Composition dependence of photoluminescence of GaAs$_{1-x}$Bi$_x$ alloys

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Room temperature photoluminescence (PL) spectra have been measured for GaAs$_{1-x}$Bi$_x$ alloys with Bi concentrations in the 0.2%–10.6% range. The decrease in the PL peak energy with increasing Bi concentration follows the reduction in bandgap computed from density functional theory. The PL peak energy is found to increase with PL pump intensity, which we attribute to the presence of shallow localized states associated with Bi clusters near the top of the valence band. The PL intensity is found to increase with Bi concentration at low Bi concentrations, peaking at 4.5% Bi. © 2009 American Institute of Physics. [DOI: 10.1063/1.3191675]

The anomalously large bandgap reduction associated with bismuth alloying of GaAs has attracted attention to this material system for long wavelength semiconductor devices.[1,2] Bismuth incorporation also strongly enhances the spin-orbit coupling, which makes bismide alloys interesting for spintronic applications where strong coupling between the spin orientation and the linear motion of electrons is desirable.[3,4] Until recently incorporation of high Bi concentrations into epitaxial GaAs films has been problematic due to the strong tendency for Bi to surface segregate during film growth. The Bi concentration in the bismide alloys can be significantly increased by reducing the growth temperature and arsenic flux, and recently GaAs$_{1-x}$Bi$_x$ alloys with Bi concentration up to 10.6% have been grown successfully by molecular beam epitaxy (MBE).[5] The anomalous growth conditions required to incorporate Bi raise questions as to whether the electronic properties of the high bismuth concentration alloys are good enough for the material to be useful in devices. To address this question, we present measurements of the room-temperature photoluminescence (PL) of GaAs$_{1-x}$Bi$_x$ alloys as a function of the Bi concentration in the 0.2%–10.6% range. A PL spectrum with a record long wavelength emission of 1.44 μm is achieved from a GaAs$_{1-x}$Bi$_x$ sample with 10.6% Bi. The excitation density is found to have a significant effect on the PL peak energy and linewidth.

GaAs$_{1-x}$Bi$_x$ samples, consisting of a 450 nm GaAs buffer layer, a 30–40 nm GaAs$_{1-x}$Bi$_x$ layer, and 300 nm GaAs capping layer, were grown on semi-insulating GaAs (100) substrates in a solid source MBE system, equipped with Ga-type effusion cells for Ga and Bi, and a two-zone valved cracker source for As$_2$. Substrate temperature is monitored by optical bandgap thermometry during growth. The GaAs$_{1-x}$Bi$_x$ epilayers were grown at a reduced growth rate ($\sim$1 nm/min), lower substrate temperature (270–300 °C), and lower As$_2$ overpressure compared with usual GaAs growth conditions. We controlled the Bi concentration by varying the As$_2$ flux, Bi flux, and growth

temperature.[5] The Bi concentration was determined by high-resolution x-ray diffraction.[6] The effects of Bi concentration and the excitation intensity on the PL peak energy and linewidth were investigated. The PL was excited with a 532 nm frequency-doubled diode-pumped YLF laser with 20 ns long pulses at an average power of 0.5–2.6 mW and a 2 kHz repetition rate. The excitation intensity was varied over a wide range with a combination of neutral density filters, changes in the laser spot size, and diode laser power.

