Hot-phonon-assisted absorption at semiconductor heterointerfaces monitored by pump-probe second-harmonic generation

Y. D. Glinka*
U.S. Army Aviation and Missile RDEC, Redstone Arsenal, Alabama 35809, USA
and Nano and Micro Devices Center, University of Alabama in Huntsville, Huntsville, Alabama 35899, USA

N. H. Tolk
Department of Physics and Astronomy, Vanderbilt University, Nashville, Tennessee 37235, USA

X. Liu, Y. Sasaki, and J. K. Furdyna
Department of Physics, University of Notre Dame, Notre Dame, Indiana 46556, USA
(Received 31 January 2008; published 17 March 2008)

We provide the evidence for the hot-LO-phonon-assisted absorption at semiconductor heterointerfaces. The process is demonstrated with GaAs/GaSb interface when the photon energy is tuned below the band-gap energy for GaAs, but it is in a great excess for GaSb. The excitation of carriers in GaAs in the vicinity of the heterointerface is shown to be assisted by hot LO phonons generated in GaAs and GaSb within the relaxation of hot carriers in GaSb. The effect has been observed in the ultrafast pump-probe experiment through the interfacial-electric-field-induced second-harmonic generation response.

DOI: 10.1103/PhysRevB.77.113310 PACS number(s): 78.20.Jq, 73.40.−c, 78.66.Fd, 78.67.Pt

Light with a frequency ω is able to excite free carriers in the direct-band-gap semiconductors if the photon energy is in excess of the band-gap energy, $\hbar\omega > E_g$, where $\hbar$ is the reduced Planck's constant. However, if the photon energy is tuned just below the band gap, an excitation of virtual carriers is also possible if the semiconductor is subjected to an electrostatic field. As this takes place, the virtual occupation rate monotonically increases with decreasing the detuning energy $(E_g - \hbar\omega)$.[1,2]

In the current Brief Report, we report on the excitation of real carriers in GaAs in the vicinity of the unbiased GaAs/GaSb heterointerface by an ultrashort laser pulse with photon energy just below E_g for GaAs. The excitation energy deficit is shown to be compensated by the energy of the nonequilibrium (hot) longitudinal optical (LO) phonons generated in GaSb and GaAs due to the relaxation of energetic (hot) carriers in GaSb. Because the time of LO-phonon emission is comparable with the photon-mediated virtual state lifetime in GaAs, the hot-LO-phonon-assisted absorption process becomes possible. Since the dynamical interfacial electric field at the GaAs/GaSb heterointerface is formed exclusively by the joint excitation of carriers in both GaAs and GaSb materials, the process has been detected through the pump-probe interfacial-electric-field-induced second-harmonic generation (IEFISHG) response. Accordingly, the photon energy dependence of the IEFISHG signal in the range of the GaAs absorption edge reveals a resonant feature occurring LO-phonon energy below the band-gap energy for GaAs. Such a hot-LO-phonon-assisted absorption in the vicinity of the GaAs/GaSb interface is a reason for the real carrier excitation in GaAs with photon energy of less than E_g $(\hbar\omega + \hbar\omega_{LO} > E_g)$. The mentioned process is similar to that occurring in the time-resolved anti-Stokes Raman scattering,[3,4] assuming that the laser photon energy is tuned below E_g and so the energy of scattered photon in the anti-Stokes mode matches it.

Our experiments were carried out at 4.3 K on a GaAs (100 nm)/GaSb (500 nm)/InAs (20 nm) heterostructure with In-Sb interface type between the GaSb and InAs layers. The details regarding the sample growth have been previously discussed.[5] A mode-locked $Ti:Al_2O_3$ laser has been tunable in the range of 873 nm (1.42 eV) to 800 nm (1.55 eV). The pump and probe beams of 350 fs pulses were set up to be cross polarized with the laser spot size on the sample of about 100 μm. The p polarized probe beam of 80 mW average power was channeled through an optical delay stage. The pump beam, after chopping at a frequency of 800 Hz, was of 130 mW average power. The average power of the pump and probe beams has been kept to be unchanged over the tunability range of the laser used. The pump beam was incident normally on the sample, whereas the probe beam was directed to the sample at the angle of 45°. The IEFISHG response was measured in p polarization as a function of probe-to-pump delay times and detected by a photomultiplier tube through a lock-in amplifier.

