Electron–phonon relaxation at the Au/WSe₂ interface is significantly accelerated by a Ti adhesion layer: time-domain ab initio analysis

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Thermal transport at nanoscale metal–semiconductor interfaces via electron–phonon coupling is crucial for applications of modern microelectronic, electro-optic and thermoelectric devices. To enhance the device performance, the heat flow can be regulated by modifying the interfacial atomic interactions. We use ab initio time-dependent density functional theory combined with non-adiabatic molecular dynamics to study how the hot electron and hole relaxation rates change on incorporating a thin Ti adhesion layer at the Au/WSe₂ interface. The excited charge carrier relaxation is much faster in Au/Ti/WSe₂ due to the enhanced electron–phonon coupling, rationalized by the following reasons: (1) Ti atoms are lighter than Au, W and Se atoms and move faster. (2) Ti has a significant contribution to the electronic properties in the relevant energy range. (3) Ti interacts strongly with WSe₂ and promotes its bond-scissoring which causes Fermi-level pinning, making WSe₂ contribute to electronic properties around the Fermi level. The changes in the relaxation rates are more pronounced for excited electrons compared to holes because both relative and absolute Ti contributions to the electronic properties are larger above than below the Fermi level. The results provide guidance for improving the design of novel and robust materials by optimizing the heat dissipation at metal–semiconductor interfaces.

1. Introduction

The increasing demand and ongoing trend for versatile, high-speed and high-density electronics are pushing the limits for miniaturization of electronic devices to atomic thickness. As silicon-based devices are approaching their limit to keep up with Moore’s law, there is a need for an alternative semiconductor material that can continue to shrink the size of electronic devices while maintaining their efficiency. As atomically thin two-dimensional (2D) semiconductors, transition-metal dichalcogenides (TMDs) are potential candidates for silicon replacement in low power devices owing to their stability, long life and tunable band gap.1–4 However, the true capability of TMDs is masked by their large contact resistance at interfaces, which necessitates the optimization of such devices to control the interfacial properties.5

Thermal resistance at interfaces can inhibit the removal of excess heat that can compromise with reliability and degrade the performance of ultrasmall devices.6 In metals, electrons govern the transfer of energy, while lattice vibrations or phonons are responsible for the heat flow in semiconductors. At interfaces, two phenomena are likely to occur: first, the electrons in metals couple to the phonons in metals and then the phonons in metals transfer energy to the phonons in semiconductors; second, the electrons in metals couple directly to the phonons in semiconductors. A comprehensive understanding of the thermal equilibration of excited electrons with the lattice is crucial for various applications.7 Experimentally, time-resolved pump–probe laser techniques are used to advance the understanding of energy transfer processes occurring over pico- and sub-picosecond time scales.8–12 Over the years, a number of theoretical models have been developed to mimic these experimental techniques.13–16

The most popular approach, the two-temperature model (TTM), considers that the irradiation of a metal surface with an ultrashort laser pulse creates thermodynamic non-equilibrium electron distribution,17,18 as the optical pulse can only
couple directly to electrons; the temperature of the phonon subsystem remains unaffected due to the large difference in the electronic and lattice heat capacities ($C_p \gg C_v$). Over tens or a few hundreds of femtoseconds, the electronic subsystem equilibrates to the Fermi–Dirac distribution at a higher temperature through electron–electron scattering. Thereafter, the electrons equilibrated at an elevated temperature redistribute their energy to the phononic subsystem until the two temperatures become equal. The rate of energy transfer depends on the electron–phonon coupling constant $G$ and the temperature difference of the two subsystems.\textsuperscript{11} The coupling is thus enhanced under the conditions of a strong non-equilibrium between the electron and phonon subsystems. The TTM theory was first confirmed experimentally by Eesley, who studied the evolution of non-equilibrium between the electronic and vibrational states using ultrafast pump–probe spectroscopy.\textsuperscript{19}

Using the TTM, Majumdar and Reddy derived an analytical expression to study how the electron–phonon coupling in metals affects the thermal boundary resistance across metal/non-metal interfaces.\textsuperscript{20} Chen et al. proposed an improvement to the TTM by introducing a temperature dependent electron–phonon coupling constant, $G_{\text{eff}}$.\textsuperscript{21} However, this method is only valid for materials that have a constant density of states (DOS) over all the electron temperature range until the Fermi temperature is reached. Further modifications to this model were introduced by Zhigilei and co-workers.\textsuperscript{22} They calculated the electron–phonon coupling constant using electronic structure calculations and studied the temperature dependence of the electron–phonon coupling factor for several different metals accounting for variations in the chemical potential and electron density of states beyond free electron theory as the degree of electron–phonon thermal nonequilibrium increased.

