13 time resolved spectroscopy 1

When the semiconductor is excited, electrons in the valence band are excited to the conduction band. The excited electrons transits to the ground state (valence band) directly or via impurity levels. Of course these phenomenon dos not occur at instantaneously, and the phenomenon is necessary needs time.

What are processes the electrons experienced? One of the experimental investigation method of that is time resolved spectroscopy.

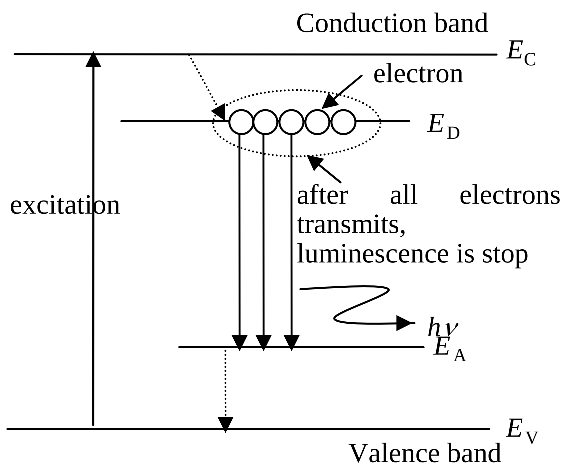

Fig. 13-1 luminescence model

13.1 time resolved spectroscopy of PL

When a light, which energy is larger than a band gap energy of a semiconductor, is incident to the semiconductor, electrons at a ground state are excited to higher levels. Since the electrons with higher energy is not stable, after lifetime, electrons recombine by radiative recombination process (emitting photon) or non-radiative recombination process (emitting phonon), and transit to lower levels. When all excited electrons are recombined, photon emitting and phonon emitting stop (here after, only photon emitting are discussed). If the light incident is continuously, photon emitting (luminescence) is continuously because excited electrons are supplied continuously.

What will happen if the light incident stops? In this case, since supplying of the excited electrons stops, when all excited electrons recombine, luminescence stops. By simple consideration, many excited electrons may cause higher recombination probability and therefore higher luminescence intensity. From the above, by observation of luminescence depending on time (= time resolved spectroscopy) lifetime of the electrons can be estimated.

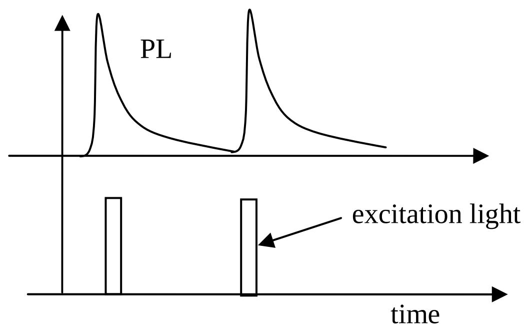

Fig. 13-2 decay curve of luminescence

Here, how long suitable interval between excitation and not excitation is? How long suitable excitation duration? When excitation light is incident into sample, luminescence must stop, therefore the interval must longer than lifetime of the electrons. A resolution of time corresponds to incident time of the excitation light. Therefore if you want to observe by high time resolution, you should use short pulse. A lifetime of phosphorescence is from few ms to s, therefore it is enough that the excitation light source is lamp + chopper (chopping frequency is few kHz). On the other hand, lifetime of the DPA recombination luminescence and the exciton recombination luminescence are ns ~ ps. Therefore for DAP and exciton, pulse laser with high reputation (few tenth MHz) is used.

13.2 excitation light source for time resolved spectroscopy

In this section, excitation light sources for time resolved spectroscopy will be explained shortly (in other lectures, often pulse lasers may be explained).

● pulse lasers

①An example of Q-switch Nd^{3+}YAG (or $Nd^{3+}YVO_4$) is shown in Table 13-1. Usually, a reputation frequency is few tenth Hz, a pulse width is few ns and energy per one pulse is relatively large. If non-liner optical crystal is used, IR, UV, and green light can be generated. Stability of the pulse intensity is not good. This light source is convenient because it is not so expensive and operation is easy. Here in Table 13-1, SHG, THG and FHG are second, third, and fourth harmonic generation.

