Supporting Information

GaAsSe Ternary Alloy Nanowires for Enhanced Photoconductivity

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Experimental Details

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Experimental Details

The structure and composition of the products were analyzed by scanning electron microscopy (SEM, Hitachi S-4700), field-emission transmission electron microscopy (FETEM, FEI TECNAI G², 200 kV), high-voltage TEM (Jeol JEM ARM 1300S, 1.25 MV), and energy-dispersive X-ray fluorescence spectroscopy (EDX). Fast Fourier-transform (FFT) images were generated by the inversion of the TEM images using Digital Micrograph GMS1.4 software (Gatan Inc.). A tilt holder (Dual Orientation Tomography Holder 927, Gatan Co.) was used for the TEM measurements. High-resolution XRD patterns were obtained using the 9B and 3D beam lines of the Pohang Light Source (PLS) with monochromatic radiation. X-ray photoelectron spectroscopy (XPS) measurements were performed using the 8A1 beam line of the PLS. The UV-visible absorption spectra of the samples were recorded using a spectrometer (Cary 5000, Agilent Tech.). Photoluminescence measurements were carried out at 8 K using a He-Cd laser (λ = 325 nm) or Ar ion laser (λ = 514.5 nm) as the excitation source.

The Raman spectra of individual NWs were measured with a homemade micro-Raman system at room temperature. The spectral resolution is about 1 cm⁻¹. Raman scattering signals were obtained in a back-scattering configuration using a 100× objective (NA 0.9) and an Ar ion laser with a wavelength of 514.5 nm. The laser spot size was approximately 1 μm, which, in combination with the imaging capabilities of the microscope, allowed for routine single-wire identification. Raman spectrum represents the total average of the spectrum excited from the corresponding volume of NWs. A laser power below 0.5 mW was used to avoid heating effects.

Photolithography was used to deposit Ti (20 nm)/Au (80 nm) electrodes on a silicon substrate with a 300-nm-thick thermally grown silicon oxide layer by sputtering using a patterned mask. The Ti film underneath the Au film was used to improve the adhesion of Au
films to the substrate. The distance between the electrodes was about 2 µm. The NWs were
dispersed in isopropyl alcohol (IPA) and the solution (0.5 µL) was dropped between the
patterned electrodes. The NWs were aligned using the dielectrophoresis (DEP) force, which
maintained their position after the solution dried out. A Pt top electrode was deposited on the
contact position of the NW using a focused ion beam (FIB). The Pt deposition was limited to
the contact regions to avoid possible contamination over the entire NW. The distance between
the Pt electrode pads was 5-15 µm. The thickness of the Pt films was 80-100 nm. We measured
the $I-V$ curves of the Au-GaAsSe NW-Au photodetectors on a probe station with parametric
test equipment (Agilent E5270A). The Au electrode pads were in direct contact with the Au
probe tips (diameter = 5 µm). A light emitting diode (Mightex System LEDs, 365 nm, max 650
mW corresponding to 60 mW cm$^{-2}$) was used as the light source.

Field effect transistors were fabricated by following procedure. Photolithography was used
to deposit Cr (20 nm)/Au (130 nm) electrodes on a silicon substrate with a 300-nm-thick
thermally grown silicon oxide layer, by sputtering using a patterned mask. The highly B-doped
Si ($p$-Si) substrate (resistivity < 0.005 Ω·cm) was used for a back gate. The NWs were dispersed
by applying a drop of its IPA solution onto a patterned Si substrate. The samples were then
coated with a layer of poly(methyl methacrylate) (PMMA, A4, Microchem. Co.), and the
electrode patterns were created in an electron-beam lithography process. After developing, the
samples were loaded in an electron beam evaporator, and 20 nm of Cr was deposited, followed
by 130 nm of Au. After the lift-off process, the samples were usually annealed to remove the
fabrication residues. The electrical transport properties were measured in a commercial probe
station (WWIT Co. VPX-10) with the Au probe tip. The gate effect was measured at ambient
conditions (300 K), and the potential was applied using the Au probe tip.
### Table S1. Comparison of photosensitivity, responsivity, and detectivity of GaAs0.7Se0.3 NW photodetector with previous reported work on GaAs, GaAsSb, and InAs NWs.

