Bandgap measurements and the peculiar splitting of E_2^H phonon modes of $\text{In}_x\text{Al}_{1-x}\text{N}$ nanowires grown by plasma assisted molecular beam epitaxy

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ABSTRACT

The dislocation free $\text{In}_x\text{Al}_{1-x}\text{N}$ nanowires (NWs) are grown on Si(111) by nitrogen plasma assisted molecular beam epitaxy (PAMBE) in the temperature regime 490 °C – 610 °C yielding In composition ranges over $0.50 \leq x \leq 0.17$. We study the optical properties of these NWs by spectroscopic ellipsometry (SE), photoluminescence (PL) and Raman spectroscopies, since they possesses minimal strain with reduced defects comparative to the planar films. The optical bandgap measurements of $\text{In}_x\text{Al}_{1-x}\text{N}$ NWs are demonstrated by SE where the absorption edges of the NW samples are evaluated irrespective of substrate transparency. A systematic Stoke shift of 0.04 – 0.27 eV with increasing x was observed when comparing the micro-photoluminescence spectra with the Tauc plot derived from SE. The micro-Raman spectra in the NWs with $x = 0.5$ showed two-mode behavior for $A_1(\text{LO})$ phonons and single mode behavior for E_2^H phonons. As for $x = 0.17$, i.e. high Al content, we observed a peculiar E_2^H phonon mode splitting. Further, we observe composition dependent frequency shifts. The 77 to 600 K micro-Raman spectroscopy measurements show that both AlN-like and InN-like modes of $A_1(\text{LO})$ and E_2^H phonons in $\text{In}_x\text{Al}_{1-x}\text{N}$ NWs are redshifted with increasing temperature, similar to that of the binary III group nitride semiconductors. These studies of the optical properties of $\text{In}_x\text{Al}_{1-x}\text{N}$ nanowires will path the way towards lasers and light-emitting diodes in the technologically important wavelength of the ultra-violet and visible range.

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INTRODUCTION

The study of group III nitride alloys is an exciting area of research owing to their enormously potential applications in electronic and optoelectronics devices such as high frequency transistors, solar cells, light emitting diodes (LEDs), laser diodes (LDs) and photodetectors¹⁻⁶. Among them, InAlN ternary alloys are attractive since they span the solar spectrum from deep UV 6.2 eV to near IR ≈ 0.7 eV by varying In (Al) content^{7,8}. Additionally, these alloys are extensively used in distributed Bragg reflectors and high electron mobility transistors^{9,10}. On the other hand, low In content ($\approx 17\%$) InAlN is an alternative for AlGaIn cladding layers in LEDs and LDs due to reasonably high refractive index contrast (4-7%) with GaN resulting in better optical blocking layer with the formation of crack free material^{9,11,12}, which is also lattice matched to GaN⁷. Despite these promising applications, $\text{In}_x\text{Al}_{1-x}\text{N}$ is least studied and understood alloy among the other ternary alloys of group III-nitrides, mainly due to the difficulty in preparation of high quality material. The large difference in the growth temperatures of AlN ($\sim 850^\circ\text{C}$) and InN ($\sim 450^\circ\text{C}$)¹³⁻¹⁵, atomic radii of In and Al and low thermal stability of Indium hinder the material quality thereby promoting severe phase segregation and compositional inhomogeneities. As a result, $\text{In}_x\text{Al}_{1-x}\text{N}$ exhibits large band bowing parameter, Stoke's shift, and unconventional phonon mode splitting in comparison with other ternary nitride alloys. For group III-nitride ternary alloys the nonlinear dependence of bandgap on the composition introduces band bowing parameter (b) which varies from one alloy to the other. For example, AlGaIn has the value of ≈ 1 eV¹⁶ and the ambiguity in earlier reported bandgap values of InN have led to the inaccurate determination of bowing parameter for InGaIn¹⁷ and InAlN alloys over the entire composition range. However, after experimental observation of accurate low bandgap value (≈ 0.7 eV) for InN^{14,18}, the most accepted bowing parameter for InGaIn and InAlN alloys has been found to be ≈ 2.8 eV^{19,20} and ≈ 5 eV²¹⁻²³, respectively.

