Electroluminescence and Spectral Shift of CdS Nanoparticles on Si Wafer

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Abstract: Preparation of CdS nanoparticles, device fabrication, and electroluminescence properties at room temperature of CdS nanoparticles on silicon substrates are reported. 86-meV spectral shift of free exciton transition due to passivation of p-hydroxyl thiophenol group around nanoparticles is found. Controlled process conditions such as heat treatment and/or with oxygen-rich environment are experimented and found to have significant influences on emission spectra. Radiative recombination corresponding to oxygen-impurity level, 273 meV below bandgap energy, presents in samples prepared in oxygen-rich environment. In addition to such mechanism, coalescence of nanoparticles into bulk form also exists and contributes to enhanced luminescence.

1. Introduction

Low-dimensional structures including nanoparticles or quantum dots (QDs) are supposed to provide significant enhancement in the density of states, so increasing the probability of light emission. Those low-dimensional structures can be epitaxially grown on bulk materials like GaAs wafers or separately formed by chemical methods. The former way is very selective on the grown substrates. Also, QDs are usually formed with only a scarce area density. In contrast, nanoparticles formed by chemical methods have the following advantages. First, they can be applied on any substrates. Second, area or volume density can be very high. The process to fabricate monodispersive nanoparticles is inexpensive and facile to industrial application. Stimulated emission and optical gain had been demonstrated in CdS quantum dots by methods of optical pumping [1], [2]. This encourages the employment of electrical pumping to realize efficient nanoparticle-based light emitting devices.

In this work, we demonstrate the applications of CdS nanoparticles on silicon substrate. The fabrication of light emitting active layer is simply the spin-coating technique. Electroluminescence (EL) can be easily achieved by quantum tunneling of carriers into the nanoparticles. The easy EL on Si wafers shows a promising way to monolithically integrate functions provided by nanoparticles and conventional integrated circuitry based on Si. Moreover, light emitting part of opto-electronic integrated circuits can be made after traditional process of electronic part. No special care is needed, compared with thermal and chemical budgets of epitaxial technology.

The experiments here include study of nanoparticle EL behavior in different environments. Heat treatment and mixture of solution is used. Spectroscopy of CdS nanoparticles is significantly influenced by the process temperature and the surrounding oxide. Radiative recombination due to free exciton in CdS is discovered in

those experiments, with pronounced energy shift due to organic coating of nanoparticles. As additional treatment is applied, bound-exciton radiative recombination of oxygen impurity emerges, and coalescence of CdS nanoparticle into bulk form presents. Because the nanoparticles are small (~5nm), compared to bulk materials, a relatively large surface contact area with environment results. The total amount of impurity states formed by diffusion of oxygen or other contaminants is thus quite severe and passivation, in our case organic p-hydroxyl thiophenol group, proves to be important. Moreover, the large interface area causes the light emission due to the impurity states to be significant, demonstrating another use of nanoparticles in addition to intrinsic quantum states provided by the low-dimensional structures.

2. Preparation of CdS Nanoparticles

We have synthesized redispersable nanoparticle powder of CdS by modification of Pietro's method [3]. Cadmium acetate dihydrate ($\text{Cd}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$, 0.80 g, 3.0 mmole) was dissolved in 20 ml mixed solvent of acetonitrile, methanol, and water with volume ratio 1:1:2. Another solution containing disodium sulfide nanohydrate ($\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$, 0.36 g, 1.5 mmole) and p-hydroxyl thiophenol (0.56 g, 4.4 mmole) in the same solvent system was added into vigorously stirred cadmium acetate solution. The whole system was stirred for 18 hours without light illumination. After removing solvent and purifying by centrifuge, we obtained 0.70 g yellow solid aggregate of CdS nanoparticles capped by p-hydroxyl thiophenol. Fig. 1 shows the TEM image. The diameter of the spherical CdS nanoparticles is about 5 nm. The TEM image of those nanoparticles is taken by the following procedure. The prepared solution is dipped onto carbon-film-coated copper plate and reabsorbed. Sparsely distributed nanoparticles are obtained.

By replacing part of cadmium acetate with manganese acetate, we prepared Mn doped CdS nanoparticles with different concentrations of manganese (5 %, 10 % and 20 %, in molar %). All such

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semiconductor nanoparticles can be re-dispersed in ethanol and other polar solvents. With ultrasonic vibration and percolation, solutions for spin-coating purpose are produced.

Figure 1. TEM image of p-hydroxyl thiophenol capped CdS nanoparticles.

