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Droplet epitaxy of zinc-blende GaN quantum dots

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ABSTRACT

Zinc-blende GaN quantum dots were grown on 3C-AlN(0 0 1) by a vapor–liquid–solid process in a molecular beam epitaxy system. We were able to control the density of the quantum dots in a range of 5×10^{8}–5×10^{12} cm^{-2}. Photoluminescence spectroscopy confirmed the optical activity of the GaN quantum dots in a range of 10^{11}–5×10^{12} cm^{-2}. The data obtained give an insight to the condensation mechanism of the vapor–liquid–solid process in general, because the GaN quantum dots condense in metastable zinc-blende crystal structure supplied by the substrate, and not in the wurtzite crystal structure expected from free condensation in the droplet.

1. Introduction

Wide-bandgap quantum dots (QDs) based on group-III nitrides are of great interest for their possible applications in optical and quantum optical devices. Single photon emitters based on wurtzite GaN single quantum dots have shown photon anti-bunching and triggered single-photon generation [1]. However the "built-in" electric fields induce a quantum confined Stark effect, leading to a reduced recombination probability of electrons and holes in confined states and consequently low repetition rate photonic devices. The metastable zinc-blende (cubic) phase of AlN (c-AlN) and GaN (c-GaN) has no polarization fields in (0 0 1) growth direction [2]. Consequently, the radiative recombination time of c-GaN QDs was measured to be two orders of magnitude below the recombination time of wurtzite GaN QDs [3]. For cubic GaN only one method to fabricate self-organized GaN QDs has been reported so far, the Stranski–Krastanov (SK) growth [4].

In this text, we report an alternative growth method of c-GaN quantum dots by droplet epitaxy, a vapor–liquid–solid (VLS) process. In droplet epitaxy liquid Ga droplets are created and subsequently nitridated to fabricate GaN quantum dots [5]. Droplet epitaxy has the advantage of size and density control of the QDs in a wide range from 5×10^{8} to 5×10^{12} cm^{-2}. Especially the low density is of great importance for applications as single photon emitters. Here the minimum spatial separation of the QDs has to be in the order of the emission wavelength.

2. Experimental procedure

We have grown the c-GaN QDs and the c-AlN confinement in a Riber 32 MBE system. Standard Ga and Al effusion cells and the Oxford Instruments N plasma cells were used. The growth process was monitored in situ by reflection high energy electron diffraction (RHEED). The surface structure of the grown layers, with and without GaN QDs, was analyzed with atomic force microscopy (AFM). The optical activity was measured by photo-luminescence (PL) spectroscopy.

3. Results and discussion

At first a 30 nm c-AlN (0 0 1) layer is grown on 3C-SiC (0 0 1) substrate at 730 °C substrate temperature by plasma assisted molecular beam epitaxy (PAMBE) [6]. Fig. 1(a) shows the RHEED pattern of the AlN surface in [1 1 0] azimuth before the deposition of droplets. Long thin streaks, including the streaks of a twofold surface reconstruction, can be observed. These streaks indicate a smooth two-dimensional (2D) surface [7]. AFM measurements, not shown here, reveal an atomically smooth AlN surface with a RMS roughness of 0.2 nm.

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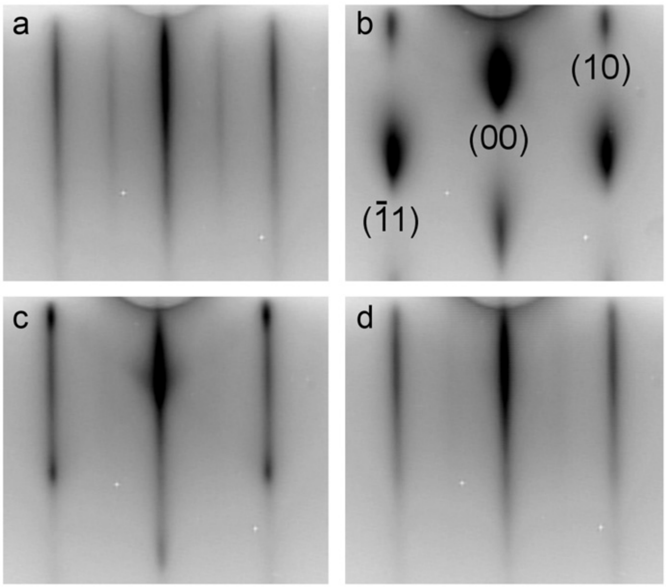

