Supplementary information

Long-lived modulation of plasmonic absorption by ballistic thermal injection

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Supplementary materials for: Long-lived modulation of plasmonic absorption by ballistic thermal injection

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MATERIALS AND METHODS

A. TDTR measurements and two-temperature analysis

Our time-domain thermoreflectance (TDTR) measurements can be conceptually understood as follows. First, the sub-ps pump pulse excites electronic carriers in the metal, which quickly (10’s of fs) scatter and decay into a ‘hot’ Fermi-Dirac distribution. At this stage, the electronic subsystem is at a greatly elevated temperature, while the phononic subsystem remains cold (i.e., approximately at its initial temperature). In the case of metals in contact with dielectrics (e.g., Al$_2$O$_3$), these hot carriers are spatially confined to the metal and can neither traverse the metal/dielectric interface nor directly couple their energy to electrons or phonons in the insulator. Instead, they couple to and lose energy to the phononic subsystem (i.e., the lattice) of the metal film. Following this electron-phonon coupling, phonon-based thermal conduction out of the metal and into the insulator over hundreds of picoseconds to nanoseconds. The entire process is monitored via temporal changes in the metal’s thermoreflectance: the reflectance signal decays with time as the surface of the metal film loses energy to the underlying substrate via phonon interactions at the metal/non-metal interface [1–4].

Conversely, when Au is in direct contact with a different metal (e.g., Au/Ti or Au/Pt interfaces [5–8], the excited electrons are no longer confined and can directly couple energy across the metal/metal interface, leading to an ‘instantaneous’ (sub-picosecond) temperature rise of electrons in the underlying metal. These hot-electrons in the underlying metal can subsequently lose energy to the phononic subsystem more quickly than those in the Au, which creates a sub-surface temperature rise. This sub-surface heating leads to a bi-directional heat flux originating from some depth under the Au/air surface, and manifests as a temporally delayed rise in the thermoreflectance signal as heat is conducted back into the Au through the lattice (e.g., ‘back-heating’). This back-heating signature is thus a strong indication of electron energy transfer from the Au film into the underlying metal film [8]. This phenomenon acts as a transient thermal diode: the injection of energy from Au to the buried metal substrate occurs on sub-picosecond time-scales, whereas the

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lattice-mediated ‘back-heating’ occurs on hundreds of picoseconds to nanoseconds.

We perform additional two-temperature model calculations on our TDTR data to verify the injection of thermal energy from Au to CdO on ultrafast time-scales, leading to a shift in the optical properties of only a thin-heated region of the CdO. As outlined in a number of previous works, one can empirically interpret the temporal dynamics of a pump-probe reflectivity experiment via a semi-classical ‘two-temperature’ model (TTM) [9–11]. As photons only couple their energy to electrons, on ultrafast timescales, the lattice of a metal will remain cold, while the electronic subsystem rapidly gains energy/increases in temperature. Within hundreds of femtoseconds to a few picoseconds, with this time scale being determined by the temperature differential between the electronic and phononic subsystems as well as an electron-phonon coupling factor, the electrons lose their energy to the lattice, which begins to heat up. Ultimately, this energy transfer follows two governing equations,

\[
\begin{align*}
C_e(T_e) \frac{\delta T_e}{\delta t} &= \nabla \cdot (\kappa_e \nabla T_e) - G(T_e - T_p) + S(t) \\
C_p(T_p) \frac{\delta T_p}{\delta t} &= \nabla \cdot (\kappa_p \nabla T_p) + G(T_e - T_p)
\end{align*}
\]

where \(C_e\) and \(C_p\) are the heat capacities of the electrons and phonons, respectively, \(T_e\) and \(T_p\) are the temperatures of the electrons and phonons, respectively, and \(\kappa_e\) and \(\kappa_p\) are the thermal conductivities of the electrons and phonons, respectively. \(G\) represents the electron-phonon coupling factor and \(S(t)\) is the laser heating source, which includes the relevant parameters of the ultrafast pump pulse. In our multi-layer TTM calculations, we use literature values for the relevant Au parameters, as well as experimentally measured/calculated values for the CdO films.

As shown in Fig. S1a, we find that the TTM captures the experimental data for CdO with various dopant/carrier concentrations very well, regardless of the fact that we only use one fitting parameter in our calculations: the electron-electron thermal boundary conductance between the two layers. Further, this semi-classical model, that does not invoke any aspects of electron transport/diffusion, but only considers temperature gradients within the layers, results in qualitatively similar findings to those observed in our transfer-matrix model of the infrared differential
reflectance measurements. Indeed, as shown in Fig. S1b, hot electrons in the Au rapidly deposit their energy to electrons within a thin layer in the CdO prior to equilibrating with the Au lattice itself, leading to an increase in the electron temperature of the CdO following optical excitation of the Au, consistent with our DFT calculations. Following this period of strong interfacial non-equilibrium, the system eventually relaxes to a thermal distribution as expected from Fourier Law, as shown in Fig. S1c.

