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Photogenerated plasmons in $GaAs_{1-x}Bi_x$

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Light scattering measurements in the dilute isoelectronically doped alloy $GaAs_{1-x}Bi_x$ reveal a large free electron population photogenerated by continuous-wave laser excitation at low temperature. Low-temperature time-resolved photoluminescence of the bismuth related near-band-gap states show carrier lifetimes of several nanoseconds. The authors attribute this to trapping of photoexcited holes at bismuth pair or cluster states located near the valence band maximum. © *2007 American Institute of Physics*. [DOI: 10.1063/1.2770760]

The need for semiconductor materials lattice matched to GaAs with band gap energies in the near-infrared spectral range has been growing due to the rapid progress in optical communications and photovoltaic technologies. Recently, isoelectronically doped $GaAs_{1-x}N_x$, for which the band gap can be changed significantly by just a few percent of nitrogen doping, has been studied intensely for the above applications, but the reduced electron mobility fundamentally limits its use for practical devices.[1] $GaAs_{1-x}Bi_x$ is a more promising alloy material in this regard because it also exhibits a giant band gap lowering with Bi doping;[2] however, the Bi incorporation is calculated to mainly perturb the valence band,[3] thus holding promise for better device performance.

Spectroscopic studies[2,4,5] have explored the effect of Bi on the host band structure, but there has been little experimental work on the nature of the Bi-related states expected to occur near the band extrema. From an applications point of view, recent results[6] showing good electron mobility in GaAsBi are extremely encouraging, but leave open questions about the occupation of Bi-related states by photocreated electrons and holes. Light scattering is a useful tool for this, as there are particular signatures that identify a mobile carrier population (plasma). Together with time-resolved luminescence, we show that hole trapping at Bi pair and cluster states results in an unusually long low-temperature lifetime and a large steady-state electron population under continuous wave (cw) excitation.

The samples used in our study are 0.2–0.3-μm-thick $GaAs_{1-x}Bi_x$ layers (x=0.4%, 0.8%, 1.4%, and 3.1%) grown by molecular beam epitaxy on (001) GaAs substrates. Details on the growth conditions can be found in Ref. 7. Temperature dependent Raman spectra and photoluminescence (PL) spectra were measured in a pseudobackscattering geometry using a triple spectrometer equipped with a nitrogen-cooled charge coupled device (CCD) detector. The samples were excited with various powers using a using a dye laser (190–1.93 eV). The spectra were obtained in the configuration $(\mathbf{E}_i\mathbf{E}_s)=(YY)$, where $\mathbf{E}_i$ and $\mathbf{E}_s$ are the incident and scattered electric field polarizations, respectively, and Y is the [110] crystal direction. For zinc blende structure crystals, in the (YY) scattering geometry, the longitudinal optic (LO) phonon is Raman active but the transverse optic (TO) phonon is not. PL was time resolved using a streak camera. Samples were excited with a 2 MHz pulse train selected from a 100 fs, 800 nm Ti:sapphire laser. 80 pJ was focused to a spot diameter of 35 μm.

Figure 1 illustrates 8 K combined PL and Raman spectra of $GaAs_{1-x}Bi_x$ for x=0% and 1.4%. The signal from undoped GaAs (lower curve) exhibits a broad PL peak at 1.874 eV due to hot carriers recombining at the spin-orbit split off valence to conduction band transition $E_0+\Delta_0$. This PL peak is very close to the value of the $E_0+\Delta_0$ transition energy previously measured at 4.2 K.[8] The zone center LO phonon and the very weak forbidden TO are also seen as sharp fea-

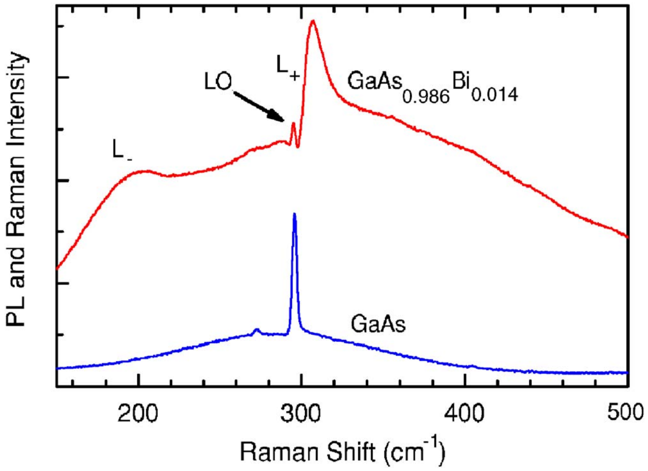

FIG. 1. (Color online) Emission spectra of GaAs and $GaAs_{0.986}Bi_{0.014}$, measured in the (YY) scattering geometry at 8 K. The excitation energy was adjusted for $E_0+\Delta_0$ resonance in both cases, 1.901 eV for GaAs and 1.909 eV for $GaAs_{1-x}Bi_x$. The same features are also seen in the x=0.8% and 3.1% samples. Note that the apparent PL peak positions are modified by their different excitation energies.

