Synopsis

The key aspect of this thesis is to understand the photoinduced carrier dynamics in low dimensional systems by employing time resolved optical pump-terahertz probe (OPTP) spectroscopy. Ultrafast pulsed laser (Ti: Sapphire regenerative amplifier, 1 KHz repetition rate) with central wavelength 800 nm and 70 fs pulse width has been used to carry out all the experiments. The thesis is divided into four parts: (a) general introduction of terahertz spectroscopy, experimental techniques and data analysis (Chapter 1 and Chapter 2), (b) understanding the photoexcited carrier dynamics in graphene family including monolayer graphene (Chapter 3), bilayer graphene (Chapter 4), hydrogenated graphene (Chapter 5) and reduced graphene oxide (Chapter 6), (c) understanding the photoexcited carrier dynamics in one-dimensional single walled carbon nanotubes and double walled carbon nanotubes, (Chapter 7) and (d) understanding photoexcited carrier relaxation in few layer MoS_2 laminate, monolayer $MoSe_2$ and their comparison with bulk transition metal dichalcogenides (TMD) such as MoS_2, WS_2 and $MoTe_2$ (Chapter 8).

Chapter 1 reviews the background electromagnetic theory to interpret light-matter interaction and the important physical parameters to be derived from time resolved terahertz spectroscopy. This chapter also gives brief introduction of the systems studied in this thesis. In particular, the electronic band structure and density of states of the graphene and carbon nanotube family, are presented which will be needed for quantitative understanding of their photoinduced terahertz conductivity.

Chapter 2 briefly describes the fundamental principles of generation and detection of terahertz pulse as well as characterization of the terahertz pulse generated in our experimental set up. The experimental details of time resolved optical

pump-terahertz probe spectroscopy are presented. The details of data acquisition techniques and the overview of data analysis for different systems are discussed.

Chapter 3 presents experimental results on single layer graphene.**[Ref. 1,2]** The chapter starts with frequency dependent terahertz measurements of two unexcited monolayer graphene samples: as-prepared single layer graphene (HSLG) (unintentionally hole doped with Fermi energy E_F at $\sim$ -180 meV) and nitrogen doped compensated graphene (LSLG) (with E_F $\sim$-10 meV). This is followed by OPTP experiments where the samples are photoexcited by 800 nm 70 fs optical pulse. After photoexcitaion, the conductivity in HSLG decreases whereas that of LSLG increases i.e, real part of photoinduced conductivity $\Delta\sigma_{Re}(\omega)$ is negative in HSLG and positive in LSLG throughout the spectral window 0.5-2.5 THz. To understand the opposite signs, we incorporate intraband scattering along with the generation of secondary hot carriers due to Coulomb interaction of photoexcited carriers with the existing carriers. Furthermore, the cooling of photoexcited carriers is analyzed using a supercollision model incorporating relaxation of hot carriers by disorder assisted high energy acoustic phonon emission.**[Ref. 1]** To understand the spectral dependence of $\Delta\sigma(\omega)$, we empirically fitted the data by using Drude-Lorentz conductivity model, as proposed in earlier reports in literature. To go beyond this empirical approach, we quantitatively evaluate frequency dependent conductivity $\sigma(T_e, \omega)$ using semi-classical Boltzmann transport equation, T_e being the carrier temperature at quasi-equilibrium after photoexcitation.**[Ref. 2]** This requires evaluation of energy dependence of different scattering rates for carrier dynamics such as short-range disorder scattering, long-range Coulomb scattering, acoustic phonon scattering, surface optical phonon scattering. We show that this approach quantitatively explains the spectral dependence of both real and imaginary part of $\Delta\sigma(\omega)$ for differently doped graphene at different delay times. A comparison of experimental $\Delta\sigma(\omega)$ with the calculated photoconductivity gives estimate of disorder density and the relative combination of different scattering mechanisms.

Chapter 4 presents the photoinduced terahertz conductivity $\Delta\sigma(\omega)$ of Bernal stacked bilayer graphene (BLG) with different dopings and disorder densities.**[Ref. 3]** The real part of dynamic conductivity $\Delta\sigma(\omega)$ ($\Delta\sigma_{Re}(\omega)$) is positive throughout the

spectral range 0.5-2.5 THz in low doped BLG as compared to negative $\Delta\sigma_{Re}(\omega)$ on low frequency and positive on the high frequency side of the spectra for the high doped BLG. Like in single layer graphene, semi-classical generalized Boltzmann transport equation is used to understand quantitatively the frequency dependence of $\Delta\sigma(\omega)$. We show that the short-range impurity scattering is the most dominant scattering mechanism as compared to other processes. The calculated dynamic conductivity captures experimental observations as a function of lattice temperature varying from 300 K to 4 K, without any empirical fitting procedures adopted so far in the literature and pave a way to understand intraband conductivity of photo-excited hot carriers in 2D materials.

