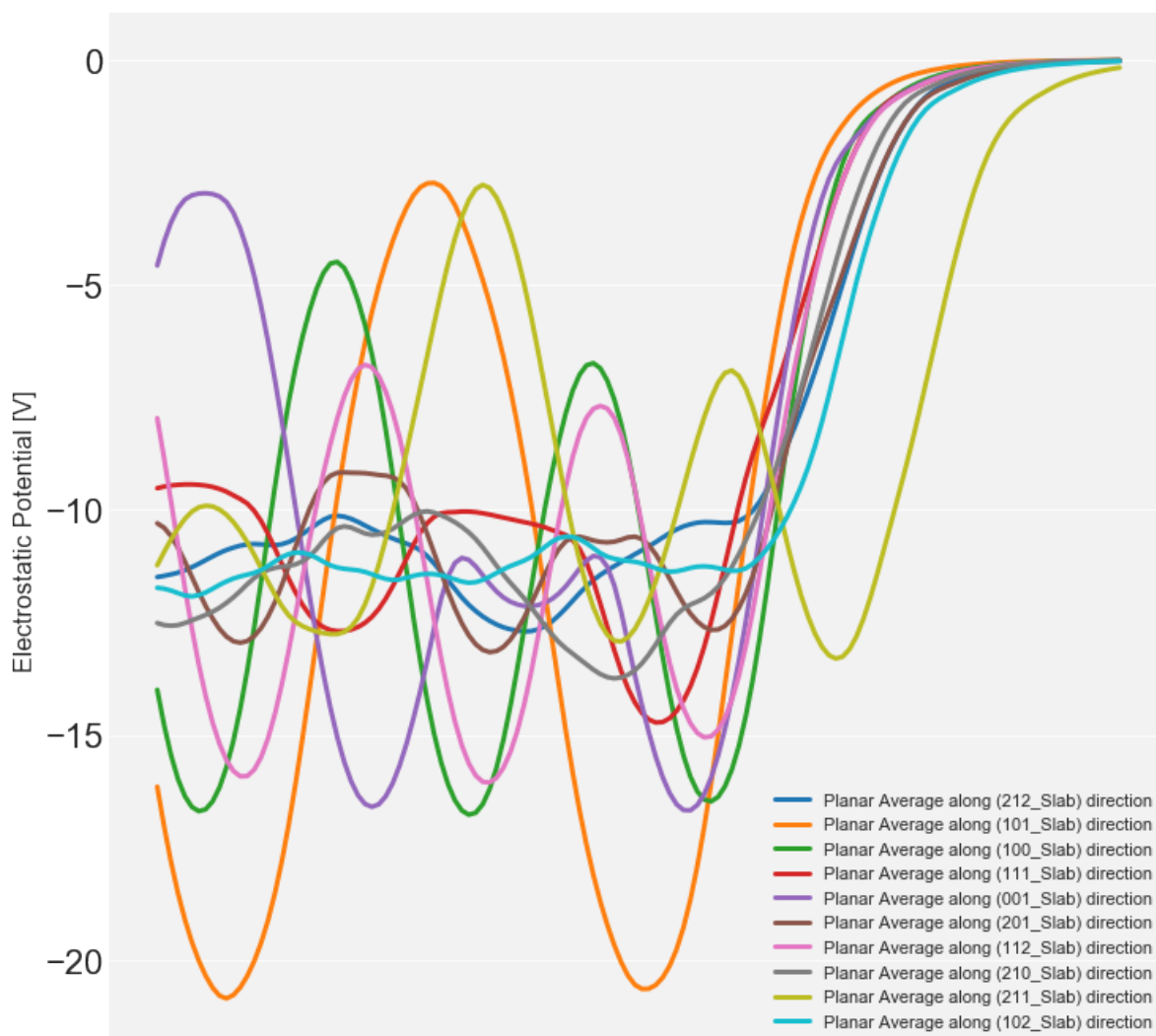


```

In [50]: %matplotlib inline
fig, ax = plt.subplots(1, 1, figsize=(12, 12))
textsize = 22
mpl.rcParams['xtick.labelsize'] = textsize
mpl.rcParams['ytick.labelsize'] = textsize
plt.rcParams['legend.title_fontsize'] = 22
for i, k in enumerate(planar_data):
    half = int(len(planar_data[k])/2)
    ax.plot((planar_data[k]-planar_data[k][350])[half-100:half+40],
            label=f"Planar Average along ({k}) direction", lw=3)
    ax.set_ylabel('Electrostatic Potential [V]', fontsize=16)
    ax.get_xaxis().set_visible(False)
    ax.grid(True)
    ax.legend(fontsize=11)
plt.setp(ax, facecolor=((0.95, 0.95, 0.95)))
plt.show()
#print(f"Using plateaus in the centre of each slab: Offset (Bi rela
tive to Sb) = {macro[91]-macro[270]:.4f} V")