The TTM has been frequently used to study numerous bulk systems in the past; however, the assumption of the quasi-equilibration of electron energy is troublesome for nano-sized metallic systems.\textsuperscript{23,24} In bulk metals, the electron energy equilibrates due to the Cherenkov generation of acoustic waves, but this mechanism is absent in the case of nano-sized metallic systems.\textsuperscript{25} For ultrasmall systems, energy carrier dynamics are fast, and the energy distributions are highly out of equilibrium. This inspires time-domain atomistic simulations in such regimes to mimic the ultrafast laser measurements.

The electron–phonon energy transfer across interfaces is strongly influenced by the interfacial atomic interactions.\textsuperscript{26} A transition metal film, usually Ti, is often inserted at the interface to alter the electronic and optical response, as well as increase the adhesion of poorly bonded layers.\textsuperscript{27–30} Giri et al. demonstrated that on incorporation of a thin Ti adhesion layer between an Au slab and a non-metal substrate, the electron–phonon coupling is enhanced resulting in accelerated energy relaxation.\textsuperscript{31} The increase in energy exchange near the interface is rationalized by the strengthened bonding between Au and the non-metal substrate when a Ti layer is included. Zhou et al. used time-domain \textit{ab initio} analysis and observed that the relaxation between electrons and phonons is accelerated on placing a Ti adhesion layer on gold films.\textsuperscript{32,33} Freedy et al. used time-domain thermo-reflectance to report that the high thermal conductance at Au–Ti–WSe$_2$–HOPG interfaces is due to the strong interaction of a Ti adhesion layer with WSe$_2$ at the interface.\textsuperscript{29}

In this paper, we use \textit{ab initio} time-dependent density functional theory (TD-DFT) within the Kohn–Sham (KS) framework, combined with non-adiabatic (NA) molecular dynamics (MD), to study how the thermal relaxation of excited charge carriers at the Au/WSe$_2$ interface is influenced when a Ti adhesion layer is sandwiched between Au and WSe$_2$ resulting in Au/Ti/WSe$_2$. Tungsten diselenide (WSe$_2$) is a 2D transition metal dichalcogenide that consists of a strongly bound Se–W–Se sandwich weakly stacked with other layers by van der Waals interactions.\textsuperscript{34–36} For the interface, a gold (Au) slab is considered because of its simple structure and the available literature that makes the comparative study between experiments and theory convenient.\textsuperscript{37} Time-domain NA-MD is efficient to probe the non-equilibrium processes that are critical for a wide-range of applications in nanostructures, semiconductors and at interfaces.\textsuperscript{38–50} It mimics time-resolved pump–probe laser experiments and aids us to gain insight into processes that occur on a sub-picosecond scale.

2. Computational details and methodology

A mixed quantum-classical approach is employed to investigate the non-equilibrium dynamics of excited electron relaxation. The electronic evolution is studied quantum mechanically using KS-DFT and the nuclear trajectory is obtained using classical MD. NA-MD is used to model electron–nuclear interactions.\textsuperscript{51–59}

Initially, geometry relaxation, and electronic structure and MD calculations are performed using the Vienna \textit{ab initio} simulation package (VASP), which uses plane wave basis sets to describe the periodic structure.\textsuperscript{60–62} The Perdew–Burke–Ernzerhof (PBE) generalized gradient DFT functional described the nonlocal exchange and correlation contribution to the electronic energy.\textsuperscript{63} The projector-augmented wave (PAW) approach is used to express the interactions between ionic cores and valence electrons.\textsuperscript{64} The following VASP pseudopotentials were used: PAW PBE Au 06Sep2000, PAW PBE Ti 08Apr2002, PAW PBE W 08Apr2002 and PAW PBE Se 06Sep2000. The van der Waals interactions at the interface were described using the DFT-D3 method.\textsuperscript{65} The cutoff energy for the plane wave basis set was set at 400 eV. The electronic energy and ionic forces were converged to 10$^{-6}$ eV and 0.02 eV Å$^{-1}$, respectively.

