Vapor-liquid-solid Growth of III-Nitride Nanowires and Heterostructures by Metal-Organic Chemical Vapor Deposition

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ABSTRACT

We report flexible synthesis of III-Nitride nanowires and heterostructures by metal-organic chemical vapor deposition (MOCVD) via a catalytic vapor-liquid-solid (VLS) growth mechanism. Indium is used as an in-situ catalyst to facilitate and sustain the stability of liquid phase droplet for VLS growth based on thermodynamic consideration. The employment of mesoporous molecular sieves (MCM-41) helps to prevent the coalescence of catalyst droplets and to promote nucleation statistics. Cathodoluminescence (CL) of GaN nanowires shows near band-edge emission at 370nm, and strong E_2 phonon peak is observed at room temperature in Raman scattering spectra. Both binary GaN and AlN nanowires have been synthesized by MOCVD. Three-dimensional AlN/GaN trunk-branch nanostructures are reported to illustrate the versatility of incorporating the VLS mechanism into MOCVD process.

INTRODUCTION

One-dimensional III-Nitride nanowires and heterostructures offer unique features as nanoscale building blocks for nanoelectronics, photonics, and hybrid biological/chemical systems. The majority of nanowires have been synthesized based on catalytic reaction through vapor-liquid-solid (VLS) growth mechanism.[1] The synthesis of III-Nitride nanowires is performed primarily by a near-equilibrium, tube furnace technique which does not offer optimum control or flexibility.[2] There is nevertheless a need to enrich the functionality and complexity of the individual building blocks *in-situ* by using modern heteroepitaxial practices such as molecular beam epitaxy (MBE) and metalorganic chemical vapor deposition (MOCVD).[3] Recently we reported our observations in preparing III-Nitride nanowires using a conventional cold wall MOCVD system.[4] Here we report on structural and optical characterization of AlN and GaN nanowires and three-dimensional (3D) AlN/GaN heterostructures synthesized by MOCVD.

EXPERIMENTAL DETAILS

Synthesis of the nanowires was carried out in a commercial horizontal MOCVD reactor (Aixtron 200/4 HT-S) using trimethylgallium (TMGa), trimethylaluminum (TMAl), trimethylindium (TMIn), and ammonia (NH_3) as sources. Both nitrogen and hydrogen were used as the carrier gas. Unless otherwise specified, growth temperature and pressure were 900 °C and 50 mbar, respectively. Scanning electron microscopy (SEM) was performed using a FEI XL30 Field Emission ESEM. High-resolution transmission electron microscopy (TEM) and electron diffraction (ED) were performed using a FEI Tecnai 20 Field Emission TEM and JEOL 2010 FasTEM.

RESULTS AND DISCUSSION

Prerequisites of VLS growth include: (1) low supersaturation to diminish vapor-solid (VS) growth for growth selectivity; (2) formation and retention of liquid phase droplets to facilitate vapor adsorption and maintain growth; (3) nucleation sites with appropriate crystallographic orientations as starting point for unidirectional growth. For compound III-Nitride nanowire growth, NH_3 flow needs to be adjusted to accommodate the low supersaturation requirement while maintaining the stoichiometry. TMGa (TMAl for AlN nanowires) flow of 1-10 μmol/min and NH_3 flow of 20 sccm are characteristic of our typical growth condition at 900°C and 50 mbar reactor pressure.

Droplet stabilization and template control

To increase the sustainability of the liquid droplets and alleviate the sensitive dependence on stoichiometry, indium is introduced during the growth of III-Nitride nanowires as a "solvent" agent or in-situ catalyst. Adding indium during GaN growth enhances the thermodynamic tendency of liquid formation over a wide range of ammonia and gallium partial pressures, thus greatly expanding the domain of liquid phase in the alloy phase diagram.[5] Polycrystalline alumina substrate is chosen to facilitate the nucleation events and prevent coalescence of liquid phase droplets. Alumina substrates were pretreated with Ni catalyst by E-beam evaporation of