```



Work Function, Ionisation Potential and Electron Affinity

Hybrid DFT was used to give an accurate description of the electronic structure, for which vanilla GGA DFT has several well-known shortcomings. See <https://pubs-rsc-org.libproxy.ucl.ac.uk/en/content/articlelanding/2013/TC/c3tc31863j> (<https://pubs-rsc-org.libproxy.ucl.ac.uk/en/content/articlelanding/2013/TC/c3tc31863j>) (Scanlon & Watson paper) for comparisons. Specifically, a modified PBE0 hybrid DFT functional, with 17% exact Hartree-Fock exchange, was used, to give an indirect bandgap of 0.68 eV, in agreement with the experimental value of ~ 0.7 eV. With this functional, the direct gap is calculated as 2.79 eV, in close agreement with the experimental value of 2.6 - 2.8 eV.

```
IMPHPC: pbe0aexx0.17 > bandgap OUTCAR
      E_g    E_VBM  E_CBM  kpoint_VBM      kpoint_CBM
direct  2.792  4.574  7.366  0.50 0.50 0.00  0.50 0.50 0.00
indirect 0.676  6.690  7.366  0.00 0.00 0.00  0.50 0.50 0.00
```

```
IMPHPC: pbe0aexx0.17 > grep E-fermi OUTCAR
E-fermi :   6.9027      XC(G=0): -8.7738      alpha+bet : -12.3981
```

```
In [12]: import numpy as np
```

```
In [10]: vbm = 6.690
cbm = 7.366
fermi = 6.9027
electrostatic_offsets = {'001': -11.1349, '101': -
                        11.4181, '100': -11.0539, '212': -11.1611}
ionisation_potentials = {}
electron_affinities = {}
work_functions = {}
for key, val in electrostatic_offsets.items():
    ionisation_potentials[key] = vbm + val
    electron_affinities[key] = cbm + val
    work_functions[key] = fermi + val
print("Ionisation Potentials: (i.e. VBM wrt Vacuum)")
for k,v in ionisation_potentials.items():
    print(f"Surface Orientation: {k} -> {v:.2f} V")
print("\nElectron Affinities: (i.e. CBM wrt Vacuum)")
for k,v in electron_affinities.items():
    print(f"Surface Orientation: {k} -> {v:.2f} V")
print("\nWork Functions: (i.e. Fermi Level wrt Vacuum)")
for k,v in work_functions.items():
    print(f"Surface Orientation: {k} -> {v:.2f} V")
```

Ionisation Potentials: (i.e. VBM wrt Vacuum)

Surface Orientation: 001 -> -4.44 V

Surface Orientation: 101 -> -4.73 V

Surface Orientation: 100 -> -4.36 V

Surface Orientation: 212 -> -4.47 V

Electron Affinities: (i.e. CBM wrt Vacuum)

Surface Orientation: 001 -> -3.77 V

Surface Orientation: 101 -> -4.05 V

Surface Orientation: 100 -> -3.69 V

Surface Orientation: 212 -> -3.80 V

Work Functions: (i.e. Fermi Level wrt Vacuum)

Surface Orientation: 001 -> -4.23 V

Surface Orientation: 101 -> -4.52 V

Surface Orientation: 100 -> -4.15 V

Surface Orientation: 212 -> -4.26 V

I've chosen these surface terminations to calculate the potential offsets, as they are the most stable surface miller indices (accounting for > 91% of the predicted Wulff shape surface area (see above)).