Table 13-1 Q-switch Nd^{3+}YAG (or $Nd^{3+}YVO_4$)			
order	wavelength (nm)	energy(mJ)	pulse width (ns)
Fundamental	1064	~1000	~10
SHG	532	~300	1~2
THG	355	~100	2~3
FHG	266	~80	3~4

②N_2 (nitrogen) laser

Oscillation wavelength is 337.1 nm, pulse width is sub ns ~ few ns, energy per one pulse is sub mJ and reputation frequency is few tenth Hz. Stability of this laser is not good. The N_2 laser can be made by yourself and is inexpensive. It is convenient light source.

③dye laser

A dye laser is excited by the lasers mentioned above (N_2, and Q-switch Nd^{3+}YAG lasers). Of course, this laser can be excited other lasers such as mode lock laser. Pulse width of the dye laser is slightly narrower than the excitation laser (① and ②). Oscillation wavelength depends on dye and if you choice dye and excitation source rightly, dye laser can oscillate from UV to IR region.

④Mode locked Ti: sapphire laser

Ti: sapphire laser is a mode locked laser by Kerr effect. This is very famous laser very narrow pulse laser. The pulse width is ca. 25~100 fs, oscillation wavelength is 700~1000 nm, and average output power is few 100 mW. Using by non-linear optical crystal, SHG can be generated and the wavelength of the SHG is UV ~ VIS. Output power is very stable. Ability of this laser is very high but very expensive. Other very narrow pulse laser (fs operation) are Er doped fiber laser and Cr:Forste laser.

●pulse compression

When a light passes through Ti:sapphire crystal, self-phase modulation is occurred by the Kerr effect. Since refractive index changes by Kerr effect, new light with other frequency components appears and then spectrum in wavelength domain is spread, and lower frequency light is out on ahead and higher frequency light is out with delayed from the Ti:sapphire crystal. That is, the spectrum in time domain is spread. By using a number of prisms, negative GVD (group velocity dispersion) (negative GVD= longer wavelength is larger refractive index = longer wavelength is slower light velocity) is occurred. Therefore if red light pass through negative GVD elements (such as prisms) the red light becomes slower, and blue light becomes faster, and then pulse is compressed (See Fig. 13-3).

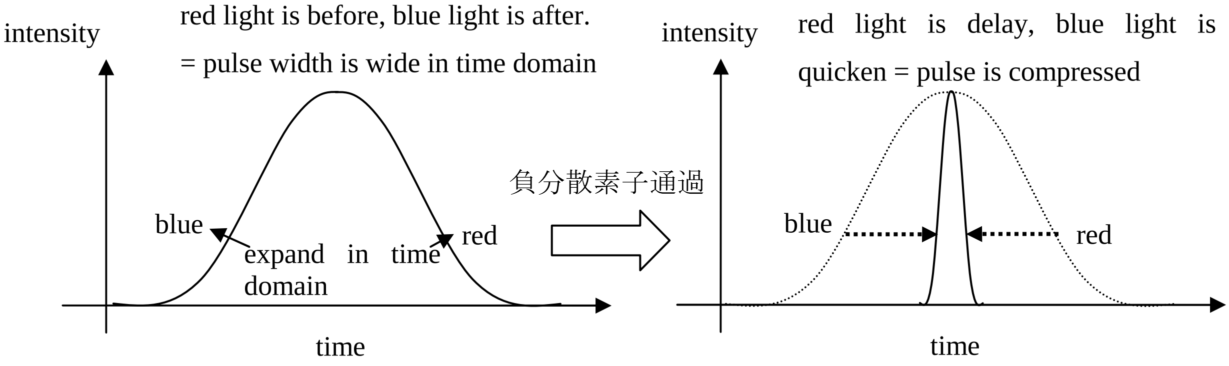

Fig. 13-3 pulse compression

●relationship between spectral width and pulse width

When GVD in the Ti:sapphire cavity (= that is, in the laser) is compensated completely, phase of all frequency components in the spectrum become same and therefore the pulse becomes Transform- Limited Pulse, that is, the pulse becomes the shortest pulse. A relationship between time spectrum and wavelength spectrum of light pulse is Fourier conjugate, and relationship between pulse width (time domain) Δt and spectral width (frequency domain) $\Delta\nu$ is uncertainty relationship of

$$\Delta t \Delta\nu \geq k .$$

where, Δt and $\Delta\nu$ are Full Width Half Maximum (FWHM). k depends on pulse shape, and for Gaussian $k = 0.441$ and for sech^2 shape $k = 0.315$ (for Ti:sapphire, in many case, the pulse shape is sech^2).

