Strong Hot Carrier Effects Observed in a Single Nanowire Heterostructure

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ABSTRACT:

We use Transient Rayleigh Scattering to study the thermalization of hot photoexcited carriers in single GaAsSb/InP nanowire heterostructures. By comparing the energy loss rate in single bare GaAsSb nanowires which do not show substantial hot carrier effects with the core-shell nanowires, we show that the presence of an InP shell substantially suppresses the LO phonon emission rate at low temperatures leading to strong hot carrier effects.

Keywords: Hot Carrier Effects, Hot Phonons, Thermalization
**Introduction**

One of the barriers to efficiency in standard solar cells is the substantial loss of solar energy to heat as carriers thermalize before they are collected electrically. There is therefore substantial interest in controlling the thermalization process to reduce such losses and thereby increase the overall efficiency.\(^1\) – \(^5\) When electrons and holes are created with substantial excess energy, they first rapidly relax (< 1 ps) through the emission of longitudinal optical (LO) phonons through polar Frohlich interactions.\(^6\) This creates a large non-thermal distribution of LO phonons which must equilibrate to the lattice temperature. In many materials, such as GaAs, GaSb and the ternary alloy GaAsSb, these non-thermal LO phonons can efficiently thermalize through the Klemens channel where a single zone center LO phonon decays into two counterpropagating LA phonons. However, in materials such as InP where \(\hbar\omega_{LO} > 2\hbar\omega_{LA}\), this thermalization process is inhibited and so the LO phonon populations can remain in a non-thermal state for extended periods which inhibits cooling of the electrons and holes resulting in a pronounced hot carrier effect.\(^7\), \(^8\)

The subject of hot carrier effects in semiconductors has been of strong interest for the past twenty years since it was first realized that optical phonon emission could be strongly suppressed in certain materials or structures.\(^9\) – \(^11\) Substantial progress in understanding hot carrier thermalization in bulk and two dimensional materials has been made, but much less is known about how thermalization dynamics might be changed in semiconductor nanostructures.\(^12\), \(^13\) Numerous measurements have shown that hot carrier effects are more prominent in InP materials than GaAs-based nanowires,\(^14\) while others have shown that hot carrier effects are more dominant in thinner nanowires,\(^15\) and terahertz measurements have shown that strong stacking fault disorder can enhance hot carrier effects even further.\(^16\) – \(^18\)

Here, we show for GaAsSb nanowires, which should not show hot carrier effects, growth of a surrounding InP shell can dramatically impact the thermalization dynamics of photoexcited carriers. We use transient Rayleigh scattering to measure directly the average energy per carrier as a function of time in single nanowires at 10 K and 300 K and so extract the energy loss rate for nanowires and nanowire heterostructures.

**Experimental Details:**

Semiconductor GaAs\(_{0.7}\)Sb\(_{0.3}\) core-only and GaAs\(_{0.7}\)Sb\(_{0.3}\) \(\backslash\) InP core-shell nanowires (NWs) were grown via the vapor-liquid-solid (VLS) growth method using gold catalysts and metal-organic vapor phase epitaxy (MOVPE).\(^19\), \(^20\) Figure 1a shows an SEM image of the morphology of the core-only and core-shell NWs. Fig. 1b shows a TEM image of a cross-section of a core-shell NW which displays the hexagonal inner core with non-polar \(\{110\}\) facets surrounded by outer truncated triangular-shaped InP shell with A-polarity \(\{112\}\) facet which inherits the zinc blende (ZB) twin free structure from the GaAs\(_{0.7}\)Sb\(_{0.3}\) core.
Under lattice-matched conditions GaAs$_{0.5}$Sb$_{0.5}$/InP heterostructures have been shown to display a type II band alignment with holes confined to the GaAsSb valence band with a 0.4 eV InP barrier, while the electrons are confined to the InP conduction band with a relatively modest GaAsSb barrier. In these GaAs$_{0.7}$Sb$_{0.3}$/InP nanowires, the GaAsSb core is under tensile strain while the InP shell is under compressive strain. It is expected that the type I to type II transition should occur at approximately 30 to 40% Sb. Thus our expectation is that the holes are strongly confined to the GaAsSb core, while the electrons see nearly flat-band conditions in the CB between the core and shell.

