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Laser writing of the electronic activity of N- and H-atoms in GaAs

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We use a focussed laser beam to control the electronic activity of N- and H-atoms in a dilute nitride Ga(AsN)/GaAs quantum well. Our approach yields submicron resolution in the spatial manipulation of the electronic properties and can provide an alternative method to masking techniques for H-defect engineering and in-plane patterning of the band gap energy. © *2011 American Institute of Physics*. [doi:10.1063/1.3610464]

The controlled incorporation of impurities in a semiconductor crystal during or after the synthesis is routinely used to tailor electronic properties and has played a key role in the discovery of physical phenomena and their exploitation in device applications. Among various elements, nitrogen and hydrogen in III-V compounds have revealed intriguing effects of fundamental interest and technological importance. The incorporation of a small concentration ($\sim$1%) of N-atoms onto the anion sublattice of a III-V crystal induces a large reduction of the band gap energy[1,2] and an unusual response to external perturbations, such as hydrostatic pressure.[1] On the other hand, H-atoms are highly mobile and reactive elements that passivate both deep and shallow crystal defects and impurities in semiconductors.[3,4] In particular, the incorporation of hydrogen in III-N-Vs acts to neutralize the electronic activity of N through the formation of N-H complexes, thus reversing the effect of the N-atoms on the band structure of the host crystal.[5,6]

In this letter, we use a focused laser beam to control the electronic activity of N- and H-atoms in a Ga(AsN)/GaAs quantum well (QW). Our laser writing technique and micro-photoluminescence (μPL) studies provide real-time *in-situ* characterisation and control of the N-H complex dissociation and of the band gap energy of Ga(AsN). This technique yields submicron resolution in the spatial manipulation of the electronic properties and could provide an alternative route to masking methods for H-defect engineering and in-plane patterning of the band gap energy[7,8] for nanophotonics[9] and photovoltaics.[10]

In this study, we use a Ga(AsN)/GaAs QW sample (V-sample) grown by molecular beam epitaxy (MBE) on a (100)-oriented GaAs substrate. This structure has the following layer composition, in order of growth: an undoped GaAs buffer layer grown at 600 °C, a 6 nm Ga(AsN) (N = 0.9%) QW and a 30 nm undoped GaAs cap layer both grown at 500 °C. The N-content was determined by high resolution x-ray diffraction (HRXRD) measurements and further supported by PL studies showing that the Ga(AsN) QW PL emission is red-shifted by 0.13 eV relative to the GaAs PL emission ($T = 300$ K). The as-grown sample was hydrogenated by ion beam irradiation using a Kaufman source. The hydrogenation was performed at 300 °C with an ion-beam energy of 100 eV and H-doses of 4×10^{16}, 6×10^{16}, and 8×10^{16} ions/cm^2. We refer to these hydrogenated samples as H1, H2, and H3, respectively.

Our experimental set-up for μPL measurements comprises an XY linear positioning stage, an optical confocal microscope equipped with a nanofocusing system, and a spectrometer with a 150 g/mm grating equipped with a liquid-nitrogen cooled (InGa)As array photodetector. The laser beam was focused to a diameter $d < 1$ μm using a 100 × objective, and the μPL spectra were measured at several points by moving the sample with respect to the laser beam. The μPL intensity maps were obtained by integrating the local PL intensity in the spectral range of interest. For the laser exposure experiments, we used laser beams of wavelength $\lambda = 515$ nm or 633 nm, powers P_a in the range 10-120 mW ($\lambda = 515$ nm) and 0.01-15 mW ($\lambda = 633$ nm), and exposure times t_a up to 180 s.

The incorporation of hydrogen in Ga(AsN) leads to the formation of several complexes including complexes H-N-H with C_{2v} and C_{1h} symmetry and higher order clusters. Complexes with C_{1h} symmetry were recently probed by infrared spectroscopy[6] and are responsible for the neutralization of the electronic activity of nitrogen and its effect on the band gap energy of GaAs, thus causing a blue shift of the PL emission.[5] This effect is shown in Figure 1(a) for an hydrogenated Ga(AsN) QW (H2-sample). We now consider how this neutralization effect can be reversed locally using a focussed laser beam, which acts to dissociate the complex, thus restoring the electronic activity of nitrogen. Figure 1(b) shows the μPL spectra of the H2-sample measured at low power (1.8 mW) after sample exposure to a focussed laser beam ($d \sim 1$ μm) of wavelength $\lambda = 515$ nm and power $P_a = 10$ and 30 mW for a time $t_a = 15$ s. It can be seen that the effect of the laser exposure is to restore the QW emission observed in the virgin V-sample. A typical laser exposed spot can be resolved in the μPL map of Figure 1(b). The QW PL intensity distribution inside the spot has an approximately Gaussian form with a full width at half maximum that corresponds closely to the size of the laser spot diameter ($\sim$1 μm). Similar μPL spectra and μPL maps were observed in all hydrogenated samples under various laser exposure

