PHYSICAL REVIEW B **83**, 081309(R) (2011)

Upconversion of infrared photons to visible luminescence using InAs-based quantum structures

David M. Tex and Itaru Kamiya*

Toyota Technological Institute, Nagoya 468-8511, Japan

(Received 10 January 2011; published 17 February 2011)

We report on the upconversion of infrared photons to visible using a quantum structure based on an InAs wetting layer (WL) embedded in AlGaAs grown by molecular beam epitaxy. The grown structures are characterized by photoluminescence, and it is found that the upconversion center is a real intermediate state induced by the WL. The temperature dependence suggests that the intermediate state is of an exciton nature, which is supported by the result of an eight-band $\mathbf{k} \cdot \mathbf{p}$ calculation.

DOI: 10.1103/PhysRevB.83.081309 PACS number(s): 78.55.Cr, 78.60.−b, 78.66.Fd, 78.67.De

Upconversion has been reported in many semiconductor systems, such as heterojunctions,[1–7] InAs/GaAs quantum dots (QDs),[8,9] and even bulk semiconductors.[10–12] This phenomenon is not restricted to semiconductors, however.[13] Upconversion, also referred to as anti-Stokes photoluminescence (PL), in semiconductor materials is usually explained in terms of Auger processes[1] or two-step two-photon absorption (TS-TPA)[2], which have in common that carriers from the ground state are excited to a high-energy state via an intermediate state (virtual or real) using two photons. In the low-excitation density regime, virtual states are negligible for upconversion; instead, a real state has to promote the carriers to be excited to higher energy levels.

To date, in all reported upconversion structures based on InAs/GaAs, the performance is limited by relaxation via the donor-acceptor states of GaAs.[8,9,14] GaAs is widely used since it offers comparable easy yet high-quality growth. However, the use of AlGaAs as barrier expands the upconversion limit from the far infrared to the near infrared (NIR) and enables upconversion to the visible light range, which is attractive from the practical point of view. In this report, we show evidence of upconversion from the NIR to the visible using InAs/AlGaAs-based structures, and propose a model that accounts for the origin of the upconversion.

We performed PL measurements on InAs/AlGaAs structures grown on GaAs (001) wafers by molecular beam epitaxy. Following a 100-nm GaAs buffer and 100-nm $Al_{0.22}Ga_{0.78}As$ growth, the InAs-based active region was grown. The active layer consists of an InAs layer sandwiched between GaAs/AlGaAs quantum wells (QWs) with a barrier layer of 30 nm: multi-QWs (MQWs) beneath and a single QW (SQW) on top, as described schematically in Fig. 1(a). The structure between the GaAs and the InAs layer was grown at 650 °C. Then the growth was interrupted and InAs was deposited at a 500 °C substrate temperature and immediately capped with the top GaAs/AlGaAs QW structure. The amount of InAs deposited was either 0, 1.0, or 2.2 ML (calibrated from the QD formation critical thickness of 1.7 ML). During the growth of the AlGaAs on the InAs layer the temperature was gradually raised. The thickness of the QWs is adjusted so as to give distinguishable PL emission above the WL peak.

In these structures we can classify four intermediate states (upconversion centers): (i) the GaAs band edge, (ii) the GaAs donor-acceptor complex, (iii) an InAs-layer-induced intermediate state, and (iv) an impurity-induced intermediate state in the top SQW. In the GaAs buffer beneath the AlGaAs buffer the GaAs band gap, which is referred to as GaAs BG [triangles in Fig. 1(b)], will provide carriers if excited in Stokes configuration. The upconversion mechanism is most likely an Auger process.[15] In the same region the upconversion center responsible for the donor-acceptor (D/A) pair upconverted PL (UPL) in GaAs will also be excited under the experimental conditions employed. The intermediate state is probably a long-living impurity complex state. However, this upconversion center does not affect the region of interest in this report (see below). It is referred to as the D/A complex. We point out that AlGaAs/GaAs interfaces do not seem to introduce any significant UPL centers in our samples, in accordance with references.[7,16]

The UPL center related to the InAs layer is referred to as the InAs center [circles in Fig. 1(b)]. As discussed later, we believe that the UPL mechanism is an excitonic Auger process. In the top GaAs SQW, impurities similar to those in the GaAs buffer are incorporated depending on the growth conditions such as the background pressure and substrate temperature. UPL centers formed by such impurities are called impurity centers (squares in Fig. 1). The UPL mechanism is assumed to be similar to that of the D/A complex, although with a shorter lifetime due to recombination centers in the barrier.