![Figure 1: a) SEM image of GaAs$_{0.7}$Sb$_{0.3}$ and GaAs$_{0.7}$Sb$_{0.3}$/InP nanowires. (b) TEM cross section image of GaAs$_{0.7}$Sb$_{0.3}$/InP. (c) Chematic band structure of type II GaAs$_{1-x}$Sb$_x$/InP nanowire.](image)

In these transient Rayleigh Scattering experiments, a Coherent Chameleon Ti:Sapphire laser with 150 fs 1.5 eV pulses with parallel polarization photoexcites a single nanowire. The change in the polarized scattering efficiency is monitored by a delayed mid-infrared output pulse (150 fs) from a Coherent Chameleon OPO laser with energies ranging from 0.79 eV - 1.13 eV (1100 to 1570 nm). The polarization of the probe beam oscillates at 100 KHz between parallel and perpendicular to the NW using a photelastic modulator, and the scattered light from the NW is detected using a LN2 cooled InSb detector and a lockin amplifier. Using a mechanical delay line, the probe pulse can be delayed relative to the pump pulse (-100 to 2000 ps) so as to investigate the change in the scattering efficiency as the carriers decay. To measure the changed scattering efficiency, the pump pulse train is chopped at 800 Hz and the output of the first lockin is detected by a second lockin amplifier tuned to this frequency. Thus we measure

$$\Delta R' = R'_\text{on} - R'_\text{off}$$

where $R' = R_\parallel - R_\perp$. The normalized TRS scattering efficiency

$$\Delta R'/R' = (R'_\text{on} - R'_\text{off})/R'_\text{off}$$

has a derivative-like behavior as a function of energy and depends on the geometry of NW and the change of both the real and imaginary part of complex index of refraction which is function of energy, carrier density and temperature.

**Measurements:**
Figure 2 (a) shows the time decay of the core-only and core-shell NWs at 10 K (blue) at a fixed 0.83 eV probe energy just below the band edge. The core-only NW decays rapidly to background with a 10 ps exponential decay, while the core-shell NW shows a remarkable 1800 ps exponential decay. This indicates that photoexcited carrier recombination in the core only GaAsSb nanowire is dominated by nonradiative surface recombination. The InP shell clearly passivates the surface states resulting in a much longer lifetime. Whether the band alignment is type II is an open question. In contrast, at room temperature (Fig. 2(b), 300 K), the core only wire shows a similar 10 ps fast decay, while the core-shell exhibits a slightly longer 150 ps time decay. This is consistent with the conduction band of the InP shell providing only very weak confinement of ~30 meV.

**Figure 2:** Exponential decay fitting of selected TRS carrier dynamics data for core-only (solid circle) and core-shell (unfilled circle) nanowires at 10 K (blue) and 300 K (red) at 0.83 eV probe energy.

By measuring the energy dependence of the polarized scattering efficiency one can obtain a more detailed look at the carrier dynamics. Figure 3 shows such TRS spectra measured at ~ 10 K lattice temperatures at three different delay times of the probe pulse for (a) GaAs$_{0.7}$Sb$_{0.3}$ core-only and (b) GaAs$_{0.7}$Sb$_{0.3}$ / InP core-shell nanowires. As described by Montazeri et al., the zero crossing point of NWs TRS spectra occurs approximately at the band gap of the structure. The lineshape is critically dependent on the density and temperature of the electron and hole distributions. The core-only NWs display a zero crossing around 0.9 eV which is slightly
shifting to the lower energy at later times. The lineshape is very broad at early times and narrows at later times which is indicative of filling of the conduction and valence bands with a dense and hot electron hole plasma which decays and thermalizes at later times. The behavior of the core-shell nanowires is very similar but extends over much longer time scales. Fig 4. shows TRS spectra for core-only and core-shell nanowires at 300 K. The behavior of the lineshapes for the core-only NWs is very similar to that at low temperature, while the lineshape for the core-shell NWs exhibits much more rapid decay and thermalization with time, consistent with the change in the time decays at room temperature.

Figure 3: Theoretical fitting (blue lines) of TRS spectrum data in three different selected delay time at low temperature for (a) core-only and (b) core-shell nanowires.
Figure 4: Theoretical fitting (Red lines) of TRS spectroscopy data in three different selected delay time at room temperature for (a) core-only and (b) core-shell nanowires.

**Theoretical Modeling:**

As noted previously, the lineshape of TRS spectra is sensitive to only three things: the density and temperature of the electron-hole plasma and the diameter of the nanowire. Through band filling, the absorption (the complex part of the index of refraction) of the nanowire is modified by the presence of the electrons and holes. In turn, the real part of the index of the refraction is also modified. The solid blue lines (red lines) in Figure 3 (Figure 4) illustrate the line-shape of the theoretical modeling of $\Delta R'/R'$ based on the following assumptions:

1. The electrons and holes are in thermal equilibrium at all times because of the extremely rapid carrier-carrier scattering rate.
2. The sum of the heavy and light hole densities in the valance band equals the density of electrons in the conduction band.
3. When the pump is off, the background carrier density and temperature is assumed to be $10^{15}$ cm$^{-3}$ and 10 K (300 K) for low temperature (room temperature) experiments.