| Materials            | I_{dark} | I_{light} | Photosensitivity$^b$ | Responsivity (A W$^{-1}$)$^c$ | Detectivity (Jones)$^d$ | Ref.$^e$ |
|----------------------|----------|-----------|----------------------|-------------------------------|------------------------|----------|
| GaAs                 | 0.03 nA at 3 V | 30 nA | 1000$^a$          | 0.030                        | --                     | [11] S1  |
| GaAs                 | 1 nA at -5 V  | 50 nA | 50                 | --                           | --                     | S2       |
| GaAs/AlGaAs core/shell | 10$^{-2}$ nA at 2 V | 1 nA | 1000$^a$          | 0.57                         | 7.20 × 10$^{10}$      | [15] S3  |
| GaAs                 | 7.18×10$^{-4}$ pA | 18 pA | 2493               | 25                           | 9.04 × 10$^{12}$      | [43] S4  |
| GaAs                 | 4 nA at 5 V   | 11 nA | 2.8$^e$            | 1.45×10$^5$                  | 1.48 × 10$^{14}$      | [18] S5  |
| GaAsSb               | 90 nA at -3 V | 3 μA | 33.3               | 1463                         |                       | S6       |
| InAs                 | 2 nA at -2 V  | 5 nA | ~3                 | 5300                         |                       | S7       |
| GaAs0.7Se0.3         | 1 nA at 2 V  | 1.4 μA | 1400               | 4.5×10$^4$                   | 1.8 × 10$^{13}$       | Present work |

$^a$ We estimated the value using the data in the text.

$^b$ Photosensitivity (= (I_{light}-I_{dark})/I_{dark}), where I_{light} and I_{dark} is the current under dark condition.

$^c$ Spectral responsivity ($R$), defined as the photocurrent generated when light of unit intensity shines on the effective area of NW, can be expressed as $R = \Delta I/A$, where $P$ is the incident light intensity (= 60 W cm$^{-2}$) and $A$ is the effective area of NW.

$^d$ Specific detectivity ($D^*$) in a unit of Jones (i.e., cm · Hz$^{1/2}$ W$^{-1}$). When the noise from dark current is small, it can be defined as $D^* = R (A/2eI_{dark})^{1/2}$.

$^e$ The number in the bracket represents the reference number in the text.
Figure S1. SEM images and EDX spectrum of GaAs$_{1-x}$Se$_x$ ($x = 0, 0.2, 0.3, \text{ and } 0.5$) and (GaAs)$_{1-x}$(Ga$_2$Se$_3$)$_x$ ($x = 0.8 \text{ and } 1$).
Figure S2. (a) XRD pattern over the full 2θ range, and (b) magnified (111) and (220) peaks. The GaAs (red color) and Ga$_2$Se$_3$ (blue color) reference peaks are indexed using the appropriate JCPDS Card; cubic phase GaAs (JCPDS Card No. 80-0016; F43m, $a = 5.654$ Å) and cubic phase Ge$_2$Se$_3$ (JCPDS Card No. 05-0724; F43m, $a = 5.429$ Å).

The reference peaks were shown at the bottom and top; cubic zinc blende (ZB) phase GaAs (JCPDS Card No. 80-0016; F43m, $a = 5.654$ Å), and cubic ($\alpha$) phase Ge$_2$Se$_3$ (JCPDS Card No. 05-0724; F43m, $a = 5.429$ Å). The lattice constant of $\alpha$-Ga$_2$Se$_3$ is 4.0% smaller than that of GaAs. The XRD peaks of GaAs and Ga$_2$Se$_3$ matched those of the cubic phases. As $x$ increases, the peak position blue shifts continuously from the ZB GaAs phase. The (111) and (220) peaks are displayed over a magnified scale in (b) and (c), respectively. The composition ($x$) was determined using Vegard’s law (i.e., $d = (1 - x) d_{GaAs} + x d_{Ga2Se3}$) based on the peak position of the end numbers GaAs and Ga$_2$Se$_3$. The peak width of $x > 0.5$ is larger than that of $x \leq 0.5$, especially $x = 1$. This is correlated with the higher degree of crystalline defects which is correlated with the TEM images and XPS data.
Figure S3. (a) [Se]/[Ga] and (b) [As]/[Ga] (obtained using EDX data as shown in Figure S1) versus $x$ (calculated by the XRD data as shown in Figure S2). The red and blue dotted lines represent the calculated values using the composition of $(\text{GaAs})_{1-x}(\text{Ga}_2\text{Se}_3)_x$ and GaAs$_{1-x}$Se$_x$, respectively.

