First principles studies of the surface and opto-electronic properties of ultra-thin $t$-Se

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ABSTRACT: Selenium is an important earth-abundant and non-toxic semiconductor with numerous applications across the semiconductor industries. Selenium has drawn attention from scientific communities for photovoltaics and imaging devices. Its usage as a photosensitive material largely involves the synthesis of the amorphous phase ($a$-Se) via various experimental techniques. However, the ground state crystalline phase of this material, known as the trigonal selenium ($t$-Se), has not been extensively studied for its optimum electronic and optical properties. In this work, we present systematic studies based on density functional theory (DFT) for ultra-thin $(10\bar{1}0)$ surface slabs of $t$-Se. We report the surface energies, work function, electronic and optical properties as a function of number of layers for $(10\bar{1}0)$ surface slabs to access its suitability for applications as a photosensitive material.

KEYWORDS: Selenium, ultra-thin-film, $(10\bar{1}0)$ surface, DFT, surface energy, work function, optical and electronic properties.
1. Introduction

Selenium (Se) is a well known photovoltaic material, with its first studies dating back to the late 1800’s [1, 2]. Commonly found in metal sulfide ores [3], Se is an earth-abundant material with a low melting point of \( \sim 220^\circ \text{C} \), a relatively simple and stable crystalline structure, and a relatively large direct band-gap [4].

There are a few allotropes of Se, among them the thermodynamically stable triagonal Se (\( t \)-Se)\(^1\). \( t \)-Se has been observed to have a large optical absorption coefficient across a wide range of wavelengths. A large absorption coefficient and a low melting point are attractive properties that facilitate the fabrication of large scale amorphous Se (a-Se) photovoltaic devices through vacuum deposition techniques.

Amorphous selenium has been the subject of research firstly for its application in xerographic photocopiers [5, 6], then as a medium for direct X-ray imaging [7, 8, 9, 10], as well as for applications in composite films used in photocells [11, 12, 13]. More recently research into Se’s potential application as a general use photon detector with a potential wide wavelength application from the visible to UV [14, 15]; see [16] for a useful summary.

A new application of Se as a photon detector is foreseen in gas and liquid based noble element particle detectors. Noble element detectors have become ubiquitous in searches for dark matter

\(^1\)sometimes referred to as hexagonal or crystalline Se
and as a medium for detection of neutrino-nucleus interactions [17, 18]. The detection of the scintillation light arising from particle interactions is a key component. The scintillation light for the most common noble element detectors (Argon & Xenon) sits in the vacuum ultraviolet (VUV) spectrum (128nm – 175nm) or (9.7 eV – 7.1 eV). Conventional photon detectors such as photomultiplier tubes (PMT’s) and multi-pixel photon counters (MPPC’s) have diminished quantum efficiency at these wavelengths prompting both alternative detection techniques utilizing wavelength shifting coatings [19] and the development of new VUV sensitive MPPC’s [20]. Each of these approaches comes with their own complications, from the unintended behavior of the wavelength shifters [21, 22] to the small active surface areas of the individual VUV sensitive detectors [23]. In this landscape, techniques utilizing thin films of photosensitive semiconductors offers an opportunity for the development of alternative photon detector designs using new materials, such as a-Se.

Some experimental work measuring the properties of Se based photon detector in the UV spectrum has taken place [24, 25, 9, 14, 15], but little theoretical work modeling and understanding the opto-electronic properties of Se exists for photons in this frequency range. This work serves as a starting point for such calculations to better understand the properties that a selenium based detector might have for photons in the VUV spectrum. We begin with calculations for t-Se modeling ultra-thin films which can be configured as fully relaxed free-standing layers. From these calculations, the surface energies can show the stability of ultra-thin layers of t-Se and the density of states (DOS), band structures, band gaps, and work function. These can illuminate the optoelectronic properties, such as absorption coefficient, reflectivity, refractive index, and electron loss function for Se in the wavelength range most relevant for noble element detectors. In future works, the transition from t-Se to a-Se structures will be enabled by the theoretical calculations presented here.

