GaN nanorod assemblies on self-implanted (111) Si substrates

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Abstract

Periodic arrays of GaN nanostructures are fabricated by MBE growth on self-implanted (111) Si substrates. Nanocapillary condensation is found to be an effective catalytic process fostering the formation of epitaxially aligned GaN nanorods in company with the thin film matrix. Changes of Si substrate surface morphology prior to deposition as a result of ion bombardments are responsible for the enhanced nanorod growth. This is attributed to the nanocapillary condensation of Ga droplets that serve as a medium to the vapor–liquid–solid growth of nanorods out of its supporting matrix.

In order for functional nanostructures to have practical device-application values, one must first be able to fabricate them in a controllable fashion, e.g., by lithography. Many nanostructures of alluring geometries have been reported in the literature, ranging from flexible and often entangled nanowires to epitaxial spikes of nanorods standing on supporting base materials [1,2]. For these nanostructures to form, very thin metallic layers were often used as a catalyst [2]. These catalytic metals act as the seeds for nucleation. They can also foster nanostructure growth. Use of metal catalysts depresses a material’s melting-point due to the alloying effect. This enables metal droplets to form on top of the fledgling nanostructures, be they the better-aligned nanorods or entangled nanowires and whiskers. As nanostructure growth commences, the nanodroplets continue to stay on top. The alloyed droplets are the source that provides what is needed for the continuing growth of the nanostructures. Such mechanism of nanostructure formation is known as vapour–liquid–solid (VLS) growth [3].

In VLS growth, traces of catalysts unavoidably would contaminate the growing material and alter its electronic band structure. Therefore, we believe that, if one can replace such extrinsic seeding procedure with an intrinsic means, say by use of the same atomic constituents, the contamination problems can then be solved. To this end, we introduced in an earlier publication a concept of nanocapillary condensation and elucidated its effects on the nanorod growth out of a supporting matrix [4,5]. Essentially, it uses nanocapillaries as a seed in lieu of the extrinsic catalytic seeding based on foreign elements.

In this work, we envisage a method to produce such capillary effects by ion beam surface engineering [6]. Through self-implantation of Si into Si substrates, we were able to control the growth of nanorod arrays. Periodic patterns were realized first by traditional UV lithography, then followed by Si ion self-implantations. The defects, especially vacancies generated as a result of self-implantation, under the influence of a heating process, provide the necessary driving force for nucleation and growth in the implanted area. The density of nanorods in the patterned arrays can be controlled by the energy and dosage of the self-implantation that determines the vacancy concentration near the free surface.
Linear strip arrays of masks 10 μm in width and in separation were first patterned on Si (111) substrates by conventional UV-lithography such that masked and unmasked regions alternate themselves. The samples were then implanted with 40 keV Si ions to a dosage ranging from $5 \times 10^{13}$/cm$^2$ to $7 \times 10^{14}$/cm$^2$ at room temperature. The Si beam current was kept below 150 nA to avoid excessive target heating. Due to the nature of forward momentum transfer by ion implantation, an interstitial-rich region takes shape close to the end of projectile range deep in the substrate, leaving behind a vacancy rich region close to the free surface [7].

Using Monte Carlo ion implantation simulation, viz. by the transport of ions in matter (TRIM) calculations [8], we see that there indeed is such a profile of defect population, as given in Fig. 1 where, as represented by negative Si concentration, a net vacancy rich region is formed within the topmost 40 nm or so of the near-surface region. By contrast, the positive concentration region represents the excessive Si self-interstitials because of the implanted Si ions. The depth distributions of the vacancies and the self-interstitials of Si can be tailored through proper selections of the Si implantation energy.

The vacancies produced by implantation can become a trap to diffusing atoms, but they can also conglomerate, which would then lead to a rough surface. Namely, the kinetics of formation for the islands, or surface morphology in general, can be dramatically affected by the interactions of the diffusing atoms with the vacancies. The clustering of vacancies are more conspicuous at high temperature where Oswald ripening process dictates that smaller ones will get smaller and eventually diminish, while larger ones will get even larger.

Point defect migration and clustering via annealing process are a complex phenomenon, but simple arguments have been attempted based on tight binding calculations [9]. From these studies, it is understood that, since $E_{b,\text{Interstitials}} > E_{b,\text{Vacancies}}$ [9,10], vacancies may move around more freely than the self-interstitials of Si would. Hence vacancy-clusters will form more easily in the near-surface region where the concentration of vacancies is high. Aggregations of vacancies led to the formation of serpentine grooves on the Si substrate surfaces, as shown in Fig. 2(a) in which the Si substrate was implanted with Si to a dose of $3 \times 10^{14}$/cm$^2$. The widths of the grooves are on order of 2–5 nm.

After implantation, the (1 1 1)-Si substrates were transferred into an ultra high vacuum MBE chamber to grow desired nanostructures. We followed the common practices of MBE growth by first heating the substrates to 810 °C for 50 min in order to rid of HF contaminants which might remain from the substrate cleaning. The GaN islands nucleate and grow out of the serpentine grooves in accordance with the Si morphology. As the islands grow further, they eventually fill the grooves and then enclose the whole plateau regions in valleys. When the walls of islands grow over the valleys of the plateaus, these valleys shrink, establishing the precursors to the nanotrenches and nanocapillary tubes that eventually would bring the condensation of Ga droplets into effect.