The assignment of phonon modes for InAlN alloys consisting of atoms with large mass difference has remained elusive, and a common consensus has not arrived yet. For the case of mixed crystals ($\text{A}_x\text{B}_{1-x}\text{C}$), the earlier modified random element isodisplacement (MREI) theoretical calculations by Chang *et al.* provided a necessary condition to be satisfied to exhibit two-mode behavior of long wavelength optical phonons. The condition for two-mode behavior is either $m_A < \mu_{BC}$ or $m_B < \mu_{AC}$, whereas for single mode behavior it is $m_A > \mu_{BC}$ and $m_B > \mu_{AC}$, where m is atomic mass and μ is reduced mass²⁴. For example, reduced mass of A and C atoms is $\mu_{AC} = \mu_A \mu_C / (\mu_A + \mu_C)$. In accordance with this MREI theory, experimentally also, both single and two-mode behaviors are

observed for III-V ternary semiconducting alloys. For instance, AlGaAs and InAlAs show two-mode behavior of LO phonons^{25,26}, while AlGaN and InGaN exhibit two-mode behavior for E_2^H and single mode behavior for $A_1(LO)$ phonons²⁷⁻²⁹. On the other hand, in recent years, the two-mode behavior of both $A_1(LO)$ and E_2^H modes of InAlN alloys is ambiguously reported^{8,30-32}. Though two-mode behavior of E_2^H optical phonons was predicted theoretically, so far experimentally this has been erroneously observed which can be attributed to the experimental limitations such as lack of suitable single excitation source for entire composition range and overlapping of InAlN related phonon peaks with that of the underlying substrate or any other intermediate layers^{31,33,34}. However, recently in 2009 Kang *et al.* reported a systematic evolution of two-mode behavior of $A_1(LO)$ mode in InAlN with Al composition $0.03 \leq x \leq 0.80$, where dual behavior of E_2^H mode was not observed in their measurements³⁴. Prior to this report in 2001, Naik *et al.* misinterpreted two-mode behavior of $A_1(LO)$ to E_2^H splitting which is later corrected by Kang *et al.*³⁰ These two groups have prepared InAlN samples on sapphire substrate that exhibits Raman peaks close to the $A_1(LO)$ dual mode of InAlN which may introduce difficulty in understanding mode behavior.

In order to understand the ambiguity in phonon mode splitting of $In_xAl_{1-x}N$ alloys, careful and systematic experiments are needed to be performed by varying growth parameters such as temperature, In (Al), N flux and thickness. For this study, the formation of $In_xAl_{1-x}N$ nanowires (NWs) is pursued since they possess reduced dislocation density, large surface to volume ratio, low strain as compared to the 2D layers³⁵. $In_xAl_{1-x}N$ nanowires are grown on Si(111) substrate by PAMBE with control of substrate temperature from 490 °C to 610 °C in steps of 40 °C. Surface morphology and structural quality of the NWs are examined by AFM, FESEM, TEM and SAED. Further, to study the optical properties such as bandgap, Stoke's shift and two-mode behavior of $In_xAl_{1-x}N$ phonons spectroscopic ellipsometry, micro-photoluminescence (μ PL) and micro-Raman spectroscopy are carried out.

II. EXPERIMENTAL DETAILS

The growth experiments of $In_xAl_{1-x}N$ NWs A-D presented here are performed by Veeco 930 Gen radio frequency-plasma assisted molecular beam epitaxy (RF-PAMBE) system. Samples A, B, C, and D are grown at 490, 530, 570 and 610 °C, respectively. A combination of an ion pump and a cryo pump is used to accomplish a base pressure of 3×10^{-11} Torr and oxygen partial pressure $< 10^{-12}$ Torr, as determined by a residual gas analyzer (RGA). The Si(111) substrates were chemically