We calculate the energy dependence of the absorption by using direct band-to-band transition theory when the conduction band and valance bands are occupied by hot electrons and holes respectively. As shown previously, the TRS efficiency ($\Delta R'/R'$) depends only on the diameter of the NW and the change in the real and imaginary part of complex index of refraction:
\[
\frac{\Delta R'}{R'} = \frac{\Delta(R_{||} - R_{\perp})}{R_{||} - R_{\perp}} \sim \text{Re} \left[ e^{i\theta} \Delta n \right]
\]

Where \( \theta \) is the modulation phase factor that depends on the NW diameter, and \( \Delta n = \Delta n + i \Delta k \) is change of the complex index of refraction due to the occupied conduction and valence bands, where \( n \) is the index of refraction and \( k \) is proportional to absorption based on the \( k = (\lambda/4\pi)\alpha \) formalism. Thus the derivative-like lineshape of \( \Delta R'/R' \) is expressed as

\[
\frac{\Delta R'_{(E,t)}}{R'_{(E,t)}} = \text{Re} \left[ A e^{i\theta} \left( \Delta n + i \frac{\lambda}{4\pi} \Delta \alpha \right) \right]
\]

\[
= A \{ \cos(\theta_{(r)})[n(E_{N_e}(t), T_{e/(t)}) - n(E_{N_e}, T_0)] - \frac{\lambda}{4\pi} \sin(\theta_{(r)})[\alpha(E_{N_e}(t), T_{e((t)}) - \alpha(E_{N_e}, T_0)] \}
\]

Where \( A \) is an overall arbitrary amplitude factor. The individual time-resolved TRS spectra are modeled using this formula to extract the time-dependent carrier density and temperature in addition to the NW diameter. The absorption coefficient \( \alpha(E, N, T) \) is calculated using

\[
\alpha[E, N, T] = \frac{\pi^2 e^2 \hbar^3 B}{n^2 E^2 (2\pi)^3} \int_0^{E - E_g} \rho_c[E'] \rho_v[E' - E] \left( f_l[E - E_g - E'] - f_u[E'] \right) dE'
\]

Where \( B \) is the radiative bimolecular coefficient, \( n \) is the average index of refraction that we have used the average values from the literature, \( \rho_l[E] \) is the 3D density of states in the conduction / valence band, \( f_l[E] = (1 + \exp[(E - E_F)/k_B T])^{-1} \) is the Fermi-Dirac distribution probability that upper / lower states involved in the transition are occupied by electrons, with the quasi-Fermi energy \( E_F[N, T] \) related to both the carrier density \( N \) and temperature \( T \), and \( E' \) is the upper state energy above the conduction band minimum. Using the Kramers-Kronig relation we transform the calculated absorption coefficient to acquire the index of refraction \( n[E, N, T] \) as a function of energy, carrier density and temperature.

To fit TRS spectra as a function of time, the absorption coefficient and index of refraction (\( \alpha \) and \( n \)) are calculated as a function of energy, carrier density and temperature (E, N, T) until the spectra are best fit to the resulting lineshapes calculated using the expression for \( \Delta R'/R' \).
Figure 5: (a) Carrier temperature, and (b) normalized carrier density from modeling of TRS spectroscopy data at different measured delay time. (a) Shows carrier temperature of core-only and core-shell nanowires at low lattice temperature. In (b) normalized carrier density of core-only and core-shell nanowires at low lattice temperature have been marked on TRS time scan data with pink hexagonals and orange squares respectively. Initial carrier density for core-only nanowires is around $4 \times 10^{18}$ and for core-shell nanowires is about $2 \times 10^{18}$.

By minimizing the difference between the theoretical line-shape and the data points, we are able to determine the electron-hole density and temperature for each delay time. The fits displayed in Fig. 4 result in nanowire diameters of 70 nm and 130 nm for core-only and core-shell nanowires, which are consistent with cross-sectional TEM measurements.\textsuperscript{20} The time-dependent density and temperature extracted from the fits of spectra at 10 K (Fig. 4(a)) are shown in Figure 5. The temperature (Fig. 5 a) of the photoexcited electrons and holes in the core-only NWs drops from 400 K to 200 K in 20 ps, while in the core-shell NWs it takes nearly 2000 ps to drop to 140 K from the same initial temperature. The orange squares (pink hexagons) in Fig. 5b show the normalized carrier densities in the core-shell (core only) NWs at times after photoexcitation which shows good agreement with the time decays shown previously. The initial carrier density for core-only nanowires is around $4 \times 10^{18}$ and for core-shell NWs is about $2 \times 10^{18}$. The fits confirm that the carrier density in the core-shell NWs takes 600 times longer to decay. This is perhaps suggestive with a type-II band alignment of the electron and hole wave functions, but not conclusive.
Figure 6: (a) Carrier temperature, and (b) normalized carrier density from modeling of TRS spectroscopy data at different measured delay time. (a) Shows carrier temperature of core-only and core-shell nanowires at room lattice temperature. In (b) normalized carrier density of core-only and core-shell nanowires at room lattice temperature have been marked on TRS time scan data with purple hexagonals and green squares respectively. Initial carrier density for core-only nanowires is around $5 \times 10^{18}$ and for core-shell nanowires is about $6.3 \times 10^{18}$.

