The Formation of Hexagonal-shaped InGaN-nanodisk on GaN-Nanowire Observed in Plasma Source Molecular Beam Epitaxy

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ABSTRACT

We report on the properties and growth kinetics of defect-free, photoluminescence (PL) efficient mushroom-like nanowires (MNWs) in the form of ~30nm thick hexagonal-shaped InGaN-nanodisk on GaN nanowires, coexisting with the conventional rod-like InGaN-on-GaN nanowires (RNWs) on (111)-silicon-substrate. When characterized using confocal microscopy (CFM) with 458nm laser excitation, while measuring spontaneous-emission at fixed detection wavelengths, the spatial intensity map evolved from having uniform pixelated emission, to having only an emission ring, and then a round emission spot. This corresponds to the PL emission with increasing indium composition; starting from emission mainly from the RNW, and then the 540 nm emission from one MNWs ensemble, followed by the 590 nm emission from a different MNW ensemble, respectively. These hexagonal-shaped InGaN-nano-disks ensembles were obtained during molecular-beam-epitaxy (MBE) growth. On the other hand, the regular rod-like InGaN-on-GaN nanowires (RNWs) were emitting at a shorter peak wavelength of 490 nm. While the formation of InGaN rod-like nanowire is well-understood, the formation of the hexagonal-shaped InGaN-nanodisk-on-GaN-nanowire requires further investigation. It was postulated to arise from the highly sensitive growth kinetics during plasma-assisted MBE of InGaN at low temperature, *i.e.* when the substrate temperature was reduced from 800 ^{o}C (GaN growth) to <600 ^{o}C (InGaN growth), during which sparsely populated metal-droplet formation prevails and further accumulated more indium ad-atoms due to a higher cohesive bond between metallic molecules.

Keywords: InGaN / GaN, Nanowires, Catalyst-free Growth Kinetics, Nitrogen-plasma Source Molecular Beam Epitaxy, Confocal Microscopy, Photoluminescence Spectroscopy, Scanning Electron Microscopy

1. INTRODUCTION

Anisotropic epitaxial growth of free-standing GaN [1, 2] and InGaN nanowires [3, 4] presents a key technological advancement in material structure for light-emitter technology. The catalyst-free [5-7] and spontaneous growth of nitrogen-polar GaN nanowires [8] based on nitrogen-plasma-source-based molecular beam epitaxy (MBE) eliminated the use of foreign metal, such as gold catalyst [9], which act as non-radiative recombination center and constitute material incompatibility with silicon foundry technology. The catalyst-free growth technology led to the subsequent demonstration of visible and white InGaN/GaN quantum-disk-in-nanowires light-emitting diodes (LEDs) on silicon [2, 10-14] and SiO_2/Si [15]. Structurally, the nanostructures circumvented the thermal mismatch and lattice mismatch associated with heteroepitaxy integration, *i.e.* growth of InGaN/GaN on the dissimilar substrates. Nanostructures thus prepared exhibited no threading dislocations, showing no quantum efficiency rollover, *i.e.* efficiency droop, low Auger recombination coefficient $\sim 10^{-33}$ $cm^6.s^{-1}$ [16], and reduced quantum confined stark-effect in LEDs application. A plethora of promising devices was also demonstrated based on GaN nanowires, such as optically pumped single GaN nanowire laser based on photonic crystal microcavity [17], and vertically-integrated dielectric-mirror-clad polariton-lasers operating at room temperature [18-20].

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New nanostructures with different form factor (size and shape) and material composition will further enable growth of material structure with unique physical properties (thermal and lattice structure) for wavelength tuning and bandgap engineering of active region and thus enable creation of novel devices. In this investigation, we present the properties and the growth kinetics of defect-free and photoluminescence-efficient mushroom-like nanowires (MNW) in the form of ~30nm thick hexagonal-shaped InGaN-nanodisk-on-GaN-nanowire grown using Molecular Beam Epitaxy (MBE).