3. CdS Light-Emitting Diodes on Si: Fabrication and Results

The CdS light emitting diodes (LEDs) are fabricated in different conditions. They are described in three parts according to the investigation of EL spectrum under those conditions. Although the primitive CdS nanoparticle EL could be found for all conditions, heat treatment and oxygen environment are discovered to have significant effects on the spectrum. Physical mechanisms for radiative recombination in these EL samples are different.

3-1. No heat treatment

A schematic of the CdS-nanoparticle LED is shown in Fig. 2. The fabrication steps are as follows. First, a low resistivity (doping $\sim 10^{15} \text{cm}^{-3}$) silicon wafer is used as the substrate. Acetone, methanol, and DI water are used for subsequent clean procedure. The wafer is placed on spinner with several dips of the previously mentioned four CdS and CdS:Mn nanoparticle solutions. A spin speed of 4000 rpm for 60 sec is used. For the EL investigation in this part, the wafer is placed in a chamber, in which 75-mmHg air pressure and room temperature are maintained for 5 minutes to remove ethanol solvents. The thickness of CdS nanoparticle layer can be as large as 500 nm, verified by surface profile scan. Therefore, volume density is very high, but relative high level of resistance also presents.

Subsequently, both top and bottom metal contacts are defined by thermal evaporation. The top semi-transparent contact layer is 10nm gold, and the bottom is 150nm gold. Before the deposition of the Au layer, a 3-nm adhesion layer of chromium had been evaporated for both contacts. After voltage bias is applied, EL through top thin layer can be seen by naked eye. A monochromator (CVI CM110) and photomultiplier is used to record the spectrum. In every spectrum

measurement, the slit width 0.6 mm is used for maximum detection and correct spectral measurement.

Figure 2. Schematic of the CdS nanoparticles EL device on Si wafer.

Samples made on n- and p-type Si wafers show different current-voltage (I-V) curves, as shown in Fig. 3. Both have rectifying I-V curves, but with opposite polarities. Those deposited on n-type silicon (solid line) exhibit large current when the electrode above the CdS nanoparticles is positively biased and small current at the opposite bias. Those deposited on p-type silicon exhibit reverse-polarity behaviors. This rectifying effect corresponds to metal-insulator-semiconductor tunneling effect. To be specific, the thin potential barrier of organic coating and low substrate doping level result in Schottky-diode-like behavior [4]. The EL spectrum corresponds to radiative recombination of carriers confined within CdS nanoparticles. Carriers are supplied by tunneling current.

Figure 3. I-V curves of devices on n-type and p-type Si, respectively.

The EL can be observed only when the devices are forward biased for both types. The forward bias is defined in conventional ways, referred to the electrical polarity with large current. The carrier injection and current flow for samples on the n-type substrate is illustrated in Fig.4. For samples on the n-type substrate, the silicon Fermi level has to be raised so that electrons are able to tunnel through the potential barrier of p-hydroxyl thiophenol group. Within CdS nanoparticles, part of the injected carriers recombine radiatively, part of them get trapped in defect levels, and part of them tunnel into the adjacent nanoparticles. Electrons trapped in oxide-impurity level could also radiatively transit to

valence band later on. Such process becomes significant if we immerse the nanoparticles into high concentration of oxygen surrounding environment, which will be further investigated in Section 3.2.

The turning point around 3V in Fig.3 corresponds to the start of carrier recombination process. Only after the applied bias overcome the potential barrier of p-hydroxyl thiophenol group between the CdS nanoparticle and the metal (or silicon), the radiative recombination process could start. This is also confirmed by light-voltage measurement.

Figure 4. Schematic of electron transport and transition in the device.

Both spectra of CdS and CdS doped with Mn are the same, as illustrated in Fig. 5. The spectrum peak at 526.5nm (2.355eV) is red-shifted from bulk CdS A-exciton transition energy, 2.441eV (508nm) at room temperature. [5] The energy red-shift of 86 meV does not come from quantum confinement within the nanoparticles, since such effect increases the exciton energy when the particle size decreases [6], [7]. It is the capping p-hydroxyl thiophenol group that gives modification of the emission peak position. CdS nanoparticles coated with polyvinyl alcohol also show such energy shift in absorption spectrum [8], where photoluminescence at 2.42eV (10K) is observed. Other studies [9], [10] have shown different shift level with different coating treatment.

