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On the mechanisms of spontaneous growth of III-nitride nanocolumns by plasma-assisted molecular beam epitaxy

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ABSTRACT

A study of the GaN nanocolumns nucleation and growth by molecular beam epitaxy on Si(111) is presented. Ga droplets with different diameters (340–90 nm) were deposited on the substrate, prior to growth, to determine any effect on the nanocolumns size and distribution. Results indicate that there is no difference in nanocolumnar size and density whether Ga droplets are used or not, meaning that Ga droplets do not act as catalysts for the nanocolumns nucleation. In addition, Ga droplets were never observed on the nanocolumn tips upon growth termination. These findings rule out the *vapor–liquid–solid* mechanism. Instead, driven by a strong lattice mismatch nanocolumnar nucleation occurs spontaneously by Volmer–Weber growth mechanism, whereas nitrogen excess prevents the nucleation sites coalescence. Further nanocolumnar growth proceeds by direct Ga incorporation on the nanocolumns top and by Ga diffusion along the nanocolumns sidewalls up to their apex. Related to this diffusion mechanism, we found that Ga droplets, when used, may act as reservoirs to feed Ga atoms to the neighboring nanocolumns. Nanocolumns preserve a constant diameter if growth conditions are not modified because of a strong metal ad-atom diffusion length along their sidewalls. The effect of using AlN buffer layers on the nanocolumnar growth and morphology is also addressed.

1. Introduction

Even though spontaneous growth of GaN nanocolumns has been achieved by a number of groups using molecular beam epitaxy (MBE) [1–5] little is still known about the mechanism behind this peculiar growth mode that, as has been shown, does not require catalyst, but only adequate growth conditions, namely the III/V ratio and growth temperature. The understanding of this growth mechanism is essential to control the nanocolumns diameter, density, and distribution, and also to achieve nanocolumnar growth on different substrates and buffer layers, avoiding the simultaneous appearance of rough compact layers (so-called "faceted matrix") and nanocolumns [5].

The growth of Si whiskers [6] or III–V nanocolumns [7–9] was generally attributed to a *vapor–liquid–solid* (VLS) process. According to it, Si whiskers grow from Si:Au liquid droplets that are preferential sites for Si atoms incorporation from the vapor phase. The droplet, whose diameter roughly determines that of the whisker, remains generally at the whisker top upon growth termination, unless its full consumption stops the growth earlier. The droplet formation is compulsory to grow the whisker by VLS, as recently shown by Hannon et al. [10].

The spontaneous growth of In(Ga)N and Ga(Al)N nanocolumns by plasma-assisted MBE (PAMBE) without the help of metal catalysts (Ni or Au) on a wide variety of substrates, either buffered or bare (Ref. [11] and others therein) cannot be explained in terms of a VLS process. Guha et al. [3] suggested that a *selective-area growth* on GaN islands, formed upon nitridation of Ga droplets, was responsible for the MBE growth of nanocolumns on Si substrates. However, the lack of detail on the growth conditions and on the size and density of the "seeding" Ga droplets or GaN

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islands prevents us from drawing conclusions on whether the nanocolumns actually grew on and only on these nucleation sites. Calleja et al. [12] suggested that Ga droplets could act as catalysts, the idea behind this suggestion being that *very small* Ga droplets ("*clusters*") formed spontaneously at the nucleation stage, could promote the nanocolumns growth in a similar way as that proposed by Guha et al. [3].

This work presents the study of the spontaneous nucleation and growth mechanisms of GaN nanocolumns on Si(111) substrates, though conclusions that will be drawn may apply to other III-nitride nanocolumns and substrates. The effect of Ga droplets pre-deposited on the substrate ("*droplet-patterned substrates*") on the nanocolumns nucleation process, as well as on their size, density, and distribution is addressed. Should the VLS mechanism be responsible for the GaN nanocolumnar growth under these conditions, the Ga droplets would act as preferential nucleation sites, giving rise to localized growth of nanocolumns with similar diameters as that of the droplets. New experimental results are presented and discussed, providing hints to clarify how nucleation occurs; how the nanocolumns grow; and how to avoid the simultaneous appearance of nanocolumnar and compact morphologies. All samples used for droplet-patterned experiments were grown on bare Si(111) substrates to avoid potential effects of buffer morphology, thickness, strain differences, or crystalline quality on the nucleation process.

2. Experimental procedure

Ga-droplet patterns were generated by exposing the substrate to a Ga flux at 560 °C at which Ga desorption is negligible [1]. This exposure was monitored by reflection high energy electron diffraction (RHEED) showing that the high diffraction orders vanished after 0.5 monolayers (ML) of Ga deposition [13], turning the (7×7) reconstruction into an (1×1) one. The remaining (1×1) reconstruction faded out progressively with increasing exposure to Ga until finally disappearing beyond 10 ML coverage.

