Chapter 3: Fundamental concepts of experiment

3.1 Photoluminescence (PL) and Absorption

Photoluminescence is a common and useful tool for semiconductor optical analysis. Some of important material properties, like band gap, composition, doping type, carrier transport, lifetime, size of material, etc… can be obtained by PL. For semiconductor quantum structures, like quantum dot, the photoluminescence spectra line position can be tuned by quantum dot size (See Figure 3.1.1). When an incident laser irradiates on the semiconductor, if the laser energy is higher than the band gap, it creates electron-hole pair (if the electron and hole attracted each other by Coulomb interaction, it is also called exciton). The generated hot electron and hole release kinetic energy by emitting phonons, and then respectively drop from the excited state to the bottom of conduction band and top of valence band. Finally, the fluorescence emission occurs while the electron and hole recombines. However, several non-radiative transitions, like defect trapping, dislocation, surface of grain boundary, phonon scattering, and Auger process etc, might exist to compete with the radiative transition.

Different from the absorption, the luminescence mainly contributes to exciton recombination from its band edge level. The difference of energy between Fermi-energy and photon emission is so called Stokes shift. The type of exciton formation can be divided into (i) free exciton, which means the electron and hole bind together only by Coulomb force (ii) electron-hole pair bounded by neutral or charged donor (iii) electron-hole pair bounded by neutral or charged acceptor. Except the band to band transition, the exciton recombination processes are depicted as follows: (i) The free electron and hole recombination (ii) donor electron and valence band hole recombination (iii) conduction band electron and acceptor hole recombination (iv) donor electron and acceptor hole recombination. (See Figure 3.1.2)

3.2 Time-Tagged Time-Resolved (TTTR) Photoluminescence

The time-resolved recording is based on the precise measurement of the relative times between a fluorescence photon and the excitation laser pulse. Since with the periodic excitation like pulse laser, the data collection may be obtained over multiple cycles. The reference for the timing is the corresponding excitation pulse (see Figure 3.2.1 (a). At the same cycle duration, the first arrival fluorescence photon may trigger (or stop) the SPAD and then form a time-tag. The time tag function addresses the single photon absolute arrival time and performs multi channel scaler (MCS, or time trace) (see Figure 3.2.1 (b)), which means the fluorescence intensity as a function of time, the single photon events are accumulated into bins or channel of several ms. Furthermore, according to the emission photon and laser pulse related time interval, the fluorescence lifetime histogram is then formed by the superposition of multiple cycles (See Figure 3.2.1(c)).

In the ideal case, the measurement is established on the principle of one emission photon per excitation pulse. However, if there is more than one photon produced by each excitation pulse, the later photon of front cycle may over represent on the behind cycle. Therefore, in order to avoid this “pile-up” effect, it is crucial to keep the probability of cycles with more than one photon low. In order to maintain single photon statistics, but still hold the high count rate for quick data collection, the parameter which is so-called dead-time has been defined. This quantity describes the time the system can not register photons while it is processing a previous photon event. Besides, the standard SPAD and TCSPC electronics saturate at few hundred kilo counts per second.

3.3 On/Off time histogram

By the phenomena model, the statistical analysis of fluorescence intermittency reveals power-law distribution. From the MCS trace, we defined the on time (or the off time) as the interval of time when the intensity remain above (or below) a threshold intensity we chose. The frequency distribution is given by the histogram of *on* or *off* events of length τ:

$$N(\tau_{on/off}) = \sum_{\tau} [\text{events of length } \tau_{on/off}]$$

and the on(off) histogram obey the inversed power law

$$N(\tau_{on/off}) = At^{-m} \qquad (1)$$

3.4 Burst size histogram

From the MCS trace, we defined the on time (or the off time) when the intensity remain above (or below) a threshold intensity we chose. A burst is defined as the part of the MCS trace from the point, where it crosses the threshold upwards, to the next point, where it crosses the threshold downwards. The burst size denotes that the integrated intensity of the on-time interval.