Figure 1(a) shows room temperature PL spectra of the GaAs$_{1-x}$Bi$_x$ samples. The PL peak shifts to lower energy
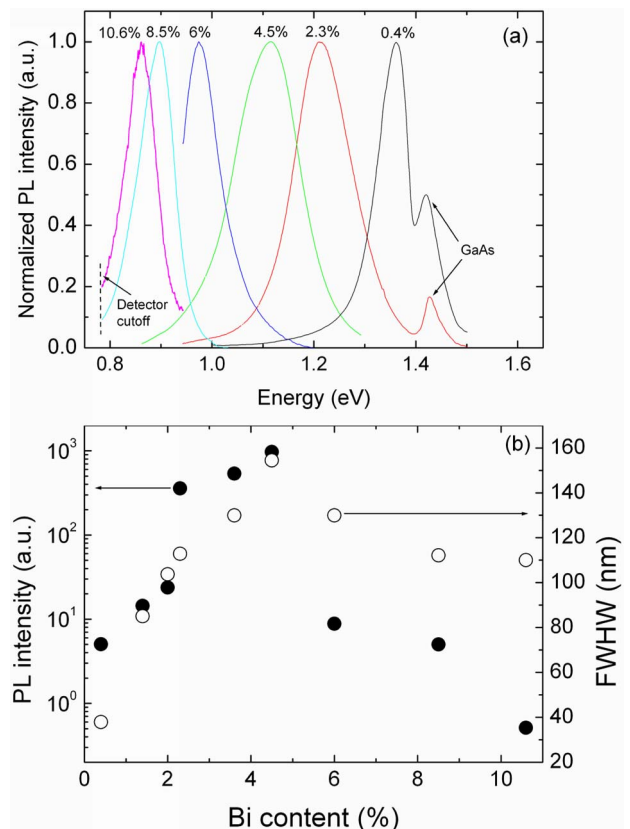

FIG. 1. (Color online) (a) PL spectra of GaAs$_{1-x}$Bi$_x$ samples and (b) Bi concentration dependence of PL intensity and linewidth.
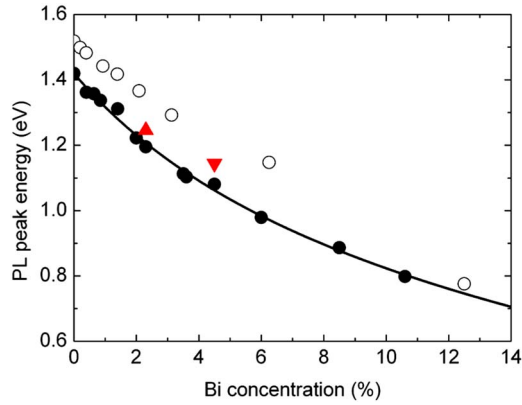
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FIG. 2. (Color online) PL peak energy as a function of Bi concentration: experimental data (solid circles) and theoretical calculations (open circles). The solid line is a fit to the experimental data using a Bi concentration dependent bowing coefficient. The triangular symbols are the PL peak energies for samples with $x=2.3\%$ and 4.5% under maximum excitation intensity.

with increasing Bi concentration as expected. The PL intensity and linewidth [Fig. 1(b)] are functions of Bi concentration, with both parameters peaking at ~4.5%. It is a surprise to see the intensity enhancement. In fact the integrated PL intensity of the sample with the highest PL intensity, the 4.5% sample, was only a factor of 3 lower than the PL from a bulk $p+$ doped GaAs reference wafer, a known strongly luminescent material. Although it is well known and understood that introduction of isoelectronic impurities leads to an enhancement in the PL efficiency in an indirect gap semiconductor, such as GaP:N,[7] the same effect is not expected to occur in a direct bandgap material such as GaAs, if we simply consider the potential effect of the electronic wave function localization to the interband transition matrix element. In fact, one would expect the incorporation of a highly lattice mismatched impurity such as Bi to introduce defects, and thus degrade the material quality. In addition the GaAs was grown at a substantially lower than optimal temperature, which itself might be expected to result in the formation of defects that lead to nonradiative recombination. However, there is a subtle effect that should be taken into account. The introduction of the Bi impurities forms localized electronic states near the valence band maximum[3,8] and they serve as trapping centers for the formation of bound holes, which effectively reduces the loss to the nonradiative centers. It is noteworthy that a similar mechanism has been proposed for the strong light emission from GaInN alloys.[9] However, eventually higher Bi concentrations might produce more defect centers that diminish the benefit.

