Ga$_2$Se$_3$ Defect Semiconductors: The Study of Direct Band Edge and Optical Properties

Ching-Hwa Ho*

**ABSTRACT:** Direct band edge is a crucial factor for a functional chalcogenide to be applied in luminescence devices, photodetectors, and solar-energy devices. In this work, the room-temperature band-edge emission of III–VI Ga$_2$Se$_3$ has been first observed by micro-photoluminescence ($\mu$PL) measurement. The emission peak is at 1.85 eV, which matches well with the band-edge transition that is measured by micro-thermoreflectance ($\mu$TR) and micro-transmittance ($\mu$T) for verification of the direct band edge of Ga$_2$Se$_3$. The temperature-dependent $\mu$TR spectra of Ga$_2$Se$_3$ show a general semiconductor behavior with its temperature-energy shift following Varshni-type variation. With the well-known high carrier mobility, transition-metal dichalcogenides (TMDCs) MX$_2$ (M = W, Mo, Re and X = S, Se) have been enthusiastically studied due to their scientific merits and good flexibility, such as smooth surface, in-plane optical anisotropy, and thickness-tunable band gap modulation. From the research works on TMDCs and III–VI compounds, band-edge characteristics turn out to be a key reason for further application of these layered semiconductors in optoelectronics, electronics, or photocatalysis devices. Based on the characteristics, it is interesting that bulk TMDCs (e.g., MoS$_2$) are usually indirect semiconductors, but they would become direct band-gap compounds by thinning their thicknesses close to a monolayer limit. On the other hand, for the III–VI layered chalcogenides, the band-edge property is opposed to the other TMDCs because of these native advantages of high luminescence efficiency and direct band edge in the III–VI Ga$_2$Se$_3$, it is important for further studying the structure, band edge, and optical properties of Ga$_2$Se$_3$, a rarely studied III–VI defect semiconductor.

Ga$_2$Se$_3$ is one of the important members of III–VI compounds, which crystallizes in a defect zinclende structure as the natural sphalerites. Unlike the III–V semiconductors such as GaAs and InP owning a stronger covalent bond, the misvalency of the III and VI elements usually makes a III–VI compound, possessing different stoichiometries, diversified crystal phases, and also changing lattice forms. Thus, GaSe and Ga$_2$Se$_3$ are the general constituents of stoichiometry existing in the gallium selenides. There are three crystalline phases of $\alpha$, $\beta$, and $\gamma$ structures that can be found in the Ga$_2$Se$_3$ crystals obtained by different growth temperatures. Sphalerite $\alpha$-Ga$_2$Se$_3$, usually crystallizes in a defect zinchblende structure possessing a cubic unit cell, which may be the most stable phase in the defective Ga$_2$Se$_3$ crystal owing to its higher growth temper-
The cubic \( \alpha \)-Ga\(_2\)Se\(_3\) may also be a fundamental unit for building \( \beta \) (monoclinic)\(^{28}\) and \( \gamma \) (orthorhombic)\(^{29}\) phases in a Ga\(_2\)Se\(_3\) lattice. This result implies that the three phases of \( \alpha \), \( \beta \), and \( \gamma \)-Ga\(_2\)Se\(_3\) are essentially comparable structures with equivalent axes marked as \([100]_\beta = [112]_\alpha\), \([010]_\beta = [110]_\alpha\), and \([001]_\beta = [112]_\alpha\), as displayed in Figure 1d.\(^{30}\) For a perfect zinblende structure of a III–V compound like GaAs, the stoichiometric content ratio of Ga/As should be 1:1. Nevertheless, for a defect zinblende structure of \( \alpha \)-Ga\(_2\)Se\(_3\), the stoichiometry ratio of Ga/Se is only 2:3. Consequently, one-third of the cations (Ga) would be vacant with respect to that of the anions (Se) in all of the phases of Ga\(_2\)Se\(_3\). The crystalline structure and lattice form are similar to its Ga\(_2\)S\(_3\) counterpart.\(^{31,32}\) Thus, the structural vacancies of Ga (\( V_{Ga} \)) in a defect zinblende Ga\(_2\)Se\(_3\) would be ordered in the lattice and they might be an important factor for determination of the crystal structure and band structure of the Ga\(_2\)Se\(_3\) defect semiconductor. Some experimental and theoretical works on the determination of band gap using optical absorption,\(^{26}\) DC photoconductivity,\(^{26}\) UV-visible diffuse reflectance,\(^{33}\) and density-function calculations\(^{34}\) had been done; however, multidisciplinary gaps ranging from 1.79 to 2.4 eV were obtained. There is still lack of evidence on the photoluminescence emission of Ga\(_2\)Se\(_3\) at room temperature for verification of its direct band edge in the defect semiconductor.

![Figure 1](https://dx.doi.org/10.1021/acsomega.0c02623)

Figure 1. (a) X-ray diffraction pattern of Ga\(_2\)Se\(_3\) from 2\( \theta \)= 20 to 90\(^\circ\). The peak indices of the diffraction planes are indicated. (b) Representative scheme of the defect zinblende structure of cubic \( \alpha \)-Ga\(_2\)Se\(_3\). (c) Atomic arrangement of the \{111\} plane (preferred orientation) in the defect zinblende structure. (d) Comparison of cubic \( \alpha \)-Ga\(_2\)Se\(_3\) and monoclinic \( \beta \)-Ga\(_2\)Se\(_3\) defect semiconductors. They are approximately equivalent with the unit-cell volume of \( \beta \)-Ga\(_2\)Se\(_3\) being about 3 times as large as that of \( \alpha \)-Ga\(_2\)Se\(_3\) along the \( \beta \)-[010] (\( \alpha \)-[110]) direction.