In this work, we present density functional theory based first principles studies of t-Se (10T0) surface slabs having up to 15 atomic layers (45 atoms per unit cell). The paper is structured into three sections, the first describes the method of simulation for t-Se (bulk and surface) using density functional theory (DFT) and the details of computational, thermodynamic, and optical modeling. The next section overviews the most important results pertaining to the optoelectronic properties. We conclude by outlining the next phase of the work. A supplemental section is provided at the end to give additional numerical and graphical details where relevant.

2. Methods

The theoretical framework of this work is based on the density functional theory (DFT) [26, 27] implemented with the projector augmented wave method (PAW) [28, 29] as in Vienna ab initio simulation package (VASP) [30, 31]. Even though local magnetic structures are not expected, all the calculations performed in this work with spin polarization to allow additional freedom in electronic relaxations. For crystal structures and slabs visualization, VESTA [32] was used throughout the work.

Figure 1 shows the crystal structure of t-Se which contains three selenium atoms per unit cell. Figure 2 shows a typical slab geometry of stacked t-Se used in the calculations.
Figure 1. The crystal structure of t-Se in (a) unit cell representation, which is viewed from (b) a, (c) b, and (d) c lattice directions. The solid red line represents the boundary of a unit cell. Se atoms form a helical chain along c lattice direction. \( d \) is the distance between two consecutive Se atoms in the helical chain, and \( \theta \) is the bond angle of Se atoms in that chain.

2.1 Computational Details

In this work, generalized gradient approximation (GGA) functional by Perdew–Burke–Ernserhof (PBE) \([33, 34]\) for the exchange-correlation energy is deployed. Since selenium atoms in t-Se are layered along [10\( \bar{1} \)0] and [01\( \bar{1} \)0] directions, as shown in Figure 1 and the inter-layer distance is over 4 Å, we have included van der Waals corrections (vdW) to GGA-DFT through zero damping DFT-D3 method of Grimme \([35]\). The crystal structure of trigonal selenium with experimental lattice constants and bond lengths \([4, 36, 37, 38]\) and GGA and GGA+vdW optimized lattice parameters are summarized in Tables 1 and 2.

### Lattice parameters for t-Se

|                                | a (Å) | b (Å) | c (Å) | \( \alpha (^\circ) \) | \( \beta (^\circ) \) | \( \gamma (^\circ) \) |
|--------------------------------|-------|-------|-------|-----------------------|---------------------|----------------------|
| Experiment \([4, 36, 38]\)      | 4.366 | 4.366 | 4.954 | 90                    | 90                  | 120                  |
| GGA                            | 4.504 | 4.504 | 4.504 | 90                    | 90                  | 120                  |
| GGA + vdW                       | 4.184 | 4.184 | 5.127 | 90                    | 90                  | 120                  |

Table 1. Experimental and DFT (GGA and GGA+vdW) optimized lattice parameters of t-Se. The van der Waals corrections (vdW) were applied through the zero damping DFT-D3 method of Grimme \([35]\). Since GGA overestimates lattice parameter, the inter-layer separation increases by 0.138 Å. However, with van der Waals corrections to GGA, the inter-layer separation decreases by 0.182 Å than the experimental lattice. On the other hand, the bond length increases up to 0.058 Å due to the helical chain stretching along [0001] directions as tabulated in Table 2.

|                                | Bond length, \( d \) (Å) | Bond angle, \( \theta (^\circ) \) |
|--------------------------------|--------------------------|----------------------------------|
| Experiment \([4, 37, 38]\)      | 2.373                    | 103.07                           |
| GGA                            | 2.405                    | 103.62                           |
| GGA + vdW                       | 2.431                    | 103.98                           |

Table 2. Bond length, \( d \) between two consecutive atoms in selenium helical chain and the bond angle, \( \theta \) as depicted in Figure 1.

