Scaling of four-photon absorption in InAs

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By monitoring the nonlinear absorption of picosecond laser pulses as a function of lattice temperature, we identify four-photon absorption in bulk InAs. Optical bandgap scaling of this process is consistent with a calculation obtained from fourth-order perturbation theory for allowed–allowed–allowed–forbidden transitions. A model of nonlinear absorption based on laser-induced impact ionization disagrees with the experimental results. © 1997 Optical Society of America [S0740-3224(97)02905-6]

1. INTRODUCTION

Two-photon absorption (2PA) in solids is a well-known and extensively characterized nonlinear optical process.[1] Higher-order multiphoton absorption, however, has received comparatively little study. Three-photon absorption (3PA) has been found with CdS,[2] HgCdTe,[3] AlGaAs,[4] ZnS,[5] GaP,[6] ZnSe,[7] and various alkali halides.[8] Experiments dealing with even higher-order multiphoton absorption in solids are rare and somewhat controversial.[5,8] Jones *et al.* have reported four-photon absorption (4PA) by use of photoacoustic absorption techniques and specially prepared samples of KBr and NaCl.[8] These measurements are sensitive to sample purity and are complicated by the fact that high-order multiphoton absorption occurs very close to the material damage threshold. Additionally, the multiphoton absorption rate inferred from these experiments does not follow the expected pulse-width scaling.[9] Watkins *et al.* attributed the phase-conjugate reflectivity that they obtained from germanium to an electron–hole plasma generated by six-photon absorption.[10] These experiments also took place just below the damage irradiance. Subsequently, James and Smith showed that the abrupt appearance of photocarriers in Ref. 10 was most likely caused by impact ionization.[11]

Using picosecond CO_2 laser pulses, we have deduced the presence of 4PA in bulk samples of InAs without ever encountering optical damage (maximum irradiance, <0.1 of the damage threshold). We reached this conclusion by studying nonlinear absorption at two different temperatures: 300 K and 15 K. When cooled, the semiconductor band-gap expands from 0.36 to 0.42 eV, changing the 4PA rate. By examining temperature scaling of the data, as opposed to extracting a representative multiphoton absorption coefficient, we eliminate substantial experimental and theoretical error. Our experiment supports a fourth-order perturbation calculation of multiphoton absorption derived by Wherrett.[12]

A rigorous, first-principles calculation of multiphoton absorption in semiconductors is cumbersome. Although estimates can be made, there is considerable latitude available when attempting to evaluate multiplicative constants of the multiphoton absorption coefficient. Factors such as the polarization of the light and its orientation to the crystal axis, relative contributions of the light- and heavy-hole bands, excitons, band nonparabolicity, valence-band anisotropy, and the existence of many possible intermediate states have to be addressed.[12] As a consequence, it has proved difficult to compare derived multiphoton coefficients with experimental results, even for the low-order 2PA process. In the case of 2PA, agreement to within a factor of 2 is considered excellent; anything better is probably fortuitous.[13] Higher-order transitions present correspondingly greater difficulty as both experimental and theoretical uncertainties are magnified. Therefore measurement of the wavelength and material scaling of multiphoton absorption can provide important insight because most of these uncertainties are removed by normalization.

This study was motivated by the high rate of multiphoton excitation that is expected to occur in narrow-gap semiconductors. It is important, however, to eliminate the possible role of impact ionization, which can become more prevalent as the semiconductor bandgap shrinks.[14] This was the proposed cause of nonlinear absorption in previous work with room-temperature InAs using 1-ns CO_2 layer pulses.[15,16] In this effect, infrared laser light couples into the carrier system by free-carrier absorption (FCA). When a fraction of carriers in the heated distribution acquires an energy of approximately E_g (relative to the band edge), an inverse-Auger scattering event can take place, leading to the generation of electron–hole pairs. The excess carriers increase the differential absorption of the laser light.

We analyze the laser-induced impact-ionization rate for the conditions of our experiment. This is a fairly involved calculation, done in several steps. First, the electron temperature is determined as a function of laser irradiance. The temperature-dependent ionization rate is then estimated, which determines the generated carrier

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density. The laser pulse is convolved temporally and spatially with the photocarrier distribution to yield the nonlinear absorption. Because we are interested in lattice temperature scaling, however, the problem is simplified substantially. We find that the rate of electron heating is significantly different at the two experimental temperatures. At 15 K, carrier cooling is much more efficient than at room temperature, owing to the small phonon population ($N_q + 1$) in the terminal states. This means that more laser power is needed to initiate impact ionization at 15 K. A 15 K sample requires 2–3 times the irradiance needed to achieve the same nonlinear absorption seen at 300 K. The experiment shows an irradiance difference of only 1.2–1.4, which is too small to be consistent with impact ionization by laser-heated carriers.