2. EXPERIMENTAL DETAILS

The InGaN-on-GaN-nanowire sample was grown on silicon (111) substrate using a molecular beam epitaxy (MBE) system having ultra-high purity gallium and indium sources, in conjunction with nitrogen-plasma source and conditions similar to references [21, 22]. The native oxide was removed from the substrate surface before epitaxy by the standard technique, which involves a rinse in HF-H_2O solution and heat treatment in the growth chamber at 900 °C for 30min at the vacuum level of 1×10^{-9} Torr. The substrate temperature was lowered to 800 °C and a few monolayers of Ga were deposited with a gallium flux of 1.5×10^{-7} Torr in the absence of nitrogen flux. The catalyst-free growth was initiated with binary GaN grown to a nominal thickness of 150nm GaN at 800 °C under nitrogen-rich conditions. A growth interruption was introduced whereby the growth temperature was reduced to < 600 ^{o}C, and the indium shutter was opened to continue with the InGaN nanowires growth to a nominal thickness of 500 nm. The optical properties and morphology of the nanowires were studied using scanning electron microscopy (SEM), and confocal microscopy (CFM) as well as micro-photoluminescence (PL) spectroscopy, respectively. Both CFM and PL are equipped with CCD-based spectrometer.

3. RESULTS AND DISCUSSION

On the same sample we observe two types of nanostructures, *i.e.* the InGaN-mushroom-cap on GaN nanowires, henceforth, the mushroom-like nanowires (MNW) growth in the form of ~30nm thick hexagonal-shaped InGaN-nanodisk on GaN nanowire, coexisting with the conventional rod-like InGaN-on-GaN nanowires (RNW), see Fig.1(a) and (b) respectively. It is noted that the MNWs in Fig.1(a) were observed at the round spots with diameter of ~30-40 μm, which is the grey-color round spot in the optical microscope picture in Fig.1(c), while the region outside the round spots were overgrown with RNWs (purple-color region outside the round spot). The round grey color spots were sparsely populated and more of such feature were found close to the MBE substrate holder retainer pins, which facilitated heat dissipation and therefore local temperature is lower than the central area region. At the center of the round spot, in addition to the MNWs, chunky materials with irregular shapes were found indicating severe distortion of the crystal structure, likely due to the formation of polycrystalline materials with dislocations formation.

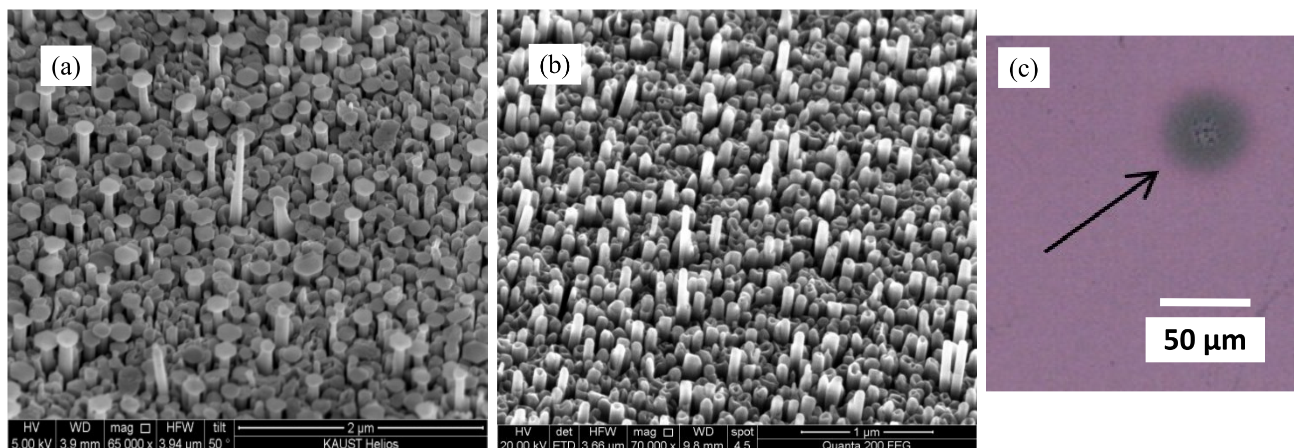

Fig.1 Scanning electron microscopy (SEM) images of (a) InGaN-mushroom-cap on GaN nanowires (MNW), and (b) InGaN-on-GaN nanowires. The microscope picture in (c) shows the grey-color region (as indicated by a pointed arrow) where MNWs was found, and the purple-color region where the conventional RNWs were observed.