According to the amount of impurities in the cap region, the five samples can be divided into two groups: (i) X, Y, and Z, whose caps are grown at the low temperature (LT) of ≈610 °C, and (ii) A and C, with caps grown at the high temperature (HT) of ≈650 °C. The former results in observable UPL from the impurity centers, while in the latter, it is negligible.

The samples are investigated by PL, using a Ti-sapphire laser as a variable excitation source between 700 and 1000 nm for anti-Stokes PL and a semiconductor diode laser at 532 nm for Stokes PL. The influence of the 532-nm line was carefully checked to avoid mixed PL and UPL. The PL is analyzed with a monochromator with a 300-nm focal length and a Si-CCD detector, cooled down to −70 °C. The sample is placed in an evacuated cryostat with a temperature variable between room temperature and 4 K.

PL peak assignments are summarized in Table I. The thick dotted line (i) in Fig. 2(a) shows the PL of the AlGaAs band gap region of sample A in the Stokes configuration (532-nm excitation, 0.5 W/cm^2). The thin dotted Gaussian curves represent the deconvoluted contributions from the AlGaAs exciton (BG), AlGaAs band to acceptor (eA), MQW,

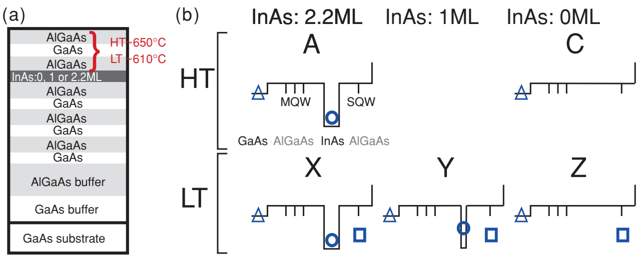

FIG. 1. (Color online) (a) Schematic description of the sample structure and (b) the corresponding conduction-band-minimum lineup. Upconversion centers of interest are indicated by circles, triangles, and squares (see text). In (b) the samples are grown from left to right. SQWs in samples A and C were grown at a high temperature (HT), ≈650 °C; samples X, Y, and Z, at a low temperature (LT), ≈610 °C.

TABLE I. Table of peak positions. The WL peak for X is red-shifted due to the larger amount of deposited InAs (overall rougher surface). Sample A has different peak positions due to its lower Al content and thinner SQW.

Peak	A (nm)	C (nm)	X (nm)	Y (nm)	Z (nm)
MQW	704	695	696	696	697
SQW	709	716	713	714	712
WL	721	–	724	718	–

SQW, and the WL formed by 2.2-ML InAs, from the short to the long wavelength. This WL peak corresponds to the 1-ML InAs/AlGaAs QW and thereby we define the WL as the first monolayer of InAs on the AlGaAs layer. Changing the excitation wavelength to 775 nm (10 W/cm^2) brings all the states in the observed window into the anti-Stokes configuration [solid (blue) spectrum (ii), Fig. 2(a)], and UPL whose intensity is about a thousandth of Stokes PL is observed. The UPL is mainly composed of those from the eA, the WL and the MQW. By further changing the excitation wavelength to cross GaAs BG, not only does the intensity fall, but also results in a qualitatively different UPL spectrum as shown by the thin (red) curve (iii) [Fig. 2(a); 855-nm excitation, 10 W/cm^2]. The UPL is now dominated by that from the WL, and those from the SQW and the MQW are weaker in intensity. This spectrum shows evidence of upconversion of photons from the infrared (855 nm) to the visible range (720 nm), at reasonably low excitation intensities (observable down to 0.5 W/cm^2), using an intermediate state in our sample structures.