The two systems under investigation, Au/WSe$_2$ and Au/Ti/WSe$_2$, were set up using the VESTA software.\textsuperscript{66} The Au/WSe$_2$ system is made up of an Au slab cut at the (111) lattice plane, and it has five layers of Au atoms at the interface with monolayer WSe$_2$. The supercell contains 40 Au, 12 Se and 6 W atoms. Au/Ti/WSe$_2$ was constructed by placing a Ti (001) monolayer of total 8 atoms sandwiched between the Au slab
and the WSe$_2$ monolayer of the same dimensions. To avoid spurious interactions with periodic slabs, a vacuum layer of 20 Å was introduced perpendicular to the surface. A 5 × 5 × 1 Monkhorst–Pack mesh was used for structural optimization, molecular dynamics and DOS calculations.

After geometry optimization at 0 K, the temperature was raised up to 300 K using repeated velocity rescaling to mimic the experimental conditions. Following thermalization, MD simulations were performed for a total of 4 ps in a microcanonical ensemble with a time step of 1 fs. Adiabatic state energies and the NA coupling (NAC) matrix were computed for the geometry at every time-step. In total 1000 stochastic surface hopping realizations for each of the 50 geometries sampled from the MD trajectory as initial conditions were used for electron–nuclear evolutions. The 4 ps trajectory was replicated twice to obtain longer time results for NA-MD.

Electronic basis states can be represented in several ways, however, for computational convenience, a Slater determinant constructed using KS orbitals is preferred. In the KS representation of DFT, the electron density of a system is used to describe the evolution of all its electronic properties. It is represented by the sum of densities of all occupied single electron KS orbitals:

$$\rho(t) = \sum_{\alpha=1}^{N_e} |\Phi_\alpha(r, t)|^2$$

where $N_e$ is the total number of electrons. The equations of motion for single particle time-dependent KS orbitals is obtained by applying the time-dependent variational principle to the expectation value of the KS density functional,

$$i\hbar \frac{\partial}{\partial t} \Phi_\alpha(r, t; R) = H(r, t, R) \Phi_\alpha(r, t; R)$$

where $H(r, t, R)$ is a functional of the total electron density, and hence the equations of each particle are coupled and not independent. The nuclear degrees of freedom are treated parametrically and they evolve on the respective adiabatic state using the quantum force, e.g., the Hellmann–Feynman force. The time-dependent KS orbitals can be expanded in terms of the adiabatic KS orbital computed for a given nuclear configuration, $R(t)$, using time-dependent coefficients,

$$\Phi_\alpha(r, t) = \sum_{k=1}^{N_e} c_{\alpha k}(t) \hat{\Phi}_k(r; R(t))$$

Combining eqn (2) and (3) produces equation-of-motion for the expansion coefficients:

$$i\hbar \frac{\partial c_{\alpha k}(t)}{\partial t} = \sum_{k=1}^{N_e} c_{\alpha k}(t) \left( \epsilon_k \delta_{\alpha k} + d_{\alpha k} \cdot \dot{R} \right)$$

where $\epsilon_k$ is the energy of the $k^{th}$ adiabatic KS orbital, and $d_{\alpha k}$ is the NAC vector between adiabatic states $j$ and $k$. The coupling arises from the dependence of adiabatic electronic states on the nuclear trajectory. The dot product of the NAC with the nuclear velocity is numerically calculated by taking the overlap of the adiabatic wavefunctions of the two states at sequential time steps.

$$d_{\alpha k} \cdot \dot{R} = -i\hbar \left< \hat{\Phi}_k | \nabla_R | \hat{\Phi}_\alpha \right> \cdot \frac{dR}{dt} = -i\hbar \left< \hat{\Phi}_j | \frac{\partial}{\partial R} | \hat{\Phi}_k \right>$$