RESULTS AND DISCUSSION

Figure 1a shows the powdered X-ray diffraction (XRD) pattern of Ga\(_2\)Se\(_3\) grown by the chemical vapor transport (CVT) method. A Cu K\( \alpha \) radiation (containing K\( \alpha_1 \)= 1.5406 and K\( \alpha_2 \)= 1.5444 Å) was used as the X-ray source. Several sharp peaks of (111), (200), (220), (311), (222), (400), (331), (420), and (422) are found, which index to a cubic \( \alpha \)-Ga\(_2\)Se\(_3\) phase of zinblende structure [JCPDS card no. 05-0724].\(^{27}\) The crystal structure of the \( \alpha \)-Ga\(_2\)Se\(_3\) phase is the defect zinblende structure, as shown in the representative scheme in Figure 1b, where 1/3 cation (Ga) atoms are vacant with respect to the anionic (Se) sites, owing to a perfect zinblende structure of 1:1 cation to anion ratio (e.g., GaAs). Thus, Ga vacancy (\( V_{Ga} \)) can be ordered in the zinblende lattice, and it would also contribute to the crystal and band structures of Ga\(_2\)Se\(_3\). From Figure 1a, the interplanar spacings measured from XRD are \( d_{(111)} = 3.145\), \( d_{(200)} = 2.726\), \( d_{(220)} = 1.927\), \( d_{(311)} = 1.645\), \( d_{(222)} = 1.574\), \( d_{(400)} = 1.364\), \( d_{(331)} = 1.254\), \( d_{(420)} = 1.220\), and \( d_{(422)} = 1.114\) Å. The values of interplanar spacings render an averaged cubic lattice constant of \( a = 5.45\) Å for \( \alpha \)-Ga\(_2\)Se\(_3\). As shown in Figure 1a, the strongest XRD peak is the (111) plane. The (111) plane has the most close-pack facet and is one of the frequently occurring orientations inside a cube-like structure of diamond, zinblende, pyrite,\(^{35}\) or chalcopyrite (denoted as (112)) compounds.\(^{36}\) The representative scheme of the atomic arrangement of the \{111\} plane in the defective zinblende Ga\(_2\)Se\(_3\) is shown in Figure 1c. Essentially, it is a honeycomb structure, which would fundamentally build a trigonal-shaped facet occurring in the crystals with a cubic phase. Figure 1d shows a contrast of an atomic scheme between cubic \( \alpha \)-Ga\(_2\)Se\(_3\) and monoclinic \( \beta \)-Ga\(_2\)Se\(_3\).\(^{28}\) In general, the unit-cell volume of \( \beta \)-Ga\(_2\)Se\(_3\) is 3 times as large as that of \( \alpha \)-Ga\(_2\)Se\(_3\), formed along the [010] (\( \alpha \)-[110]) direction. The crystal axes of [001] and [100] (\( \beta \) phase) are also equivalent to those of [112] and [112] (\( \alpha \) phase) in the Ga\(_2\)Se\(_3\) defect semiconductor.

Figure 2a displays the micro-photoluminescence (\( \mu \)PL) spectrum of a Ga\(_2\)Se\(_3\) microcrystal (\( \sim \)80 \( \mu \)m in size) on the \{111\} plane in the energy range of 1.5–2.2 eV at room temperature. The right inset shows the crystal image of the Ga\(_2\)Se\(_3\) sample under excitation with a 532 nm laser using a 50\( \times \) objective lens. A clear PL peak at \( \sim 1.85\) eV is observed owing to the band-edge free exciton (BEFX) combined with the bound exciton (BX) and defect emissions occurring in the \( \alpha \)-Ga\(_2\)Se\(_3\) sample (i.e., sample S1). The inference of the free-exciton (FX), BX, and defect emission in Ga\(_2\)Se\(_3\) can be verified by the temperature-dependent \( \mu \)PL spectra obtained from the other sample (i.e., sample S2), as displayed in the left inset of Figure 2a. At a low temperature of \( \sim 160\) K, both free-exciton (FX \( \sim 1.945\) eV) and bound-exciton (BX \( \sim 1.822\) eV) peaks are simultaneously detected in the \( \mu \)PL spectrum similar to the free-exciton (FX), BX, and defect emission in Ga\(_2\)Se\(_3\). As the temperature increases, the PL intensity of the BX feature decreases faster than that of the FX emission due to the bound exciton (BX) defect effect from the impurity or defect state inside the Ga\(_2\)Se\(_3\) microcrystal caused by the increasing temperature. Because of the free to bound behavior, the BX emission would decrease promptly and the FX emission can finally dominate the main PL emission peak at 300–320 K, as shown in the left inset of Figure 2a. At 320 K, the emission peak of Ga\(_2\)Se\(_3\) is at about 1.835 eV. The thermal-ionization temperature of the BX emission is about 26 meV for Ga\(_2\)Se\(_3\). The BX feature is inferred to be an acceptor-bound exciton in \( \alpha \)-Ga\(_2\)Se\(_3\). As shown in
Figure 2. (a) Room-temperature µPL spectrum of Ga₂Se₃. The left inset shows temperature-dependent bound-exciton (BX) and free-exciton (FX) emissions of an additional Ga₂Se₃ sample for verification of the direct band edge. The right inset displays the microscopic image of the Ga₂Se₃ microcrystal. (b) µRaman spectrum of Ga₂Se₃. The inset shows some of the vibrational atomic movements in the fundamental GaSe₃ sp³ unit.