To determine the origin of the UPL, a more detailed trend of the MQW, SQW, and WL peak intensities for samples A and C is given in the PL excitation (PLE) spectra in Figs. 2(b) and 2(c), respectively. For sample A [Fig. 2(b)], resonance at the GaAs BG (816.5 nm) is clearly seen for all three peaks, and also, a crossover in the intensity between MQW and SQW. For sample C (without InAs), the same trend is observed above GaAs BG excitation, but no observable UPL signal for below GaAs BG. This is clear evidence that the UPL observed by 855-nm excitation in sample A is induced by the InAs layer. The PLE for sample A below GaAs BG shows that carriers are excited to the InAs center (a state in the InAs layer region, whose nature is unknown at this stage) and then further excited to the quantum states in the WL, SQW, and MQW. To prove that UPL from the InAs-center is also possible for InAs deposition below the QD formation limit, a reference UPL signal induced by a UPL center different from the InAs center is favored. It is introduced by growing the SQW at a low temperature (samples X, Y, and Z). UPL spectra for the three samples for an excitation wavelength of 855 nm measured at 4 K are shown in Fig. 3, all three showing a distinct peak at about 713 nm corresponding to the SQW. The MQW peak at around 696 nm is observed only in sample X with 2.2-ML InAs, from which the strongest WL peak among these three samples is also observed at around 720 nm, indicating that the number of InAs centers is highest. The WL peak is slightly blue-shifted for sample Y. In sample Z (without InAs) the same spectrum, except for the WL peak, is obtained. By raising the sample temperature to 24 K, UPL spectra shown in the inset of Fig. 3 are observed. For samples X and Y we note a decrease in the SQW UPL intensity and almost no decrease in WL UPL. A different behavior is observed in sample Z, that is, a prominent decrease in the SQW UPL. These results indicate that the UPL of the SQW for samples X, Y, and Z is realized through two

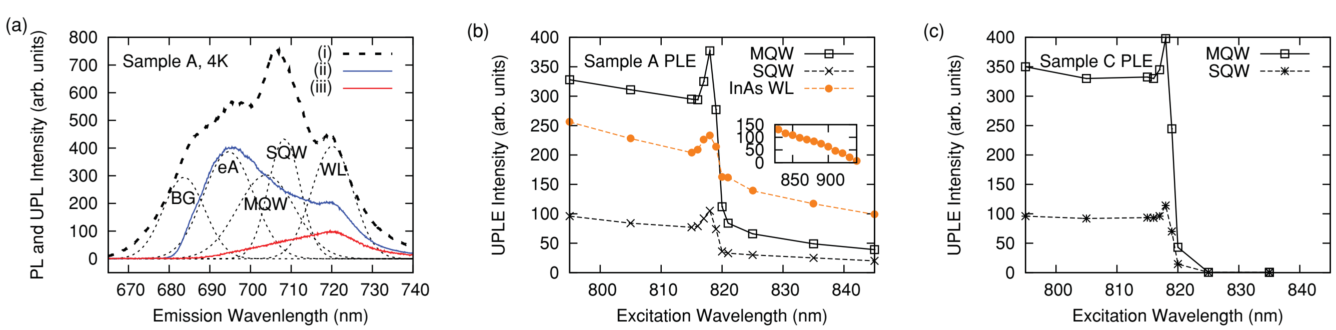

FIG. 2. (Color online) (a) PL spectra of the AlGaAs band gap region for sample A excited at (i) 532 nm, (ii) 775 nm, and (iii) 855 nm measured at 4 K. The thick dotted line obtained at 532 nm (i) is deconvoluted into contributions from the AlGaAs exciton (BG), AlGaAs band to acceptor (eA), MQW, SQW and InAs WL, shown by the thin dotted lines. Line (ii) is magnified by a factor of 500, and line (iii) by 1000, to compare them with the Stokes signal. Therefore, we estimate that the upconversion efficiency is of the order of 0.1% (power dependence ≈1.25). (b) PLE spectra for sample A; the inset shows WL UPL from 830 to 940 nm. (c) PLE spectra for sample C. The similarity of the UPL signals below GaAs BG values between (b) and (c) illustrates good reproducibility.

