Journal of Luminescence 196 (2018) 264–269

Contents lists available at ScienceDirect

Journal of Luminescence

journal homepage: www.elsevier.com/locate/jlumin

Plasmon coupled photoluminescence from silver coated silicon quantum dots

Sioma Debela*, Belayneh Mesfin, Teshome Senbeta

Department of Physics, Addis Ababa University, Addis Ababa, Ethiopia

ARTICLE INFO

Keywords:
Local field
Surface plasmon
Spectral absorption
Radiative recombination
Photoluminescence

ABSTRACT

The surface plasmon enhanced photoluminescence (PL) emission of silver coated Si/SiO_2 quantum dots (QDs) is investigated theoretically and numerically for different parameters of the QDs. Due to the interaction of radiation with the silver coat, a local surface plasmon oscillation is established which in turn results in a considerable resonant enhancement of the local field in the QDs. The local field enhancement factor inside of the silver coated spherical Si/SiO_2 QDs is solved using the Laplace equation. Utilizing this enhancement factor, the plasmon enhanced radiative recombination rate, the spectral absorption, and the PL intensity of ensembles of silver coated Si/SiO_2 QDs embedded in a SiO_2 host matrix are studied. The induced electric field increases the overlapping of the electron and hole wave functions in the QDs leading to an increase in radiative recombination rate, spectral absorption, and the PL intensity. Moreover, by varying the thickness of silver coat and SiO_2 spacer, the surface plasmon resonance frequency can be tuned to the longer wavelength regions in the visible spectrum. This enhances the coupling between surface plasmon resonance frequency of the silver coat and the energy gap of silicon QDs. It is found that the radiative recombination rate, spectral absorption and photoluminescence intensity increase up to 3 folds compared to the QDs without a metal coat.

1. Introduction

Silicon is the most dominant material in the microelectronics world. Nevertheless, the electron-hole radiative recombination in the bulk material is forbidden because of the fundamental property of the silicon band structure [1,2]. On the other hand, silicon quantum dots (Si-QDs) show quantum confined luminescence at wavelengths in the visible and near infrared region [1,3]. Despite their high emission efficiency, Si-QDs suffer from low radiative decay rates as compared to those of direct band gap semiconductors [4]. To improve this state of affairs, the resonant effects of surface plasmons (SP) on PL emission attract a great deal of attention [4–10].

In particular, A. Inoue et al. [11] reported that a significant amount of PL emission enhancement of Si-QDs occurs when the emission energy lies in the vicinity of the localized surface plasmon resonance of gold NP. On the other hand, recent experimental work of S. K. Srivastava et al. [12] revealed the surface plasmon coupled emission of quantum confined excitons in the Ag_2O layer in a composite nanorod composed of silver core and Ag_2O shell.

The stretching in the energy gap of silicon quantum dots, which are sufficiently smaller than the Bohr exciton radius of the material ($\sim 5\ nm$) as a consequence of quantum confinement [13] favors the coupling of the energy gap of the QD with the SP energy of the metal coat. The plasmon coupled emission becomes more important for sufficiently smaller Si-QDs when the energy gap of the QD is close to the local surface plasmon resonance energy.

When the $Si/SiO_2/Ag$ QD (shown in Fig. 1) is illuminated by a radiation field, a local field is induced inside and outside of the metal coat as a result of polarization. This field significantly changes the interaction of the optically generated electrons and holes in the QD emitter. The induced field enhances the coupling between the electron and hole wave functions in the QD. The coupling between the electron and hole wave functions gets its maximum value at the local surface plasmon resonance frequency of the metal coat.

In an ensemble of such QDs, the spectral absorption and emission intensity strongly depends on the thickness of the metal coat, the size of Si-QD, thickness of spacer, and the dielectric functions of the different layers in the Si/SiO_2 /Ag QDs structure as well as the surrounding environment. By tuning the energy gap of a typical mean sized QDs in the ensemble to the local surface plasmon energy of the silver coat, enhancement of the spectral absorption and PL emission could be achieved.

