Transient transition from free carrier metallic state to exciton insulating state in GaAs by ultrafast photoexcitation

X C Nie¹, Hai-Ying Song¹, Hai-Xiang Zhang¹, Peng Gu¹, Shi-Bing Liu¹, Fan Li¹, Jian-Qiao Meng¹, Yu-Xia Duan⁴ and H Y Liu⁴

1 Strong-field and Ultrafast Photonics Lab, Institute of Laser Engineering, Beijing University of Technology, Beijing 100124, People’s Republic of China
2 Department of Chemistry and Chemical Engineering, College of Environmental and Energy Engineering, Beijing University of Technology, Beijing 100124, People’s Republic of China
3 Hunan Key Laboratory of Super-microstructure and Ultrafast Process, School of Physics and Electronics, Central South University, Changsha, Hunan 410083, People’s Republic of China
4 School of Physics and Electronics, Central South University, Changsha, Hunan 410083, People’s Republic of China

E-mail: haiyun.liu@bjut.edu.cn

Keywords: exciton, metal–insulator transition, ultrafast pump–probe spectroscopy

Abstract

We present systematic studies of the transient dynamics of GaAs by ultrafast time-resolved reflectivity. In photoexcited non-equilibrium states, we found a sign reverse in reflectivity change $\Delta R / R$, from positive around room temperature to negative at cryogenic temperatures. The former corresponds to a free carrier metallic state, while the latter is attributed to an exciton insulating state, in which the transient electronic properties is mostly dominated by excitons, resulting in a transient metal–insulator transition (MIT). Two transition temperatures ($T_1$ and $T_2$) are well identified by analyzing the intensity change of the transient reflectivity. We found that photoexcited MIT starts emerging at $T_1$ as high as $\sim 230$ K, in terms of a dip feature at 0.4 ps, and becomes stabilized below $T_2$ that is up to $\sim 180$ K, associated with a negative constant after 40 ps. Our results address a phase diagram that provides a framework for the inducing of MIT through temperature and photoexcitation, and may shed light on the understanding of light–semiconductor interaction and exciton physics.

1. Introduction

Metal–insulator transition (MIT) has been of great interest for the past half century in different branches of condensed matter physics, ranging from semiconductors to strongly correlated electronic systems [1, 2]. It is of great value in fundamental quantum many–body physics in solids [3]. By implementing ultrafast photoexcitation, a growing interest has been devoted to light–induced MIT in strongly correlated systems, through melting of charge-density-wave (CDW) in low–dimensional CDW crystals [4–6], resonant phonon–driven in manganites [7, 8], etc. In semiconductors, transient MIT can be induced by the interplay between free carriers and excitons, for example, a exciton-dominated abrupt change was experimentally found in photoluminescence dynamics below 49 K in GaAs [9]. Further researches have explored the formation dynamics of excitons and exciton Mott transition in GaAs quantum wells [10–15], Si [16–18] and Ge [19] by time–resolved spectroscopy.

GaAs is a typical direct band-gap semiconductor with a face-centered cubic Bravais lattice [20, 21], as shown in figure 1(a). Both the top of the valence band (TVB) and the bottom of the conduction band (BCB) lie at $\Gamma$ (where $\Gamma$ is the center of the first Brillouin zone). It is well known that exciting GaAs by near–infrared photons above the band-gap around room temperature generates hot free carriers including free electrons in TVB and holes in BCB, resulting in a transient metallic state. Unlike free carriers, excitons are pairs of electrons and holes in semiconductors, which can be operated in optoelectronic devices, for example, excitonic integrated circuit for signal processing and communication through the direct transform between photons and excitons [22]. More interestingly, exciton–mediated superconductivity has been proposed in heterostructures based on semiconductors [23, 24], indicating a way of realizing light–induced superconductivity in 2D semiconductor
crystals [25]. It is of importance to conduct comprehensive investigation on the interplay between photons, free carriers and excitons, and their contributions to physical properties.