The spontaneous emission was collected using from the MNWs and RNWs regions using PL spectroscopy with 473nm laser excitation having a laser beam spot of between 1-2 μm. As shown in Fig.2(a), a broad PL spectrum with 3 main peaks covering the entire visible wavelength range was measured for the MNWs spot; while a narrower PL spectrum

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with peak emission at 490nm was observed for the RNW region (see Fig.2(b)). With arbitrary Gaussian fittings, five peaks were obtained with three main peaks located at 500nm, 570nm and 710nm, as well as two other peaks at 610nm and 640nm. The peaks were originated from MNWs with varying indium compositions.

In order to ascertain the spatial distribution of the PL peaks and therefore the distribution of indium composition, the area shown in Fig.1(c) was characterized using confocal microscopy (CFM) with 458nm laser excitation. This is done by measuring the spontaneous emission map with detection wavelength swept at ~10nm steps. With increasing detection wavelength, the spatial spontaneous emission map as shown in Fig.3(a)-(c), respectively, changes from pixelated emission from the whole area, to having only an emission ring, and then a round emission spot. This corresponds to the PL emission with increasing indium composition; starting from emission mainly from the RNW, and then the emission from the MNWs at 540nm, and the emission from MNWs at 590 nm. The spatial maps of MNWs with varying indium composition indicated that the indium composition increases from the circumference of the round spot towards the center. It is hence clear that local accumulation of indium occurred during growth, and hence facilitated the formation of these unique mushroom-like nanowires (MNWs).

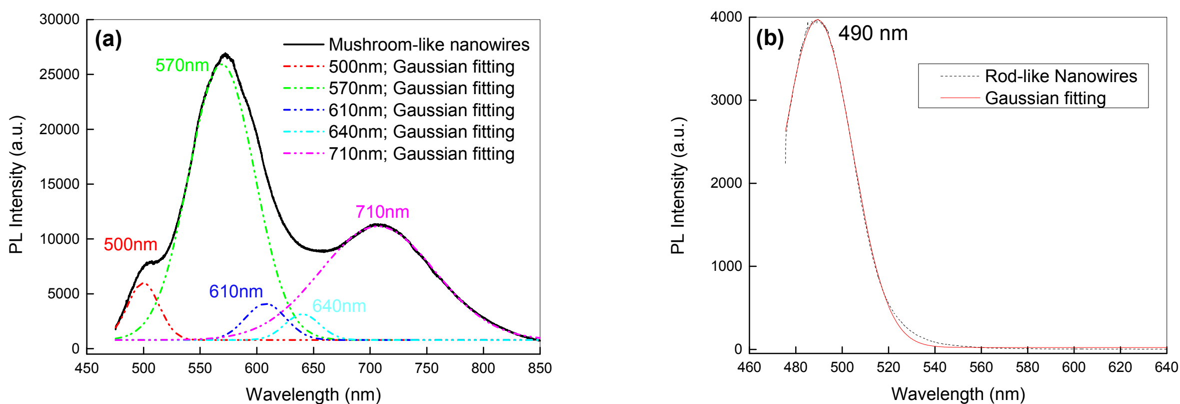

Fig.2 The photoluminescence spectra (black curve) of the sample at the region having: (a) the InGaN-mushroom-cap on GaN nanowires (MNWs), and (b) the conventional rod-like nanowires (RNWs). The spectrum for MNWs was fitted with five arbitrary Gaussian curves with peak wavelengths located at 500nm, 570 nm, 610 nm, 640 nm, and 710 nm, while the spectrum for the RNWs was fitted with single Gaussian curve. Both spectra were measured using 325 nm and 473 nm laser excitation, respectively.