The calculated [Se]/[Ga] value for the $(\text{GaAs})_{1-x}(\text{Ga}_2\text{Se}_3)_x$ composition is plotted by the red dotted line. The experimental [Se]/[Ga] values, obtained using the EDX data, matched with the calculated values, as $x$ approached to 1. However, the experimental values show a large deviation from the calculated ones in the range of $x = 0-0.5$. They are rather matched with the calculated values using the GaAs$_{1-x}$Se$_x$ composition (linear line as shown by the blue dotted line). Therefore, in the range of $x \leq 0.5$, the Se would substitute the As with the GaAs$_{1-x}$Se$_x$ composition.

The experimental data of [As]/[Ga] decreases almost linearly with $x$ over the whole range. However, the [As]/[Ga] value is only 0.9 for GaAs NWs, probably due to the oxygen binding with Ga, indicating that the [As]/[Ga] values have large experimental errors. Furthermore, there is not much difference in the calculated GaAs$_{1-x}$Se$_x$ and $(\text{GaAs})_{1-x}(\text{Ga}_2\text{Se}_3)_x$ compositions. Therefore, it is difficult to determine which composition the experimental data follows using the As composition.
Figure S4. (a) HRTEM and corresponding FFT images of GaAs$_{1-x}$Se$_x$ ($x = 0.2$) NW at the [011] zone axis. The single-crystalline NW has the [011] growth direction. The SAED pattern for the round tip at the [1 1 3] zone axis reveals the orthorhombic phase AuGa (JCPDS No. 07-0126, Pbnm, $a = 6.937$ Å, $b = 6.267$ Å, $c = 3.447$ Å). (b) HAADF STEM image, and EDX elemental mapping (using the Au L-, Ga K-, As K-, and Se K-shell peaks) and (c) corresponding EDX line-scanned profiles along the axial direction reveals the atomic ratio of Ga:As = 1:1 at the NW and Au:Ga = 1:1 at the tip.
Figure S5. (a) HRTEM and corresponding FFT images of GaAs$_{1-x}$Se$_x$ ($x = 0.5$) NW; (i) 50 nm thick GaSe shell (zone axis = [100]) sheathing the nanoparticle has $d_{003} = 7.94$ Å, which is consistent with the rhombohedral phase $\gamma$-GaSe (JCPDS Card No. 81-1971; R3m, $a = 3.730$ Å and $c = 23.860$ Å); (ii) the polygonal shaped nanoparticle (zone axis = [111]) consisted of the orthorhombic phase AuGa (JCPDS No. 07-0126, Pbnm, $a = 6.937$ Å, $b = 6.267$ Å, $c = 3.447$ Å). The crystallographic directions of AuGa are not matched with those of NW; (iii) the single-crystalline NW (zone axis = [011]) has the [011] growth direction. (b) HAADF STEM image, EDX elemental mapping (using the Au L-, Ga K-, As K-, and Se K-shell peaks) and (c) corresponding EDX line-scanned profiles along the axial direction confirmed that the composition of polygonal nanoparticle and shell is Au:Ga = 1:1 and Ga:Se = 1:1, respectively. The NW part shows the composition of Ga:As:Se = 1:0.5:0.5.
Figure S6. (a) HRTEM and corresponding FFT images of $\text{(GaAs)}_{1-x}\text{(Ga}_2\text{Se}_3)_x$ ($x = 0.7$) NW at the $[01 \overline{1}]$ zone axis; (i) the nanoparticle tip consisted of polycrystalline $\alpha$-$\text{Ga}_2\text{Se}_3$ phase (JCPDS Card No. 05-0724; F43m, $a = 5.429$ Å); (ii) the NW was grown along the $[011]$ growth direction. (b) HAADF STEM images and (c) EDX elemental mapping (using the Au L-, Ga K-, As K-, Se K-, and O-K shell peaks) shows that the tip has Ga:Se = 2:3 composition and 10%-doped As. There is 50 nm-size round shaped Au nanoparticle inside 200 nm-size $\text{Ga}_2\text{Se}_3$ tip. The sheathing of Au nanoparticle with the $\text{Ga}_2\text{Se}_3$ indicates that the Ga depletion from the Au-Ga alloy nanoparticle is accompanied by the growth of $\text{Ga}_2\text{Se}_3$ after the termination of NW growth.
Figure S7. Survey XPS scanned spectrum of GaAs$_{1-x}$Se$_x$ ($x \leq 0.5$) and (GaAs)$_{1-x}$(Ga$_2$Se$_3$)$_x$ ($x > 0.5$) using the photon energy of 600 eV. As $x$ increases, the As composition decreases while the Se composition increases.
Figure S8. Raman spectrum of GaAs$_{1-x}$Se$_x$ ($x \leq 0.5$) and (GaAs)$_{1-x}$(Ga$_2$Se$_3$)$_x$ ($x > 0.5$) NWs. Raman signals were obtained using an Ar ion laser with a wavelength of 514.5 nm.

