PICO-SECOND SPECTROSCOPY OF HIGHLY EXCITED SEMICONDUCTORS

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ABSTRACT

The importance of pico-second spectroscopy in the investigation of highly excited semiconductors is pointed out with a survey of dynamical aspects of phenomena to be studied. The present status of technical aspects of pico-second spectroscopy is reviewed. Some results of pico-second experiments performed recently for CdSe are described. Finally, it is emphasized that the study of coherent interactions of highly excited states, especially of the Bose-condensed state, with radiation fields is very important.

Pico-second spectroscopy is very important in investigating the physics of highly excited semiconductors. Most of phenomena due to high intensity excitation effects in semiconductors, especially in direct gap materials such as CdS, GaAs and CuCl, take place with time constants in the pico-second range, *i.e.* 10^{-12} - 10^{-9}s. By using pico-second spectroscopic technique one may obtain firsthand information on dynamical processes in such transient phenomena. Any other method of study, such as ordinary spectral analysis, gives only secondhand information, and may not substitute for the direct measurement in the time domain.[1] Some pioneering work recently made by the author's group and also by some others has already proven how pico-second spectroscopy is useful and important in the field under discussion.

First let us survey dynamical aspects of phenomena to be studied (Fig.1). When electrons and holes are created by the band-to-band transition in high densities, they will relax emitting longitudinal optical phonons with a time constant in an order of magnitude of 10^{-13} - 10^{-12} s, or they will spatially diffuse from the surface into the interior of a crystal with a time constant of probably 10^{-12} - 10^{-11} s.

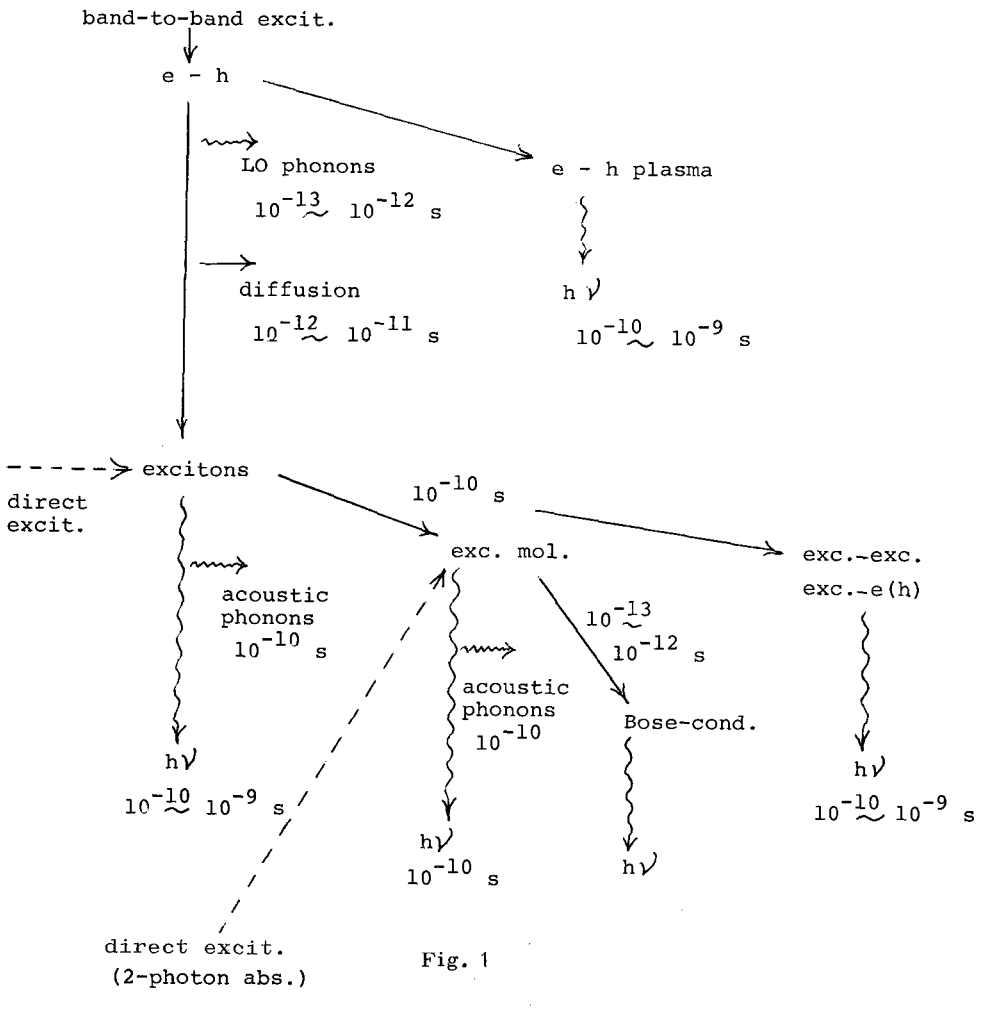

Fig. 1

In some conditions, electron-hole plasma will be generated, which will be annihilated radiatively in a lifetime of 10^{-10} - 10^{-9} s.

