GaN nanocolumn arrays with diameter <30 nm prepared by two-step selective area growth

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A new method of two-step selective area growth (SAG) by RF-plasma-assisted molecular beam epitaxy is developed, enabling the growth of uniform arrays of thin GaN nanocolumns (NCs) with diameters <50 nm. In the SAG, the migration-enhanced epitaxy mode with an alternating supply of Ga and active nitrogen was employed during the initial growth of NCs on small-nanohole-patterned substrates to complete the crystal nucleation in the nanoholes. Once the nucleation occurred, the growth mode to the simultaneous supply of Ga and nitrogen is immediately switched. In the second step, the growth temperature is increased and the nitrogen flow rate to suppress the lateral growth rate is decreased. A high-density uniform array of very thin NCs in a triangular lattice with a diameter of 26 nm and a lattice constant of 60 nm is demonstrated; the NC density is 3.2×10^{10} cm^{-2}.

Introduction: GaN nanocolumns (NCs), which are independent one-dimensional nanocrystals, were first fabricated on (0001) sapphire substrates [1, 2] and then on (111) Si substrates [3] through self-assembly by RF-plasma-assisted molecular beam epitaxy (RF-MBE). The self-assembled GaN NCs have been utilised in the fabrication of InGaN-based light-emitting diodes (LEDs) on Si [4–7]. However, randomness of the size and position of the NCs was inevitably introduced by the self-assembly of NCs, which is initiated by random and spontaneous nucleation, frequently resulting in the multicolour emission of LEDs in microscale areas [5]. At the same time, precise control of the NC size and position was achieved by the development of selective area growth (SAG) [8–11]. However, the uniform arrays of GaN NCs fabricated by SAG had NC diameters (D) larger than ~100 nm [8–12]. It was therefore considered a challenge to grow well-ordered thin GaN NCs with $D < 100$ nm, even though the diameter of self-assembled NCs typically varies from 50 to 100 nm [1, 5]. In axial InGaN/GaN heterojunction NCs, the in-plane spatial separation of electrons and holes occurs, reducing the internal quantum efficiency (IQE) [13]. According to a theoretical prediction, however, reducing the NC diameter to 40 nm significantly increases the electron–hole ground state overlap, thus providing a promising approach for achieving a higher IQE [14]. In this Letter, we report having developed a two-step SAG method for improving the growth control of thin NCs and having demonstrated a high-density array of very thin NCs in a triangular lattice with $D = 26$ nm and a NC density of 3.2×10^{10} cm^{-2}. The lattice constant (L) was 60 nm.

Nucleation of NCs: Prior to the growth, Ti mask patterns for SAG were prepared on metal-organic-chemical-vapour-deposition-grown GaN templates on (0001) sapphire substrates by electron beam lithography (EBL) and inductively coupled plasma (ICP) etching. First, a Ti film of 5 nm thickness was deposited by electron beam evaporation. On the Ti film, ZEP520A resist of 180 nm thickness was spin coated, then triangular lattice nanohole patterns with various L and D were drawn by EBL. The subsequent ICP etching process transcribed the resist pattern to the nanohole arrays. By growing NCs on the patterned substrate in two growth modes, the initial nucleation behaviour of the NCs was first investigated. One was the normal growth mode of RF-MBE, having a simultaneous atomic supply of Ga and N, and the other was a migration-enhanced epitaxy (MEE) mode with an alternating atomic supply; the shutter sequence in each mode is shown in Fig. 1. In the normal growth mode, the substrate temperature was 870°C, the N flow rate was 1.0 sccm and the growth time was 15 min. In the MEE mode, they were 840°C, 2.0 sccm, and 30 min with the Ga and N shutters opened and closed alternately every 1.5 s. The Ga beam flux was fixed at 3.0×10^{-4} Pa for both growth modes. Top-view SEM images of NCs ($L = 70$ nm) grown in the normal mode and MEE mode are shown in Figs. 2*a* and *b*, respectively; uniform nucleation in the initial growth was obtained for the MEE mode. Fig. 2*c* shows the missing NC ratio, which was defined as the number of missing NCs divided by the number of nanoholes, against nanohole diameter. In SAG, the NCs are grown in the nanoholes at mask openings. Under the nitrogen supply, Ga is supplied to the surface of the substrate and diffuses on the Ti mask surface to be absorbed at the nanoholes. The crystal quickly fills up the circular nanoholes and then the lateral growth of the NCs proceeds outwards along the *a*-axis, finally forming the stable hexagonal side facets (*m*-faces) of the NCs [9]. Once crystal nucleation occurs in the nanoholes, GaN NCs grow preferentially along the *c*-axis, because the lateral growth rate along the *m*-axis is extremely slow [9]. However, for small nanoholes with diameters <40 nm, crystal nucleation randomly occurred at the nanoholes in the normal growth mode, causing the missing NC ratio to rapidly increase with decreasing nanohole diameter, as shown in Fig. 2*c*. To overcome this problem, we lowered the growth temperature and increased the N flow rate to enhance the crystal nucleation in the nanoholes. In addition, NC growth was performed in the MEE mode, in which the alternating supply of species was expected to promote the migration of Ga adatoms. As a result, the crystal nucleation was substantially improved and NC arrays without missing NCs were prepared on the nanohole pattern with a diameter down to 15 nm (see Fig. 2*c*). For the normal growth and MEE modes on a nanohole pattern with diameter of 36 nm and $L = 70$ nm, the growth rates of the GaN NCs were evaluated to be 7.0 and 4.1 nm/min, respectively. The MEE mode with a lower growth rate was time consuming in the growth of NCs, although the crystal nucleation occurred for a very thin nanohole pattern.

