

Isotype heterojunction solar cells using *n*-type Sb₂Se₃ thin films

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ABSTRACT: The carrier type of the emerging photovoltaic Sb₂Se₃ was evaluated for both thin films and bulk crystals via a range of complementary techniques. X-ray photoelectron spectroscopy (XPS), hot-probe, Hall effect and surface photo-voltage spectroscopy showed films and crystals synthesized from Sb₂Se₃ granulate material to be *n*-type with chlorine identified as an unintentional *n*-type dopant via secondary ion mass spectrometry analysis. The validity of chlorine as a dopant was confirmed by synthesis of intrinsic crystals from metallic precursors and subsequent deliberate *n*-type doping by the addition of MgCl₂. Chlorine was also shown to be a substitutional *n*-type shallow dopant by density functional theory calculations. TiO₂/Sb₂Se₃ *n-n* isotype heterojunction solar cells with 7.3% efficiency are subsequently demonstrated, with band alignment analyzed via XPS.

INTRODUCTION.

Antimony selenide (Sb₂Se₃) solar cells are a comparatively recent addition to the thin-film photovoltaics family. Sb₂Se₃ has numerous selling points as a PV material: it has high optical absorption of >10⁵ cm⁻¹, a 1.18 eV direct bandgap ¹, contains no scarce or high toxicity elements such as In, Te, Cd or Pb, is a simple binary material minimizing secondary phase concerns and has a nano-ribbon grain structure ², suggesting that isotropic charge transport should be realizable and the recombination rates of grain boundaries should be greatly reduced ³. Although a seemingly obvious candidate as a PV material, the first thin-film device efficiency of note was not reported until as recently as 2009 by

Messina *et al*, who utilized a solution deposition process to achieve 0.66% power conversion efficiency (PCE) ⁴. It wasn't until the work of the Tang group, demonstrating ~2% efficiency in early 2014 by either thermal evaporation⁵ or a hydrazine-based solution process ⁶, that interest in the technology started to increase. The field has rapidly developed since, primarily through vapor transport deposition techniques for Sb₂Se₃ and an ITO/CdS/Sb₂Se₃ device structure to achieve PCE of 5.6% in 2015, 6.5% in 2017 ⁷, 7.5% in 2018 ⁸ and 9.2% in early 2019 ⁹. This rapid growth in efficiency means Sb₂Se₃ has already exceeded the performance levels of long studied binary inorganics of high potential such as FeS₂ and SnS ^{10,11}. Research at the University of Liverpool has focused on the use of the well-established CdTe deposition technique of close space sublimation (CSS) ¹²⁻¹⁴ to develop a cell platform which produces material with preferable orientations compared to thermal evaporation routes, i.e., nano ribbons oriented perpendicular to the interface ². The use of CSS necessitated the development of an alternative SnO₂:F/TiO₂/Sb₂Se₃ device structure due to excessive interdiffusion with CdS, but yields carrier concentrations >10¹⁷ cm⁻³ ² and PCEs of over 6.6% ¹⁵ with open circuit voltages (*V*_{oc}) beyond the current state of the art. Given the rapid growth of performance, this technology should easily exceed 10% PCE in the near future. Key to achieving this goal however will be development of a comprehensive understanding of the Sb₂Se₃ material, to align with the encouraging early stages of cell development.

A key assumption that has been made in the emergence of Sb₂Se₃ solar cells is that the absorber is predominantly *p*-

type. Inorganic thin film solar cells almost universally utilize *p*-type absorbers, with the exception of BiS₂¹⁶. The majority of reported Sb₂Se₃ devices also adopt the TCO/CdS/Sb₂Se₃ structure, common to CZTS, CIGS and CdTe¹⁷, again all of which are *p*-type absorbers. The natural assumption is therefore that we have simply incorporated Sb₂Se₃ as an alternative *p*-type absorber into the existing device architecture. However, the actual carrier type of Sb₂Se₃ is somewhat unclear and is often assumed to be *p*-type rather than measured. Work on high purity single crystals showed the material to be insulating¹⁸, something supported by recent density functional theory calculations¹⁹ which suggested significant mid-gap pinning due to native defects.

There are some reports of carrier type determination in solar cell material, although the results are typically from a single group and often inconclusive. Liu *et al.*⁵ report Seebeck analysis showing *p*-type character of thermally evaporated thin films, but subsequently draw the band structure based on XPS analysis with a near insulating Fermi level. Zhou *et al.*²⁰ found *p*-type conductivity via cyclic voltammetry and Hall measurements, although Hall effect data were not shown. The same group have also latterly reported some *n*-type and insulating character in devices. Zhou *et al.*²¹ also suggested the formation of *n*-type Sb₂Se₃ regions near to the CdS interface due to Cd out-diffusion from the CdS layer, with the remainder of the Sb₂Se₃ layer being *p*-type. The mechanism by which Cd may act as an *n*-type donor is unclear, however. Recent work by the same group has further suggested Sb₂Se₃ to be insulating and a CdS/Sb₂Se₃/CuSCN device to function as a *n-i-p* structure²². How the insulating character of the material was determined was not specified.

In this paper we conclusively demonstrate *n*-type character of both single crystals and thin films of Sb₂Se₃ via a range of analysis techniques. We identify chlorine impurities as the source of the *n*-type doping and subsequently demonstrate MgCl₂ as an effective deliberate *n*-type dopant for single crystal Sb₂Se₃. We thereby establish that the TCO/TiO₂/*n*-Sb₂Se₃/Au device structure produced is in fact an isotype *n-n* heterojunction device.

EXPERIMENTAL.

Thin film and cell fabrication: Sb₂Se₃ cells discussed in this work were deposited on the commercial SnO₂:F (FTO) coated soda-lime glass TEC10 from NSG ltd. The device structure was glass/FTO/TiO₂/Sb₂Se₃/Au. TiO₂ layers were first deposited via RF sputtering to a thickness of ~10 nm at room temperature followed by a two-stage spin coating process. A 250 µl concentration of 0.15 M titanium isopropoxide (TTIP) in ethanol solution was deposited on a 50 × 50 mm substrate at 4000 rpm followed by 275 µl of 0.3 M TTIP in ethanol. The substrates were then air annealed at 500 °C for 30 min. Sb₂Se₃ layers were deposited using Alfa Aesar 5N granulate material via CSS using a two stage process¹⁵. Firstly, a compact “seed” layer was deposited to ensure good coverage. This was done under vacuum at a source temperature of 350°C with the substrate temperature being ramped from 250 °C to 390 °C over a period of five min. A second stage to deposit a larger grained film was

then performed under 10 Torr of nitrogen at source and substrate temperatures of 460 °C and 410 °C respectively, giving a film thickness of ~1.5 µm. Sb₂Se₃ source material is used for multiple (>100) depositions following an initial “bake” process performed at temperatures higher than used for growth to establish a consistent material baseline. No post growth processing of CSS material was employed. 0.1 cm² gold back contacts were finally added via thermal evaporation.