cleaned using HF:H₂O (1:3) to remove the surface oxide and rinsed with acetone, isopropyl alcohol and deionized water before loading into the MBE chamber. Later, thermally degassed in introduction chamber at 200 °C for 30mins, further cleaning was carried out in preparation chamber at 600 °C for 60 mins and in the growth chamber at 900 °C for 30 mins. While cooling the substrate down to the growth temperature phase transition of 1×1 to 7×7 is observed at ≈795 °C by *in-situ* reflection high-energy electron diffraction (RHEED) which is a clear evidence of the removal of native oxide. During growth, the nitrogen plasma source is operated with the flow rate of 1 standard cubic centimeter per minute (sccm) and RF-power of 350 W and group III metals are supplied by standard Knudsen cell with beam equivalent pressure (BEP) values of (In) 1.35×10^{-8} and (Al) 2.10×10^{-8} Torr. The corresponding chamber pressure is $\approx 1.5 \times 10^{-5}$ Torr. Atomic force microscope and Field Emission Scanning Electron Microscopy (FESEM) are employed to characterize the surface morphologies of the formed In_xAl_{1-x}N NWs. The thickness of the samples is measured by stylus step and cross sectional view of FESEM images which is found to be ≈200 nm. Transmission Electron Microscopy (TEM) studies are carried out using Titan with electron beam energy of 300 keV. The optical constants and bandgap of samples are obtained using *ex-situ* Horiba-HJ UVISSEL variable angle spectroscopic ellipsometry (SE) performed in reflection geometry while the angle of incidence is ≈65°. The band edge emission and evolution of phonon modes for grown samples are obtained using Aramis room temperature μ PL and micro-Raman spectroscopy with excitation line as He-Cd laser of 325 nm with power of 200 mw. Thorlab LMU-40×-NUV having numerical aperture (NA) of 0.5 is used as objective lens. To probe deep UV emission of NWs, Varian spectrometer with Xenon flash lamp as excitation source is used. Temperature dependent micro-Raman measurements are carried out in the range 77 to 600 K.

III. RESULTS AND DISCUSSION

To investigate the root mean square (rms) roughness, surface morphology and thickness of samples, AFM and FESEM are carried out. Fig 1(a-d) show the AFM surface topography scans and the corresponding insets (right and left) show the FESEM images (plan and cross sectional view) for In_xAl_{1-x}N samples A-D grown at 490, 530, 570 and 610 °C. The AFM scans and the FESEM insets represent the nanowire surface morphology. The surface roughness values acquired from AFM scans of $5 \times 5 \mu\text{m}^2$ area are measured to be ≈10.7, 8.5, 3.2 and 16 nm for samples A-D, respectively. The density of nanowires is calculated from the plan view FESEM images which are found to be

10^{10} , 1.8×10^{11} , 8×10^{10} , $2 \times 10^{10} \text{ cm}^{-2}$ for samples A-D, respectively. The average diameter of NW is $\approx 25 \text{ nm}$ for samples A-C and it is $\approx 65 \text{ nm}$ for sample D. From the cross sectional FESEM images, the length of the nanowires determined to be $\approx 200 \text{ nm}$. The larger NW diameter and relatively low density for sample D is due to the higher lateral mobility of Al adatoms at higher growth temperature. All the samples consist of tapered nanowires. This tapering takes place during the growth of the nanowires owing to the shadow effect^{36,37}. Thus, irrespective of the growth temperature all samples exhibit tapered nanowire morphology with varying NW density and rms surface roughness.

In order to inquire the crystalline structure and quality of the $\text{In}_x\text{Al}_{1-x}\text{N}$ NWs, TEM measurements are carried out and the results are shown in Fig 2. Fig 2 (a) shows bright field TEM images of a typical $\text{In}_x\text{Al}_{1-x}\text{N}$ NWs of sample C which clearly depicts that the NWs are tapered with increasing diameter from bottom ($\approx 25 \text{ nm}$) to top ($\approx 50 \text{ nm}$) while the length is $\approx 200 \text{ nm}$. Fig 2(b) shows the high-resolution image of the stack of c-planes which is acquired from top part of $\text{In}_x\text{Al}_{1-x}\text{N}$ NW. Fig 2(c) shows the selected area electron diffraction (SAED) pattern for bright field image Fig 2(a) taken along the $\langle 10\bar{1}0 \rangle$ zone axis infers single crystalline wurtzite $\text{In}_x\text{Al}_{1-x}\text{N}$ NWs that grow along the $\langle 0002 \rangle$ direction. The absence of dislocation lines in the NWs depicts good structural quality of the formed $\text{In}_x\text{Al}_{1-x}\text{N}$ NWs. However, the observed contours/fringes are due to the thickness variation and slight bend that accommodated along the NW³⁸. The absence of fringes at the top half of the NW is resulting from the constant thickness. Thus, the $\text{In}_x\text{Al}_{1-x}\text{N}$ NWs that grown on Si(111) substrates are single crystalline c-oriented and dislocation free exhibiting wurtzite crystal structure.