Excitons are formed from pairs of electrons and holes first in a hot state, and then the relaxation takes place with the emission of acoustic phonons, the time constant of which will be 10^{-10} s. Excitonic molecules will be formed from two single excitons, provided the electrons and holes have antiparallel spins. In some conditions, exciton-exciton and exciton-electron (or-hole) collision processes accompanied by the emission of a photon take place. The radiative dacay times of

single excitons and excitonic molecules and those of the collision processes are in an order of magnitude of 10^{-9} - 10^{-10} s. If the necessary conditions are satisfied, excitonic molecules will exhibit the Bose condensation. Even if excitonic molecules are directly created by the two-photon absorption, some time will be required for the excitonic molecules to make rearrangement for the condensation as a result of repulsive interactions. The time required will be as short as 10^{-12} - 10^{-13} s.

Utilizing the technique of pico-second spectroscopy, it is possible to directly pursue these dynamical processes in the time domain. Further it should be noticed that the study of coherent interactions of highly excited states, especially of the Bose-condensed state, with radiation fields is very important. This will be mentioned later, but it is pointed out here that for this study pico-second technique is indispensable.

Next the present status of technical aspects of pico-second spectroscopy[1] will be briefly reviewed, and what we can do with this technique at present will be described. As pico-second pulse sources, mode-locked neodymium glass lasers producing 1.06 μm pulses or ruby lasers producing 694 nm pulses are usually used. The duration of pulses is 7 ps for glass lasers and 10 - 15 ps for ruby lasers. As to the peak power of output pulses, it is not difficult to obtain 1 GW, which gives excitation density of 1 - 10 GW/cm^2 corresponding to 10^{27} - 10^{28} photons/cm^2·s. By utilizing second (or higher) harmonic generation, higher frequency pulses are obtained. In ordinary semiconductors, if one gives band-to-band excitation using a 10 ps pulse at excitation density of 1 GW/cm^2, the number of electron-hole pairs generated is 10^{20} cm^{-3} in case of one-photon absorption, while 10^{17} cm^{-3} in case of two-photon absorption. These numbers are usually enough to observe high density excitation effects.

These mode-locked lasers are difficult to operate with high re-

petition rates. Therefore, one must measure the spectrum of a pico-second pulse to be measured with one-shot operation of laser. For this purpose a television camera system is very useful. The system very recently constructed by the author's group[2] has high sensitivity, which is 10^5 times that of high sensitive photographic films, and high spectral resolution of about 0.5 Å. Using this system it is possible to catch the spectrum of luminescence produced by excitation of a pico-second pulse as a one-frame picture of television and to reproduce it on the chart of a recorder.

Time-resolved spectroscopy in the pico-second region is possible to perform by using an ultrafast shutter, which is operated by utilizing the optical Kerr effect in CS_2. The time resolution is 10 ps. Combining this shutter and an optical delay system, one can pursue the time change of emission spectra in the pico-second region.

It is possible to produce a white pico-second pulse by making a strong pico-second laser pulse pass through glass, CCl_4 or some other substances. Using such a pulse, one can observe spectra of absorption induced by pico-second pulse excitation. In the pico-second spectroscopy of highly excited semiconductors, it is very important to produce frequency-tunable pico-second pulses. There are at least two ways; one is to use the lasing of dyes and the other is to use the optical parametric effect. In both cases, mode-locked neodymium lasers or ruby lasers are used for pumping. The parametric laser seems to be superior to the dye laser at least in two points. The first is that it covers a wider tuning range extending from visible to infrared. The second is that it can be operated in a single mode, so that the beam quality is better.

Kushida and coworkers[3] in our laboratory are attempting to generate tunable pico-second pulses with high power by pumping a $LiNbO_3$ crystal as a parametric crystal with the second harmonic pulses (530 nm) of a neodymium glass laser. The tuning is made by changing the tempera-

ture of the crystal. The generation of pico-second pulses with wavelengths of 640 to 900 nm has been confirmed. Efforts are being made to increase the output of the pulses and to make the spectral width narrower. Attainment of a peak power of 100 MW in the above wavelength range is expected in the near future. The second harmonics of these tunable pulses could be used to directly create excitonic molecules through two-photon absorption in some important materials such as CuCl and CdS, if they are strong enough to give excitation density of 10 - 100 MW/cm^2.