In this paper we present systematic studies of the dynamics of photoexcited free carriers and excitons in bulk n-type GaAs (100), in a wide range of lattice temperatures and excitation densities. We observe a transient MIT in the system, i.e., from a free carrier metallic state to an exciton insulating state, by decreasing temperature. The exciton insulating state starts emerging and gets stabilized at unexpected temperatures as high as \( \sim 230 \text{ K} \) and \( \sim 180 \text{ K} \), respectively. In addition, our results reveal that photoexcitation can effectively induce MIT in semiconductors, providing a way for the control of MIT and the understanding of exciton physics in semiconductors.

2. Results

Ultrafast time-resolved reflectivity based on femtosecond laser is employed to elucidate the electronic dynamics of n-type GaAs (100), doped by Si with carrier level at \( \sim 10^{17} \text{ cm}^{-3} \). The sample size is about \( 3 \times 3 \times 0.4 \text{ mm} \). The optical pulses were generated by a Ti:sapphire laser amplifier system (repetition rate of 1 kHz, pulse duration at 35 fs and central wavelength of 800 nm) and splitted by a beam splitter into intense pump and weak probe pulses. The pump and probe excitation densities are 0.05–0.36 mJ cm\(^{-2}\) (i.e. 1.3–9.6 \( \times 10^{19} \) photos cm\(^{-2}\), taking into account the penetration depth \( \sim 150 \text{ nm} \) of the 800 nm laser beam) and 4 \( \mu \text{j} \text{ cm}^{-2} \) respectively. Both pump and probe were focused onto the sample, with spot sizes at \( \sim 0.4 \text{ mm} \) (pump) and \( \sim 0.2 \text{ mm} \) (probe) in diameter. The reflected probe signal was collected by a Si-based detector and a lock-in amplifier. The temporal evolution of the pump-induced change in the probe reflectivity (\( \Delta R \)) was measured by scanning the delay time between pump and probe pulses, using a motorized delay line. The sample was mounted on a cryostat with a temperature sensor embedded close by, allowing a precise control of temperature in the range of 6–300 K.
Figure 1(b) shows the mechanism of ultrafast time-resolved reflectivity. The system is excited by a pump beam to non-equilibrium states and tracked by a subsequent probe beam. The reflectivity change of probe is collected to study the transient dynamics of the system, such as light-induced phase transition, electron scattering process, collective modes and so on. Figure 1(c) shows time-resolved reflectivity changes induced by photoexcitation for different pump fluences at lattice temperatures of 6 K and 300 K, respectively. At room temperature, all transient reflectivity changes indicate a metallic feature in terms of $\Delta R/R > 0$, owing to the above-gap excitation in which the pump photon energy (1.55 eV) is greater than the direct band-gap ($E_{\text{gap}} \sim 1.42$ eV) in GaAs. The absorption of pump photons generates a large number of hot free carriers, including free electrons in the conduction band and holes in the valence band in non-equilibrium states [26], giving rise to a rapid increase of transient reflectivity [27, 28]. The reflectivity curves at 300 K show a rise edge immediately after photoexcitation, followed by a peak feature around 1 ps, indicating a non-thermal carrier re-distribution. Subsequent transient reflectivity rapidly decreases, corresponding to a thermalize process, in which the photoexcited electrons and holes thermalize among themselves into a Fermi–Dirac distribution, with temperatures that are typically higher than that of the lattice, in a few hundreds of femtoseconds primarily via carrier–carrier scattering [29, 30]. Within a couple of picoseconds the electrons and holes then thermalize with each other to reach a common temperature via electron–hole scattering [31]. Then the transient reflectivity change decays back to a positive constant after 40 ps, corresponding to the cooling process, in which the thermalized carrier distribution continues to cool to the lattice temperature by further interactions of the carriers with the lattice primarily via carrier–phonon scattering [32–34]. The constant shows no change in our measurement for up to 300 ps, suggesting a stable transient metal stable phase. This is most likely due to a carrier heat diffusion process or an interband relaxation process, in which electron–hole pairs recombine by either radiatively (emitting photons) on a time scale of hundreds of picoseconds to nanoseconds in direct-gap semiconductors or non-radiatively, such as Auger recombination or carrier trapping, within tens to hundreds of picoseconds depending on the carrier density. On the other hand, we observe a sign reverse to negative for the transient reflectivity change at 6 K ($\Delta R/R < 0$) after photoexcitation, consisting of a well-defined dip feature at 0.4 ps and a negative constant from 40 ps to more than hundreds of ps, indicating a new non-equilibrium phase distinct from the transient metallic state at 300 K.

