Chapter 2 Optical Measurement Theory and Instrument

2-1. Photoluminescence (PL)

2-1.1 Theory of photoluminescence

Luminescence is an electromagnetic (EM) radiation phenomenon due to excessive thermal radiation or incandescence in physical system. With regard to luminescent semiconductors, when energy of incident photon is equal or beyond the energy bandgap, it will excite the electron of valence band into conduction band through bandgap. Semiconductors generate recombination radiation from excited state to ground state. Absorption will also happen when an electron is excited to higher energy level from neutral acceptor energy level and it can also transit to ionization donor energy level from valence band or transit to conduction band from ionization acceptor energy level. Those phenomena can explain the energy band or impurities in the semiconductor successfully.

Photoluminescence which inspects optical property of luminescent semiconductor materials is a strong and nondestructive technology. According to analytic data of photoluminescence, we can know the kind of impurities, bandgap, and impurity activation energy etcetera from the spectra. We can estimate the composition of the compound from the peak intensity of PL spectra. Using photoluminescence can investigate the internal interface of hetero-structure that general physical or electronic measurements can not measure.

Luminescence process includes three procedures: (1) Excitement, (2) Heat balance, (3) Recombination. Incident light generates electron-hole pairs and recombines to generate photons after heat balance. Impurities and defects form various energy levels in the bandgap and their corresponding energy will generate radiation by radiation recombination process or generate absorption by nonradiation recombination process.

Luminescence of semiconductors can divide two types:

(1) Radiative transition

When an electron drops to lower energy state from higher energy state, it will probably occur radiative transition regardless of intrinsic state or energy state formed by impurities. Therefore, the system is not a balanceable condition and we assume that excited phenomena will generate electron-hole pairs in semiconductors. Firstly, we consider some basic transitions [19-21]:

(I) Band-to-band transition

Band-to-band transition is the relationship of free-electrons and holes. Those transitions usually occur in direct bandgap materials such as Ⅲ-Ⅴ compounds where the electron-hole pairs will generate radiation recombination effectively between conduction band and valence band.

(II) Free exciton transition

If the material is very pure, an electron and a hole will attract each other to form exciton. Then, they will recombine to generate a very narrow spectrum. In Ⅲ-Ⅴ compounds, free exciton energy state usually describes Wannier-Mott approximation. It also says that carriers presume no relationship with charged particles which generate Coulomb force each other. And energy of free exciton can be expressed as Equation 2.1-1.

$$E_n = \frac{2\pi^2 m^* e^4}{h^2 \varepsilon^2 n^2} \tag{2.1-1}$$

In this equation, m* is effective mass, h is Planck constant, ε is dielectric constant, and n is quantum number.

Because of the existence of excitons, the transition energy in bandgap can be expressed as Equation 2.1-2.

$$h\nu = E_g - E_n \tag{2.1-2}$$

However, there are probably several mechanisms to result in non-radiative transition. Those transitions will compete with radiative transition to result in lower luminescence.

(III) Free-to-bound transition

The transition is free-to-bound transition between energy bands of materials and impurity energy level. This transition is between the impurity and one of energy bands such as from conduction band to acceptor or from donor to valence band. Not in zero degree, the impurity is just occupied partly to cause that some impurity centers are neutral and others are ionized. If the kind of impurity is donor, it probably has two transitions:

(a) The electron reaches to ionization donor energy level (e^-D^+)

(b) The hole reaches to neutral acceptor energy level (h-D)

If the spectrum is the range of infrared light, the transition is (a). Because of small energy, the phonon radiation will provide effective competition and the radiative efficiency will be very low. The transition of (b) is very near the basic energy bandgap and this phenomenon is observed in many semiconductors. The energy of radiative photon is E_g-E_b and E_b is bound energy of shallow impurity energy level.

