REVIEW ARTICLE

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Ultrafast Spectroscopy of Semiconductors: A Review on Experimental Methods

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Abstract

The advancement of picosecond and femtosecond pulsed lasers made optical spectroscopy a more powerful tool that has been used in the fields of physics, chemistry, and biology. This method is mainly used to study the dynamical properties of various substances such as metals, semiconductors, and superconductors. Ultrafast non-equilibrium carrier excitation of the semiconductor and subsequent relaxation processes occurring on different time scales have become an important area of semiconductor research. Numerous experimental approaches have been employed to explore these dynamic processes in both semiconductors and their nanostructured. In this article, we have discussed dynamic phenomena that occur in optically excited semiconductors on time scales from a few hundred femtoseconds to nanoseconds. Among the most widely employed experimental techniques is the ultrafast pump-probe technique, which makes it easier to investigate dynamical phenomena in semiconductors. This article provides a comprehensive explanation of the basic principles underlying the ultrafast pump-probe technique. Additionally, it highlights significant experimental discoveries obtained through the investigation of semiconductor quantum wells and quantum dots.

Keywords: Ultrafast spectroscopy, Pump-probe spectroscopy, Quantum dots, Quantum wells.

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Introduction

Optical spectroscopy is a powerful technique to investigate optical, electronic, and vibrational properties of various materials including metals, semiconductors, and superconductors. One can get invaluable information on many aspects such as electronic band structures, phonons, coupled phonon-plasma modes, single particle excitation spectra of electrons and holes, and properties of defects, surface, and interfaces by using the popular techniques including absorption, reflection, luminescence, and light-scattering spectroscopies.[1-7] Optical spectroscopy became more powerful after the invention of picosecond and femtosecond pulsed lasers. Ultrafast spectroscopy has become a prominent way to investigate nonequilibrium, non-linear and transport properties of bulk and semiconductor nanostructures.[1] In the past these have been extensively investigated using continuous wave (CW) spectroscopies[8] and after the invention of ultrashort lasers, fundamental dynamical processes related to energy relaxation and thermalization of photo-excited carriers[9] have been studied in a nanosecond (ns) to a few femtoseconds (fs) time scales. Investigations of optical properties of bulk and semiconductor nanostructures reveal the most basic processes in the solid-state physics such as scattering with acoustic and optical phonons and exciton-exciton interaction,[10,11] dephasing dynamics,[12] coherent oscillations,[13] quantum beats,[14] etc. have been intensively studied in a GaAs-based semiconductors. Experimental techniques such as Pump-Probe Reflectivity/Transmissivity,[2,15-17] Excitation correlation spectroscopy have been developed to investigate the dynamics of photo-excited carriers in semiconductors. The nonlinear optical properties of semiconductors have been also studied by using these experiments. This review paper aims to explore various ultrafast experimental methods utilized for studying the dynamical phenomena in semiconductors and semiconductor nanostructures. Some of these techniques focus on providing insights into coherent dynamics, while others use to explore incoherent dynamics. There are certain techniques that offer information about both coherent and incoherent dynamics.

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Optical Excitation of Semiconductor

In a typical semiconductor, the conduction and valence bands are separated by a bandgap energy (Eg) that

corresponds to a photon energy (ħω) falling within the range of near infrared (IR) to near ultraviolet (UV) region. Under equilibrium conditions at low temperature, the valence band is occupied by electrons while the conduction band remains empty. When a light with an energy equal to or greater than the band gap is incident upon a semiconducting material, the photons are absorbed by the material. Consequently, some of the electrons in the valence band are excited to the conduction band, creating a hole (an electron vacancy) in the valence band. The behavior of this electron-hole pair is significantly influenced by the Coulomb interaction. The Coulomb interaction between the electron and hole leads to the formation of an exciton, which can be likened to a hydrogen atom-like quasiparticle.[18-20]