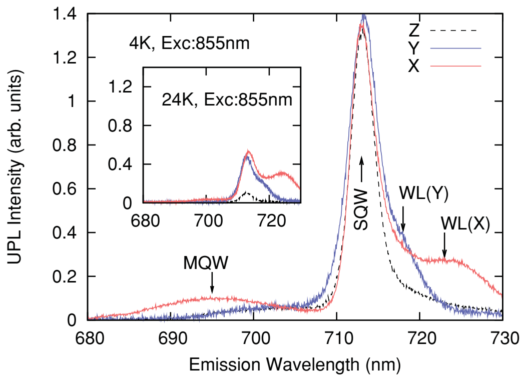

FIG. 3. (Color online) UPL spectra for samples X (2.2-ML InAs), Y (1.0-ML InAs), and Z (no InAs) excited at 855 nm, 10 W/cm^2, measured at 4 K. Data are normalized to the deconvoluted SQW reference. Inset: data obtained at 24 K.

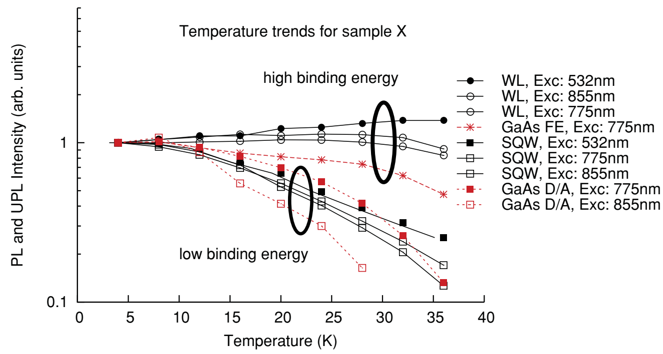

FIG. 4. (Color online) Temperature dependence of four PL peaks [SQW, WL, GaAs free exciton (FE), and GaAs donor/acceptor (D/A)] in Stokes (filled symbols) and anti-Stokes (open symbols) configurations, normalized by the 4 K data.

paths: (1) the impurity center and (2) the InAs center. At 24 K, nonradiative recombination of the impurity center is enhanced, resulting in the reduction in SQW UPL intensity for sample Z. In samples X *and* Y, carrier flow from the InAs center, which is less sensitive to temperature, make up for the loss of the impurity center. This is the proof that InAs centers exist even below QD formation limit. UPL from an InAs layer below the QD formation limit, however, seems to be weaker than that from above, suggesting that either QDs or a rougher surface induces more InAs centers. The advantage of using a reference UPL signal lies in the possibility of inferring the carrier flow in the sample. Consistent with our model, which we applied to explain the results for sample A, the InAs center generates free carriers, that is, the upconverted carriers may recombine at a location far away from the InAs center. The above result also implies that the carrier transfer from the impurity center to states other than the SQW is negligible. Therefore, the impurity center is considered as a source of bound carriers.

To classify the upconversion centers, we consider the binding energy of the electron hole pair to the centers. The temperature dependence in the different excitation regions reveals the intrinsic binding energy of each upconversion center. Four PL/UPL peak trends of sample X are summarized in Fig. 4: (i) the GaAs free exciton, (ii) the GaAs D/A, (iii) the SQW, and (iv) the WL. It is observed that the Stokes configuration results in a higher binding energy compared to the anti-Stokes for all peaks. This can be explained by a change in the dominant excitation mechanisms (Stokes—relaxation only; anti-Stokes—first excitation from the UPL center, then relaxation). When PL or UPL involves two intermediate states, the temperature trend represents the feature of the state with the weaker binding energy. For the WL, this means that the binding energy for the WL quantized state is higher than that of the InAs center.

