Supporting Information

Ultrafast Carrier Dynamics of CdTe: The Surface Effects

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Calculation of the change of the refractive index

Above-gap photoexcitation generates electron-hole plasma in a material, which cause a change in the refractive index, n. The four main contributions as a result of these free carriers are the effects of band filling (BF), bandgap renormalization (BGR), free-carrier absorption (FC), and lattice-temperature increase following the carrier-phonon coupling (LT). The methods to calculate these effects are outlined as follows.[1]

1. Band Filling. The index of refraction is expected to be modified if additional carriers are injected into a band and block the absorption of light at corresponding wavelengths owing to the Pauli Exclusion Principle, which forbids fermions to occupy the same quantum states at the same time. For materials with a direct bandgap E_g, the change in the absorption coefficient α_0 modeled for parabolic band structures at the photon energy $E \geq E_g$ is[1]

$$\Delta\alpha_{\mathrm{BF}}(N,P,E)=\frac{\sqrt{E-E_g}}{E}\{C_{hh}[f_v(E_{ah})-f_c(E_{bh})-1]+C_{lh}[f_v(E_{al})-f_c(E_{bl})-1]\},$$

where N and P are the densities of electrons and holes in conduction and valence bands, respectively; C_{hh} and C_{lh} are the absorption constants associated with heavy holes (hh) and light holes (lh), respectively; and $f_v(E_a)$ and $f_c(E_b)$ are the probability of a valence band state of energy E_a being occupied by an electron and that of a conduction band state of energy E_b being occupied by an electron, respectively. An estimate of the values of C_{hh} and C_{lh} may be obtained by fitting the experimental absorption spectra for the sum $C = C_{hh} + C_{lh}$ and considering the reduced effective masses of the electron-hole pairs for different bands.[1-2]

An important feature of the model is the assumption of quasi-neutrality, i.e. $N = P$. For a given photon energy $E \geq E_g$, the values of E_a and E_b are well-defined as a result of the conservation of energy and momentum,

$$E_{ah,al}=\left(E_g-E\right)\frac{m_e}{m_e+m_{hh,lh}}-E_g$$

$$E_{bh,bl}=\left(E-E_g\right)\frac{m_{hh,lh}}{m_e+m_{hh,lh}}$$

where m_e, m_{hh}, and m_{lh} are the effective masses of electrons, heavy holes, and light holes, respectively, and the zero of the energy scale is defined at the minimum of the conduction band. The probabilities $f_v\left(E_{ah,al}\right)$ and $f_c\left(E_{bh,bl}\right)$ are given by the Fermi-Dirac distribution,[1]

$$f_v\left(E_{ah,al}\right)=[1+e^{\left(E_{ah,al}-E_{F_v}\right)/(k_BT)}]^{-1}$$

$$f_c\left(E_{bh,bl}\right)=[1+e^{\left(E_{bh,bl}-E_{F_c}\right)/(k_BT)}]^{-1}$$

where E_{F_v} and E_{F_c} are the Fermi energies of the valence and conduction bands, respectively, k_B is the Boltzmann constant, and T is the absolute temperature. The carrier-density-dependent E_{F_v} and E_{F_c} are estimated using Nilsson's formula,[3]

$$E_{Fc} = \left\{ \ln\left(\frac{N}{N_c}\right) + \frac{N}{N_c}\left[64 + 0.05524\frac{N}{N_c}\left(64 + \sqrt{\frac{N}{N_c}}\right)\right]^{-\frac{1}{4}} \right\} k_B T,$$

$$E_{Fv} = \left(-\left\{ \ln\left(\frac{P}{N_v}\right) + \frac{P}{N_v}\left[64 + 0.05524\frac{P}{N_v}\left(64 + \sqrt{\frac{P}{N_v}}\right)\right]^{-\frac{1}{4}} \right\} - E_g \right) k_B T.$$