From the above, spectral width in wavelength domain is wider, pulse width in time domain is narrower.

●pulse width spread by optical elements (such as lens)

Usually, refractive index of optical elements composed with glass has positive dispersion (shorter wavelength is larger refractive index) . Therefore, by passing through optical elements such as lens and prism, pulse width of the light is spread. (but it is not necessary to mind above if the pulse width is larger than ca. 100fs).

From the above, in the case of few fs ~ few tenth fs, the light is collected by concave mirror and mirrors are used instead of corner cube.

●peak power, how to calculate energy

◆how to calculate peak energy of one pulse E (J) from average power.

If reputation frequency and average power are defined as f (Hz) and P_{av}(W), respectively,

$$E(\mathrm{J}) = P_{av}(\mathrm{W}) / f(1/\mathrm{sec}) .$$

◆how to calculate peak power P_{max}(W) from peak energy E (J)

if pulse width is defined as Δt (sec),

$$P_{max}(\mathrm{W}) = E(\mathrm{J}) / \Delta t(\mathrm{sec}) .$$

For example, from the parameters of reputation frequency of 80 MHz, average output power 500 mW and pulse width 100 fs, these are general condition of Ti:sapphire laser, peak power per one pulse is 62.5 kW. You can find it is very high intensity because power of the laser pointer is usually less than 1 mW.

●relationship between cavity length and reputation frequency

The reputation frequency of the mode-lock laser is defined by the cavity length of the laser. In the cavity, only one pulse must be existed since if there are two pulses, these pulses are affected by each other.

In the laser cavity, pulse is generated at laser gain medium (such as Ti:sapphire crystal), the pulse propagates to mirror, the pulse is reflected by the mirror, and then the pulse returns to the laser gain medium. As mentioned above, there must be one pulse in the cavity, therefore, when the pulse returned to the laser gain medium, next pulse is generated in the medium, that is, the pulse makes a round trip with the time calculated by reciprocal number of reputation frequency.

From the above, if cavity length, reputation frequency and velocity of the light in vacuum are defined as L (m), f (Hz) and c (m/sec), respectively,

$$2L = c / f \ .$$

For example in the case of $f = 80$ MHz, $L = 1.875$ m. Here reputation frequency of the mode locked laser of Spectra-Physics (SP) and Coherent, they are very famous laser supplier, are 80 MHz and 76MHz.

If you want to excite a mode-locked dye laser by other mode-locked laser, cavity length of the dye laser must be same of the excitation mode-locked laser.

13.3 observation system:(1): PMT

Most simple observation system is PMT+oscilloscope. Here, important reminders are shown.

① time domain characteristics of PMT

A time domain characteristic of fast PMT will be explained here. The time domain characteristic of PMT mainly depends on dynode. The time domain characteristic also depends on supplied voltage. Figure 13-4 shows output characteristic of PMT when a delta function shape pulse, which pulse width is much shorter than response time of PMT, is incident into the PMT.

The time during from 10% to 90% output is called as climbing time and the time during from 90% to 10% is called falling time. The time between incidence of photon at photoelectron surface and output of signal from anode is called electron transit time. Usually falling time is 2~3 times longer than climbing time. FWHM of the PMT output signal is ca. 2.5 times of climbing time. The parameters mentioned above are shown in catalogs. Therefor you should choose suitable PMT with considering the PMT parameters and life time of luminescence. Usually the climbing time and falling time are few ns ~ few tenth sec. Time response of a line focus type dynode and a metal channel type dynode are relatively faster than that of a box type dynode and a Venetian blind type dynode are slower. (details are shown in PMT catalogs).

Time response is improved by increasing of supplied voltage. The higher supplied voltage causes faster electron transit velocity and therefore climbing time, falling time and electron transit time are shortened. In generally, time response is improved by proportion of reciprocal value of square root of supplied voltage. However, higher supplied voltage causes larger noise (larger dark current).