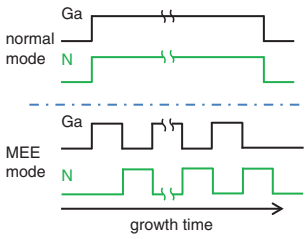

Fig. 1 *Time-sequence diagrams of Ga and N shutters for normal mode and MEE mode*

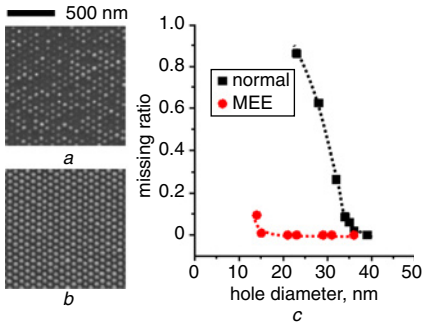

Fig. 2 *Top-view SEM images and missing NC ratio against nanohole diameter for SAG on nanohole patterns with L = 70 nm*

a Normal mode for hole diameter of 28 nm
b MEE mode for hole diameter of 23 nm
c Missing NC ratios for normal and MEE modes plotted by black squares and red circles, respectively

Two-step SAG growth: To fabricate thin NC arrays without missing NCs, while suppressing the lateral growth, the two-step SAG growth mode was employed. In this growth mode, the initial growth was performed with the MEE mode for 30 min, and once the crystal nucleation occurs the growth mode is immediately switched to the normal growth mode. Then, GaN NCs were grown for 1 h. The growth on the underlying circular nanoholes with the diameter of ~11 nm resulted in NCs with $D = 26$ nm; thus the lateral growth rate was evaluated to be 5 nm/h, which is comparable with the reported value for the nitrogen flow rate of 1.0 sccm [9]. Figs. 3*a–c* show top-view SEM images of sample A with $L = 200$ nm and $D = 165$ nm, sample B with $L = 100$ nm and $D = 65$ nm, and sample C with $L = 60$ nm and $D = 26$ nm, respectively. Fig. 3*d* shows a birds-eye-view SEM image of sample C; the height of sample C was evaluated to be 364 nm. A histogram of the NC diameter for sample C is shown in Fig. 4. The standard deviation of D was 2.4 nm, which is within the resolution of the SEM image. Thus, a high-density uniform array of very thin NCs was fabricated.

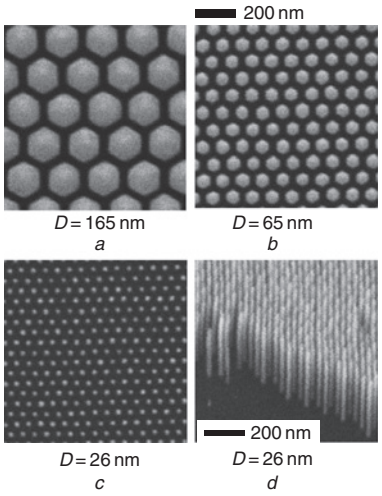

Fig. 3 *SEM images of NCs grown by two-step SAG method*
a Sample A ($L = 200$ nm and $D = 165$ nm)
b Sample B ($L = 100$ nm and $D = 65$ nm)
c, *d* Sample C ($L = 60$ nm and $D = 26$ nm)

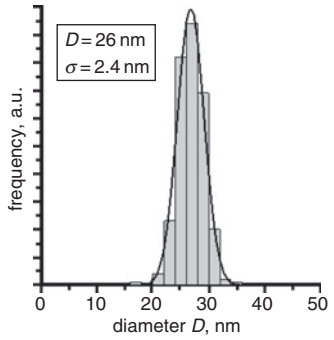

Fig. 4 *Histogram of NC diameter of sample C*
Solid line indicates Gaussian fitting curve; average NC diameter 26 nm, standard deviation 2.4 nm

Conclusion: To enable the growth of high-density uniform arrays of thin NCs with diameters <50 nm, the method of two-step SAG by RF-MBE has been developed. We successfully fabricated high-density arrays of very thin NCs in a triangular lattice with $D = 26$ nm and $L = 60$ nm. The NC density was 3.2×10^{10} cm^{-2}.

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