Due to their unique physical properties, semiconductor nanowires (NWs) have attracted enormous attention as promising active materials for future electronic and optoelectronic devices. In particular, ternary alloy NWs have been demonstrated to create a uniform stoichiometric system that can be synthesized with facile growth methods without introducing complex heterojunctions. They also offer a great flexibility of tunable band gap by changing the relative composition of their alloys such as In$_x$Ga$_{1-x}$N (1.12–3.43 eV), Al$_x$Ga$_{1-x}$N (3.4–6.2 eV), and Cd$_x$Se$_{1-x}$ (1.73–2.44 eV), which is advantageous for various device structures. Recently, indium gallium arsenide (In$_x$Ga$_{1-x}$As) NWs have become of great interest due to their variable band gap, spanning from the near-infrared to the infrared region (0.34–1.42 eV). In addition to the benefits arising from this tunable band gap in photovoltaics, the electrical properties of In$_x$Ga$_{1-x}$As NWs could also be modulated as needed in lowering the off-state leakage current while maintaining a high electron mobility in electronic devices. Despite the success in the synthesis of completely tunable compositions, important relationships among the electrical, optical, and structural properties and chemical composition in this NW material system still have not been well studied until now. Understanding all of this would be essential to design and implement In$_x$Ga$_{1-x}$As NWs for more advanced technological applications.

In this study, we present the synthesis of composition-tunable In$_x$Ga$_{1-x}$As NWs by a simple two-step growth method and correlate the electrical, optical, and structural properties with the NW stoichiometry. The experimental results illustrate a well-controlled, uniform growth of single-crystalline NWs with a smooth surface and low defect concentration for all stoichiometric compositions. X-ray diffraction (XRD) and UV–vis optical absorption measurements confirm the complete composition tuning and band gap engineering over the entire range for the material system. More importantly, the
electrical properties of In$_x$Ga$_{1-x}$As NWs, when configured as back-gated field-effect transistors (FETs), reveal composition-dependent behaviors. Specifically, decreasing the In content of NWs would increase the band gap and $I_{ON}/I_{OFF}$ ratio, but this is attained at the cost of electron mobility degradation. All of this suggests that a careful device design consideration manipulating the ternary NW composition and electrical properties is required to achieve optimal device performances.

**RESULTS AND DISCUSSION**

The In$_x$Ga$_{1-x}$As NWs used in this study were synthesized by a two-step catalytic chemical vapor deposition (CVD) method previously reported.$^{19}$ In order to produce the complete composition-tunable NWs, different ratios of InAs and GaAs source powder were used, e.g., InAs:GaAs = 1:1, 1:3, 1:9, and 1:14 in weight ratio. This mixture ratio predetermined the available vapor pressure of In and Ga precursors under a specific source temperature; therefore, it has a significant influence on the final composition of the grown ternary NWs. As shown in Figure 1a, the In concentration of as-grown NWs decreases with the In content in a predetermined mixture, while the composition of NWs was determined by energy-dispersive X-ray spectroscopy (EDS). For example, for each mixture ratio, around 30 NWs were randomly chosen as candidates for the EDS point scan in the NW body to statistically determine the composition (see Supporting Information Figure S1 for representative EDS spectra). The 95% confidence interval for the average composition is also depicted by the error bar for each mixture ratio, demonstrating the tight control over the NW stoichiometry with this simple powder mixing technique. Notably, this tunability covers almost the entire composition range of In$_x$Ga$_{1-x}$As (0.2 < $x$ < 0.75) and could be further refined by tuning the powder mixture ratio. Furthermore, during the growth, a two-step method is utilized to optimize the NW growth yield and morphology. As previously reported, this method can significantly reduce the kinked morphology and surface coating in In-rich InGaAs NWs, while in this study, by carefully adjusting the growth parameters, such as nucleation temperature, growth temperature, and growth time, as-grown NWs can have the desirable morphology in all composition ranges. As demonstrated in Figure 1b–e, In$_{0.64}$Ga$_{0.36}$As, In$_{0.45}$Ga$_{0.55}$As, In$_{0.3}$Ga$_{0.7}$As, and In$_{0.22}$Ga$_{0.78}$As NWs all exhibit a smooth surface and nontapered characteristics along the entire NW length, favoring subsequent device fabrication and performance. Also, the NW density of each composition range is sufficient (>10 $\mu$m$^{-2}$) for large-scale assembly (see Supporting Information Figure S2) by the contact printing method and is promising to produce spatially composition-graded InGaAs NW arrays. More importantly, the diameter statistics of NWs in different composition domains (see Supporting Information Figure S3) have demonstrated a tight control over the NW diameter. By summarizing diameters of 100 NWs for each composition range, we obtained average diameters ranging from 21 to 34 nm (corresponding to plus or minus one standard deviation) for all as-grown NWs utilizing the same catalyst dimensions. The composition-independent diameter here can further eliminate the possibility of excess NW lateral growth under certain stoichiometries and can prepare a consistent platform for a subsequent comparison study among different NW properties. This again highlights the simplicity and potency of our two-step method for the synthesis of uniform, completely composition tunable NWs.