Next some of the results of pico-second experiments recently performed in the author's laboratory will be described.[4-7] As to CdSe, absorption spectra of single excitons and their time-change in the pico-second region were measured with white pico-second pulses. It was found that the absorption line of the n=1 A-exciton shifts to the high energy side if the crystal is simultaneously excited intensely by pico-second neodymium laser pulses. The blue shift is ascribed to the cutting-down effect of the conduction and valence band edges caused by the formation of high density excitons. A shift as large as 4 meV was observed, which corresponds to the number of excitons of 5×10^{16} cm^{-3}. The time-change measurements of this blue shift showed that the shift becomes the maximum at 20 ps after the pulse excitation and then disappears at 50 ps. The time resolution was 10 ps, so that the data were not accurate enough, but these results are regarded as indicating that it takes about 20 ps for the formation of n=1 A-excitons from electron-hole pairs after band-to-band excitation. The disappearance of the blue shift at 50 ps may be ascribed mainly to the formation of excitonic molecules.

Spectra of excitonic molecule luminescence (M-line) in CdSe were observed under excitation with 1.06 μm pico-second pulses through two-photon absorption. It was found that a sharp line appears under some excitation conditions, which is not seen in the spectra under excitation

by nano-second pulses from a nitrogen laser. The position of the sharp line coincides with that expected for excitonic molecules at the k=0 state. These results have been interpreted as indicating the attainment of the Bose condensation of excitonic molecules. This sharp line is observed only by two-photon pico-second excitation, and not by one-photon pico-second excitation.

Further the time-dependence of the M, P_M, and P luminescence lines in the pico-second region was measured in CdSe. The P_M line is produced by the collision of two excitonic molecules, and the P line is due to the collision of two single excitons. It was observed that the M line reaches the maximum at 100 ps after the pulse excitation and decays with a time constant of 100 ps, and that the P_M and P lines show maxima at 200 and 300 - 350 ps with decay constants of 100 and 350 ps, respectively. Also for GaAs, the time dependence of the P line and the emission line due to electron-hole liquid was measured.[2] Both lines show nearly the same behavior, rising up at about 300 ps and decaying with time constants of about 300 ps. Very recently, the decay of excitonic molecule luminescence in CuCl was measured, and was found to have a time constant of 300 ps.

Recently Hanamura and Inoue[8] studied theoretically population dynamics of single excitons and excitonic molecules. They showed on the basis of some assumptions that the time-dependence of the concentration of single excitons and excitonic molecules is expressed by simple kinetic equations. In the case where single excitons are directly excited by a pico-second pulse, their calculation shows that the concentration of excitonic molecules has the maximum around at $t=\alpha^{-1}$, α being the reciprocal time constant of the radiativel decay of excitonic molecules. The above-mentioned experimental results are understood by this calculation.

Finally, it is emphasized that the study of coherent interactions of highly excited states, especially of the Bose-condensed excitonic

molecules, with radiation fields is very important. To obtain conclusive evidence for the attainment of the Bose condensation, it will be required to experimentally reveal the coherent nature of the Bose-condensed state. We must challenge this important target.

Two-kinds of coherent interactions of Bose-condensed excitonic molecules have been discussed theoretically by Hanamura.[9] One is super-radiance and the other is self-induced transparency. The Bose-condensed excitonic molecules should have a common phase, and the transverse relaxation time will be quite long, probably determined by the radiative decay time. Such excitonic molecules emit radiations cooperatively and spontaneously. The intensity of the radiation should be proportional to the square of the number of excitonic molecules. This corresponds to the case of super-radiance. Since the Bose-condensed excitonic molecules are expected to have a much longer relaxation time than uncondensed molecules, it will be possible to observe self-induced transparency.

From experimental points of view, the observation of self-induced transparency will be easier than that of super-radiance. From this observation, one may obtain some important information on the relaxation properties of the condensed excitonic molecules, which are closely connected with their coherent nature. To make this observation, one must directly create excitonic molecules by means of two-photon absorption and look at the propagation of an exciting light pulse through a crystal. In such experiments, we need tunable pico-second pulses with sufficient intensity. It is hoped that the use of such laser pulses is realized in the near future so that we could obtain fruitful outcomes on this important problem in the physics of highly excited semiconductors.

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