# **Epitaxial Growth of InN Nanorods on Nitridated Chromium Nanoislands under the In-rich Regime**

Kai-Hsuan Lee<sup>1</sup>, Sheng-Po Chang<sup>2,\*</sup>, Kuang-Wei Liu<sup>2</sup>, Ping-Chuan Chang<sup>3</sup>, Shoou-Jinn Chang<sup>2</sup>, Tse-Pu Chen<sup>2</sup>, Hung-Wei Shiu<sup>1,4</sup>, Lo-Yueh Chang<sup>1,4</sup>, and Chia-Hao Chen<sup>1</sup>

<sup>1</sup>Nano Science Group, National Synchrotron Radiation Research Center, Hsinchu 30076, TAIWAN
<sup>2</sup>Institute of Microelectronics & Department of Electrical Engineering, Center for Micro/Nano Science and Technology, Advanced Optoelectronic Technology Center, National Cheng Kung University, Tainan 70101, TAIWAN
<sup>3</sup>Department of Electro-Optical Engineering, Kun Shan University, Yung-Kang Dist., Tainan 71003, TAIWAN
<sup>4</sup>Department of Physics, National Tsing Hua University, Hsinchu 30013, TAIWAN
\*E-mail: <a href="mailto:changsp@mail.ncku.edu.tw">changsp@mail.ncku.edu.tw</a>.

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Vertically aligned inverted-cone-like InN nanorods were epitaxially grown on Si (111) substrate by molecular beam epitaxy (MBE) using AlN buffers and nitridated chromium (NC) nanoislands under In-rich environment. The Al droplets were limited to between NC nanoislands so that the lateral diffusion was suppressed. The spot-like AlN nuclei aided the subsequent growth of InN nanorods more uniform and well aligned. X-ray diffraction (XRD) of InN nanorods exhibits a hexagonal phase and (0002) oriented growth. The structural analysis performed by Raman scattering indicates that InN nanorods are wurtzite-type InN crystals with low structural disorders and defects, which contain low concentrations of electrons. The photoelectron spectra depict the considerably reduced surface states and In-In bonds of InN nanorods, while the valence band spectra reveal the presence of surface band bending in InN nanorods. The InN nanorods are free from charge trapping effects due to Fermi-level pinning, which may deplete the carriers.

Keywords: InN, nanorods, nitridated chromium, nanoislands, molecular beam epitaxy

# **1. INTRODUCTION**

InN marks the lower band gap limit achievable within the group III-nitride semiconductor family [1-3]. Its narrow band gap, the existence of a surface accumulation layer, and the smallest effective mass, which were recently observed and debated by many research groups, extend the application area of full spectrum solar cell and high-power/high-frequency electronics [4-6]. The

physical and optical properties strongly rely on the quality of InN crystals, which are difficult to grow because of the low dissociation temperature of InN and the lack of an appropriate substrate [7-9]. Dissociation can be avoided by growing at low enough temperatures by molecular beam epitaxy (MBE). The generation of extended defects during heteroepitaxial growth on mismatched substrates can be eased using different types of buffer layers that accommodate the mismatch. For example, Wu et al. have provided the direct evidence of 8:9 commensurate heterojunction formed between InN and AlN on Si (111) substrate [10]. Sánchez-García et al. have pointed that the layer morphology of InN can be controlled by tuning the III/V ratio. Under N-rich condition, it is inclined to form InN nanorods [11]. As the In molecular flux is increased towards In-rich condition, the structure of InN evolves to a more compact morphology free of columnar features. In addition, it has been reported that growth under In-rich conditions gives rise to In segregation in the InN [12]. Thus, the preparation of high quality InN nanorods under the In-rich regime has proven challenging. In order to achieve controlled synthesis and self-organized formation of InN nanorods in In-rich environment, the template-assisted growth technique by virtue of AlN buffers on nitridated chromium (NC) nanoislands was selected in this study for the subsequent directional growth of InN nanorods along the c-axis. The NC nanoislands can be simply regarded as the "nucleation promoter" to interrupt the film-like growth of AlN. The lateral diffusion of Al droplets was limited between NC nanoislands and AlN was thus grown relatively discontinuous as the spot-like grains. These spot-like AlN nucleation sites can be precisely controlled by tuning the size and density of underlying NC nanoislands and are able to achieve uniform and well aligned InN nanorods.