This paper is organized as follows. In Section 2, material and wavelength scaling of 4PA based on two perturbation calculation approaches is presented. Experiments that reveal the bandgap scaling of 4PA in InAs are discussed in Section 3. A calculation of laser-induced impact ionization is developed in Section 4 and is compared with the experimental results. The impact-ionization model is shown to be an inadequate description of the experiment, which puts the 4PA interpretation on firmer footing. Scaling of 4PA agrees with Wherrett's calculation[12] by use of fourth-order perturbation theory.

2. SCALING OF MULTIPHOTON ABSORPTION

There are two approaches for calculating the multiphoton absorption rate in a two-band semiconductor. The first scheme uses first-order perturbation theory with Volkov-type dressed wave functions, which incorporate acceleration of the electrons (and holes) by the oscillating electromagnetic field.[17–19] For m-photon absorption, there is a single, virtual interband transition and $m-1$ virtual self-transitions. In a second method, Wherrett uses the maximum available interband excitations and de-excitations.[12] Only one self-transition is needed for even-order transitions (such as 2PA and 4PA), and none is employed for odd-order (e.g., 3PA) transitions. In odd-order multiphoton absorption, all intermediate states are obtained by transitions across the semiconductor bandgap, i.e., allowed–allowed transitions. For 2PA in semiconductors, it was shown previously that these two approaches give identical wavelength and material scaling.[13] This is expected, as both methods incorporate a single cross-gap excitation and a self-transition (i.e., allowed–forbidden).

For higher-order multiphoton absorption the situation changes. We define the m-photon excitation rate of excess electron–hole pairs ($\Delta N_e = \Delta N_H$) in the usual way:

$$\frac{\mathrm{d}N_e}{\mathrm{d}t} = \frac{\mathrm{d}N_H}{\mathrm{d}t} = \frac{K_m I^m}{m\hbar\omega}, \tag{1}$$

where I is the laser irradiance and K_m is the nonlinear absorption coefficient. In the case of 3PA, dressed-wave-function perturbation predicts that K_3 scales as[19]

$$K_3^{(A)} \propto \frac{1}{n^3 E_g^7} \frac{\left(\dfrac{3\hbar\omega}{E_g} - 1\right)^{5/2}}{\left(\dfrac{3\hbar\omega}{E_g}\right)^9} \tag{2}$$

(n is the linear refractive index), whereas Wherrett's third-order calculation yields

$$K_3^{(B)} \propto \frac{1}{n^3 E_g^7} \frac{\left(\dfrac{3\hbar\omega}{E_g} - 1\right)^{1/2}}{\left(\dfrac{3\hbar\omega}{E_g}\right)^9} \tag{3}$$

when only allowed–allowed–allowed transitions are included (i.e., self-transitions are not used). In 4PA, K_4 scales as

$$K_4^{(A)} \propto \frac{1}{n^4 E_g^{11}} \frac{\left(\dfrac{4\hbar\omega}{E_g} - 1\right)^{7/2}}{\left(\dfrac{4\hbar\omega}{E_g}\right)^{13}} \tag{4}$$

when derived from dressed-wave-function, first-order perturbation theory. Wherrett's fourth-order model gives

$$K_4^{(B)} \propto \frac{1}{n^4 E_g^{11}} \frac{\left(\dfrac{4\hbar\omega}{E_g} - 1\right)^{3/2}}{\left(\dfrac{4\hbar\omega}{E_g}\right)^{13}} \tag{5}$$

for three cross-gap transitions and a single self-transition. If multiplicative constants (wavelength- and material-independent parameters) are ignored, the calculations can be compared. We have, for both K_3 and K_4,

$$\frac{K_m^{(A)}}{K_m^{(B)}} = \left(\frac{m\hbar\omega}{E_g} - 1\right)^2. \tag{6}$$

The difference in scaling of K_m arises from two additional self-transitions needed in the dressed-wave-function calculation. Clearly, there can be substantial discrepancies in the predicted scaling of m-photon absorption when $m\hbar\omega$ approaches E_g. In Fig. 1, the 4PA coefficients (normalized at 300 K) given by relations (4) and (5) are plotted for InAs as a function of E_g.