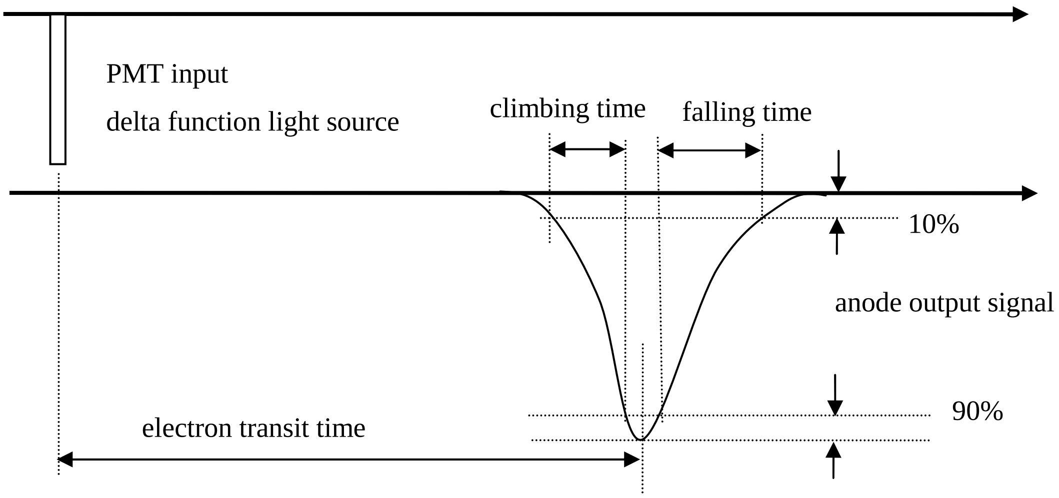

Fig. 13-4 climbing, falling, and electron transit times

②reflection and impedance matching

Usually, a characteristic impedance of a coaxial cable which connects a PMT and an oscilloscope is 50Ω. However, since a characteristic impedance of the oscilloscope is not 50 Ω, the electrical signal (= detected light by PMT) is reflected at an entrance of the oscilloscope and the reflected signal are multiple reflected between oscilloscope and PMT.

To reduce the multiple reflections, the characteristic impedance of the oscilloscope, the coaxial cable and other connected things must be matched. The high-grade oscilloscope often has a function that input impedance can be changed to 50Ω. But if the oscilloscope does not have such a function, a terminator which can convert the characteristic impedance to 50Ω must connect to the oscilloscope. Figure 13-5 shows decay curves of luminescence observed by with impedance matching and without impedance matching. As shown in Fig. 13-5, without impedance matching, there are pulses on the decay curve.

A propagation velocity of the electromagnetic wave is proportional to a reciprocal value of refractive index, that is, proportional to a reciprocal value of square root of dielectric constant. For coaxial cable of 50Ω, polyethylene which dielectric constant is 2.66 is used. Therefore the propagation velocity of the electromagnetic wave in the coaxial cable is 66% of the velocity of the light in the vacuum. From this, during 1 ns, electric signal propagates $3 \times 10^8 \, (\text{m/s}) \times 0.66 = 20$ cm. If you cannot eliminate reflected pulse completely, the coaxial cable should be longer as the reflected pulse cannot return to the oscilloscope during the reputation of observation time.

③observation system

An observation system of the time resolved spectroscopy by PMT is almost as same as the observation system of the PL. After observation of the PL, the wavelength of the monochromator is moved to the observed wavelength and connection of an output cable of the PMT changes from an photon counter to a oscilloscope.

By the self- trigger mode of the oscilloscope, the observed result is often unstable, therefore a part of an excitation light is detected by PD and an output signal from the PD is used as reference signal for trigger.

In generally, by the oscilloscope, time resolution is ~ns and reputation is few MHz (these properties are depends on the oscilloscope). The highest reputation frequency is few MHz, therefore you cannot use mode-locked laser for an excitation source of this observation system because the reputation frequency is so high.