Crystal growth: Sb₂Se₃ single crystal samples were grown using a vertical Bridgman melt-growth method. The crystal growth method was identical for all samples, with the only difference being in the source material used. For single crystals utilising the non-intentionally doped Sb₂Se₃ (5N purity Alfa Aesar), the source material granulate was used with no further additives. Undoped Sb₂Se₃ bulk crystals, were synthesised from metallic Sb (6N purity Alfa Aesar) and Se (5N purity Alfa Aesar). 8 g in total of metallic Sb and Se shot were added to a 16 mm diameter quartz tube. The elements were weighed to achieve a ratio close to stoichiometry, with a small (~0.01 at%) Se excess observed in the weighed elements. Ampoules were heated to 615 °C then held for 24 hr to allow full reaction and homogenisation, before cooling to 300 °C at 1.5 °C/min. For MgCl₂-doped single crystals, (0.1 ± 0.02) at% solid MgCl₂ was weighed, added to the undoped Sb₂Se₃ powder formed by the above process, and mixed. Sealed ampoules were lowered into a vertical single-zone furnace with the ampoule tip being held at the peak temperature point of 620 °C, set to be just above the 611 °C melting point of Sb₂Se₃²³. A lowering rate of 1.15 mm/hr through the furnace, for 7 days, with a temperature gradient of 6 °C/cm, was used. This produced crystals of 3 cm in length with the first 1.5-2 cm being large grained polycrystalline and the remaining section confirmed to be single crystal. Further details are given in the paper by Hobson *et al.*²⁴.

Hot-point probe technique: Hot-point probe was carried out using an in-house system. Samples were contacted with gold contacts and gold point probes with a heat source attached to one probe. The current generated was monitored via a Keithley 2400 source meter as current was found to produce more consistent data than voltage for analysis of calibration samples.

Electronic transport measurements: For transport measurements, including Hall effect, square samples of ~3 mm lateral size were cleaved from larger Sb₂Se₃ crystals doped with Cl. Thicknesses of the crystals used were in the 0.4 to 1 mm range. Indium contacts were soldered on the crystals in a van der Pauw geometry²⁵. Four-terminal resistances were then measured DC using a Keithley 2400 source-measure unit in conjunction with a Quantum Design Physical Property Measurement System (PPMS) (in perpendicular magnetic fields to 60 or 90 kOe) or a Janis Corporation flow cryostat in an electromagnet (to 10 kOe). All presented measurements were done at 300 K. Care was taken to select appropriate excitation currents to avoid non-Ohmic response and/or self-heating.

Surface photovoltage measurement: Surface photovoltage measurements (SPM) were carried out using a Vibrating Kelvin Probe (probe diameter = 2 mm) (KP Technology, UK)

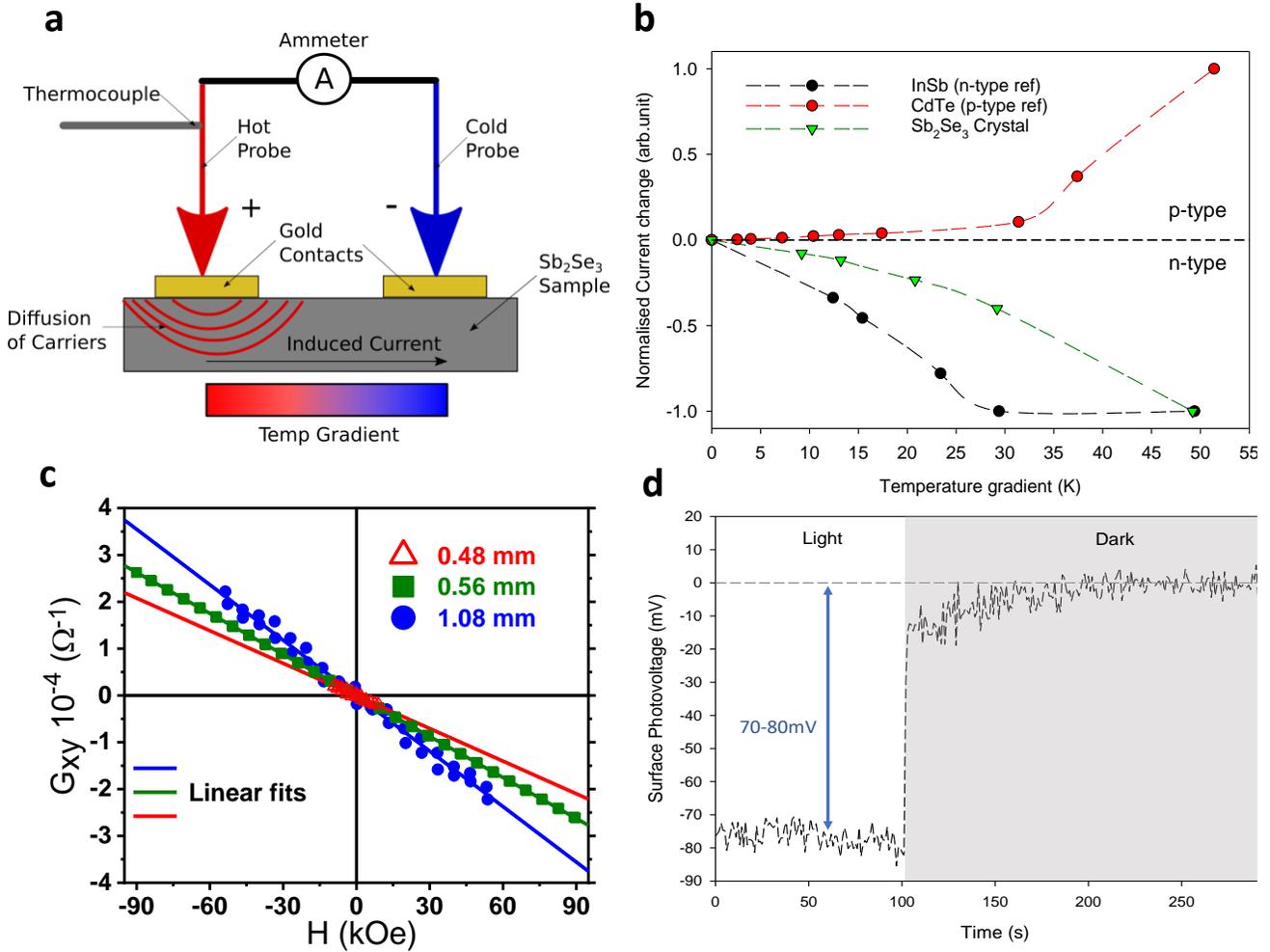


Figure 1. a) Hot probe measurement setup for bulk carrier type determination, b) Normalized hot probe data for Sb_2Se_3 bulk crystal grown from Sb_2Se_3 granulate with *p*-type and *n*-type reference crystals, c) Hall conductance (G_{xy}) vs. applied magnetic field (H) for three Sb_2Se_3 crystals with different thicknesses (0.48, 0.56, and 1.08 mm). The straight lines are linear fits to the corresponding data, which had zero field backgrounds subtracted and d) Surface photovoltage measurement of a $\text{TiO}_2/\text{Sb}_2\text{Se}_3$ device back surface.

to determine the surface work function in the dark and under illumination. All the measurements were done in constant N_2 flow. To illuminate the whole surface, light from a 150 W quartz tungsten halogen lamp was incident on the sample using an optical fiber and lens at an angle of 45° with respect to the sample surface. This configuration allows illumination and probing from the same side. The work function of the Kelvin probe was calibrated by a freshly cleaved highly ordered pyrolytic graphite surface.