The effective densities of states in the conduction and valence bands are N_c and N_v, respectively, given by

$$N_c = 2\left(\frac{m_e k_B T}{2\pi\hbar^2}\right)^{3/2},$$

$$N_v = 2\left[\frac{\left(m_{hh}^{3/2} + m_{lh}^{3/2}\right)^{2/3} k_B T}{2\pi\hbar^2}\right]^{3/2}.$$

Table S1 gives a summary of the aforementioned parameters calculated using the generally accepted values of m_e, m_{hh}, and m_{lh}. Then the change in the refractive index can be obtained using the Kramers-Kronig relation,[1]

$$\Delta n_{\mathrm{BF}}(N,P,E) = \frac{\hbar c}{\pi}\mathbb{P}\int_0^\infty \frac{\Delta\alpha_{\mathrm{BF}}(N,P,E')}{E'^2 - E^2}dE'$$

where c is the speed of light and $\mathbb{P}$ indicates and the principal value of the integral, which is computed numerically as a function of the carrier density at the probe wavelength of 1030 nm.

2. Bandgap Renormalization. When the density of photoinjected carriers exceed a critical density χ_{cr} (which is associated with the effective Bohr radius of an electron-hole pair in a material), the wavefunctions of the carriers start to interfere with each other as they relax toward the band minima and the phenomenon of Coulomb screening becomes important. Together with the Pauli Exclusion Principle, the resulting quantum effect is the lowering (raising) of the conduction (valence) band edge, leading to the shrinkage (renormalization) of the bandgap.

Bennet, Soref, and Del Alamo[1] modeled this effect by considering

$$\Delta\alpha_{\mathrm{BGR}}(N,P,E) = \frac{C}{E}\sqrt{E - E_g - \Delta E_{\mathrm{BGR}}(N,P)} - \frac{C}{E}\sqrt{E - E_g}$$

when $N = P \geq \chi_{cr}$. For CdTe, $\chi_{cr} \approx 4.2 \times 10^{17}$ cm^{-3}, and the change in the bandgap may be approximated by[1]

$$\Delta E_g = \frac{\kappa}{\epsilon_s}\left(1 - \frac{N}{\chi_{cr}}\right)^{1/3}$$

where ϵ_s is the static dielectric constant, κ is a dimensionless parameter that was fitted to be ~0.21 for CdTe. Thus, the resulting change in the index of refraction as a function of the carrier density can be calculated similarly using the aforementioned Kramers-Kronig relation at 1030 nm.

3. Free-Carrier Absorption. Free carriers can absorb photons and move to higher energy states within a band. Based on the Drude model, the refractive index change is given by[1]

$$\Delta n_{\mathrm{FC}}(N,P,E) = -\frac{e^2 h^2}{8\pi^2 \epsilon_0 n_0 E^2}\left[\frac{N}{m_e} + P\left(\frac{m_{hh}^{1/2} + m_{lh}^{1/2}}{m_{hh}^{3/2} + m_{lh}^{3/2}}\right)\right]$$

where ϵ_0 is the permittivity of free space. Calculation of Δn_{FC} as a function of the carrier density is straightforward.

4. Lattice Thermalization. Following the above-gap excitation by photons with an energy of E_{ex}, the hot carriers will transfer their excessive energy to the lattice via the carrier-phonon coupling. As a result, the lattice temperature will rise in few picoseconds and the initial increase is approximately

$$\Delta T_0 = \frac{N_{\mathrm{peak}}}{\rho C_{latt}}\left(E_{ex} - E_g - E_{F_c} - E_{F_v}\right),$$

where N_{peak} is the initial peak value of the carrier density, and ρ and C_{latt} are the density and the specific heat of CdTe, respectively. Subsequently, the temperature of the lattice near the surface will slowly decrease due to thermal diffusion into the bulk, given by[4]

$$\Delta T(t) = \Delta T_0 \exp(\alpha^2 D_{th} t)\, \mathrm{erfc}\left(\alpha\sqrt{D_{th} t}\right)$$

for sufficiently large t, where D_{th} is the thermal diffusivity and is related to the thermal conductivity κ_{th} by $D_{th} = \kappa_{th}/(\rho C_{latt})$.