(IV) Donor-acceptor pair recombination

The transition is between donor and acceptor. After optical pumping, the electrons and holes will be bounded at D^+ and A^- locations to generate neutral D_0 and A_0 centers. Some neutral donor electrons will recombine with neutral acceptor holes radiatively in equations and they can be expressed as following equations.

$$D_0 + A_0 \rightarrow h\nu + D^+ + A^- \qquad (2.1\text{-}3)$$

The radiative energy of those transitions is:

$$E_{DA} = h\nu = E_g - \left(E_D - E_A\right) + \frac{Q^2}{\varepsilon R_{DA}} \qquad (2.1\text{-}4)$$

Here, E_D and E_A is donor and acceptor bound energy, respectively. Q is charge number, ε is dielectric constant, and R_{DA} is the distance between donor and acceptor. Bigger R_{DA} will cause lower probability to transit.

(2) Non-radiative transition

Some opportunities which cause non-radiative transition will compete with radiative recombination transition and influence luminescent efficiency negatively. They can describe as below:

(I) Because of thermal oscillation to generate phonons;

(II) Recombination on the surface state includes two dimensional dislocation, and agglomerative boundary et al. through step-wise transition which causes loss energy. It also calls cascade process;

(III) Impurity locations are often not radiative recombination centers;

(IV) Loss energy of trapped carriers will excite other carriers in the lattice and emit non-radiative loss energy by Auger process.

2-1.2 Photoluminescence measurement system

Firstly introduce our photoluminescence measurement system as showed in Fig. 2-1. The excited light source is continuous wave Helium-Cadmium Laser which is manufactured by Melles Griot Company. Its main peak is 325 nm. This multimode laser is no particular polarization and its output power is 30 mW. Laser focuses on the sample through three reflectors and a focal lens which focal length is five centimeter. The spot diameter is about 0.3 mm after focusing and the power density reaches 21 W/cm^2 on the surface of the sample. The excited luminescence of the sample is also through this focal lens which forms the confocal route with another focal lens in front of the spectrometer.

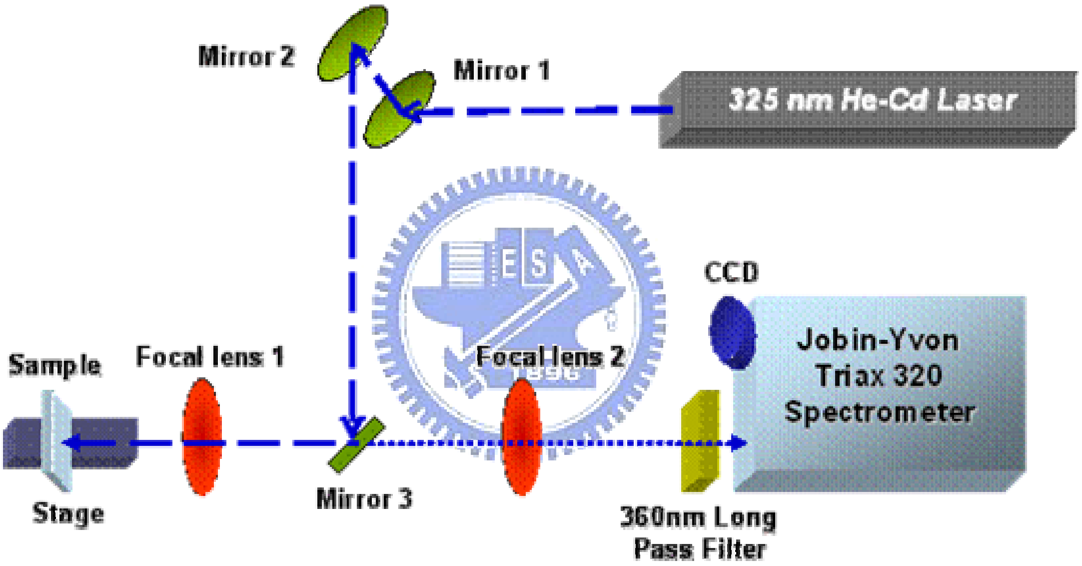

Fig. 2-1: Diagram of photoluminescence measurement system

The type of the spectrometer is Jobin-Yvon Triax-320 monochromator. It includes three kinds of gratings and the stripe density per centimeter are 1200, 1800, and 300 respectively. In the measurement, we use that the stripe density is 1200 gratings. In order to avoid laser entering the spectrometer directly, we place a wavelength filter which filters wavelengths under 360 nm in front of the spectrometer. The exit of the spectrometer is detected by Charge Couple Device (CCD).