④example of observation result of decay curve

Figure 13-5 shows a decay curve of a luminescence from $CaGa_2S_4:Ce^{3+}$ excited by LD (405 nm, pulse width few ns) and detected by PMT + oscilloscope. As shown in Fig. 13-5, without terminator the signal shows multiple reflections and shows no decay (it may be oscillated). With the terminator of 50Ω, the multiple reflections are eliminated and the decay curve can be observed, but signal intensity is reduced.

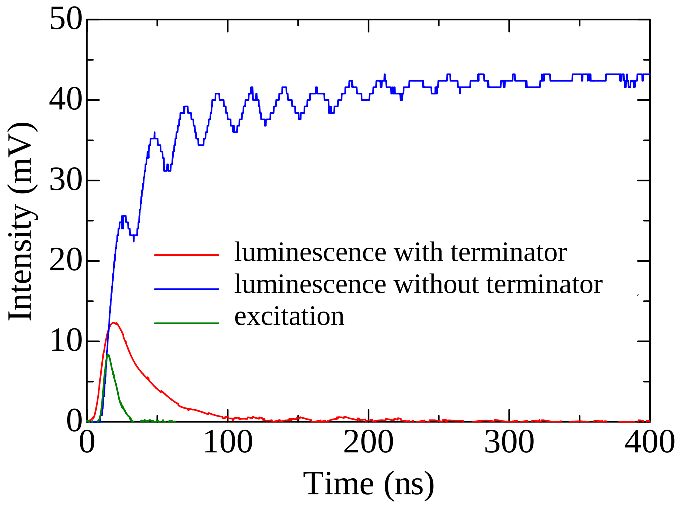

Fig. 13-5 PD decay curve observed by PMT

13.4 observation system (2): streak camera

A streak camera consists with input optical system, high speed sweep electronic circuit, streak tube, output optical system, detection system and PC for data treatment. Among the consisting elements, the streak tube and the high speed sweep electronic circuit are related to time resolved spectroscopy.

Figure 13-6 shows schematic diagram of the streak camera. A luminescence from the excited sample is incident into a slit, a relay lens provides an image of the luminescence passes through slit on the photoelectric surface. The image converted into photo electrons. A number of the photo electron is proportional to photon numbers and the electrons are emitted to accelerating electrode. The photo electrons are accelerated by the accelerating electrode and incident into deflecting field.

In the deflecting field there is one-pare of deflection plate. At a moment the electrons pass through the deflection plates, high speed sweep voltage is applied to the deflection plates and the electrons are swept from upper to lower side. The sweep must be synchronized with the electron passing, therefore a part of excitation light is detected and the detected light is used as trigger.

Usually streak camera has several sweep mode, fast sweep, slow sweep and high reputation sweep. If the luminescence intensity is low, high reputation sweep mode must be used and the detected light must be integrated.

The swept electrons are incident into micro channel plate (MCP) and at MCP a number of electrons are amplified, and then the amplified electrons are incident into a phosphor screen, and at last the electrons are converted into optical image again. The output relay lens provides an image of the converted optical image on the phosphor screen of the 2 dimensional CCD camera, and then the data was treated by the PC. From the above, the position of the electron on the phosphor surface is determined by a moment that the electron is incident into the photo electron surface, that is, a moment that the electron passes through the deflection plates. Therefore from a vertical distribution of the light intensity, time distribution is determined. The horizontal axis of the streak image corresponds to input image. Therefore if the light is dispersed by grating before the light incidence into the streak camera, decay curves depend on wavelength can be obtained.

The fastest time resolution of the streak camera is sub ps. Therefore the streak camera is suitable for a observation of very fast phenomenon, however it is very expensive.