The contribution of the lattice temperature increase to the refractive index change can be calculated by

$$\Delta n_{LT} = \frac{\partial n}{\partial T}\Delta T$$

where the derivative $\frac{\partial n}{\partial T}$ has been experimentally studied in an early study.[5] Compared to the BF, BGR, and FC effects, the LT contribution to the transient reflectivity at early times is on the order of 10^{-4} and hence relatively small.

Table S1. Parameters for calculation of the refractive index change at T = 300 K

Parameter (Unit)	Value
E_g (eV)	1.513
m_e (m_0)	0.09
m_{hh} (m_0)	0.8
m_{lh} (m_0)	0.1
C ($cm^{-1}s^{-1/2}$)	5.0×10^{12}
C_{hh} ($cm^{-1}s^{-1/2}$)	3.5×10^{12}
C_{lh} ($cm^{-1}s^{-1/2}$)	1.5×10^{12}
ϵ_s	10.2
n_0 (λ = 515 nm)	3.1
n_0 (λ = 1030 nm)	2.83
N_c (cm^{-3})	6.8×10^{17}
N_v (cm^{-3})	1.9×10^{19}
χ_{cr} (cm^{-3})	4.2×10^{17}
κ	0.21
ρ ($g\ cm^{-3}$)	5.86
C_{latt} ($J\ g^{-1}\ K^{-1}$)	0.209
κ_{th} ($W\ cm^{-1}\ K^{-1}$)	0.075

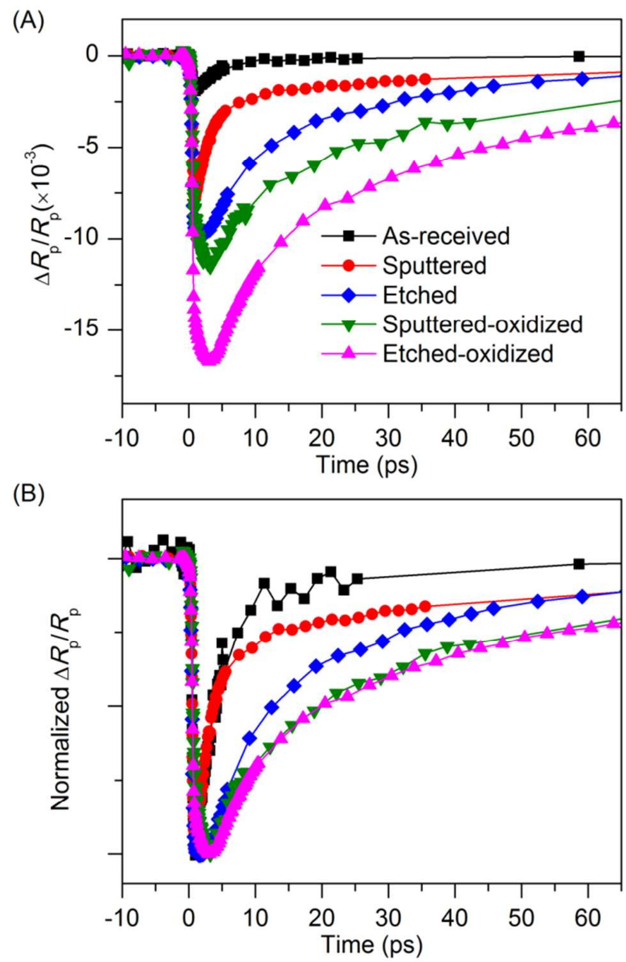

Figure S1. Two-color transient reflectivity results of CdTe(111)B with different surface conditions. (A) Absolute values of $\Delta R_p/R_p$ as a function of time. (B) Normalized $\Delta R_p/R_p$. The transient of the as-received surface is the result of a 5-point moving average for noise reduction.

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