3. EXPERIMENT

A grating-tuned CO_2 laser produces subnanosecond pulses at $\lambda = 10.6\ \mu$m by means of an optical free-induction-decay pulse slicing scheme.[20] Zero-background autocorrelation measurements of the temporal profile reveal an initial pulse of ~125-ps duration containing 75% of the total energy, followed immediately by a weaker second pulse lasting ~400 ps. Pulses are generated at a rate of 1 Hz, and all the data points represent a five-shot average. An uncoated, 1-mm-thick sample of bulk n-InAs ($N_e \sim 8 \times 10^{16}\ \mathrm{cm}^{-3}$) is mounted on a cold finger in a closed-cycle helium cryostat. A thin

layer of indium between the sample and cold-finger fixture ensures good thermal contact. Two temperature diodes verify proper operation of the cryostat. Pyroelectric detectors monitor transmission of the focused laser pulses ($\omega_0 = 64\ \mu$m) through the semiconductor. The sample is tilted approximately 30 ° (s polarization) to eliminate complications from Fabry–Perot fringes. The absolute irradiance is known with an accuracy of ±20%.

The nominal bandgap of InAs is 0.42 eV at 15 K and 0.36 eV at room temperature. Four-photon absorption is therefore the lowest-order multiphoton process available at $\lambda = 10.6\ \mu$m ($\hbar\omega = 0.117$ eV). Open-aperture Z scans are made by translation of the cryostat through the focus of a positive-lens telescope.[21] Data derived from a sequence of Z scans are shown in Fig. 2, in which nonlinear transmission is plotted as a function of irradiance in the sample. In the two scans, only the sample temperature (i.e., semiconductor band gap) is varied. The abscissa represents peak irradiance inside the sample. Although the absolute irradiance is not known to better than 20%, the relative position of the data points at the two temperatures is accurate to within 5%.

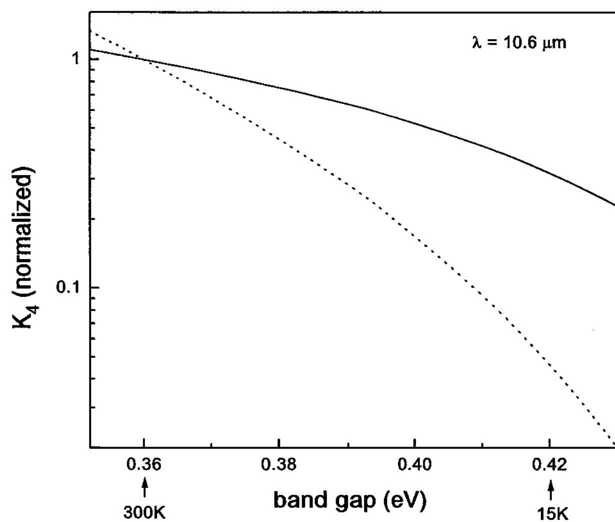

Fig. 1. Bandgap scaling of 4PA in InAs at 10.6 μm obtained from relation (4) (dotted curve) and relation (5) (solid curve). The curves are normalized at room temperature ($E_g = 0.36$ eV).

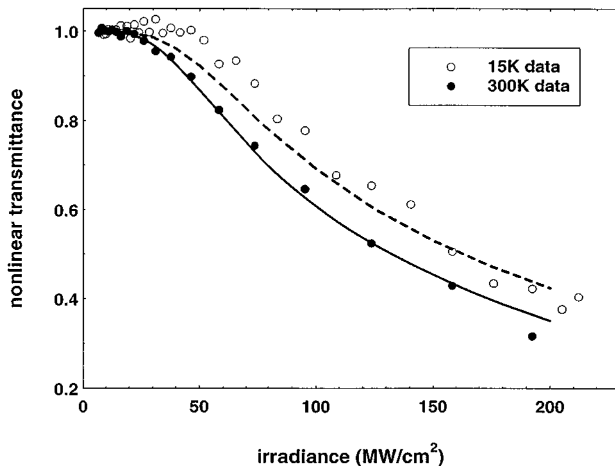

Fig. 2. Nonlinear transmission of InAs at 300 and 15 K. The solid curve through the room-temperature data is obtained by adjustment of the 4PA coefficient (K_4). The dashed curve is derived from the solid one by appropriate scaling of K_4 for a wider semiconductor bandgap by use of relation (5).

Compared with room temperature, equivalent nonlinear absorption at 15 K takes place at an irradiance that is 1.2–1.4 times higher. The data are fit with the common model for nonlinear beam propagation in the presence of multiphoton absorption and FCA.[1] We solve Eq. (1) along with the following nonlinear absorption equation ($m = 4$):

$$\frac{\mathrm{d}I}{\mathrm{d}z} = -K_m I^m - [\sigma_e(I)N_e + \sigma_H(I)N_H]I, \tag{7}$$