We conclude that the temperature trends of the UPL peaks represent the intrinsic binding energy of the upconversion centers themselves. The InAs-center-induced UPL mechanism is exciton-like, due to the high binding energy, while that via the impurity center is impurity-like, with a low binding energy and localized nature, that is, the inability to produce free upconverted carriers.

The details of the InAs-center-mediated UPL remain unclear. However, from the experimental results it is likely that upconversion is induced by intermediate states in the two dimensional (2D) InAs islands. The islands exist in the samples with InAs below and beyond QD critical thickness,[17] explaining the UPL from sample Y with only 1-ML InAs. Similar reports have been made, namely, that the upconversion center lies not in the QD ground state itself, but rather, in the WL.[8,9,14] These reports show UPL for InAs/GaAs QD systems only. In the present work, the roughness of the AlGaAs surface is likely to induce more InAs islands and, consequently, more InAs centers. As a result, UPL can be observed from samples with InAs less than the QD formation limit.

Based on this idea, a 1D numerical calculation for the confined states in 2D InAs islands was performed. We used an eight-band $\mathbf{k} \cdot \mathbf{p}$ model including spin-orbit coupling and boundary conditions as introduced by Burt[18] and explicitly written for eight bands by Foreman.[19] We used material parameters presented by Vurgaftman *et al.*[20] for InAs and parameters given by Eppenga *et al.*[21] for the AlGaAs alloy. In brief, the results show a confined energy 230 to 300 meV lower for 2- and 3-ML islands, compared to the WL (=1 ML) state. This corresponds to intermediate states from 845 to 890 nm if the strain energy in the 2- and 3-ML island is as high as for the 1-ML WL. This result is fairly consistent with the PLE shown in the inset in Fig. 2(b).[22]

Given these results, we propose the following model. When the In shutter is opened an extended single-layer WL is grown on the AlGaAs surface together with smaller multilayered islands (2 ML or thicker). Due to the small band gap compared to the spin split-off band, the island states are considerably smaller than the wetting layer state. We believe these island states to serve as the intermediate state for upconversion (Fig. 5). In extended islands the confined excitons have a reasonably large cross section and a lifetime that is sufficient for an exciton to transfer its energy to another by direct overlap.[22] The confinement due to further lateral extension of the randomly sized islands introduces a continous change in the energy of the intermediate states, which implies a continous UPLE spectra [inset in Fig. 2(b)]. For such island states to contribute to UPL at below GaAs BG excitation, the island must exceed a certain size.

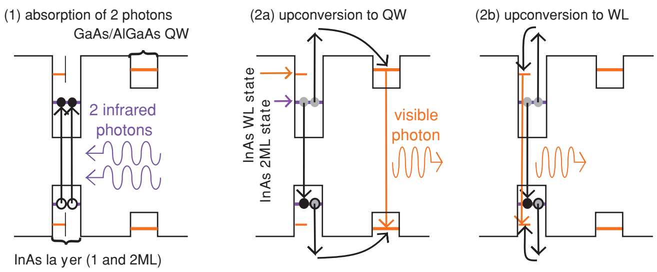

FIG. 5. (Color online) Sketch of the upconversion mechanism. (1) Two photons create two excitons in the 2-ML InAs island state. (2a) One exciton recombines and transfers its energy to the other exciton, whose electron and hole are excited and then relax to the GaAs/AlGaAs QW. (2b) Relaxation to the WL.

In conclusion, we observed upconverted visible PL by exciting intermediate states induced in an InAs layer in an InAs/AlGaAs system with infrared photons. We propose a model that includes three important upconversion centers (GaAs BG, InAs center, impurity center), together with the mechanisms that explain the data consistently, and focuses on the nature of the InAs-layer-induced UPL center. The temperature dependence and PL excitation spectra show that UPL from the InAs-induced intermediate state can be observed from the InAs WL or islands above a certain size, which produces free carriers of excitonic character. The existence of such a state can be verified theoretically with an eight-band $\mathbf{k} \cdot \mathbf{p}$ calculation. Based on the results, we believe that InAs islands 2 or 3 ML in height are the origin of such intermediate states. QD formation does not seem to affect the ability of the WL for UPL, and we showed that QD formation is not necessarily needed for UPL. We emphasize that the excitation densities used in the experiments are as low as the lowest reported in upconversion in InAs/GaAs systems. The use of InAs/AlGaAs instead opens new possibilities for device applications for upconversion devices such as photovoltaic due to the generation of free carriers instead of impurity-induced carriers, resulting in localized UPL. We believe that the upconversion efficiency may be improved by control of the shape of the InAs 2D islands through precise control of the growth conditions.