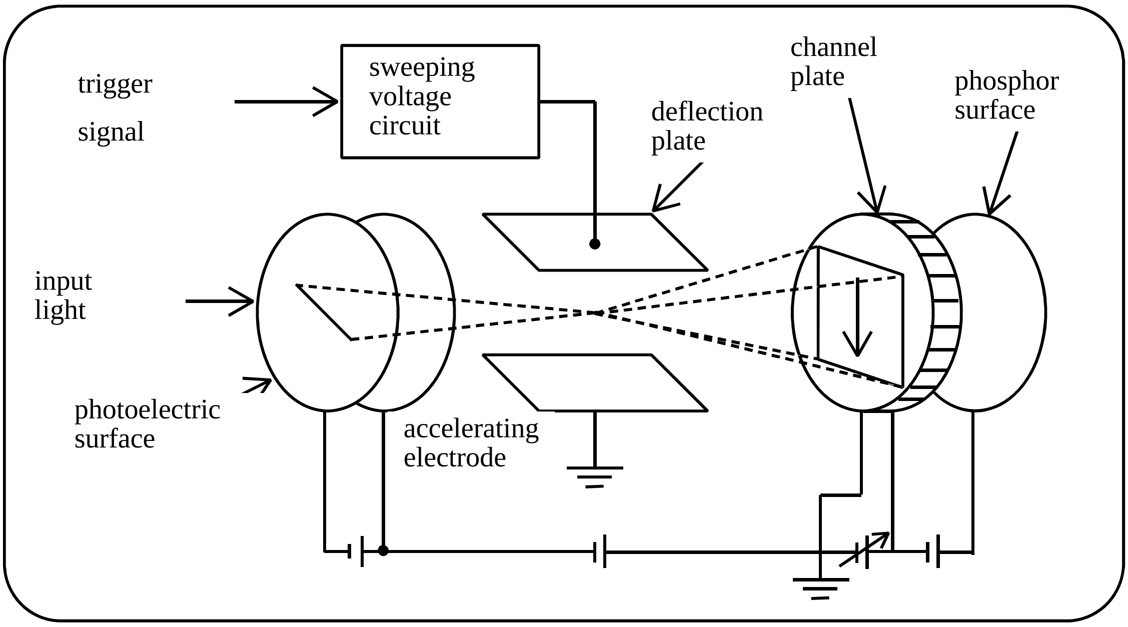

Fig. 13-6 streak camera

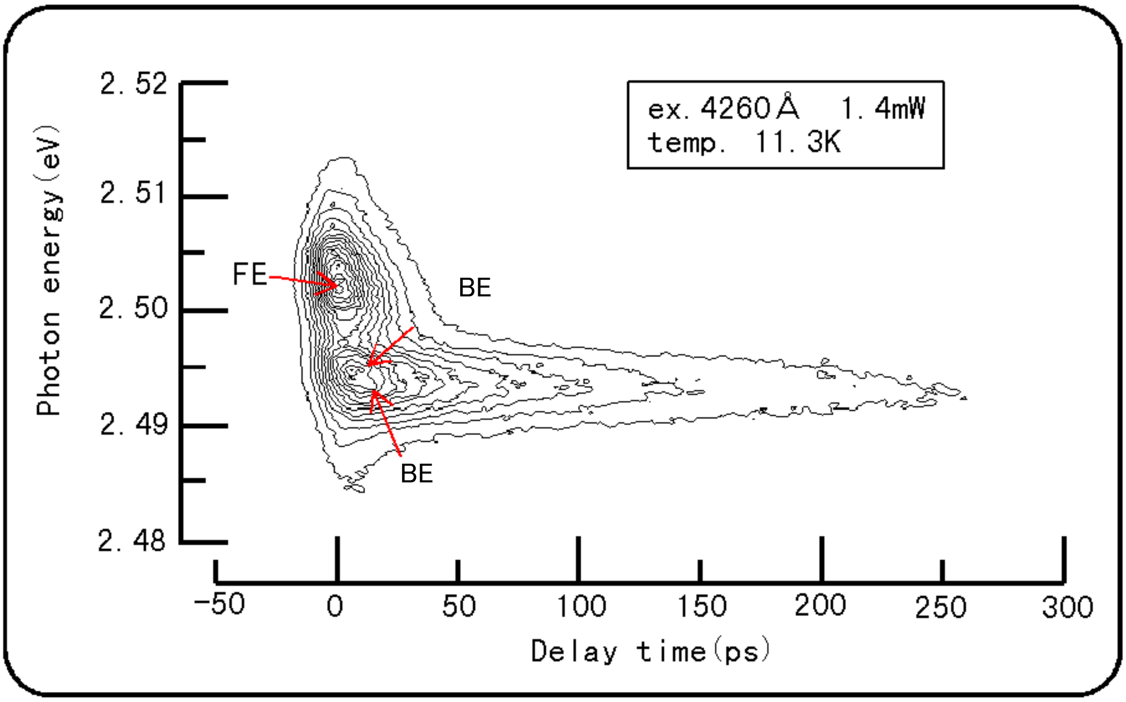

Fig. 13-7 time resolved excition luminescence from $CuGaS_2$ observed by streak camera