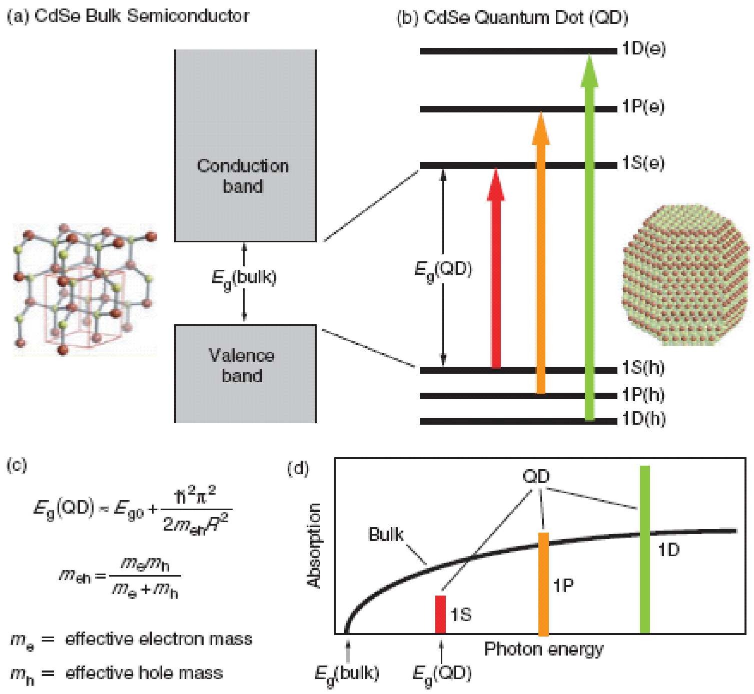

Figure 3.1.1 (a) CdSe bulk has the continuous band structure (b) CdSe QD has discrete level feature and (c) its energy level correspond to the size of QD. (d) The energy function of bulk and QD.

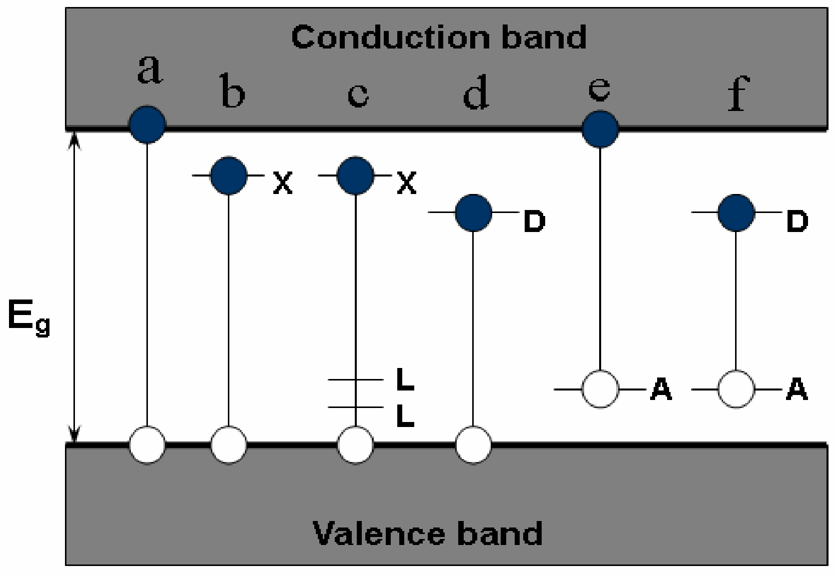

Figure 3.1.2 Carrier recombination radiative process: (a) the conduction band electron to valence band hole, (b)free exciton recombination, (c) free exaction with phonon recombination, (d) donor electron to valence band hole, (e) conduction band electron to acceptor hole, (f) donor electron to acceptor hole