This work was supported by the Strategic Research Infrastructure Project of the Ministry of Education, Sports, Science and Technology, Japan.

*Corresponding author: sd09501@toyota-ti.ac.jp

[1] W. Seidel, A. Titkov, J. P. André, P. Voisin, and M. Voos, Phys. Rev. Lett. **73**, 2356 (1994).

[2] R. Hellmann, A. Euteneuer, S. G. Hense, J. Feldmann, P. Thomas, E. O. Göbel, D. R. Yakovlev, A. Waag, and G. Landwehr, Phys. Rev. B **51**, 18053 (1995).

[3] F. A. J. M. Driessen, H. M. Cheong, A. Mascarenhas, S. K. Deb, P. R. Hageman, G. J. Bauhuis, and L. J. Giling, Phys. Rev. B **54**, R5263 (1996).

[4] Z. P. Su, K. L. Teo, P. Y. Yu, and K. Uchida, Solid State Commun. **99**, 933 (1996).

[5] J. Zeman, G. Martinez, P. Y. Yu, and K. Uchida, Phys. Rev. B **55**, R13428 (1997).

[6] Y. H. Cho, D. S. Kim, B. D. Choe, H. Lim, J. I. Lee, and D. Kim, Phys. Rev. B **56**, R4375 (1997).

[7] H. M. Cheong, B. Fluegel, M. C. Hanna, and A. Mascarenhas, Phys. Rev. B **58**, R4254 (1998).

[8] C. Kammerer, G. Cassabois, C. Voisin, C. Delalande, Ph. Roussignol, and J. M. Gerard, Phys. Rev. Lett. **87**, 207401 (2001).

[9] P. P. Paskov, P. O. Holtz, B. Monemar, J. M. Garcia, W. V. Schoenfeld, and P. M. Petroff, Appl. Phys. Lett. **77**, 812 (2000).

[10] E. J. Johnson, J. Kafalas, R. W. Davies, and W. A. Dyes, Appl. Phys. Lett. **40**, 993 (1982).

[11] L. G. Quagliano and H. Nather, Appl. Phys. Lett. **45**, 555 (1984).

[12] D. Kovalev, J. Diener, H. Heckler, G. Polisski, N. Künzer, F. Koch, Al. L. Efros, and M. Rosen, Phys. Rev. B **61**, 15841 (2000).

[13] F. Auzel, Chem. Rev. **104**, 139 (2004).

[14] G. Cassabois, C. Kammerer, R. Sopracase, C. Voisin, C. Delalande, Ph. Roussignol, and J. M. Gérard, J. Appl. Phys. **91**, 5489 (2002).

[15] D. M. Tex and I. Kamiya (to be published).

[16] F. A. J. M. Driessen, Appl. Phys. Lett. **67**, 2813 (1995).

[17] T. R. Ramachandran, R. Heitz, P. Chen, and A. Madhukar, Appl. Phys. Lett. **70**, 640 (1997).

[18] M. G. Burt, J. Phys. Condens. Matter **11**, R53 (1999).

[19] B. A. Foreman, Phys. Rev. B **56**, R12748 (1997).

[20] I. Vurgaftman, J. R. Meyer, and L. R. Ram-Mohan, J. Appl. Phys. **89**, 5815 (2001).

[21] R. Eppenga, M. F. H. Schuurmans, and S. Colak, Phys. Rev. B **36**, 1554 (1987).

[22] D. M. Tex and I. Kamiya (to be published).