Figure 2 shows the PL peak energy of $GaAs_{1-x}Bi_x$ samples as a function of Bi composition. Room temperature PL is an approximate measure of bandgap, although strictly speaking the bandgap for such a strongly perturbed semiconductor cannot be precisely defined.[10]

The PL emission wavelength is found to monotonically increase with Bi concentration up to 1.44 μm for 10.6% Bi. To the best of our knowledge, this is the longest reported PL wavelength at 300 K from a $GaAs_{1-x}Bi_x$ alloy. The composition dependence of the bandgap of a semiconductor alloy is usually described by introducing a bowing parameter b. For the ternary system $GaAs_{1-x}Bi_x$, the relationship is

$$E_{GaAs_{1-x}Bi_x} = xE_{GaBi} + (1-x)E_{GaAs} - bx(1-x), \qquad (1)$$

where $E_{GaAs_{1-x}Bi_x}$, E_{GaBi}, and E_{GaAs} are the bandgap energies of $GaAs_{1-x}Bi_x$, GaBi, and GaAs, respectively. As the bandgap of GaBi is unknown, there are two parameters, E_{GaBi} and b, in the above equation. The bowing parameter, b, is typically assumed to be independent of alloy composition. However, for the $GaAs_{1-x}Bi_x$ alloy investigated here, fitting with a constant bowing coefficient would result in an unreasonable band gap energy value of 29.9 eV for GaBi, compared with the calculated value of -1.45 eV.[11] We instead define a bowing parameter that decreases monotonically with increasing Bi concentration,[12] as follows:

$$b(x) = \alpha/(1 + \beta x). \qquad (2)$$

By substituting Eq. (2) into Eq. (1), we get a good fit, as shown in Fig. 2, with physically reasonable parameters: E_{GaBi}, α, and β are -0.36, 9.5, and 10.4, respectively.

In order to better understand the composition dependence of the PL peak energy or the bandgap energy of the $GaAs_{1-x}Bi_x$ alloy, we performed band structure calculations using a first-principles pseudopotential method to obtain the dependence of the bandgap on Bi composition. The alloy is simulated by a supercell approach, i.e., an ordered array of Bi atoms on As sites embedded in a GaAs matrix that is constructed using multiple cubic unit cells. This simplification is found to give quite accurate bandgap shifts for low Bi concentrations,[3] even though in the real sample the doping is likely to be closer to a random than an ordered distribution. We note that the calculation for the high concentration region is not as accurate as for the low Bi concentration region. For instance, the bandgap is found to depend on the selection of the unit cell. We find that the bandgap reduction is larger if the supercell is built on the primitive cell of the zinc-blende structure rather than the cubic cell. Nevertheless, the computation should still be able to provide a semiquantitative account for the band structure change. The comparison between the experimental data and the calculations are indeed in good agreement, as shown in Fig. 2, except for a temperature induced bandgap shift because the calculation is for $T=0$ K. Empirical corrections are applied to the nonlocal pseudopotentials in order to compensate the well-known bandgap error due to the local density approximation in the density functional theory.[13]

Figure 3(a) shows the excitation intensity dependence of the PL peak energy for $GaAs_{1-x}Bi_x$ samples with various Bi concentrations. There are two important observations: (1) the PL peak shifts to a higher energy with increasing excitation intensity, the shift being more significant for higher Bi concentrations and (2) the PL bandwidth increases with increasing excitation density. These types of dependences are often observed in highly perturbed system, such as $GaAs_{1-x}N_x$,[14] as a result of the existence of localized states introduced here by Bi incorporation. Such localized states are expected to form near the top of the valence band and are localized at regions with high local Bi concentration [as illustrated schematically in the inset in Fig. 3(a)]. At low excitation intensity, only the localized states with the highest binding energies participate in PL. In this case the PL peak energy (E_{PL}) is the smallest. With increasing excitation intensity the recombination lifetime is reduced. In this case the holes have less time to thermalize down into the localized state distri-
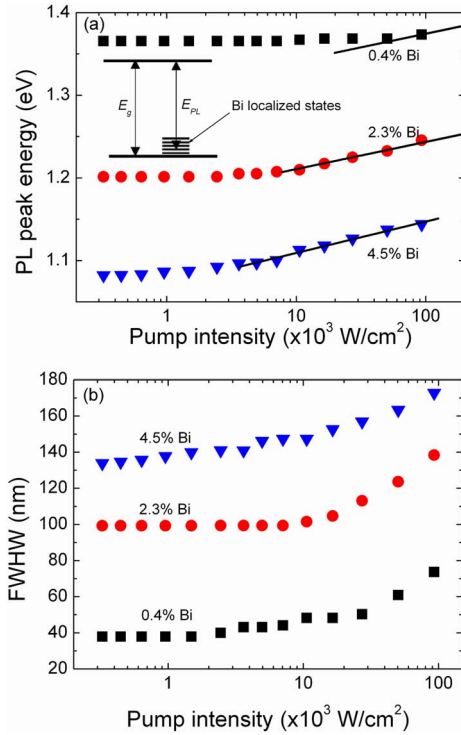
FIG. 3. (Color online) (a) Pump intensity dependence of PL peak energy for GaAs$_{1-x}$Bi$_x$ samples with various Bi concentrations and (b) effect of pump intensity on PL linewidth of GaAs$_{1-x}$Bi$_x$. The solid line for the 4.5% sample in (a) is a fit to the data according to the model discussed in the text. Two lines with the same slope are plotted through the data for the 0.4% and 2.3% samples for reference. The inset shows a schematic energy level diagram for a GaAs$_{1-x}$Bi$_x$ alloy, with Bi localized states.