Fig. 1. RHEED patterns: (a) reflections of the c-AlN layer, long thin streaks indicate a smooth 2D surface. (b) Reflections of c-GaN droplet QDs, the spotty reflections indicate 3D islands of cubic crystal structure. (c) Reflections of the c-AlN layer after 4 ML QD overgrowth, the smaller FWHM of the spotty reflections indicate partially strained GaN QDs. (d) Reflections of the c-AlN after 30 ML QD overgrowth, long thin streaks indicate a smooth 2D surface.

In step 2 the equivalent of 3 monolayers (MLs) of Ga is deposited on the AlN surface at 350 °C substrate temperature. The strong cohesion force between the Ga atoms induces the formation of droplets. The size and distance between the Ga droplets can be controlled by a combination of amount of deposited Ga, substrate temperature and time before nitridation [5]. During the deposition of Ga the RHEED pattern shows a strong overall decrease in intensity. In step 3 the Ga droplets are exposed to the N plasma beam for 3–10 min. Here two different nitridation methods can be applied. In method A the nitridation is exclusively carried out at Ga deposition temperature. Afterwards the substrate temperature is increased to 730 °C in order to desorb excess Ga from the surface. In method B the nitridation is performed during a slow increase in the substrate temperature ramping to 730 °C. In both cases the RHEED image shows a strong increase in intensity and the appearance of spotty reflections. Fig. 1(b) shows the RHEED pattern after the nitridation of the Ga droplets. The spotty reflections are a result of an electron transmission component through three-dimensional islands on the surface [7]. Therefore, the spotty reflections are an indication of quantum dots on the surface. The broadening of the reflections can be explained by a change in lattice parameter of the upper part of the QD due to partial relaxation. All reflections in the RHEED pattern indicate zinc-blende crystal structure. Reflections of the wurtzite lattice would be alongside the diagonal of the (-11) reflection to the (10) reflection, but are absent [8]. Confirmation of the nano-size of the 3D islands is obtained by AFM measurements of uncapped GaN QDs. Fig. 2(a) shows an AFM image of a $1\times1\ \mu m^2$ area of the AlN surface covered with GaN QDs grown by method A. The average width of the QDs is 10 nm, the height 2.5 nm and the average distance between the QDs is about 100 nm, resulting in a density of $5\times10^{9}\ cm^{-2}$. Fig. 2(b) shows a 3D close-up of the same area measured in Fig. 2(a) with pronounced GaN QDs. Depositing the same amount of Ga but applying nitridation by method B changes the size and density of the QDs, as shown in Fig. 2(c). In this case a QD width of 20 nm, a height of 3 nm and a distance of 30 nm can be determined, resulting in a density of $2\times10^{11}\ cm^{-2}$. The difference in size and density of the GaN QDs can be explained by the nitridation method. At growth temperature a phase equilibrium of liquid Ga and solid GaN exists inside the droplet [9]. Further GaN condensation requires supersaturation of Ga, and consequently GaN growth occurs during the desorption of the excess Ga at higher temperatures. In method A no additional N is supplied during Ga desorption. As N solubility in Ga is lower than 1%, only a small amount of N is available to form GaN [9]. During the heating process Ostwald ripening results in larger, but more distant QDs [10]. In method B additional nitrogen is supplied during the heating and Ga desorption process. The additional nitrogen has two effects on the GaN QD formation. The first effect is the growth of more GaN compared to method A, simply because more nitrogen is available. The second effect is related to the nitrogen termination of the surface, increasing the surface potential and strongly decreasing the diffusion length of the Ga adatoms [11]. This leads to the trapping of Ga inside the droplets until nitridation and reduces Oswald ripening. Consequently, the density of the GaN QDs fabricated with method B is higher.