The optical constants of samples A-D are acquired using *ex-situ* Horiba-HJ UVISEL spectroscopic ellipsometry (SE). Although, all samples exhibit nanowire morphology as shown in Fig 1(a-d), the surface rms roughness values are less than 20 nm . When the rms roughness of the surface is $< \lambda/10$, λ is wavelength, such surface can be treated as uniform layer for SE studies³⁹. Thus, the SE measurements are feasible for $\text{In}_x\text{Al}_{1-x}\text{N}$ NW samples used in the present study. In order to obtain energy dependent refractive index (n) and extinction coefficient (k) values, the following equations (1) and (2) are used.

$$\rho = \frac{r_p}{r_s} = \tan \Psi \exp(i\Delta) \quad (1)$$

$$(n + ik)^2 = \sin^2 \theta \left[1 + \tan^2 \theta \left(\frac{1 - \rho}{1 + \rho} \right)^2 \right] \quad (2)$$

Where Ψ and Δ are standard ellipsometric parameters respectively indicate the amplitude ratio and phase difference between p and s-polarizations. These parameters are related to the complex ratio ($\rho = r_p/r_s$) of the Fresnel reflection coefficients r_p and r_s for light polarized parallel (p-polarization) and perpendicular (s-polarization) to the plane of incidence as described in Equation (1). The parameters n , k and θ in Equation (2) are refractive index, extinction coefficient and angle of incidence (65°), respectively^{39,40}. Fig 3(a-d) show energy dependent Ψ , Δ , n and k plots. Here refractive index values are presented only in the transparent region ($E \ll E_g$) of the samples⁴¹. As shown in Fig 3(c) the energy dependent refractive index decreases by increasing the growth temperature from sample A to D. The observed noticeable change for samples A and D could be due to the reasonably large variation of growth temperature. Additionally, deep kinks which are shown by arrows in Fig 3(d) also shift to higher energy as increasing the growth temperature for samples A-D. These variations in energy dependent refractive index and extinction coefficient can be attributed to the growth temperature dependent In composition in the respective samples.

Further, to investigate the optical band gap values of Samples A-D room temperature (RT) μ PL and spectroscopic ellipsometry (SE) are carried out. Fig 4 (a-d) show PL spectra (Y-axis) and SE absorption squared Tauc plots (alternate Y-axis) for $\text{In}_x\text{Al}_{1-x}\text{N}$ samples A-D. The band edge emission values obtained by μ PL for samples A-C are 2.16, 2.50 and 3.19 eV, respectively. Owing to the limitations of μ PL setup we measure the band to band transition as ≈ 4.48 eV for sample D in the deep UV region using Varian spectrometer having Xenon Flash lamp as excitation source. As represented by vertical down arrows, Fig 4 (a-c) show a shoulder at higher energy of PL spectra with increasing intensity from samples A to C, which could be due to the inhomogeneity of In incorporation in $\text{In}_x\text{Al}_{1-x}\text{N}$ crystal lattice. On the other hand, optical transmission measurements can be employed to attain the band gap of a material which is solely limited to the samples that grown on transparent substrates. However, irrespective of the transparency of substrate in the UV-Visible region, the band gap information for $\text{In}_x\text{Al}_{1-x}\text{N}$ NWs/Si can be accomplished by calculating optical absorption coefficient (α) using its relation with extinction coefficient k and wavelength $\alpha = 4\pi k/\lambda$. Here energy dependent extinction coefficient k is previously obtained by means of spectroscopic ellipsometry (SE) as described in Fig 3. For direct optical transitions, the relationship between