B. Time-dependent density functional theory (TDDFT)

The non-equilibrium evolution of the coupled electronic and nuclear degrees of freedom is modeled by combining real-time time-dependent density functional theory (TDDFT) with nonadiabatic molecular dynamics (NAMD). Real-time TDDFT [12] describes evolution of electronic properties of a system using its time-dependent electron density, \( \rho(t) \), which is constructed from single-electron Kohn-Sham (KS) orbitals, \( \Psi_n(r,t) \)

\[
\rho(t) = \sum_{n=1}^{N_e} |\Psi_n(r,t)|^2
\]  

(3)

Here, \( N_e \) is the number of electrons. The equations-of-motion for the time-dependent KS orbitals is derived using the time-dependent variational principle. Applying the time-dependent variational principle to the expectation value of the KS Hamiltonian gives a set of coupled equations of motion for the KS orbitals,

\[
i\hbar(\partial / \partial t)\Psi_n(r,R,t) = H(r,R,t)\Psi_n(r,R,t)
\]  

(4)

where \( r \) and \( R \) are electron and nuclear coordinates, respectively. The nuclear degrees of freedom \( R \) are treated parametrically, and their evolution is obtained from classical trajectories propagated using a quantum force, e.g. the Hellmann-Feynman force for the currently occupied adiabatic electronic state in surface hopping (SH), or the average force in the mean-field (Ehrenfest) approach.

In the current implementation of real-time TDDFT, [13] the time-dependent KS orbitals \( \Psi_n(r,t) \) are constructed from a set of adiabatic KS orbitals, \( \Phi_i(r;R(t)) \), with their corresponding
time-dependent coefficients $C_i(t)$

$$\Psi_n(r, t; R) = \sum_k C_{nk}(t) \Phi_k(r; R(t))$$  \hspace{1cm} (5)

Substituting Eq. 3 into Eq. 2 gives equations-of-motion for the expansion coefficients,

$$i\hbar (\partial / \partial t) C_{nk}(t) = \sum_j C_{nj}(t) (\varepsilon_j \delta_{jk} + d_{jk})$$  \hspace{1cm} (6)

Here, $\varepsilon_j$ is the energy of the adiabatic state $j$, and $d_{jk}$ is the nonadiabatic (NA) coupling between adiabatic states $j$ and $k$.

$$d_{jk} = -i\hbar \langle \Phi_j | \nabla_R | \Phi_k \rangle (dR/dt) = -i\hbar \langle \Phi_j | d/dt | \Phi_k \rangle$$  \hspace{1cm} (7)

The NA coupling reflects the dependence of the electronic wavefunctions on the nuclear coordinates. The NA coupling is a form of electron-phonon coupling.

Fewest Switch Surface Hopping (FSSH) is the most popular approach for modeling electron-vibrational dynamics in molecular, condensed matter and nanoscale systems [14]. It combines a classical, fully atomistic, non-perturbative description of vibrational dynamics with a quantum mechanical description of electrons. The method uses output from the deterministic time-dependent Schrödinger equations to evaluate probabilities of transitions between electronic states, and to perform Monte Carlo type stochastic sampling of electronic transitions correlated with nuclear motions. In particular, FSSH prescribes the following probability of hopping between adiabatic electronic states $j$ and $k$ within a time interval $dt$ based on the time-dependent coefficients, Eq. 4,

$$dP_{jk} = \left(-2Re(\alpha_{jk}^* d_{jk} \dot{R})/\alpha_{jj}\right)dt; \alpha_{jk} = c_j^* c_k$$  \hspace{1cm} (8)

If the probability is negative, it is set to zero. A hop from state $j$ to $k$ is allowed only when the state population flows from $j$ to $k$. A uniform random number between 0 and 1 is generated in each time step and compared to the hopping probabilities from the currently occupied states to all other states, in order to determine whether a hop will happen. The energy exchange between the electronic and nuclear degrees of freedom during the hop is assumed instantaneous. The total electron-vibrational energy is maintained constant by rescaling nuclear velocities along the direction of the NA coupling. If there is not enough kinetic energy along the NA coupling direction to
accommodate an increase in the electronic energy, the hop is rejected. The current implementation of FSSH applies the classical path approximation (CPA) in order to achieve significant computational savings \[15\]. The FSSH-CPA scheme replaces the velocity rescaling and hop rejection rules by scaling the hopping probability upward in energy with the Boltzmann factor, which guarantees the microscopic detailed balance and leads to quantum-classical thermodynamic equilibrium in the long-time limit.

