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Growth of InGaN nanopyramid arrays on Si for potential photovoltaic applications

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ABSTRACT

InGaN/Si multijunction solar cells form a cost-effective approach for full-spectrum photovoltaics. However, heteroepitaxial InGaN films with high In content are highly defective. To overcome this, nanostructured InGaN growth is explored in this work. Ordered arrays of $In_xGa_{1-x}N$ nanopyramids were grown by metalorganic chemical vapor deposition on AlN(0001)/Si(111) substrates in a selective area heteroepitaxy approach. The effect of growth temperature and pressure on the morphology, structure and photoluminescence of the nanopyramids, and their In content x were studied. Reduction in temperature increases x but temperatures $<750\,^{\circ}C$ are correlated with lower structural quality, polycrystalline deposits and In droplet formation. To maintain the quality, a moderately high temperature ($\sim 775\,^{\circ}C$) may be used. Together with lower pressure, x can be improved. This also enhances the growth rate and improves nanopyramid size uniformity. Nanopyramid arrays generally exhibit greater lattice tilt than their control films due to dislocation bending. While lattice twist is increased with higher x, it is offset by epitaxial lateral overgrowth. Compared to control films, nanopyramid samples consistently yielded higher x, lower average reflectance ($<5.5\%$) and a multi-fold increase in photoluminescence intensity with tunable emission from 3.05 eV to 1.93 eV.

1. Introduction

$In_xGa_{1-x}N$ is a promising semiconductor for full-spectrum photovoltaic applications due to a combination of some desirable characteristics. These include a bandgap that is tunable from 0.7 eV to 3.4 eV by varying the In content x from 1 to 0, high absorption coefficients, and high carrier mobilities [1–5]. Excellent radiation resistance [1], and strong phonon bottleneck effects that slow down cooling of hot carriers [6] further potentially make this alloy suitable for this application. However, achieving high quality InGaN films remains extremely challenging due to lattice mismatched growth on GaN which is typically also grown on mismatched substrates such as sapphire, silicon carbide or silicon. The large lattice mismatches between GaN and InGaN (up to $\sim 11\%$ for InN) and between GaN and the substrate [7] are major reasons for the high dislocation and defect densities in the material. Phase separation attributed to the large difference in interatomic spacing between GaN and InN further compounds the issue [8]. While increased growth temperatures have been shown to improve the structural quality of InGaN, the incorporation of InN is inadvertently reduced due to the high volatility of N over InN [9]. Good quality, high In content InGaN films thus remain a challenge.

To integrate highly lattice mismatched semiconductor materials, Hersee et al. and Alizadeh et al. have proposed a nanoheteroepitaxial approach utilizing nanoscale growth initiation sites [10,11]. Through the three-dimensional strain relief mechanism available to nanoscale nuclei, it is hypothesized that strain-free and defect-free material can be grown. Even for defective seed layers containing pre-exisiting dislocations, selective area growth through nanoporous templates can substantially reduce or “filter” off threading dislocations (TDs),

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leading to high quality re-grown nanostructures. Previous work in this aspect has concentrated on the selective area growth of GaN nanostructures "homoepitaxially" over GaN seed layers to achieve nearly defect-free GaN [12–16], and "heteroepitaxially" on AlN buffer layers albeit with little discussion of the structure [17]. For the growth of InGaN, strain-relaxed nanostructure growth is expected to provide the additional benefit of suppressing phase separation and improve compositional tunability that currently plagues the InGaN thin film community [18,19].

Further, the integration of III-nitrides with Si is of great commercial interest due to the production potential enabled by the availability of low-cost, large size and high crystalline quality Si wafers from the Si microelectronics industry. InGaN/Si monolithic tandem solar cells would thus offer a cost-effective approach towards achieving broad solar spectral absorption and high efficiency photovoltaics [20]. Here, a buffer layer of AlN is required to prevent Ga melt-back etching of Si [21,22] and undesired nitridation of Si [23,24]. The layer is kept thin and multilayer AlN/AlGaN/GaN buffers are avoided to maintain a low resistance electrical contact between InGaN and Si for a monolithic vertically integrated electrical device architecture [25–28]. Due to the much larger lattice mismatch between InGaN and AlN, and the pre-existing high dislocation densities within AlN, defect and dislocation densities are expected to be substantially increased compared to growth of InGaN on better quality thicker GaN films. Thus, combined with relatively low growth temperatures, bulk InGaN films grown on Si by molecular beam epitaxy (MBE) or metalorganic chemical vapor deposition (MOCVD) are typically much rougher compared to GaN films, and defective as indicated by the weak photoluminescence intensities [29,30].