In the analysis of the simulation, we find that the inter-layer separation decreased after van der
Waals corrections were applied due to enhanced long-range interactions. In addition, the cohesive energy per atom calculated by GGA + vdW (2.734 eV) for bulk t-Se is 0.203 eV lower than the GGA (2.937 eV) computed value. The cohesive energy per atom was calculated using the following formula:

$$E_c = \frac{NE_{\text{atom}} - E_{\text{bulk}}}{N}$$

(2.1)

where $E_{\text{bulk}}$ is the total energy of bulk selenium per unit cell, $N$ is the total number of atoms in a unit cell, and $E_{\text{atom}}$ is the energy of a single selenium atom in a cubic box of dimension 10 Å. The experimental cohesive energy is 2.25 eV/atom [39], which indicate that GGA+vdW agrees better with the experimental value compared to the GGA-only calculation of cohesive energy. The binding between the Se atoms in the t-Se crystals is significantly weaker when compared to the binding, for example, of Si (4.62 eV/atom) [40].

Since selenium atomic layers along [10\overline{1}0] and [01\overline{1}0] directions are arranged in the same geometric fashion in t-Se crystals, atomic layers from a unit cell were stacked along [10\overline{1}0] direction only with a 25 Å vacuum for modeling slabs. A schematic of a six-layers (1 × 1) slab oriented in the [10\overline{1}0] direction is presented in Figure 2.

Figure 2. A schematic of a (1x1) slab geometry for stacked selenium atomic layers in [10\overline{1}0] direction. Each simulation box that contains stacked selenium layers has a fixed 25 Å vacuum along [10\overline{1}0].

All slabs considered in this work for surface properties calculations were geometrically optimized without any symmetry constrained. Atoms in the simulation box could relax in all three lattice directions, and we name these relaxed layers as “free-standing” layers. Throughout the relaxation, cell volumes with vacuum layers (25 Å) were kept fixed. The convergence criteria for the electronic self-consistent loop was set equal to or less than 1×10^{-8} eV/Å. All the ions were relaxed until the Hellman-Feynman force was equal to or less than 0.001 Å. The kinetic energy cut off for
the plane-wave basis set was 400 eV. Se 4s\(^2\) 4p\(^4\) is the valence electron configuration considered for this work. Each atomic layer in a (1 \(\times\) 1) slab contains three selenium atoms. In this work, the largest (1 \(\times\) 1) slab contains 15 atomic layers (45 atoms). The Brillouin zone was sampled by a 1 \(\times\) 21 \(\times\) 21 gamma centered \(k\)-mesh for slabs having up to 10 layers (30 atoms) and by a 1 \(\times\) 15 \(\times\) 15 gamma centered \(k\)-mesh for slabs containing more than 10 layers.

### 2.2 Modeling of Surface Stability

For the characterization of the stability of the [10\(\bar{1}0\)] surface of \(t\)-Se, the surface energy, \(\gamma\) was calculated using the following formula:

\[
\gamma = \frac{1}{2A} [E_{\text{tot}}(N) - NE_{\text{Bulk}}]
\]

(2.2)

where \(E_{\text{Bulk}}\) is the total energy of bulk selenium per unit cell, \(N\) is the number of layers, \(E_{\text{tot}}(N)\) is the total energy of \(N\)-number of layers, and \(A\) is the surface area.

To avoid inconsistencies in the surface energies, \(\gamma\) in Eq. (2.2) resulting from a separate bulk calculation for \(E_{\text{Bulk}}\), a well-established method is to derive \(E_{\text{Bulk}}\) from a least square fitting of \(E_{\text{tot}}(N)\) curve by re-writing the Eq. (2.2) in the form:

\[
E(N) = NE_{\text{Bulk}} + 2A\gamma
\]

(2.3)

The slope in Eq. (2.3) provides the required \(E_{\text{Bulk}}\) to calculate \(\gamma\) from Eq. (2.2). This method is tested thoroughly in previous works [42, 43, 44]. In our case, the fitted values and separate bulk calculations for \(E_{\text{Bulk}}\) are very close to one another as summarized in Table 3. In particular, for both GGA and GGA + vdW calculated energies, the difference is within 0.01 eV. Details of the convergence for the surface energies and the least square fitting techniques are given in Figure 4 and section 3.1.