### 2. EXPERIMENTAL METHODS

InN nanorods in this study were grown on Si (111) substrates by a MBE system equipped with a radio frequency (RF) plasma source. The In source (7N pure metal) was loaded in a standard effusion cell and the nitrogen source (6N pure nitrogen gas) was further purified by a nitrogen purifier and fed into an RF plasma generator. Prior to loading into the MBE chamber, the Si substrates were cleaned using standard solvent and buffer hydrofluoric acid solution to remove native oxides. Seven kinds of growth template were prepared to investigate the growth of InN nanorods under the In-rich regime. Among them, the sample without buffer layer (sample A), with a 40-nm-thick AlN buffer layer (sample B) and with a 80-nm-thick AlN buffer layer (sample C) was deposited onto the Si substrate by MBE, respectively. Another Si substrate was deposited by a Cr layer by RF magnetron sputtering with RF power of 50 W and then transferred into the MBE chamber at 700 °C for 30 min with  $N_2$  plasma to form NC nanoislands (sample D). In order to optimize the best template for subsequent growth of InN nanorods, the combination of NC nanoislands and AlN buffers were implemented as well. The sample with sputtered Cr layer at an RF power of 25 W (sample E), 50 W (sample F) and 100 W (sample G) was firstly prepared, respectively. Thereafter, they were all transferred into the MBE chamber to form NC nanoislands and 80-nm-thick AlN buffer layer were then deposited at a substrate temperature of 890 °C. After the formation of growth templates, InN nanorods began to evolve on them under In-rich condition at 450 °C for 4hr. The general set of growth conditions includes background pressure,

nitrogen flow rate, and RF-plasma power, which were kept at  $10^{-9}$  Torr, 1.2 SCCM and 350 W, respectively.

Surface morphologies of the samples and size distribution of the InN nanorods were characterized by a field-emission scanning electron microscope (FESEM), which is operated at 5 keV. Crystallography of the InN nanorods were determined by using X-ray diffraction (XRD, source:  $CuK_{\alpha l}$ ,  $\lambda$ =1.5405 Å) system to confirm the growth orientation. Room-temperature micro-Raman measurements were made in the backscattering configuration using the 533 nm line of an Ar<sup>+</sup> laser as the exciting source. The crystallinity and structural properties of InN nanorods were examined by a high resolution transmission electron microscopy (HRTEM: JEOL JEM-2100F) attached to an energy-dispersive X-ray spectrometer (EDXS). The TEM samples used in this study were prepared by focused ion beam (FIB). Photoelectron spectra (PES) were measured by an ultra-high vacuum PES system with a base pressure of approximately 10<sup>-10</sup> Torr at the 09A1 beam line of the National Synchrotron Radiation Research Center (NSRRC), Hsinchu, Taiwan. All photoelectron spectra were collected in normal emission and the calibration of electron binding energy (BE) was performed with the Fermi edge of a clean gold reference sample.

## **3. RESULTS AND DISCUSSION**





 WD
 mag
 HV
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 HFW
 1
 1
 mm

 S2
 S2
 mm
 50000 x)
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 0
 2.59 µm
 5EM



D



**Figure 1.** (a)-(g) Top view FESEM images of InN nanorods on different growth templates under the In-rich regime.

Figure 1 (a)-(g) show the FESEM images and morphologies of InN nanorods on Si substrate under the In-rich regime by different design of growth templates. Figure 1 (a) shows the InN directly grown on Si substrate without any buffer layer. During the initial growth stages, the nuclei were formed for the continuous growth. However, the growth of the nuclei was stopped when they were surrounded by stable planes with high-index planes {01-12} [13]. As a result, triangular shape three dimensional (3D) InN nanoislands with large density were observed, rather than the one dimensional (1D) InN nanorods. The AlN buffer layer apparently aided the self-assembly of the InN nanostructures, which the nuclei were surrounded by low-index planes, {10-10} and {0001}, continuously grew into 1D nanorods. Because of the In-rich growth condition and the AlN which formed a long and continuous grain, the lateral growth rate was higher than the vertical growth rate. Since the growth of film-like AlN provided a lateral growth path, the merging of the InN nanorods occurred during the growth process, as shown in Fig. 1 (b). As the thickness of AlN increased from 40 to 80 nm, the coalescence of the inter-rods was reduced and the merging of the InN nanorods was rarely observed, as shown in Fig. 1 (c). Nevertheless, the morphology is not identical and all the nanorods are far from freestanding and well aligned. Therefore, the NC nanoislands were prepared as a template to grow