UPS/XPS/HAXPES analysis: Ultraviolet photoemission spectroscopy (UPS) was performed using a He(I) discharge lamp in combination with a hemispherical electron-energy analyser (PSP Vacuum Technology) with a 120 mm radius to detect photoelectrons, operated at a pass energy of 2 eV. X-ray photoemission spectroscopy (XPS) was performed using a SPECS monochromatic Al $K\alpha$ ($h\nu = 1486.6$ eV) x-ray source operated at 250 W and the same analyser as for the UPS measurements using a pass energy of 10 eV. The nar-

rower line width of the UPS source means a better resolution is achieved with UPS over XPS. Hard X-ray Photoelectron Spectroscopy (HAXPES) was performed at the I09 beamline at the Diamond Light Source. A double-crystal Si (111) monochromator was used to select 5921 eV photons. A Si (004) channel-cut crystal was employed to monochromate the beam, improving the resolution. The end station is equipped with a VG Scienta EW4000 electron analyzer with $\pm 30^\circ$ angular acceptance. In all photoemission experiments performed, binding energies are stated with respect to the Fermi level, which was calibrated using the Fermi-edge of a metal (cleaned polycrystalline silver or gold), also allowing the resolution of the systems to be determined ($\Delta_{UPS} = 0.13$ eV, $\Delta_{XPS} = 0.43$ eV, $\Delta_{HAXPES} = 0.28$ eV). Bulk crystal samples were cleaved in situ to expose a clean surface, and all measurements were performed at room temperature. CSS thin films were measured using XPS and HAXPES without any in situ preparation.

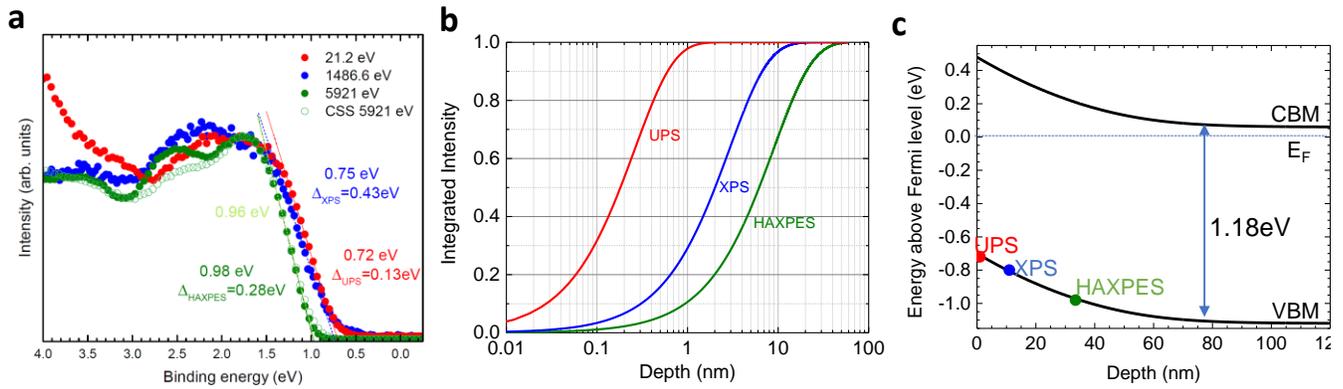


Figure 2. a) Valence band spectra from a cleaved bulk crystal measured using HAXPES (5921.0eV), XPS (1486.6eV) and UPS (21.2eV) with a CSS thin film measured by HAXPES for comparison (thin film and crystal HAXPES data overlaps). Values are the VBM to fermi level separation determined, with Δ values being the resolution of the technique; b) The integrated photoemission signal intensity as a function of depth for the three different photon energies used calculated using the TPP model of inelastic mean free paths; c) determined band bending at the back surface from photoelectron measurements.

SIMS analysis: Time of Flight Secondary Ion Mass Spectrometry (SIMS) of thin films was performed using an ION-TOF V instrument. The analysis beam was 25 keV Bi^{3+} with an analysis area of 50 microns square. The depth profiling beam was 1 keV Cs^+ operated with a raster size of 200 microns square. To minimise the SIMS matrix effect, CsM^+ cluster secondary ions were selected to obtain compositional depth profiles. Quadrupole SIMS of bulk crystals was performed using a Hiden Analytical gas ion gun and quadrupole detector. A beam of O^{2-} ions rastered over a $500 \times 500 \mu\text{m}$ area was used to sputter the sample using a beam energy of 5 keV at a current of 300 nA,

DFT calculations: Calculations were performed using Density Functional Theory (DFT) within periodic boundary conditions using the Vienna Ab Initio Simulation Package (VASP).²⁶⁻²⁹ The screened hybrid exchange correlation functional HSE06 was used³⁰ for electronic structure with geometry optimization of both bulk and defect supercells of Sb_2Se_3 . Due to the layered nature of the Sb_2Se_3 structure, the D3 dispersion correction from Grimme et al. was also included in all calculations,³¹ while spin-orbit coupling (SOC) was included for all bulk electronic structure calculations. Defect calculations were performed using the HSE06+D3 method on a $1 \times 3 \times 1$ supercell (60 atoms) with a Γ centered $2 \times 2 \times 2$ k-point mesh and a plane-wave energy cutoff of 350 eV. Spin-orbit coupling effects were not included in these calculations due to their expense and minimal structural effects; the relativistic renormalisation at the k-points considered is also small (~ 0.1 eV). To account for the 'finite size effects' of the supercell and restore the dilute defect model, three corrections were used. Firstly, a correction is necessary to ensure that the electrostatic potential of the host and defect supercells are aligned³². Secondly, defects within supercells may interact with their own periodic images, causing the formation of a defect band; if this defect level is shallow, it may interact with a conduction or valence band, leading to erroneous filling with electrons and affecting the total energy. To counteract this, a 'band filling' correction was applied³³. Thirdly, charged defects may interact

with each other coulombically, due to the long range behavior of such effects, and so a further 'image charge' correction is required. In this report, we use the formalism of Murphy et al., as this accounts for anisotropy in the dielectric constant of the material, an effect which is strong for Sb_2Se_3 .³⁴

Device characterization: Current-voltage (J - V) measurements were performed under AM1.5 illumination provided by a TS space systems solar simulator. Capacitance voltage measurements were performed using a Solatron impedance analyzer. For external Quantum Efficiency (EQE) measurement a Bentham PVE300 system was used

RESULTS.