The fits to 300 K spectra (see Fig. 4(b)) result in the same 70 nm and 130 nm diameters for the core-only and core-shell NWs. The density and temperature extracted from these fittings at room temperature are shown in figure 6. These fits show exhibit extremely rapid carrier thermalization in the core-only nanowires from 500 K just after the pump pulse to 320 K within ~20 ps. The core-shell NWs show a slower thermalization from 550 K to 320 K within 150 ps (Figure 6(a)). The normalized carrier densities obtained from the fits are shown in figure 6(b) with purple hexagons for core-only NWs and green squares for core-shell NWs. These points display a good agreement with the related TRS time scan. The initial densities that are obtained are $5 \times 10^{18}$ for the core-only NWs and $6.3 \times 10^{18}$ for the core-shell NWs.

From the fits to the time-resolved scattering spectra from these nanowires it is possible to draw a number of conclusions. The first is that the InP shell clearly passivates non-radiative surface states in the GaAsSb nanowires at both 10 K and 300 K resulting in substantially longer recombination lifetimes in the core-shell nanowires. The much larger lifetime enhancement observed at low temperatures perhaps indicates that the band alignment of the core-shell NW is marginally type-II with electrons confined to the InP with a 30 meV confinement energy. However, the carrier temperature dynamics also indicate that the presence of the InP shell clearly...
causes a substantial slowing of the thermalization times. GaAsSb (like GaAs) is not known as a material which shows substantial hot carrier effects. In the following sections we quantify the change in the energy loss rate in the core-shell NWs.

**Carrier Thermalization:**

Through this fitting process we can determine the electron and hole densities (their quasi Fermi energies) and temperature as a function of time. We can therefore calculate the dynamic change in the average energy per particle of electrons and holes using the expression:

\[
E = \frac{3}{2} k_B T \frac{F_{3/2}(\eta)}{F_{1/2}(\eta)}
\]

Where \( \eta \) is the quasi-fermi energy and \( F_i(\eta) \) is the ith fermi integral defined as usual. Using this result and the measured dynamics of the temperature and Fermi energies for electrons and holes we can plot (see Fig. 7) the average energy per electron hole pair as a function of time after photoexcitation for both the core-only and core-shell nanowires at 10 K. One can see that the average energy per electron hole pair falls much more rapidly with time for the core-only nanowire than for the core-shell nanowire.

![Figure 7: Average energy per for core-only (solid line) and core-shell (dot line) nanowires at 10 K.](image)

The thermalization of electrons and holes is determined by the scattering (emission) rate of the carriers with optic and acoustic phonons which determines their energy loss rate.\(^{10,32,33}\) From the average energy per pair, we can calculate the energy loss rate (ELR) versus time
simply by calculating a numerical derivative. The ELR calculated in this way is shown in Fig. 8(a) for the core-only NWs and Fig. 8(b) for the core-shell nanowires. The difference between the core only and core-shell nanowires is immediately obvious as the ELR for the core only is three orders of magnitude larger than for the core-shell nanowires.

![Diagram showing the ELR for core-only and core-shell nanowires](image)

**Figure 8:** (a,b) dE/dt and carriers energy loss rate due to optical and acoustic phonon emission for core-only and core-shell nanowires respectively at 10 K. Dash lines in these graphs show energy loss rate due to LO phonon emission calculated by Ridley expression. (c,d) Effective relaxation time of LO phonons for core-only and core-shell nanowires respectively. Dash line in graph (d) shows Effective relaxation time of LO phonons for core-shell nanowires calculated by Ridley expression.

Indeed, the reduction in the energy per particle reflects the thermalization of the carriers as a function of time. The derivative dE/dt of this function shows the dynamics of the energy loss rate (ELR) as a function of time. Because the thermalization process is dominated by emission of both optic and acoustic phonons, it is clear that:

\[
\langle \frac{dE}{dt} \rangle = \langle \frac{dE_{\tau^*,N(t),T(t)}}{dt} \rangle_{LO} + \langle \frac{dE_{E_{ac,N(t),T(t)}}}{dt} \rangle_{AC}
\]

The left side of the equation is determined directly from the TRS measurements. Hot carrier effects in semiconductors occur because of a large suppression of the LO emission rate because of hot phonons which cannot down convert efficiently to acoustic phonons. On the
other hand, if one knows the acoustic deformation potential the ELR for acoustic phonons is quite well understood. This means that it is possible to extract the LO phonon ELR simply by subtracting the ELR for acoustic phonons directly from $\frac{dE}{dt}$ calculated from the TRS data.

For example, $\frac{dE}{dt}$ from the TRS data for the core-only nanowires shows a total ELR which is $\sim 10^{10}$ eV/s, on the other hand given the deformation potential of 1.6 eV the acoustic phonon ELR is just below $10^8$ eV/s. This means that the thermalization of hot carriers in the core-only nanowire is completely dominated by optic phonon emission which explains the rapid decrease in temperature of the carriers (see Fig. 8 a).

