Fabrication, characterization and applications of novel nanostructures based on dilute nitride semiconductors

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Dilute nitride semiconductors are III-V alloys in which small percentages of nitrogen atoms are included on the group V sublattice. These N isoelectronic impurities (namely, impurities having the same valence of the atoms they replace) considerably modify the physical properties of the host material, leading to many surprising effects. For example, in the case of GaAs$_{1-x}$N$_x$ ($x \approx 1\%$), a large decrease of the bandgap energy and a deformation of the conduction band structure have been observed [1, 2, 3].

Even more surprising are the effects of hydrogen incorporation in these alloys. Indeed, H completely reverses the effect of N impurities, due to the formation of stable N-2H complexes (“passivation” of N impurities) [4]. As a consequence, a complete recovery of the N-free material bandgap is achieved, as well of all other electronic and structural properties of N-free GaAs [5].

Beyond their relevance for fundamental research, dilute nitrides are attractive for the fabrication of nanostructures, such as quantum dots (QDs) and quantum wires (QWRs). QDs are semiconductor nanostructures surrounded by another semiconductor material with greater energy gap, so that electrons and holes are quantum confined in all spatial directions. Thanks to their 0-D density of states, QDs exhibit atomic-like electronic and optical properties and they could find applications in the field of quantum information as single photon sources [6]. QD fabrication requires to modulate on a nanometer scale the electronic properties of semiconductors (in particular the bandgap energy) in the growth plane, a difficult task to be achieved. Bottom-up techniques rely on random self-assembly processes: this way dots with good optical quality can be obtained but there’s no control over their size, shape, and position [7]; on the other hand, top-down methods allow fabrication of highly uniform dots, but with a poor optical quality because of air exposed surfaces produced by chemical treatments [8].

In many applications both a high optical efficiency and a good control over dot positioning are crucial: for instance, integration with optical microcavities, that could allow the observation of cavity effects [9] and enhance the efficiency of QD-based single photon sources [10].

The first goal of my PhD thesis will be the optimization of an innovative technique for QD and QWR fabrication that relies upon selective hydrogenation of dilute nitride heterostructures, able to overcome the limitations of the previously mentioned methods. QDs will be then integrated into properly designed photonic crystal cavities in order to enhance their emission rate through the Purcell effect and possibly to observe other cavity effects. Samples will be characterized by means of optical spectroscopy techniques in order to study their electronic properties and verify their possible use as single photon emitters.

The project can be divided in three steps, as described in the following:
1) Fabrication of III-V semiconductor quantum dots

Effects related to hydrogen incorporation in dilute nitrides can be exploited to realize nanostructures with arbitrary shape and size and well-defined position [11]. Indeed, by patterning a GaAsN/GaAs quantum well with hydrogen-opaque metallic masks with nanometer size it’s possible to hydrogenate only selected regions of the sample, thus creating regions of untreated GaAsN surrounded by regions having the physical properties of N-free GaAs. Therefore, a spatial modulation of the bandgap energy in the growth plane is achieved (a technique referred to as “in plane bandgap engineering” [11]). Figure 1 sketches the process, showing the simulated distribution of H and N atoms and the spatial profile of the valence and conduction bands. Previous experiments have proved the feasibility of this technique: wires and dots fully controlled in their size and position have been fabricated and quantum confinement effects have been observed in these systems [12, 13].

Figure 1: Sketch of the fabrication process: distribution of H, \( n_H \), and N, \([N]\), atoms below the mask (left panels) and bandgap modulation in the growth plane (right, top panel) and perpendicular to it (right, bottom panel)

Deposition of metallic masks will be performed by electron beam lithography (EBL) at the facilities of the CNR Institute of Photonics and Nanotechnologies in Rome. EBL, a powerful technique to create a pattern onto the surface of a sample, ensures a spatial resolution in the 10 nm range. Schematically, the sample is covered with a thin positive resist layer and then exposed to an electron beam which increases the solubility of the resist in an appropriate developing solvent, thus the exposed part of the resist can be removed. Then a thin Ti layer is deposited on the sample surface and the desired pattern is transferred onto the substrate through a lift-off process of the remnant resist with a different solvent. In this way, very uniform array of dots were obtained, as shown in Fig. 2 by scanning electron microscope (SEM) images. However, in the case of dots having diameter equal or smaller than 100 nm, some dot may be missing in the array or its shape be defective because of the lift-off process. In this process, indeed, unwanted parts of the deposited Ti layer can be removed, giving rise to slightly different dot shapes and sizes (see for example the 80 nm dot in Fig. 2).
To overcome these problems, different strategies will be tested, for example using a HSQ (Hydrogen silsesquioxane, $\text{H}_8\text{Si}_8\text{O}_{12}$) negative resist to directly pattern the sample, without depositing metallic masks. HSQ provides a very high spatial resolution (below 10 nm [14, 15]), it is opaque to hydrogen, and therefore it can be effectively used in place of Ti.

Hydrogen irradiation will be performed by means of a Kaufman source, which uses $\text{H}^+$ ions with 100 eV energy; different hydrogenation conditions (sample temperature and H dose) will be employed in order to optimize the optical properties of QDs, especially to minimize the emission linewidth.

