

Phonon-induced photoconductive response in doped semiconductors

Kui-juan Jin,^{1,*} Jiandi Zhang,² Zheng-hao Chen,¹ Guo-zhen Yang,¹ Z. H. Chen,³ X. H. Shi,³ and S. C. Shen^{3,4}
¹Laboratory of Optical Physics, Institute of Physics and Center for Condensed Matter Physics, Chinese Academy of Sciences,
 P. O. Box 603, Beijing 100080, China

²Department of Physics, Florida International University, Miami, Florida 33199

³National Laboratory for Infrared Physics, Shanghai, Institute of Technical Physics, Chinese Academy of Sciences,
 Shanghai 200083, China

⁴Department of Physics, Fudan university, Shanghai 200433, China

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We present an unusual photoconductive response in doped GaAs and InP semiconductor epitaxial layers and demonstrate that such a response is due to the longitudinal optic (LO) phonon-induced Fano resonance instead of the traditional kinetic mechanism. Theoretical calculations based upon the present mechanism are in excellent agreement with the experimental results and the developed formalism should be universally applicable to the related photoconductive processes of other doped semiconductors.

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The understanding of the photoconductivity in doped semiconductors such as the semiconductors with shallow donors/impurities is an important issue in semiconductor community. The study of photoconduction not only gains a great insight of the doping effects on the electronic structure but also offers valuable guidance for semiconductor devices. In general, photoconduction involves various processes such as photoexcitation, photogeneration, carrier transportation, and recombination, thus it is normally much more complicated than simple absorption process. For the last forty years many mechanisms have been introduced for the interpretations of photoconductivity phenomena.^{1,2} Particularly, the photoconductivity which involves LO-phonon excitations has attracted much attention,³⁻⁷ partially because of the fundamental importance of electron-phonon coupling. The main feature in such photoconductive processes is a *negative* photoconductive response due to LO-phonon emission process and the traditional kinetic mechanism developed by Stocker *et al.*⁷ has been generally recognized as a reasonable qualitative explanation.

In this letter, however, we present a peculiar photoconductive feature in the vicinity of single LO-phonon energy in both the high purity GaAs and InP semiconductor epitaxial layers with shallow donors. This feature exhibits an asymmetric line shape with a *weak negative* but a *strong positive* photoconductive response, which can not be understood based upon the established mechanisms.³⁻⁷ We demonstrate quantitatively that the Fano resonance which was initially introduced by Fano⁸ for atomic systems is indeed the mechanism for the observed strong positive photoconductive response. For the present doped semiconductors, this Fano resonance process is originated from the quantum-mechanical interference between the transition from a donor state to an electron continuum state and the one from a donor state to a LO-phonon state. Based on this mechanism we calculated the line shape of the photoconductivity and achieved an excellent agreement between experimental and theoretical results. More importantly, the new quantum mechanical formalism developed here should be universally applicable to the related photoconductive processes in other doped semiconductors.

The high quality InP (GaAs) samples used for the measurements was an unintentionally doped epitaxial layer with the thickness of 5.2 μm (5 μm), which was grown on a Fe-doped semi-insulating InP (a Si-doped semi-insulating GaAs) substrate with a V80H GSMBE system. Pure In Ohmic contacts were alloyed to sample at 40 °C in N_2 atmosphere for 1 min. Hall measurement gave a carrier concentration of $2.70 \times 10^{14} \text{ cm}^{-3}$ and an electron mobility of 4070 cm^2/Vs for InP ($8.0 \times 10^{14} \text{ cm}^{-3}$ and 6400 cm^2/Vs for GaAs) at room temperature, a carrier concentration of $1.17 \times 10^{14} \text{ cm}^{-3}$ and an electron mobility of $1.12 \times 10^5 \text{ cm}^2/\text{Vs}$ for InP ($7.0 \times 10^{14} \text{ cm}^{-3}$ and $6.9 \times 10^4 \text{ cm}^2/\text{Vs}$ for GaAs) were obtained at 77 K. The measurements of the photothermal ionization (PTI) spectra of the samples were performed with a Bruker IFS-113V Fourier transform spectrometer. All the measurements were taken at 4.2 K.