absorption coefficient α and the photon energy E can be expressed as $\alpha E = A(E-E_g)^{1/2}$, where A is constant, and E is incident photon energy. The direct optical band gap (E_g) is determined by the standard procedure of extrapolating the linear part of the squared absorption coefficient times Energy of incident photon to its zero value. Thus, the measured optical absorption edge values for samples A-D are 2.43, 2.58, 3.24 and 4.52 eV, respectively. These values are higher than the respective observed PL band edge emission due to the Stoke's shift that is associated with localization of the carriers just below the conduction band minimum^{42,43}. The samples A and B with higher In content exhibit the shoulders at ≈ 2.00 eV as shown in Fig 4(a and b), which is consequence of the free carrier absorption⁴⁴. Samples C and D show a small linear region before the absorption edge which is due to the Urbach tail states⁴⁵. For samples A-D obtained Stoke's shift values are 0.27, 0.08, 0.05 and 0.04 eV which are much less than the reported values⁸. The value of minimal Stoke's shift decreases with PL emission energy for samples A-D.

The estimation of Indium composition for samples A-D is accomplished using the nonlinear dependence of band-gap on the composition of $\text{In}_x\text{Al}_{1-x}\text{N}$ in terms of Vegard's law

$$E_g^{\text{InAlN}} = xE_g^{\text{InN}} + (1-x)E_g^{\text{AlN}} - x(1-x)b \quad (3)$$

where b is the bowing parameter that depicts the deviation from a linear interpolation of band gap values between E_g^{InN} and E_g^{AlN} , here reported bowing parameter ~ 5 eV is used²¹⁻²³. E_g^{InN} and E_g^{AlN} are the band gap values of intrinsic InN, and AlN^{46,47} and E_g^{InAlN} is the value of the emission energy deduced from the μPL data analysis. The values of In composition (x) are thus estimated to be 0.48, 0.43, 0.33 and 0.17 for samples A-D, respectively. As expected, the PL band edge and Absorption edge values exhibit the blue shift with decreasing In composition. We notice that the observed Stoke's shift not only decreases with decreasing indium composition but also decreases with increasing PL emission energy for samples A-D.

In order to address the ambiguity in understanding the dual mode nature of $A_1(\text{LO})$ and E_2^{H} phonons, micro-Raman spectroscopy measurements are carried out in back scattering geometry on $\text{In}_x\text{Al}_{1-x}\text{N}$ NW samples A-D having composition $0.50 \leq x \leq 0.17$ and the results are shown in Fig 5. In order to avoid any overlapping of substrate peaks with $A_1(\text{LO})$ and E_2^{H} modes of $\text{In}_x\text{Al}_{1-x}\text{N}$ having In composition $0.50 \leq x \leq 0.17$, in present study samples are grown on Si(111) substrates. In Raman phonon mode evolution, AlN-like and InN-like $A_1(\text{LO})$ two-mode behavior is observed for all the

samples and peak at 521 cm^{-1} is represented by asterisk stems from Si substrate as shown in Fig 5 (A-D). In Fig 5d, obtained micro-Raman signal for $\text{In}_x\text{Al}_{1-x}\text{N}$ phonon modes is enlarged by 30 times so as to observe any change in mode behavior. This weak signal is consequence of the reduced resonant excitation effect³⁰ owing to the reason that the band gap (4.48 eV) of $\text{In}_x\text{Al}_{1-x}\text{N}$ with $x=0.17$ is larger than the laser excitation line of 3.8 eV used in this study. The extremely low intense broad peak at higher frequency is deconvoluted for guiding the eyes, and attributed to InN-like and AlN-like $A_1(\text{LO})$ two-mode behavior as shown in Fig 5d. In addition to this, we observe a clear splitting of E_2^{H} mode into InN- and AlN-like two-modes for sample D consisting of low In ($x=0.17$) whereas In-rich $\text{In}_x\text{Al}_{1-x}\text{N}$ samples (A-C) show single mode behavior for E_2^{H} phonons and two-mode behavior for $A_1(\text{LO})$ phonons. The splitting of E_2^{H} mode is in good agreement with the MREI theoretical model calculations reported by Grille and coworkers in 2000³³. The peak positions of InN-like $A_1(\text{LO})$, AlN-like $A_1(\text{LO})$ and E_2^{H} phonon modes are listed in Table I for samples A-D. It has been observed that with decreasing In composition the peak positions of AlN-like and InN-like $A_1(\text{LO})$ and E_2^{H} modes shift to high frequency.