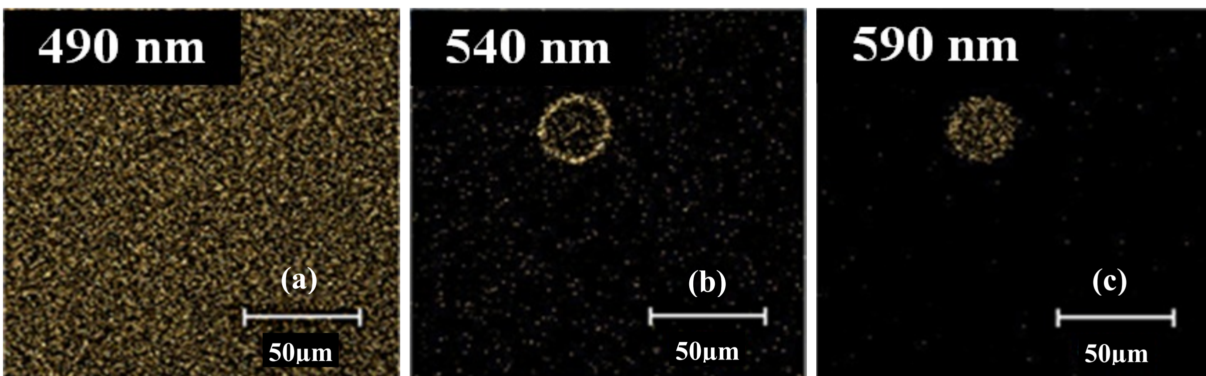

Fig.3 The confocal microscope (CFM) based photoluminescence map of InGaN nanowire at detection wavelength of (a) 490nm, (b) 540 nm, and (c) 590 nm. Spatially uniform emission from the rod-like InGaN NW was detected at 490 nm, while the 25 µm diameter region showed a clear transition from a ring emission peaking at 540 nm (emission from crystalline InGaN-nano-disk on GaN-NW, *i.e.* mushroom-like NW), to a uniform circular emission towards 590 nm (and beyond) detection wavelength (a mixed of crystalline/polycrystalline/amorphous (In)GaN).

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The spontaneous growth of GaN nanowires proceeded without the use of catalyst, and is governed by the kinetic processes [8, 22]. As shown in the schematic of Fig.4(a), during the high temperature growth (800 ^{o}C) of the GaN nanowires, the impinging gallium flux gets adsorbed (physical attachment) on the silicon (111) substrate. These ad-atoms either gets desorbed or continues to migrate before they eventually nucleate the initial basal GaN nanowires after combining with nitrogen species. Since the gallium ad-atoms have enough kinetic energy, they will diffuse up the length of the nanowires and nucleate on top of the nanowires as well as diffuse away from the basal GaN nanowires at high growth temperature (long ad-atoms diffusion length). The preferential growth along [0001], or c-direction under nitrogen-rich conditions and high temperature led to rod-like GaN nanowire growth. In addition, the direct impingement of gallium flux on the nanowire also contributed to GaN nucleation at the top. Such growth mechanism is common for the RNW and MNW during GaN growth, and hence rod-like structures were formed for both types of nanowires.

Although the nanowires growth were conducted using group-V rich conditions, the growth interruption time between 800 to < 600 ^{o}C in preparation for InGaN growth provided time and the required activation energy for the dissociation of GaN; desorption of gallium and dissociation of GaN at high temperature limit, and local accumulation of gallium during the lower temperature limit (close to <600 ºC) as mentioned. We now turn to explaining the kinetics behind the local formation of MNW. While the rod-like InGaN growth proceeded in a manner similar to that of rod-like GaN described in the above (see steps 1-4 in Fig.4(a)), the InGaN mushroom-disk growth is postulated to proceed through steps 1-2 as shown in Fig.4(b) due to a short migration length of ad-atoms. It is postulated to arise from the highly temperature sensitive growth kinetics during plasma-assisted MBE of InGaN during the temperature transition, *i.e.* when the substrate temperature was reduced from 800 ^{o}C (GaN growth) to <600 ^{o}C (InGaN growth), during which sparsely populated group-III metal-droplet formation prevails and further accumulated incoming indium ad-atoms due to higher cohesive bond between metallic molecules and lower substrate temperature < 600 ^{o}C. This is typically found during the growth of nitride epitaxy at intermediate growth regime or III/V ratio ~ 1, (see microscope picture in Fig.5), where the droplets in the size of tens of micrometer were routinely found. Similar mechanism led to the droplet formation.