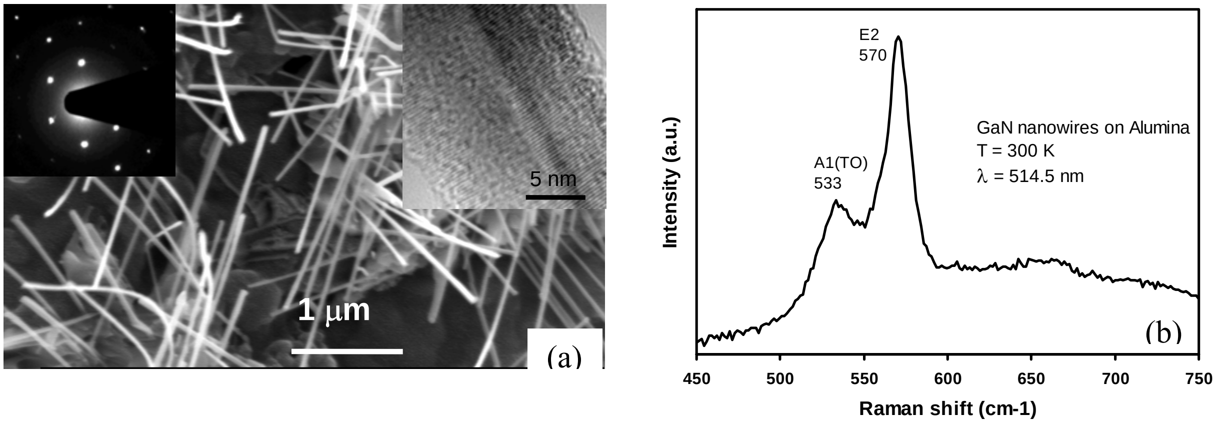

Figure 1. (a) SEM image of GaN:In nanowires on MCM-41 templates. Inset: High resolution TEM (right) and electron diffraction images (left); (b) Room temperature Raman spectra from GaN nanowires on alumina templates.

8Å thick Ni thin film. The effect of varying the amount of indium has been studied, with TMIn/TMGa ratios of zero, 2:1, 7:1, 14:1 and 20:1. For growth without indium, short rods and sub μm crystallites are observed. At the In/Ga ratio of 2:1, the growth occurs in the shape of ~1 μm long tapered rods with sharp tips. GaN nanowires obtained with the In/Ga molar flow ratio of 14 exhibited an average diameter of 90 nm and length of 1 to 2 μm after 30 min of growth. An excess of indium is observed at the molar ratio of 20, manifested by the appearance of the large indium droplets together with the nanowires.

To enhance the yield and control of nucleation, mesoporous molecular sieves (MCM-41)[6] consisting of hexagonal arrays of silicate materials with well-defined pore sizes of nominally 3.5 nm are employed. Figure 1 (a) shows a SEM image of In-doped GaN nanowires on MCM-41 templates, using identical growth procedure to that on the alumina substrate. We have observed the increase in nanowire density, accompanied by a reduction in diameter to 30-40 nm. We speculate that the MCM-41 template serves at least two purposes: (1) a surface with high curvature will facilitate the perturbational optimization of crystallographic orientation and enhance nucleation events; (2) a high surface area (≥2000 m^2/g) will prevent the sintering and coalescence of liquid phase droplets and result in a tighter control of the dimensions of nanowires. X-ray diffraction 2θ-Ω scans (not shown) confirmed the presence of GaN diffraction peaks. These wires were dispersed through sonication in ethanol onto TEM grids. Selected area electron diffraction (inset of Figure 1(a)) and SEM indicates the wires are oriented along the $[10\underline{1}0]$ direction. The $(10\underline{1}0)$ plane (m-plane) has been identified[7] to have the lowest surface energy with the formation of Ga-Ga dimer reconstruction, consistent with the notion that VLS growth proceeds through a Ga-rich liquid-solid interface.

Optical characterization

The Raman spectra are recorded in backscattering geometry at room temperature with 514.5nm line Ar^+ laser light source. Raman scattering spectra reveal the A_1 (TO) mode at 533 cm^{-1} and E_2