Figure 2a, the PL line widths (i.e., 1.85 eV peak) of the samples S1 and S2 at 300 K range from ∼0.1 to ∼0.4 eV. The values are larger than those of the general direct semiconductors like GaAs. The emission peak of PL may also contain the contribution of defects inside Ga₂Se₃. Moreover, in comparison with its GaSe counterpart, the PL quantum efficiency of Ga₂Se₃ in Figure 2a is approximately 25% lower than that of the GaSe at room temperature.13,23

Figure 2b shows the µRaman spectrum of the Ga₂Se₃ microcrystal from 100 to 500 cm⁻¹. There are about five Raman peak features, at A¹′ ~ 119 cm⁻¹, A₁ ~ 156 cm⁻¹, A₂ ~ 190 cm⁻¹, A¹ ~ 240 cm⁻¹, and F₃ ~ 289 cm⁻¹. that can be detected in the α-Ga₂Se₃ microcrystal, similar to previous ordered Ga₂Se₃.38 Most of the mode frequencies are indexed to the internal and external vibrations of the tetrahedral GaSe₃ groups in the zincblende Ga₂Se₃. In the defect semiconductors of Ga₂X₃ (X = S, Se), even Ga₃S₃ is crystallized in a defect wurtzite structure (β),37 and 1/3 Ga vacancies are still ordered in the Ga₃X₃ lattice similar to that of α-Ga₂Se₃. The atomic arrangement of the wurtzite {0001} plane also resembles that of zincblende (111) on the top layer surface of Ga₂X₃ (see Figure 1c). Thus, the measured Raman frequencies of Ga₃S₃ are observed to shift to higher frequencies (i.e., A¹ ~ 147 cm⁻¹, A₁ ~ 233 cm⁻¹, A₂ ~ 280 cm⁻¹, A¹ ~ 307 cm⁻¹, and F₃ ~ 386 cm⁻¹)31,40 as compared to those of Ga₂Se₃ in Figure 2b due to the shrinkage of the Ga–X bond length inside the GaX₄ tetrahedra.37 The symmetric GaSe₃ sp³ unit inside the zincblende structure has vibration modes at the Γ center represented by Γ = A₁ + E + F₁ + F₃.39,41 Four standard vibrations of atomic movement, ν₁(A₁), ν₂(E), ν₁(F₁), and ν₂(F₃), in the GaSe₃ molecule are depicted in the inset of Figure 2b for contrast. All of the full-width at half-maximum (FWHM) values of the Raman peaks (A¹′−F₃) in Figure 2b range from 15 to 38 cm⁻¹ by Raman fits. The FWHM values are higher than those of the Raman peak observations in GaAs and Si with a zincblende and diamond structure for identification of the defect zincblende character of Ga₂Se₃.

To further identify the direct band edge of Ga₂Se₃, µTransmittance and µTR measurements of the Ga₂Se₃ microcrystals are, respectively, carried out. The experimental results of µTransmittance and µTR spectra at 300 and 20 K are shown in Figure 3a,b, respectively. Modulation spectroscopy of a semiconductor, like TR measurement,42,43 has been proven to be a very powerful technique for the characterization of excitons, direct band edge, and interband transitions in the semiconductor’s band structure.44 The derivative spectral line features suppress unintentional spectral background and emphasize the direct critical-point transitions in the band structure. As shown in Figure 3a, the direct band-edge transition of µTR feature matches well with the center-edge position of the µTransmittance spectrum at E₆ = 1.85 eV. In comparison with the µPL peak in Figure 2a, the E₆ µTR feature is in agreement with the PL emission of Ga₂Se₃ to verify its direct band edge. The agreement of the E₆ position in the µTR and µTransmittance spectra can also be found in Figure 3b, where the value of the band-edge transition blue shifts to E₆ ≈ 2.0 eV at 20 K. Figure 3c shows the temperature-dependent µTR spectra of α-Ga₂Se₃ between 20 and 320 K. For comparison purpose, the 2D contour plot of µTR spectra is also depicted in Figure 3d for contrast. The direct band-edge feature (E₆) shows enhanced amplitude at 20 K, while it demonstrates an energy red shift and line-shape broadened character when the temperature increased to 320 K, such as the general semiconductor behavior. The broadened E₆ µTR feature is likely owing to the intrinsic defect (like VGa) and alloy scattering effect existing inside the Ga₂Se₃ crystal at higher temperature. There is a small µTR feature D present in the lower-energy side (i.e., T > 260 K) in Figure 3c. It is likely caused by a defect transition in Ga₂Se₃.

The occurrence of the direct band edge of Ga₂Se₃ can be attributed to the spherical-like Ga 4s orbital constituting the lowest conduction band, while the Se 4p state hybrid with Ga 4p + 4s electrons constructs the top of the valence band,36 similar to the defect semiconductor counterpart Ga₃S₃.45 Figure 3e shows the temperature dependence of band-edge transition energies (with representative error bars) from 20 to 320 K for the E₆ transition in Ga₂Se₃. The solid squares are the experimental data obtained from µTR measurement and the solid line is the least-square fit to a Varshni-type formula expressed as E₆(T) = E₆(0) − αT²/β(T + T₀),46 where E₆(0) is the energy at 0 K, the Varshni constant α is related to the strength of an electron (exciton)–phonon interaction, and β is closely related to the Debye temperature of the material. The obtained values of the fitting parameters for the direct band edge of Ga₂Se₃, E₆(0) = 2.005 ± 0.002 eV, α = (7.1 ± 0.7) × 10⁻⁴ eV/K, and β = 120 ± 40 K. The values are similar to those obtained by its III–VI defect semiconductor counterparts such as In_xS_y in cubic phase (or a tetragonal phase),47 wherein the defect crystal still owns one-third of the cation vacancy’s ordered arrangement in the crystal.