To model the excited electron relaxation dynamics, a method that can efficiently describe the transitions between electronic states is desired. For the work in this paper, we used the global flux surface hopping (GFSH) method within the classical path approximation as implemented in the PYXAID program. GFSH is a generalization of the fewest switches surface hopping, which is the standard method for modelling electron–phonon relaxation dynamics in condensed matter. The probability of electronic transitions between electronic states is calculated using the solution of the time-dependent Schrodinger equation.

$$dP_{jk} = \left( - \frac{2Re\left( a_{jk}^* d_{jk} \dot{R} \right)}{d_{jj}} \right) dt$$

where $a_{jk} = \epsilon_j^* \epsilon_k \cdot$ and $j$ and $k$ are the electronic states under consideration and $dt$ is the time interval. If $dP_{jk}$ is negative, the transition probability is set to zero. To determine if a transition to a state will occur, the probability of the transition is compared with a random number uniformly generated between 0 and 1 at every time step. The detailed balance between transitions upward and downward in energy is achieved by accepting transitions upward in energy with the Boltzmann probability, reflecting the probability that sufficient kinetic energy is present in the motion along the direction of the NAC that induces the transition.

3. Results and discussion

On geometry relaxation of both systems under investigation, Au/WSe$_2$ and Au/Ti/WSe$_2$, the structural integrity of all materials in the supercell is preserved. WSe$_2$ displays a small- scale sliding on the incorporation of a Ti adhesion layer between the Au slab and the WSe$_2$ monolayer, Fig. 1. The distance between WSe$_2$ and the nearest Au layer in Au/WSe$_2$ is 2.807 Å, while the nearest Au layer–Ti layer and Ti layer–WSe$_2$ distances in Au/Ti/WSe$_2$ are maintained at 2.236 Å and 2.265 Å, respectively. The average Au–Ti distance is similar to that observed and calculated in the Au/Ti interfacial system in the absence of the WSe$_2$ monolayer indicating that WSe$_2$ has little influence on the interaction between Au and Ti. The two Se layers in WSe$_2$ are in different chemical environments altogether. The distance between Se and Ti which is in direct contact with the Au slab in Au/WSe$_2$ and the Ti layer in Au/Ti/WSe$_2$ is termed “Se-con”, while the W–Se distance for which Se is not in direct contact to any other element is called “Se-non”, Fig. 1.

The thermal effects when the temperature is raised up to 300 K and the inclusion of the Ti adhesion layer between the Au slab and the WSe$_2$ monolayer have notable impacts on the geometry and interlayer distance of all materials in the system,
Titanium interacts with WSe$_2$ and lengthens the W–Se bond length at 0 K, however, in the case of Au/Ti/WSe$_2$, the average W–Se bond length at 300 K is exactly equal to the bond length at 0 K, however, in the case of Au/Ti/WSe$_2$, the W–Se bond bond elongates by 0.002–0.003 Å. Titanium interacts with WSe$_2$ and lengthens the W–Se bond distance (2.588 Å), indicating that Ti leads to bond scissoring in WSe$_2$, which results in increased elemental W and Ti-Se bonding characters. Overall, the influence of the Ti–WSe$_2$ interactions on the system geometry is much stronger than the thermal effects, Table 1.

To characterize the electronic structure, the projected density of states (PDOS) of the optimized geometry is computed as shown in Fig. 2a. The PDOS is derived by separation of the total density of states into contributions from Au (red), Ti (green) and WSe$_2$ (blue). The Fermi level is set to zero. This journal is © The Royal Society of Chemistry 2022