In order to investigate the sign reverse and the corresponding dynamics in detail, we performed temperature-dependent experiments for pump fluence at 0.05, 0.16, 0.22 and 0.36 mJ cm$^{-2}$, as depicted in figures 2(a)–(d). The peak feature at $\sim$1 ps and the positive constant around 300 K become suppressed with decreasing temperature and vanishes below 150 K. In the meanwhile, a negative dip at $\sim$ 0.4 ps starts emerging at $\sim$ 200 K (figures 2(b) and 2(c)) and gets enhanced in the cooling process, with a negative constant at lower temperature. As conveyed by figures 2(e)–(h), the intensity changes of transient reflectivity as a function of temperature are selectively extracted for delay times at 0.4, 50 and 100 ps. The curves for 50 and 100 ps are coincident with each other, confirming a long-surviving transient state. Two critical temperatures are identified by crossing to the zero baseline: Firstly, the negative dip at 0.4 ps $\Delta R/R < 0$ ($t = 0.4$ ps) emerges around $T_1$; Secondly, the damped negative constant $\Delta R/R < 0$ ($t \geqslant 50$ ps) forms below $T_2$. It is interesting to note that, in the region between $T_1$ and $T_2$, we find the change of reflectivity first produces a negative dip at 0.4 ps, which damps into a positive constant, suggesting a possibly composite state. To investigate the dynamics of the dip at 0.4 ps right after pump stimulation, we primely fit the relaxation processes by exponential functions, as indicated by the black dotted lines in figures 3(a)–(d). We found that above $T_1$, the curves have to be fitted by a double-exponential function containing a fast decay ($\sim 1$ ps) and a slow decay ($\sim 10$ ps), while below $T_1$ the fast decay elongates after 0.4 ps and the curves can be well fitted by a single-exponential function. The decay time curves as a function of temperature $\tau(T)$ in figures 2(e)–(h) show slope changes around $T_1$ and $T_2$, suggesting different dynamical origins below and above the transition temperatures.

Figure 3 presents the influence of excitation density, by varying pump fluence from few percent to 0.36 mJ cm$^{-2}$, at fixed temperatures of 300, 150 and 6 K. For $t > 0$, $\Delta R/R$ is constantly positive at 300 K (figure 3(a)) and increases with increasing pump fluence, while $\Delta R/R$ is all negative at 6 K (figure 3(c)) and shows a opposite behavior with increasing pump fluence. Remarkably, at 150 K (figure 3(b)), the variation of pump fluence induces a sign reverse of $\Delta R/R$ from positive to negative, suggesting a light-control of transient phase transition. Qualitatively analysis of $\Delta R/R$ at 0.4 and 50 ps are shown in figures 3(d) and (e). Obviously, the intensity changes of transient reflectivity for 300 K get enhanced below 0.11 mJ cm$^{-2}$ with a linear dispersion and saturate at higher pump fluence. At 150 K, the intensity changes of transient reflectivity start a positive-negative reverse at 0.11 mJ cm$^{-2}$ in terms of the dip feature at 0.4 ps, and completely turn to negative above 0.22 mJ cm$^{-2}$ characterized by the flat feature around 50 ps. For 6 K, the first negative dip at 0.4 ps linearly increases its magnitude while the damped constant (around 50 ps) saturates above 0.15 mJ cm$^{-2}$. The decay time of the fast dynamics within 10 ps at 6 K linearly increases from 1.3 to 2.7 ps with increasing pump fluence, as indicated in figure 3(f).
Figure 2. Time-dependent reflectivities of GaAs. (a)–(d) Transient reflectivity changes as a function of pump-probe delay measured at various temperatures, for pump fluences at 0.05, 0.16, 0.22 and 0.36 mJ cm$^{-2}$, respectively. The black dashed lines are exponential fits to 10 ps. (e)–(h) Intensity changes of transient reflectivity at the delay time of 0.4 ps (blue circles), 50 ps (red triangles) and 100 ps (brown open squares) as a function of temperature. The pink circles are decay time constant $\tau$ for the 0.4 ps dip feature obtained by fitting curves in (a)–(d). The black arrows mark two critical temperatures $T_1$ and $T_2$, at which the changes of transient reflectivity vary from positive to negative.