To understand the effect of temperature on AlN-like and InN-like phonon mode behavior in $\text{In}_x\text{Al}_{1-x}\text{N}$ NWs, temperature dependent μ -Raman spectroscopy measurements are carried out over the temperature range of 77 to 600 K for samples B and D. Since the grown $\text{In}_x\text{Al}_{1-x}\text{N}$ alloys have nanowire morphology, the effect of substrate strain on over grown layer is presumably low. The samples B and D are chosen for temperature dependent measurements as they exhibit splitting for different phonons $A_1(\text{LO})$ and E_2^{H} as shown in Fig 5. Fig 6 (a) and (b) show the temperature dependent μ -Raman spectra obtained at four different temperatures for samples B and D, respectively. The phonon modes in Fig 6(a) and (b) are red shifted with increasing temperature due to the thermal expansion of the lattice. Notably, temperature dependent studies also exhibit clear splitting of $A_1(\text{LO})$ mode for sample B and splitting of both E_2^{H} and $A_1(\text{LO})$ modes for low In content sample D. However, signal to noise ratio is remarkably low for sample D as discussed in Fig 5, there is a clear evidence of two-mode behavior for E_2^{H} and $A_1(\text{LO})$ phonons in the spectra obtained at low temperatures (77-200 K). Thus, the signal for $A_1(\text{LO})$ splitting is clearly visible for sample B and similarly the AlN-like and InN-like two-mode behavior for E_2^{H} phonon modes are observed for sample D even up to 600 K. Further, Fig 6(c and d) show the experimental data points from the temperature dependent frequency shifts for AlN-like and InN-like $A_1(\text{LO})$ modes in sample B and AlN-like and InN-like E_2^{H} phonon modes for sample D. These data points are fitted using the

equation (4) which is a proposed empirical relation for diamond⁴⁸ and later on used for group III
nitride materials^{49,50}.

$$\omega(T) = \omega_0 - \frac{P}{\exp(Q\hbar\omega_0 / k_B T) - 1} \quad (4)$$

where ω_0 , P and Q are fitting parameters and ω_0 represents the phonon mode frequency at 0K. As shown in Fig 6(c and d), it has been observed that this empirical relation fits the temperature dependent frequency shifts for $\text{In}_x\text{Al}_{1-x}\text{N}$ phonon dual modes as well. The fitting parameters are listed in Table II. This red shifted modes with increasing temperature for low In content sample D further confirms that the existence of dual mode behavior for E_2^H phonons in addition to the $A_1(\text{LO})$ phonons. Thus, the two-mode behavior of $A_1(\text{LO})$ and E_2^H phonons in $\text{In}_x\text{Al}_{1-x}\text{N}$ NWs are redshifted with increasing temperature. This redshift is similar to that of the binary III group nitride semiconductors^{49,50}.

IV. CONCLUSIONS

In summary, vertically aligned $\text{In}_x\text{Al}_{1-x}\text{N}$ NWs are grown on Si(111) substrates by plasma assisted MBE which are shown to be dislocation free NWs having wurtzite crystal structure characterized by TEM and SAED pattern. The optical bandgap and splitting of phonon modes of $\text{In}_x\text{Al}_{1-x}\text{N}$ NWs grown on Si(111) substrates are studied. Energy dependent optical constants and optical bandgap are measured by spectroscopic ellipsometry (SE). We showed that the absorption edge of grown layer can be measured independent of substrate transparency using SE. The composition of In for sample A-D is estimated to be $0.50 \leq x \leq 0.17$ using PL band edge emission values in conjunction with the SE absorption edge, which decreases with increasing growth temperature. The blue shift in the optical absorption edge with decreasing In incorporation is found to be in accordance with the trend of PL band edge emission values. The observed minimal Stoke's shift, attributed to In inhomogeneity induced localized carrier states, that decreases with blue shifted PL band edge emission as lowering In content in $\text{In}_x\text{Al}_{1-x}\text{N}$ NWs. We experimentally demonstrate the splitting of E_2^H phonon mode for low In content sample that is in good agreement with earlier theoretical calculations. The single mode for E_2^H and two-mode behavior for $A_1(\text{LO})$ phonons are observed for $\text{In}_x\text{Al}_{1-x}\text{N}$ NWs with high Indium incorporation. Moreover, the frequency shifts for $A_1(\text{LO})$ and E_2^H phonons have proven to be composition dependent. In temperature dependent micro-