We were able to determine the carrier type of bulk Sb_2Se_3 crystals grown from granulate source material using a hot probe technique³⁵, shown schematically in Figure 1a. Two metal probes were contacted to a sample surface, with one probe being in contact with a heat source. The hot probe thermalizes carriers in the vicinity causing a diffusion current of free carriers which can be read through an external ammeter. Depending on the majority carrier type of the material this produces either a positive or negative current gradient with temperature. The sign of the current gradient can thus be used to determine the carrier type of unknown materials, for instance when calibrated with reference to known n or p -type materials. This technique has the advantage of not requiring any specific sample preparation, being applicable even for relatively low doping densities and being a bulk measurement technique (*i.e.*, it is independent of doping variations at the surface or contacting barriers³⁵). Figure 1b shows hot probe data recorded for both bulk crystal Sb_2Se_3 , along with known compound semiconductor single crystal reference samples of InSb (n -type) and CdTe (p -type). The current values were assessed over an ~ 50 K range and have been normalized to allow easy comparison, as the magnitude of current recorded is highly sample specific. The data show a negative gradient for Sb_2Se_3 indicating that it is n -type. This was confirmed by comparison to both reference samples, which showed the expected positive p -type and negative n -type gradients.

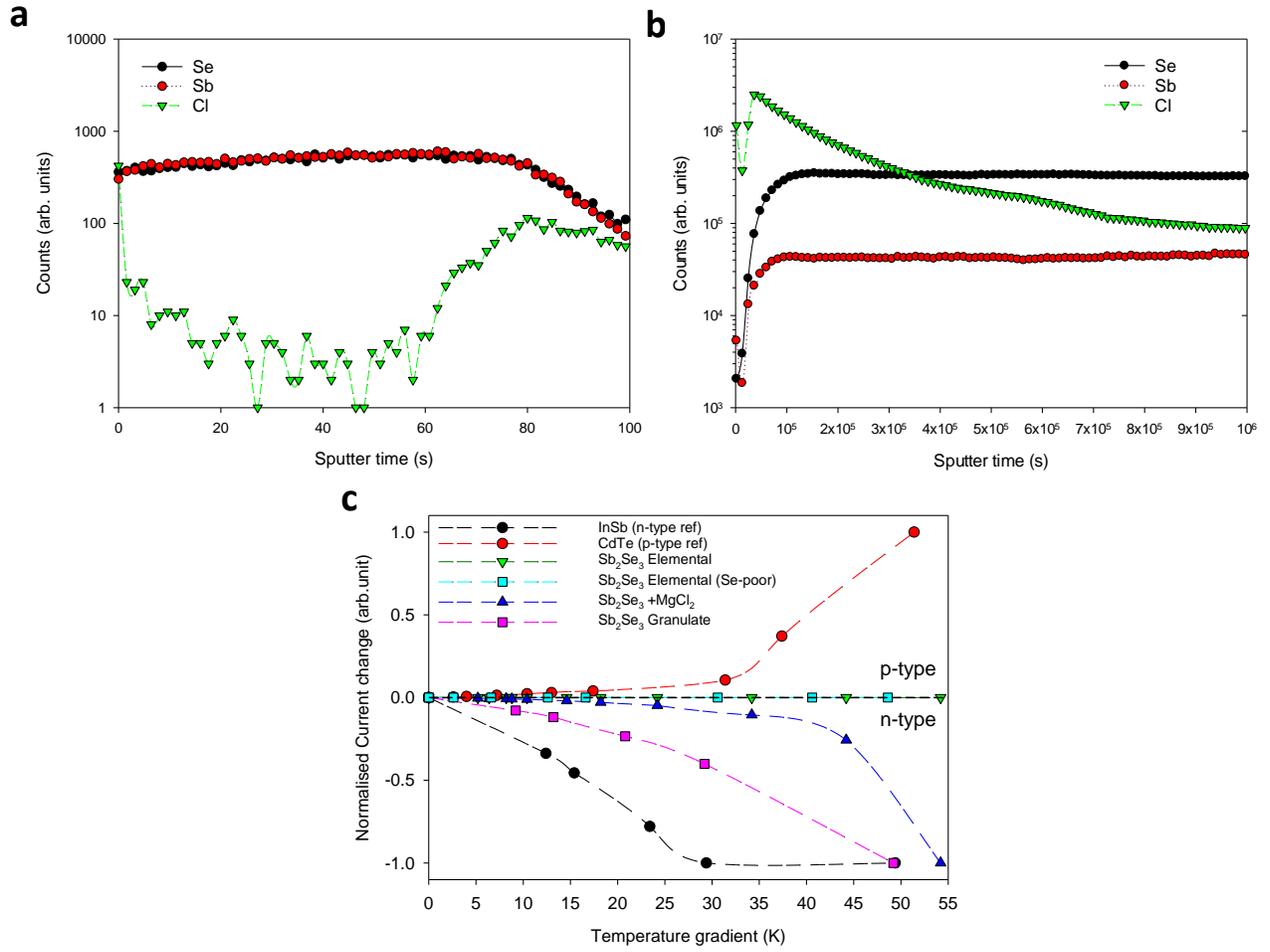


Figure 3. a) SIMS of Sb_2Se_3 cell structure, b) SIMS analysis of a crystal grown from Sb_2Se_3 source material, c) hot probe comparison of carrier type in Sb_2Se_3 crystal grown from Sb and Se elemental precursor material, with addition of MgCl_2 , under Se-poor conditions and comparison with growth from Sb_2Se_3 granulate precursor .

The majority carrier type of single crystal material was also confirmed via Hall effect measurements. Fig. 1c shows the 300 K Hall conductance (G_{xy}) vs. applied magnetic field for three Sb_2Se_3 crystals of different thickness: 0.48, 0.56 and 1.08mm. The Hall conductance G_{xy} is defined as $G_{xy} = \frac{R_{xy}}{R_S^2(0)}$ where R_{xy} is the Hall resistance and $R_S(0)$ is the sheet resistance at zero applied field. In all cases, simple linear behavior with negative slope is found. Given the magnitude of the signal, the sizable mobility (see below), and the absence of non-linearity to 90 kOe, we conclude a single dominant carrier type, definitely electrons, i.e. n-type behavior. This is in accord with the results obtained from hot-probe in Fig. 1a, and other data discussed below, all of which indicate

n-type carriers. The Hall coefficients, $R_H = -\frac{1}{|n|e}$, from the slopes of the straight-line fits in Figure 1c yield electron densities n of 3.99×10^{16} , 3.98×10^{16} , and $3.30 \times 10^{16} \text{ cm}^{-3}$ for the three crystals. The room temperature resistivities (ρ) were 6.54, 5.46, and 6.04 $\Omega \text{ cm}$, giving carrier mobilities μ of 24.0, 28.7, and 31.3 $\text{cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ respectively. The n , ρ , and μ values are thus in very reasonable agreement in these three crystals, the mobilities being easily large enough to

rule out potential complications with non-diffusive transport³⁶.

We note that thin-film layers produced by CSS from Sb_2Se_3 granulate material were not able to be measured by either Hall effect or hot probe measurements. Hot probe did not yield a sufficient signal to give a clear sign determination, whilst Hall measurements were frustrated by high resistivity, high contact resistance and low apparent mobility. The measurement issues here may be a result of the material anisotropy and the necessity for the films to be deposited on an insulating substrate, i.e., glass. A large amount of prior work was required to optimize film orientation on FTO/ TiO_2 for device application^{2,15}. Use of a glass substrate thus likely results in a non-favorable film orientation, and low mobility in the plane of the measurement³⁷.