vertically aligned InN nanorods. We observed that the size and density of the NC nanoislands were dependent on the thickness of Cr coating, i.e., the controllable growth can be achieved via tuning the thickness of Cr layer by changing the RF-plasma power during sputtering. Figure 1 (d) shows the growth of InN nanorods directly on NC nanoislands. Inhomogeneous distributed InN nanorods with irregular shapes were observed when only using NC nanoislands as buffers. The combination of NC nanoislands and AlN buffers were hence intuitionally carried out. However, the optimal values of size and density of the NC nanoislands should be estimated by tuning RF power. Figure (e), (f) and (g) show the morphologies of InN nanorods on AlN/NC nanoislands with sputtered Cr layer at an RF power of 25 W, 50 W and 100 W, respectively. At the beginning, numerous Cr nanoislands of approximately 100 nm in size were distributed on the Si substrate at an RF power of 25 W (sample E). Upon the nitridation process, the Cr-coated surface aggregated nano-sized metal droplets at high temperatures and immediately to form NC nanoislands. As the RF power increased to 50W (sample F), the increased thickness of Cr layer induced more and larger Cr metal droplets to increase the density and the size of the NC nanoislands. As the RF power further increased to 100W (sample G), the density of the nanoislands was supposed to increased accordingly; however, the nanoislands also reaggregated and increased the size of the NC nanoislands, leading to decrease the density of NC nanoislands. After the formation of NC nanoislands on Si substrate, the AlN buffers were introduced. The Al droplets were limited to between NC nanoislands so that the lateral diffusion of the metal droplets was more difficult, i.e., the lateral growth of AlN were inhibited by NC nanoislands. These spot-like AlN nuclei aided the subsequent growth of InN nanorods more uniform and vertically aligned. In sample E, the roots of the InN nanorods seem to connect with each other, as shown in Fig. 1 (e). This should be attributed to the larger lateral growth rate for the InN nanorods under In-rich regime, which means the density and size of NC nanoislands were too low to sustain the vertical growth of InN nanorods. In sample G, the diameter of InN nanorods were enlarged because of the growth on larger nucleation sites, while the reduced density of nucleation sites failed to provide enough seeds to growth of InN nanorods. The alignment of vertical InN nanorods on Si substrate was thus undesirable and disorderly nanostructures with irregular shape were observed in the bottom region. Therefore, the growth condition of sample F is most appropriate in terms of crystallography and morphology aspects.

Figure 2 show  $2\theta$ - $\omega$  X-ray diffraction (XRD) of InN nanorods and their orientation growth for all samples. The peak at  $2\theta$ =31.3° is identified as InN (0002), which suggests the c-orientation of the nanorods. Another peak signals reveal InN (10-11) at  $2\theta$ =33.1° and InN (10-13) at  $2\theta$ =56.9°, which were diffracted by the sloped sides of the tip. The signals of CrN were only detected in sample D, E, F and G, which are consistent with our initial design. From sample A to B, the main peak was changed from InN (10-13) to InN (0002). This indicates that the growth of InN crystals was turned to 1D nanorods instead of 3D InN nanoislands upon the implement of AlN buffers. As the thickness of AlN increased from 40 to 80 nm (sample C), the peak intensity of InN (0002) began to weaken considerably. Fortunately, the NC nanoislands can be utilized to drive InN nanorods to grow vertically with highly (0002)-orientation. Among them, the individual nanorods had an identical morphology and all the nanorods well aligned in sample F, which indicates that the 50 W is the optimal RF power for sputtered Cr layer to form NC nanoislands. This is also confirmed by the FESEM images in Fig. 1.



Figure 2. (a)-(g) XRD profiles of InN nanorods on different growth templates under the In-rich regime.



**Figure 3.** (a)-(g) Room-temperature polarized Raman spectra of InN nanorods on different growth templates under the In-rich regime.

Figure 3 shows room-temperature polarized Raman spectra of InN nanorods for all samples obtained in the backscattering configuration [z(xx)z], in which  $E_2$  (high) and  $A_1$  (LO) symmetry modes are allowed. The z direction is parallel to the hexagonal axis, and the x and y directions are mutually orthogonal and have arbitrary orientations in the plane normal to z. The measured first-order polarized Raman spectra are seen to be consistent with the selection rules for the wurtzite structure [14].

As shown in Fig. 3, the line at 520 cm<sup>-1</sup> is the first-order phonon of the Si substrate. The large full width at half maximum (FWHM) value of the  $E_2$  mode for sample A (~10.83 cm<sup>-1</sup>) suggests the presence of a considerable amount of structural defects, which can result in a high concentration of electrons in InN [15]. In contrast, the FWHM of the  $E_2$  mode for sample F (~4.1 cm<sup>-1</sup>) is consistent with the literature data for InN with good crystalline quality [16].