In the far-infrared PTI spectra of the samples, all phonon-assisted transition features were revealed in both InP (Ref. 4) and in GaAs (Ref. 5). In InP, for example, there is a dominant feature at the wave number of 45.32 cm^{-1} (the 1s to 2p transition of the donor states), accompanied with a weak peak appears at 52.07 cm^{-1} (the 1s to 3p transition) and a broad continuum at even higher frequencies (the 1s to continuum transition). However, an abnormal feature with an asymmetric line shape appears in both GaAs and InP. As shown in Figs. 1 and 2, this asymmetric feature occurs at frequency of 296.1 cm^{-1} just above the LO phonon ($\hbar\omega_{LO} = 294.5 \text{ cm}^{-1}$) for GaAs and at the frequency of 349.2 cm^{-1} just around the LO phonon ($\hbar\omega_{LO} = 349.5 \pm 0.3 \text{ cm}^{-1}$) for InP. For both systems, a weak dip but a strong peak appear at the incident photon frequencies just around ω_{LO} , characterizing the line shape of the feature.

This unusual feature in InP has been qualitatively interpreted⁴ based upon the kinetic mechanism.⁷ In Ref. 4, the dip below $\hbar\omega_{LO}$ in the photoconductive response was explained as a momentum lost process of electrons with positive wave vectors \mathbf{k} in the direction of the electric potential gradient by the LO phonon emission, while the peak above $\hbar\omega_{LO}$ was interpreted as a net momentum gain process of the electrons with negative wave vectors \mathbf{k} . However,

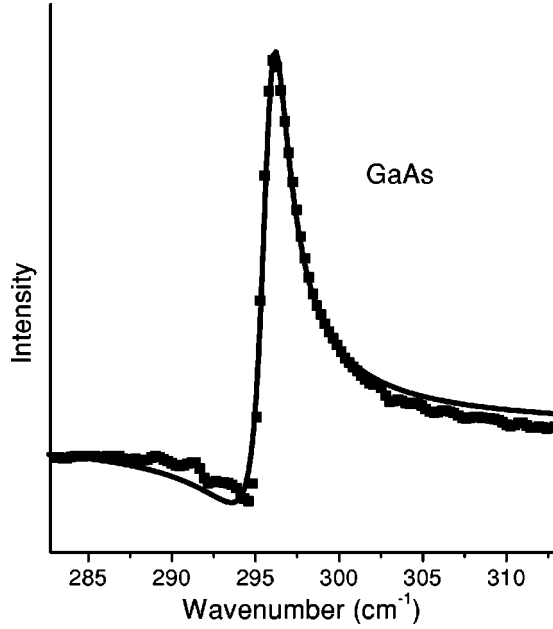


FIG. 1. The experimental photothermal ionization spectrum (solid square) and corresponding theoretical result (solid line) based upon the Fano resonance process for high purity GaAs epitaxial layers with shallow donors. The experimental data were taken at 4.2 K.

a very important consequence of this simple kinetics picture was missing in Ref. 4. As the distributions of electrons in the conduction band with both the positive and negative wave vectors \mathbf{k} are nearly the same, these two reverse processes would result in nearly the same magnitude of both dip and peak in photoconductive responses. This is not the case. In fact, for both InP and GaAs the peaks are much more intense

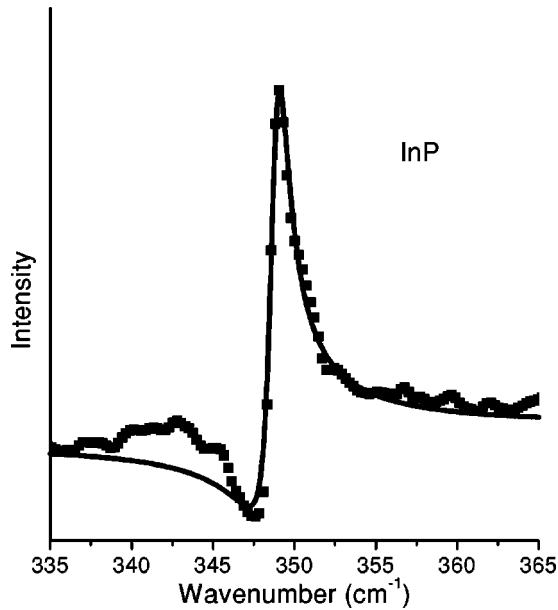


FIG. 2. The experimental photothermal ionization spectrum (solid square) and corresponding theoretical result (solid line) based upon the Fano resonance process for high purity InP epitaxial layers with shallow donors. The experimental data were taken at 4.2 K.