Chapter 5 presents terahertz photoconductivity studies of monolayer graphene for different levels of hydrogenation (graphane) after 800 nm femtosecond optical pump excitation.**[Ref. 4]** We provide quantitative understanding of unique spectral dependence of photoconductivity $\Delta\sigma(\omega)$ using Boltzmann transport equation. The real part of terahertz photo-conductivity ($\Delta\sigma_{Re}(\omega)$), which is negative in doped pristine graphene, becomes positive after hydrogenation. It is shown that the carrier scattering rate dominated by disorder-induced short-range scattering, though sufficient for pristine graphene, does not explain the observed complex $\Delta\sigma(\omega)$ for graphane. A model is proposed wherein the graphane is taken to be heterogeneous with effective conductivity as a weighted sum of conductivities of two parts: one dominated by Coulomb scattering coming from trapped charge impurities in the underlying substrate and other dominated by short-range scattering coming from disorder, surface defects, dislocations and ripples in graphene flakes. A finite band gap opening due to hydrogenation is shown to be a key factor in determining $\Delta\sigma(\omega)$ of graphane.

Chapter 6 relates to the studies of photoexcited carrier dynamics in reduced graphene oxide (RGO).**[Ref. 5]** The real and imaginary parts of conductivity spectra clearly reveal low frequency resonances, attributed to the energy gaps due to the van Hove singularities in the density of states flanking the Dirac points arising due to the relative rotation of the graphene layers. Further, optical pump induced terahertz conductivity is positive, pointing to the dominance of intraband scattering

processes. The relaxation dynamics of the photo-excited carriers consists of three cooling pathways: the faster (∼450 fs) one due to optical phonon emission followed by disorder mediated large momentum and large energy acoustic phonon emission with a time constant of a few ps (called the super-collision mechanism) and a very large time (∼100 ps) arising from the deep trap states. The frequency dependence of the dynamic conductivity at different delay times is analyzed in term of Drude-Smith model.

Chapter 7 discusses frequency dependent photoconductivity in terahertz range after 800 nm optical pump excitation in (6,5) semiconducting single walled carbon nanotube (SWCNT) and double walled carbon nanotubes (DWCNT) containing both metallic and semiconducting tubes.**[Ref. 6]** We find the real part of photoconductivity ($\Delta\sigma_{Re}(\omega)$) of SWCNT to be positive on low frequency and negative on the high frequency side of the terahertz spectra. In contrast, DWCNT shows negative $\Delta\sigma_{Re}(\omega)$ on low frequency and positive on the high frequency side of the spectra. The contrasting behavior is explained once again using Boltzmann transport theory where the scattering rate is energy dependent. Taking the scattering rate to be dominated by short-range disorder scattering as in graphene, we show that the model captures the experimental features for SWCNT as well as DWCNT. Both the semiconducting and metallic nanotubes in DWCNT are shown to contribute to the observed photoconductivity.

Chapter 8 presents the dynamics of photo-induced carriers in a free standing MoS_2 laminate consisting of a few layers (1 to 6 layers) using time resolved OPTP spectroscopy.**[Ref. 7]** Upon photoexcitation with the 800 nm pump pulse, the terahertz conductivity increases due to absorption by the photoinduced charged carriers. The relaxation of the non-equilibrium carriers shows fast as well as slow decay channels, analyzed using rate equation model incorporating defect assisted Auger scattering of photoexcited electrons, holes and excitons. We show that though the excitons generated after photoexcitation are not directly probed by the terahertz, they indirectly impact on charge carrier dynamics through blocking the defect states necessary for defect mediated Auger scattering of charge carriers. The fast relaxation time occurs due to the capture of electrons and holes by defects via Auger processes

resulting in non-radiative recombination. The slower relaxation arises since the excitons get bound to the defects, preventing the defect assisted Auger recombination of the electrons and the holes. We have also studied monolayer $MoSe_2$ by OPTP spectroscopy which shows fast electron and hole capture dynamics and the results are compared with monolayer MoS_2.**[Ref. 8]**

To compare the above relaxation dynamics with that of bulk, we extend the experiments to probe the charge carrier dynamics in bulk TMDs - MoS_2, WS_2 and $MoTe_2$.**[Ref. 9]** Here also we use rate equations model including defect assisted Auger scattering of electrons, holes and the excitons to describe the carrier relaxation dynamics. Thus we can extract the temporal evolution of electron, hole and exciton densities in photoexcited TMDs. It is seen that the screened Coulomb interactions in the bulk results in longer carrier relaxation compared to monolayer and a few layer TMDs. Our results provide a comprehensive understanding of the non-equilibrium carrier kinetics in systems where defect assisted Auger processes dominate and should be applicable to other 2D systems.