**Figure 4.** Zoomed-in view of the Raman spectra in low branch of wave number for InN nanorods on different growth templates under the In-rich regime.

**Table 1.** Parameters of the room-temperature Raman spectra for seven samples. The abbreviation "Rel.intensity" denotes for the intensity of  $A_1(LO)$  peak normalized to the  $E_2$  phonon peak intensity.

sample	Raman shift (PLP <sup>-</sup> peak) [cm <sup>-1</sup> ]	FWHM ( $E_2$ peak) [cm <sup>-1</sup> ]	Rel. intensity [A <sub>1</sub> (LO) peak] [a. u.]
А	449	10.83	1.35
В	454	7.18	1.40
С	448	7.27	1.07
D	438	6.06	1.06
E	451	8.92	1.48
F	430	4.40	0.74
G	452	10.31	1.39

The intensity of  $A_1$  (LO) line peak in the Raman spectra is also an indication of structural disorder. It can be observed that the lowest  $A_1$  (LO) peak intensity as well as the narrowest FWHM of the  $E_2$  peak in sample F enable the growth of high quality InN crystals, as shown in Tab. 1.

In addition to  $E_2$  and  $A_1$  (LO) modes allowed by polarization selection rules in the  $[z(xx)z^-]$  configuration, the Raman spectrum in this configuration has a broad and weak feature at lower wave number side, as shown in Fig. 4 (a)-(g). We assigned this feature to the lower coupled plasmon-LO-phonon (PLP<sup>-</sup>) mode arising in polar semiconductors due to interaction of the longitudinal optical modes through the macroscopic field with collective excitations of free carriers [17]. This feature approaches and coincides with the position of  $A_1$  (TO) phonon line at frequency of ~448 cm<sup>-1</sup> in InN with a very high electron concentration and shifts to larger wave number with increasing carrier concentration [18]. It can be seen in Tab. 1 that the position of PLP<sup>-</sup> peak in sample F has the slight shift and does not overlap with  $A_1$  (TO) phonon peak. This suggests that the concentrations of free carriers in InN nanorods of sample F are low with limited structural disorder and defects.

Figure 5 and 6 display a series of In 4d and N 1s core-level spectra taken in normal emission for all proposed samples, respectively. The representative spectra were taken with the photon energies (hv) of 380 and 580 eV.





Figure 5. Resolved photoelectron spectra (hv=380 eV) for the In 4d core electrons of InN nanorods on different growth templates under the In-rich regime.





Figure 6. Resolved photoelectron spectra (hv=580 eV) for the N 1s core electrons of InN nanorods on different growth templates under the In-rich regime.

All peaks have been fitted using a Shirley background (incorporating a linear component) and Voigt (mixed Lorentzian-Gaussian) line shapes. Figure 5 depicts a fit to the In 4d core-level spectra. In our fit, four components are resolved, which in the order of high to low BE correspond to bulk In-N environment, surface state, In-In metallic bonds and N 2s orbital. The existence of surface states is a signature of InN nanorods with clean surfaces while the In-In bonds are originated from the surface metallic In droplets during growth under In-rich regime.

**Table 2.** Parameters of the In 4d bonding state components in a fit. The abbreviation "rel. A", "BE", "VBM" and "CLS" denotes for the relative area from each component, binding energy, valence band maximum and core-level shift (relative to the In-N state), respectively. Note that BE, VBM and CLS are in unit of eV.

		In-	·N	S		In-	In	N	2s	VBM
hv (eV)	sample	rel. A	BE	rel. A	CLS	rel. A	CLS	rel. A	CLS	
380	А	0.8138	18.62	0.0761	-0.49	0.0535	-1.18	0.0566	-3.53	1.90
	В	0.8282	18.67	0.0652	-0.63	0.0461	-1.29	0.0606	-3.37	2.30
	С	0.7673	19.09	0.1079	-0.97	0.0974	-1.62	0.0273	-4.82	0
	D	0.7607	18.57	0.0243	-0.48	0.05	-1.17	0.165	-3.60	1.94
	Е	0.8009	18.43	0.0425	-0.35	0.0446	-1.05	0.112	-3.58	1.94
	F	0.8684	18.54	0.0416	-0.54	0.0371	-1.01	0.0529	-3.45	1.76
	G	0.858	18.55	0.0429	-0.46	0.0452	-1.09	0.0538	-3.43	1.76

**Table 3.** Parameters of the N 1s bonding state components in a fit. The abbreviation "rel. A", "BE" and "CLS" denotes for relative area from each component, binding energy and core-level shift (relative to the In-N state), respectively. Both BE and CLS are in unit of eV.