Figure 3. Transient reflectivity changes of GaAs after a series of excitation fluence at temperatures 300 K (a), 150 K (b) and 6 K (c). (d) and (e) Typical intensity changes at delay times 0.4 and 50 ps as a function of pump fluence, for different temperatures of 6 K (red squares), 150 K (brown triangles) and 300 K (blue circles), respectively. (f) Decay time constant of the dip feature at 0.4 ps at 6 K by exponential fits. The red line is used to guide the linear increment. The error bars are obtained from fits.
measurements by varying excitation wavelength from 785 to 815 nm, using narrow band pass filters. Light-induced free carriers (b) and exciton (c) in a direct band-gap semiconductor. (d) Phase diagram of GaAs, with constant error bars of ±10 K to guide the eye. \( T_1 \) is the starting temperature of free carrier/exciton composite state, and \( T_2 \) is the exciton stable temperature. The color-areas are obtained by parabolic fits of \( T_1 \) and \( T_2 \) as a function of pump fluence. The left insets illustrate photoexcited free carriers and excitons (electron–hole pairs). The inset curves on the right side are typical transient reflectivity changes in different phase regions.

3. Discussion

We now turn to the interpretation of the negative reflectivity changes (\( \Delta R/R < 0 \)) at cryogenic temperatures. One possibility is high-energy carriers by multi-photon absorption, similar to second harmonic pumping, which produces occupied high-energy conduction band states above the probe frequency, resulting in reduced dielectric function and reflectivity at the probe frequency [28]. However such a reason can be excluded since the lifetime of the occupation of high-energy conduction band states is less than 2 ps as observed in [28], due to fast intraband scattering, much less than the long-time state for at least hundreds of ps observed in our experiments. The fact that the sign reverse is temperature-dependent at weak excitation density (figure 2(a)), suggests an intrinsic phase transition rather than the multi-photon absorption mechanism.

In order to check further the role of the excitation energy on \( \Delta R/R \) time evolution we performed few measurements by varying excitation wavelength from 785 to 815 nm, using narrow band pass filters, with pump fluence at 0.14 mJ cm\(^{-2}\). Considering the energy differences are 58 meV (between 785 and 815 nm) and 28 meV (between 800 nm and 815 nm), we chose two temperatures at 204 and 123 K with bandgaps smaller than 815 nm by such differences. As shown in figure 4(a), \( \Delta R/R \) curves have almost no changes with different excitations, indicating that the result is insensitive to the energy difference (at least 58 meV) between bandgap and excitation in our wavelength regime.