The range of the laser light tunability covers the range of the direct fundamental absorption edge of GaAs $(E_g = 1.52$ eV). In contrast, the photon energy is much higher than E_g for GaSb and InAs, pointing to the hot carriers to be excited in the corresponding layers [Fig. 1(a)]. As a result of the photoexcitation ($N \approx 2.2 \times 10^{17}$ cm^{-3} within InAs and GaSb layers), the electrons and holes relax in all the layers. This can be proven by taking into account the absorption coefficients of the materials and the Beer law distribution of photoexcited carriers. Accordingly, since the absorption coefficient of GaSb and InAs for 1.5 eV light is $\sim 0.5 \times 10^5$ cm^{-1},[6,7] the average absorption length is estimated $\sim$200 nm. As a result, at normal light incidence, 10% of the incident light is absorbed in the InAs cap layer, while the GaSb and GaAs layers absorb 82.5% and 7.5% of the light, respectively. This estimation proves that the interfacial electric fields can be formed at both of the heterointerfaces

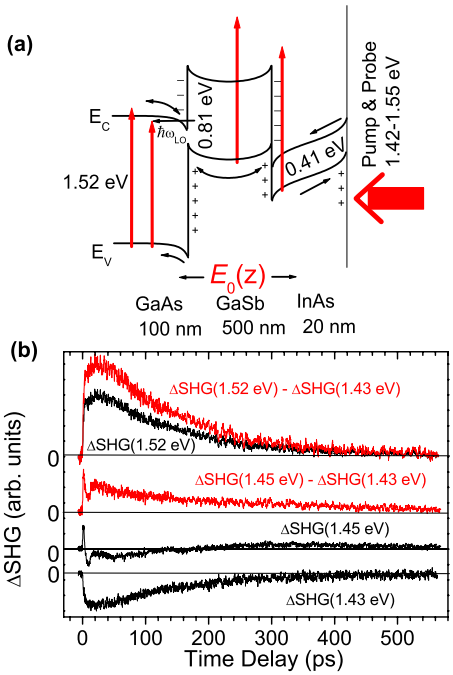

FIG. 1. (Color online) (a) The schematic representation of the band alignment of the GaAs/GaSb/InAs heterostructure. (b) The TIEFISHGC traces measured at the photon energy indicated are shown in black. Traces shown in red/gray are the difference of signals measured with $\hbar\omega > 1.43$ eV and that taken with $\hbar\omega = 1.43$ eV. The individual trace baselines are arbitrarily shifted for better observation.

(GaAs/GaSb and GaSb/InAs) and have to be comparable in the magnitude. As a result of the carrier-carrier thermalization, carrier-LO-phonon relaxation, and subsequent diffusion, the photoexcited carriers accumulate at the heterointerfaces inducing the band bending.[8] As a result of the charge separation, the electric fields at the heterointerfaces are formed. The delayed probe beam hence interacts with the system, which is subjected to the interfacial electric field that varies slowly compared with the frequency of light (dc field). The coupling of one dc electric field and two optical fields with the third-order nonlinear susceptibility $[\chi^{(3)}(-2\omega;\omega,\omega,0)]$ gives rise to the IEFISHG response, which has normally been used to study the dc electric fields at semiconductor interfaces.[5,9,10]

Accordingly, the IEFISHG intensity for two adjoining semiconductors [denoted by (1) and (2)] in the electric dipole approximation is given by[11]

$$I^{2\omega} = (|\chi(1)^{(2)}_{ijk} + \chi(2)^{(2)}_{ijk}|^2 + |3[\chi(1)^{(3)}_{ijkz} + \chi(2)^{(3)}_{ijkz}]E_{0z}(z,t)|^2)(I^{\omega})^2 \pm (6E_{0z}(z,t)|[\chi(1)^{(3)}_{ijkz} + \chi(2)^{(3)}_{ijkz}] \times [\chi(1)^{(2)}_{ijk} + \chi(2)^{(2)}_{ijk}]|\cos\phi)(I^{\omega})^2, \quad (1)$$