As is usually the case (from what I can tell from a quick scan of the literature), the work function is indeed surface-dependent, but not massively variable between the most stable surfaces (depending on your reference though, I suppose...). In this case, the work function varies over ~0.4 V.

The fact that the 100 termination gives the highest (least negative) value, suggests that 'thicker' SnO platelets will have higher work functions, compared to the thinner platelets.

Below is the calculated surface-area-normalised values (using the predict Wulff shape):

```
In [16]: normalized_wulff_areas = {'212': 0.160, '101': 0.111, '100': 0.205,
'001': 0.437}
total = np.sum(list(normalized_wulff_areas.values()))
for dictionary in [ionisation_potentials, electron_affinities, work_
_functions]:
    surface_weighted = 0
    for key, val in normalized_wulff_areas.items():
        surface_weighted += (val/total)*(dictionary[key])
    dictionary["Wulff-shape surface weighted"] = surface_weighted
print("Wulff shape surface-weighted values:")
print(f"Ionisation Potential: (i.e. VBM wrt Vacuum) -> {ionisation_
potentials['Wulff-shape surface weighted']:.2f} V")
print(f"Electron Affinitie: (i.e. CBM wrt Vacuum) -> {electron_affi
nities['Wulff-shape surface weighted']:.2f} V")
print(f"Work Function: (i.e. Fermi Level wrt Vacuum) -> {work_funct
ions['Wulff-shape surface weighted']:.2f} V")
```

Wulff shape surface-weighted values:

Ionisation Potential: (i.e. VBM wrt Vacuum) -> -4.47 V

Electron Affinitie: (i.e. CBM wrt Vacuum) -> -3.79 V

Work Function: (i.e. Fermi Level wrt Vacuum) -> -4.25 V

Calculated ionisation potential: 4.47 eV

Other (slightly-older theory) calculation(s): 4.4 eV (<https://doi.org/10.1021/cm401343a>)
(<https://doi.org/10.1021/cm401343a>)

Calculated electron affinity: 3.79 eV

Other (slightly-older theory) calculation(s): 3.7 eV (<https://doi.org/10.1021/cm401343a>)
(<https://doi.org/10.1021/cm401343a>)

Calculated work function: 4.25 eV

Experimental work function measurements: 4.3 eV (<https://doi.org/10.1063/1.4916664>)
(<https://doi.org/10.1063/1.4916664>) (UPS, SnO Films - i.e. the 001 surface, for which the calculated work function is 4.23 eV), 4.9 eV (<https://doi.org/10.1021/cm401343a>)(Kelvin
(<https://doi.org/10.1021/cm401343a>)(Kelvin) probe), 5.2 eV
(<https://iopscience.iop.org/article/10.1088/0957-4484/27/33/335603/meta>)
(<https://iopscience.iop.org/article/10.1088/0957-4484/27/33/335603/meta>)

Seems to match up pretty damn well with experiment....

Again, these calculations give the ionisation potential, electron affinities and work functions **with respect to vacuum** (i.e. essentially corresponding to measurements in vacuum or air (wouldn't massively affect surface dipoles in this case)), and so solvent effects could still affect these values.

I don't know if any of this is useful / relevant, but hopefully it is! If there's any other particular analysis you think would be interesting / possible, let me know.

Appendix

Electrostatic Potential Plots