In order to overcome the growth challenges of InGaN that is further compounded by its growth on thin AlN buffer layers on Si, we proposed a nano selective area heteroepitaxy (nano-SAHE) approach which will be reported in a separate work. Here, a nano-SAHE InGaN nanopyramid array grown by continuous flux MOCVD on AlN(0001)/Si(111) substrate is found to exhibit increased internal quantum efficiency compared to the planar control film. This is indicative of improved structural quality and arises from dislocation confinement to the nanopyramid core, dislocation bending to the pyramidal free surface, and dislocation filtering by the mask. At the same time, In content is increased by strain relaxation and growth on $\{1-101\}$ planes. While site-controlled growth of InGaN [31,32] and InN [33] nanostructures has been performed, this employed GaN seed layers. Growth of InGaN nanostructures directly on AlN/Si substrates has yet to be performed by other groups to the best of our knowledge. In this work, we explore this approach further by examining the influence of growth conditions on the In content, morphological, structural, and PL qualities of the InGaN nanostructures. We believe our work on nano-SAHE of InGaN will advance efforts towards achieving improved quality InGaN where other techniques have had limited success. This is likely to have direct implications not only in the development of InGaN/Si tandem solar cells, but in other areas requiring improved quality, high In content InGaN.

2. Experimental method

Nanopatterned samples used for nano-SAHE consist of AlN(0001)/Si(111) substrates over which a nanoporous SiN_y mask template (~110 nm thick) was fabricated. The latter, defined by nanoimprint lithography, bears a hexagonal array (10 mm by 10 mm) of pores ~210 nm in diameter with a period of 300 nm. SiN_y was employed as the mask material as opposed to more commonly used SiO_2, to reduce oxygen incorporation during growth. The close-packed axis of the array is oriented parallel to the $[-1-12]$ direction of the Si(111) substrate to ensure the edge-to-edge close-packed arrangement of subsequently grown InGaN nanopyramids. Such a configuration, together with the narrow period, allows a dense array of nanostructures to be obtained, greatly increasing the light-capturing area for photovoltaic application.

Continuous flux MOCVD was performed in an EMCORE/Veeco D125 system which comprises a Rotating Disc Reactor (RDR). Two series of experiments were performed. In the first, the reactor pressure was maintained at 300 Torr while the growth temperature was varied between 700 °C and 800 °C. In the second series, a relatively high growth temperature of 775 °C was employed while the reactor pressure was varied between 70 Torr and 300 Torr. For all cases, the flow rates of TMIn, TMGa NH_3, and N_2 were kept constant at 51.1 μmol/min, 12.5 μmol/min, 18 slm, and 6 slm respectively. This corresponds to a V/III ratio of ~9200 and TMIn/(TMIn+TMGa) molar flow ratio of 0.80. All growth durations were kept at 40 min. In each run, a nanopatterned substrate was used along with a bare AlN(0001)/Si(111) substrate which serves as the control sample. The heights of the nanopyramids in SA-NHE are at least 220 nm while the thicknesses of the control films are ~130 nm or more.

Sample morphology was examined with field emission scanning electron microscopy (FESEM) using a Nova NanoSEM 230, and with atomic force microscopy (AFM) using a Bruker Dimension Icon®. Compositional and structural characteristics were studied with high-resolution X-ray diffraction (HRXRD) in a PANalytical X'Pert Pro-MRD X-ray diffractometer utilizing the Cu Kα1 line with a wavelength of 1.540598 Å. Transmission electron microscopy (TEM) was performed with a JEOL JEM-2100 with an accelerating voltage of 200 keV. Room temperature micro-photoluminescence (μ–PL) measurements was further carried out in a Renishaw Ramascope 2000 setup using the 325 nm line from a He–Cd laser as the excitation source. The instrument has a spatial resolution of ~1 μm, allowing measurement to be localized to the patterned region. The laser spot size ~40 μm has a power ~10 mW. Total reflectance measurements were performed with an integrating sphere at a sample incidence angle of 8° in a Bentham/IVT PVE300 setup.

3. Results and discussion

3.1. Effect of growth temperature

3.1.1. Morphology

At 300 Torr, over the range of growth temperatures (700 °C–800 °C) investigated, nano-SAHE at each pore of the SiN_y template resulted in the formation of an InGaN hexagonal nanopyramid bound by six facets. Fig. 1 shows the FESEM images of the nanopyramids. The inclination angle of each facet from the basal plane is determined by AFM to be ~62°, confirming that these are $\{1-101\}$ planes. These slow growing, energetically stable planes, frequently encountered in III-nitrides growth [33–37], are responsible for the observed shape, in accordance to Wulff's theory [38].

In general, not all facets are of the same size, resulting in nanostructure asymmetry and size non-uniformity. This was further studied by examining the morphology attained under reduced reactor pressure P as discussed later in Section 3.2.1. It is known that a reduction in P increases the mass transport of reactants through the boundary layer in MOCVD [39]. According to Lundskog et al., the increased arrival rate of adatoms will favor growth in the adsorption regime which will degrade uniformity [40]. On the contrary, we found the size uniformity of InGaN nanopyramids is notably improved. In another work by Miao et al., asymmetry of GaN nanopyramids has been correlated to stacking fault formation [41]. However, in our work, stacking faults are present in both asymmetric and symmetric InGaN nanostructures