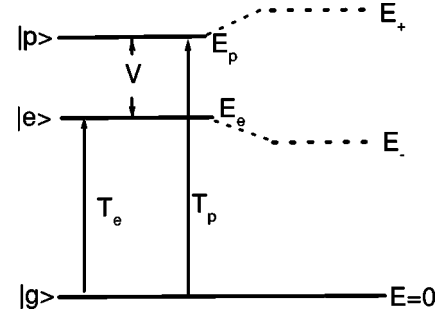


FIG. 3. A schematic illustration of the basic mechanism for the photoconductive response involving in a Fano resonance from the coupling between a ground state to conduction continuum transition and the ground state to a LO-phonon state transition.

and sharper than the dips, indicating that the positive photoconductive response is much stronger than the negative one. Therefore, such an explanation can not reproduce the unusual line shape of the observed feature. Recently a Monte Carlo simulation of the photoconductive response for GaAs based on the Stocker's kinetic mechanism has been quantitatively carried out.⁹ However, the simulation result has shown the same magnitude of the dip and peak, clearly indicating the kinetic model is not proper to understand the experimental data.

To understand this puzzling line shape, we suggest a more plausible mechanism involving a more complex Fano resonance which has been served as a model and observed in a large number of very different physical (such as atomic,⁸ molecular,¹⁰ and semiconducting¹¹⁻¹⁵) systems. In general, a Fano resonance occurs when transitions, whatever the excitation mechanism is, couple a discrete state and a continuum to a common ground state and when the discrete state is quantum-mechanically coupled to the continuum with matrix element V . The Fano resonance observed here occurs when the direct transition from a donor state to the conduction band interferes with the indirect transition from an electronic donor state to a LO-phonon state of the semiconductor.

For the system we are studying, the $1s$ donor state of the shallow impurity serves as the common ground state in the Fano resonance. As the energy of the discrete LO phonon state having the same symmetry as the photon conductive transitions falls within the conduction band continuum, interference between the phonon discrete state and the electron continuum takes place. Figure 3 schematically shows the system with two excited states coupled by a matrix element V . Suppose that $T_e = \langle N, \phi_e | H_{el}(\hbar\omega_l) | \phi_0, N \rangle$ is the direct transition matrix element of the electron from the ground state $|g\rangle = |\phi_0, N\rangle$ with the phonon number N to the continuum $|e\rangle = |\phi_e, N\rangle$ with the energy E_e . $T_p = \sum_e \langle N+1, \phi_0 | H_{ep} | \phi_e, N \rangle \langle N, \phi_e | H_{el}(\hbar\omega_l) | \phi_0, N \rangle / (\hbar\omega_l - E_e)$ is the matrix element of the indirect transition from the ground state to a phonon state $|p\rangle = |\phi_0, N+1\rangle$ with the energy $E_p = \hbar\omega_0$. $V = \langle N+1, \phi_0 | H | N, \phi_e \rangle$ is the matrix element of electron-phonon interaction. This electron-phonon coupling produce a mutual repulsion of the level E_p and E_e to positions E_{\pm} which are the roots of the secular equation $(E_0 - E)(E_e - E) - V^2 = 0$. Similar to the approximation for Ra-

man scattering in bulk semiconductor¹³ and quantum well¹⁴ systems, we assume here for simplicity that both T_e and V are both constant for each level $|e\rangle$ in the continuum. The line shape of the spectrum of the photonconductive response at LO phonon energy is proportional to

$$I(E) = \frac{\sum_{a=\pm} |\langle a|H|g\rangle|^2 \delta(E_a - E) - |\langle p|H|g\rangle|^2 \delta(E_p - E)}{|\langle e|H|g\rangle|^2}. \quad (1)$$

The second term in Eq. (1) is the rate of indirect transition from the ground state to the unperturbed phonon state, and the corresponding transition process is that an electron absorbs the photon and makes the transition to the conduction band state and immediately emits an optical phonon with the same frequency of the photon by returning to the ground state. The first term presents a photon adsorption process. In this process, an interference exists between two amplitudes for the $|g\rangle \rightarrow |e\rangle$ transition, namely between the direct transition with amplitude T_e and the indirect transition $|g\rangle \rightarrow |p\rangle \rightarrow |e\rangle$ with amplitude $T_p(E - E_p)^{-1}V$. It can be obtained by the very similar derivation done by Fano⁸ and Klein,¹³ thus Eq. (1) can be further written as

$$I(E) = D(E) \frac{(q + \varepsilon)^2}{1 + \varepsilon^2} - D(E_p) \frac{T_p^2}{T_e^2}, \quad (2)$$