bution before they recombine, so that the corresponding PL peak shifts higher in energy. In Fig. 2, the two triangle symbols show the PL peak energies of the 2.3% and 4.5% samples under maximum pump intensity.

For a better understanding of the experimental results, we derive the relationship between the peak PL emission energy and the pump intensity. The binding energy of the holes will increase progressively with time as they thermalize into the distribution of localized states above the top of the valence band. This thermalization terminates when the hole recombines, at which time the hole will have thermalized to a depth,[15]

$$\varepsilon = k_B T \ln(\omega_0 \tau), \tag{3}$$

where τ is the recombination lifetime, T is the temperature, and ω_0 is an attempt-to-escape frequency. If we neglect nonradiative recombination, the PL pump intensity, I, is proportional to the rate of radiative recombination, G, where G is given by

$$G = Bnp. \tag{4}$$

In this equation B is a parameter characterizing the radiative recombination rate; n and p are densities of electrons and holes. The recombination lifetime is inversely proportional to the carrier density,

$$\tau = \frac{1}{Bp}. \tag{5}$$

By substituting Eqs. (4) and (5) into Eq. (3) and using $n=p$ for the intrinsic case, we find the relationship between ε and the pump intensity, I,

$$\varepsilon = -\frac{kT}{2} \ln I + \text{constant}. \tag{6}$$

Using Eq. (6), we do a linear fit to the curve in Fig. 3(a) for the 4.5% Bi sample. The slope of the fitted straight line is $-kT/2 = -0.0143$. The observed intensity dependence agrees with the model since the solved temperature, 332 K, is consistent with the measurement temperature. Lines with the same slope are also plotted through the data for the 0.4% and 2.3% samples in Fig. 3(a) for reference. We believe that the intensity dependent shift is smaller for the low Bi concentration samples because the density of Bi-related localized states is lower.

Figure 3(b) shows the excitation intensity dependence of the PL linewidth for the GaAs$_{1-x}$Bi$_x$ samples. At low excitation intensity (<1 kW/cm^2), no obvious PL linewidth change was observed. At higher intensity the PL linewidth increases monotonically with pump intensity. Although we have not attempted to model the intensity dependence of the linewidth, we believe this effect can also be explained by emission from a distribution of localized states.

In summary, we have demonstrated room temperature PL with emission wavelength up to 1.44 μm in GaAs$_{1-x}$Bi$_x$ alloys with Bi concentrations up to 10.6%. The PL intensity is found to increase with increasing Bi concentration, peaking at $\sim$4.5% Bi, which is a positive indication for light emitting devices made from this material. The increase in PL intensity is in striking contrast with the effects of alloying with N, another strongly lattice mismatched and isoelectronic impurity, where the PL intensity falls rapidly with increasing N concentration. The excitation intensity has a significant effect on the PL peak energy and linewidth, which is attributed to the effects of Bi-induced localized states above the top of the valence band.

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