To evaluate the functional performance of Ga₂Se₃ for further solar-energy and optoelectronic device applications, the photoelectric conversion and photodetection behavior of as-grown Ga₂Se₃ crystals were also investigated. A larger as-grown Ga₂Se₃ crystal was cut and polished into a size of 0.3 × 0.2 × 0.04 cm³. The crystal was selected for fabrication in a Cu/Ga₂Se₃ Schottky solar cell (SSC), as shown in the representative scheme in the
inset of Figure 4a. A mica-clamped copper mesh contacting the Ga2Se3 surface acts as the top electrode of the SSC. The Ga2Se3 crystal was mounted on a copper sample holder using a silver paste for the bottom electrode. Figure 4a shows the surface photovoltaic (SPV) response spectrum of the Cu/Ga2Se3 SSC structure in the energy range between 1.5 and 5 eV. The spectrum was normalized to the spectral light intensity. Figure 4b depicts the representative energy-band diagram of the Cu/Ga2Se3 SSC structure. Essentially, the as-grown Ga2Se3 is a p-type semiconductor as confirmed by our Hall measurement. The dark resistivity of Ga2Se3 is about 145 Ω·cm and Hall mobility is ∼11 cm²/V·s at 300 K. The p-type behavior of Ga2Se3 would make the SSC structure with downward band bending near the Cu/Ga2Se3 rectified junction, as displayed in Figure 4b. When the photon is incident (hν ≥ Eg), the electron–hole pair is generated and then the electron–hole pair is separated by a built-in electric field of the Schottky junction. Thus, the SPV response voltage for different wavelengths in the SSC can be measured. As shown in Figure 4a, with E > 1.85 eV (Eg), the SPV response spectrum starts to increase, and the responsivity reaches a maximum intensity of ∼6.2 mV/μW at 2.25 eV. Then, the SPV responsivity is gradually decreased with the incident photon energy increasing up to 5 eV. The decrease of SPV is dominated by the surface-recombination effect of the Ga2Se3 sample, which reduces the net excess carriers and forms a photoresponse peak near the band gap. The SPV spectrum in Figure 4a still reveals a good responsivity of Ga2Se3 in the visible range from 1.9 to 3.1 eV.

Figure 4c shows the photocurrent photoresponsivity spectrum in a Ga2Se3 photoconductor at room temperature. The size of the Ga2Se3 crystal is similar to that for the SPV measurement. The photoconductivity (PC) value is measured by applying 30 V to the Ga2Se3 photoconductor, and the chopped frequency (f) is set at 30 Hz. The inset of Figure 4c depicts the experimental setup for the PC measurement, where the photocurrent is derived from a load resistor and the incident light is chopped with different frequencies to evaluate the PC responsivity of the Ga2Se3 photoconductor. In Figure 4c, the photocurrent responsivity spectrum of Ga2Se3 clearly shows a photocurrent peak of ∼2.25 μA/μW occurring at 1.93 eV near and above the band edge (Eg). The residual absorption below Eg (i.e., 1.65–1.85 eV) is detected, which may be caused by imperfect states (defect and impurity) inside the Ga2Se3 defect semiconductor. The inset in Figure 4d shows the band scheme of the Ga2Se3,
photoconductor operating under the application of an external electrical field. Unlike the SSC structure in Figure 4b, the separation of the photogenerated electron and the hole might depend on applying the external field, and the path of carrier transport should be much longer (distance) than that in the Schottky junction in Figure 4b. If there is a trap state or trap level (E_t) in the band gap of the defect semiconductor (e.g., Ga_2Se_3), the thermal bounce of electrons and holes between E_v and E_i would prolong the PC lifetime of the Ga_2Se_3 photoconductor. Thus, when the chopped frequency of the incident light is increased, the peak photocurrent value decreases, owing to a longer lifetime \( \tau \) in the Ga_2Se_3 defect semiconductor. The peak photocurrent versus chopped frequency f at 1.93 eV (operation see Figure 4c) is shown in Figure 4d. The frequency range is set from 30 to 1000 Hz and the maximum photocurrent responsivity decreases exponentially with f. The hollow triangles in Figure 4d are the experimental data and the solid line is fitted to the expression

\[
I(f) = I_0 \exp(- \tau f)
\]

where \( I_0 \) is the DC photocurrent responsivity (f = 0 Hz) and \( \tau \) is the lifetime of the photoconductor. The obtained values of the fitting parameters in Figure 4d are \( I_0 = 3.24 \) A/W and \( \tau = 12.5 \) ms. The efficiency for generation of photocurrent in a photoconductor is known as the responsivity (R). The DC responsivity is \( R = 3.24 \) A/W and \( R = 2.25 \) A/W at 30 Hz for the Ga_2Se_3 photoconductor (under bias = 30 V at \( E = 1.93 \) eV, \( \lambda = 642 \) nm). The lifetime \( \tau \) is closely related to photoconductive gain \( \Gamma \), defined as \( \Gamma = \tau / \tau_{trans} = \tau \mu V^2 / l \), where \( \tau_{trans} \) is the mobility, and \( l \) is the transit time of electron across the photoconductor. Thus, \( \Gamma \) is dependent on the bias (V) and geometry (l) we can further use a normalized gain, which is expressed by the product of lifetime, mobility, and quantum efficiency as

\[
\Gamma = \tau \mu \eta = (\Gamma / \mu) (1 / V^2) \mu \eta / P (E / q) \Gamma^{-1}
\]

\[
= (1 / V^2) R (E / q)
\]

where R is the responsivity given by \( R = i_p / P \), and \( q \) is the charge. The DC responsivity of Ga_2Se_3 is \( R = 3.24 \) A/W. Substituting the channel length \( l = 0.2 \) cm and bias \( V = 30 \) V at \( E = 1.93 \) eV in eq 2, the normalized gain of the Ga_2Se_3 photoconductor can be determined to be \( \Gamma_n = 8.34 \times 10^{-3} \) cm^2/V. The responsivity R of a photoconductor depends on the photocurrent but is independent of the dark current \( I_{dark} \). In the real case of a photodetector’s application, the dark current and noise current are the drawbacks of the detector while they should be taken into account for the evaluation of the photodetector performance. Thus, detectivity (\( D^* \)) is defined as the figure-of-merit of a photodetector and is given by