<table>
<thead>
<tr>
<th>Table 1</th>
<th>Calculated average W–Se bond length, average Ti–Se bond length, interface distance between Au and either WSe$_2$ or Ti (D 1), Fig. 1, and interface distance between WSe$_2$ and Ti (D 2) at 0 K and 300 K</th>
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<tbody>
<tr>
<td>Average W–Se bond length</td>
<td>Average Ti–Se bond length</td>
</tr>
<tr>
<td>0 K</td>
<td>300 K</td>
</tr>
<tr>
<td>Normal</td>
<td>2.548 Å</td>
</tr>
<tr>
<td>Au/WSe$_2$</td>
<td>2.544 Å</td>
</tr>
<tr>
<td>Au/Ti/WSe$_2$ Se-con</td>
<td>2.588 Å</td>
</tr>
<tr>
<td>Au/Ti/WSe$_2$ Se-non</td>
<td>2.539 Å</td>
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As evident from the data in Table 1. On heating, the system expands, and as a result, the average inter-layer distance increases by ∼0.027 Å for both Au–WSe$_2$ and Au–Ti. However, there is no significant change in Ti–WSe$_2$ (0.003 Å) distance. In Au/WSe$_2$, the average W–Se bond length at 300 K is exactly equal to the bond length at 0 K, however, in the case of Au/Ti/WSe$_2$, the W–Se bond bond elongates by 0.002–0.003 Å. Titanium interacts with WSe$_2$ and lengthens the W–Se bond distance (2.588 Å), indicating that Ti leads to bond scissoring in WSe$_2$, which results in increased elemental W and Ti-Se bonding characters. Overall, the influence of the Ti–WSe$_2$ interactions on the system geometry is much stronger than the thermal effects, Table 1.

The right panels of Fig. 2 show charge densities of the electronic states at the Fermi level for both systems under consideration. In the case of Au/WSe$_2$, the density of the Fermi level is completely localized on Au, and there is no contribution from WSe$_2$. As understood from the PDOS, the band gap of WSe$_2$ encompasses the Fermi level, and hence WSe$_2$ does not contribute to the charge density. In the case of Au/Ti/WSe$_2$...
WSe$_2$, the charge density is delocalized on the whole system, while it is most dense at Ti, indicating that Ti supports the most mobile electrons in the system. Furthermore, the Fermi level charge density of Au/Ti/WSe$_2$ shows contributions from W, reflecting the increased DOS of WSe$_2$ near the Fermi energy, resulting from WSe$_2$ distortion due to interaction with Ti and the Fermi-level pinning. The charge density contribution by Au is sparse and less dense, compared to contributions from Ti and W, as well as the charge density of Au in Au/WSe$_2$ at the Fermi level.

Electrons and phonon subsystems interact, leading to elastic and inelastic electron–phonon scattering. Elastic scattering results in dephasing of the electronic states by randomization of the phase of the electronic wavefunction, and it is measured by the pure-dephasing time. \(^\text{78-80}\) Inelastic scattering leads to energy exchange between the electrons and phonons, and it is characterized by the NAC. Here, we focus on the electron–phonon energy exchange. The coupling strength between two electronic states is directly related to the localization of the wavefunction of the corresponding electronic states, see eqn (5). The magnitude of NAC determines the frequency and time-scale of NA transitions between the electronic energy levels. In surface hopping, a sequence of NA transitions governs the electron–phonon relaxation rate. Fig. 3 shows the phonon-induced NAC of both systems for ±50 electronic states around the Fermi energy, \(i.e.,\) the highest occupied molecular orbital (HOMO). As expected, both the plots are diagonally symmetric confirming that the magnitude of state \(i\) coupling to state \(j\) or state \(j\) coupling to state \(i\) is equal. The diagonal data points (black) have zero NAC magnitude because the electronic states do not couple to themselves. The brighter purple-red traces in the plot correspond to the coupling between consecutive electronic states. The rest of the non-diagonal part represents the electronic states that differ by two or more. The NAC between distant states is much weaker than the coupling between neighbor states, indicating that the electron–phonon energy relaxation occurs by small energy transitions, and that large energy hops are possible occasionally.

The NAC strength is much larger in Au/Ti/WSe$_2$ compared to Au/WSe$_2$ throughout the plot, Fig. 3. In the presence of the Ti adhesion layer, the DOS is relatively dense around the Fermi level, and the coupling strength is generally higher for states closer in energy. Ti is the dominant element contributing to the electronic states in the corresponding energy region. Furthermore, eqn (5) shows that the NAC is directly related to nuclear velocities, and nuclear velocities are inversely pro-

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Fig. 2 Projected density of states (PDOS) in the left panel and charge densities of the Fermi level in the right panel of (a) Au/WSe$_2$ and (b) Au/Ti/ WSe$_2$. 

