Room Temperature Electroluminescence from Mechanically Formed van der Waals III–VI Homojunctions and Heterojunctions

Nilanthy Balakrishnan, Zakhar R. Kudrinskyi, Michael W. Fay, Garry W. Mudd, Simon A. Svatek, Oleg Makarovsky, Zakhar D. Kovalyuk, Laurence Eaves, Peter H. Beton, and Amalia Patanè*

Room temperature electroluminescence from semiconductor junctions is demonstrated. The junctions are fabricated by the exfoliation and direct mechanical adhesion of InSe and GaSe van der Waals layered crystals. Homojunction diodes formed from layers of p- and n-type InSe exhibit electroluminescence at energies close to the bandgap energy of InSe ($E_g = 1.26$ eV). In contrast, heterojunction diodes formed by combining layers of p-type GaSe and n-type InSe emit photons at lower energies, which is attributed to the generation of spatially indirect excitons and a staggered valence band lineup for the holes at the GaSe/InSe interface. These results demonstrate the technological potential of mechanically formed heterojunctions and homojunctions of direct-bandgap layered GaSe and InSe compounds with an optical response over an extended wavelength range, from the near-infrared to the visible spectrum.

1. Introduction

Over recent years there has been a resurgence of interest in exfoliable layered crystals following their integration into graphene-based devices. These materials are often referred to as van der Waals (vdW) solids due to the weak interlayer coupling. Atomically thin layers of large band gap insulators such as hexagonal boron nitride have been exploited as tunnel barriers. Substrates for graphene, and as quasi-epitaxial protective layers, while metal chalcogenides such as MoS$_2$ and WSe$_2$ are attracting increasing interest as optoelectronic materials. It is now established that these dichalcogenides have a thickness-dependent electronic band structure, including a transition from indirect- to direct-band gap for single monolayers, a property that has stimulated recent studies of photodetection and photovoltaic effects. By exploiting the ease with which atomically thin layers of these materials can be produced by mechanical exfoliation, it is now possible to assemble van der Waals heterostructures layer by layer, with properties that are quite distinct from those of the bulk starting materials. Among the vdW crystals, the III–VI layered semiconductors, such as GaSe and InSe, provide an important class of direct-band gap semiconductors. Recent work has included the exfoliation and growth by a vapor phase technique of thin films of GaSe, the demonstration of strong quantum confinement effects in InSe, whose direct-band gap can be tuned in the near infrared spectral range when the crystals are exfoliated into nanometer-thick flakes, and the direct-indirect band gap crossover occurring in the single monolayer limit. These properties differ from those of other vdW crystals (e.g., MoS$_2$, WS$_2$...), which become direct only as single monolayers. Despite their promise as optoelectronic materials, electroluminescence (EL) has to date not been reported in the III–VI layered crystal junctions, and, to our knowledge, has not yet been reported for any vdW heterostructure fabricated using exfoliation and mechanical adhesion between layered crystals.

In this work we demonstrate room temperature electroluminescence from van der Waals semiconductor junctions with atomically flat interfaces, which are fabricated by exfoliation and direct mechanical adhesion of III–VI layered crystals. Homojunction diodes formed from layers of p- and n-type InSe exhibit EL at energies ($h\nu = 1.23$ eV) close to the band gap energy of InSe ($E_g = 1.26$ eV). In contrast, heterojunction diodes formed by combining layers of p-type GaSe and n-type InSe emit photons at lower energies ($h\nu = 1.1–1.2$ eV), which we attribute to the generation of spatially indirect excitons and a staggered valence band lineup for the holes at the GaSe/InSe interface. Our results demonstrate the technological potential...
The primitive unit cells of heterojunction, we used InSe and GaSe, and optical image of a junction device.