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tures. The upper curve shows that the addition of 1.4% Bi to GaAs results in several dramatic changes. The $E_0+\Delta_0$ PL is more intense, broader, and the absolute energy of its peak has dropped by 12 meV, a combined effect of the bismuth-induced band gap reduction[2] and increase in the spin-orbit splitting.[5] There are also two features, L_+ and L_-, observed above and below the LO phonon energies which have the same polarization selection as the LO phonon. These are the upper and lower branches of the coupled modes, or coupled plasmon-LO phonon modes (CPLOMs), between the photoexcited plasma and the LO phonon. CPLOMs in doped GaAs have a well-defined frequency that is a function of the electron density, and thus serve as a direct probe of the free carrier density. Their observation in *isoelectronically* doped GaAsBi is unexpected, since normally an electron-hole plasma excited by a cw laser is not observed from undoped GaAs, unless the GaAs is buried below $Al_xGa_{1-x}As$.[9] In fact, it has been shown that a very small surface recombination velocity is needed for the photoexcited (by a cw laser) plasmon to be observed in an undoped semiconductor.[10] Thus, there needs to be a mechanism, such as an electronic state which can trap photoexcited carriers, to modify the recombination of electrons and holes to explain the observation of CPLOMs in GaAsBi. We will show below that the Bi pairs and cluster states located above the valence band maximum serve as traps for the photogenerated holes which hinder the recombination of the photoexcited carriers, allowing for the observation of the electron plasma in GaAsBi.

Figure 2 shows the results of varying this plasma density through the temperature dependence and the excitation power dependence of Raman spectra for $GaAs_{0.986}Bi_{0.014}$. Both the L_+ and the L_- are being suppressed in intensity and redshifted in frequency with either increasing temperature or decreasing excitation power. In particular, the L_+ mode merges toward the LO phonon at temperatures over 96 K or at excitation powers below 5 mW. The frequency shifts of the L_+ mode are shown as insets in each figure. The power dependence can be easily understood from the nature of the plasma in GaAsBi. Since the plasma is due not to charged dopants, but rather from photoexcited carriers, higher excitation power generates more carriers which lead to higher intensity and frequency of the plasmon. The temperature dependence, however, is not so straightforward and in fact runs opposite to the normally expected dependence for thermally generated intrinsic carriers. We believe that this peculiar temperature dependence is associated directly with the influence of Bi-related electronic states. Because bismuth is less electronegative than the arsenic atom it replaces, it is a potential minima for holes, and thus the Bi and Bi cluster states are energetically located close to the valence band maximum (VBM). The isolated Bi atom had been predicted to form a bound state;[11] however, a recent calculation[3] using larger supercells and more extensive analysis of the origin of the VBM concluded that the isolated Bi state is actually resonant in the valence band. This leaves the possibility that Bi pairs or clusters form potential wells deep enough to bind excitons. Experimentally, below-band-gap transistions are indeed observed in low-temperature PL of GaAsBi,[12] showing energy spacing and saturation behavior that are consistent with the expected Bi cluster states. At low-to-midexcitation density they dominate the PL. It is possible that at low temperature, holes are trapped at these sites, thus lowering the rate of electron-hole recombination. Equivalently, the spatially localized Bi states are composed of wave functions from multiple wave vector points in the valence band, which gives them a non-Γ character, reducing their wave function overlap with the free electrons.