To further shed light on the NW crystal structure, as depicted in Figure 2a, we performed XRD analysis for nine different NW compositions obtained with further control in the NW growth condition in each source powder mixture ratio. The XRD patterns indicate that the grown NWs belong to the cubic zinc blende (ZB) structure, including our pure GaAs and InAs NWs. The peaks correspond to the (111) plane shifting from $2\theta = 25.7^\circ$ (InAs NWs) to $2\theta = 27.1^\circ$ (GaAs NWs) with the plots ordered with decreasing In concentration in between, suggesting the NWs are not phase separated. The full-width at half-maximum (FWHM) of the (111) peaks is $\sim 0.45^\circ$ and $0.42^\circ$ for the InAs and GaAs NWs, respectively, while the FWHM values of the (111) peaks for the ternary In$_x$Ga$_{1-x}$As NWs are close to $\sim 0.5^\circ$, except for the In$_{0.22}$Ga$_{0.78}$As NWs of $\sim 0.73^\circ$, which can
be attributed to the nonoptimized growth conditions in this particular NW stoichiometry. Compared with thin-film In$_x$Ga$_{1-x}$As materials, the FWHM of NWs is higher, which could arise from the distribution of bond lengths for a random alloy and size-dependent broadening effect. Figure 2b shows the lattice constant determined from the XRD pattern as a function of In concentration. This result (red dots) agrees with Vegard’s law approximation in which a near-linear relationship is established between the lattice spacing and NW alloy composition. As the In concentration of NWs increases, the lattice constant increases almost linearly.

In order to demonstrate the detailed structural information of the NW body, high-resolution transmission electron microscopy (HRTEM) was performed for NW samples in different composition domains. As shown in Figure 2c–f, all four NWs exhibit single-crystalline ZB structure. No significant amount of stacking faults or twin-plane polytypic defects were found in these samples; however, the NW growth directions vary among the characterized NWs as presented in Figure 2c–f with the dominant directions in both (111) and (311). Since the NWs are grown randomly on the amorphous substrate, obtaining a mixed growth orientation is not unexpected here. More importantly, the lattice constants concluded from HRTEM images agree well with the results extrapolated from XRD peaks using Bragg’s law (see Supporting Information Table S1). Although the lattice constant of In$_{0.28}$Ga$_{0.72}$As nano-whiskers is reported as ~5.76 Å, slightly lower than that in our In$_{0.3}$Ga$_{0.7}$As NWs, it can be due to the different strain-induced mechanism of the underlying substrates here. Notably, the measurement accuracy in determining lattice constants can be further improved utilizing high-resolution XRD or collecting more HRTEM data in the future; in any case, this highly correlated result suggests that our growth scheme has excellent control over the crystal structure of ternary In$_x$Ga$_{1-x}$As NWs.

As one of the most important features in ternary NWs, the tunable band gap could be typically determined by photoluminescence (PL) emission or optical absorption. In this study, we have performed
adapt a de
discrete thorough statistical studies to quantify the
technology, and this enable In
value here suggests that the composition-tunable
photodetectors or solar cells. Moreover, most of the
any phase segregation.
study the electrical behaviors of NW with di
certified NW field-effect
involving wavelengths of 800–1900 nm, such as
particles.28 On another hand, by
the band gap energy for each stoichiometric NW sample
energy as a function of In composition, a red line is
extrapolation of the absorption edge to zero absorbance. The absorption onset value red-shifts when the
In concentration increases (data not shown). It is also
noted that the resulting band gap energies follow the
same trend as two-dimensional In,Ga,As materials.27
As the In concentration increases, the band gap
energy falls from ∼1.54 (pure GaAs NWs) to ∼0.65 eV
(In,Ga,As NWs); therefore, this manipulation can enable In,Ga,As NWs to be used in applications
involving wavelengths of 800–1900 nm, such as
photodetectors or solar cells. Moreover, most of the
band gap values determined here are higher than the
bulk values in the literature, which could be attributed
to the quantum confinement effect of NWs, leading
to larger band gap energies, similar to the previously
reported studies of In,Ga,As nanocones and nanowires.