On the other hand the 10 K measurements in the core-shell nanowires shows a radically different behavior. While the total ELR starts at $10^9$ eV/s it fall rapid to mid $10^7$ eV/s and decreases slowly after that. Calculations of the acoustic phonon ELR shows that the late time ELR is completely determined by the acoustic phonon ELR. By subtracting the acoustic phonon ELR from $\frac{dE}{dt}$, we therefore obtain the dynamics change in the optic phonon ELR in the core-shell nanowires. This shows that the optic phonon ELR dominates at times less than 200 ps after the pump pulse but falls rapidly below the acoustic phonon ELR at later times (see Fig. 8 b).

The dash lines in Fig. 8 a, b display the ELR due to LO phonon emission based on Ridley expression. In this calculation, LO phonon ELR depends on carrier temperature and density, lattice temperature and reabsorption of LO phonons which represent by a coefficient in that formalism. For a given 0.0025 reabsorption coefficient ELR due to LO phonon emission is pretty close to carrier ELR in core-only nanowire and it has nice corresponding with other method of calculation. But in core-shell nanowire by using same value of reabsorption coefficient (0.0025), ELR is close to our calculation using another method but in the late time it is $\sim 10^9$ eV/s which is much higher than carriers ELR. Since this coefficient depends on the material features and it should be constant for whole carriers decay time, there should be some physical quantity which change over time.

The optic phonon ELR is just related to the emission rate of the optic phonons through $\frac{\hbar}{\omega}/\tau^*$, where $\tau^*$ is the time between optic phonon emissions. This shows that the optic phonons emission rate for the core-only nanowires is $\sim 2$ ps, while that for the core-shell nanowires at 10 K is 10 ps at the earliest times but rapidly increases by three orders of magnitude to 4000 ps by 1 ns after the pump pulse (see Fig. 8 c, d). The dash line in Fig. 8 d shows $\tau^*$ for ELR calculation of LO phonons based on Ridley expression with 0.0025 reabsorption coefficient. We see that it has a constant value of $\sim 2$ ps for whole relaxation time which that constant value does not explain ELR of our TRS measurement. Essentially emission of optic phonons is nearly completely suppressed in the core-shell nanowires within 200 ps.

Similar analysis of TRS data taken at room temperature (300 K) shows that the optic phonon emission time for core-only nanowires drops to 100 fs, while that for the core-shell nanowires remains stable at 5 ps. This implies that even at room temperature hot carrier effects are not negligible in GaAsSb/InP nanostructures (see Fig. 9). The dash lines in this graph is ELR based on Ridley expression with 0.025 reabsorption coefficient. This coefficient is 10 times larger than 10 K value and the calculations shows the nice corresponding with other method of calculation for core-only nanowires, but for core-shell nanowires LO phonons ELR is almost one order of magnitude larger than TRS results for total ELR and consequently it gives one order magnitude smaller $\tau^*$. 


Discussion:

The conclusion from the previous analysis is that a GaAsSb semiconductor nanowire made of material which should not show hot carrier effects, shows very strong hot carrier effects at low temperatures if a thin 10 nm InP shell is added to the nanowire. There are only two ways this can happen: First, the Frohlich interaction which describes the interaction of the electrons and optic phonons is suppressed in some way, or second, the anharmonic decay of the optic phonons is somehow strongly suppressed in the core-shell nanowires resulting in much longer lifetimes and so a buildup in the nonthermal population of the optic phonons results. Over the past decade there has been intense interest in phonon engineering whereby one can use nanoscale heterostructures to tune the phonons in a material and also their interactions.\textsuperscript{39,40} Spatial confinement of phonons in nanostructures have been shown to strongly impact their dispersion, group velocity and density of states.\textsuperscript{39,41,42}
While there have been a few papers which claim theoretically that the electron-phonon coupling can be impacted by the presence of a heterostructure, most conclusions are that such an effect is small. On the other hand, there are a number of papers which indicate that a shell can strongly impact the acoustic phonons in the nanowire, particularly if there is a large impedance mismatch between the core and the shell. The impedance, defined as \( \eta = \rho v_s \), where \( \rho \) is the density and \( v_s \) is the sound velocity in the material, is substantially larger (40\%) for the GaAsSb core than in the InP shell. Thus the outer shell is “softer” than the core, and this has been shown to deplete the density of states of the phonons in the core and confining the phonons to the shell, particularly for large wavevectors (high frequencies). A number of papers have shown theoretically that the thermal conduction in both two- and one-dimensional structures can be strongly suppressed with the addition of a softer cladding layer. Others have shown that the mobility in the core can be enhanced by suppression of the acoustic phonon modes in the core. Similarly, Stroscio and Dutta has shown that in a nanostructure where the optic phonons are confined while the acoustic phonons are not that the anharmonic decay of the optic phonons is suppressed, resulting in a factor of two longer lifetimes.