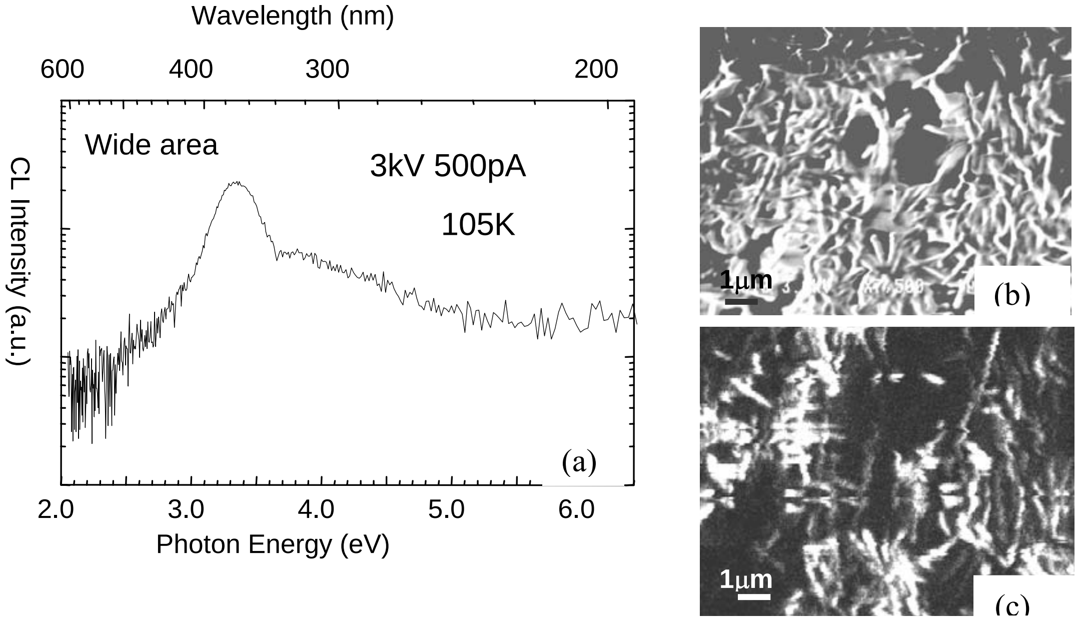

Figure 2. (a) Wide area CL spectrum at 105 K; (b) SEM image of GaN nanowires on alumina substrate; (c) monochromatic CL map of the same area at 370nm (3.35eV).

mode around 570 cm^{-1}, see Figure 1 (b), which is close to the Raman peaks from bulk GaN.[8] The strong E_2 peak indicates the hexagonal wurtzite crystal phase in GaN nanowires. Previous report suggests that the broadening of Raman peak is related to the phonon confinement in the size dispersed nanometer sized materials which causes the uncertainty in phonon wave vector.[9]

Figure 2 (a) shows the wide area cathodoluminescence (CL) spectrum at low temperature (105 K), exhibiting the near band-edge emissions at 370 nm (3.35eV). SEM image of GaN naonowires on alumina (also at 105 K, figure 2 (b)) is shown together with the monochromatic CL map (Figure 2 (c)) obtained at 3.35eV detection energy on the same area of the sample. The correlation between the SEM image and CL map indicates that the near-band edge emission originates with the 1D GaN nanowire structures. Strain and crystallographic defects caused by the large surface-to-volume ratio, large lattice mismatch and difference in thermal expansion coefficients between the substrate and growing material, could influence the unit cell size in nanosize structures, leading to the peak emission wavelength shift relative to bulk GaN. The change of lattice constant in the nanowires is corroborated by the shifts of [10$\underline{1}$0] [10$\underline{1}$1] and [0002] peaks in the X-Ray diffraction measurements.

3-D trunk/branch structures

A distinct advantage of using MOCVD platform is the flexibility of rapid modulation of vapor species for doping and heterostructures. By replacing TMGa with TMAl of an identical flow rate, we have achieved the synthesis of AlN nanowires under same growth condition. Having established the synthesis procedures for binary GaN and AlN nanowires, we attempted[10] AlN/GaN superlattice heterostructures toward a proof-of-concept illustration of nanoscopic tailoring by MOCVD. Figure 3(a) shows a TEM image of these structures, representing a surprising departure from single 1D nanowires to complicated 3D trunk-branch nanostructures. Selected area electron diffraction indicated that the trunk is consisted of a [10$\underline{1}$0] oriented GaN core (30 nm in diameter), as is described earlier, and a polycrystalline AlN sheath of 5-10 nm thick. Roughening in the sheath region was observed under high-resolution TEM, possibly due to highly strained growth of AlN on the GaN facets. Nanoscale compositional analysis by EDS indicated the existence of AlN (or high Al-fraction AlGaN) branches with indium tips. We note