where N_e and N_H are the electron and the hole concentrations, respectively. Given the picosecond time scale, recombination and diffusion are ignored.[22,23] These equations are integrated numerically with the measured laser temporal profile[24] and the Gaussian beam spatial distribution. The calculation shows that the preponderance of nonlinear absorption is derived from free holes generated by multiphoton transitions across the bandgap. The first term on the right-hand side of Eq. (7) represents the intrinsic 4PA process, which leads to a comparatively minor fraction of the overall loss, even for picosecond pulses. For example, a pulse duration of <0.5 ps is needed to make the intrinsic 4PA comparable with absorption from the photocarriers at 150 MW/cm^2. Both the electron (σ_e) and the hole (σ_H) absorption cross sections are considered, but it is dipole-allowed transitions from the heavy- to the light-hole band that are by far the strongest component of FCA and of the total nonlinear loss.[25,26] Intraband transitions are indirect and much weaker, as they require participation of LO phonons to conserve momentum. Therefore it is absorption by heavy holes generated as a result of 4PA that drives the nonlinear absorption. Note that both absorption cross sections have been written as a function of irradiance. The irradiance dependence of FCA and its role in interpretation of the data are discussed later in this paper.

In Fig. 2, the room-temperature data are fit with the 4PA model described by Eqs. (1) and (7), assuming an irradiance-independent hole cross section of $\sigma_H = 8 \times 10^{-16}$ cm^2.[25] K_4 is the only adjustable parameter ($K_4 = 5 \times 10^{-6}$ cm^5/MW^3). To obtain the curve at 15 K, we scale K_4 by using Eq. (5) with a larger bandgap ($\Delta E_g = 60$ meV) and employ a hole cross section of $\sigma_H = 1.2 \times 10^{-15}$ cm^2, appropriate for low temperature.[25] There were no free parameters used to scale the room-temperature curve to 15 K. Within the measurement uncertainty, the data are consistent with the predicted bandgap scaling by use of Wherrett's fourth-order perturbation approach. In contrast, the experimental points sharply disagree with the scaling predicted by relation (4). Defining the ratio $\Gamma = K_4(300\ \mathrm{K})/K_4(15\ \mathrm{K})$, we find that $\Gamma = 3.1$ with Wherrett's model, whereas the dressed-wave-function calculation gives $\Gamma = 21.5$. This difference is significant and easily resolved by our experiment.

We estimate $10^{-6} < K_4 < 10^{-5}$ cm^5/MW^3 from the room-temperature data, compared with theoretical predictions. Although we cannot determine K_4 to better than an order of magnitude, note that the nonlinear absorption is characteristic of $\chi^{(9)}$ [$\chi^{(7)}$ owing to 4PA followed by linear absorption of photocarriers], so experimental uncertainties get magnified substantially in the extraction of K_4. Wherrett's fourth-order perturbation calculation[12] gives $K_4 = 1.2 \times 10^{-4}$ cm^5/MW^3. The first-order perturbation calculation with dressed wave functions made by Brandi and de Araujo[19] yields $K_4 = 3.7 \times 10^{-7}$ cm^5/MW^3. A similar calculation by Keldysh[17] gives $K_4 = 4.2 \times 10^{-7}$ cm^5/MW^3. These numbers are all in reasonable agreement with experiment, given the order-of-magnitude accuracy expected from the calculations. We emphasize that it is the relative behavior of K_4 as a function of the temperature-dependent bandgap that is of primary significance here. Indeed, the point of the calculation in Ref. 12 was to establish scaling relations for multiphoton absorption—not to obtain quantitative agreement with measured values. Our results are consistent with scaling of 4PA as calculated by Wherrett with fourth-order perturbation theory by use of the maximum number of (virtual) cross-band excitations.

We now consider the possibility of residual 3PA that is due to band-tail states. At 15 K, $E_g - 3\hbar\omega \cong 70$ meV, and 3PA is of no concern. At room temperature, $E_g - 3\hbar\omega \cong 9$ meV, i.e., the three-photon energy is slightly below the bandgap. The room-temperature data in Fig. 2 can be fit reasonably well with a model based on 3PA, leading to $K_3 \approx 10^{-4}$ cm^2/MW^3. We measured 3PA at 9.54 μm ($3\hbar\omega > E_g$) and obtained $K_3 \cong 3 \times 10^{-4}$ cm^2/MW^3.[27] The question is whether band-tail states can support a rate of three-photon excitation at 10.6 μm that is comparable with 9.54 μm. As there is no precise definition for the optical band-gap energy in a semiconductor, linear absorption spectra for InAs are consulted.[28,29] Linear absorption gives a direct measure of the density of optically coupled states in the spectral region of interest. The linear absorption is nearly 2 orders of magnitude smaller for $3\hbar\omega = 0.351$ eV ($\lambda = 10.6$ μm) compared with $3\hbar\omega = 0.39$ eV ($\lambda = 9.54$ μm). Therefore we expect the 3PA coefficients at 9.54 and 10.6 μm to be significantly different, which does not support a residual 3PA interpretation of the 10.6-μm data. Also, fits of the room-temperature data with a 3PA model underestimate nonlinear absorption in the high-irradiance regime. Finally, we contend that the similarity of the data at the two temperatures depicted in Fig. 2 suggests that the same physical mechanism is operative.