On another hand, by fitting the absorption
energy as a function of In composition, a red line is
obtained that is similar to the one proposed by Goetz
et al. with the bowing parameter (b = −0.475 eV).27
Typically, this bowing parameter is a measure of crystal
field fluctuation29 or nonlinear effect30 arising from
the anisotropic binding, and this b value is found to
be a lot smaller than those of other reported NW material systems;31–33 as a result, this relatively small
value here suggests that the composition-tunable
In,Ga,As NW system has a good miscibility without
any phase segregation.

In addition to the band gap energies, in order to fully
study the electrical behaviors of NW with different
chemical stoichiometry, back-gated NW field-effect
transistors were fabricated with the same configuration
as previously reported.19 We have performed
several thorough statistical studies to quantify the
difference among these NW samples. Specifically, we
adapt a definition of I_{ON}/I_{OFF} ratio ≈ 10^3 as the criterion
to describe the NW devices being completely turned
off or delivering no current in their “OFF” state. Again,
this criterion is chosen on the basis of the typical I_{ON}/I_{OFF} ratio (∼10^3) reported in state-of-the-art InAs NW
devices, and again the main motivation to develop this
ternary In,Ga,As NW material system is to alleviate
the small I_{ON}/I_{OFF} ratio in the small band gap InAs NWs
without sacrificing electron mobility.34,35 In this case,
the so-called “turn-off ratio” is calculated as the number
of turn-off devices divided by the total number of
∼100 devices measured in each NW stoichiometry. As
shown in Figure 4a, the turn-off ratio is the highest for
the p-type GaAs NW-FET (red color) and then decreases
gradually as the In concentration increases. This reduc-
tion probably corresponds to the decreased band gap
of In-rich NWs, which can lead to a significant amount

![Figure 3](image-url) (text continues...)
METHODS

**Nanowire Synthesis.** To synthesize In$_x$Ga$_{1-x}$As NWs with different chemical stoichiometry, InAs and GaAs source powder in various mixture ratios (1:1, 1:3, 1:9, and 1:14 in wt %) were loaded in a boron nitride crucible. The growth substrates were SiO$_2$/Si wafer pieces with 50 nm thick thermal oxide on the top. The Au thin films of 0.5 nm thickness were used as the catalysts for all NW growth. Considering the different evaporation velocity of source powders, different source temperatures were used for each mixture ratio. For example, for a 1:1 mixture, 800 °C was used, while for a 1:9 mixture, 850 °C was used for the source temperature. The growth temperatures, including both nucleation and growth steps, were adjusted carefully as well to produce the highly crystalline NWs. For example, for the 1:3 mixture, the nucleation temperature was set at 620 °C and growth temperature at 550 °C while for the 1:14 mixture, the temperatures were 650 and 580 °C, respectively.

**Material Characterizations.** All material characterizations were performed on the NWs obtained in the 0–1 cm region of growth substrates in order to establish a consistent study on the chemical stoichiometry. Specifically, the XRD characterization was carried out in a Philips powder diffractometer using Cu Kα radiation. The scanning step was set to be 0.001°, and each step time was 1 s in order to increase the accuracy of the measurement. To resolve the lattice constant, we first obtained the position of the (111) peak from the XRD pattern, which is essentially the value of 2θ. Then we applied Bragg’s law: nλ = 2d_{hkl} sin θ with λ = 1.54 Å. From the d$_{hkl}$ value that we calculated, the lattice constant could be calculated by d times $\sqrt{h^2 + k^2 + l^2}$. The SEM images were taken from an FEI/Philips XL30 scanning electron microscope, and TEM images were taken using a Philips CM-20 transmission electron microscope. HRTEM images were observed with a JEOL 2100F transmission electron microscope. To prepare the TEM samples, NWs were first harvested in high-purity ethanol solution and then drop-casted on a Cu grid. The UV–vis optical absorption measurement was performed in an ultraviolet–visible–near infrared spectrophotometer with an integrating sphere (PE Lamda 750).

**Supporting Information Available:** Comparison of NW lattice constants obtained from HRTEM versus XRD; SEM images of the NWs with different chemical compositions; representative EDS spectra within the NW body; NW diameter statistics; selected UV–vis absorption of In$_{0.45}$Ga$_{0.55}$As NW; and electrical transfer characteristics of NW FETs. These materials are available free of charge via the Internet at http://pubs.acs.org.

REFERENCES AND NOTES

3. Duan, X. F.; Huang, Y.; Cui, Y.; Wang, J. F.; Lieber, C. M. Indium Phosphide Nanowires as Building Blocks for