Nevertheless, n-type character of thin-film device layers was able to be confirmed by surface photovoltage measurement (SPV) using a Kelvin probe (KP). SPV measurements were carried out on the free back surface of a complete $\text{TiO}_2/\text{Sb}_2\text{Se}_3$ device structure, where the film orientation is optimized. SPV measurements show that the surface work function decreased under illumination (Figure 1d). This can

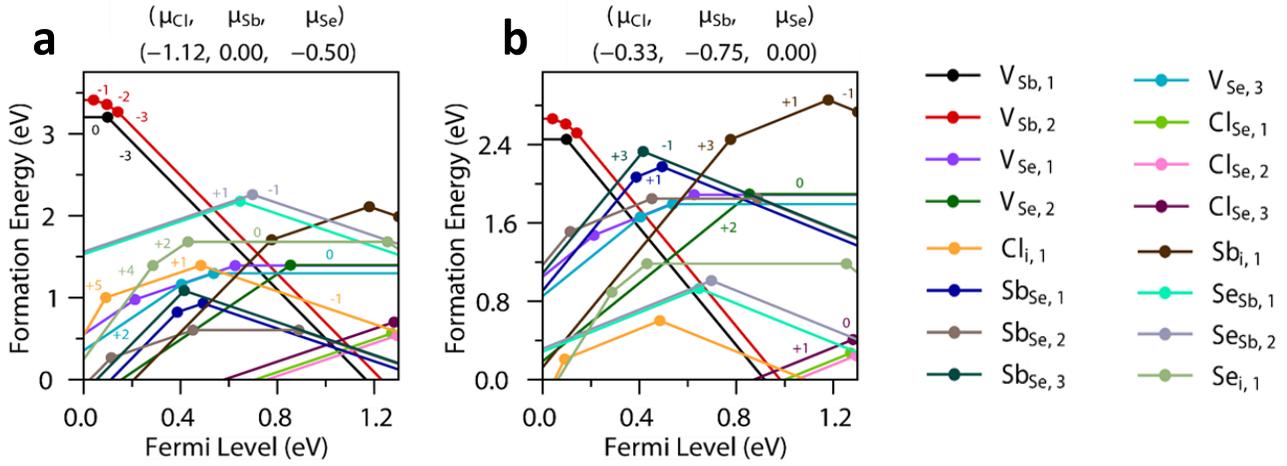


Figure 4. Defect transition level diagrams for Sb_2Se_3 doped with Cl under limiting chemical potential conditions (A) Sb-rich and (B) Se-rich, plotting defect formation energy (eV) against the position of the Fermi level above the valence band maximum. Defect labels are given in the legend, charge states are given by the labels adjacent to the lines (with parallel lines sharing the same charge state), and transition levels are represented by filled circles.

be explained by the upward, i.e., from bulk to surface band bending, due to the trapping of electrons (the majority carrier of the semiconductor) on the surface. Upon illumination, the trapped electrons are screened by the photo-generated hole which moves to the surface due to the band bending. This screening of electrons decreases the band bending, causing a decrease in surface work function. In this case, the effect is amplified due to the presence of the TiO_2 interface where the photo-generated holes encounter an energetic barrier. The SPV measurement thus identified n -type behavior of the thin film Sb_2Se_3 material also, in agreement with the single crystal measurements.

Further validation of the n -type character of the material was sought through a range of photoelectron spectroscopy techniques (UPS, XPS and HAXPES), which were used to determine the work function at a range of penetration depths. Photoelectron spectroscopy work primarily focused on single crystal material as this provided a cleaner signal, and crystals could be in-situ cleaved at the van der Waals bonds, removing the potential influence of surface oxide phases³⁸. Confirmatory XPS and HAXPES analyses were also carried out on thin film layers to check consistency with the crystal data.

Figure 2a shows photon-energy-dependent photoemission of the valence band spectra of a cleaved bulk Sb_2Se_3 crystal for UPS, XPS and HAXPES analysis with a CSS-grown thin film HAXPES profile for comparison. The valence band maximum (VBM) to Fermi level separation is estimated by extrapolating the leading edge of the valence band photoemission to zero (Figure 2a). The higher the photon energy used, the higher the kinetic energy of the generated photoelectrons and the greater the effective probing depth, as illustrated in Fig. 2b. The UPS spectrum probes the Fermi level and valence band position at ~ 1 nm from the back surface compared to up to ~ 30 nm for HAXPES. This depth-dependent photoemission allows not only determination of doping type via the Fermi level position, but also an estimate of the band bending at the surface, as shown in Fig. 2c. The Fermi

level position in the bulk has been estimated using Hall-determined shallow doping levels (i.e., $\sim 10^{16}$ - 10^{17} cm^{-3}). For all depths probed the Fermi level is always above the middle of the band gap, demonstrating that the Sb_2Se_3 is n -type. This depth dependent analysis also indicates upward band bending at the back surface, with the material being more highly n -type away from the back surface. This corresponds to the presence of a surface electron depletion layer which may be modelled by solving the Poisson equation³⁹. HAXPES analysis of CSS deposited thin film material showed good agreement with the cleaved single crystal. In both cases the material was found to be n -type and with the VBM to Fermi level position being near identical, 0.98eV for bulk crystals and 0.96eV for CSS films, with the bandgap being 1.18eV.

Recent density functional theory work on native defect formation energies by Savory *et al.*¹⁹, identified that Sb_2Se_3 should be natively insulating due to the midgap pinning influence of vacancy defects. Based on this analysis, and the comparatively high doping levels observed in our material, it seemed likely that our material contained unintended n -type extrinsic dopants. Clearly, impurities can arise at various points in the sample preparation. However, as both thin film and single crystal samples displayed similar n -type doping, but no common fabrication steps, it was suspected that contamination arose from the granulate Sb_2Se_3 source material (5N purity Alfa Aesar), which was common to both thin films and crystals.

TOF-SIMS analysis was initially performed on a complete cell structure, as a screening process to identify possible contaminants. A number of expected contaminants were observable in the soda lime glass layer (e.g., Na, Mg, Ce), but the only contaminant observed in all samples at significant levels within the Sb_2Se_3 layer was Cl. Figure 3a shows SIMS profiles for Sb, Se and Cl in a $\text{TiO}_2/\text{Sb}_2\text{Se}_3$ CSS deposited device (a similar Cl content was found for other CSS and thermally evaporated Sb_2Se_3 device structures, Figure S1). The