4. LASER-INDUCED IMPACT IONIZATION

In their nonlinear transmission measurement of InAs with a 1-ns CO_2 laser, Jamison and Nurmikko concluded that intraband excitation gave conduction electrons sufficient energy to induce inverse-Auger scattering, i.e., impact ionization of electron–hole pairs.[15] In a separate publication, we present a model of laser-induced carrier heating for InSb.[30] This calculation is based on the framework proposed by James,[16] in which the carrier temperature (greater than the lattice temperature) is determined by the balance of laser heating by FCA and cooling by LO-phonon emission. This model is appropriate for InAs, since LO-phonon scattering is the primary energy exchange mechanism with the lattice for carrier temperatures greater than 30 K.[31]

A brief outline of the carrier heating analysis is as follows. We reasonably neglect lattice heating by the 125-ps laser pulse; a simple heat capacity calculation shows that $\Delta T < 1$ K. Carrier–carrier scattering is sufficiently frequent ($N_e = 10^{16}$–10^{17} cm^{-3}) to establish a carrier temperature in a Fermi–Dirac distribution on the time scale of the experiment.[32,33] A carrier temperature (in this case it is electrons) is deduced from the following energy balance equation[16]:

$$\sigma_e(T_E)I(t) = \left\langle \frac{\mathrm{d}E}{\mathrm{d}t} \right\rangle_{\text{LO phonons}}, \tag{8}$$

where σ is the temperature-dependent FCA cross section, I is the laser irradiance, E is the carrier energy, and the angle brackets represent an average over the electron distribution. This relation allows the electron temperature (T_E) to be determined as a direct function of the laser irradiance. This is valid on the 100-ps time scale of the present experiment, as can be verified by assessment of the dynamic energy balance derived from the Boltzmann equation.[34] The electron distribution acquires the requisite temperature so that phonon emission balances carrier heating by the laser. On the time scale of the experiment, this balance is achieved instantaneously. For laser pulse widths approaching the LO-phonon rate (<10 ps), Eq. (8) is no longer valid, and a model incorporating the dynamics of carrier heating and cooling must be used.

We determine the electron temperature for the conditions of our InAs experiment and then estimate the rate of impact ionization. Our calculation includes nonparabolicity in the density of states, phonon absorption as well as emission, dynamic screening of the Fröhlich potential by the coupled plasmon–phonon system,[35–38] nonparabolic overlap of conduction-band wave functions,[38] and a temperature-dependent FCA cross section.[16,39] In the latter effect, the electron temperature scaling of σ_e is obtained in a separate calculation and is normalized to previously measured linear values (where $T_L = T_E$).[26] Recent measurements have shown that the anharmonic decay of LO phonons occurs with a characteristic time of a few picoseconds in InAs,[40] which is more than an order of magnitude shorter than the time scale of the experiment. Therefore hot-phonon effects are ignored.

Once the laser-induced electron temperature is computed, the next step is to determine the rate of impact ionization. Jamison and Nurmikko[15] and James[16] used the random-k calculation of Kane[41] to model the ionization rate (w) in a parabolic band:

$$w(E) \approx A\left(\frac{E - E_g}{E_g}\right)^{7/2}, \tag{9}$$

where E is the kinetic energy of an electron relative to the conduction-band edge ($E > E_g$) and A is a constant. The rate of carrier generation by impact ionization is

$$\frac{dN_e}{dt} = \frac{dN_H}{dt} = \eta N_e = \sum_{E_j > E_g} w(E_j)N_j. \qquad (10)$$

The conduction band is partitioned into discrete energy intervals $[\Sigma N_j(E) = N_e]$ to yield the impact-ionization coefficient (η) for a given electron temperature. In our calculation, the energy interval is taken as $E_{j+1} - E_j = 1$ meV.

Conduction-band nonparabolicity is obtained from Kane's $\mathbf{k}\cdot\mathbf{p}$ band-structure theory[42]:

$$\frac{\hbar^2 k^2}{2m^*} = E(1 + aE), \qquad (11)$$

where the nonparabolic coefficient $a = 1/E_g$. With expansion to first order in a, we find that relation (9) is modified as follows:

$$w(E) \approx A\left(\frac{E - E_g}{E_g}\right)^{7/2}\left(1 + \frac{31}{12}\frac{E - E_g}{E_g}\right). \qquad (12)$$

Here we have followed the procedure used to derive relation (9), retaining only the highest-order term involving energy in a very lengthy expression. Evaluating the constant A from Kane's theory is difficult, as it involves several interband overlap integrals. Following James,[16] we set $A = 5 \times 10^{12}\ \mathrm{s}^{-1}$, although there is reason to suspect that this number is far too large. This is discussed briefly later in this section.