The simulation cell is formed from five layers of CdO and three layers of Au atoms to imitate the experimental thickness ratio of the CdO and Au films. The simulation cell contains 138 atoms total, including 60 Cd, 60 O and 18 Au atoms. A 20 Å vacuum layer is placed in the direction perpendicular to the slab, in order to eliminate spurious interactions between slab images in the 3D periodic simulation. Additional calculations are performed on two thicker slabs, containing eight layers of CdO and four layers of Au, and ten layers of CdO and five layers of Au, respectively. The geometric and electronic structure calculations, and adiabatic molecular dynamics (MD) are carried out using the Quantum Espresso package \[16\], \[17\]. The simulations use the PBE functional with Hubbard parameters 12 eV for Cd and 8 eV for O, taken from references \[18\], \[19\] in order to obtain the proper alignment of the Au Fermi energy and the CdO band edges. The plane-wave basis set energy cutoff is set to 820 eV. A \(4 \times 6 \times 1\) k-point mesh grid is used.

After the structure optimization, the system is brought up to 300 K in the canonical ensemble using the Andersen thermostat. Then, a 5 ps trajectory is obtained in the microcanonical ensemble and used for the subsequent NAMD simulations. The adiabatic state energies and NA are calculated for each step of the MD run. The 5 ps NA Hamiltonian obtained this way is iterated several times in order to simulate longer time dynamics. The nuclear dynamics of the system is rather simple, involving no long term atomic rearrangements, and therefore 5 ps are sufficient to sample nuclear motions that drive the electron dynamics. The NAMD calculations are carried out using the quantum-classical FSSH technique implemented within the time-dependent KS scheme with the PYXAID code \[15\], \[20\]. 1000 initial geometries are sampled from the 5 ps MD trajectory, and 100 stochastic realizations of the FSSH process are generated for each geometry.

Because \textit{ab initio} simulations can only be performed with modest simulation cells, the current
setup is much smaller than the experimental system, and therefore, the simulation should be taken as a model demonstrating semi-quantitatively the mechanisms of the measured processes.

C. Optical pump-Infrared probe measurements

To monitor the epsilon-near-zero (ENZ) condition of the doped CdO film following excitation of the Au film, we utilize a second pump-probe system to measure the differential reflectivity. This experiment relies on a 400 femtosecond laser operating at its fundamental wavelength of 1040 nm with a repetition rate of 500 kHz. The output is split into two paths; the first path is frequency-doubled to a wavelength of 520 nm, which operates as the pump pulse. This pump goes through a mechanical delay stage, chopped at a frequency of 451 Hz, and then focused to the surface of the Au metal film at the Au/air interface. The other portion of the beam is passed through an optical parametric amplifier, where the signal is filtered out and the idler output operates as the probe; this probe beam is varied in 10 nm increments from 3400-4200 nm and focused onto the Au surface at the CdO/Au interface. The sapphire/100 nm CdO/Au sample is mounted on a goniometer to allow for high-precision in defining the incident angle of the probe beam. Although the ENZ resonance for this structure has minimal angular-dependence and inhibits reflection at the plasma frequency from 30 to 70 degrees, the peak absorption occurs at 55 degrees and is thus where we perform the majority of our experiments. Note, the probe beam is p-polarized for the majority of our experimental results as only this polarization is sensitive to the ENZ mode. We repeat the wavelength sweep with s-polarized and find no measurable differential reflectance signal; this is due to both the lack of response of the CdO as well as the inherently low (i.e., nearly zero) optical response of Au at infrared wavelengths. Additionally, we repeat these experiments with the use of a 15 nm hafnia buffer layer between the Au and CdO as was done with our TDTR experiments; again, no differential reflectance signal is observed at these wavelengths. This buffer layer provides two critical pieces of information. First, it ensures our optical response is not due to heating of the gold and is truly sensitive to only the CdO ENZ mode. Second, the hafnia layer is optically transparent to the 520 nm pump beam; thus, if any light were transmitting through the
15 nm Au metal film and optically exciting the CdO, the hafnia would not inhibit this factor and lead to a response in our pump-probe measurements.