Time-resolved ultrafast optical spectroscopic techniques are utilized for the examination of carrier dynamics in semiconductors. These techniques involve the use of ultrashort laser pulses, typically 100 femtoseconds, to optically excite the semiconductors. By employing laser pulses with energy higher than the bandgap energy, a non-equilibrium population of electrons and holes is generated in the conduction and valence bands, respectively. The presence of strong Coulomb interaction among the charged carriers leads to a rapid randomization of momentum within a time scale of less than 100 femtoseconds.[21] Even after momentum randomization, the carrier distribution remains non-thermal. Various scattering processes, including carrier-carrier and carrier-phonon scattering, defect scattering, and carrier capture,[22-25] contribute to the redistribution of energy within the carrier population, ultimately bringing the system to a state of thermal equilibrium characterized by a temperature. Generally, carrier thermalization occurs within a time scale of a few picoseconds (ps). However, the exact thermalization time depends on several factors, such as carrier density, band structure, and the strength of interaction with phonons. Despite reaching thermal equilibrium, the thermalized carriers may still possess a significant excess energy, and the temperature of the carrier distribution function is typically higher than the lattice temperature. Moreover, the temperature can differ between the subsystems of electrons and holes. The hot carriers endeavor to equilibrate with the lattice by interacting with various phonon modes of the semiconductor. The carrier temperature gradually approaches the lattice temperature within a time scale ranging from 1 to 100 ps. Investigating the dynamics of hot carrier cooling provides valuable insights into the processes of carrier-carrier, carrier-phonon, and phonon-phonon scattering.[26, 27] Eventually, in the isothermal regime, all carriers and phonons reach a state of equilibrium with each other, characterized by a common temperature known as the lattice temperature. However, the system is still not in the thermodynamic equilibrium state as there are excess electron and hole populations compared to the thermodynamic equilibrium state of the semiconductor. The recombination of free electron-hole pairs and excitons occurs through either radiative or non-radiative processes, ultimately leading the semiconductor to return to its thermodynamic equilibrium within a time frame ranging from hundreds of picoseconds to a few nanoseconds.[24, 28, 29]

Ultrafast Experimental Techniques

Following the photoexcitation with ultrafast laser pulses, a range of steady-state and dynamical processes take place in semiconductor nanostructures such as multi-quantum-wells (MQWs) GaAs and InAs quantum-dots (QDs), as mentioned earlier. To explore the non-equilibrium carrier dynamics and dephasing dynamics of the carrier, various experimental techniques have been widely employed, including excitation correlation spectroscopy (ECS)[30] and pump probe reflectivity/transmittivity.[31] The details of these experiments are covered in the section that follows, along with an explanation of their underlying theories and the detection systems used to examine the signal.

Time-resolved ultrafast pump-probe spectroscopy

Pump-probe spectroscopy is a highly effective method employed to investigate the behavior of carriers in semiconductors and other materials within the time range of picoseconds to nanoseconds.[1,15-17, 31-33] In a pump-probe experiment, a pump pulse, which is a laser pulse with high intensity, is directed onto the sample to excite the carriers, resulting in a non-equilibrium state. Consequently, the optical properties of the irradiated region of the sample, including refractive index, absorption, reflectivity, and transmittivity, undergo changes. These pump-induced alterations can be examined by a delayed weak pulse known as the probe pulse. By analyzing the modulated reflectivity or transmittivity of the probe pulse as a function of the delay between the pump and the probe, valuable insights into the various relaxation processes occurring in the sample within the picosecond to nanosecond time scale can be obtained. In pump-probe spectroscopy, two primary geometrical configurations are commonly utilized: pump-probe differential reflectivity (PPDR) and pump-probe differential transmission (PPDT). Both configurations provide valuable information regarding carrier dynamics in both coherent and incoherent regimes.

The majority of pump-probe experiments are conducted using either reflection geometry or transmission geometry. Figure 1 illustrates a conventional and standard setup for pump-probe differential reflectivity (PPDR). In this setup, a femtosecond laser pulse is emitted from a Ti: sapphire laser system and divided into two beams, namely the pump beam and the probe beam, using a 50/50 beam splitter (BS). The pump beam passes through a retroreflector that is mounted on a computer-controlled motorized translation stage. By adjusting the position of the retroreflector on the translation stage, an additional optical path difference (delay) is introduced between the pump and probe pulses. The average intensities of the pump and probe beams are