### 2.3 Modeling of Optical Properties

In order to calculate the optical properties, we calculated the frequency-dependent complex dielectric function in the independent particle picture using VASP. The expression for the real (\(\varepsilon_1\)) and imaginary (\(\varepsilon_2\)) parts of the dielectric function (\(\varepsilon = \varepsilon_1 + i\varepsilon_2\)) as a function of photon frequency (\(\omega\)) were as in ref. [45]. Using the following formulas, the optical absorption coefficient (\(\alpha(\omega)\)), reflectivity (\(R(\omega)\)), refractive index (\(n(\omega)\)) and the electron energy loss function (\(L(\omega)\)) were calculated for all the (10\(\bar{1}0\)) surface slabs and bulk \(t\)-Se:

\[
\alpha(\omega) = \frac{\sqrt{2}\omega}{c} \sqrt{\sqrt{\varepsilon_1(\omega)^2 + \varepsilon_2(\omega)^2} - \varepsilon_1(\omega)}
\]

(2.4)

\[
R(\omega) = \frac{\sqrt{\varepsilon_1(\omega) + i\varepsilon_2(\omega)} - 1}{\sqrt{\varepsilon_1(\omega) + i\varepsilon_2(\omega)} + 1} = \frac{(n - 1)^2 + k^2}{(n + 1)^2 + k^2}
\]

(2.5)

\[
n(\omega) = \sqrt{\frac{\varepsilon_1(\omega)^2 + \varepsilon_2(\omega)^2 + \varepsilon_1(\omega)}{2}}
\]

(2.6)
\[ L(\omega) = \frac{\varepsilon_2(\omega)}{\varepsilon_1(\omega)^2 + \varepsilon_2(\omega)^2} \] (2.7)

Where the extinction coefficient \( k(\omega) \) is defined as

\[ k(\omega) = \sqrt{\frac{\varepsilon_1(\omega)^2 + \varepsilon_2(\omega)^2 - \varepsilon_1(\omega)}{2}} \] (2.8)

3. Results and Discussion

The results of the simulation are discussed in four subsections. Section 3.1 focuses on the stability analysis and reports the surface energies of (10\(\overline{1}0\)) surface for \( t \)-Se slabs containing up to 15 atomic layers. Section 3.2 shows the calculated work function to further understand the stability of those layers. Section 3.3 reports the calculated electronic properties such as band structures, band gaps and the density of states. Lastly, Section 3.4 presents the calculated optical properties for all the relaxed layers considered in this work. As described above, all the calculations have considered the van der Waals corrections separately, along with GGA-DFT.

3.1 Surface Energies

The GGA calculated converged surface energy for free standing (10\(\overline{1}0\)) \( t \)-Se surface slabs is 160.22 mJ/m\(^2\). When van der Waals interactions are added, the converged energy becomes approximately 16 mJ/m\(^2\) higher, which is 176.24 mJ/m\(^2\). This increment is expected due to the long-range vdW interaction term added to the Kohn-Sham Hamiltonian. Our calculated values are in reasonably good agreement with experimentally measured surface energies of selenium (175 - 291 mJ/m\(^2\)) [46, 47]. The surface energies shown in Figure 3 are calculated values with respect to the number of layers in the slab model; numerical values are presented in Table 5 of Supplemental Material.

![Surface energy vs. number of layers](image)

**Figure 3.** GGA and GGA + vdW calculated surface energies \( \gamma \) (mJ/m\(^2\)) as a function of the number of layers for fully relaxed \( t \)-Se (100) surface slabs.

As a convergence criteria of surface energies calculation, the incremental energy per formula unit, or atomic layer, was calculated using the following formula

\[ \text{Incremental energy per layer} = \frac{\text{Converged energy with vdW}}{\text{Converged energy without vdW}} - 1 \]
\[ \Delta E_{\text{per formula unit}} = E_{\text{tot}}(N+1) - E_{\text{tot}}(N), \tag{3.1} \]

where \( \Delta E_{\text{per formula unit}} \leq 0.01\text{eV} \) (for both GGA and GGA + vdW). This is reported as a function of the number of layers, as shown in Figures 3(b).

In addition, the total energies of layers are reported as a function of the number of layers, see Figures 3(c), to obtain the slope from a least square fitting to estimate for the energies of bulk selenium \( (E_{\text{Bulk}}) \).