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The measurement in the current process is chosen to match the experiments. The electronic subsystem is nearly as heavy as Au. Se is twice heavier than Ti, however, it has no contribution near the Fermi energy and contributes to the WSe$_2$ conduction band. Se contributes to the WSe$_2$ valence band, however, the DOS in that energy region is strongly dominated by Au, Fig. 2. Overall, the NAC strength is expected to be larger in the region where Ti electronic states are dominant. Consequently, the influence of the Ti adhesion layer should be more significant above the Fermi energy.

The photoexcited charge carriers dissipate their energy by coupling to phonons. The rate of relaxation through manifold states depends on the strength of respective NAC, Fig. 3. Fig. 4 shows the evolution of the average energy of the charge carriers in the two systems beginning at high and low energy initial conditions: 3.1 and 1.55 eV in the case of electrons, and −3.1 and −1.55 eV in the case of holes. The initial conditions are chosen to match the experiments. The electronic subsystem is pumped at 400 nm, corresponding to ~3.1 eV. The 3.1 eV of energy is distributed between the electron and the hole. The initial conditions represent two limiting cases. Either half of the energy is given to the electron and half to the hole, resulting in 1.55 eV excitation of each, or all energy is given to either the electron or hole. Because the dense d-band of Au starts about 1.7 eV below the Fermi level, as seen in the rapidly rising DOS in Fig. 2, majority of the carriers are excited from around this energy, and the symmetrical initial condition provides a better representation of the experiments.

As expected for all quantum dynamical systems, the dynamics is Gaussian in the beginning. The exponential regime, associated with participation of many states, is achieved relatively fast. The Gaussian regime of quantum dynamics gives rise to the Zeno effect, in which continuous measurement of the quantum system effectively slows down the dynamics. The measurement in the current process is associated with electronic wavefunction dephasing due to elastic electron–phonon scattering. Because the relaxation occurs through the dense manifolds of electronic states, the elastic pure-dephasing process is slow relative to the frequency of inelastic quantum transitions. The Fermi energy level is set to zero in Fig. 4, and the decay time is obtained by fitting the data to an exponential function, $A \exp(-t/\tau)$. While no experimental time-traces are available in the literature for the systems under investigation, time-resolved data are available for the systems composed of Au films on other semiconductor substrates, including Si, SiO$_2$, TiO$_2$ and Al$_2$O$_3$, with and without Ti adhesion layers. The measured timescales are similar to those obtained in the present calculations.

In the case of Au/WSe$_2$, there is a steep decrease in the electronic DOS above ~1.5 eV, Fig. 2. Consequently, the decay of holes starting from ~1.5 eV is much slower than the decay of holes beginning at ~3.1 eV, Fig. 4c. The frequency of transitions is slow in the region where electronic states are sparse. Moreover, it is slower when electronic states are contributed by Au compared to Ti due to Au heavier mass, slower velocity, and smaller NAC, eqn (5). Therefore, on addition of Ti, the involvement of Ti states after ~1.5 eV substantially increases the relaxation rate of holes, Fig. 4d. Overall, the relaxation of holes is faster in the presence of Ti. Similarly, the hot electron decay is faster in Au/Ti/WSe$_2$ compared to Au/WSe$_2$, Fig. 4a and b, while the timescales of electron decay beginning at different energy levels are comparable within each system due to the homogeneous DOS above the Fermi level, Fig. 2. Notably, the influence of the Ti adhesion layer is more pronounced for the relaxation of hot electrons compared to holes. This can be rationalized by the more significant Ti contribution to the DOS above the Fermi level in Fig. 2b.