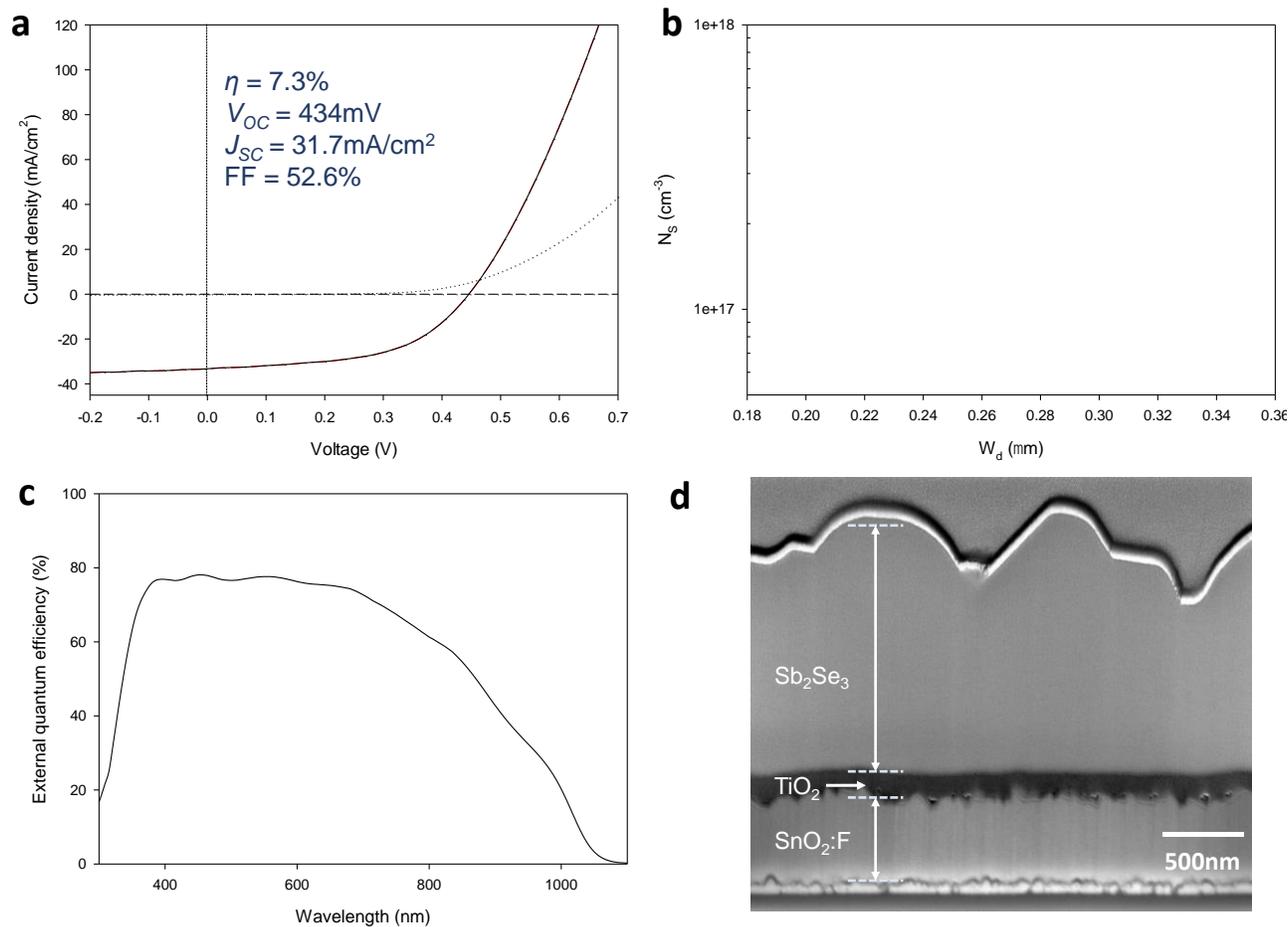


Figure 5. a) JV curve for TiO₂/Sb₂Se₃ isotype junction, b) Shallow doping density versus depletion width calculated from capacitance voltage measurement, c) External quantum efficiency curve, d) SEM cross section of device structure.

Cl signal appears lower towards the free back surface (0 s sputter time), but there is accumulation primarily in the region near the Sb₂Se₃/TiO₂ interface (60-80 s sputter time). The presence of chlorine could not be otherwise accounted for, and was identified as a potential *n*-type dopant via substitution on a Se-site. Quadrupole SIMS analysis of single crystal material, figure 3b, demonstrated an even higher Cl content in the bulk crystal material. It was therefore strongly suspected that Cl contamination of the Sb₂Se₃ feedstock was the cause of *n*-type doping. The Sb₂Se₃ feedstock was able to be pinpointed as the source of Cl contamination as crystals and thin films shared no common fabrication steps. The only commonality between the two sample types was the source material.

Verification of Cl as the active dopant was done in two parts. Firstly, bulk crystals were fabricated from high purity metallic Sb and Se source material, rather than from Sb₂Se₃ granulate (i.e., with removal of extrinsic impurities in granulate source material). These high purity samples were found to be highly insulating, with no measurable carrier type even by hot probe, as shown in Figure 3c. Secondly, to definitively establish the role of Cl, the insulating material was reground into powder and mixed with MgCl₂ (0.1 at%), a convenient Cl source used for CdTe cell processing¹⁷, before being recrystallized. MgCl₂ was additionally selected as, if active, Mg would be a *p*-type dopant via Mg_{Sb}, so Mg could be discounted as a source of any *n*-type doping observed. X-

ray diffraction (XRD), Figure S3, showed no evidence of structural change or secondary phases as a result of Cl incorporation. Regardless formation of secondary phases such as SbCl₃ is not a concern given its low melting point and the fabrication temperatures used. Hot probe analysis of the resultant crystal showed addition of Cl converted insulating material to *n*-type (Figure 3c). This is a clear demonstration that i) on the basis of native defects Sb₂Se₃ is insulating and ii) Cl is an effective *n*-type dopant, with MgCl₂ being a suitable chlorine source for doping. Further to this we also produced crystals grown from Sb and Se elemental precursors but with a Se deficiency i.e. Se-poor conditions. This was done to rule out the possibility of selenium vacancies acting as a *n*-type dopant as has previously been suggested⁴⁰. As shown in Figure 3c Se-poor conditions produced no shift from insulating behavior and there was no indication that *n*-type character resulted from native defects.

DFT calculations were then performed to examine the potential of Cl in Sb₂Se₃ as a dopant. Chlorine was introduced as a substitution on all 3 symmetry-inequivalent Se sites, as well as an interstitial into a $1 \times 3 \times 1$ (60 atom) supercell which was used in the previous ab initio study on the intrinsic defects of the Sb₂Se₃ system¹⁹. As such, the defect formation energies are directly comparable to the intrinsic calculations. Figure 4 depicts the transition level diagrams under the two relevant chemical potential limits of Sb₂Se₃ – a)

