Optical properties of Nd-doped InGaAsP epilayers

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Abstract

The optical properties of Nd-doped InGaAsP epilayers grown by liquid phase epitaxy (LPE) have been studied by photoluminescence and Raman scattering. The full width at half maximum (FWHM) of the photoluminescence peak has been found to decrease as the doping amount of Nd element increases. The narrowest value of the FWHM of PL peak is 7.5 meV, which is smaller by about 46% than that of the undoped InGaAsP and better than previous reports on similar composition layers. Using a spatial correlation model, we found that the asymmetric broadening of the lineshape of the Raman signal is not influenced by the Nd doping. We hence conclude that the introduction of the Nd element can greatly reduce the residual impurities of LPE-grown layers, but the Nd element is not incorporated into the epitaxial layers during the purification.

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1. Introduction

Optical devices operating in the near-infrared region at the wavelength of 1.1–1.6 μm have been developed on the basis of InGaAsP quaternary solid solutions. Liquid phase epitaxy (LPE) is one of the useful methods for growing high-quality InGaAsP epilayer because the LPE growth is at thermodynamic equilibrium [1–3]. Unfortunately, one drawback of the LPE growth is the unavoidable residual impurities, which arise from the melt, substrate, source materials and growth ambient during the growth. Various methods have been used to reduce the concentration of the residual impurities [4–7]. Recently, doping rare-earth elements into III–V semiconductors has been demonstrated to be an effective method of reducing the amount of residual impurities in LPE-grown layers [8–11]. The rare-earth elements are known for their chemical activity as the

gettering agent to efficiently reduce the impurities which act as donors in III–V semiconductors. It has been shown that the residual impurities (for example, S, Se, Si, C, Te, O, etc.) can interact with the rare-earth elements such as Gd, Yb, Er, Ho to form stable compounds and the impurities can thus be removed during the LPE growth [8–11]. Using this method, the rare-earth elements can produce III–V materials with low carrier concentration and increase the carrier mobility.

So far, most research on the rare-earth doping of semiconductors have focused on the gettering ability of impurities due to the presence of rare-earth elements. The investigation on the purification mechanism of the rare-earth doping is still limited. One interesting topic regarding the purification mechanism is whether the rare-earth elements are incorporated into the epitaxial layers during purification [12]. Nakagome et al. suggested that the rare-earth elements should be incorporated into the active layers during the LPE growth [13–15]. However, recent studies reported that the resultant compound, which consist of rare-earth elements and impurities are insoluble in the liquid phase and do not enter into the solid phase after purification [8–10]. Raman

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spectrum, which is a powerful tool to obtain valuable insight into the microscopic nature of the solids, may be an effective way to resolve this problem. If the resultant compounds are captured by the solid phase, the growth layers should generate stress or produce potential fluctuation in the rare-earth doped layers. It is known that the stress in solids can cause a Raman shift of optical phonons and the potential fluctuations due to imperfections can breakdown the $q = 0$ Raman selection rule, leading to the broadening and asymmetry of the Raman line shape [16–18]. Therefore, Raman scattering can offer an effective technique to evaluate the microscopic variation of the rare-earth doped semiconductors.

In this paper, we study the optical properties of Nd-doped 1.55 μm -InGaAsP epilayers by photoluminescence and Raman scattering. The full width at half maximum (FWHM) of PL peak has been found to reduce as the doping amount of Nd element increases. The line shapes of Raman scattering were analyzed according to a spatial correlation model. It is found that the Raman scattering of InGaAsP epilayers is not influenced by the rare-earth doping, indicating the resultant compounds, originated from the chemical reaction of the rare-earth elements and impurities, are not captured by the epilayers during the growth. The wavelength with 1.3–1.55 μm range are very attractive for both emitters and detectors in the long-distance wide-bandwidth fiber-optical communication systems due to their low attenuation and dispersion. Understanding the optical properties of 1.55 μm -InGaAsP epilayers is expected to be important in the technological field of optical communications.

2. Experiment

Nd-doped InGaAsP layers were grown by LPE using a horizontal graphite sliding boat. After cleaning, the LPE system was heated at 670 $^{\circ}\text{C}$ for 0.5 h to homogenize the melt completely. The temperature was cooled down to 640 $^{\circ}\text{C}$, and the substrate was contacted with InGaAsP quaternary melt. The epilayer was grown by the super-cooling rate of 0.3 $^{\circ}\text{C}/\text{min}$. During the growth process, the system is flushed with purified hydrogen to maintain the atmospheric pressure. After growth, the melt was slid away from substrate and the graphite boat was rapidly cooled down to room temperature to avoid thermal damage of the grown layer. The samples were mounted on the cold finger of a closed-cycle helium crystal and characterized by photoluminescence and Raman scattering. The low-temperature photoluminescence measurement was carried out to evaluate the quality of the InGaAsP layers. An Ar-ion laser ($\lambda = 488 \text{ nm}$) was used to excite the sample at $T = 13 \text{ K}$. The luminescence signal was dispersed with a monochromator and detected with a germanium photodiode. Raman measurements were performed in the backscattering configuration at room temperature by using a photon counter.