Note that as the valleys shrink sufficiently when islands impinge upon each other, as described above, triangular or hexagonal voids are formed. Thereafter the nanotrench would be elevated as the film grows thicker. The voids existing among the impinged islands are essentially what later form the nanocapillaries. However, the existence of nanocapillaries is a necessary but not sufficient condition for the nanorod formation. The size and aspect ratio of a nanocapillary determines the efficiency of Ga atoms’ capillary condensation.

![TRIM simulation of 40 keV Si ions implanted into Si substrate. The defect concentrations are normalized to a single Si ion implanted.](image)

![SEM morphology by field emission of sample implanted with dose of $3 \times 10^{14}$/cm$^2$. Right: Fast Fourier transform (FFT) of the respective images, showing consistent increase of periodicity (a) after pre-annealing, (b) after buffer growth on implanted area, and (c) un-implanted area.](image)
Nanoscopic clustering mechanism is a subject of active ongoing research [11], we must note. Thus our arguments stand to be tested by more future experiments. But, in any case, while the morphology appears quite random to the naked eye, the Fourier transform of Fig. 2(a) demonstrates that the serpentine surface structure for the as-implanted Si still possesses certain degree of anisotropy and periodicity. A fourfold symmetry is obvious, though it is unclear to us why such symmetry element of morphology would exist on a (111) Si-surface. However, the periodicity along the orthogonal axes showing an interference pattern on the x–y coordinate axes of the Fourier domain suggest of a multiple-slit-like periodic structure of the morphology.

After the GaN (0001) buffer layer was grown under an equivalent N/Ga pressure ratio of ~100 at 550 °C substrate temperature, the morphology of the implanted area, as Fig. 2(b) shows, smeared out and became more isotropic and uniform as judged form the rounder and narrower long wavelength components of the Fourier spectrum. As for the un-implanted region which also went through the same thermal processes, Fig. 2(c) shows that the morphology seems to be finer, but its continuous Fourier components of the long wavelength region are much similar to those of Fig. 2(b) for GaN grown over the implanted region. However, for the un-implanted region, the GaN morphology retains much of the slit-like nature, as judge by its on-axis Fourier patterns, while the implanted area does not. In the meantime, the period of interference pattern has increased, reflecting a decrease of inter-slit spacing in the real space, namely, the surface morphology.

Because of the diminished multiple-slit-like interference pattern, we thus conclude that the islands of the implanted regions are larger in sizes as seen from the surface morphology and its Fourier pattern. This is most likely a consequence of the defect congregation at high temperature. Moreover, as mentioned earlier, though island impingements necessarily produce nanotrenches and the underlying nanocapillaries, only when the size and aspect ratio of the nanocapillary tubes are proper, will condensation of Ga droplets take place. The lower density of nanorods in the un-implanted region, hence, may be indicative of the less favorable conditions for nanocapillary condensation.

GaN (0001) nanorods accompanying the matrix thin films were grown with equivalent N/Ga pressure ratio ~30 on the GaN buffer shown in Fig. 2(b) and (c). The N2 plasma power was ~500 W and substrate temperature was ~720 °C for the film deposition. Under these conditions, nanorods would sprout from the nanotrenches of proper dimensions. Typical patterns of aligned GaN nanorods on (111)-Si substrates are shown in Fig. 3. The density of nanorods strongly depends on the implanted ion dosages. The nanorods can be classified into two categories. One is in hexagonal or triangular shape with size ranging from 30 to 80 nm, while the other is larger and appears to be merged from multiple nanorods. It is not clear why these two types of nanorods came to coexist, but we speculate that since implantation was performed at room temperature, point defects might have migrated and clustered together even before pre-annealing. Therefore, the diffusion and migration mechanisms of vacancies or Si self-interstitials and the ensuing GaN growth would naturally be different from the un-implanted case. However, better understandings will depend on more systematic future work. But, at any rate, with increasing dosages, it is understandable that defects may effectively agglomerate into larger sizes. Hence, nanotrenches and the underlying nanocapillaries, consequently, would become larger as well. Starting at a dosage of 5 × 10^14/cm², as seen from Fig. 3, coalesced nanorods became dominant with average diameter > ~100 nm.
In summary, we have fabricated GaN nanorods into patterned arrays by the modifications of (111)-Si substrate surfaces. This was achieved by controlling the near surface defect chemistry via Si self-implantation. Before high temperature annealing, serpentine grooves already formed on the as-self-implanted areas of the Si substrates. Such self-implantation led the GaN buffer layer to exhibit a morphology that is more smeared in granular feature as compared to that of the un-implanted area. The as-implanted Si substrate and GaN films grown on the un-implanted substrate areas both demonstrate multiple-slit-like structures, as demonstrated in the periodic pattern on the $x$ and $y$ axes of the Fourier domains.

Enriched vacancy concentration near the free-surface instigated nano- or micro-clustering of vacancies and hence the formation of grooves. These grooves then serve as the nucleation sites for the GaN island formation. Impinging islands grow out of the grooves and then extend inward to cover the Si plateaus. This gives rise to the nanocapillaries. Condensation of Ga liquids into the nanocapillaries and followed by reacting with the nitrogen plasma constitutes the VLS growth mechanism of the nanorods. Implantation of Si self-ions into Si substrates fosters the formation of nanoclusters of vacancies which led to surface morphologies favorable for the nucleation and growth of the nanorods.

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