where ϕ is the relative phase difference between the second- and third-order susceptibilities, which is constant at the given experimental configuration. Here, we take into account that the interfacial electric field due to the charge separation at an interface is directed along the axis perpendicular to the sample surface (z axis) and can be represented by a simple rise-decay function,

$$E_{0z}(z,t) = AH(t)[1 - \exp(-t/\tau_R)]\exp(-t/\tau_D), \quad (2)$$

where τ_R and τ_D denote the rise-time and decay-time constants of the dc electric field, which we associate with the accumulation of carriers at the heterointerfaces and carrier recombination, respectively, $H(t)$ is the Heaviside step function that accounts for the pump-probe cross-correlation time, and A is the amplitude of the dc electric field. Only second and third terms in Eq. (1) may contribute to the transient interfacial-electric-field-induced second harmonic generation change (TIEFISHGC) signal. However, the second term is not a quadratic-in-field term because such a process should be described by a nonlinear susceptibility of the higher order $[\chi^{(4)}_{ijkzz}(-2\omega;\omega,\omega,0,0)]$. Since $(\chi^{(3)}_{ijkz})^2$ can never be transformed into $\chi^{(4)}_{ijkzz}$, the second term in Eq. (1) does not have any physical meaning. Hence, only linear-in-field term will contribute to the TIEFISHGC signal, the sign of which depends on the direction of the dc electric field along the z axis. The sign $\pm$ in Eq. (1) distinguishes the opposite direction of the field. The total intensity of the TIEFISHGC signal is resulted from the interference of contributions in the form of Eq. (1) from both of the heterointerfaces and hence is determined by the strength of the interfacial electric fields by their directions and by the value of the third-order susceptibilities $\chi^{(3)}_{ijkz}(-2\omega;\omega,\omega,0)$ for each of the materials.

Specifically, the TIEFISHGC signal from the GaSb side of the heterointerfaces is expected to be dominant since the out-of-resonance value of the third-order susceptibility for GaSb is at least 1 order of magnitude larger than that for GaAs and InAs.[12] Moreover, our data suggest that even a resonant enhancement of $\chi^{(3)}_{ijkz}$ for GaAs near the band-gap energy due to the excitonic and interband transitions[13] is incapable of making $\chi^{(3)}_{ijkz}$ for GaAs to be comparable with that for GaSb. Since GaSb in the vicinity of both of the heterointerfaces dominantly contributes to the TIEFISHGC signals and because of the linear dependence on the interfacial field strength, one can manipulate with TIEFISHGC signals in accordance with algebraic rules.

Figure 1(b) shows an example of the TIEFISHGC signals. The signal can be either negative or positive depending on the photon energy applied. The dc field at the GaAs/GaSb interface is formed exclusively when carriers in the GaAs layer are optically excited. Accordingly, if the photon energy is tuned to be not high enough to excite carriers in GaAs, the accumulation of both holes excited in GaSb and electrons excited in InAs at the GaSb/InAs heterointerface forms the dc field at it. In contrast, if the photon energy is tuned to excite carriers in GaAs, in addition to the latter process, the accumulation of both holes excited in GaSb and electrons excited in GaAs at the GaAs/GaSb heterointerface creates the dc electric field, which is oppositely directed to that at the GaSb/InAs heterointerface [Fig. 1(a)]. Thus, the TIEFISHGC signal can be induced by the dc field at single heterointerface (GaSb/InAs) or at two heterointerfaces (GaAs/GaSb and GaSb/InAs) depending on how far the

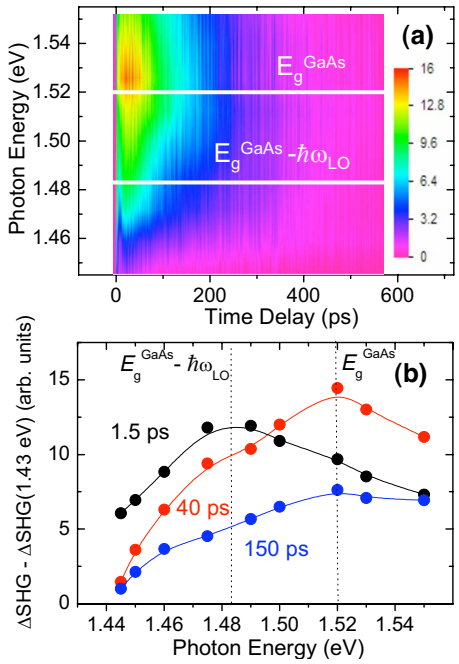

FIG. 2. (Color online) (a) $\hbar\omega$-time mapping of the dc field at the GaAs/GaSb interface. The IEFISHG intensity color/gray scale key is shown on the right. (b) The corresponding photon energy dependences extracted from (a) at the time delays indicated. The vertical dotted lines show the position of E_g for GaAs and $E_g-\hbar\omega_{\mathrm{LO}}$.