Around room temperature, above-gap excitation by 800 nm (1.55 eV) effectively produces hot free carriers, as shown in figure 4(b). The band-gap increases up to \( \sim 1.52 \) eV upon cooling to 6 K, in which excitons play a major role after photoexcitation. As shown in figure 4(c), an exciton is a photon-excited heavy electron–hole pair glued by the Coulomb interaction [21, 35, 36]. Excitons may be easily thermalized to free carriers at room temperature by absorbing lattice energy, which is much higher than the exciton binding energy. Without the Coulomb interaction and exciton contribution, the light absorption coefficient of semiconductors with a direct band-gap can be simply described by the function \( \alpha(\hbar \omega) \propto \sqrt{\hbar \omega - E_{\text{gap}}} \), for \( \hbar \omega > E_{\text{gap}} \). However, at cryogenic temperatures when the band-gap enlarges and the lattice energy becomes comparable or even smaller than the exciton binding energy, exciton survives and contributes to a robust peak in the vicinity of the band edge [37]. In contrast to free carriers, an exciton can be treated as an hydrogen-like bosonic particle [38], with exciton Bohr radius of 11 nm for GaAs [39], leading to reduced conductivity and optical reflectivity, which are typically transient insulating behaviors. Accordingly, the photon-induced transient state characterized by \( \Delta R/R < 0 \) (\( t > 0 \)) can be attributed to an exciton insulating state. The dip at 0.4 ps is probably due to the ultrafast formation...
of intense exciton density after light irradiation, which decays into a constant probably by the interaction with lattice, corresponding to the exponential fits shown in figure 3(f).

Figure 4(d) summarizes the phase diagram of GaAs by extracting transition temperatures $T_1$ and $T_2$ from our results in figure 2. The dome-like phase diagram consists of three regimes: (1) above $T_1$, photoexcitation effectively produces free carriers, giving rise to positive $\Delta R/R$ and a free carrier metallic state; (2) below $T_2$ is a transient exciton insulating state, in which the system holds a transient insulating property with negative $\Delta R/R$, due to the population and stabilization of excitons; (3) between $T_1$ and $T_2$, pump pulses immediately stimulates a fast negative dip at $\sim 0.4$ ps in $\Delta R/R$, which decays into a constant positive, noted as exciton and free carrier composite state in which excitons and electrons coexist/compete with each other. The optimal pump fluence is between 0.15 and 0.2 mJ cm$^{-2}$, where $T_1$ and $T_2$ reach their maximums ($\sim 230$ and 180 K). Below 0.15 mJ cm$^{-2}$ both $T_1$ and $T_2$ drop rapidly due to the generation of only weak exciton density, while above 0.2 mJ cm$^{-2}$ they decrease probably due to the approaching of Mott density. The fact that the insulating state emerges when the metallic state is suppressed below $T_2$, as shown in figure 3(b), provides a possible way of control MIT by photoexcitation in semiconductors.

4. Conclusion

In our measurements, $T_1$ and $T_2$ are found to be as high as $\sim 230$ K and $\sim 180$ K, respectively, in sharp contrast to the exciton insulating temperature previously observed at 49 K [9]. The difference is probably due to that highly intense pump pulses in our case induce high density of exciton, which elongates the exciton lifetime (figure 3(f)), and stabilizes the exciton insulating state, while low excitation density causes only uncorrelated excitons [40, 41], yet theoretical work for such a light-enhanced exciton insulating state is required.

In conclusion, we have investigated the transient dynamics in GaAs by ultrafast pump-probe optical reflectivity. Our results reveal that ultrafast photons effectively populate free carriers and excitons above $T_1$ and below $T_2$, giving rise to transient metallic and insulating states, respectively. We find that MIT can be induced by varying either temperature or excitation density. More quantum effects induced by the overlap of exciton wave functions at high exciton densities, such as biexciton, exciton Mott transition and Bose–Einstein condensation, require further ultrafast experiments and theoretical studies on semiconductors.

Acknowledgments

The authors gratefully acknowledge support from the National Natural Science Foundation of China (Grant No. 51705009) and NSAF of China (Grant No. U1530153). H Y Liu thanks the Sea Poly Project of Beijing Overseas Talents (SPPBOT).