The process of Ga deposition and re-evaporation (*flush-off*) to control the droplet patterning was studied by reflectivity measurements (Fig. 1). The Ga flux used was the same required to further grow the GaN nanocolumns ($\phi_{Ga}=1.7\times10^{-7}$ Torr, 0.13 ML/s). Different amounts of Ga were deposited at 560 °C and sequentially flushed-off at 700 °C. The reflectance decay time during Ga desorption at 700 °C is found to be a linear function of the Ga deposition time (Fig. 2), providing an estimate of the Ga coverage and a reproducible method for droplet patterning. Since metallic Ga forms liquid droplets on a Si surface in order to reduce the surface tension [14], droplet patterning at 560 °C as a function of the Ga coverage, from 8 to 62 ML, produced Ga droplets of different diameters and densities (see Table 1).

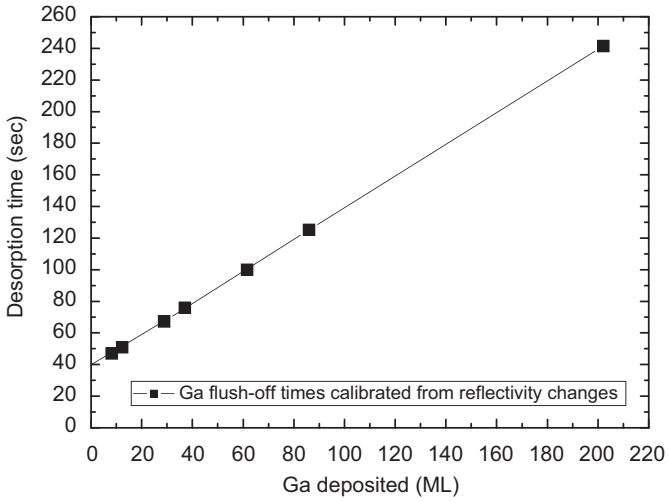

Fig. 2. Ga desorption times at 700 °C as a function of the Ga deposition times (measured in MLs), derived from experiments like those in Fig. 1. Data is taken at 700 °C.

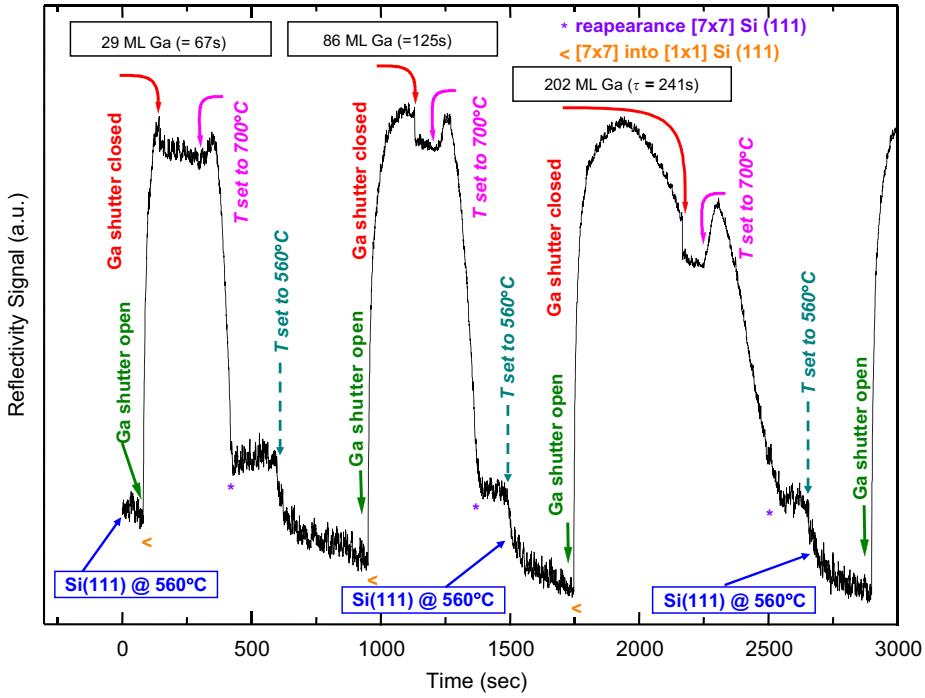

Fig. 1. Reflectivity changes during the deposition and flush-off of different amounts of Ga. (*) symbols indicate when the 7×7 Si(111) RHEED reconstruction reappears (Ga is gone), whereas (<) symbols indicate when the 7×7 turns into a 1×1 reconstruction (Ga on the surface).