photon energy is tuned below E_g for GaAs. We experimentally found that such a critical photon energy is $\hbar\omega=1.43$ eV. Accordingly, the negative TIEFISHGC signals taken with photon energy $\hbar\omega\leqslant 1.43$ eV are attributed to those induced by the dc electric field at the GaSb/InAs interface. Further increase in the photon energy gives rise to another positive component of the signal, which compensates the negative contribution [Fig. 1(b)]. Finally, if the photon energy is tuned above E_g for GaAs, the positive component becomes dominant. This means that it is induced by the dc electric field at the GaAs/GaSb interface because of the oppositely directed fields at the heterointerfaces. By extracting the contribution from the GaSb/InAs interface ($\hbar\omega=1.43$ eV) from the total TIEFISHGC signal measured with $\hbar\omega>1.43$ eV, one can get the dynamics of the dc electric field at the GaAs/GaSb interface. This is exemplified in Fig. 1(b) for two TIEFISHGC traces taken with different photon energies.

Figure 2(a) represents the corresponding $\hbar\omega$-time mapping of the dc field at the GaAs/GaSb interface, which combines ten TIEFISHGC traces taken at different photon energies. The strength of the dc electric field at the GaAs/GaSb interface is high enough even if the photon energy is still below E_g for GaAs. Another peculiarity is the existence of a sharp dip at short time delays and photon energies below E_g for GaAs, which disappears as the photon energy approached E_g for GaAs. This is illustrated in Fig. 3 for one of the difference of the traces. The fit to the data by using Eq. (2) allows one to recognize two components. The first component manifests itself at short time delays. Accordingly, the interfacial electric field at the GaAs/GaSb interface initially

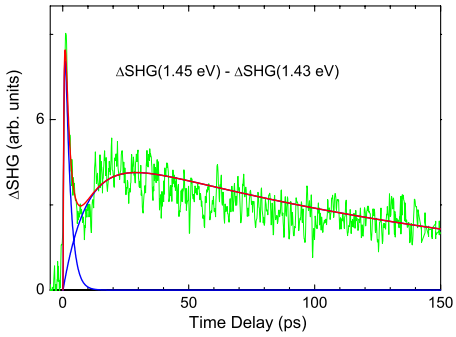

FIG. 3. (Color online) The difference of the TIEFISHGC traces taken with $\hbar\omega=1.45$ eV and $\hbar\omega_{\mathrm{LO}}=1.43$ eV. The result of the fit is shown in red/gray. The fit components are shown in blue/dark gray.

rises up with a constant of $\tau_R\approx 0.5$ ps and then decays with a constant of $\tau_D=2$ ps. The second component both rises up and decays slowly, $\tau_R=10$ ps and $\tau_D=170$ ps, respectively.

It is evident that all the peculiarities of the dc electric field variation reflect the changes in the density of oppositely charged carriers at the heterointerface. The carrier density at the GaAs/GaSb interface, in turn, is affected by the rate of carrier excitation in both GaAs and GaSb, by the rate of the relaxation of both hot electrons and hot holes in GaSb due to the electron-phonon and hole-phonon couplings, and also by diffusion of carriers toward the heterointerface. If the photon energy is tuned below E_g for GaAs, the absorption in GaAs is expected to occur as a transition into the photon-mediated virtual state in GaAs, which is coupled with hot phonons generated in GaSb and GaAs in the vicinity of the heterointerface due to the cooling of hot carriers in GaSb. The hot-LO-phonon-assisted process discussed is similar to that occurring in the time-resolved anti-Stokes Raman scattering,[3,4] assuming that the laser photon energy is tuned below E_g for GaAs and so the energy of scattered photons in the anti-Stokes mode matches it.