Micro-Raman spectra were measured for the individual NWs using a 514.5-nm excitation source. The Raman spectra of GaAs NW consisted of the transverse optical (TO) and a longitudinal optical (LO) mode peaks at 267 and 286 cm$^{-1}$, respectively. The Ga$_2$Se$_3$ NWs and bulk crystal show two broad peaks at 250 and 300 cm$^{-1}$, originated from the TO and LO branches, respectively. As $x$ increases, the intensity of Ga$_2$Se$_3$ peaks increases, while that of GaAs peaks decreases, indicating that the composition is tuned effectively.
Figure S9. Power dependence of photocurrents for (a) $x = 0$ (GaAs) and (b) GaAs$_{1-x}$Se$_x$ ($x = 0.3$) NWs. The photocurrents vs. light intensity is plotted in the inset of Figure 5a.
Figure S10. Source-drain current ($I_{SD}$) vs. gate voltage ($V_G$) curves for GaAs$_{1-x}$Se$_x$ ($x \leq 0.5$) and (GaAs)$_{1-x}$(Ga$_2$Se$_3$)$_x$ ($x > 0.5$) at room temperature (300 K); (a) $x = 0$ (GaAs), (b) $x = 0.3$, (c) $x = 0.7$, and (d) $x = 1$ (Ga$_2$Se$_3$).

The reproducible source-drain current ($I_{SD}$) as a function of (back) gate voltage ($V_G$) at 2-40 V bias voltage of source-drain ($V_{SD}$) was obtained from the field-effect transistor (FET) device under ambient condition (300 K). For GaAs$_{1-x}$Se$_x$ ($x = 0$ and 0.3), the current increases with increasingly negative $V_G$, indicating the characteristics of $p$-type semiconductors. The threshold voltage for current onset ($V_{th}$) is about 0 and -20 V, respectively. In contrast, (GaAs)$_{1-x}$(Ga$_2$Se$_3$)$_x$ ($x = 0.7$ and 1) show the current increase with increasing the positive $V_G$, corresponding to a behavior of $n$-type semiconductors, with $V_{th} = 30$ and 12 V, respectively. For $x = 0.5$, the enhancement of current by gate potential is negligible (not shown here).
The photographs and AFM images of each electrode are shown for the distance between the electrodes and the diameter of NWs.