Monte Carlo calculations of impact ionization in InAs by Brennan and Hess[43] and by Brennan and Mansour[44] used a rate based on the theory of Keldysh.[45] This formulation gives a quadratic dependence of electron energy in the expression for $w(E)$. We have included quadratic energy scaling as well as relations (9) and (12) in our analysis of impact ionization in InAs. Our model leads to six different curves, derived from three formulations of impact ionization and two treatments of the conduction-band overlap integral in the carrier heating analysis.[30] We obtain a range of numbers set by the extrema of these curves. The calculations give the laser-induced impact ionization rate of electron–hole pairs, which is used in place of multiphoton excitation to analyze nonlinear absorption in the semiconductor.

In Figs. 3(a) and 3(b), the calculated nonlinear absorption due to impact ionization is compared with the experimental data at 300 and 15 K, respectively. The two dashed curves represent the range set by the various models at each temperature. There are three significant discrepancies between the calculated curves and data points that do not support an interpretation based on impact ionization. First, the calculations underestimate the nonlinear absorption, although agreement is within an order of magnitude. Second, the slope of the calculated nonlinear absorption curves is a more gradually decreasing function of irradiance compared with the data. This is caused by substantial transmission leakage in the outer radial portions of the Gaussian beam. Finally, and most important, the predicted temperature scaling of laser-induced impact ionization is not consistent with the data. To interpret the calculated temperature scaling, we compare corresponding edges of the range depicted in Fig. 3. More precisely, only corresponding calculations (at 300 and 15 K) treating carrier heating and impact ionization in exactly the same way are compared. In this manner, much of the theoretical uncertainty is removed, as relative position of the curves is the key issue. We find that equivalent nonlinear absorption is predicted to occur at an irradiance that is approximately 2–3 higher at 15 K than at 300 K. The discrepancy increases as the irradiance increases. Experimentally, the data differ by only 20–40% throughout the measured irradiance range. Note that by looking at lattice temperature scaling of nonlinear absorption, the choice of a specific quantum-mechanical description of impact-ionization scattering is irrelevant. The larger difference predicted by the calculations at the two lattice temperatures can be traced directly to the carrier cooling process—specifically, the LO-phonon scattering rate.

At $T_L = 15$ K, carrier cooling is more efficient because of a relatively small phonon population in the final states, which helps maintain a lower electron temperature. Additionally, more laser irradiance is needed to heat cold

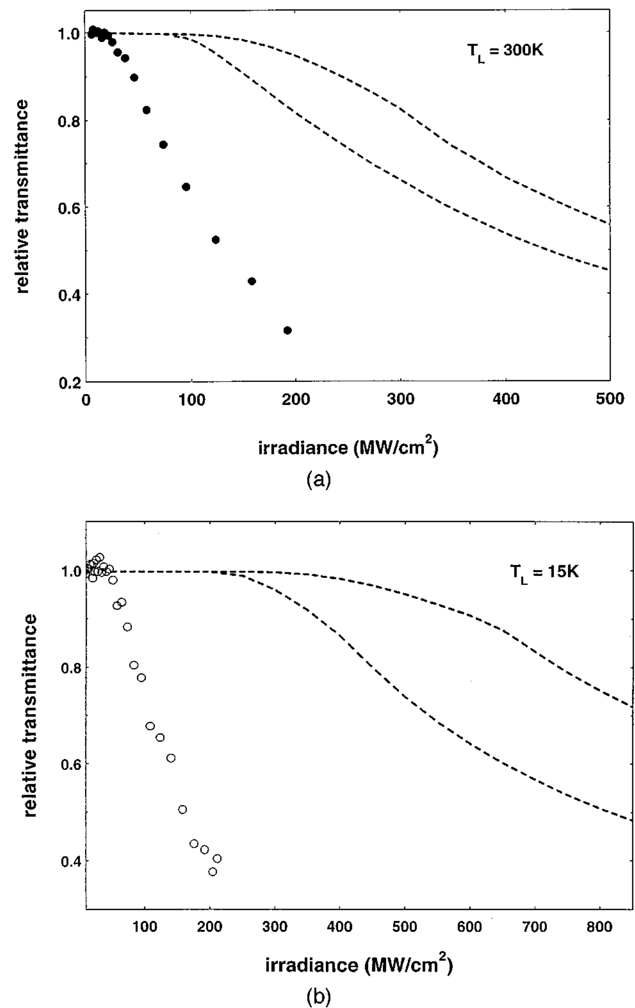

Fig. 3. Calculated nonlinear absorption due to impact ionization at lattice temperatures of (a) 300 K and (b) 15 K. The plotted points are the same experimental data shown in Fig. 2. The two dashed curves in each plot represent the high and the low ranges obtained from six different formulations of the problem. To evaluate temperature scaling, the corresponding high and low curves in each plot are compared.

electrons to a given temperature. As the onset of impact ionization depends primarily on electron temperature (a 14% wider bandgap at low temperature is much less important), a greater rate of laser energy deposition is needed to attain nonlinear absorption at low temperature. We conclude that the predicted temperature scaling of impact ionization is not consistent with the experimental evidence.