The rate of emission of LO phonons by hot carriers in GaSb can be estimated from the polar Frohlich interaction,[14]

$$\frac{1}{\tau_{e\text{-}ph}}=\frac{e^2}{4\pi\hbar}\left(\frac{2m^*\hbar\omega_{\mathrm{LO}}}{\hbar^2}\right)^{1/2}\left(\frac{1}{\varepsilon_\infty}-\frac{1}{\varepsilon_s}\right), \tag{3}$$

where $\tau_{e\text{-}ph}$ is the electron-phonon interaction time, e is the electron charge, $\hbar\omega_{\mathrm{LO}}=29$ meV is the LO-phonon energy in GaSb, $m^*=0.041m_e$ is the electron effective mass in the Γ valley (m_e is the free-electron mass), and ε_∞ and ε_s are the high-frequency and static dielectric constants. Hence, the time required to emit single LO phonon by hot electrons in GaSb is as long as 454 fs. Using the effective masses for light and heavy holes in GaSb, $m_{lh}=0.05m_e$ and $m_{hh}=0.4m_e$, the following times can be obtained for the hole-phonon interactions: 415 and 145 fs, respectively. If the hot electrons and holes in GaSb relax by emitting LO phonons in GaAs, the corresponding times are 410, 371, and 131 fs, respectively. The obtained values are comparable with the virtual state lifetime in GaAs, which is assumed to be of the order of the laser pulse duration (350 fs) despite the fact the lifetime of virtual carriers is measured by the inverse detuning from the band edge and is much shorter than 350 fs mentioned.[1,2]

Thus, one can argue that the excitation of carriers in GaAs may involve the hot LO phonons in GaSb and GaAs generated within the relaxation of hot carriers in GaSb. The corresponding rule for the excitation process is $\hbar\omega+\hbar\omega_{\mathrm{LO}}>E_g$.

The electrons photoexcited in GaAs within the hot-LO-phonon-assisted absorption become confined at the heterointerface, while the photoexcited holes move inward GaAs as a consequence of the band bending and do not contribute to the interfacial field. Since the hot-LO-phonon-assisted absorption produces the carriers with close-to-zero energies, the electron accumulation at the GaAs/GaSb interface occurs fast enough. The charge balance condition requires the same number of holes to be accumulated in the GaSb side of the heterointerface. This process leads to the rise of the dc electric field with a constant of $\tau_R \approx 0.5$ ps. However, the low-energy carriers are able to pick up an additional energy from hot phonons during their lifetime. Therefore, once the excitation is complete, the carriers photoexcited in GaAs can be heated up by hot LO phonons until the hot phonon subsystem gets cooled down. The heating of electrons in GaAs, which were initially confined at the heterointerface, leads to their delocalization, resulting in a decrease of the strength of the dc field at the heterointerface. Thus, the decay of the field with a constant of $\tau_D=2$ ps is a measure of the lifetime of the hot LO-phonon subsystem. The latter value is consistent with those obtained for numerous semiconductors for which the anharmonic three phonon (Ridley) decay process, LO$\rightarrow$TO+LA, has been proposed.[14,15] However, we note here that in the discussed case, the relaxation of hot phonons in GaSb in the vicinity of the heterointerface is governed by their energy transfer to free carriers, which have been photoexcited in GaAs through the hot-LO-phonon-assisted process.

The second much longer component of the interfacial field rise ($\tau_R=10$ ps) overlaps in time the carrier heating process and is caused by the relaxation and diffusion of holes photoexcited in GaSb. As this takes place, the electrons photoexcited in GaSb move away from the interfaces inward the GaSb layer and accumulate in the central area of it. The accumulation of holes at the heterointerface partially returns the delocalized electrons in GaAs to it, restoring the dc field at the heterointerface. This process corresponds to the rise of the dc electric field with a constant of $\tau_R=10$ ps. Finally, the interfacial fields decay with a constant of about 170 ps, which we associate with carrier recombination.