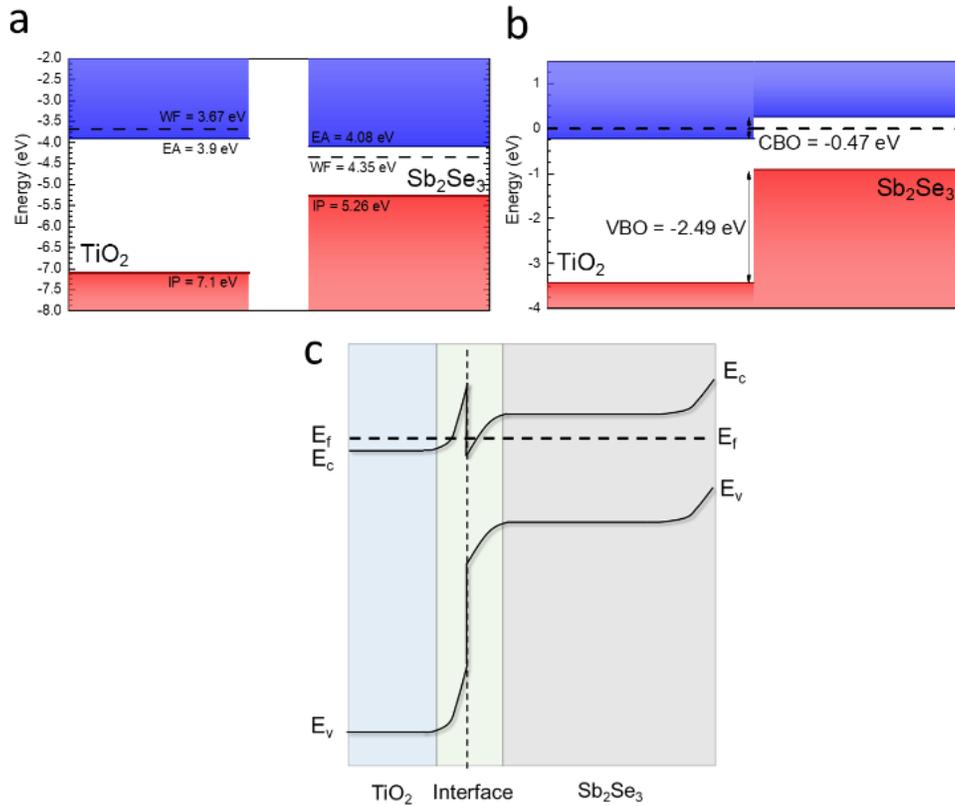


Figure 6. a) TiO₂ and Sb₂Se₃ energy level positions determined from XPS analysis showing electron affinity (EA), work function (WF) and ionization potential (IP) of each material, b) band alignment of TiO₂/Sb₂Se₃ interface and c) proposed band structure of TiO₂/Sb₂Se₃.

Sb-rich, Se-poor and b) Se-rich, Sb-poor. SbCl₃ was the most stable Sb-Cl phase at $\mu(\text{Sb})=0$, and so its formation energy was used for the chemical potential of Cl in the Sb-rich limit, while the *P*-43n phase of SeCl₄ was the limiting Cl-containing phase in the Se-rich limit. In both chemical potential limits, Cl_{Se} is a dominant defect, with low formation energies (<0.5 eV) on all 3 Se sites. The Se² position at the edge of the Sb-Se 1D ribbons is the most favourable to substitute; in all cases, this defect is likely to act as a shallow donor, with the +1/0 transition level always occurring within 25 meV of the conduction band edge. The Cl interstitial shows amphoteric behaviour, similar to both Sb_i and Se_i – the interstitial region of Sb₂Se₃ allows stable situations for both Cl acting in negative and positive oxidation states – although the -1 charge state dominates for most Fermi level positions.

The primary effect of Cl doping will be to significantly shift the Fermi level position and modify Sb₂Se₃ from intrinsic to *n*-type. In both chemical potential conditions, Cl_{Se} will be compensated by V_{Sb} below the conduction band edge, however, moving E_F from mid-gap in the intrinsic regime to within 0.3 eV of the conduction band edge. This will lead to significantly higher electron concentrations. We can quantify this effect using the SC-Fermi package,⁴¹ which self-consistently solves for the Fermi energy given a set of defect formation energies assuming thermodynamic equilibrium and overall charge neutrality. Considering the intrinsic defects alone¹⁹, the calculated Fermi levels lie almost exactly

at the mid-gap: 0.632 eV above the VBM for Sb-rich and 0.641 eV for Se-rich. With the Cl defects included, the Fermi level shifts to 1.057 eV in the Sb-rich regime, only ~0.23 eV below the HSE06+D3 conduction band position and aligning extremely well with the observed experimental conduction band/workfunction separation. The predicted concentration of electrons from a Fermi-Dirac distribution at 300 K is only $6.3 \times 10^{14} \text{ cm}^{-3}$, significantly greater than that from the intrinsic defects alone, but far from that observed experimentally. Furthermore, in the Se-rich regime, the Fermi level is shifted to 0.944 eV, and the predicted electron concentration is $7.9 \times 10^{12} \text{ cm}^{-3}$. This model, however, assumes that the defect concentrations are at their equilibrium concentrations at 300 K, whereas the synthesis of the material occurs at much higher temperature. At elevated temperatures, defects will be more prevalent and some of these may be retained in the films. To model this situation, SC-Fermi can calculate the self-consistent Fermi level at 300 K, but where the defects are fixed at their concentrations for fabrication temperatures of 700 K. For both chemical potential regimes, this shifts the Fermi level to ~1.27 eV and increases the predicted electron concentration to $2.5 \times 10^{18} \text{ cm}^{-3}$ (Se-rich) or to $2.1 \times 10^{20} \text{ cm}^{-3}$ (Sb-rich). In reality, the defect concentrations in the synthesized samples will lie somewhere between these two extremes, in line with the 10^{16} - 10^{17} cm^{-3} electron concentration observed experimentally.

Complete solar cell structures were fabricated from the granulate source material established to be *n*-type doped due to the presence of Cl. Figure 5a shows *J-V* data for a TiO₂/Sb₂Se₃ device with associated *C-V* data converted into shallow doping (N_s) versus depletion width (W_d) in figure 5b, and EQE in figure 5c. Compared to cell structures reported in our prior work,^{2,15} the efficiency has been increased by the inclusion of a sputtered TiO₂ layer, prior to solution deposition of a thicker TiO₂ film. This creates uniform TiO₂ coverage, as seen from the cross-sectional SEM image in Figure 5d, reducing shunting losses occurring due to the TiO₂ layer and thus improving the FF. This structure has so far yielded a peak PCE of 7.3% with $V_{oc} = 434$ mV, $J_{sc} = 31.7$ mA/cm² and FF = 52.6%. From analysis of capacitance voltage measurements (Figure 5b), the apparent doping density, now established to be donor doping, was $\sim 10^{17}$ cm⁻³. The increase to $>10^{17}$ cm⁻³ at $W_d < 0.2\mu\text{m}$ is due to the influence of the back contact, as commonly observed for CdTe solar cells⁴², rather than a genuine increase in doping.

Critically, given our identification of the absorber as *n*-type, the device clearly does not have the standard *p-n* junction architecture, and as such our TiO₂/Sb₂Se₃ device is better described as a *n-n* isotype heterojunction^{43,44}. An important point of note is to recognize that *J-V* and *C-V* analyses of a device junction in isolation cannot determine the *majority carrier type* of the absorber. *C-V* measures the capacitance change of the depletion region extending with applied bias, from which the carrier density, but not type, of the absorber may be inferred. For thin film PV devices, including Sb₂Se₃ ones, it is a common assumption that they operate as a one-sided *p-n* junction and *CV* data is then interpreted using the appropriate *CV* relation. However, the *p* and *n* designations simply relate to the fermi level position relative to the mid-gap. The direction of carrier flow is essentially independent of such classifications and is determined by the *relative* fermi level positions of the two partner layers, as well as the conduction and valence band offsets. If carrier flow under illumination is in the same direction, a *n-n*, or indeed *p-p*, isotype junction is essentially indistinguishable from a *p-n* junction by the *J-V* and *C-V* behavior alone⁴³.