There are limits to the validity of this analysis, beyond which some of the assumptions of the model break down. When the rate of impact ionization becomes sufficiently high, it can act as an effective carrier-cooling mechanism by removing electrons from the high-energy tail of the distribution. When this occurs, Eq. (8) is no longer valid. Indeed, impact ionization can be self-limiting in the sense that it restricts the increase of carrier temperature and hence the growth of the ionization rate. We estimate that cooling by impact ionization becomes comparable with LO-phonon emission at $>300\ \mathrm{MW/cm^2}$, which is higher than any irradiance encountered in the experiments. The concept of electron temperature may be invalid at sufficiently high irradiance, when a significant number of energetic carriers get removed from the distribution. Therefore the model is best suited for describing the onset of nonlinear absorption. The cooling effect, however, will lead to a reduction of nonlinear absorption with increasing irradiance. This would tend to flatten out the calculated curves depicted in Fig. 3 and result in an even greater disparity with the data.

Previous studies have been made of the temporal evolution of impact ionization in narrow-gap semiconductor electronic devices.[46–48] In bulk InSb, intervalley transfer (Gunn effect) of conduction electrons having energy many times the bandgap has been obtained with pulsed electric fields.[46] Satellite valley scattering is observed for several nanoseconds before impact ionization becomes significant. It is reasonable to assume that a similar situation exists with InAs. Measurements and simulations of impact ionization in InAs show that the scatter rate is of the order of $10^9\ \mathrm{s}^{-1}$ at fields immediately below the threshold for intervalley transfer.[49,50] This suggests that impact ionization is not important on the picosecond time scale of our pulsed laser experiments. In particular, the rate constant (A) in relations (9) and (12) may be over estimated. Note that in our model of free-carrier heating by the laser pulse the electrons are thermalized and isotropically distributed in momentum space. In pulsed field experiments, the carrier distribution tends to exhibit anisotropy in momentum space, and a temperature description is usually not appropriate.

Our carrier heating analysis assumes that the infrared laser light heats only the electrons—hot holes have been ignored. This assumption must be treated with some care, however, as the hole absorption cross section can be almost 2 orders of magnitude larger than the electron cross section in narrow-gap semiconductors at CO_2 laser wavelengths,[25,26,51] leading to efficient coupling of laser energy into the carrier system. The InAs sample is n-type material, in which the electron concentration significantly exceeds the hole concentration. A small hole concentration is needed to obtain acceptable linear infrared transmission. The hole temperature will in general be different from the electron temperature,[52] and the excess energy in the holes will be distributed among far fewer carriers. A relatively small concentration of hot holes would not contribute significantly to the electron temperature.[53] Moreover, experiments with GaAs reveal that the holes can be much cooler than electrons, because of the additional energy loss conduit available in the valence bands of III–V semiconductors (i.e., deformation potential scattering).[54] The difficulty of directly exciting holes is borne out by the inability to obtain unambiguous evidence for hole impact ionization in narrow-gap p-type semiconductors with pulsed electric fields.[55,56]

Using a pump–probe arrangement to study 2PA in InAs, Elsaesser *et al.* have observed a transient increase of FCA when the two-photon energy is significantly above the bandgap ($\Delta E = 2\hbar\omega - E_g = 135\ \mathrm{meV}$).[23] This can leave excited carriers in the conduction band and in the light-hole band, thereby raising the temperature of both electrons and holes. Since intervalence band absorption dwarfs photon absorption by conduction electrons, their observed transient absorption change is most likely originating in the heavy-hole band. Photoexcitation energy supplied to light holes transfers rapidly to the heavy-hole band, which thermalizes on a subpicosecond time scale.[57,58] As the temperature of heavy holes increases, the population in initial states of the heavy-hole–light-hole band transition increases, and absorption rises. When the holes cool ($\sim 10^{-11}$ s), the transient absorption disappears. This effect may be important in our room-temperature data at high irradiance, since $\Delta E = 4\hbar\omega - E_g \approx 100\ \mathrm{meV}$, and may be less of a factor at 15 K, where $\Delta E \approx 50\ \mathrm{meV}$. The calculated nonlinear absorption would tend to be too low in the high-irradiance regime, which is evident in the room-temperature fit shown in Fig. 2. Based on the data of Elsaesser *et al.*,[23] an uncertainty of 2 is estimated for σ_H, which has been incorporated in our extracted value of K_4. The behavior of the heavy-hole–light-hole optical transition in the presence of multiphoton excited hot carriers is an interesting avenue for further study.