mined from separate Hall effect measurements of electrons and holes of \(10^{15}\) cm\(^{-3}\) crystals with room temperature concentrations of \(10^{15}\) cm\(^{-3}\) and intentionally Cd-doped InSe crystals have lattice parameters of \(4.002\) Å and \(3.755\) Å. For the heterojunction, we used \(n\)-InSe and \(p\)-GaSe crystals with room temperature concentrations of electrons and holes of \(10^{15}\) cm\(^{-3}\) and \(10^{15}\) cm\(^{-3}\), respectively, which were determined from separate Hall effect measurements.\(^{[19]}\) For the homojunction, the undoped and intentionally Cd-doped InSe crystals have majority carrier concentrations of \(10^{15}\) cm\(^{-3}\) (\(n\)-type) and \(10^{13}\) cm\(^{-3}\) (\(p\)-type).\(^{[20]}\) The cleaved facets of InSe layered crystals are atomically smooth, contain a low-density of surface states and have stable and reproducible photoluminescence properties (see Supporting Information S1).

Flakes with areas between 1 µm\(^2\) to 1 cm\(^2\) and with thicknesses from 1 nm to 10 µm were prepared from as-grown crystals by mechanical exfoliation using adhesive tape. An individual large (~1 cm\(^2\)) flake of thickness of ~1–10 µm was then laid onto another layered crystal so that the adhesive van der Waals force between the layers forms an homojunction (e.g., \(n\)-InSe on \(p\)-InSe) or an heterojunction (e.g., \(p\)-GaSe on \(n\)-InSe). Indium Ohmic contacts were then formed on the top and bottom layers, Figure 1b. As illustrated in Figure 2a,b for a \(p\)-GaSe/\(n\)-InSe heterojunction, cross-sectional images acquired using transmission electron microscopy (TEM) and high-resolution TEM (HRTEM) show an atomically flat interface between the layers; elemental mapping using energy-dispersive X-ray (EDX) spectroscopy reveals a well-defined, abrupt transition going from the InSe to the GaSe layer along the c-axis (Figure 2c); also, the Fourier analysis of the HRTEM images indicate that the layers are generally misaligned in the plane perpendicular to the c-axis (see Supporting Information S2). These structural and compositional studies provide evidence for the high-quality of the crystal surfaces and the weak interface interaction between the different layered crystals, which form an abrupt junction despite the simple mechanical contact method used to form the junction and the large lattice mismatch, i.e., \(\varepsilon = |a_{\text{InSe}} - a_{\text{GaSe}}|/ a_{\text{InSe}} = 6\%\), between InSe and GaSe.

The room temperature current–voltage characteristics, \(I–V\), of the InSe homojunctions fabricated using the van der Waals mechanical contact technique show rectification with low leakage current densities in reverse bias, see Figure 3a. The \(I–V\) curve departs from a simple ideal diode equation indicating dominant recombination on defect-related states at the junction. Similar diode characteristics were also measured...
mostly absorbed near the surface (<1 μm) where the recombination time is short and photocarriers recombine before being collected at the p-n junction, which is >1 μm below the n-InSe top-layer. The heterojunction exhibits a similar behavior except that in this case the sharp cut-off is at \( \nu \sim 2 \text{ eV} \) due to the interband photon absorption in the top p-type GaSe layer, whose band gap energy is \( E_g = 2.05 \text{ eV} \) at \( T = 300 \text{ K} \).[23] Since all our junctions are based on flakes with thickness \( t \geq 1 \mu \text{m} \), quantum confinement effects are not significant. Layers of thickness \( t \leq 20 \text{ nm} \) would be required to observe a measurable increase of the direct band gap with decreasing \( t. \)[14]