ORCID iDs

Hai-Ying Song @ https://orcid.org/0000-0001-7454-0542

References

[1] Mott N F 1968 Rev. Mod. Phys. 40 677[10]
[2] Mott N F 1973 Contemp. Phys. 14 401
[3] Chemla D S and Shah J 2001 Nature 411 549
[4] Tomelj A, Schäfer H, Städtler D, Beyer M, Biljakovic K and Demsar J 2009 Phys. Rev. Lett. 102 066404
[5] Petersen J C et al 2011 Phys. Rev. Lett. 107 177402
[6] Liu H Y et al 2013 Phys. Rev. B 88 045104
[7] Polli D, Rini M, Wall S, Schoenlein R W, Tomioka Y, Tokura Y, Cerullo G and Cavalleri A 2007 Nat. Mater. 6 645
[8] Tobey R I, Prabhakaran D, Boothroyd A T and Cavalleri A 2008 Phys. Rev. Lett. 101 197404
[9] Amo A, Martin M D and Viña I 2006 Phys. Rev. B 73 035205
[10] Zhang Q, Wang Y R, Gao W L, Long Z Q, Watson J D, Manfra M J, Belyanin A and Kono J 2016 Phys. Rev. B 94 104510
[11] Petersen J C et al 2011 Phys. Rev. Lett. 107 177402
[12] Yoon H W, Sturge M D and Pfeiffer LN 1997 Solid State Commun. 104 287
[13] Kappei L, Szczytko J, Morier-Genoud F and Deveaud B 2005 Phys. Rev. Lett. 94 147403
[14] Rossbach G, Levrat J, Jacopin G, Shahmohammadi M, Carlin J-F, Ganière J-D, Butté R, Deveaud B and Grandjean N 2014 Phys. Rev. B 90 201308(R)
[15] Manzke G, Semkat D and Stolz H 2012 New J. Phys. 14 095002
[16] Suzuki T and Shimano R 2009 Phys. Rev. Lett. 103 057401
[17] Suzuki T and Shimano R 2012 Phys. Rev. Lett. 109 046402
[18] Suzuki T and Shimano R 2011 Phys. Rev. B 83 085207
[19] Sekiguchi F and Shimano R 2015 Phys. Rev. B 91 155202
[20] Blakemore J S 1982 J. Appl. Phys. 53 R123
[21] Harrison P and Valavanis A 2016 Quantum Wells, Wires and Dots: Theoretical and Computational Physics of Semiconductor Nanostructures (New York: Wiley)
[22] High A A, Novitskaya E E, Butov I V, Hanson M and Gossard A S 2008 Science 321 229
[23] Allender D, Bray J and Bardeen J 1973 Phys. Rev. B 7 1020
[24] Cotlet O, Zejtinoglou S, Sigrist M, Demler E and Imamoglu A 2016 Phys. Rev. B 93 054510
[25] Kavokin A and Lagoudakis P 2016 Nat. Mater. 15 599
[26] Othonos A 1998 J. Appl. Phys. 83 1789
[27] Shank C V, Auston D H, Ippen E P and Teschke O 1978 Solid State Commun. 26 567
[28] Auston D H 1978 Solid-State Electron. 21 147
[29] Nuss M C, Auston D H and Capasso F 1987 Phys. Rev. Lett. 58 2355
[30] Lin W Z, Fujimoto L G, Ippen E P and Logan R A 1987 Appl. Phys. Lett. 50 124
[31] Shah J 1999 Ultrafast Spectroscopy of Semiconductors and Semiconductor Nanostructures (Berlin: Springer)
[32] Cho G C, Kutt W and Kurz H 1990 Phys. Rev. Lett. 65 764
[33] Kash J A, Tsang J C and Hvam J M 1985 Phys. Rev. Lett. 54 2151
[34] Kuznetsov A V and Stanton C J 1995 Phys. Rev. B 51 7555
[35] Frenkel J 1931 Phys. Rev. 37 1276
[36] Wannier G H 1937 Phys. Rev. 52 191
[37] Sturge M D 1962 Phys. Rev. 127 768
[38] Keldysh L V and Kozlov A N 1968 Sov. Phys.—JETP 27 521
[39] Yu P Y and Cardona M 2010 Fundamentals of Semiconductors: Physics and Materials Properties (Berlin: Springer) p 282
[40] Fehrenbach G W, Schafer W, Treusch J and Ulbrich R G 1982 Phys. Rev. Lett. 49 1281
[41] Prasankumar R P, Upadhyya P C and Taylor A J 2009 Phys. Status Solidi b 246 1973