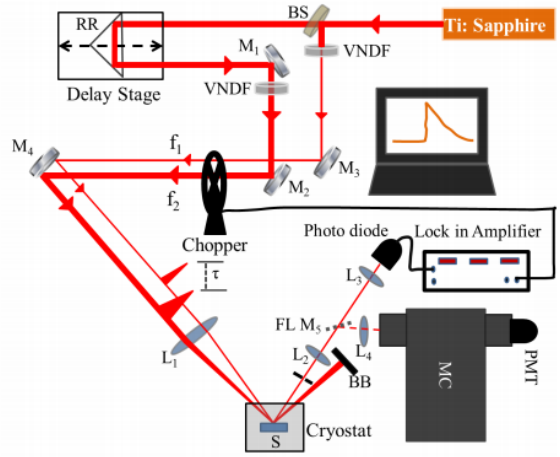

Figure 1: Schematic diagram of the Pump-probe differential reflectivity setup. Symbols: BS:-Beam Splitter, M1-M4: -Mirrors, FL M5 :-Flip Mirror, VNDF:- Variable Neutral Density Filter, RR:- Retro Reflector, f1 and f2: chopping frequency, L1-L4: Lenses, BB:- Beam Blocker, MC:-Monochromator, S:- Sample.[31]

controlled using a variable neutral density filter (VNDF). The intensity ratio of the probe beam to the pump beam is maintained at approximately 1:10. It is worth noting that the influence of the probe beam is intentionally kept lower than that of the pump beam to prevent excessive excitation of the sample. Both the pump and probe beams are focused onto the sample using a single lens (L1). The reflected probe beam from the sample is collected by a Si photodiode, and the signal from the photodiode is then sent to a lock-in amplifier. The pump-probe differential reflectivity ($\Delta R = R_{0n} - R_{off}$) signal, where R_{on} (R_{off}) represents the reflectivity in the presence (absence) of the pump beam, is measured using lock-in detection technique. To calculate $\Delta R/R_0$, the reflectivity of the probe beam (R_0) is measured by chopping the probe beam in the absence of the pump beam. This ΔR signal represents the time and spectrally integrated pump-probe differential signal. Additionally, the ΔR signal can be dispersed into a monochromator to perform a spectrally resolved pump-probe reflectivity (SRPPR) measurement.[31]

Figure 2, adopted from the reference,[34] illustrates the temporal evolution of the differential reflectivity signal obtained from a GaAs multi quantum wells (MQWs) sample with a thickness of 17.5 nm, measured at a temperature of 4 K. The signal comprises two main components: one exhibiting a rapid decay that persists for up to 15 ps, and another displaying a slower decay that can be observed for up to 100 ps. To analyze the experimental data, a double decay function was employed for fitting. The exponential fit outcome suggests that the coherence process signature experiences a rapid decay with a rate of approximately 0.8 ps. On the other hand, the dynamics of the signal are elucidated by the interactions between radiative excitons prior to their radiative recombination, which takes place in a typical time of about 2 ps, representing the lifetime of the incoherent heavy-hole exciton.

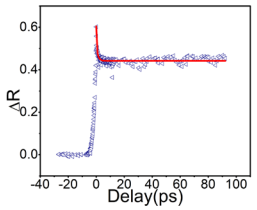

Figure 2: The typical time evaluation of differential pump-probe reflectivity signal for heavy-hole exciton observed on 17.5 nm GaAs MQWs sample. Red line represents the double exponential fit to extract the coherence phenomena and life time of heavy-hole-exciton.[34]

Excitation Correlation Spectroscopy (ECS)

The picosecond excitation correlation spectroscopy (ECS)[30] is another powerful technique to investigate carrier dynamics in semiconductors and their nano-structures. This technique has been used in the past to study hot carrier cooling and recombination dynamics.[35-40] ECS specifically probes the time-resolved dynamics of the nonlinear photoluminescence (PL) signal. This technique is similar to the pump-probe spectroscopy, the only major difference is that the correlation in PL signal from pump and probe pulses is measured as a function of delay. Both excitation beam (pump and probe) has the same intensity in this technique. The delay between the two pump-pulses is introduced by the variable delay stage. It is suitable to monitor any nonlinear processes in carrier dynamics. The main features of this technique are (i) the number of photons incident on the sample is constant over one cycle of the laser pulse regardless of the set delay (τ) between the two excitation pulses, (ii) the array detector measures the spectrally-resolved but time-integrated (over many cycles of laser pulses) PL signal emanating from the sample at a given delay, (iii) the measurement is repeated as a function of delay to get the time evolution of the signal.[30] The EC signal is defined as[30]

$$EC(\tau, \hbar\omega) = PL_{12}(\tau, \hbar\omega) - PL_{12}(\tau = 0, \hbar\omega)$$

where, $PL_{12}(\tau, \hbar\omega)$ is the steady-state PL signal measured at an energy with a delay between both beam incident on the sample. The EC signal as a function of delay would be zero if there were no nonlinearity in the PL spectrum.[30] A sign of PL nonlinearity is a nonzero EC signal.

