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A comparative study of photo-, cathodo- and ionoluminescence of GaN nanowires implanted with rare earth ions

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ABSTRACT

GaN nanowires (NWs) implanted with Europium, Praseodymium and Erbium ions were analysed by Photoluminescence (PL), Cathodoluminescence (CL) and Ionoluminescence (IL). The red $^5D_0 \rightarrow {}^7F_2$ and $^3P_0 \rightarrow {}^3F_2$ luminescence of the Eu^{3+} ($4f^6$) and Pr^{3+} ($4f^2$) ions, respectively, was optically activated after the lattice damage was recovered by thermal annealing. On the contrary, for the case of the erbium implanted NWs no intra-$4f^{11}$ transitions were identified in the visible and infra-red spectral range. Besides the lanthanide luminescence, the heat treated GaN NWs exhibit the band edge recombination and a deep level emission in the yellow spectral range when the samples are excited by photons, electrons and protons with energies of 3.8 eV, 5.0 keV and 2.0 MeV, respectively. At RT, the dependence of GaN NW luminescence intensity with the illumination/irradiation time was analysed using PL, CL and IL. The effects of the different excitation mechanisms are discussed to explain the observation that the broad emission bands suffer a luminescence quenching for the GaN NWs irradiated with energetic particles and photons. The influence of the irradiation on the optical properties of the GaN NWs is discussed and models for the recombination processes are established.

1. Introduction

Semiconductor nanowires (NWs) have been widely studied since they constitute ideal building blocks for functional nanoscale electronic and photonic devices [1]. NW heteroepitaxy has the advantage that numerous combinations of materials can be achieved since the NW synthesis prevents formation of dislocations originating from lattice mismatch [2]. The growth of these nanostructures has been reported for several materials, including nitride compounds [3]. Among the various techniques that can be employed in the growth of gallium nitride (GaN) nanowires the most used ones are molecular beam epitaxy (MBE), metal organic chemical vapour deposition (MOCVD) and hydride vapour phase epitaxy (HVPE) [4–7].

GaN NWs have been doped in order to modify their electrical, optical and magnetic properties. However doping these NWs is a difficult task due to low diffusion coefficients inhibiting ex-situ doping by diffusion [1] and the "self purification" effect posing challenges for in situ doping during growth [8]. One approach to doping these nanostructures is by ion implantation [1]. This method is a key technology in the semiconductor industry and allows the introduction of dopants in a controlled way and without the limitations of the solubility of the dopant in the matrix [9]. The major disadvantage of this approach is the fact that defects are created during the implantation and thus post-implant thermal treatments are usually required in order to recover the crystal, which is difficult in nanostructures since they exhibit a low thermal stability when compared to bulk materials [1].

Nitride systems proved to be important technological materials for lighting applications and one approach to tune visible light emission is based on the incorporation of rare-earth (RE) ions in the nitride hosts [9,10]. For further RE based optical device developments the understanding of the luminescence stability should be tested under harsh ambient conditions. A worthy method to explore the produced effects is by using ion beam excitation impinging on the doped NWs. In a general way, the ion irradiation is expected to produce damage and modifications in the lattice structure leading to changes in the optical centres luminescence intensity [11].

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In this work we report a comparison between photo-, cathodo- and ionoluminescence properties of GaN NW samples doped with different RE ions. In all the cases, the excitation sources provide band to band excitation with 3.8 eV photons, 5.0 keV electrons and 2.0 MeV protons.

NWs were implanted with europium, praseodymium and erbium ions, followed by thermal annealing treatments in order to recover the lattice damage and promote the RE ion activation. In addition, the mechanisms responsible for the observation of the yellow band in the implanted NWs are also discussed.

2. Experimental details

The GaN NWs were grown by radio frequency plasma-assisted molecular beam epitaxy (MBE) on (1 1 1) Si substrates, as reported elsewhere [5]. A thin (2–3 nm) AlN buffer layer was deposited prior to the NW growth which was performed for 2 h at 880 °C in nitrogen rich conditions. The samples were implanted to a fluence of 1×10^{13} at/cm^2 with Er, Pr or Eu ions at 150 keV. The implantation was carried out at room temperature and along the *c*-axis of the vertically aligned NWs. Post-implant rapid thermal annealing (RTA) was performed for 30 s at 1000 °C in flowing N_2 using a halogen lamp furnace.

Room temperature (RT) Raman spectroscopy (Horiba Jobin Yvon HR800) was measured in backscattering configuration by exciting the samples with the 532 nm laser line of a Ventus-LP-50085 (Material Laser Quantum).

Steady state photoluminescence (PL), performed with an angle of 90° between the laser beam and the sample surface, was generated using the 325 nm light from a cw He–Cd laser and an excitation power density less than 0.6 W cm^{-2}. The samples were mounted in a cold finger of a closed-cycle helium cryostat and the sample temperature was controlled in a range from 14 K to RT. The luminescence was measured using a dispersive system SPEX 1704 monochromator (1 m, 1200 mm^{-1}) fitted with a cooled Hamamatsu R928 photomultiplier tube.