From the linear region of the $I_{SD}$-$V_G$ curve (see the linear fit line), the transconductance ($g_m = \left| \frac{\partial I_{SD}}{\partial V_G} \right|$) can be obtained by extrapolation. The channel mobility, $\mu$, was estimated to be $\text{cm}^2\text{V}^{-1}\text{s}^{-1}$ using the equation,

$$\mu = g_m L^2 \frac{1}{V_{SD}} \left( \frac{1}{V_{SD}} \right) \left( \frac{\ln(4h/d)}{2\varepsilon\varepsilon_0 L} \right)_m = g_m \left( \frac{1}{V_{SD}} \right) \left( \frac{(\ln(4h/d))_m}{2\varepsilon\varepsilon_0 L} \right),$$

where $h$ is the thickness of SiO$_2$ (300 nm), $L$ is the channel length (1 $\mu$m), $d$ is the NW diameter.
(based on the value measured by AFM images), \( \varepsilon \) is the relative dielectric constant of \( \text{SiO}_2 \) (3.9), \( \varepsilon_0 \) is the dielectric constant of vacuum \( (8.85 \times 10^{-12} \text{ J C}^{-2} \text{ m}^{-1}) \), the gate capacitance per unit area \( C_G \) is \( \frac{2\pi\varepsilon\varepsilon_0L}{\ln(4h/d)} \) and \( V_{SD} \) is the bias voltage between the source and drain. The

\[
\left( \frac{\ln(4h/d)L}{2\pi\varepsilon_0} \right) = \frac{ln\left(\frac{1200}{d(x)}\right)}{216864 \times 10^{-12}} \times \frac{(L(\mu m) \times 10^{-6})}{ln\left(\frac{4}{h(d)}\right) L(\mu m)} \times \frac{1200}{d(x)}.
\]

The carrier concentration \( (\text{cm}^{-3}) \) is calculated using the equation: \( n = \left( \frac{\sigma}{e\mu} \right) \), where \( e \) is 1.602 times \( 10^{-19} \) coulombs and \( \sigma = \left( \frac{I_{SD}}{V_{SD}} \right) \times \left( \frac{L}{\pi r^2} \right) \), where \( r \) is radius \( \left( = \frac{D}{2} \right) \) of NW is the conductivity. Table S1 summarized the results.

**Table S1.** Characteristics of \( \text{GaAs}_{1-x}\text{Se}_x \) \((x \leq 0.5)\) and \( (\text{GaAs})_{1-x}(\text{Ga}_2\text{Se}_3)_x \) \((x > 0.5)\) NWs measured by FET devices. The experimental data has 10% uncertainty.

| \( X \) \( (\text{Se}) \) | \( D \) \( (\text{nm}) \) | \( L \) \( (\mu \text{m}) \) | \( V_{SD} \) \( (\text{V}) \) | \( g_m \) \( (\text{A V}^{-1}) \) | type | \( \frac{ln(4h/d)L}{2\pi\varepsilon_0} \) | \( \mu \) \( (\text{cm}^2\text{V}^{-1}\text{s}^{-1}) \) | \( \frac{I_{SD}}{V_{SD}} \) | \( \sigma \) \( (\text{S cm}^{-1}) \) | \( n \) \( (\text{cm}^{-3}) \) |
|---|---|---|---|---|---|---|---|---|---|---|
| 0 | 130 | 1.8 | 2 | \( 1.1 \times 10^{-9} \) | \( p \) | 1.9 \( \times 10^8 \) | 0.10 ± 0.01 | 1.1 \( \times 10^8 \) | 1.5 \( \times 10^{-2} \) | 9.3 \( \times 10^{17} \) |
| 0.3 | 310 | 2.3 | 40 | \( 2.2 \times 10^{-11} \) | \( p \) | 1.4 \( \times 10^8 \) | 7.9 (± 0.8) \( \times 10^5 \) | 1.9 \( \times 10^{-10} \) | 5.8 \( \times 10^{-5} \) | 4.6 \( \times 10^{18} \) |
| 0.7 | 250 | 1.8 | 10 | \( 4.1 \times 10^{-10} \) | \( n \) | 1.3 \( \times 10^8 \) | 5.3 (± 0.5) \( \times 10^{-3} \) | 2.0 \( \times 10^{-10} \) | 7.2 \( \times 10^{-5} \) | 1.3 \( \times 10^{17} \) |
| 1 | 320 | 0.75 | 5 | \( 1.3 \times 10^{-9} \) | \( n \) | 4.6 \( \times 10^7 \) | 1.2 (± 0.1) \( \times 10^{-2} \) | 1.0 \( \times 10^{-8} \) | 9.4 \( \times 10^{-4} \) | 4.9 \( \times 10^{17} \) |
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