Figure 13-7 shows time resolved free exciton (FE) and bound excitons (BE) luminescence spectrum from $CuGaS_2$. The excitation source is the second harmonic of the mode-locked Ti:sapphire laser

13.5 observation system(3): pump probe method

When lights with angular frequencies ω_1 and ω_2 are incident into a non-linear optical crystal, lights with angular frequencies $\omega = \omega_1 + \omega_2$ (sum frequency) and $\omega = \omega_1 - \omega_2$ (difference frequency) are generated. By using the sum frequency light or difference frequency light, very fast phenomena can be observed.

It is assumed that when a sample is excited ("pump" the sample), the sample shows 500 nm luminescence. The luminescence is incident into a non-linear optical crystal, and with proper delay a very stable (in intensity domain) and very narrow pulse with 830 nm (= probe light) is incident into the non-linear optical crystal. the 500 nm luminescence and probe light are overlapped in the non-linear optical crystal. If the light of 500 nm and 860 nm are incident into the non-linear optical crystal at the same moment, sum frequency light of $(1/500+1/860)^{-1}=316$ nm is generated. An intensity of the sum frequency light is proportional to the product of 500 nm luminescence intensity and the probe intensity. In this case, the intensity of the probe light is constant, therefore, the intensity of the sum frequency light is proportional to the intensity of the sum frequency light. If the delay time of incident of the probe light is controlled, the intensity of the sum frequency light against to the delay time corresponds to decay curve of the 500 nm luminescence. The observation method like this is called “pump-probe method”.

Figure 13-10 shows an actual observation system. A second harmonic of the Ti:sapphire laser $2\omega = 430$ nm is generated by incident a fundamental light of Ti:sapphire laser $1\omega = 860$ nm into a non-linear optical crystal of LBO. At the exit of the LBO 1ω and 2ω are mixed. At the exit of the LBO, 1ω and 2ω are separated by a beam splitter which reflects 1ω and transmits 2ω. 1ω is incident into LBO2 via the delay time. On the other hand 2ω excites the sample, and then the luminescence generated by the excited light collected on the LBO2. If optical path length of the pass 1（＝BS→CC→M2→LBO2）and pass2（＝BS→M1→sample→LBO2）are same, the luminescence and probe light are incident into LBO2 at same time. If delay line is lengthened by 150 μm, round trip optical path length is lengthened by 300 μm. If the light speed is assumed as 3×10^{8} m/s, 300 μm corresponds to 1 psec. That is, as delay line is lengthened by 150 μm, probe light is incident into LBO2 with 1 ps delaying. At LBO2 sum frequency light of probe light and luminescence is generated. At behind of LBO2, an aperture is inserted to cut the luminescence and probe light, but passes through sum frequency light and the sum frequency is incident into the PMT. If pulse width of probe light is narrower than 1 ps and delay line can be controlled with accuracy of 150 μm, the decay curve can be observed with 1 ps resolution. Usually for pump probe method, the corner cube (see fig. 13-10) is on the stage with a micrometer, and the stage can move with accuracy of ca. 150 μm.

In the case of the observation of like that, the optical pass length of pass 1 and pass 2 must be same length. For example, if you want to the observation region is from excitation to 100 ps, differences between pass 1 and 2 must be less than 15 mm. To generate sum frequency light very high intense light is necessary, the luminescence and probe light must be collected very small (less than 0.1 mm of diameter). The luminescence and probe light must be overlapped at LBO2 in space domain. However since the light collected light is very small, overlapping is very difficult. In addition, if the observation system is not aligned accuracy, when length of the delay line is varied, overlapping is deviated. In particular if the life time of the luminescence is long and variation length of the delay line is longer than few cm, the deviation may become larger. Therefore the alignment of the observation system like that is very difficult. In addition, intensity of the sum frequency light is week, the observation like that is very difficult.

Therefore, this observation method is very high resolution, but for the experienced.