Figure 5. EL Spectrum of CdS with direct vacuum treatment

The spectrum fits into Lorentzian shape with

scattering time of 6 fs. The FWHM is 42 nm. Such broad spectrum indicates dispersion of particle size. The emission mechanism could be radiative recombination of free exciton in CdS nanoparticles, with red-shift effect due to p-hydroxyl thiophenol group. With special heat treatment, the organic group decomposes, so CdS nanoparticles contact one another. Thus the spectrum becomes free exciton emission of bulk CdS. Then no red-shifted peak is observed, as will be explained in Section 3.2. As a result, possibility of bound exciton origin due to doped impurity is excluded in these samples.

3.2 Heat treatment by rapid thermal annealing

The CdS nanoparticles are spin-coated on Si wafer, as described in previous section. These samples are subsequently treated by rapid thermal annealing (RTA) with temperature 425°C for 5 minutes. The annealing process takes place with 75-mmHg air pressure. No observable ash of the organic p-hydroxyl thiophenol group presents, but the organic chemical is expected to decompose. I-V curves resemble that in section 3.1. EL spectrum depicted in Fig. 6 shows two peaks. One is at 513.7nm and another at 571.5nm. The former peak stands for bulk CdS signal (A exciton). This spectral lobe can be fitted by Lorentzian shape with scattering time of 8 fs and FWHM 40 nm. This investigation indicates that p-hydroxyl thiophenol group has influences on the emission wavelength, but has no significant effect on the emission strength of the radiative recombination process.

Figure 6. The EL Spectrum of CdS particles after heat treatment.

The 571.5nm peak results from the trapped carriers in oxide-impurity levels [9]. High temperature environment and the decomposition of p-hydroxyl thiophenol group cause the diffusion process of oxygen into the nanoparticles to occur. This proves p-hydroxyl thiophenol group to be effective overcoat of CdS nanoparticles against oxygen before it decomposes. The oxide-impurity levels also induce radiative transition. The peak magnitude at the spectral lobe is smaller than the magnitude at 513.7nm, indicating that the emission from oxide-impurity levels is weaker than that resulted from the CdS nanoparticles. However, light power from this sample is stronger than that in Section 3.1. The reason may be due to the participation of oxide-level

luminescence.

3.3 Effect of surrounding oxides

To further study the effect of oxide-impurity related signal, we immersed the CdS nanoparticles into high oxygen concentration environment. The nanoparticle solutions had been separately mixed with SOG (spin-on-glass) 315FX and SiO₂ nanoparticles (average diameter of 12 nm, dissolved in isopropyl alcohol). The cleaned silicon substrate is spin coated with the two kinds of mixture solution. Both samples are treated by 425°C RTA to sinter the SiO₂ glass.

Figure 7. EL spectrum for CdS nanoparticles mixed with SOG and mixed with SiO₂ nanoparticles.

EL spectra of the mixture of CdS nanoparticles with SOG and SiO₂ nanoparticles are shown in Fig. 7. The peak at 513.7 nm (2.414 eV) is A exciton signal of bulk CdS at temperature 65°C. The peak at 571.5 nm (2.414 eV) corresponds to radiative transition due to carriers trapped in oxide-impurity levels, as mentioned in previous section. Details of spectrum fitting will be discussed later. The magnitude of light emission in these samples is ten times stronger than that from unheated samples in Section 3.1, for the same carrier injection condition. The reason for significantly enhanced EL may be two-fold. The spectra shown in Fig. 7 indicate two mechanisms. First, the coalescence of CdS nanoparticles into bulk form results in less broadening spectrum around 513.7 nm. Since the potential barrier of p-hydroxyl thiophenol group disappear due to decomposition, carriers in bulk powders stay for enough time (about ns transition lifetime) to recombine radiatively between each tunneling process. The coalescence of CdS nanoparticles hence increases luminescence. Second, relative magnitude of oxide-impurity-level luminescence is much stronger than that in Section 3.2. Highly increased concentration of oxide-impurity levels, which are supplied by SOG or SiO₂ nanoparticles, contributes to the enhancement of internal quantum efficiency. Even with comparatively small oxygen concentration (around 1% mol ratio), the EL due to such level overwhelms that of CdS nanoparticles. The magnitude difference between mixture with SOG and SiO₂ nanoparticles comes from excess dangling Si-O bond of the latter case. With the

same sintering time, the latter mixture makes oxygen diffusion easier.