To assess the functionality of our device structure, band positions were determined for device layers via XPS. Figure 6a shows work function, electron affinity and ionization potential values determined for Sb₂Se₃ and TiO₂ thin films via XPS analysis (raw data is given in supplementary information Figure S2). The “natural” band alignment of the two layers based on VBM, CBM and Fermi level positions is shown in Figure 6b with a proposed band diagram for the resultant structure in Figure 6c. The TiO₂ layer was measured with a degenerate Fermi level position, indicative of significant downward band bending at the surface⁴⁵. The bulk of the TiO₂ film will likely have non-degenerate doping, however this surface Fermi level position is considered more representative for junction formation. When the Sb₂Se₃ and TiO₂ layers are brought into contact, electrons flow from the material with the higher fermi level (TiO₂: -3.67eV) to the lower fermi level (Sb₂Se₃: -4.35eV), creating a built-in potential V_{bi} in the same direction as would be anticipated for a *p-n* junction. A spike and trough occur in the near-inter-

face region due to the charge transfer. The respective conduction and valence band offsets also favor electron extraction through the TiO₂. Compared to an equivalent *p-n* junction architecture, the built-in voltage will be reduced but this has essentially been traded off for the benefit of higher carrier concentration. This demonstration of Sb₂Se₃ solar cells being based on an *n-n* isotype junction begs a number of questions; i) which carrier type is truly optimal for performance of such solar cells? ii) can device designs be improved on the basis of an *n*-type absorber? iii) are *p*-type doping processes required, and iv) can *p-n*, or indeed *p-i-n/n-i-p*, junction structures be fabricated by controlled doping approaches? Finally, we would emphasize that our results do not imply all reported Sb₂Se₃ solar cells, from varied deposition processes and source materials, are *n*-type. The Cl contamination, and thus *n*-type doping, appears results from a synthesis step of the Sb₂Se₃ granulate material. As this is an industrial process which we do not have access to, it is difficult to identify the specific source. It is also not possible to say whether this is a common contaminant which will be present in Sb₂Se₃ material purchased from all manufacturers. Rather, we would suggest researchers working on such devices be advised to carefully determine the carrier type of the material being used, rather than assuming *p*-type character. We have however demonstrated a route for Sb₂Se₃ synthesis from metallic precursors by which the doping can be more consistently controlled. This work clearly shows how the presence of extrinsic impurities can have a profound and unexpected effect on the material, and on devices built from it.

CONCLUSION.

In this work we have demonstrated that Sb₂Se₃ can be utilized as an *n*-type absorber layer to produce isotype thin film solar cells. This was shown via a range of complementary analyses on both thin film solar cell and bulk crystal material. The source of the *n*-type doping in devices was identified to be Cl impurities in the Sb₂Se₃ source material, leading to *n*-type carrier concentrations in the range of 10^{16} - 10^{17} cm⁻³. This was verified through the fabrication of insulating bulk crystals from pure metallic (i.e. Cl-free) precursors, which were subsequently doped *n*-type via addition of Cl from MgCl₂. DFT calculations of associated Cl defect levels showed the Cl substitutional on the Se sites to be a shallow donor level with low formation energy, although the Cl_i defect could introduce a potential deep level compensating defect.

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Author Contributions

TDCH prepared and characterized bulk crystal samples under the guidance of KD. LJP and OSH prepared thin films and solar cells with assistance from JDM. JS, HS, LAMJ, TF and MJS performed photoelectron spectroscopy measurements and analysis with assistance from PKT and TL and input from TDV and VD. CNS and DOS performed DFT calculations. Hall measurements were carried out by BD, supervised by CL. PKN and SM performed SVM measurements with input from HJS. Cross sectional cell images were produced by LB, SIMS analysis by GZ and MAF. JDM coordinated the project and prepared the manuscript, with input from all authors.

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Supplementary information

Supporting information is available and contains secondary ion mass spectrometry of different thin film Sb_2Se_3 devices, secondary electron cut-off and valence band maxima obtained from x-ray photoelectron spectroscopy analysis of TiO_2 and Sb_2Se_3 thin films and X-ray diffraction data of Sb_2Se_3 crystals with and without the addition of Cl. The Supporting Information is available free of charge at <https://pubs.acs.org>.

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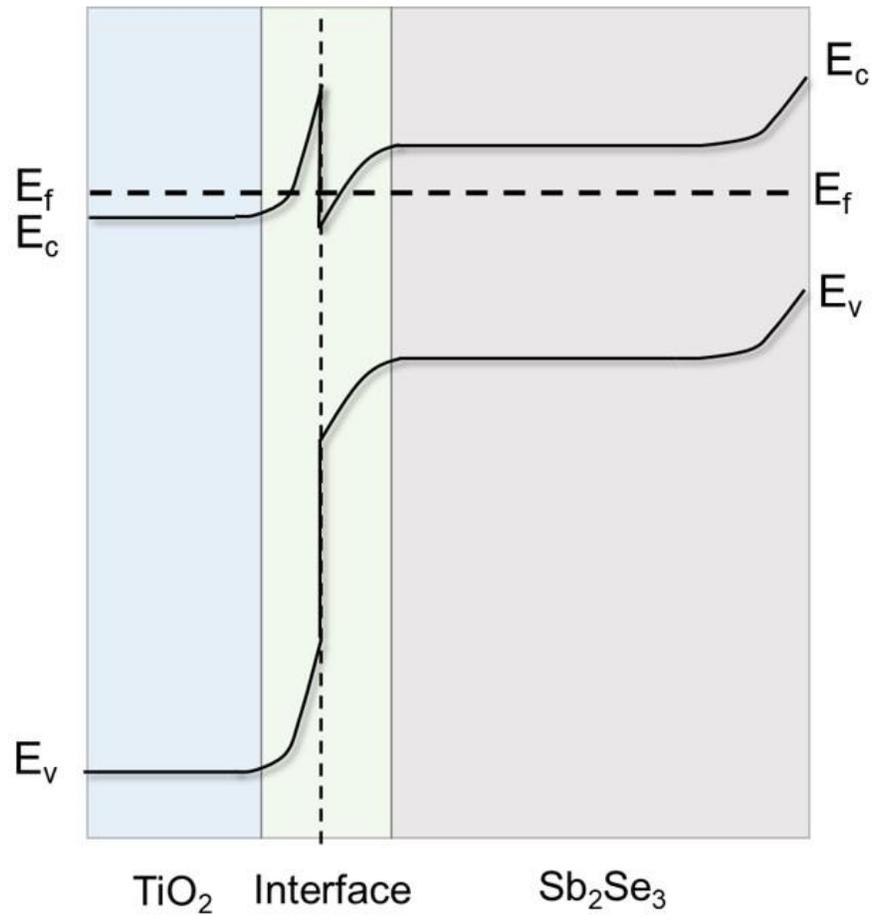


Table of Contents artwork