\[
D^* = \frac{R \cdot \Delta f}{\sqrt{2 \cdot e \cdot I_{dark}}}
\]

assuming unit bandwidth (i.e., \( \Delta f = 1 \) Hz) and \( A \) being the lateral area of the photoconductor. \( I_{dark} \) is the dark current density of the Ga_2Se_3.
photoconductor is \( \sim 30 \) Hz, as seen from Figure 4d, the detectivity is calculated to be \( D^* \sqrt{\Delta f} = 2.5 \times 10^{10} \) Jones (cm-Hz\(^{1/2}\)-W\(^{-1}\)). Table 1 lists the values of responsivity (\( R \)), normalized gain (\( \Gamma_a \)), and detectivity (\( D^* \)) of Ga\(_2\)Se\(_3\) together with those of III–VI compounds and transition-metal dichalcogenides (TMDCs) are also included for comparison. For the Ga\(_2\)Se\(_3\) defect-free type photoconductor operated at 642 nm, the value of detectivity \( D^* \) is close to those of the other III–VI GaSe field-effect phototransistors measured at 532 and 254 nm \(^{51, 52}\) of the visible and ultraviolet region, while the responsivity \( R \) of Ga\(_2\)Se\(_3\) is slightly larger than that of the layered GaSe, which is not defect type. The high detectivity of the Ga\(_2\)Se\(_3\) implies lower dark current \( I_{dark} \) of the photodetector and the value of \( D^* \) is comparable to its defect semiconductor counterpart, cubic \( y\)-Ga\(_2\)S\(_3\) operated at 350 nm owing to the larger direct band gap of Ga\(_2\)S\(_3\).\(^{53}\) For a In\(_2\)Se\(_3\)/MoS\(_2\) heterostructure (HS) field-effect transistor (FET) at \( \lambda = 450 \) nm, the \( R \) value is similar to that of Ga\(_2\)Se\(_3\) at 642 nm, while the detectivity of Ga\(_2\)Se\(_3\) is greater than that of the HS FET, likely owing to the lower dark current in the Ga\(_2\)Se\(_3\) photoconductor. In comparison with the GaSe photo-FET\(^{51}\) and WSe\(_2\) FET,\(^{55}\) the normalized gain \( \Gamma_a \) of Ga\(_2\)Se\(_3\) is larger than those of GaSe and WSe\(_2\). The higher normalized gain of Ga\(_2\)Se\(_3\) is likely due to the longer lifetime \( \tau \) of the photoconductor caused by its native defect character.

![Image](https://example.com/image.png)

**Table 1. Comparison of Values of Responsivity (\( R \)), Normalized Gain (\( \Gamma_a \)), and Detectivity (\( D^* \)) of Ga\(_2\)Se\(_3\), Layered III–VI Chalcogenides, and TMDCs**

| chalcogenides and detector type | \( \lambda^* \) (nm) | \( V^* \) | \( l^* \) (\( \mu \)m) | \( R \) (A-W\(^{-1}\)) | \( \Gamma_a \) (cm-V\(^{-1}\)) | \( D^* \) (Jones) | rel |
|-------------------------------|------------------|---------|-----------------|-----------------|-----------------|-----------------|----|
| Ga\(_2\)Se\(_3\) photoconductor | 642 | \( V_{bias} = 30 \) V | 2000 | 3.24 | \( 8.34 \times 10^{-3} \) | 2.5 \times 10\(^{10} \) | this work |
| GaSe FET | 532 | \( V_{p} = -18 \) V, \( V_{in} = 10 \) V | 47 | 0.9 | | | 8.08 \times 10\(^{11} \) | 51 |
| GaSe photo-FET | 254 | \( V_{p} = 1 \) V, \( V_{in} = 5 \) V | 20 | 2.8 | \( 1.1 \times 10^{-5} \) | | | 2.36 \times 10\(^{11} \) | 52 |
| \( y\)-Ga\(_2\)S\(_3\) FET | 350 | \( V_{p} = -40 \) V, \( V_{in} = 1 \) V | 15 | 61.3 | | | | 1.52 \times 10\(^{10} \) | 53 |
| In\(_2\)Se\(_3\)/MoS\(_2\) HS FET | 450 | \( V_{p} = 60 \) V, \( V_{in} = 1 \) V | 15 | 4.47 | | | | 1.07 \times 10\(^{9} \) | 54 |
| WSe\(_2\) FET | 655 | \( V_{p} = 5 \) V, \( V_{in} = -5 \) V | 5 | 5750 | \( \sim 1 \times 10^{-3} \) | | | 5.3 \times 10\(^{10} \) | 55 |

\( \lambda^* \) is the excitation wavelength, \( V \) is the applied bias, and \( l \) is the channel length of the photodetector.

**EXPERIMENTAL SECTION**

**Crystal Growth.** Ga\(_2\)Se\(_3\) single crystals were grown by the chemical vapor transport method using ICl\(_3\) as the transport agent. The starting-material powders with a stoichiometric composition of Ga (99.999% pure) and Se (99.999% pure) were first prepared. The starting materials together with appropriate amount of the transport agent ICl\(_3\) (10 mg/cm\(^3\)) were cooled with liquid nitrogen and were then sealed in a vacuum of \( \sim 10^{-6} \) Torr inside a quartz ampoule. The growth temperature was set as 850 → 780 °C with a gradient of \( -3.5 \) °C/cm for simultaneously growing two ampoules of Ga\(_2\)Se\(_3\). The reaction was kept for 280 h for growing large single crystals. After the growth, several bulk crystals and microcrystals with a size ranging from hundred cubic micrometers to hundred cubic millimeters and showing a dark red color were obtained. Powder XRD measurement was implemented using the Cu K\(_\alpha\) line as the X-ray source. The result showed a zincblende phase of the as-grown Ga\(_2\)Se\(_3\) crystals.