The question is whether in the present case of a 70 nm diameter GaAsSb core and a 10 nm thick InP shell such confinement effects could be relevant. Two estimates of size scales where phonon confinement effects can be seen are when the diameter of the wire is either comparable to \( \lambda_T = h v_s / k_B T \) or the diameter of the wire is less than the phonon mean free path, \( d_{MFP} = 3K / (C V v_s) \). At 10 K the thermal wavelength is approximately 20 nm while the mean free path is typically >200 nm. Moreover, recently Balandin et al showed using Brioullin scattering that confinement of acoustic phonons can be observed at room temperature even in GaAs wires which are 130 nm in diameter. We conclude therefore that confinement of phonons is certainly applicable for the 10 nm InP shell, and the core should certainly show effects at low temperatures. The fact that the hot carrier effects in the core-shell nanowire are stronger at low temperature may reflect the temperature dependence of the thermal phonon wavelength and the mean free path.

**Conclusions:**

We have shown using Transient Rayleigh Scattering in both bare GaAsSb NW and a GaAsSb/InP core-shell NW that the presence of the InP shell strongly influences hot carrier effects in these structures. For the GaAsSb core essentially no hot carrier effects are seen, and the thermalization of photoexcited carriers is completely dominated by optic phonon emission at both 10 K and 300 K. On the other hand, in the GaAsSb/InP core-shell NW at 10 K the optical phonon emission is seen to be completely suppressed at times longer than 200 ps and so thermalization is determined almost completely by acoustic phonon deformation potential scattering. At 300 K, thermalization of hot carriers in the core shell NW is determined by the optic phonon emission, but strong hot carrier effects are still observed with the emission rate reduced by an order of magnitude from the bare core NW. This provides the first evidence that it
might be possible to use concepts from *phononic engineering* to control hot carrier effects in semiconductors.

**ACKNOWLEDGEMENTS:**

We acknowledge the financial support of the NSF through grants DMR 1507844, DMR 1531373 and ECCS 1509706, and the financial support of the Australian Research Council.
REFERENCES:

(1) Knig, D.; Casalenuovo, K.; Takeda, Y.; Conibeer, G.; Guillemoles, J. F.; Patterson, R.; Huang, L. M.; Green, M. A. Hot Carrier Solar Cells: Principles, Materials and Design. *Phys. E Low-Dimensional Syst. Nanostructures* **2010**, *42* (10), 2862–2866.

(2) Le Bris, A.; Rodiere, J.; Colin, C.; Collin, S.; Pelouard, J. L.; Esteban, R.; Laroche, M.; Greffet, J. J.; Guillemoles, J. F. Hot Carrier Solar Cells: Controlling Thermalization in Ultrathin Devices. *IEEE J. Photovoltaics* **2012**, *2* (4), 506–511.

(3) Conibeer, G. J.; König, D.; Green, M. A.; Guillemoles, J. F. Slowing of Carrier Cooling in Hot Carrier Solar Cells. *Thin Solid Films* **2008**, *516* (20), 6948–6953.

(4) Le Bris, A.; Lombez, L.; Laribi, S.; Boissier, G.; Christol, P.; Guillemoles, J. F. Thermalisation Rate Study of GaSb-Based Heterostructures by Continuous Wave Photoluminescence and Their Potential as Hot Carrier Solar Cell Absorbers. *Energy Environ. Sci.* **2012**, *5* (3), 6225–6232.

(5) Le Bris, A.; Guillemoles, J. F. Hot Carrier Solar Cells: Achievable Efficiency Accounting for Heat Losses in the Absorber and through Contacts. *Appl. Phys. Lett.* **2010**, *97* (11).

(6) Lassnig, R. Polar Optical Interface Phonons and Fröhlich Interaction in Double Heterostructures. *Phys. Rev. B* **1984**, *30* (12), 7132–7137.

(7) Fritsch, J.; Pavone, P.; Schröder, U. Ab Initio Calculation of the Phonon Dispersion in Bulk InP and in the InP(110) Surface. *Phys. Rev. B* **1995**, *52* (15), 11326–11334.

(8) Vallée, F. Time-Resolved Investigation of Coherent LO-Phonon Relaxation in III-V Semiconductors. *Phys. Rev. B* **1994**, *49* (4), 2460–2468.

(9) Gornik, E.; Stradling, R. A.; Findlay, P. C.; Kotitschke, R. T. Suppression of Lo Phonon Scattering in Landau Quantized Quantum Dots. *Phys. Rev. B - Condens. Matter Mater. Phys.* **1999**, *59* (12), R7817–R7820.

(10) Othonos, A. Probing Ultrafast Carrier and Phonon Dynamics in Semiconductors. *J. Appl. Phys.* **1998**, *83* (4), 1789–1830.