		N-In		N-H <sub>2</sub>		N-H <sub>3</sub>		N-O	
hv (eV)	sample	rel. A	BE	rel. A	CLS	rel. A	CLS	rel. A	CLS
580	А	0.5238	396.52	0.3684	0.70	0.1078	1.50		
	В	0.54	396.39	0.3997	0.69	0.0603	1.7		
	С	0.0118	396.38					0.9882	3.02
	D	0.6495	396.46	0.3505	0.85				
	Е	0.6367	396.54	0.3633	0.76				
	F	0.6745	396.78	0.3255	0.84				
	G	0.608	396.64	0.392	0.88				

The chemical shifts of the three additional components relative to the In-N state located at ~18.5 eV and their corresponding occupied percentage of the whole spectral area are provided in Tab. 2. It was found that the area occupations of surface states and In-In bonds were considerably reduced by means of InN nanorods grown on NC nanoislands and/or AlN buffers, which suggests that high quality InN crystals can be achieved in those cases. Figure 6 displays a fit of the N 1s core-level spectra. In sample A, two additional components were needed in the model function at higher branch of BE in addition to the main peak of N-In bonding. The two feature are assigned to N bonding to

hydrogen: N-H<sub>2</sub> and N-H<sub>3</sub> with a chemical shift of 0.7 and 1.5 eV relative to the N-In state located at  $\sim$ 396.5 eV. As shown in Tab. 3, it was found that the N-H<sub>3</sub> bond disappeared and the areal percentage of N-H<sub>2</sub> bond were reduced by means of InN nanorods grown on NC nanoislands and/or AlN buffers, which means that a larger percentage of N-In bonds formed. This result is also consistent with the reduced surface states and In-In bonds in In 4d core-level spectra. It should be mentioned that the N-O bonds were only formed in the case of sample C with a chemical shift of 3.02 eV. The higher electronegativity of O (3.4) than N (3.0) renders a charge transfer from N to O. Correspondingly, the In-N peak shifted toward higher BE in In 4d core-level spectrum in sample C. This should be attributed to the charge transfer from In to N. Note that there is no In-O component present in In 4d core-level spectrum, indicating that the formation of N-O bonds is presumably caused by the nitrogen dangling bond due to the excess In metal droplets, but not by the oxidation of InN nanorods. The extremely high percentage of In-In bonds seen from Tab. 2 provides the supporting evidence as well.



**Figure 7.** Photoelectron spectra (hv=380 eV) of InN nanorods on different growth templates under the In-rich regime for determination of the energy separation between VBM and surface Fermi-level ( $E_V$ - $E_F$ ).

Figure 7 shows the valence band spectra for all proposed samples. All photoelectron spectra were collected in normal emission with incoming photon energy of 380 eV to examine the presence or absence of surface band bending for InN nanorods. The valence band maximum (VBM) positions ( $E_V$ ) were determined from linearly extrapolating the leading edges of valence band spectra. The surface band bending ( $V_B$ ) can also be determined from the difference between the bulk and surface Fermi level ( $E_F$ ) positions with respect to the VBM. Under flat surface band conditions, the measured surface  $E_V$ - $E_F$  should be very close to the bulk value (the lowest value in present is 0.5±0.1 eV for *in situ* cleaved a-plane InN surface) [19]. Therefore, a downward band bending can be inferred if the surface  $E_F$  lies much higher in energy above the conduction band minimum (CBM) than the bulk  $E_F$ . In sample

A, the surface Fermi level position of the surface of InN nanorods maintains at 1.9 eV above the VBM, indicating that it is under strong band bending conditions ( $V_B$ =1.4 eV) and electron accumulation. The surface of InN nanorods bend downwards much more in sample B while the overlap of  $E_V$  and  $E_F$  in sample C indicates the In-rich environment due to the excess In metal droplets on the surface of InN nanorods during growth. In sample F,  $V_B$  is estimated to be 1.26 eV, which indicates that the surface electron accumulation is alleviated in this case. It should be noted that two valence band onsets develop in sample D: one at 1.94 eV BE and the other at 0.06 eV BE, which correspond to the VBM and the surface state of InN nanorods, respectively.