For white light excitation with incident power of 100 mW/cm\(^2\), the n-InSe/p-InSe diodes produce an open-circuit voltage of \( V_{oc} \sim 0.6 \text{ V} \) and a short-circuit current density of \( J_{sc} \sim 0.7 \text{ mA/cm}^2 \). A larger photore- sponse (\( V_{oc} \sim 0.6 \text{ V} \) and \( J_{sc} \sim 7.5 \text{ mA/cm}^2 \)) is observed in the heterojunction since in this case the larger band-gap upper GaSe layer acts as a transparent window for the transmission of light. For an ideal junction, using the band diagrams of the isolated layers[23] and taking into account the energy position of the Fermi-levels (Figures 3a and 4a), we estimate that \( V_{oc} = 0.7 \text{ V} \) (homojunction) and \( V_{oc} = 0.8 \text{ V} \) (heterojunction), close to the measured values of \( V_{oc} \). The experimental \( V_{oc}\)-values can vary slightly in different junctions, thus indicating a possible contribution of crystal defects and impurities to the band alignment. In summary, these diodes exhibit sensitivity to light in the near infrared and visible range of the electromagnetic spectrum at a level that is comparable or better than that reported in the current literature for photodetectors based on other van der Waals crystals, such as MoS\(_2\) and WS\(_2\), which require exfoliation into single layers to become direct-band gap semiconductors.[7–10]

We now examine the EL properties of these junctions. In the homojunction, the EL peak is centered at \( \nu \sim 1.23 \text{ eV} \) at lower energy with respect to the photoluminescence (PL) emission, Figure 3b. Also, the EL spectrum reveals a weak inflection point at the energy of the PL peak energy, suggesting that the red-shifted EL spectrum arises from the re-absorption of photons in the n-type InSe top-layer. To confirm this attribution, we have used the energy dependence of the absorption coefficient, \( \alpha(\nu) \), of InSe as derived from the measured PC spectrum and the value of \( \alpha = 10^4 \text{ cm}^{-1} \) at the energy of the free exciton absorption at \( T = 300 \text{ K} \).[23] Hence we have derived: i) the emission spectrum, \( I_e(\nu) \), using the relation \( I_e(\nu) = \alpha(\nu) \exp(-\nu/k_B T) \); and ii) the effect on this spectrum of the re-absorption of photons through an InSe layer of thickness \( t \), i.e., \( I_e(\nu) = I_e(\nu) \exp[-\alpha(t) \nu] \). As shown in Figure 3b, with increasing...
To understand this behavior we need to consider the band alignment at the heterojunction interface: the conduction minimum (CB) of GaSe lies above that of InSe by $\Delta E_c = 0.9$ eV whereas the valence band (VB) edge of InSe lies below ($\Delta E_v = -0.1$ eV) that of the larger band gap GaSe, resulting in a staggered line up for the holes\(^{(22)}\) (inset of Figure 3a).

Consequently, the injection of holes and electrons from the p-GaSe and n-InSe can lead to the formation of spatially indirect excitons with a recombination energy ($h\nu = 1.15$ eV), which is below the energy of the direct indirect exciton in InSe, as we observe.

The Raman mode at 116 cm\(^{-1}\) responds to the energy of non-polar optical phonons in InSe\(^{(14–16)}\). In \(\gamma\)-InSe, each unit cell has 12 atoms and 36 vibration modes. The Raman mode at 116 cm\(^{-1}\) is the dominant mode observed in the Raman spectra under non-resonant conditions (see ref. \[15\] and Supporting Information S4). Thus we attribute the EL emission to phonon-assisted electron-hole recombination at the junction interface. Coupling to lattice vibrations can be influenced by local electric fields arising from surface dipoles due to the local atomic structure and charge distribution at the surface of the layers; the degree of coupling to the phonons also increases with the strength of localization particularly for holes due to their larger mass. To estimate the strength of carrier-phonon coupling, we describe the intensity ($I$) of the main EL emission in Figure 5 by Equation (1):

$$I(h\nu) = \sum_{\sigma} \frac{S}{m!} e^{-S} \exp\left(-\frac{(\Delta E_{\sigma} - h\nu - m\hbar\nu_p)^2}{2\sigma^2}\right)$$