![Figure 4. GGA and GGA + vdW optimized (a) surface area (Å²), (b) incremental energy \( \Delta E \) (eV) at each layer, and (c) energy \( E_{\text{tot}} \) (eV) of free-standing t-Se (10\overline{1}0) surface slabs as a function of the number of layers (N). The figure in (a) shows that surface area converges within 0.01(0.02) Å² for GGA(GGA +vdW) optimized layers while (b) shows the incremental energy, \( \Delta E \) convergence within 0.01 eV. Energies for bulk selenium, \( E_{\text{Bulk}} \) derived from least square fitting in (c) are very close to separate bulk calculations which are within 0.001 eV per unit cell as in Table 3.](image)

Once \( E_{\text{Bulk}} \) is found, \( \gamma \) was calculated following Equation 2.2 and were tabulated in Table 5. From Figure 4, the layer-to-layer incremental energy saturates after seven layers for both GGA and GGA+vdW. However, the surface energy does not converge for GGA+vdW till twelve layers; there is a small fall in the value after eleven layers. The fall is due to the combined effect of larger surface area and higher layer-thickness per unit layer as the number of layers increased.

The higher surface energy resulting from GGA + vdW calculations can also be explained from Figure 5 which shows that the rate at which the layer thickness increases with subsequent number of layers is higher for GGA calculated values than the GGA + vdW. This is due to the layer thickness for GGA + vdW-relaxed slabs being less and thus the inter-layer interaction increases, resulting in slightly higher surface energies.

| Total Energy (eV) of t-Se per atomic layer or formula unit | GGA | GGA + vdW |
|---------------------------------------------------------|-----|-----------|
| Bulk                                                   | -10.450 | -11.059 |
| Least square fitting                                   | -10.451 | -11.058 |

**Table 3.** Total energy, \( E_{\text{bulk}} \) (eV), per atomic layer for bulk t-Se derived from separate bulk calculation and a least square fitting. Note that, each atomic layer or a unit cell contains three selenium atoms.
Figure 5. (Left) GGA and GGA + vdW optimized (10\overline{1}0) surface slab thickness for t-Se as a function of the number of layers. It is found that slab thickness increases almost linearly as the number of layers increases. However, the slab thickness for GGA + vdW optimized layers are less than GGA only optimized layers. For example, it is up to 3.82 Å less for a 15 layers slab. (Right) Difference between GGA and GGA + vdW optimized slab thickness. As the number of the layers increases, the slab thickness difference also increases. These results are summarized in Table 6 in the Supplemental Material.

3.2 Work Function

Figure 6. GGA and GGA + vdW calculated (a) work function $\phi$ (eV) of fully relaxed t-Se (10\overline{1}0) surface slabs up to 15 atomic layers. (b) a schematic of the electrostatic potential $E_{tot}$ (eV) for a four-layer slab calculated using the formula, $\phi = E_V - E_F$. Where $E_V$ is the vacuum level and $E_F$ is the Fermi level.

To assess the surface stability further, we have calculated the work function of (10\overline{1}0) surface of t-Se. The work function of a semiconductor corresponds to the least amount of energy required to remove an electron from the bulk through the surface so that the electron no longer interacts with the material. It can be calculated as

$$\phi = E_V - E_F$$ (3.2)
where $E_V$ is a vacuum level energy, a reference value within the slab model, and $E_F$ is the Fermi level. Within the slab model employed for the present study, the $E_V$ is defined as the saturated electrostatic potential energy as depicted in Figure 6(b). A higher work function indicates a higher stability of a surface, i.e., the surface is less reactive. The calculated work function for (10\overline{1}0) surface slabs are presented in Figure 6(a) as a function of the number of layers. A single atomic layer of selenium has the highest work function (5.4 - 5.5 eV). As the number of layers increases, the work function decreases and tends to converge toward 5.1 eV for GGA optimized slabs. For GGA + vdW optimized slabs, this value is slightly lower but comparable to the bulk selenium surface work function (5.11 eV). Since minute changes in the surface configuration can change work function significantly, GGA + vdW optimized layers have lower values than the GGA relaxed layers. However, such higher values of work function for both cases (GGA and GGA+vdW) show good surface stability of the slabs considered for this work. Note, from four atomic layers, free-standing slabs have almost the same work functions as the bulk surface.