275 Raman measurements 0 K phonon energies are determined for these phonon modes which exhibit
 276 redshift with increasing temperature. Thus, the behavior of split phonon modes of the $\text{In}_x\text{Al}_{1-x}\text{N}$
 277 nanowires is similar to that of the planar binary group-III nitride compound semiconductor.

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Fig 1(a-d) show the AFM surface morphology images. The corresponding right and left insets represent the top view and cross sectional FESEM images for $\text{In}_x\text{Al}_{1-x}\text{N}$ nanowire samples A-D which are grown at 490, 530, 570 and 610 °C. The gradient color bars on each image represent the height contrast.

FIG 2 (a) The bright field TEM image of InAlN NWs (sample C) along $[11\bar{2}0]$ zone axis; (b) the high magnification dislocation-free $\text{In}_x\text{Al}_{1-x}\text{N}$ lattice; and (c) the SAED pattern obtained on $\text{In}_x\text{Al}_{1-x}\text{N}$ NW along $\langle 10\bar{1}0 \rangle$ zone axis.

FIG 3(a-d) depict the energy dependent plots for Ψ , Δ , refractive index (n) and extinction coefficient (k), respectively, as obtained from spectroscopic ellipsometry (SE).

FIG 4. The μPL band edge emission spectra (a-c), and Xenon-lamp based fluorescence spectrum (d), with SE based absorption-squared (Tauc) plots for $\text{In}_x\text{Al}_{1-x}\text{N}$ samples A-D, which are grown at 490, 530, 570 and 610 $^\circ\text{C}$, respectively.

FIG 5(a-d) show room temperature micro-Raman spectra for $\text{In}_x\text{Al}_{1-x}\text{N}$ samples A-D with In composition $0.50 \leq x \leq 0.17$ grown at 490, 530, 570 and 610 °C, respectively. The deconvoluted peaks in Fig 5(d) are guide to the eyes. The peak represented by asterisk at 521 cm^{-1} is from Si substrate.

FIG 6(a) and (b) show the temperature dependent μ -Raman spectra while (c) and (d) represent the temperature dependent frequency shifts of AIN-like and InN-like phonon modes obtained for samples B and D, respectively. The dashed/dotted lines are fit to the experimental data points (open symbols) using equation (4).

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454 Table I. Experimental parameters of InAlN samples A-D: growth temperature, PL peak energy,
455 absorption edge, Stoke's shift, indium composition and Raman shift of phonon modes.

Sample	Growth Temperature (°C)	PL (eV)	Absorption edge (eV)	Stoke's shift (eV)	Indium composition x	AlN-like $A_1(\text{LO})$ ± 0.5 (cm^{-1})	InN-like $A_1(\text{LO})$ ± 0.5 (cm^{-1})	E_2^{H} ± 0.5 (cm^{-1})
A	490	2.16	2.43	0.27	0.50	803.7	686.1	580
B	530	2.5	2.58	0.08	0.44	816.7	699.1	592.3
C	570	3.19	3.24	0.05	0.34	824.6	706.9	600.4
D	610	4.48	4.52	0.04	0.17	~835.0	~736.0	643.2 (AlN-like) 606.2 (InN-like)

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462 Table II. The obtained fitting parameters ω_0 , P and Q for the experimental data points in Fig 6.

Fitting Parameters	Sample B		Sample D	
	AlN-like $A_1(\text{LO})$	InN-like $A_1(\text{LO})$	AlN-like E_2^{H}	InN-like E_2^{H}
ω_0 (cm^{-1})	818.1	708.2	650.2	613
P (cm^{-1})	26.66	14.03	12.60	13.26
Q	0.55	0.33	0.55	0.74

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Energy (eV)