(11) Sundaram, S. K.; Mazur, E. Inducing and Probing Non-Thermal Transitions in Semiconductors Using Femtosecond Laser Pulses. *Nat. Mater.* **2002**, *1* (4), 217–224.

(12) Michael Klopf, J.; Norris, P. Subpicosecond Observation of Photoexcited Carrier Thermalization and Relaxation in InP-Based Films. *Int. J. Thermophys.* **2005**, *26* (1), 127–140.

(13) Elsaesser, T.; Woerner, M. Femtosecond Infrared Spectroscopy of Semiconductors and Semiconductor Nanostructures. *Phys. Rep.* **1999**, *321* (6), 253–305.

(14) R. Clady, P. Aliberti, N. J. Ekins-Daukes, and M. A. G. Interplay between the Hot Phonon Effect and Intervally Scattering on the Cooling Rate of Hot Carriers in GaAs and InP. *IPhotovoltaics_Research_and_Applications* **2011**, *20* (3–4), 82–92.
(15) Tedeschi, D.; De Luca, M.; Fonseka, H. A.; Gao, Q.; Mura, F.; Tan, H. H.; Rubini, S.; Martelli, F.; Jagadish, C.; Capizzi, M.; et al. Long-Lived Hot Carriers in III-V Nanowires. *Nano Lett.* 2016, 16 (5), 3085–3093.

(16) Johnston, M. B.; Whittaker, D. M.; Corchia, A.; Davies, A. G.; Linfield, E. H. Simulation of Terahertz Generation at Semiconductor Surfaces. *Phys. Rev. B - Condens. Matter Mater. Phys.* 2002, 65 (16), 1–8.

(17) Beard, M. C.; Turner, G. M.; Schmuttenmaer, C. A. Transient Photoconductivity in GaAs as Measured by Time-Resolved Terahertz Spectroscopy. *Phys. Rev. B - Condens. Matter Mater. Phys.* 2000, 62 (23), 15764–15777.

(18) Joyce, H. J.; Docherty, C. J.; Gao, Q.; Tan, H. H.; Jagadish, C.; Lloyd-Hughes, J.; Herz, L. M.; Johnston, M. B. Electronic Properties of GaAs, InAs and InP Nanowires Studied by Terahertz Spectroscopy. *Nanotechnology* 2013, 24 (21).

(19) Yuan, X.; Caroff, P.; Wong-Leung, J.; Tan, H. H.; Jagadish, C. Controlling the Morphology, Composition and Crystal Structure in Gold-Seeded GaAs$_{1-x}$Sb$_x$ Nanowires. *Nanoscale* 2015, 7 (11), 4995–5003.

(20) Yuan, X.; Caroff, P.; Wang, F.; Guo, Y.; Wang, Y.; Jackson, H. E.; Smith, L. M.; Tan, H. H.; Jagadish, C. Antimony Induced [112]A Faceted Triangular GaAs$_{1-x}$Sb$_x$/InP Core/Shell Nanowires and Their Enhanced Optical Quality. *Adv. Funct. Mater.* 2015, 25 (33), 5300–5308.

(21) Hu, J.; Xu, X. G.; Stotz, J. A. H.; Watkins, S. P.; Curzon, A. E.; Thewalt, M. L. W.; Matine, N.; Bolognesi, C. R. Type II Photoluminescence and Conduction Band Offsets of GaAsSb/InGaAs and GaAsSb/InP Heterostructures Grown by Metalorganic Vapor Phase Epitaxy. *Appl. Phys. Lett.* 1998, 73 (19), 2799–2801.

(22) Moss, T. S.; Balkansk, M. *Handbook on Semiconductors : Volume 2. Optical Properties of Solids*; North- Holland: New York, 1980.

(23) Glembocki, O. J. Modulation Spectroscopy of Semiconductor Materials, Interfaces, and Microstructures: An Overview. *1990, No. August 1990*, 2.

(24) Montazeri, M.; Wade, A.; Fickenscher, M.; Jackson, H. E.; Smith, L. M.; Yarrison-Rice, J. M.; Gao, Q.; Tan, H. H.; Jagadish, C. Photomodulated Rayleigh Scattering of Single Semiconductor Nanowires: Probing Electronic Band Structure. *Nano Lett.* 2011, 11 (10), 4329–4336.

(25) Montazeri, M.; Jackson, H. E.; Smith, L. M.; Yarrison-Rice, J. M.; Kang, J.-H. H.; Gao, Q.; Tan, H. H.; Jagadish, C. Transient Rayleigh Scattering: A New Probe of Picosecond Carrier Dynamics in a Single Semiconductor Nanowire. *Nano Lett.* 2012, 12 (10), 5389–5395.

(26) Sabbah, A. J.; Riffe, D. M. Femtosecond Pump-Probe Reflectivity Study of Silicon Carrier Dynamics. *Phys. Rev. B - Condens. Matter Mater. Phys.* 2002, 66 (16), 1–11.