In case cleaned silicon is spin coated by mixture of CdS and SiO₂ nanoparticles, soft-baked at 90°C, and treated in 75 mmHg vacuum at room temperature. No sintering process and less oxygen diffusion is expected in this situation. As a result, the measured EL spectrum resembles that of heat treatment in Section 3.2. Less oxide-impurity level signal and CdS band edge emission of no energy shift is observed.

4. Discussion

In order to gain more physical insight into light emission in CdS nanoparticles, theoretical fitting to EL spectrum in Fig. 7 is made and shown in Fig. 8. Since the spontaneous emission spectrum of bulk CdS is of exciton origin, we have (see Appendix A)

$$R_{sp}(\hbar\omega) \propto \sum_{i=A,B,C} \left| \langle u_c | p | u_v^{(i)} \rangle \right|^2 \frac{\exp\left(\frac{-E_g^{(i)} + E_B^{(i)}}{kT}\right)}{(E_B^{(i)})^3} \times \delta(\hbar\omega - E_g^{(i)} + E_B^{(i)}) \quad \dots (1)$$

The bound energies of A, B, and C exciton are 29.4 meV, 29.4 meV, and 26 meV, respectively, and the bulk bandgap energy 2.4423 eV at 65°C is adopted [5]. The matrix element p_{cv}^2 is found to be 1:0.7:8.3. With delta function substituted by the Lorentzian one, scattering time 18 fs and FWHM 29 nm is obtained, indicating reduction of size dispersion and coalescence into bulk form.

Figure 8. Theoretical fitting of spectrum in section 3.

With the energy parameters of bulk CdS given above, the energy shift due to p-hydroxyl thiophenol group in Section 3.1 is found to be 86 meV. Also, the oxide-impurity level is found to be 273 meV below the bandgap. In addition to current observation of such peak at 571.5 nm, many other similar phenomena at the spectral range, 550 nm~600 nm, as an indication of imperfect CdS crystal or nanoparticles, had also been found. Hong et. al. [5] also demonstrated broad peak of 592 nm (2.0944 eV) due to S-vacancy (in this case substituting oxygen atom). Furthermore, Okamoto. et. al. [11] ascribed their broad

peak at 650nm (1.9eV) to surface-trap-state emission, perhaps due to different process method. Previously observed transition of Mn^{2+} ion in CdS nanoparticle at 585nm (2.119eV) [10] is not clearly observed in our samples, probably due to insufficient spectral resolution in our measurement.

5. Conclusion

Chemical preparation of CdS nanoparticles ready for spin-coating and EL devices made of CdS and CdS:Mn nanoparticles on Si substrates are described in detail. EL properties are investigated. Spectral shift of free exciton transition of 86 meV due to passivation of p-hydroxyl thiophenol group around nanoparticles is discovered. Process modifications such as heat treatment and oxygen-rich environment are influential to intrinsic green emission. p-hydroxyl thiophenol group is shown to have protection effect to avoid diffusion of contaminants into nanoparticels, but cannot resist temperature deterioration above 400°C.

Radiative recombination of carriers trapped in oxide-impurity levels of 273 meV below bandgap energy presents. With the oxide-impurity levels formed at the surface of CdS nanoparticels, luminescence increases for an order of magnitude.

APPENDIX A

The bulk CdS owns three valence bands, due to spin-orbit and crystal field splitting, and the conduction band. The electrons in conduction band form excitons with valence bands, i.e. A, B, and C excitons. Consider all three types of exciton A,B, and C, we have spontaneous light emission rate as

$$R_{sp}(\hbar\omega) = \sum_{i=A,B,C} G(\hbar\omega) \frac{\pi^2 e^2}{\hbar\omega\epsilon m^2} \left| \langle u_c | p | u_v^{(i)} \rangle \right|^2 \times \sum_{(i)} \frac{1}{3} f_{ex} \delta(\hbar\omega - (E_g^{(i)} - E_B^{(i)}))$$

.....(A.1)

where photon density is $G(\hbar\omega) = \frac{\omega^2}{\pi^2 \hbar v_g^3}$

exciton radius is $a_{ex} = \frac{e^2}{4\pi\epsilon E_B^{(i)}}$

and occupation probability approximated by Maxwell-Boltzman distribution is

$$f_{ex} = \exp(E_F - (E_g^{(i)} - E_B^{(i)} / n^2))$$

Here we assume all the three types of exciton A, B and C share the same Fermi level E_F . Collecting all terms and ignore constants at nearby energy 2.42eV (512nm) and consider only the most important n=1 peak, we obtain simplified relation in (1).

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