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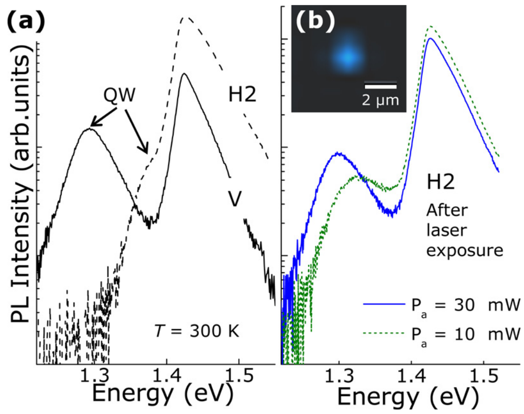

FIG. 1. (Color online) (a) μPL spectra of the H2- and V-samples ($T = 300$ K). (b) PL spectra at 300 K of sample H2 following an exposure to a focussed laser beam with power $P_a = 10$ and 30 mW ($t_a = 15$ s and $\lambda = 515$ nm). The inset shows a μPL map obtained by plotting the μPL intensity integrated in the range 1.25–1.35 eV.

conditions, i.e., laser powers, wavelengths (633 and 515 nm), and/or annealing times. We note that powers less than 2 mW do not introduce any permanent change in the electronic properties of the hydrogenated QW. Also, the PL intensity tends to decrease for laser exposures at large powers, i.e., $P_a \geq 40$ mW. These powers lead to a significant heating and a damage of the sample surface[11] due to As-desorption at high temperatures (>600 °C).[12]

This laser technique can be used to produce arrays of emitting regions or shaped emitting areas with submicron precision, see Figure 2(a). As shown in Figure 2(b), the photon energy of the emitting regions can be controlled precisely by the laser exposure conditions. In Figure 2(b), we plot the dependence of the peak energy, $h\nu$, of the QW PL emission for sample H2 as a function of the exposure time t_a at various laser powers P_a and $\lambda = 633$ nm. It can be seen that with increasing t_a, the QW PL peak energy shifts to lower energies towards the value of the QW peak energy in the V-sample. This value is approached faster and the remnant offset becomes smaller with increasing laser power.

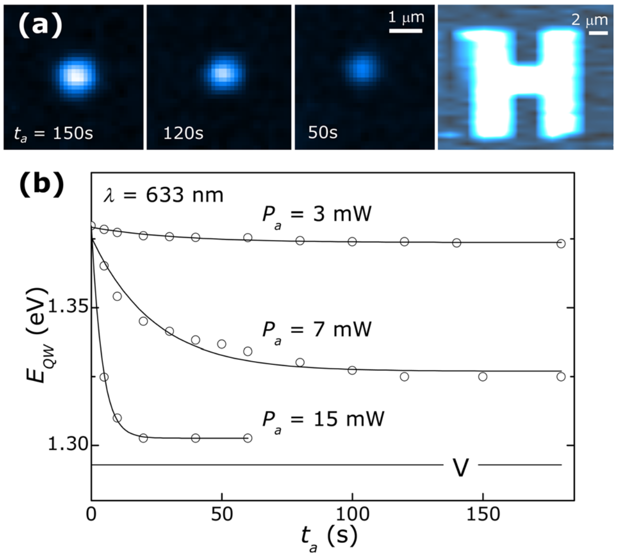

FIG. 2. (Color online) (a) Left: μPL intensity maps of sample H2 at 300 K following a laser exposure with laser power $P_a = 7$ mW, exposure times $t_a = 150$ s, 120 s, and 50 s and $\lambda = 633$ nm. Right: H-shaped emitting area written by laser ($P_a = 15$ mW, $t_a = 10$ s, $\lambda = 633$ nm) and mapped using a laser power of 0.1 mW at 300 K. (b) Dependence of the peak energy, E_{QW}, of the Ga(AsN) QW PL emission on t_a at 300 K ($\lambda = 633$ nm). Continuous lines are guides to the eye. The horizontal line corresponds to the value of E_{QW} in the V-sample.

The exposure of the sample to the laser beam induces a local heating, which we probe by acquiring the μPL spectra during *in-situ* laser exposure experiments with a focussed laser beam. As shown in Figure 3(a), the high energy tail of the GaAs μPL emission in sample H2 exhibits an exponential tail described by $\exp(-h\nu/k_BT_e)$, where T_e is the effective temperature of the photogenerated carriers. The value of T_e increases with increasing P_a (see Figure 3(b)). This increase is accompanied by an increase of the lattice temperature T_L, which we estimate by modelling the measured shift of the QW PL peak by the Varshni's law.[13] The carrier and lattice temperatures reach values of up to $T_L \sim T_e \sim 190\,^{\circ}$C at $P_a \sim 15$ mW and $\lambda = 633$ nm (Figure 3(b)). The measured increase of the lattice temperature is in qualitative agreement with that calculated numerically[14] by using the temperature dependent thermal conductivity and absorption coefficient of GaAs at $\lambda = 633$ nm.[15] Laser annealing at powers >40 mW leads to an abrupt increase of the lattice temperature. This thermal runaway effect is caused by the low thermal conductivity of GaAs at high temperatures. Our analysis shows that the laser powers required to trigger the neutralization of the effect of hydrogen on the PL emission energy of the Ga(AsN) QW corresponds to temperatures $T_L \sim T_e \sim 100\,^{\circ}$C ($P_a \sim 3$ mW), which are significantly lower than those (250-300 °C) reported before using conventional thermal annealing methods.[16]