**Figure 8.** (a) In 4d and (b) valence band spectra (*hv*=380 eV) for top surface and side facets (top and bottom) of sample F.

To investigate the electronic structure of a single InN nanorod, the In 4d core-level spectra and valence band spectra were performed to its top surface and side facets (top and bottom) of sample F. From top surface to the sidewall of InN nanorod, the change is the movement of the In 4d peak toward a lower BE with a chemical shift of 0.26 eV, as shown in Fig. 8 (b), suggesting that part of the In-N states is enriched in charge. It is believed that the electron transfer is not resulted from electron accumulation since the measured  $E_V$ - $E_F$  of side facet is slight lower than that of top surface, as shown in Fig. 8 (a). In addition, it suggests that our InN nanorods are free from charge trapping effects which may deplete the carriers, since the conduction and valence bands should bend upward at the nanorod surface due to the Fermi-level pinning [20]. Accordingly, there is no depletion space charge regions in our InN nanorods and the electrons might thus be obtained from the In metal droplets reside at the sidewall of nanorod due to the In-rich environment during growth.





В





**Figure 9.** (a) SAED patterns and (b) HRTEM image of sample F taken along [11-20] zone axis. (c) EDXS depth profile of a single InN nanorod from the apex to the substrate. (d) EDXS mapping image and spectrum measured from the region near the buffer layer.

One another feature of our nanorods is that the FHWM value of main peak in In 4d spectra at the bottom part of sidewall is broader than that at the top part of sidewall, as shown in Fig. 8 (b). The line width of photoelectron spectrum was found to increase with decreasing size of metallic nanoparticle [21]. A theoretical explanation of this effect is proposed in terms of the reduced electronic screening of the final state core hole potential [22]. This indicates that In droplets from the InN dissociation diffused from the root to the top of the nanorods. The inverted-cone-like InN nanorod with tapered sidewall would thus happen as the nanorods were lengthened. Since the substrate temperature was higher than the dissociation temperature of InN, the bottom part of the nanorods started to dissociate into In droplets and nitrogen, and thus reduced the rod diameter near the roots. In droplets were inclined to diffuse along the low-index planes and adsorbed on them, keeping reacting with the impinging nitrogen plasma flux. As a result, the In droplets at the apex of nanorod kept reacting with the impinging nitrogen plasma flux, while the roots of InN nanorods were dissociated continually. The rod diameter near the top would become larger to form the inverted-cone-like InN nanorods.

Figure 9 (a) and (b) show HRTEM image of InN nanorods for sample F and corresponding selected area electron diffraction (SAED) pattern taken from one single nanorod along the [11-20] zone axis, which confirms that the InN nanorod is single crystalline with a [0002] growth direction and is enclosed by low-index {100} planes. The HRTEM image shows that the InN nanorod has no significant extension of the dislocations or stacking faults, and the arrangement of atoms is orderly. Both the SAED pattern and the HRTEM image confirm that our InN nanorods are of excellent crystal quality. In addition, the HRTEM image shows that the lattice fringes with interplanar spacing of 0.57 and 0.31 nm corresponding to the (001) and (100) planes of wurtzite InN, in agreement with previously reported results [23-24]. Figures 9 (c) shows the EDXS depth profile of a single InN nanorod from the head region of nanorod to the substrate. It was found that In and N atoms distributed uniformly in the region of InN nanorod and the Al and Si signals is assigned to the AlN buffer layer and Si substrate, respectively. Note that the higher intensity of In signals compared to N signals reveals the In-rich growth of InN nanorods. If we zoom in the region near the buffer layer and take the EDXS mapping image, it can be observed that the CrN signals come from the NC nanoislands in the measured spectrum, as shown in Fig. 9 (d). The results of HRTEM are also consistent to the deductive inverted-cone-like shape, wurtzite hexagonal phase and high crystal quality InN nanorods on Si (111) substrate by using AlN buffers and NC nanoislands under In-rich regime.

#### **4. CONCLUSIONS**

We demonstrate the growth of InN nanorods on Si (111) substrate by using AlN buffers and/or NC nanoislands under In-rich regime. The physical and structural properties of InN nanorods can be tuned by the thickness of AlN buffers and/or the size and density of NC nanoislands. The optimal growth of InN nanorods exhibited a wurtzite hexagonal phase with high crystal quality. The InN nanorods were in inverted-cone-like shape and the possible growth mechanism was also addressed to display the controlled growth of InN nanorods on tunable nucleation structures.

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