3. Results and discussions

Fig. 1(a) and (b) show the typical 300-K and 13-K PL spectra of the undoped InGaAsP epilayers and the Nd-doped InGaAsP epilayers with Nd of 0.005 wt%, respectively. All PL spectra are normalized to the same peak intensity. In Fig. 1, the 13-K PL spectrum of undoped InGaAsP layer exhibits two peaks (denoted as A and B, respectively). The main peak A, where the photon wavelength is around 1.6 μm at room temperature, is attributed to the near band-to-band transition [8,9]. The lower-energy peak B is assigned to the transition involving the shallow-acceptor levels according to previous reports on similar samples [8,9]. It is found that the FWHM of the near band-to-band transition is reduced from 48 to 45 meV after the Nd doping of 0.005 wt% at 300 K, and more pronouncedly, from 13.9 to 9 meV at 13 K. This finding indicates that the Nd doping effectively improve the quality of InGaAsP layers at both low and room temperatures. The 13-K PL spectra of the InGaAsP epitaxial layers with various amount of Nd doping are shown in Fig. 2. The amount of the Nd elements is: (a) 0, (b) 0.005, (c) 0.011, (d) 0.031 and (e) 0.050. Basically, with increasing the amount of Nd elements, the FWHM (intensity) of PL in Nd-doped InGaAsP is reduced (enhanced). The FWHM and peak intensity of PL signals as a function of Nd amount are shown

Fig. 1. (a) 300-K and 13-K PL of undoped InGaAsP epilayers, (b) 300-K and 13-K PL of Nd-doped InGaAsP epilayers with Nd of 0.005 wt%.

Fig. 2. The 13-K photoluminescence spectra of InGaAsP epilayers as a function of doping amount of the Nd elements: (a) undoped, (b) 0.005 wt%, (c) 0.011 wt%, (d) 0.031 wt%, (e) 0.050 wt%.

in Fig. 3. As seen in Fig. 3, the PL intensity (FWHM) has a maximum (minimum) value by doping Nd elements around 0.031 wt%. To our knowledge, this minimum FWHM value of 7.5 meV, which is smaller by about 46% than that of the undoped InGaAsP, is better than previous reports on similar composition layers [10,11]. Since the FWHM of PL is related to the presence of residual impurities, narrowing effect indicates the Nd doping to InGaAsP layers can greatly reduce the residual impurities in the liquid phase, and improve the quality of LPE-grown layers. As the doping amount of Nd element is increased to 0.050 wt%, the FWHM of PL peak becomes broader than that with 0.031 wt% of Nd doping. Similar trend have been found for using rare-earth element as a gettering agent to reduce the shallow impurities [8,11]. The broadening effect of the FWHM of PL could be explained by the fact that too much gettering effect may cause a lattice mismatch or strain which will result in additional dislocations or stoichiometric defects in the epitaxial layers [8,11].

Although the rare-earth doping is an effective way to reduce the residual impurities, so far, the purification mechanism is not fully understood. Especially, whether

Fig. 3. The PL FWHM and intensity of the PL extracted from Fig. 2 as a function of the doping amount of the Nd elements. The solid line is a smooth fit of the data. The dotted lines are guide for the eye.