3.3 Electronic Properties

Here the electronic properties of (10\overline{1}0) surface $t$-Se slabs are presented. We begin with the band gap which are calculated through GGA and GGA + vdW formalism. These are shown in Figure 7. We find that the band gap ($E_g$) is the highest for one atomic layer, 1.94 eV from GGA and 1.91 eV from GGA+vdW calculations, and much higher than the bulk band gaps (see Figure 15 in Supplemental Material). As the number of layers increases, the band gap decreases and tends to reach the limit of the bulk selenium. The results can be justified by the quantum confinement effect. Note, the calculated band gaps by either GGA or GGA+vdW method is an underestimation of the experimental band gap of 1.86 eV for $t$-Se. The underestimation of band gaps is a well-known feature by the standard DFT functionals.

![Figure 7](image)

**Figure 7.** GGA and GGA + vdW calculated band gaps of fully relaxed $t$-Se (10\overline{1}0) surface slabs as a function of the number of layers.

Figures 8 and 9 show the GGA calculated band structure and density of states (DOS) respectively for the free-standing $t$-Se surface slabs at one, three, five, nine, and fifteen layers. Analysis
of these plots shows that the top of the valence band and the bottom of the conduction bands are dominated by the Se $p$ orbitals as like the case of the bulk Se. As the number of layers increases, the overall features of band composition and the density of states remain similar except the valence band maximum (VBM) shifting from G to M. However, the conduction band minimum (CBM) remains at the same point (near to M). There is an indirect to direct band gap transition as the number of layer increases.

The calculations of the bulk $\tau$-Se electronic properties including the direct and indirect band gaps and the corresponding DOS are shown in Section 5 of the Supplemental Material in Figures 15 and 16. Starting from few atomic layers, the DOS at the Fermi level and near CBM are very similar to that of the bulk. GGA + vdW calculated band structures and DOS are similar to the GGA calculated features with a slightly lower band gaps.

Figure 8. GGA calculated band structures for free-standing $\tau$-Se (10T0) surface slabs containing one, three, five, nine and fifteen layers. The Fermi level is set to 0 eV. From corresponding density of states plots, it is found that the top of the valence band and the bottom of the conduction bands are predominantly contributed by the Se $p$ orbitals. As the number of layers in the slab increases, the band gap decreases and tend to reach the band gap of the bulk $\tau$-Se.
Figure 9. GGA calculated density of states for free-standing t-Se (10\overline{1}0) surface slabs. The Fermi level is set to 0 eV. It is found that the top of the valence band and the bottom of the conduction bands are predominantly contributed by the Se p orbitals. As the number of layers in the slab increases, the band gap decreases and tend to reach the band gap of the bulk t-Se.

3.4 Optical Properties

Using the analysis presented above, the optical properties of t-Se are calculated using GGA and GGA+vdW across the photon energy range of interest and along the orientations [10\overline{1}0] and [0001], as shown in Figures 10 and 11 for relaxed free standing layers. We focus our analysis on the behavior of the optical absorption coefficient (\(\alpha\)), the reflectivity (R), the refractive index (n), and the loss function (L).

Some important observations which are apparent when comparing the optical absorption coefficient in the range relevant for the VUV spectrum of noble element detectors (e.g. 7.1 - 9.7 eV): i) after only a few atomic layers the behavior quickly begins to mimic the bulk properties suggesting that extremely thin-films will have a favorable absorption coefficient, ii) the absorption peaks near the area of our interest (\(\sim\)9 eV) in both polarizations and thus should have very favorable properties
sought in their application as a VUV photodetector.

Figure 12 shows the bulk calculations compared to data from references [24] and [25] taken for t-Se when the incident radiation is parallel and perpendicular to the Se crystal over the photon energy range of 4-14 eV. The broad spectral features show general agreement while the two data sets differ from the GGA and GGA+vdW values by 10-20% with the data being generally higher than the calculation for photon energies <5 eV and the calculations being higher than the data above 5 eV.