RT Cathodoluminescence (CL) studies were performed in a Hitachi S2500 SEM using a Hamamatsu PMA-11 charge coupling device (CCD) camera, with an acceleration voltage V_{acc} = 5 kV. The beam was defocused to a diameter of several hundreds of micrometers and the sample was tilted by 25°, thus the electron beam hits both the top surface and parts of the side facets of the NWs.

Ionoluminescence measurements were performed at the OM150 microprobe type end-station installed in IST/CTN using a 2 MeV proton beam and a beam current of ~1 nA. The ion beam induced luminescence is focused on an optical fibre, guided into a monochromator (Jobyn-Yvon/Horiba Triax 190), with a triple diffraction grating Turret (a 1200 or a 300 grooves/mm diffraction grating can be chosen), and detected with a Peltier cooled CCD device. The whole system sensitivity covers the radiation wavelength range between 300 and 1000 nm with a resolution between 0.3 and 2 nm depending on the used diffraction grating and entrance slit aperture. A more complete description may be found elsewhere [12]. The measurements were carried out at an incidence angle of 5° between the beam and the sample surface and the quadrupoles triplet system used to adjust the focused beam to irradiate an area of $\sim 250 \times 250$ μm^2 at the surface. Although inhibiting beam scanning information this geometry increases the sensitivity to the thin (~70 nm) implanted top layer of the NWs. Several consecutive measurements (acquisition time of ~20 s) were taken at each point in order to study the effect of the proton irradiation. All the presented luminescence spectra are uncorrected for the optics spectral response.

3. Results and discussion

3.1. Samples morphology and structural properties

SEM images of the NWs can be seen in Fig. 1 showing their good vertical alignment (Fig. 1a). In Fig. 1b it is possible to observe that the NWs are randomly spaced. These NWs were characterized by Raman spectroscopy and the Raman spectrum indicates that the GaN NWs have high-crystalline quality. This structure belongs to the C^4_{6v} space group and taking into account the considerations of group theory it was reported that eight sets of phonon modes are allowed at the Γ point: $2A_1 + 2E_1 + 2B_1 + 2E_2$ [13]. One of the A_1 and E_1 modes are acoustic whereas the others are optical modes [13]. Among these vibrational modes only A_1, E_1 and E_2 are Raman active. Since GaN is a noncentrosymmetric material the A_1 and E_2 modes are split into longitudinal optical (LO) and transversal optical (TO) [14]. Fig. 2 shows a typical Raman spectrum of the hexagonal GaN NWs where the A_1 TO and LO modes and one of the E_2 modes are identified. E_2^H denotes the higher frequency E_2 mode. These three modes appear at 538, 567 and 734 cm^{-1}, respectively, which is in good agreement with the values found in literature [13]. Additional modes appear at 521, 673 and 890 cm^{-1}. These modes can be attributed to defect related phonons [15] or to the relaxation of the $q = 0$ selection rule due to surface disorder of finite crystalline size allowing new modes that correspond to $q \neq 0$ phonons as reported elsewhere [14].

3.2. Rare earth luminescence in GaN NWs

Fig. 3 shows the 14 K PL (Fig. 3a, b and d) spectra upon excitation above the bandgap of the GaN NWs implanted with europium and praseodymium ions along with the RT CL (Fig. 3c and e) and IL (Fig. 3f) spectra of Eu implanted samples. After annealing rare earth optical activation was achieved for europium and praseodymium ions. The samples exhibit the trivalent Eu^{3+} $^5D_0 \rightarrow {}^7F_2$ and Pr^{3+} $^3P_0 \rightarrow {}^3F_2$ intra-4*f* transitions, overlapped with broad yellow and red emission bands. In the case of the Eu implanted sample, the $^5D_0 \rightarrow {}^7F_2$ transitions appear at 620.6, 621.6 and 622.6 nm

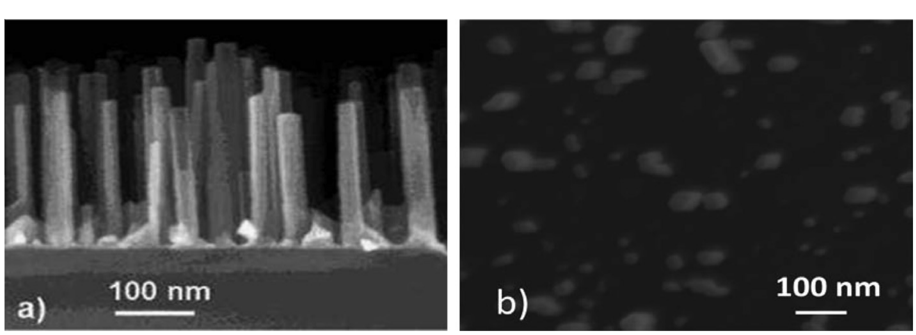

Fig. 1. (a) Side view and (b) plane view SEM images of the GaN nanowires before implantation.