We evaluate the activation energy for this neutralization effect from the temperature dependence of the increase, ΔN, in the concentration of electrically active N-atoms in the hydrogenated Ga(AsN) QW following the laser exposure. An increase in the value of ΔN is correlated to a corresponding decrease, ΔH, in the concentration of N-H complexes in the QW. To estimate ΔN, we model the laser-induced redshift of the QW PL emission by a two-level band-anticrossing model with an interaction parameter $V_N = 2.7$ eV and a N-level located at 0.23 eV above the conduction band minimum of GaAs.[2]

The values of ΔN determined under different laser exposure conditions and their dependence on the lattice and electron temperatures are plotted in Figure 3(c). The thermally activated behaviour of ΔN, i.e., $\Delta N \sim \exp(-E_a/k_BT)$, is characterized by an activation energy E_a equal to 0.43 eV and 0.86 eV, for T equal to T_L and T_e, respectively. These energies and the corresponding temperatures are significantly smaller than those obtained for out gassing of H from the sample and the thermal dissociation of N-H related complexes involving one ($E_a = 1.77$ eV) or two H-atoms ($E_a = 1.89$ eV) using HRXRD measurements of the lattice parameter during *in-situ* annealing studies at $T = 250$–$300\,^{\circ}$C.[16] Thus, we conclude that our laser writing technique is photon-assisted. Various processes can be envisaged: the photogenerated electron-hole pairs recombine and release their energy to the complex; also, they can modify its charge state, thus reducing the activation energy for the complex dissociation.[17] Similar processes are frequently observed in

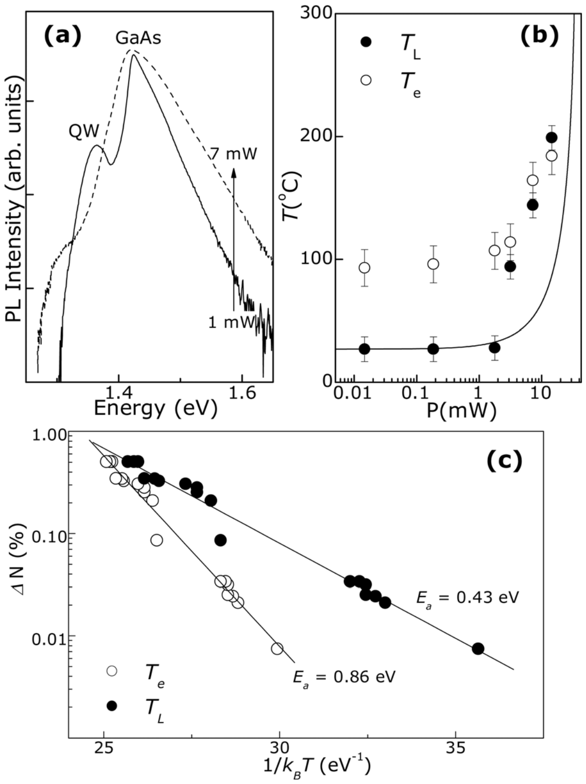

FIG. 3. (a) PL spectrum of sample H2 measured at various laser powers at 300 K ($\lambda = 633$ nm). (b) Dependence of the carrier (T_e) and lattice temperature (T_L) on the laser power ($t_a = 120$ s). The continuous line is the calculated dependence of T_L on the laser power P_a at $\lambda = 633$ nm. (c) Dependence on $1/k_BT_L$ and $1/k_BT_e$ of ΔN. The continuous lines are fit to the data by the exponential curve $\exp(-E_a/k_BT)$, where E_a is the activation energy.

photochemistry and can be responsible for the light enhanced H motion in amorphous Si[17] and the photo-induced reactivation of neutralized donors in Si-doped GaAs.[18] Further studies are now required to model and probe the laser power and λ-dependence of the photodissociation of the N-H complex and to discriminate possible contributions of thermal effects.

In conclusion, we have shown that a focussed laser beam can be used to control spatially the photoluminescence emission energy of an hydrogenated Ga(AsN) quantum well. This laser writing effect is caused by the photodissociation of N-H complexes and can be used to manipulate the electronic activity of the N- and H-atoms with submicron resolution. Laser writing of the electronic activity of H-atoms in GaAs and other III-Vs could open up interesting possibilities for low-cost and high-speed nanofabrication techniques in nanophotonics. In particular, UV laser writing and/or near-field laser irradiation[19] will help to gain further spatial control and resolution of the optical properties, which in our experiment is limited to ~0.8 μm for laser wavelengths of λ ~600 nm.

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