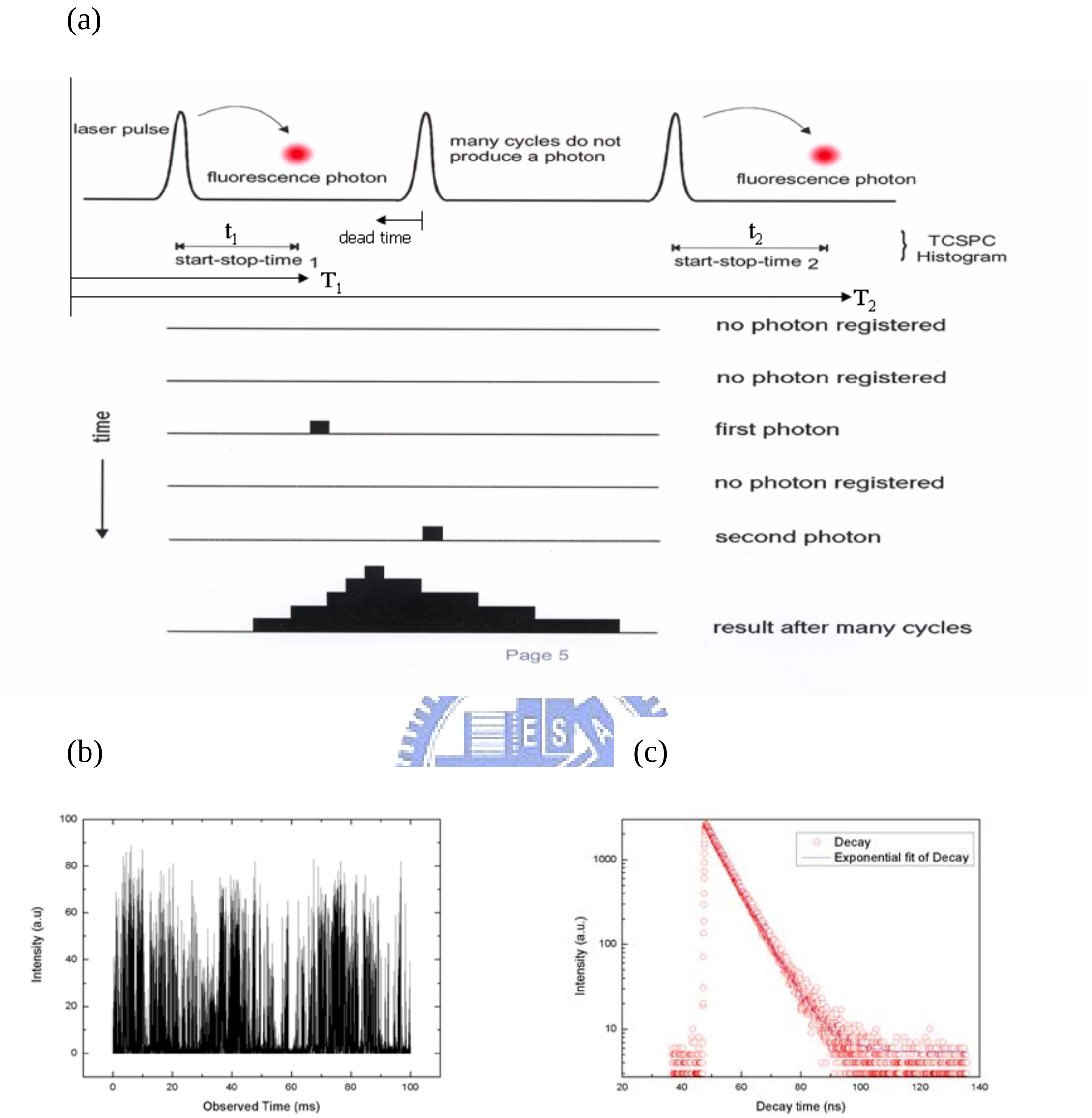

Figure 3.2.1 (a) Time-resolved lifetime histogram is formed by the statistic of counts of photon-pulse time related cycle. The acquisition can be divided into (b) Time-tag mode and (c) Time-resolved mode.