If the slits of the entrance and exit in the system are wider, the resolution of the system will decrease. But the slits are too narrow, noises will cover the signals. In the measurement, we use the slit is 0.2 mm.

2-2. Photoluminescence Excitation (PLE)

2-2.1 Theory of photoluminescence excitation

Photoluminescence excitation spectra which operate with photoluminescence spectra are useful measurements. Photoluminescence spectrum is the recombination process of energy bandgap or impurity energy level in semiconductors; Photoluminescence excitation spectrum detects specific energy of photoluminescence spectra. This method detects specific radiation energy and modulates exciting energy like absorption spectra.

2-2.2 Photoluminescence excitation measurement system

Firstly introduce our photoluminescence excitation measurement system as showed in Fig. 2-2. Photoluminescence excitation measurement system is the same as Photoluminescence measurement system except the exciting light source. The exciting light source is xenon lamp with 300 W in the photoluminescence excitation measurement system. Guide the light into double gratings monochromator (Jobin-Yvon Gemini 180) and use the stripe density is 1200 gratings. In the measurement, we use the slit is 0.2 mm and the resolution is about 4 Å.

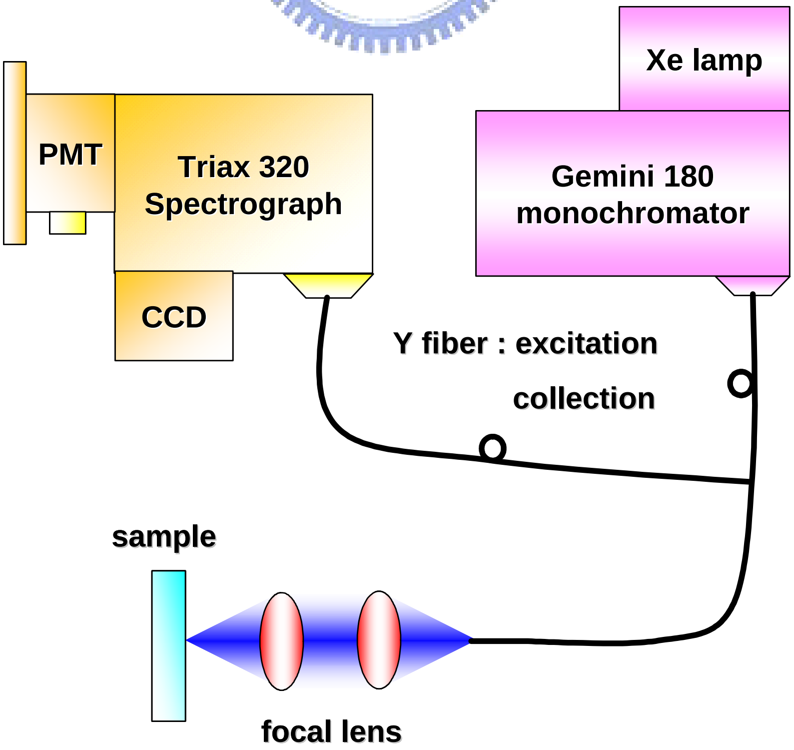

Fig. 2-2: Diagram of photoluminescence excitation measurement system

Before we measure photoluminescence excitation spectra, we must use Gemini 180 monochromator to separate 325 nm light from white light. When the light exits the slit and passes Y fiber, we let the spot size become 3 mm by the focal lens and focus on the sample. In the same method, we collect the light emitted by the sample to enter the Triax-320 monochromator. After that, fix the gratings of Triax-320 monochromator and collect the wavelength measured by photoluminescence spectra. Then, separate specific wavelength light from white light of xenon lamp by Gemini 180 monochromator which employs mechanical scanning method. After that, start our measurement.