**Micro-Raman and Micro-Photoluminescence Experiments.** The \( \mu \)Raman and \( \mu \)PL measurements were carried out in an integrated RAMaker microscope spectrometer with a 532 nm solid-state diode-pump laser as the excitation source. A light-guiding microscope (LGM) equipped with an Olympus objective lens (50X, working distance \( \sim 8 \) mm) acted as the interconnection-coupled medium between the microcrystal sample, incident and reflected lights, and the charge-coupled device (CCD) spectrometer. A Janis liquid helium open-circled cryostat equipped with a Lakeshore 335 digital thermometer controller facilitated low-temperature and temperature-dependent measurements.

**Micro-Thermal-Modulated Reflectance and Micro-Transmission.** Samples for \( \mu \)TR and \( \mu \)Transmission measurements were prepared in sheet-plate Ga\(_2\)Se\(_3\) of dimensions \( \sim 0.8 \times 0.8 \times 0.06 \) mm\(^3\) and a polished surface. For \( \mu \)TR measurement, a 150 W tungsten halogen lamp acted as the white light source. The sheet-plate Ga\(_2\)Se\(_3\) was closely attached to an Au-evaporated quartz plate. A 4 Hz heating current (\( \sim 0.5 \) A) was supplied to the Au heater periodically for thermal modulation of the lattice constant and band edge of the sample. The Janis liquid helium cryostat was also used to facilitate the temperature-dependent measurement from low to room temperature. The white light source was dispersed by a monochromator equipped with a 1200 grooves/mm grating.
for providing the monochromatic light. The monochromatic light source was coupled to the sheet-plane Ga2Se3 sample using silica fiber and passed through the LGM. The reflected light from the layered sample was collected by the LGM and coupled onto the sheet-plane Ga2Se3 sample using silica fiber. The optical alignment of the nanoflake from the layered sample was facilitated by the adjustment of a CCD imaging camera equipped in the LGM. For micro-transmission measurement, the LGM was used for guiding the incident white light of a tungsten halogen lamp onto the sheet-plane Ga2Se3 sample using silica fiber. The sample was closely mounted on the cryostat with a center hole of size ~80 μm for light transmission. The transmission light of the sample was collected by the fiber and then coupled to a CCD spectrometer.

Surface Photovoltaic Response and Photoconductivity Measurements. For SPV response measurement, a Ga2Se3 crystal of size 0.3 × 0.2 × 0.04 cm3 was attached to a copper sample holder using a silver paste; the holder acted as the bottom electrode of the measurement. The top sample surface was contacted with a copper mesh for acting as the top electrode. The incident monochromatic light source of SPV response measurement was similar to μTR. The photoexcited electron–hole pairs from the surface band-bending region were extracted from the top and bottom electrodes of the capacitor-like configuration and sent to an EG&G model 7265 lock-in amplifier. The incident light of SPV response measurement was chopped at 200 Hz. For PC measurement, the size of the Ga2Se3 crystal was made similar to that for the SPV response measurement. The two ends of the photocathode sample were coated with indium for acting as the ohmic contact electrodes. A 1 MΩ load resistor was connected in series to the sample and a bias of 30 V was applied. The chopped frequencies of incident monochromatic light were set from 30 to 1000 Hz for evaluation of frequency-dependent PC responses. All of the SPV response and PC spectra were normalized to the optical power measured using an Ophir optical power meter at each wavelength.

**AUTHOR INFORMATION**

Corresponding Author

Ching-Hwa Ho — Graduate Institute of Applied Science and Technology, National Taiwan University of Science and Technology, Taipei 106, Taiwan; orcid.org/0000-0002-7195-208X; Phone: +886-2-27303772; Email: chho@mail.ntust.edu.tw; Fax: +886-2-27303733

Complete contact information is available at: https://pubs.acs.org/10.1021/acsomega.0c02623

Notes

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**REFERENCES**

(1) Novoselov, K. S.; Geim, A. K.; Morozov, S. V.; Jiang, D.; Zhang, Y.; Dubonos, S. V.; Grigorieva, I. V.; Firsov, A. A. Electric Field Effect in Atomically Thin Carbon Films. Science 2004, 306, 666–669.

(2) Yin, Z.; Li, H.; Li, H.; Jiang, L.; Shi, Y.; Sun, Y.; Lu, G.; Zhang, Q.; Chen, X.; Zhang, H. Single-Layer MoS2 Phototransistors. ACS Nano 2012, 6, 74–80.

(3) Ovchninnikov, D.; Gargiulo, F.; Allain, A.; Pasquier, D. J.; Dumcenco, D.; Ho, C. H.; Yazyev, O. V.; Kis, A. Disorder Engineering and Conductivity Dome in ReS2 with Electrolyte Gating. Nat. Commun. 2016, 7, No. 12391.

(4) Ho, C. H.; Huang, C. E. Optical Property of the Near Band-Edge Transitions in Rhenium Disulphide and Diselenide. J. Alloys Compd. 2004, 383, 74–79.

(5) Zhou, X.; Tian, Z.; Kim, H. J.; Wang, Y.; Xu, B.; Pan, R.; Chang, Y. J.; Di, Z.; Zhou, P.; Mei, Y. Rolling up MoSe2 Nanomembranes as a Sensitive Tubular Photodetector. Small 2019, 15, No. 1902528.

(6) Sun, J.; Wang, Y.; Guo, S.; Wan, B.; Dong, L.; Gu, Y.; Song, C.; Pan, C.; Zhang, Q.; Gu, L.; Pan, F.; Zhang, J. Lateral 2D WSe2 p–n Homojunction Formed by Efficient Charge-Carrier-Type Modulation for High-Performance Optoelectronics. Adv. Mater. 2020, 32, No. 1906499.