During the final step the GaN QDs are overgrown with AlN at 730 °C substrate temperature. The initial 3–6 ML AlN adapt to the QD shape. Fig. 1(c) shows the RHEED pattern of the AlN surface after 4 ML of QD overgrowth. Long thin streaks indicate mainly a 2D surface; however, sharp spots show that there are still 3D islands on the surface. As the full width at half maximum (FWHM) of those spots is smaller than that of the previous overgrowth, it can be assumed that the GaN QDs are partially strained to the AlN cap layer. Fig. 1(d) shows the RHEED pattern of the AlN surface after 30 ML of QD overgrowth. The spotty reflections of Fig. 1(c) are no longer present, full epitaxial overgrowth of the GaN QDs can be concluded. AFM measurements of the AlN surface after GaN QD overgrowth confirm a smooth surface.

To analyze the photoluminescence of the c-GaN QDs, comparable samples with and without 30 nm AlN cap layer have been grown by method B. The samples were excited by an ArF excimer laser with $\lambda=193$ nm. The photoluminescence (PL) was detected by a liquid nitrogen cooled charge coupled device camera mounted to a grating monochromator. The sample was mounted in a temperature-controllable liquid helium cryostat to allow the PL investigations at different temperatures. Fig. 3 shows the PL spectrum of the c-GaN QD sample at 10 K. Two overlapping Gaussian shaped emission bands were identified, one at an energy of 3.61 ± 0.01 eV, marked with A, and a broader one at 3.64 ± 0.01 eV, marked with B. Since the QD transition energy is mainly influenced by the QD height, AFM has been utilized to determine the QD height. The average height of the uncapped QDs has been measured to be 3.1 nm. The theoretical work of Fonoberov and Balandin[12] on c-GaN QDs predicts an exciton ground state transition energy of 3.62 eV for QDs having a dot height of 3.1 nm above the wetting layer. This energy is in good agreement with the measured energy peak at 3.61 eV of the capped c-GaN QD sample. The existence of two overlapping emission bands can be explained by partial Ostwald ripening. Here the initial, broader QD size distribution has its emission maximum at an energy of 3.64 eV and the ripened QD size distribution has its emission maximum at an energy of 3.61 eV [10]. To exclude other possible origins of the emission, the exciton ground state transition energies for various c-GaN quantum wells (QWs) strained on c-AlN have been calculated by solving the Schrödinger equation. For a 5 ML c-GaN QW the calculated exciton ground state transition energy is 4.05 ± 0.025 eV. A list with the QW energies in the range of 1–6 ML thick c-GaN layers is shown as an inset in Fig. 3. The energy of c-plane wurtzite GaN QDs of the same size is 3.20 eV [12]. Consequently, wurtzite GaN QDs and c-GaN QWs can be excluded as origin for the 3.61 eV emission, verifying the c-GaN QDs as the emission source.

