Supporting Information

Annex 1: Discussion regarding why n and p-type semiconductors conduct differently when they are connected to low and high work function metals

In either case, the semiconductor acts as a channel, which provides a conductive path for the carriers from the metallic electrodes; electrons at the conduction band in the case of n-type semiconductors, and holes at the valence band in the case of p-type semiconductors. Before applying any voltage both electrodes are in equilibrium, therefore the difference between their electrochemical potentials is zero $(\mu_1 - \mu_2 = 0)$. However, when a positive voltage is applied to one electrode (2 in **Figure A**), a potential difference appears between the electrochemical potentials of both electrodes ($^{qV_{12}}$), which the system will try to bring back into equilibrium by moving electrons to 2 through a channel (the semiconductor). If the channel is an *n-type material*, this implies that there are states available for conduction through the electrons at the conduction band. Consequently, for low work function metal, the resulting path is energetically favorable (there are no energy barriers), and electrons can flow between the electrodes. As a result, there is current, see **Figure A**a. On the other hand, for high work function metals there is an energy barrier for electrons coming from electrode 1, therefor, no current-voltage characteristics will be measured, see **Figure A**b. Note that the difference between the electrochemical potentials and the Fermi level of the semiconductor should curve the energy bands, however it is not relevant for the current consideration, and thus for simplicity it has been omitted from the diagrams.

Alternatively, if the channel is a *p-type semiconductor*, then conduction occurs via holes at the valence band. In this case, holes from electrode 2 should recombine with electrons from electrode 1, however to achieve it they need to flow through the valence band of the semiconductor, where are the available states for conduction. According to this, for low work function metal there is an energy barrier for holes (states at the channel's valence band have lower energy than metal contact), resulting in no current, see **Figure A**c. Otherwise, for a high work function metal there is no barrier, leading to conduction, see **Figure A**d.

Another interesting case for the experiments presented in this work corresponds to the performance of an n-type semiconductor, connected both to low and high work function metals. If a positive voltage is applied to the high work function metal, electrons can move smoothly from electrode 1 to 2 through the channel without finding any energy barrier, therefore there is current, see **Figure A**e. Nonetheless, if the positive voltage is applied to the low work function metal (electrode 1), then carriers should flow from electrode 2 to the semiconductor's conduction band, but there is an energy barrier, leading to low or no conduction, see **Figure A**f.



Figure A: Schematics of electron-only and hole-only devices to illustrate the effect of differences in the electrochemical potential to the flow of carriers through the semiconductor

Annex 2: Additional Figures and Tables



Figure S1: SEM images of the process to generate a SbSel sample lamella for HR-TEM using FIB

| | FWHM (°) | | | | |
|------------|----------|--------|--------|--------|--------|
| 2theta (°) | II | III | IV | V | VI |
| 26.7 | 0.1564 | 0.1670 | 0.0925 | 0.1064 | 0.0845 |
| 27.7 | | 0.2318 | 0.1061 | 0.1125 | 0.0850 |
| 29.4 | 0.1160 | 0.1037 | 0.0651 | 0.0718 | 0.0708 |
| 29.8 | | 0.1609 | 0.0781 | 0.0948 | 0.0941 |
| 31.1 | 0.2620 | 0.1306 | 0.0725 | 0.0846 | 0.0800 |
| 32.0 | 0.1818 | 0.1717 | 0.0985 | 0.1160 | 0.0941 |
| 33.7 | | 0.1320 | 0.0669 | 0.0731 | 0.0755 |

Table S1: Full width half maximum (FWHM) values obtained from the PXRD patterns in Figure 2



Figure S2: SEM image and EDX analysis of a Mo/SbSeI sample prepared at 450°C and 2 bar



Figure S3: HR-TEM images of the Mo/SbSeI sample prepared at 450°C and 2 bar



Figure S4: HR-TEM images and EDX analysis of a Mo/SbSeI sample prepared at 450°C and 2 bar



Figure S5: HR-TEM images and EDX analysis of a Mo/SbSeI sample prepared at 450°C and 7 bar. **a-c)** HR-TEM images. **d)** SAED pattern. **e-f)** EDX linescan mappings



Figure S6: HR-TEM images and EDX analysis of a Mo/SbSeI sample prepared at 275°C and 2 bar. **a-e)** HR-TEM images. **f)** SAED pattern. **g)** EDX linescan mappings



Figure S7: a) Complete XPS spectrum of a SbSel sample (grown at 450°C, 2 bar). b) Determination of the valence band from the XPS spectra. Schematic of the valence, conduction bands, and Fermi level. Measurements performed with a PHI 5500 Multitechnique System from Physical Electronics, using a monochromatic X-ray source Al Kα line of 1486.6eV



Figure S8: Complete set of optoelectronic parameters obtained from SLG/Mo/SbSeI/CdS/intrinsic-ZnO/ITO/Ag prototype solar cells annealed ay 275°C and 300°C



Figure S9: Absorption (α·d) spectra of SbSeI measured by photothermal deflection spectroscopy (PDS). Direct bandgap calculated using the Tauc-Urbach model. Measurement performed with a PDS setup consisting of a 100 W tungsten halogen lamp, PTI 01-0002 monochromator, and Thorlabs MC1000 optical chopper