D. Optical model

Transfer-matrix method (TMM) reflectance simulations were performed with light incident on the CdO side of a Al₂O₃/CdO/Au/Air stack at an angle of incidence of 55 degrees to mimic our experimental measurements. These TMM simulations incorporate rigorous relationships between the optical parameters (plasma frequency, scattering rate, high-frequency dielectric constant) and electronic parameters (electron number density, mobility, and effective mass), consistent with previous observations [21, 22].

First, the unpumped case was simulated as a 15 nm Au/100 nm CdO stack. In this case a uniform distribution of carriers was assumed, and thus a space-charge region at the Au/CdO interface was not present. A carrier density of $\sim 6.6 \times 10^{19} \text{ cm}^{-3}$ produced a minimum in reflectance at $\sim 3800 \text{ nm}$, as is seen in the measured spectra. The effective mass for the CdO film was estimated using the non-parabolic conduction band model, with fit parameters provided from [22]. The optical mobility of the CdO was set to 150 cm$^2$ V$^{-1}$ s$^{-1}$ in order to match the linewidth of the measured spectra. The high-frequency permittivity was set to $\varepsilon_{inf/ty} = 5.5$ which is consistent with previously-reported values of CdO films with similar carrier densities. From these parameters, reflectance was calculated and recorded for the unpumped case.

Next, we fit this multilayer TMM simulation to our experimental differential reflectance, $dR/R = (R_{pumped} - R_{unpumped})/R_{unpumped}$, data. We ultimately find that these data can not be simulated using a single-layer for the CdO film. Instead, we split the CdO into two layers (e.g., Al₂O₃/(d)CdO/(100 − d)CdO/Au/Air, where $d$ is the thickness of a perturbed layer within the CdO) which provides excellent overlap to our experimental data. The best-fit values lead to the following analysis, as also outlined in the manuscript. The pump pulse heats the Au which couples its electronic energy with the CdO, forming a thin layer of high electron temperature at the Au/CdO interface ($< 5 \text{ nm}$), as determined by an increase in the effective mass within this layer.
In prior work, the effective mass in CdO has been shown to increase with increased electron temperature [23]. This interface layer is out-of-equilibrium with the bulk of the film leading to carrier migration from the bulk of the CdO to the surface layer, as demonstrated by an observed decrease in the high-frequency permittivity. Previous work has demonstrated that a rise in the carrier density at the surface was related to a proportional decrease in the high-frequency permittivity as the Fermi level is pushed to higher energy [21, 22]. Conversely, an increase in the high-frequency permittivity of the bulk of the CdO film is observed, consistent with electron diffusion towards the Au/CdO interface. Finally, we find a decrease in the damping frequency of the free electrons within this thin heated layer; as the scattering rate is inversely proportional to the effective mass, this is an unsurprising observation. Ultimately, we find excellent agreement between the calculated spectra and experimental results.

E. Non-equilibrium electronic thermal diffusion

Although our results are in well-explained by the proposed BTI mechanism, which is in excellent agreement with our TTM and TD-DFT results, we note that there could be other energy transduction mechanisms operating in-tandem with BTI. Namely, we note the possibility of non-equilibrium electronic thermal diffusion (NETD) occurring in these experiments. This process can be qualitatively described as the transfer of hot electrons from the Au into the CdO, simultaneous to the transfer of ‘cold’ holes in the same direction (Fig. S9). This mechanism would lead to a lack of ‘net charge transfer,’ as charge neutrality is ensured due to simultaneous diffusion of carriers, while still allowing for the deposition of heat, due to the increased energy of carriers flowing from Au into CdO. Under the relaxation time approximation in Boltzmann theory, one can define an electronic thermal conductivity under zero field and zero current conditions, allowing this process to occur, despite the lack of net charge transfer. More explicitly, the heat current, assuming zero field, is defined as,

\[ j_q = L^{\alpha \beta} \nabla T, \]  

(9)
where the transport coefficient, $L^{\alpha\beta}$, takes the form

$$L^{\alpha\beta} = \frac{1}{4\pi^3 \hbar T} \int d\varepsilon \tau(\varepsilon) (\varepsilon - \mu)^2 \left(-\frac{\delta f^0}{\delta \varepsilon}\right) \int dS_\varepsilon \frac{\nu^{\alpha\beta}}{|\nu|}.$$  \hspace{1cm} (10)

For the case of Au, the chemical potential, $\mu$, is approximately constant until nearly 3000 K assuming the electrons can be described by a near-equilibrium Fermi distribution, such that the heat current is proportional to the excess energy of electrons relative to the Fermi energy (e.g., $j_q \propto (\varepsilon - \varepsilon_F)$). This can arise simply from Fermi smearing rather than shifting of the Fermi level.