the rare-earth elements are incorporated into the epitaxial layers after LPE growth is still under debate. Nakagome et al. pointed out that the rare-earth elements are incorporated into the active layer during the LPE process, based on the sharp emission spectrum due to the energy transfer from the 4f intra-subshell [13–15]. On the contrary, Krier et al. demonstrated that the rare-earth elements react with the accidental impurities and form stable compounds in liquid phase, which do not enter into the grown epitaxial layers [5,19]. In order to clarify the purification mechanism using the rare-earth doping, we performed the Raman scattering measurements. If the rare-earth compounds, originate from the reaction of the rare-earth elements and impurities, are captured by the epitaxial layers, the grown layers should exhibit a change in their microscopic structure. It is known that the lineshape of Raman signal in semiconductors is associated with the structural imperfections, while the peak position of Raman signal is related to the stress change [16,20,21]. Raman scattering can hence be a suitable technique to find out the microscopic structure of the Nd-doped InGaAsP epilayers. Fig. 4 displays the Raman spectra with various amounts of Nd elements into InGaAsP layer: (a) undoped, (b) 0.031 wt% and (c) 0.050 wt%. The Raman signal peaked at 226 cm^{-1} in Fig. 4 is attributed to the InAs-like LO mode [20,21]. The same peak position of Raman signal in Fig. 4(a)–(c) indicates that no strain occurs in InGaAsP epilayers after the Nd doping. The Raman peaks in Fig. 4 have an asymmetric line shape, which can be analyzed by a spatial correlation (SC) model. According to the SC model, the spatial correlation function of the phonon for a pure compound semiconductor is infinite and the phonon eigenstates are plane waves. These lead to the usual $q = 0$ momentum selection rule of Raman scattering and the Raman spectrum shows a symmetric Lorentzian profile [$\Gamma_a = \Gamma_b$, where $\Gamma_a(\Gamma_b)$ represents the low-energy (high-energy) half width of half maximum]. The alloying or any imperfection in semiconductors may destroy the configurational symmetry and relax the q -section rule. The spatial correlation function of phonon hence become finite and the Raman spectrum reveals an asymmetric lineshape ($\Gamma_a > \Gamma_b$). Based on the SC model, we analyze

Fig. 4. The Raman spectra of InGaAsP epilayers as a function of doping amount of the Nd elements: (a) undoped, (b) 0.031 wt%, (c) 0.050 wt%.

the asymmetric Raman spectrum in Fig. 4 with a correlation function in a Gaussian form, $\exp(-2r^2/L^2)$, where L is the phonon correlation length. The Raman intensity at a frequency ω is given by a Lorentzian function modified by Gaussian distribution: [20,21]

$$I(\omega) \propto \int \frac{\exp\left(-\frac{q^2 L^2}{4}\right)}{[\omega - \omega(q)]^2 + \left(\frac{\Gamma_0}{2}\right)^2} d^3 q, \quad (1)$$

where q is the reduced wave vector in the unit of $2\pi/a$, a is the lattice constant of InAs, and Γ_0 ($= 10 \text{ cm}^{-1}$ for the InAs-like mode) is the intrinsic linewidth of phonon mode. As for the dispersion $\omega(q)$ of the LO phonon, an analytical model based on a one-dimensional linear-chain model has been used:

$$\omega^2(q) = A + \sqrt{A^2 - B\{1 - \cos(aq)\}}, \quad (2)$$

where we take $A = 2.59 \times 10^4 \text{ cm}^{-2}$ and $B = 3.58 \times 10^8 \times \text{cm}^{-4}$ for the InAs mode [22]. Eqs. (1) and (2) show that if L is finite, the q selection rule may break, and additional transitions by phonon with lower energy at $q \neq 0$ may occur, which lead to the asymmetric broadening of the Raman lineshape. The dotted curves in Fig. 4 show the calculated results of the Nd-doped InGaAsP layers, which are in good agreement with experiments. From Fig. 4, we can evaluate the asymmetric ratio (Γ_a/Γ_b) from the lineshape fitting. It is found that the asymmetric ratio (Γ_a/Γ_b) as a function of Nd amounts are almost unchanged (~ 1.77). This implies that the alloy disorder or the structural imperfection in InGaAsP layers is not affected by the Nd doping, i.e. the Nd elements are not incorporated into the LPE-grown layers after purification. The correlation length L , which is fitted from the calculation, is also evaluated in Fig. 4. It is found that the L values are all about 23 Å for the undoped and Nd-doped InGaAsP epilayers. Since L can be viewed as the average distance between two imperfections, the same L values for all samples also implies that no structural variance occurs after the Nd doping. What we have observed is thus consistent with the interpretation of Krier et al. [19], which suggested that the rare-earth elements do not incorporate into the grown epitaxial layer, but can reduce the residual impurities.

4. Conclusions

We studied the influence of doping Nd into InGaAsP on the optical properties by photoluminescence and Raman scattering measurements. The FWHM of 13-K PL peak decreases with increasing the amount of Nd doping and has a narrowest value of 7.5 meV, which is better than previous reports on similar composition layers. As a consequence, the introduction of the Nd elements can effectively reduce the residual impurities and improve the quality of LPE-grown layers. We also performed the Raman measurements to investigate the structural influence of Nd elements on

InGaAsP epitaxial layers. It is found that the peak position, asymmetric ratio, and the correlation length of the Raman signals for InGaAsP epilayers are not influenced by the Nd doping. This result suggests that the rare-earth elements are not incorporated into the epitaxial layers during the purification even the residual impurities are greatly reduced.

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