A similar analysis of the reflectance in Figure 10 and 11 shows: i) again, after only a few atomic layers the behavior quickly begins to mimic the bulk properties, ii) the reflectivity is ∼30% higher for the [0001] orientation compared to the [1010] for both GGA and GGA+vdW, iii) the GGA+vdW calculation has a higher predicted reflectance in the region between 1-6 eV, above which GGA and GGA+vdW agree with one another. Comparing our results to data a few conclusions can be drawn. Firstly, the broad spectral features show a similarity between the GGA calculation, GGA+vdW, and the data with peaks and drops occurring in roughly the same energies. In t-Se the dip shown in the data around ∼6.5 eV and its rise thereafter is interpreted as a gap in the valence band. A similar, albeit, shifted phenomenon is seen in both the GGA and GGA+vdW calculation with the GGA+vdW more closely matching the data in the region of the dip. Secondly, the magnitude of the reflectance in the region of interest (7 eV - 9 eV) seems to be lower in the GGA calculation than the data by about ∼40% and slightly less low in the GGA+vdW.

Similar comparisons for the index of refraction and the loss function follow with subsequent comparisons to data in Figure 14 having generally the same conclusions as those given above.
Figure 10. GGA calculated optical properties as a function of photon energy for free-standing $t$-Se (10T0) surface slabs having up to fifteen atomic layers. Optical properties are calculated along [10$ar{1}0$] (left panel) and [0001] (right panel) directions.
Figure 11. GGA + vdW calculated optical properties as a function of photon energy for free-standing \(t\)-Se \((10\bar{1}0)\) surface slabs having up to fifteen atomic layers. Optical properties are calculated along \([10\bar{1}0]\) (left panel) and \([0001]\) (right panel) directions.
Figure 12. Using data taken by Leiga (1968)\textsuperscript{24, 25} we can compare the calculations for bulk properties of the absorption coefficient ($\alpha$) made using GGA (Left) and GGA+vdW (Right) to experimental data taken when the photon is polarized parallel and perpendicular to the crystal. \textsuperscript{[24, 25]}

Figure 13. Using data taken by Leiga (1968)\textsuperscript{24, 25} we can compare the calculations for bulk properties of the reflectance made using GGA (Left) and GGA+vdW (Right) to experimental data taken when the photon is polarized parallel and perpendicular to the crystal. Broad spectral properties show general agreement with the shape of the spectrum having approximate agreement but the magnitude of the reflectance differing between $\sim 25 - 50\%$ across the spectrum.
Figure 14. Using data taken by Leiga (1968) we can compare the calculations for bulk properties of the Energy Loss made using GGA (Left) and GGA+vdW (Right) to experimental data taken when the photon is polarized parallel and perpendicular to the crystal.
4. Conclusion

In this work, we have employed density functional theory to systematically investigate the thermodynamic, electronic and optical properties of (10\text{\bar{1}}0) surface layers of trigonal selenium (t-Se). We find that within few atomic layers of t-Se, free standing thin films started to have bulk like properties. From the electronic structures calculations, both the valence and the conduction bands’ extrema (VBM and CBM) have Se-\textit{p} characters, so optical absorption across the band gap is highly suppressed. In addition, an indirect to direct band gap transition was observed as the number of layers increases within the slab. Overall, the optical properties matches well with the experimental results when Van der Waals corrections are included in the DFT Hamiltonian. The optical absorption peaks near the area of our interest (\sim 9 eV) and thus should have very favorable properties sought in their application as a VUV photodetector.

This work serves as a foundational starting point for theoretical calculations to better understand the properties a selenium based detector will have for photons in the VUV spectrum. The calculations have shown the surface energy, work function, electronic, and optical properties which can be derived for t-Se. Where possible, the calculations are compared to existing data. The general agreement found between the existing data for t-Se and the work done here opens up the doorway to further analysis of the amorphous state (a-Se), which is most commonly used in photon detectors and helps better understand the fundamental properties of the thin film selenium detectors which can be employed for VUV photon detection given Se’s favorable properties of high absorption coefficient, low loss function, and favorable transport properties.