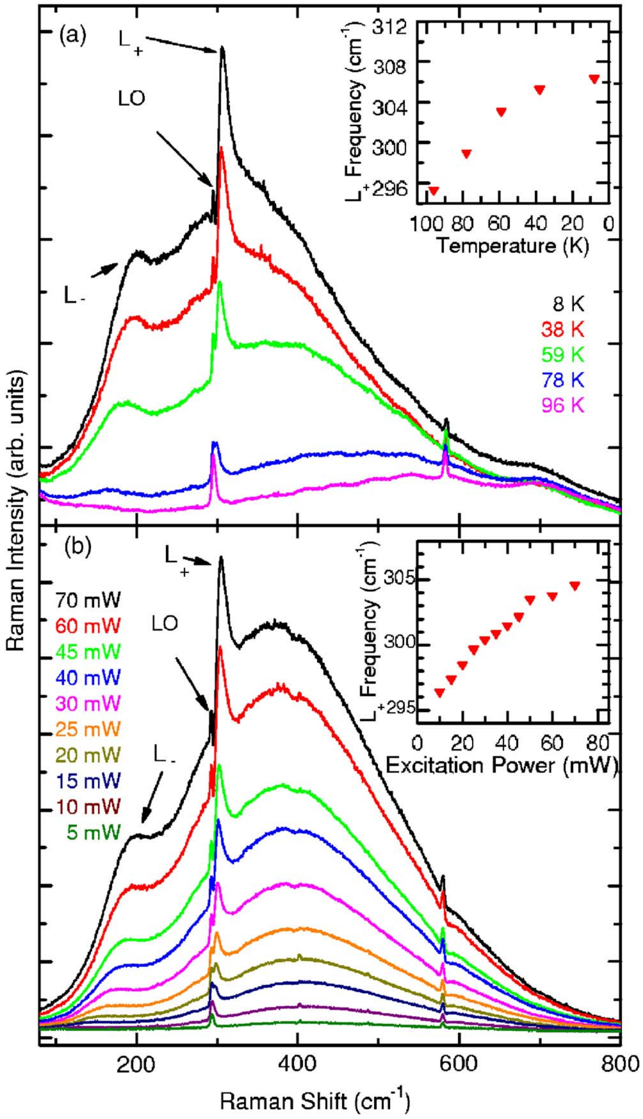

FIG. 2. (Color online) (a) Raman spectra for $GaAs_{0.986}Bi_{0.014}$ with an excitation energy of 1.901 eV at 40 mW at temperatures from 8 K (largest spectrum) to 96 K (smallest spectrum). All the spectra were taken in the (YY) geometry. Inset: Frequency of L_+ mode as a function of decreasing temperature. (b) Raman spectra for $GaAs_{0.986}Bi_{0.014}$ at 10 K with an excitation energy of 1.909 eV and excitation powers of 5 mW (smallest spectrum) to 70 mW (largest spectrum). Inset: frequency of L_+ mode as a function of excitation power. Similar temperature and power dependencies are seen in the $x=0.8\%$ and 3.1% samples.

To test this hypothesis, we have measured time-resolved PL spectra from $GaAs_{0.996}Bi_{0.004}$ in two energy ranges: first, near the $E_0+\Delta_0$ transition energy using a 1.984 eV pump beam and next, the below-band-gap region using a 1.550 eV pump beam. Figure 3(a) shows the time-integrated PL spectra near 1.44 eV. At 150 K, the PL is emitted at the Bi-lowered band gap at 1.46 eV, whereas at 45 K the below-band-gap Bi-related states dominate. The PL near 1.87 eV (shown in Fig. 1) decays very rapidly (not shown), almost as fast as the pump beam itself, at all temperatures measured, indicating that it originates from higher-lying well-defined host band edge states where carriers are undergoing rapid relaxation. Near 1.5 eV, PL from the low-temperature GaAs