To address the role of this alternative energy transfer mechanism, we perform two additional experiments. First, we perform a study with varying thicknesses of Au films deposited on CdO. We find that for the case where the Au film is sufficiently thick, such that ballistic electrons do not reach the Au/CdO interface ($\sim 80$ nm), plasmonic modulation is not observed, and there is a lack of ‘back-heating’ in our TDTR experiments. This observation is despite the fact that electrons in the Au are still heated well above room temperature, and Au electrons at the interface can still be considered ‘hot’ (e.g., above room temperature and the initial temperature of CdO, such that the carriers exist with a finite value of $(\varepsilon - \varepsilon_F)$ and thus a finite heat current exists). Under these experimental conditions, BTI is hindered, whereas one should fully expect NETD to be occurring. Additionally, we performed TDTR measurements on similarly thick platinum films (20-30 nm) in contact with CdO, and observe a similar lack of ‘back-heating’ in the Pt film. We attribute this finding to the necessary criteria of ballistic transport (e.g., the electrons are out of equilibrium with the phonons) within the metal contact upon reaching the metal-semiconductor interface; due to the large electron-phonon coupling factor of Pt, the electrons thermalize with phonons prior to reaching the Au/CdO interface, and BTI does not occur. Further, we note that within the temperature range investigated in this work, Pt has a larger shift in chemical potential than Au, and NETD should be enhanced [24]. Thus, NETD alone cannot be solely responsible for the plasmonic modulation and in-direct heating of the CdO layer observed in this work, but could
easily be playing an additional, parallel role to BTI.

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Figure S1. a) TDTR measurements with TTM fits for 15 nm Au on 100 nm Y:CdO at various dopant/carrier concentrations of the CdO film. The only fitting parameter of these calculations is the interfacial thermal resistance of the electronic subsystem. b) TTM-calculated electron temperatures near the Au/CdO interface within the first few picoseconds following optical excitation of the Au. c) TTM-calculated temperature gradient of the electronic subsystem at select times following optical excitation of the Au film. At time scales comparable to the observed non-equilibrium in our TDTR measurements, the system relaxation follows that as expected by Fourier Law.

Figure S2. Density of states of the Au/CdO system showing contributions of Au, Cd and O atoms. The Fermi energy is set to 0 eV. The Au Fermi level falls within the bandgap and is closer to the CdO conduction band than valence band.
Figure S3. Electron-phonon relaxation in the Au/CdO system. The 2.25 ps timescale is obtained by exponential fitting. The relaxation dynamics match the charge flow dynamics shown in Figure 2 of the main text.

Figure S4. Fourier transforms of energies of states localized primarily on Au (black) and delocalized between Au and CdO (red), characterizing phonon modes that couple to electrons. By entering CdO, electrons couple to higher frequency phonons that accelerate electron-phonon energy exchange. The frequencies below 100 cm$^{-1}$ can be assigned to phonons of Au [25], while the peaks of the red line between 200 cm$^{-1}$ and 400 cm$^{-1}$ can be assigned to phonons of CdO [26].
Figure S5. Optimized structures of the simulation cells with thicker Au/CdO slabs. a) 8 layers of CdO and 4 layers of Au. b) 10 layers of CdO and 5 layers of Au. Yellow, large purple and small red balls represent Au, Cd and O atoms, respectively.

Figure S6. Evolution of electron localization on Au atoms in the thicker Au/CdO systems shown in Figure S5. (a) 8 layers of CdO and 4 layers of Au. (b) 10 layers of CdO and 5 layers of Au. Zero-time corresponds to the initially-excited state.
Figure S7. Electron-phonon relaxation in the thicker Au/CdO systems shown in Figure S5. (a) 8 layers of CdO and 4 layers of Au. (b) 10 layers of CdO and 5 layers of Au.

Figure S8. Density of states of the thicker Au/CdO systems, Figure S5, showing contributions of Au, Cd and O atoms. (a) 8 layers of CdO and 4 layers of Au. (b) 10 layers of CdO and 5 layers of Au. The Fermi energy is set to 0 eV.
Figure S9. Following optical excitation of the metallic contact, there is a potential for non-equilibrium electron thermal diffusion to occur. In this case, (1) hot-electrons are first generated in the gold. At sufficiently high electron temperatures, (2) these hot-electrons traverse the interface and lie within the conduction band of the semiconductor. Simultaneous to this hot-electron transfer, there is hole movement into the semiconductor (electron from the semiconductor traversing into the Au), leading to a lack of ‘net’ charge transfer, while allowing for interfacial thermal transport to occur.