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Conflict of Interest and Data Sharing

The authors declare no conflict of interest in this work. The data that support the findings of this study are available from the corresponding author upon reasonable request.

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5. Supplemental Material

First principles studies of the surface and opto-electronic properties of ultra-thin t-Se

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5.1 Surface Properties

| Number of layers | Surface area of free-standing layers (Å²) |
|------------------|------------------------------------------|
|                  | GGA | GGA + vdW |
| 1                | 21.08 | 20.29 |
| 2                | 21.91 | 20.84 |
| 3                | 22.23 | 21.08 |
| 4                | 22.36 | 21.17 |
| 5                | 22.44 | 21.22 |
| 6                | 22.52 | 21.32 |
| 7                | 22.62 | 21.35 |
| 8                | 22.64 | 21.41 |
| 9                | 22.61 | 21.43 |
| 10               | 22.64 | 21.46 |
| 11               | 22.77 | 21.46 |
| 12               | 22.71 | 21.46 |
| 13               | 22.68 | 21.44 |
| 14               | 22.73 | 21.51 |
| 15               | 22.74 | 21.53 |

Table 4. GGA and GGA + vdW relaxed (10\bar{1}0) surface areas of t-Se as the number of layer increases for free standing layers.
Surface energies, $\gamma$(mJ/m$^2$) for (10\bar{1}0) surface slabs of t-Se

| Number of layers in slabs | GGA | GGA + vdW |
|-------------------------|-----|----------|
| 1                       | 160.22 | 176.24 |
| 2                       | 160.22 | 192.26 |
| 3                       | 160.22 | 192.26 |
| 4                       | 160.22 | 192.26 |
| 5                       | 160.22 | 192.26 |
| 6                       | 160.22 | 192.26 |
| 7                       | 160.22 | 192.26 |
| 8                       | 160.22 | 192.26 |
| 9                       | 160.22 | 192.26 |
| 10                      | 160.22 | 192.26 |
| 11                      | 160.22 | 192.26 |
| 12                      | 160.22 | 176.24 |
| 13                      | 160.22 | 176.24 |
| 14                      | 160.22 | 176.24 |
| 15                      | 160.22 | 176.24 |

Table 5. GGA and GGA + vdW calculated energies of fully relaxed (10\bar{1}0) surface slabs as a function of the number of layers. Atoms in this relaxation (free-standing layers) could relax in all three directions inside the simulation box.

| Number of layers in slabs | Slab Thickness (Å) |
|--------------------------|--------------------|
|                          | GGA    | GGA + vdW |
| 2                        | 4.583  | 4.283    |
| 3                        | 9.056  | 8.531    |
| 4                        | 14.592 | 12.690   |
| 5                        | 18.065 | 16.903   |
| 6                        | 22.628 | 21.123   |
| 7                        | 27.150 | 29.614   |
| 8                        | 31.568 | 29.614   |
| 9                        | 36.109 | 33.788   |
| 10                       | 40.604 | 38.081   |
| 11                       | 45.087 | 42.232   |
| 12                       | 49.604 | 46.427   |
| 13                       | 54.102 | 50.576   |
| 14                       | 58.617 | 54.919   |
| 15                       | 63.045 | 59.217   |

Table 6. GGA and GGA + vdW optimized slab thickness as a function of the number of layers.

5.2 Bulk Electronic Properties
Figure 15. (a) GGA and (b) GGA + vdW calculated band structures of pure bulk $t$-Se. The calculated indirect (direct) band gaps are 0.98 (1.21) eV and 0.72 (0.80) eV, respectively. The Fermi level, $E_F$, is set at 0 eV. van der Waals correction, vdW was applied through the zero damping DFT-D3 method of Grimme.

Figure 16. GGA and GGA + vdW calculated the density of states (DOS) of pure bulk $t$-Se. This figure shows that the top of the valence band and the bottom of the conduction band are mainly composed of Se $p$. Hence, the bands in Figure 15 in the energy range of (-4, 4) are contributed primarily by Se $p$. The Fermi level, $E_F$, in this figure is set at 0 eV.