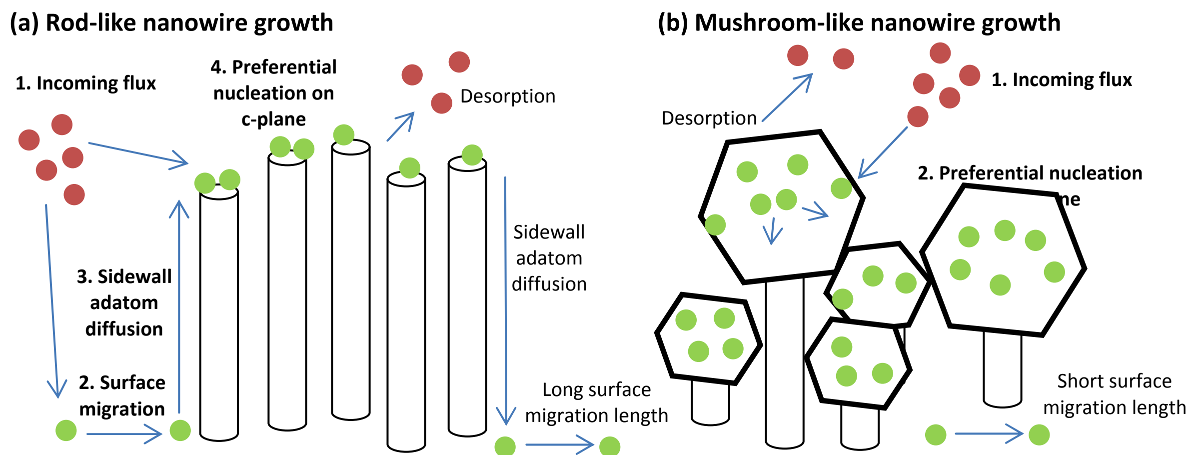

Fig.4 Schematic diagram showing growth kinetics in: (a) InGaN-on-GaN rod-like nanowire, and (b) InGaN-disk-on-GaN-nanowire or mushroom-like nanowire growth on silicon (111) substrate. The green balls represent the group-III ad-atoms on substrate surface or nanowire surface, while the red balls represent incoming or outgoing (desorption) group-III fluxes. Incoming Group-V flux is not shown. During the top InGaN growth, nitrogen-rich and local metal-rich conditions resulted in the growth of rod-structure through steps 1-4, and hexagonal-disk-structure through step 1-2 in (a) and (b), respectively.

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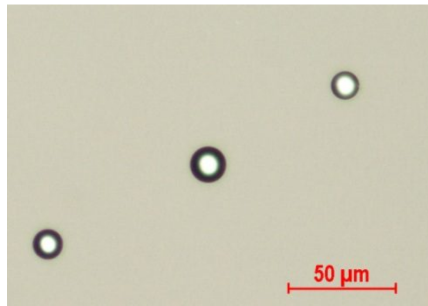

Fig.5 Microscope picture showing the typical formation of group-III droplets (the 3 circular spots) on GaN surface during growth of nitride epitaxy at temperature ~600 ^{o}C at intermediate growth regime, *i.e.* III/V ratio slightly higher than 1.

The energy dispersive X-ray spectroscopy (EDXS, not shown here) showed the basal rod of the MNWs consisted of only GaN while the hexagonal cap consisted of InGaN. This evidence allows us to further explain the formation of the hexagonal InGaN disk with the six facets corresponded to the m-planes. The presence of local metal-rich region and low InGaN growth temperature led to the two-dimensional (*2D*) growth of InGaN disk and preferential nucleation at the m-planes rather than the nucleation at the c-plane. The preferentially nucleation at the m-plane facets, instead of c-plane is also due to strain-induced lateral crystal expansion growth in the presence of more metallic species (see Fig.4(b)). The understanding of the growth mechanism suggested a potential way of pendeo-epitaxial growth [23] based on the coalescence of well-oriented InGaN hexagonal disk on hexagonally patterned substrate.

4. CONCLUSIONS

We reported on the optical properties and concurrent formation growth kinetics of the rod-like nanowires (RNWs) and mushroom-like nanowires (MNWs). It is noted that the simultaneous emission from the NRW and MNW forms white light and therefore is attractive for solid state lighting. The PL emission from the MNWs was spatially resolved using CFM, and provided the evidence of local indium accumulation during growth. The local metal-rich condition and low temperature growth of InGaN led to the growth of hexagonal cap disk and the MNW. The understanding of the growth mechanism suggested a potential way of pendeo-epitaxial growth for InGaN template substrate formation based on the coalescence of the well-oriented and equal height InGaN hexagonal disk, though the orientation control is potentially a great research challenge.

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