To further advance the understanding of the electron–phonon scattering, we obtained phonon influence spectra. They help in identifying the frequencies of the phonon modes that couple to the electronic subsystem and dissipate the electronic energy. Phonon influence spectra are obtained by computing the Fourier transform of the autocorrelation function.
tions of the energy gaps between the initial and final states in each simulation, i.e., between the hole energy level at $-3.1$ eV and the Fermi level (HOMO) at 0 eV, the hole energy level at $-1.55$ eV and the Fermi level at 0 eV, the electron energy level at 3.1 eV and the Fermi level, and the electron energy level at 1.55 eV and the Fermi level. This particular choice is made for

![Fig. 4](image_url) Evolution of electron (a and b) and hole (c and d) energy starting from high (3.1 eV) and low (1.55 eV) energy initial states in (a and c) Au/WSe$_2$ and (b and d) Au/Ti/WSe$_2$.

![Fig. 5](image_url) Phonon influence spectra for the energy gaps from the Fermi level to the high or low energy initial states for the electron relaxation (top two panels) and hole relaxation (bottom two panels) in (a) Au/WSe$_2$ and (b) Au/Ti/WSe$_2$. 

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representative purposes, since around 50 states are involved in the studied NA dynamics of both electrons and holes, and the number of energy gaps is on the order of 1000. The height of the peaks in Fig. 5 indicates the strength of the electron–phonon coupling at the corresponding frequency.

The influence spectra show only very weak signals at frequencies above 200 cm$^{-1}$. The Ti adhesion layer introduces higher frequency phonons, because Ti is lighter than any atom of the Au/WSe$_2$ system. Moreover, the electron–phonon coupling strength increases as evident from the larger peak heights. Note that while the peak intensity scale is arbitrary, it is consistent across all plots. The influence spectrum characterizing holes starting at $-3.1$ eV exhibits a strong peak at 100 cm$^{-1}$, which is not seen for the $-1.5$ eV signal, comparing the third and bottom panels in Fig. 5a. This is because Se atoms are lighter than both Au and W, and contribute to the valence band states of WSe$_2$, which participates in the relaxation of deep holes. The Ti peaks at 150 cm$^{-1}$ are stronger for electrons than holes, comparing the top two and bottom two panels in Fig. 5b. This is because Ti has a much larger absolute and relative contribution to the DOS above than below the Fermi energy, Fig. 2. We conclude that the photogenerated charges always couple to phonons in the metal, and the Ti adhesion layer makes this coupling stronger. The phonons of the WSe$_2$ semiconductor couple to the excited charges only when the energy of the charges is within the range of the conduction or valence band of WSe$_2$.

4. Conclusion

We performed ab initio quantum dynamics simulations to model two related systems: Au/WSe$_2$ and Au/Ti/WSe$_2$, and thus study the effect of a thin Ti adhesion layer on excited electron and hole relaxation dynamics at the interface between Au and WSe$_2$. Related metal–semiconductor interfaces are ubiquitous in electro-optical devices, and it is essential to optimize such devices to minimize the thermal resistance at the interfaces. It was observed that the inclusion of Ti at the interface increases the strength of the electron–phonon coupling and hence accelerates the relaxation dynamics. We thoroughly investigated the reasons behind the enhanced coupling strength. Because Au has a low DOS around the Fermi level, which falls within the WSe$_2$ band gap, even a thin Ti adhesion layer has a strong influence on the electronic properties and electron–phonon coupling in the relevant energy range. The Ti adhesion layer makes a significant direct contribution to the electronic DOS. In addition, Ti interacts strongly with WSe$_2$ to elevate the W metallic character and Ti–Se bonding, while weakening W–Se bonding. This results in Fermi-level pinning, increasing the WSe$_2$ contribution to the electronic states in the relevant energy window. Furthermore, Ti atoms are lighter by a factor of four than Au and W atoms and by a factor of two than Se atoms. Consequently, Ti atoms move faster and accelerate the electron-vibrational energy exchange. Se atoms contribute to the DOS where it is dominated by Au, and therefore, the contribution of Se to electron–phonon relaxation is less important compared to the Ti, Au and W metal atoms. By increasing the DOS and moving fast, Ti atoms increase the NAC and accelerate the charge–phonon relaxation. Because Ti has a more significant contribution to the electronic properties above than below the Fermi energy, the electron relaxation is accelerated more than the hole relaxation. These results can be used for designing modern electronic devices by altering the thermal conductance at metal–semiconductor interfaces.

Conflicts of interest

There are no conflicts of interest to declare.

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