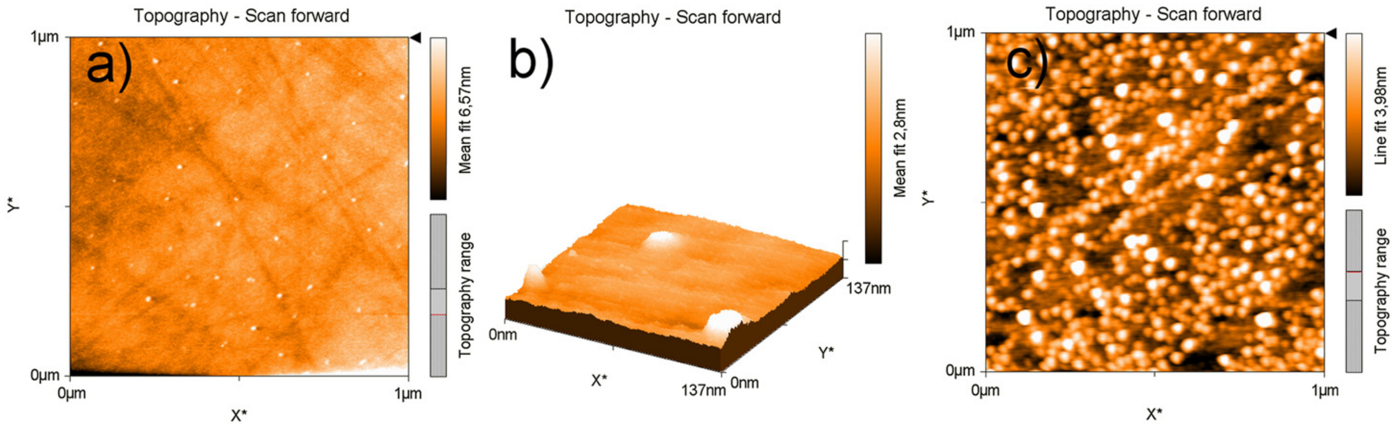

Fig. 2. AFM images: (a) $1\times1\,\mu m^2$ GaN QDs grown by method A on c-AlN, the average width of the QDs is 10 nm, the height 2.5 nm and the density $5\times10^9\,cm^{-2}$, (b) 3D close-up of GaN QDs in (a), (c) $1\times1\,\mu m^2$ GaN QDs grown by method B on c-AlN, the average width of the QDs is 20 nm, the height 3 nm and the density $2\times10^{11}\,cm^{-2}$.

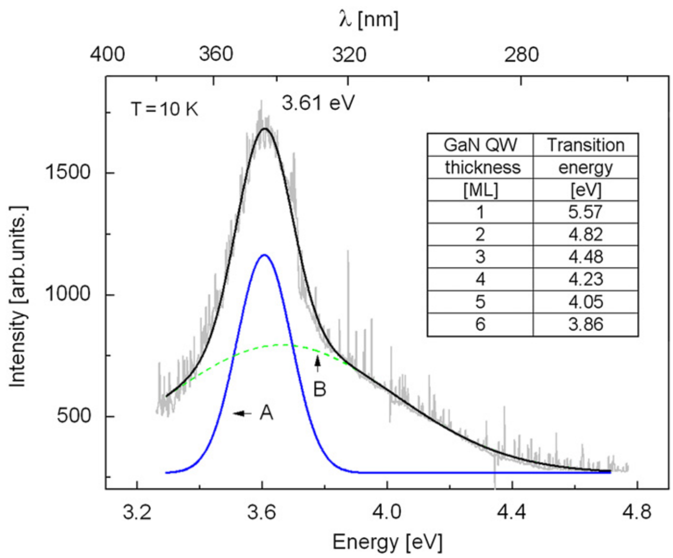

Fig. 3. Photoluminescence spectrum of c-GaN droplet QDs. Two overlapping Gaussian shaped emission bands were identified, one at an energy of 3.61 ± 0.01 eV, marked with A, and the other at 3.64 ± 0.01 eV, marked with B. The inset lists the transition energies for various c-GaN quantum wells.

Samples grown with method A have a QD density of two orders of magnitude lower than samples grown with method B and did not show PL above the noise threshold with our setup.

4. Conclusion

In summary, we have shown that droplet epitaxy can be utilized to create optically active zinc-blende GaN QDs. Samples grown with method B had a QD density of 10^{11}–$5\times10^{12}\,cm^{-2}$ and showed strong photoluminescence. Samples grown with method A had a QD density of 5×10^8–$5\times10^9\,cm^{-2}$ and did not show photoluminescence above the noise threshold. The GaN quantum dots condense in the metastable zinc-blende crystal structure supplied by the substrate, and not in the wurtzite crystal structure expected from free condensation in the droplet. This result gives an insight to the condensation mechanism of the vapor–liquid–solid process in general.

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