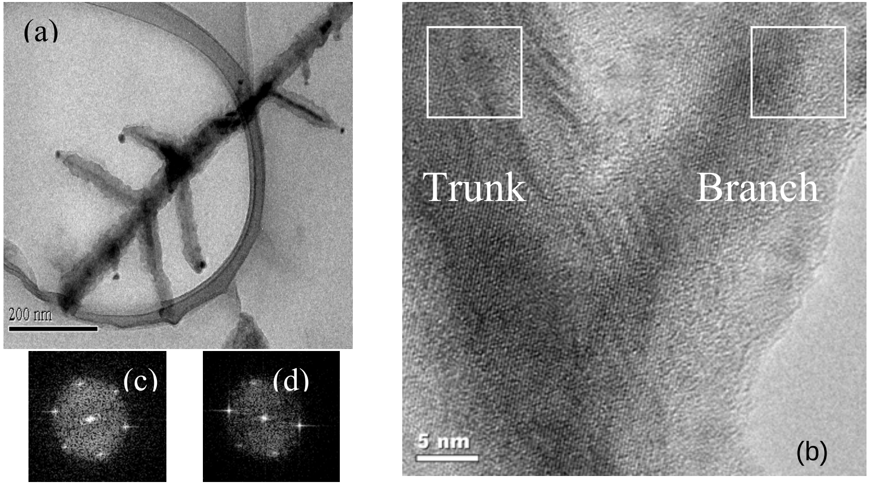

Figure 3. (a) TEM of MOCVD grown GaN/AlN nanostructures using indium catalyst on MCM-41, (b) High resolution TEM along (0001) diffraction showing [10$\underline{1}$0] lattice planes, (c) and (d) 2D FFT of boxed regions from trunk and branch respectively.

that the Al-In binary system is expected to exhibit the miscibility gap at the temperatures below 875 °C, while the miscibility of Al-Ga and In-Ga binaries is complete at the temperatures above the melting points of the constituent elements (30, 157 and 660 °C for Ga, In and Al, respectively).[11] Formation of tree-like nanostructures as controlled multiplication of nanowires networks is of contemporary interest[12] and was demonstrated recently through iterative cycles of catalyst applications, VLS synthesis, and growth interruptions. High resolution TEM image at a branch-trunk junction reveals perfect, hexagonal lattice registry throughout the vicinity of junction, see Figure 3 (b). Two-dimensional fast Fourier transform produces diffraction images (Figure 3 (c)-(d)) from the trunk and branch regions (boxed areas), which in turn indicate that the lattice planes are the $(10\underline{1}0)$ planes (m-planes), and both the GaN trunk and the AlN branch are oriented along $<10\underline{1}0>$ directions at an angle of 60°. The observed preference for the m-axis growth direction is independent of the template in our case – it is likely that under the Ga-rich VLS growth mode the $\{10\underline{1}0\}$ planes emerge as the lowest energy ones with the formation of the Ga-Ga dimmer reconstructions.[13] Vertically and laterally aligned m-axis nanowires on m-plane AlN and patterned GaN substrates were also obtained, the results of this study will be reported elsewhere. We also note that the spacings between the diffraction spots reveal that the branch has a smaller lattice constant than the trunk by approximately 1%; the exact state of strain can not be accurately assessed given the uncertainty of Al composition at the junction.

The *in-situ* formation of nano-branches, which does not occur with uniform GaN wires, is likely strain-driven to accommodate elastically the 2.4% lattice mismatch while maintaining the preferential $[10\underline{1}0]$ directions for Al(Ga)N nanowires branches. Four of the six equivalent $\{10\underline{1}0\}$ branches are observed that are at approximately 60° or 120° to the trunk, contrasting the recent reports of 90° nano-branches in cubic Si and InP systems. It points to a new degree of tunability in constructing complex three-dimensional nanostructures through strain engineering.

CONCLUSIONS

Growth of III-Nitride nanowires (GaN, AlN) and heterostructures is demonstrated by MOCVD via a catalytic VLS growth mechanism. Low temperature cathodoluminescence of GaN nanowires shows near band-edge emission at 370nm, and strong E_2 phonon peak is observed at room temperature from inelastic Raman scattering. Three-dimensional AlN/GaN trunk-branch nanostructures illustrate the versatility of incorporating the VLS mechanism into MOCVD process.

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