The paper is organized as follows. In Section 2, we present the expression of the local field enhancement factor. The effect of local field

* Corresponding author.
E-mail address: sioma2007@gmail.com (S. Debela).

https://doi.org/10.1016/j.jlumin.2017.12.010
Received 31 July 2017; Received in revised form 2 December 2017; Accepted 4 December 2017
Available online 06 December 2017

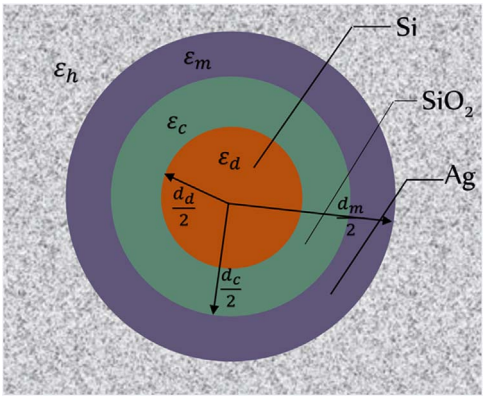

Fig. 1. Schematic diagram of a three layered spherical Si/SiO_2 /Ag QD in a SiO_2 host matrix. The central region shows the Si emitter with diameter d_d and dielectric constant ε_d, the middle layer represents the SiO_2 spacer with diameter d_c and dielectric constant ε_c, and the silver coat has a diameter d_m and dielectric constant ε_m.

enhancement in modifying the radiative recombination rate in silver coated Si-QDs is discussed in Section 3. Section 4 is devoted to the investigation of the effect of local field enhancement on the spectral absorption and PL emission of an ensemble of noninteracting silver coated Si-QDs. Section 5, summarizes the result obtained in the paper.

2. Local field enhancement factor

Consider a metal coated Si-QDs embedded in a dielectric host matrix, as shown in Fig. 1. In the electrostatic approximation, the electric field distribution inside and outside of the silver coated Si-QDs may be obtained by employing the Laplace equation $\nabla^2\Phi = 0$ in spherical coordinates, where Φ is the electric potential (see Appendix). The magnitude of the spatially constant electric field, E, inside the QD is found to be

$$E = \frac{27}{2p_m}\frac{\varepsilon_h\varepsilon_c\varepsilon_m}{\eta\varepsilon_m^2 + \beta\varepsilon_m + \varphi}E_0. \tag{1}$$

The coefficient of E_0 in Eq. (1) is the local field enhancement factor, $F = E/E_0$. Writing the complex dielectric function of the metal coat as $\varepsilon_m = \varepsilon'_m + i\varepsilon''_m$, where ε'_m and ε''_m are its real and imaginary parts, and manipulating the modulus square of the local field enhancement factor becomes

$$|F|^2 = \frac{\left(\frac{27\,\varepsilon_c\varepsilon_h}{2p_m}\right)^2(\varepsilon_m'^2 + \varepsilon_m''^2)}{[\eta(\varepsilon_m'^2 - \varepsilon_m''^2) + \beta\varepsilon'_m + \varphi]^2 + \varepsilon_m''^2(2\eta\varepsilon'_m + \beta)^2}. \tag{2}$$

The coefficients η, β, and φ depend on the dielectric functions of the host matrix, quantum dot, and the SiO_2 layer (see Appendix).

To understand the penetration of light into the Si-QD emitter in the three-layered composite NP, we may calculate the absorption coefficient (α) with the help of the Maxwell-Garnett effective-medium theory, thereby the penetration depth (d) can be computed. Accordingly, α is found to be

$$\alpha = \frac{2\omega}{c}Im\left\{\sqrt{\varepsilon_h\left[1 + \frac{\rho\chi_{cs}}{1 - \frac{1}{3}(\rho\chi_{cs})}\right]}\right\}, \tag{3}$$

where ω is the frequency of light, c is the speed of light, ρ is the density of the dipole moments in the mixture, $\chi_{cs} = 4\pi r_m^3(\delta_{sph}/2p_m\Delta_{sph})$. δ_{sph} and Δ_{sph} are given by (see Appendix) Eqs. (28) and (31), respectively.

The penetration depth of light through the composite NP can be estimated from the relation $d \sim 1/\alpha$. Typical value of d lies between 500 nm and 1μm depending on the thickness of silver shell, SiO_2 spacer, size of Si-QD, and wavelength of light. Since the typical size of the three-layered NP under consideration is below 40 nm, light can penetrate easily into the QD emitter.