which corresponds to the superposition of a zero-phonon line ($m = 0$) centered at $E_{\sigma}$ and phonon sidebands ($m > 0$) peaked at $E_{\sigma} - m\hbar\nu_p$. Here $S$ is the Huang-Rhys factor and $h\nu_p = 0.014$ eV is the measured phonon energy.\(^{(24)}\) In Figure 5, a typical EL spectrum is fitted to Equation (1) with $S = 0.6$, $E_{\sigma} = 1.16$ eV and $m = 3$. The high energy part of the EL spectrum is not described by Equation (1), thus suggesting an additional excitonic recombination mechanism involving the absorption of phonons. The specific form of the EL spectrum changes slightly from sample to sample, but the main EL band is always centered at lower energy (~0.1 eV) relative to the band gap energy of InSe, thus indicating a well-defined band lineup at the GaSe/InSe interface.
the measured fluorescence emission can be detected at room temperature in all of GaSe on InSe) between the constituent layers. Electroluminescence from electrically injected carriers is achieved even in the presence of a large lattice mismatch (≈6% for GaSe on InSe) between the constituent layers. Electroluminescence emission can be detected at room temperature in all of the measured p-n junctions thus opening realistic prospects for the implementation of these layered crystals in different sequences of layer stacking. These electroluminescent and photon sensitive junctions could be transferred on different substrates (e.g., plastics, graphene, boron nitride, etc.); since these crystals are direct-band semiconductors over a range of sequences of layer stacking. These electroluminescent and photon sensitive junctions could be transferred on different substrates (e.g., plastics, graphene, boron nitride, etc.); since these crystals are direct-band semiconductors over a range of wavelengths.

3. Conclusions

Mechanically formed van der Waals III–VI junctions have atomically flat interfaces, well-defined band lineups and radiative recombination from electrically injected carriers is achieved even in the presence of a large lattice mismatch (≈6% for GaSe on InSe) between the constituent layers. Electroluminescence emission can be detected at room temperature in all of the measured p-n junctions thus opening realistic prospects for the implementation of these layered crystals in different sequences of layer stacking. These electroluminescent and photon sensitive junctions could be transferred on different substrates (e.g., plastics, graphene, boron nitride, etc.); since these crystals are direct-band semiconductors over a range of wavelengths.

4. Experimental Section

The bulk III–VI crystals were studied by X-ray diffraction (XRD) using a DRON-3 X-ray diffractometer with a monochromatic Cu-Kα radiation of wavelength $\lambda = 1.5418 \text{ Å}$. The XRD data revealed that the InSe and GaSe crystals had $\gamma$- and $\epsilon$-phase structures, respectively. The experimental set-up for pMPL and pMEL comprised a He-Ne laser ($\lambda = 633 \text{ nm}$), an XY linear positioning stage, an optical confocal microscope system, a spectrometer with 150 and 1200 grooves/mm gratings, equipped with a charge-coupled device and a liquid-nitrogen cooled (InGa)As array photodetector. The laser beam was focused to a diameter $d \sim 1 \text{ µm}$ using 50× and 100× objectives, and the pMPL spectra were measured at low power ($P \leq 0.1 \text{ mW}$) to avoid lattice heating. For the photoconductivity studies, light from a quartz halogen lamp, dispersed through a MDR-23 diffraction grating monochromator, and modulated with a mechanical chopper, was focused onto the junction. The photocurrent signal was measured using a standard lock-in amplification technique.

For the transmission electron microscopy (TEM), high-resolution TEM and energy-dispersive X-ray (EDX) studies, a cross-sectional sample of the junctions was prepared by Ga ion beam thinning and lift-out in an FEI Quanta 3D FIB-SEM equipped with an Omniprobe micromanipulator system. Prior to lift-out, the sample was reinforced with vertical W-support straps to prevent delamination. A section between these straps was subsequently thinned to electron transparency for TEM analysis in a JEL 2100F FEG-TEM equipped with an Oxford Instruments INCA EDX system.

Acknowledgment

This work is supported by the Engineering and Physical Sciences Research Council (United Kingdom) and The University of Nottingham.

Received: April 30, 2014
Revised: June 23, 2014
Published online: August 20, 2014

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