(7) Ho, C. H.; Wu, C. C.; Cheng, Z. H. Crystal Structure and Electronic Structure of GaSe1−xSx Layered Solids. J. Cryst. Growth 2005, 279, 321–328.

(8) Jung, C. S.; Shojaei, F.; Park, K.; Oh, J. Y.; Im, H. S.; Jang, D. M.; Park, J.; Kang, H. S. Red-to-Ultraviolet Emission Tuning of Two-Dimensional Gallium Sulfide/Selenide. ACS Nano 2015, 9, 9585–9593.

(9) Wu, C. C.; Ho, C. H.; Shen, W. T.; Cheng, Z. H.; Huang, Y. S.; Tiong, K. K. Optical Properties of GaSe1−xSx Layered Semiconductors Grown by Vertical Bridgen Manifold. Mater. Chem. Phys. 2004, 88, 313–317.

(10) Ho, C. H. Thickness-dependent Carrier Transport and Optically Enhanced Transconductance Gain in III-VI Multilayer InSe. 2D Mater. 2016, 3, No. 025019.

(11) Lin, Z.; Liu, Y.; Halim, U.; Ding, M.; Liu, Y.; Wang, Y.; Jia, C.; Chen, P.; Duan, X.; Wang, C.; Song, F.; Li, M.; Wan, C.; Huang, Y.; Duan, X. Solution-processable 2D Semiconductors for High-performance Large-area Electronics. Nature 2018, 562, 254–258.

(12) Chiu, W.; Petrone, N.; Hone, J. Two-dimensional Flexible Nanoelectronics. Nat. Commun. 2014, 5, No. 5678.

(13) Chiu, C. A.; Lin, M. H.; Yeh, B. X.; Ho, C. H. Curvature-dependent Flexible Light Emission from Layered Gallium Selenide Crystals. RSC Adv. 2018, 8, 2733–2739.

(14) Guo, L. Flexible Device Applications of 2D Semiconductors. Small 2017, 13, No. 1603994.

(15) Li, H.; Huang, J. K.; Shi, Y.; Li, L. J. Toward the Growth of High Mobility 2D Transition Metal Dichalcogenide Semiconductors. Adv. Mater. Interfaces 2019, 6, No. 1900220.

(16) Ho, P. H.; Chang, Y. R.; Chu, Y. C.; Li, M. K.; Tsai, C. A.; Wang, W. H.; Ho, C. H.; Chen, C. W.; Chiu, P. W. High-Mobility InSe Transistors: The Role of Surface Oxides. ACS Nano 2017, 11, 7362–7370.

(17) Li, M.; Lin, C. Y.; Yang, S. H.; Chang, Y. M.; Chang, J. K.; Yang, F. S.; Zhong, C.; Tian, W. B.; Lien, C. H.; Ho, C. H.; Liu, H. J.; Huang, R.; Li, W.; Lin, Y. F.; Chu, J. High Mobilities in Layered InSe Transistors with Indium-Encapsulation-Induced Surface Charge Doping. Adv. Mater. 2018, 30, No. 1803690.

(18) Ho, C. H.; Liu, Z. Z. Complete-series Excitonic Dipole Emissions in Few Layer ReSe2 and ReS2 Observed by Polarized Photoluminescence Spectroscopy. Nano Energy 2019, 56, 641–650.

(19) Ho, C. H.; Yen, P. C.; Huang, Y. S.; Tiong, K. K. Photoelectrochemistry Study of the Excitonic Transitions of Rhenium Disulphide Layer Compounds. Phys. Rev. B 2002, 66, No. 245207.

(20) Mak, K. P.; Lee, C.; Hone, J.; Shan, J.; Heinz, T. F. Atomically Thin MoS2: A New Direct-Gap Semiconductor. Phys. Rev. Lett. 2010, 105, No. 136805.

(21) Kang, J.; Zhang, L.; Wei, S. H. A Unified Understanding of the Thickness-Dependent Bandgap Transition in Hexagonal Two-Dimensional Semiconductors. J. Phys. Chem. Lett. 2016, 7, 597–602.

(22) Mudd, G. W.; Svatek, S.; Ren, T.; Patane, A.; Makarovsky, O.; Eaves, L.; Beton, P. H.; Kovalyuk, Z. D.; Lashkarv, G. V.; Kudrynski,
(23) Ho, C. H.; Huang, K. W. Visible Luminescence and Structural Property of \( \text{Ga}_2\text{Se}_3(0 \leq x \leq 1) \) Series Layered Crystals. \textit{Solid State Commun.} \textbf{2005}, \textit{136}, 591–594.

(24) Ho, C. H.; Chu, Y. J. Bending Photoluminescence and Surface Photovoltaic Effect on Multilayer InSe 2D Microplate Crystals. \textit{Adv. Opt. Mater.} \textbf{2015}, \textit{3}, 1750–1758.

(25) Park, K. H.; Kim, H. G.; Kim, W. T.; Kim, C. D.; Jeong, H. M.; Lee, K. J.; Lee, B. H. Optical Properties of \( \text{Ga}_2\text{Se}_3: \text{Co}^{2+} \) Single Crystals. \textit{Solid State Comm.} \textbf{1989}, \textit{70}, 971–974.

(26) Abdal-Rahman, M.; Shaikh, H. A. E. Photoelectric Properties of \( \text{Ga}_2\text{Se}_3 \) Single Crystals. \textit{J. Phys. D: Appl. Phys.} \textbf{1996}, \textit{29}, 889–892.