For silver/gold alloys, the frequency dependent dielectric function ε_m of the metal coat is described by the modified Drude form given by [14]

$$\varepsilon_m = \varepsilon_\infty - \frac{\omega_p^2}{\omega(\omega + i\gamma)} + \varepsilon_{cp1}(\omega,\ \omega_{01},\ \omega_{g1},\ \gamma_1,\ A_1) + \varepsilon_{cp2}(\omega,\ \omega_{02},\ \gamma_2,\ A_2), \tag{4}$$

where, ε_∞ is a real constant, ω_p is the bulk plasma frequency of the metal, γ is the decay constant of plasma vibrations, ω is the frequency of radiation, ε_{cp1} and ε_{cp2} are the interband contributions to the dielectric function of the plasmonic metals. The parameter γ is the size dependent decay constant of plasma vibrations given by

$$\gamma = \gamma_{bulk} + A\frac{v_F}{a}, \tag{5}$$

where γ_{bulk} is the bulk decay constant of plasma vibrations, v_F is the velocity of the electrons at the Fermi surface, a is the thickness of silver coat and $A$is a parameter which depends on the details of the scattering process [15].

Later, we will use the local field enhancement factor, Eq. (2), with account of the complex dielectric function of the metal coat, Eq. (4), to calculate the plasmon enhanced radiative recombination rate, the spectral absorption, and PL intensity of silver coated Si-QDs.

3. Plasmon coupled radiative recombination rate

The rate of a spontaneous transition Γ_r from an excited electron-hole state $|\psi_i\rangle$ to the ground state $|\psi_f\rangle$ may be described by using Fermi's golden rule in the first-order perturbation theory as $\Gamma_r = (2\pi/\hbar)|\langle\psi_f|\widehat{H}_{int}|\psi_i\rangle|^2\delta(E_f - E_i - \hbar\omega)$ [16], where $\widehat{H}_{int}$ is the operator of the interaction Hamiltonian, $\hbar\omega$ is the emitted photon energy, E_f and E_i are the energies of the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO), respectively. Summing Γ_r over all light polarization gives [17,18]

$$\Gamma_r = \frac{4e^2\ n\ \omega}{3\ m^2\hbar\ c^3}|\langle\psi_f|\hat{p}|\psi_i\rangle|^2, \tag{6}$$

where e is the charge of an electron, n is the refractive index, ω is the transition frequency, m is the electron rest mass, c is the speed of light, $\hbar$ is Planck's constant divided by 2π, and $\hat{p}$ is the momentum operator.

The matrix element of transition $\langle\psi_f|\hat{p}|\psi_i\rangle$ can be expressed in terms of the oscillator strength f_{osc}, which can be regarded as a measure of strength of a transition from an initial state with energy E_i to a final state with energy E_f, i.e.,

$$f_{osc}(\omega) = \frac{2}{m\hbar\omega}|\langle\psi_f|\hat{p}|\psi_i\rangle|^2. \tag{7}$$

The oscillator strength is a function of the photoluminescence emission energy which for silicon QDs can be described by using the following empirical formula [19]:

$$f_{osc}[\hbar\omega(eV)] = 1.4\times10^{-5} + 5.8\times10^{-8}\exp\left(\frac{\hbar\omega(eV)}{0.332}\right), \tag{8}$$

where the size dependent f_{osc} is described via the emission energy-size relation ($\hbar\omega = 1.12 + 3.73/d_d^{1.39}$) suggested by Delerue et al. [20].

When a QD is coated with noble metals, the oscillator strength changes. The change may be described by modifying the interaction Hamiltonian of electron-hole pairs. In the dipole approximation, the interaction Hamiltonian may be written as $\widehat{H}_{int} = -F(\omega, d_d, d_c, d_m)\hat{\mu}\cdot\widehat{E}$, where $\hat{\mu}$ is the dipole moment operator and $\widehat{E}$ is the electric field operator. The matrix element of momentum operator is obtained from the dipole matrix element using the relation $\langle\psi_f|\hat{p}|\psi_i\rangle = im\omega\langle\psi_f|\hat{r}|\psi_i\rangle$ [21]. Thus, the expression for the plasmon coupled oscillator strength f_{sp} of electron-hole pairs takes the form: