1/2** 420.
[24] Gil B, Camassel J, Albert J P and Mathieu H 1988 *Phys. Rev.* B **37** 1205
[25] Miyoshi S, Yaguchi H, Onabe K, Ito U and Shiraki Y 1993 *Appl. Phys. Lett.* **63** 3506
[26] Nicklin R, Mobsby C D, Lidgand G and Hart P B 1971 *J. Phys. C: Solid State Phys.* **4** L344
[27] Moureu H and Wetroff G 1938 *C. R. Acad. Sci., Paris* **207** 915