(27) Hahn, H.; Klingler, W. Über die Kristallstrukturen von \( \text{Ga}_2\text{Se}_3 \), \( \text{Ga}_2\text{Te}_3 \) und \( \text{Ga}_2\text{Te}_5 \). \textit{Z. Anorg. Chem.} \textbf{1949}, \textit{259}, 135–142.

(28) Lübbers, D.; Leute, V. The Crystal Structure of \( \beta' \)-\( \text{Ga}_2\text{Se}_3 \). \textit{J. Solid State Chem.} \textbf{1982}, \textit{43}, 339–345.

(29) Palatnik, L. S.; Belova, E. K. Investigation of the Polymorphism of \( \text{Ga}_2\text{Se}_3 \), Selenide of Variable Composition. \textit{Inorg. Mater.} \textbf{1965}, \textit{1}, 1703.

(30) Ueno, K.; Kawayama, M.; Dai, Z. R.; Koma, A.; Ohuchi, F. S. Growth and Characterization of \( \text{Ga}_2\text{Se}_3/\text{GaAs}(100) \) Epitaxial Thin Films. \textit{J. Cryst. Growth} \textbf{1999}, \textit{207}, 69–76.

(31) Ho, C. H.; Chen, H. H. Optically Decomposed Near-band-edge Structure and Excitonic transitions in \( \text{Ga}_2\text{Se}_3 \). \textit{Sci. Rep.} \textbf{2015}, \textit{4}, No. 6143.

(32) Liu, H. F.; Ansaht Antwi, K. K.; Yakovlev, N. L.; Tan, H. R.; Ong, L. T.; Chua, S. J.; Chi, D. Z. Synthesis and Phase Evolutions in Layered Structure of \( \text{Ga}_2\text{Se}_3 \) Semiconductor Thin Films on Epitaxial GaAs (111) Substrates. \textit{ACS Appl. Mater. Interfaces} \textbf{2014}, \textit{6}, 3501–3507.

(33) Park, K.; Lee, J.; Kim, D.; Seo, J.; Lee, J. A.; Kwak, I. H.; Kwon, I. S.; Ahn, J. P.; Park, J. \text{GaAsSe} Ternary Alloy Nanowires for Enhanced Photoconductivity. \textit{J. Phys. Chem. C} \textbf{2019}, \textit{123}, 3908–3915.

(34) Peressi, M.; Baldreschi, A. Structural and Electronic Properties of \( \text{Ga}_2\text{Se}_3 \). \textit{J. Appl. Phys.} \textbf{1998}, \textit{83}, 3092–3095.

(35) Ho, C. H.; Huang, C. E.; Wu, C. C. Preparation and Characterization of Ni-incorporated Fe\text{S}_2 Single Crystals. \textit{J. Cryst. Growth} \textbf{2004}, \textit{270}, 535–541.

(36) Ho, C. H.; Lo, S. F.; Chi, P. C. Electronic Structure and El Excitons of CuInS\text{S}_2 Energy-Related Crystals Studied by Temperature-Dependent Thermoreflectance Spectroscopy. \textit{J. Electrochem. Soc.} \textbf{2010}, \textit{157}, H219–H226.

(37) Ho, C. H.; Chiuo, M. C.; Herninda, T. M. Nanowire Grid Polarization and Polarized Excitonic Emission Observed in Multilayer GaTe. \textit{J. Phys. Chem. Lett.} \textbf{2020}, \textit{11}, 608–617.

(38) Finkman, E.; Tauc, J.; Kershaw, R.; Wold, A. Lattice dynamics of tetrahedrally bonded semiconductors containing ordered vacant sites. \textit{Phys. Rev. B} \textbf{1975}, \textit{11}, No. 3785.

(39) Julien, C.; Barinier, S.; Ivanov, I.; Guittard, M.; Pardo, M. P.; Chiloulot, A. Vibrational Studies of Copper Thiogallate Solid Solutions. \textit{Mater. Sci. Eng., B} \textbf{1999}, \textit{57}, 102–109.

(40) Lucazeau, G.; Leory, J. Etude vibrationnelle de \( \alpha\)-\text{Ga}_2\text{S}_3. \textit{Spectrochim. Acta, Part A} \textbf{1978}, \textit{34}, 29–32.

(41) Heo, J.; Yoon, J. M.; Ryu, S.-Y. Raman Spectroscopic Analysis on the Solubility Mechanism of \( \text{La}^{3+} \) in \( \text{Ge}_2\text{S}_3-\text{Ga}_2\text{S}_3 \) Glasses. \textit{J. Non-Cryst. Solids} \textbf{1998}, \textit{238}, 115–123.

(42) Ho, C. H.; Tseng, C. Y.; Tien, L. C. Thermoreflectance Characterization of \( \beta'\)-\text{Ga}_2\text{O}_3 Thin-film Nanostrips. \textit{Opt. Express} \textbf{2010}, \textit{18}, 16360–16369.

(43) Ho, C. H.; Tsai, M. C.; Wong, M. S. Characterization of Indirect and Direct Interband Transitions of Anatase TiO\text{2} by Thermoreflectance Spectroscopy. \textit{Appl. Phys. Lett.} \textbf{2008}, \textit{93}, No. 081904.

(44) Aspnes, D. E. Modulation Spectroscopy/Electric Field Effects on the Dielectric Fuction of Semiconductors. In \textit{Handbook on Semiconductors} 2; Balkanski, M., Ed.; North Holland: Amsterdam, 1980; Chapter 4A, pp 109–154.

(45) Zhang, M. J.; Jiang, X. M.; Zhou, L. J.; Guo, G. C. Two Phases of \( \text{Ga}_2\text{S}_3 \): Promising Infrared Second-order Nonlinear Optical Materials with Very High Laser Induced Damage Thresholds. \textit{J. Mater. Chem. C} \textbf{2013}, \textit{1}, 4754–4760.