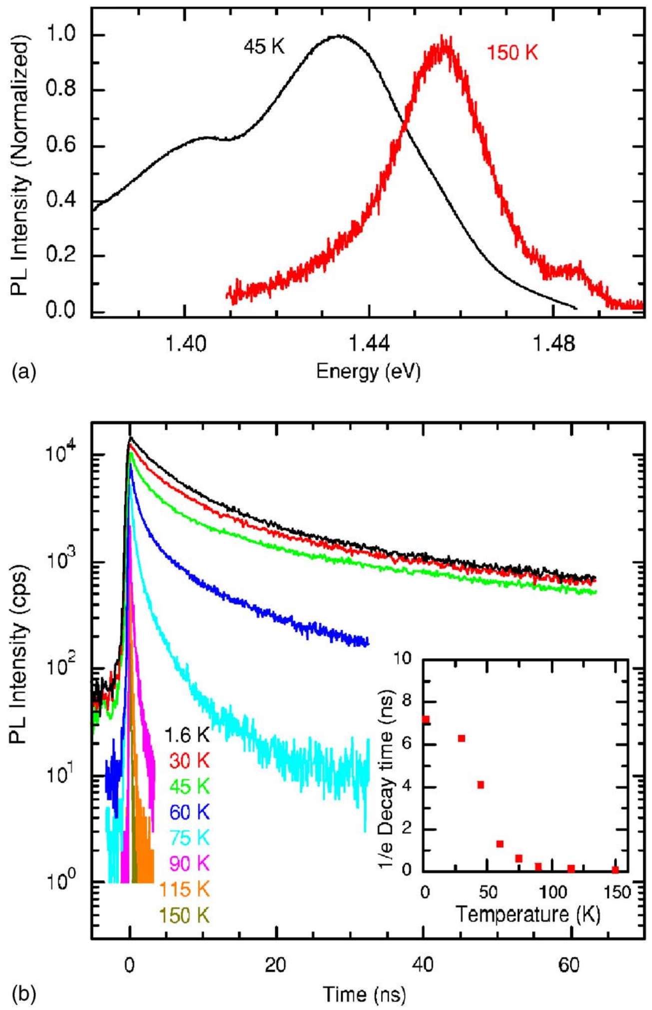

FIG. 3. (Color online) (a) Time-integrated PL spectra of $GaAs_{0.996}Bi_{0.004}$ at 45 and 150 K. The PL was filtered to block energies above 1.46 eV, and sent to a 0.27 m spectrometer/CCD. (b) Decay of the entire 1.38–1.48 eV PL spectrum shown in (a) at temperatures from 1.6 K (slowest decay) to 150 K (fastest decay). Inset: plot of the time for the PL intensity to reach $1/e$ of its maximum value as a function of temperature.

buffer layer decayed exponentially in 180 ps, as expected. However, the GaAsBi band edge and below-band-edge PL shown in Fig. 3(a) exhibit quite different behaviors. As shown in Fig. 3(b) at temperatures starting from 90 K and above, this PL decays very rapidly, similar to GaAs, but at lower temperature, it exhibits an extraordinarily long lifetime. Nearly identical time decays were also measured for the maximum bismuth concentration, $x=3.1\%$. The long-lived Bi hole states are the likely cause of this PL lifetime and hence also of the observation of the photoexcited electron plasma. In Ref. 12 it was shown that the sub-band-gap states, likely triplets or higher clusters in agreement with Ref. 3, ionize at approximately 50 K. The temperature dependence in Fig. 3(b), showing a similar transition temperature, is thus completely consistent with the behavior of the plasmon seen in Fig. 2(a). At temperatures above this, PL is dominated by the free carriers at the bandedge, which do not have a long lifetime.

To examine this in more detail, we note that the 1.6 K PL decay in Fig. 3(b) is highly nonexponential, and its power dependence (not shown) indicates that the radiative recombination itself is superlinear. The 1.6 K $1/e$ fall times shown in the inset of Fig. 3(b) will therefore underestimate the excitation density generated by the cw laser. Using the simple coupled-mode analysis in the long-wavelength limit,[13] and the effective electron mass of GaAs, electron densities corresponding to the L_+ and L_- frequencies of Fig. 2(b) are calculated and shown in Fig. 4. The results are consistent with the CPLOM model, and electron densities are seen to be a few $\times 10^{17}$ cm^{-3} with a small inequality between upper and lower branches that may be due to the wavelength dependence of the plasma frequency.[14] In addition, the clear observation of two modes, in particular, the L_+ mode with a relatively sharp linewidth and the density dependence seen in Fig. 4, points specifically to an *electron* plasma with a good mobility, as these characteristics are not seen in p-doped GaAs.[15,16] This strongly supports the models[3,5,6] of Bi achieving a technologically useful band gap reduction by modifying primarily the valence band and leaving the conduction band relatively unchanged.

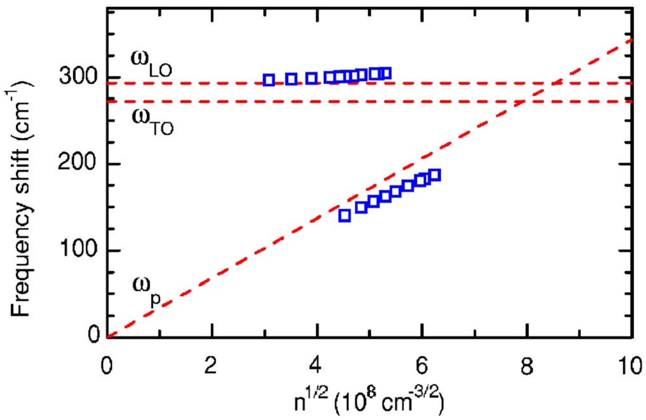

FIG. 4. (Color online) CPLOM frequencies from Fig. 2(b) plotted as a function of the square root of the carrier density calculated by solving for roots of the total longitudinal dielectric constant. Dashed lines ω_p, ω_{TO}, and ω_{LO} show the plasma frequency and the transverse and longitudinal optic phonons.

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