Because the relaxation of hot carriers photoexcited in GaSb involves many processes of carrier-LO-phonon scattering, it proceeds slowly enough. One can estimate the number of phonons required to emit by hot carriers in GaSb in order to be cooled down and reached the conduction and valence band extrema. For the case discussed in Fig. 3, the excess of the excitation energy in GaSb is 0.64 eV. Assuming that due to the electron-hole scattering, which occurs on the order of $\leqslant$100 fs,[4] the electron and hole subsystems reach the same temperature, one can estimate that 11 LO phonons in GaSb (9 LO phonons in GaAs) are required to be emitted by each photoexcited hole in GaSb before reaching the band edge. Taking into account the above-estimated times for the single LO-phonon emission, one can obtain the time required for the hot carrier energy relaxation in GaSb, which is in the range of 1.2–4.5 ps for different scattering mechanisms mentioned. The latter values are less than $\tau_R=10$ ps measured, indicating that the diffusion of relaxed holes toward the GaAs/GaSb interface also takes place.

Additional evidence for the hot-LO-phonon-assisted absorption process is a resonant feature in the photon energy dependence of the TIEFISHGC signal at time delays corresponding to the carrier-LO-phonon interaction time and the lifetime of hot LO phonons [Fig. 2(b)]. The resonant feature is energetically positioned LO-phonon energy below E_g for GaAs. The width of the resonance indicates that either the individual hot LO phonons in GaSb (29 meV) and GaAs (36 meV) or their combination may contribute to the hot-LO-phonon-assisted absorption in GaAs.

In summary, we have provided the experimental evidence for the hot-LO-phonon-assisted absorption in GaAs in the vicinity of GaAs/GaSb interface, which is realized due to the coupling of the transition into the photon-mediated virtual state in GaAs with hot LO phonons generated in GaSb and GaAs within the relaxation of hot carrier in GaSb. The process is similar to that occurring in the time-resolved anti-Stokes Raman scattring and can be observed at any heterointerfaces created by the direct band-gap semiconductors of different band-gap energies.

We gratefully acknowledge support from the (U.S.) Army Research Office and the National Science Foundation.

*Corresponding author. glinkay@uah.edu

[1] D. S. Chemla, D. A. B. Miller, and S. Schmitt-Rink, Phys. Rev. Lett. **59**, 1018 (1987).
[2] E. Yablonovitch, J. P. Heritage, D. E. Aspnes, and Y. Yafet, Phys. Rev. Lett. **63**, 976 (1989).
[3] A. K. Sood, J. Menéndez, M. Cardona, and K. Ploog, Phys. Rev. Lett. **54**, 2115 (1985).
[4] A. Othonos, J. Appl. Phys. **83**, 1789 (1998).
[5] Y. D. Glinka, T. V. Shahbazyan, I. E. Perakis, N. H. Tolk, X. Liu, Y. Sasaki, and J. K. Furdyna, Appl. Phys. Lett. **81**, 3717 (2002).
[6] S. Adachi, J. Appl. Phys. **66**, 6030 (1989).
[7] J. R. Dixon and J. M. Ellis, Phys. Rev. **123**, 1560 (1961).
[8] C. K. Sun, G. Wang, J. E. Bowers, B. Brar, H. R. Blank, H. Kroemer, and M. H. Pilkuhn, Appl. Phys. Lett. **68**, 1543 (1996).
[9] Y. D. Glinka, W. Wang, S. K. Singh, Z. Marka, S. N. Rashkeev, Y. Shirokaya, R. Albridge, S. T. Pantelides, N. H. Tolk, and G. Lucovsky, Phys. Rev. B **65**, 193103 (2002).
[10] G. Lupke, Surf. Sci. Rep. **35**, 75 (1999).
[11] N. Bloembergen, *Nonlinear Optics* (Benjamin-Cummings, New York, 1965).
[12] S. S. Jha and N. Bloembergen, Phys. Rev. **171**, 891 (1968).
[13] A. Lohner, K. Rick, P. Leisching, A. Leitenstorfer, T. Elsaesser, T. Kuhn, F. Rossi, and W. Stolz, Phys. Rev. Lett. **71**, 77 (1993).
[14] B. K. Ridley, Semicond. Sci. Technol. **4**, 1142 (1989).
[15] K. Wang, J. Simon, N. Goel, and D. Jena, Appl. Phys. Lett. **88**, 022103 (2006).