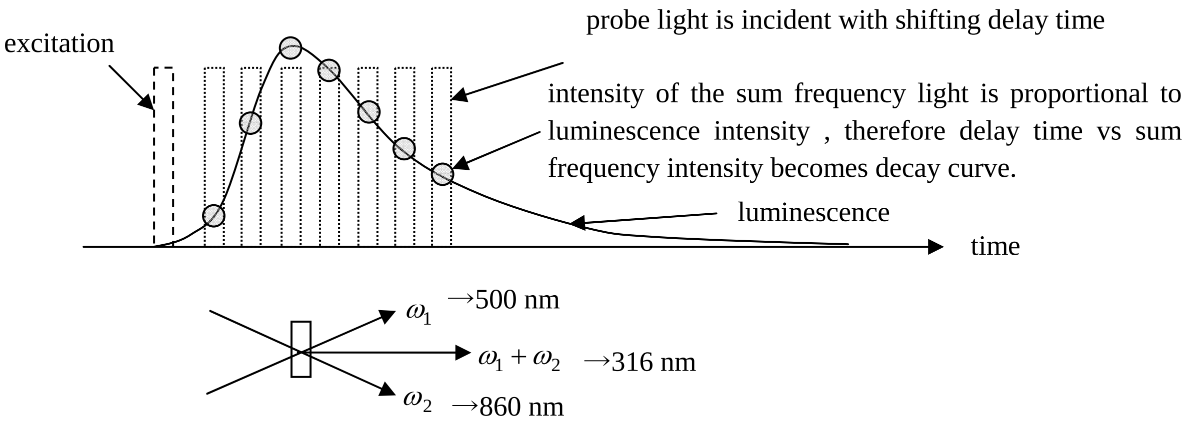

Fig. 13-9 time resolved spectroscopy of luminescence using by sum frequency

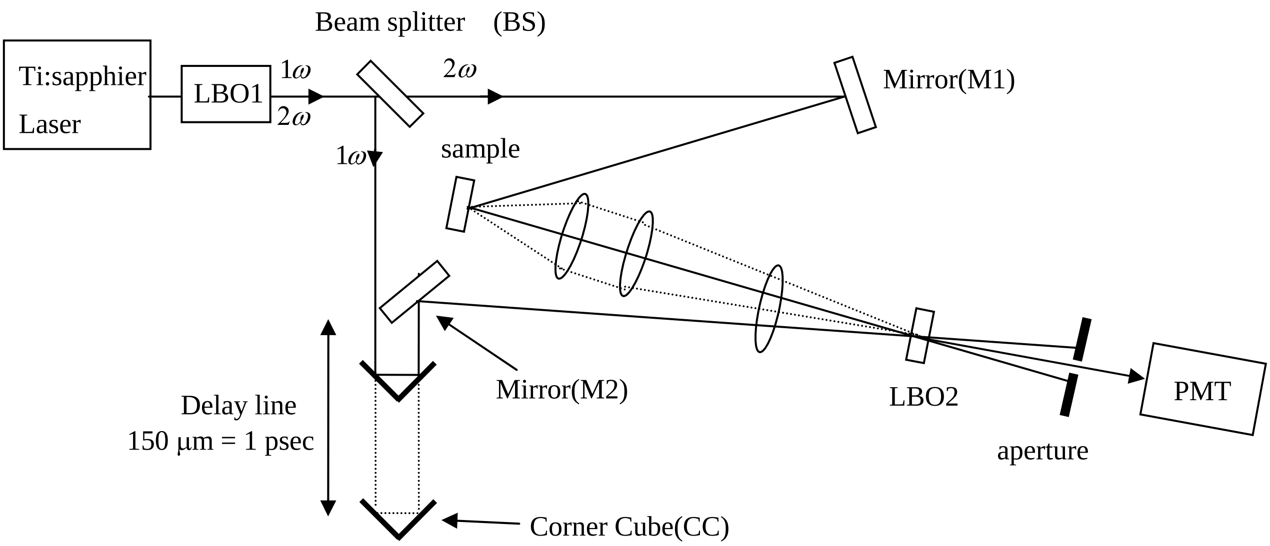

Fig. 13-10 observation system of time resolved PL by pump-probe method