The optical ray diagram of ECS setup is shown in Figure 3 adopted from Ref.[30] The femtosecond pulsed laser from the Ti: sapphire laser system is divided into two parts by the 50/50 beam splitter (BS) to generate two pulsed beams of equal intensity. One of the beams is passed through the computer-controlled delay stage consisting of a precise motorized translation stage and a retroreflector. By changing the position of the delay stage, optical path difference is introduced between the two pump pulses. The average intensity of the both beams is adjusted by the VNDF. Both beams are co-focused on the sample by the single lens-L1. The sample is mounted on a cryostat to perform the temperature dependent measurement. The emitted PL from the sample

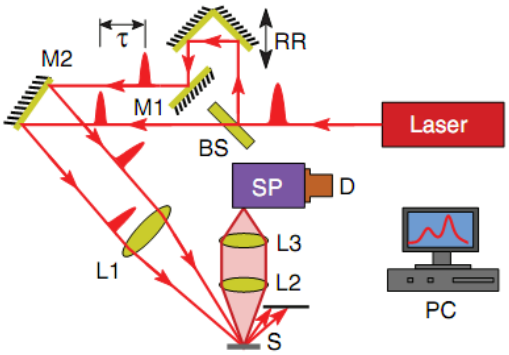

Figure 3: Schematic diagram of excitation correlation spectroscopy experimental setup. Symbols: BS:-Beam Splitter, M1-M2: - Mirrors, , RR:- Retro Reflector, L-L3: Lenses, SP:- Spectrometer, S:- Sample.[30]

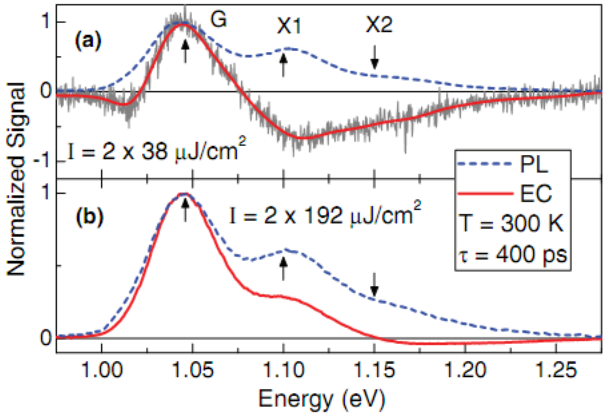

Figure 4: Time-integrated PL spectra were recorded at 400 ps and calculated corresponding EC signal for two different excitation pump fluence on the InAs/GaAs QDs sample.[30]

is collected as a function of delay by a lens-L2. Then the PL beam is dispersed by the lens-L3 onto the monochromator to get the time integrated PL spectrum.

Figure 4, adopted from Ref.,[30] exhibits the time integrated PL spectra at a delay of 400 ps (dotted line) and the corresponding calculated EC signals for two distinct excitation pump powers. This investigation employed excitation correlation spectroscopy on a self-assembled InAs/GaAs quantum dot (QDs) sample under ambient temperature conditions.[30] The QDs possess quantum energy levels as a result of the confinement effect. The redistribution of carriers into these quantum energy levels, governed by the Pauli exclusion principle,[30] generates a nonzero EC signal, which serves as an indication of nonlinearity within the quantum dots. The detailed findings are available in Ref.[30]

Conclusion

To summarize, we have briefly examined the diverse dynamic processes occurring in semiconductors after being exposed to ultrafast laser pulses. Additionally, we have presented a concise introduction to the fundamental principles underlying time-resolved nonlinear optical spectroscopic measurement methods, such as Pump-Probe spectroscopy and Excitation Correlation Spectroscopy techniques. Moreover, we have discussed the noteworthy experimental findings derived from the investigation of semiconductor quantum wells and quantum dots. Ultimately, this knowledge will play a crucial role in the field of physical science, facilitating the development of more efficient devices.

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