(27) Mittendorff, M.; Wendler, F.; Malic, E.; Knorr, A.; Orlita, M.; Potemski, M.; Berger, C.; De Heer, W. A.; Schneider, H.; Helm, M.; et al. Carrier Dynamics in Landau-Quantized Graphene Featuring Strong Auger Scattering. *Nat. Phys.* 2015, 11 (1), 75–81.

(28) Wang, Y.; Jackson, H. E.; Smith, L. M.; Burgess, T.; Paiman, S.; Gao, Q.; Tan, H. H.; Jagadish, C. Carrier Thermalization Dynamics in Single Zincblende and Wurtzite InP Nanowires. *Nano Lett.* 2014, 14 (12), 7153–7160.
(29) Leo, K.; Rühle, W. W.; Ploog, K. Hot-Carrier Energy-Loss Rates in GaAs/AlxGa1-XAs Quantum Wells. *Phys. Rev. B* **1988**, *38* (3), 1947–1957.

(30) Žukauskas, A. Second Nonequilibrium-Phonon Bottleneck for Carrier Cooling in Highly Excited Polar Semiconductors. *Phys. Rev. B - Condens. Matter Mater. Phys.* **1998**, *57* (24), 15337–15344.

(31) Pugnet, M.; Collet, J.; Cornet, A. Cooling of Hot Electron-Hole Plasmas in the Presence of Screened Electron-Phonon Interactions. *Solid State Commun.* **1981**, *38* (6), 531–536.

(32) Lyon, S. A. Spectroscopy of Hot Carriers in Semiconductors. *J. Lumin.* **1986**, *35* (3), 121–154.

(33) Schoenlein, R. W.; Fujimoto, J. G.; Ippe, E. P. Femtosecond Absorption Saturation Studies of Hot Carriers in GaAs and AlGaAs. *IEEE J. Quantum Electron.* **1988**, *24* (2), 267–275.

(34) Cardona, M.; Christensen, N. E. Acoustic Deformation Potentials and Heterostructure Band Offsets in Semiconductors. *Phys. Rev. B* **1987**, *35* (12), 6182–6194.

(35) Riddoch, F. A.; Ridley, B. K.; Ridley, B. K.; Ridley, B. K. Journal of Physics C : Solid State Physics Related Content The Electron-Phonon Interaction in Quasi-Two- Dimensional Semiconductor Quantum-Well Structures Dimensional Semiconductor Quantum-Well Structures. **1982**.

(36) Zanato, D.; Balkan, N.; Ridley, B. K.; Hill, G.; Schaff, W. J. Hot Electron Cooling Rates via the Emission of LO-Phonons in InN. *Semicond. Sci. Technol.* **2004**, *19* (8), 1024–1028.

(37) Lester, L. F.; Ridley, B. K. Hot Carriers and the Frequency Response of Quantum Well Lasers. *J. Appl. Phys.* **1992**, *72* (7), 2579–2588.

(38) Ridley, B. K.; Ridley, B. K. Hot Electrons in Low-Dimensional Structures. *Rep. Prog. Phys.* **1991**.

(39) Balandin, A. A.; Pokatilov, E. P.; Nika, D. L. Phonon Engineering in Hetero- and Nanostructures. *J. Nanoelectron. Optoelectron.* **2007**, *2* (2), 140–170.

(40) Toberer, E. S.; Zevalkink, A.; Snyder, G. J. Phonon Engineering through Crystal Chemistry. *J. Mater. Chem.* **2011**, *21* (40), 15843–15852.

(41) Stroscio; Dutta. *Phonons in Nanostructures*; 2001.

(42) Ridley, B. K. *Hybrid Phonons in Nanostructures*, first.; UK, 2017.

(43) Pokatilov, E. P.; Nika, D. L.; Balandin, A. A. Acoustic-Phonon Propagation in Rectangular Semiconductor Nanowires with Elastically Dissimilar Barriers. *Phys. Rev. B - Condens. Matter Mater. Phys.* **2005**, *72* (11), 4–7.

(44) Pokatilov, E. P.; Nika, D. L.; Balandin, A. A. Acoustic Phonon Engineering in Coated Cylindrical Nanowires. *Superlattices Microstruct.* **2005**, *38* (3), 168–183.

(45) Datta, D.; Krishnababu, K.; Stroscio, M. A.; Dutta, M. Effect of Quantum Confinement on Lifetime of Anharmonic Decay of Optical Phonons in Semiconductor Nanostructures. **2018**.

(46) Kargar, F.; Debnath, B.; Kakko, J. P.; Sañättjoki, A.; Lipsanen, H.; Nika, D. L.; Lake, R. K.; Balandin, A. A. Direct Observation of Confined Acoustic Phonon Polarization Branches in Free-Standing Semiconductor Nanowires. *Nat. Commun.* **2016**, *7*, 1–7.