where the first part in Eq. (2) is just the Fano resonant term in which $D(E)$ is the density of the continuum states

$$\varepsilon = \frac{E - E_p - V^2 R(E_p)}{\pi V^2 D(E_p)}, \quad (3)$$

and the asymmetry parameter of the Fano line shape

$$q = \frac{VT_p/T_e + V^2 R(E_p)}{\pi V^2 D(E_p)}. \quad (4)$$

The asymmetric parameter governing the line shape of the resonance is intimately linked to the transition probabilities for the discrete state and the band of unperturbed continuum states. Among them, the transition probability T_p can be expressed as $T_p = VT_e \{ \sum_e P[1/(E_p - E_e)] + i\pi \delta(E_e - E_p) \}$. The density of the electronic continuum states in the semiconductor is given as $D(E_p) = (V_0 m^* / \hbar^3 \pi^2) \sqrt{2m^*(E_p - E_b)}$, where E_b is the bottom energy of the conduction band relative to the ground state of the donor. V_0 is the bulk volume of the layer, and m^* is the effective mass of the semiconductor layer. The $R(E_p)$ can be obtained as $R(E_p) = (V_0 m^* / \hbar^2 \pi^2) [k_p \ln|(\Delta k + k_p)/(\Delta k - k_p)| - 2\Delta k]$, where $k_p = \sqrt{2(E_p - E_b)m^*/\hbar}$, and Δk represents the range of the electronic wave number associated with the photoelectron transition from the ground state to the conduction band, which can be estimated by using the uncertainty principle,

i.e., $\Delta k \approx 1/4R$, where R is the radius of the $1s$ orbital of the donor. From above equations, we can obtain the asymmetry parameter q of the Fano shape as

$$q = \frac{2}{\pi} \ln \left| \frac{\Delta k + k_p}{\Delta k - k_p} \right| - \frac{4}{\pi} \frac{\Delta k}{k_p} + i. \quad (5)$$

For the present systems q depends only on the material parameters, i.e., the effective mass, the LO phonon energy of the semiconductor, the effective radius of the donor orbital, and the bottom energy of the semiconductor layer relative to the $1s$ ground state of the donor. In our calculations, we used all these parameters from the text book or experimental data^{2,4} without any adjustment, $m^* = 0.067m_e$ for GaAs and $0.08m_e$ for InP, $R = 104 \text{ \AA}$ for GaAs and 82 \AA for InP, $E_b = 65 \text{ cm}^{-1}$ for GaAs and 60 cm^{-1} for InP, $\hbar\omega_{\text{LO}} = 294.5 \text{ cm}^{-1}$ for GaAs and 349.5 cm^{-1} for InP. q can be calculated as 1.9 for GaAs and 1.78 for InP. The second term in Eq. (2) can be further obtained as $D(E_p)(T_p/T_e) = D(E_p)V^2[R(E_p) + D(E_p)]^2$. It is obviously that this only reduces the absolute value of the photoconductive response, in the other words, it does not make any change of its line shape. The final theoretical results, as shown in both Figs. 1 and 2, are in excellent agreement with the experimental data, indicating the Fano resonance process is the true origin for the observed photoconductive features. A small discrepancy between the theoretical and experimental results around the frequency range just below the dip for either GaAs or InP is due to the theoretical renormalization by the direct transition contributions, resulting in the exclusion of irrelevant transitions appearing in the experimental data.

In summary, we observed an abnormal positive photoconductive response in the vicinity of LO-phonon energy in the semiconductor epitaxial layers with shallow donors. We showed that such a strong positive rather than negative response is indeed due to a Fano resonance process associated with the coupling between LO-phonon and electron continuum. The Fano resonance enhances greatly the electronic transition from a donor state to an electron continuum, thus leading to the unusual photoconductive feature with asymmetric line shape. The theoretical results based on the present mechanism are in excellent agreement with the experimental data, which demonstrates that Fano resonance reveals, in a clear and intuitive way, the nature of LO phonon-induced photoconductivity. We believe that the new quantum mechanical formalism developed here should be universally applicable to the related photoconductive processes in all doped semiconductors. More importantly, the mechanism of photoconductivity proposed here may be valuable for potential optoelectronic applications.

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- *Corresponding author. Lund University, Department of Physics, Solid State Theory, Slvegatan 14 A, S-223 62 Lund, Sweden; FAX: (+46) 046-2224438.
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