2) Integration of single QDs with photonic crystal cavities

The coupling of a single emitter with the modes of an optical cavity has several advantages: a more efficient photon extraction, a control over the polarization of emitted photons, and the possibility to control the dynamics of photon emission. E. M. Purcell et al. predicted an enhancement of the spontaneous emission if the energy of emitted photons is resonant with that of the cavity modes [16]. If the emitter is placed at the maximum of the cavity electric field, the rate of spontaneous emission at wavelength $\lambda$ is enhanced by the factor $F = \frac{3\lambda^3Q}{4\pi^2V}$, where $Q$ and $V$ are the quality factor and the modal volume of the cavity, respectively [16]. Among the various kinds of cavity, photonic crystal cavities (PhC) are emerging because of their ease of fabrication and the possibility to reach high $Q$ values and small modal volumes [17]. Photonic crystals are materials with a periodical modulation of the refractive index, typically achieved by etching an array of holes in a high refractive index semiconductor. The periodicity of the refractive index gives rise to frequency gaps for photons, where light propagation is forbidden. A defect in the photonic crystal breaks the periodicity and can confine light. Then, an optical cavity can be realized by simply removing one or a few holes. Resonant frequencies of the cavity are determined by refractive index, hole size, and lattice constant.

PhCs will be designed to be resonant with GaAsN QD excitonic emission and fabricated by means of EBL. As sketched in Fig. 3, once a QD has been realized, holes will be etched around it, so that the dot position coincides with the electric field maximum.
3) Optical characterization of the samples

Once fabricated, the optical properties of the samples will be investigated by means of photoluminescence (PL) and micro-PL spectroscopy. In conventional PL spectroscopy a sample is excited by photons with energy greater than that of the bandgap, thus generating electron-hole pairs. Then, excited carriers relax toward lowest energy states and afterward recombine radiatively. Investigation of a single QD requires a micro-PL setup, in which the excitation laser is focused through a microscope objective onto a spot with size smaller than 1 µm. The light emitted from the sample is then collected and analyzed by means of a 0.75 m monochromator and a N-cooled CCD camera, as shown in Fig. 4.

Because of their 0-D density of states, QDs exhibit discrete energy levels and, therefore, typical PL spectra of a single dot show very sharp features, which can be attributed to recombination of single as well as multiple or charged excitons [13]. Indeed, because of the strong confinement, also bound states of two (biexcitons) or more excitons can be observed: detailed PL spectroscopy, performed at different excitation powers and temperatures, will allow to identify all the observed peaks and fully characterize the optical spectra of a single dot. Moreover, at sufficiently low excitation power, only one peak, corresponding to recombination of a single exciton, can be observed [13]: the dot is populated by only one electron-hole pair and in this regime can act as a single photon source. To further explore
this possibility, photon correlation spectroscopy will be performed with the facilities of the Laboratory of Physics of Nanostructures at the École Polytechnique Fédérale de Lausanne. A typical setup for photon correlation spectroscopy is made of a Hanbury Brown and Twiss interferometer (see Fig. 5): a 50:50 beam splitter, two single photon detectors (typically avalanche photodiodes, APD) and a correlation electronics which measure the relative time delay $\tau$ between two detections in the two APDs. For an ideal single photon source no coincidence detection are observed and a minimum for $\tau = 0$ occurs in the histogram of photon counts as a function of the time delay.

Figure 5: Sketch of the experimental setup for photon correlation measurements

**Preliminary experimental results and perspectives**

Prior to the integration with photonic crystal cavities, preliminary measurements were performed on samples made of arrays of QDs with different diameters (ranging from 500 nm to 80 nm), in order to characterize their optical spectra and to verify the occurrence of quantum confinement effects in the smallest dots.

Photoluminescence spectroscopy were performed by exciting the samples with a $\lambda = 532$ nm vanadate:Nd laser. During the measurements, samples were kept at a temperature $T = 10$ K in a liquid-He flux-cryostat. Micro-PL spectra recorded on unpatterned GaAsN quantum well and single QDs with different sizes are shown in Fig. 6. Contrary to what observed in greater dots, PL spectra in 80 nm dots one exhibit a single narrow line corresponding to recombination from the exciton ground state. Moreover, the line is blue-shifted with respect to emission lines in greater dots and in the GaAsN quantum well, which is a clear evidence of quantum confinement effects.

Spectra acquired on a single 80 nm dot at different excitation powers are shown in Fig. 7. At the lowest laser power, a single narrow line (linewidth of about 600 µeV) is observed, while with increasing laser power other features appear, both at lower and higher energies. At even higher laser power additional lines, due to recombination of carriers from the excited states of the dot, appear at high energy.

The dependence of the intensity of the main emission lines on excitation power allows to understand their physical origin. The equation $y = Ax^p$ was fitted to the data, as shown in Fig. 7. The intensity of line 1 increases linearly with the laser power so this recombination is due to a single exciton; line 2, whose intensity has a quadratic dependence on the power, is due, instead, to recombination of a biexciton, a bound state of two excitons. The line 3 increases with an exponent $p = 1.6$ and it is due to a charged exciton, a complex made of two electrons and one hole.
These results, although preliminary, are very promising, showing that a novel route to build quantum dots is possible. However, power dependence studies on a large number of dots have to be performed to verify the uniformity of the samples. Also, photon correlation measurements are required to confirm the attribution of the emission lines and especially to verify single photon emission in the low excitation power regime.

Another issue concerns the excitonic linewidth, which is about 600 µeV at the lowest laser power. Though this value is already comparable with those obtained in site-controlled QDs [19], it is still too high. Indeed, linewidths in the range of tens of µeV, or even smaller, have been reported for self-assembled QDs [20]. One of the main line broadening mechanism in QDs is related to an excess of electric charge around the dot: different excitation schemes will be tested on our samples, for example
resonant or quasi-resonant excitation (namely, with the laser tuned to the first excited states of the dot), which were found to considerably decrease these effects [21]. Also, different hydrogenation conditions will be used. As an example, an increasing H dose could be useful to reduce the linewidth because H can bind with charged impurities neutralizing their effects.

In parallel to the optimization of the QD fabrication process, photonic crystal cavities will be designed and finally single QDs will be integrated into PhC to verify the occurrence of the Purcell effect.

References