5. DISCUSSION

Our data show that 4PA scales in a manner predicted by fourth-order perturbation theory with three interband transitions and a single self-transition, as determined in the work of Wherrett.[12] In contrast, scaling of K_4 with bandgap energy is in substantial disagreement with a Keldysh model that includes a single interband transition and three intraband self-transitions.[19] We note that the scaling obtained from a Keldysh calculation can be obtained directly from an m-order perturbation calculation with a two-band model and $m-1$ self-transitions. As pointed out by Wherrett, the magnitude of these self-transitions depends on the value of k set by the optically coupled states and is weak near the valley minima. Using the maximum number of (k-independent) matrix elements linking states across the fundamental gap leads to the highest rate of m-photon absorption and gives the best description of our experimental results.

Our experimental conditions are nearly ideal for observing 4PA. As relation (5) reveals, narrow-gap semi-

conductors give the largest values of K_4. Also, the strong absorption resonance between the heavy- and the light-hole bands at $\lambda = 10$ μm serves as a sensitive detector for generated carriers. In that sense, 4PA is not directly measured—it is absorption by generated holes that reveals its presence. Indeed, a large hole-absorption cross section (σ_H) is essential for making the observations with InAs reported here.

We comment on differences between this work and previous studies of InAs at $\lambda = 10$ μm. Jamison and Nurmikko observed nonlinear transmission of room temperature using 1-ns CO_2 laser pulses in the irradiance regime of 30–300 MW/cm^2 and attributed it to impact ionization.[15] Both their calculation of electron heating and the subsequent analysis of their experiment by James[16] assume an electronic cross section that is four times larger than that indicated by linear spectroscopic data.[26] This causes an overestimation of the excited carrier energy and a lower irradiance for the onset of impact ionization. Also, Jamison and Nurmikko derived a nonthermal carrier distribution with structure associated with the photon energy. More recent studies of carrier thermalization dynamics in GaAs indicate that a temperature description of the distribution is entirely appropriate on the time scale of their experiment.[32,33,59,60] The principal difference between the calculation in Section 4 and previous efforts is that we incorporate impact ionization in a model of nonlinear propagation through the semiconductor sample. Because electron–hole pair generation is highly nonlinear and the resulting hole absorption is large, including the spatial and the temporal characteristics of the laser beam is essential to make a meaningful interpretation of the data. Accounting for Fresnel reflection in the experiment of Ref. 15 and using their estimate of an excess hole density of the order of $\Delta p \sim 10^{15}$ cm^{-3}, we find that the observed nonlinear transmission appears to be consistent with the 4PA interpretation proposed in this paper. Reported experimental details are not sufficient, however, to allow a detailed quantitative evaluation of their data.

In a series of papers, Kovalev and co-workers studied phase conjugation and nonlinear absorption of 10.6-μm TEA CO_2 laser beams, using room-temperature n-InAs.[61–64] Strong nonlinear absorption was observed between 1 and 10 MW/cm^2 and was attributed to 3PA. As discussed in Section 3, our analysis does not support this interpretation. Although 4PA may have been present in their experiments, we note that it is difficult to make nonlinear optical measurements of semiconductors with TEA CO_2 lasers having pulses that are a considerable fraction of a microsecond in duration because of excessive energy deposition and uncertain carrier recombination processes. Additionally, lack of longitudinal-mode control leads to a heavily modulated, spiked temporal profile emitted by the TEA laser. The instantaneous peak power varies rapidly in time and is not reproducible from shot to shot. It has been pointed out that these pulses present serious problems for 2PA characterization, and we expect that the situation can only get worse when dealing with higher-order processes.[65]

In summary, we have observed four-photon absorption (4PA) with bulk InAs at $\lambda = 10.6$ μm. We believe that this is the first time a 4PA process has been used to interpret the nonlinear optical behavior of a semiconductor. This conclusion is based on bandgap scaling of multiphoton absorption, which is consistent with the predictions of a calculation by Wherrett in which the maximum number of cross-band excitations are employed. Bandgap scaling is obtained in a straightforward manner by variation of the temperature of the InAs semiconductor sample. The experimental results do not agree with scaling of 4PA obtained from a Keldysh calculation or with a model of nonlinear absorption arising from laser-induced impact ionization.

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