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Third harmonic and sum-frequency generation in ZnO quantum dots

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ABSTRACT

Within the framework of the density matrix approach we investigate the third harmonic generation (THG) and sum frequency generation (SFG) associated with the intersublevel transitions in the conduction band of a singly charged ZnO quantum dot (QD). With three optical fields incident on the dot, we obtain the third order nonlinear susceptibility resulting in the THG and the SFG processes. As compared to the bulk enhanced value of the third order nonlinear susceptibility is obtained through the electric dipole interactions of the pump fields with the electron in the QD. Results are obtained for the THG and SFG in the ZnO QD embedded in the HfO_2, Al_2O_3, AlN, and SiO_2 matrices. The results show that the dot size and the surrounding matrix significantly influence the third order nonlinear susceptibility, which is found to be relatively higher for the QD embedded in the high-dielectric constant HfO_2 matrix as compared to the other matrices.

1. Introduction

Advances in the nonlinear optical spectroscopy techniques have revealed that the optical nonlinearity associated with the low-dimensional nanostructures such as quantum well, quantum wire, and quantum dot (QD), becomes considerably large as compared to the bulk. Materials with enhanced optical nonlinearity have potential applications in nonlinear spectroscopy, ultrafast optical devices e.g. laser amplifiers, photodetectors and electro-optic modulators [1–3], optical signal processing [4]. The high speed of operation in such devices relies on the optical nonlinearity that involves intraband or interband electronic transitions during the interaction of radiation with matter. It is particularly important for quantum electronics and quantum information processing. The dipole matrix element associated with the intersublevel (ISL) transitions in nanostructures has large value which leads to the enhanced optical nonlinearity [5].

The exploitation of low dimensional semiconductor nanostructures as nonlinear optical media has resulted in important advances in nonlinear optics. Controlling the size and dimensionality of the semiconductor nanostructures is an additional way to tune their nonlinear optical properties via quantum confinement effects. Quantum confinement in a direction in quantum well leads to two dimensional step like density of electronic states. Further, quantum wire and QD allows enhancement of density of states in two and three dimensions respectively. In QD, with atomic like electronic spectra the energy spacing is a function of dot size which is advantageous for spectral tunability. The triple resonance condition can be achieved in QD. Further compared to the nonlinear bulk materials there is absence of phase matching requirement in nanoparticles

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[6]. Additionally they can be embedded into different matrices. Embedded semiconductor quantum dots have emerged as a family of materials with size dependent nonlinear optical properties.

Unlike the second harmonic generation which is observable only in the noncentrosymmetric structures, the third harmonic generation (THG) and sum frequency generation (SFG) are easily observable in both the centrosymmetric and the noncentrosymmetric structures [7]. In the literature several studies have been reported on the nonlinear susceptibility in nanostructures [8–21]. The third order nonlinear processes offer an opportunity to extend the coherent light sources to shorter wavelengths which is advantageous for the operation of the optoelectronic devices at shorter wavelengths. The enhanced THG in InAs/GaAs QDs has been demonstrated both experimentally and theoretically by Sauvage et al. [14]. The third order nonlinearity based on the exciton–exciton interaction has been reported on the nanocolloids of ZnO [18]. Kumar et al. [19] studied the THG in InAs QD. A report on the third order optical nonlinearity of ZnS QD demonstrated that it depends on the choice of the medium in which the dot is embedded [20]. To the best of our knowledge the THG and SFG in spherical ZnO QD embedded in different matrices has not been studied. We report the THG and the SFG associated with ISL optical nonlinearities in the conduction band of the ZnO QD embedded in the four different matrices HfO_2, Al_2O_3, AlN, and SiO_2.

2. Theory

Using the effective mass approximation (EMA) the Schrödinger equation for the confined electron in the wurtzite ZnO QD embedded in a matrix is given by,

$$\left[-\frac{\hbar^2\nabla^2}{2m^*}+V_{conf}(\vec{r})+\Sigma(\vec{r})+V_P(\vec{r})\right]\psi(\vec{r})=E\psi(\vec{r}) \tag{1}$$

where m^* is the effective mass of the electron in the QD, $V_{conf}(\vec{r})$ is the confinement potential due to the conduction band offset, $\Sigma(\vec{r})$ is the self energy. $V_P(\vec{r})$ is the induced potential energy due to the built-in internal electric field (F_D) for wurtzite QD.

The confinement potential $V_{conf}(r)=\begin{cases}0 & r<R\\ V_b & r\geqslant R\end{cases}$ with dot radius R and the finite barrier height V_b. The self energy $\Sigma(\vec{r})$ of the electron confined in a QD $\Sigma(r)=\frac{1}{2}\left(\frac{1}{\varepsilon_{out}}-\frac{1}{\varepsilon_{in}}\right)\frac{e^2}{4\pi\varepsilon_0 R}+\delta\Sigma$, with $\delta\Sigma\cong 0.47\frac{e^2}{4\pi\varepsilon_o\varepsilon_{in}R}\left(\frac{\varepsilon_{in}-\varepsilon_{out}}{\varepsilon_{in}+\varepsilon_{out}}\right)$ [21,22], where ε_{in} and ε_{out} are the dielectric constant of the dot material and the matrix material, e is the electronic charge and ε_0 is the permittivity of free space.

For a wurtzite ZnO QD the total polarization P_{tot} consists of the sum of the spontaneous polarization P_{SP} (polarization at zero strain) and the strain induced piezoelectric polarization P_{PZ}. The piezoelectric polarization along the c-axis due to the lattice mismatch between the dot and the matrix material is given by,

$$P_{PZ}=e_{31}(\varepsilon_{xx}+\varepsilon_{yy})+e_{33}\varepsilon_{zz}$$

where e_{ij} are the piezoelectric coefficients and ε_{ij} are the strain elements expressed as $\varepsilon_{xx}=\varepsilon_{yy}=\frac{a_{bar}-a_D}{a_{bar}}$ and $\varepsilon_{ZZ}=-2\frac{C_{13}}{C_{33}}\varepsilon_{xx}$ where a_D and a_{bar} are the lattice constants and C_{13} and C_{33} are the elastic constants.

The total built-in electric field F_D inside the spherical dot is given by [23],

$$F_D=\frac{P_{tot}^{bar}-P_{tot}^{D}}{\varepsilon_0(\varepsilon_{bar}+\varepsilon_D)}$$

where $P_{tot}=P_{SP}+P_{PZ}$ and $\varepsilon_{bar(D)}$ is the relative permittivity of the barrier (of the QD).

For the smaller dot size up to about one and half times the effective electron Bohr radii the shift in the electron energy levels due to the built in applied electric field of about ten atomic units can be neglected [24]. In addition, for the wurtzite ZnO dot-matrix structure the internal field is negligible due to the mutual cancellation of the sum of the piezoelectric and the spontaneous polarization [25].

After obtaining the required energy levels and the wave functions [21,26], we calculate the third order nonlinear susceptibility coefficient leading to THG and SFG. The different material parameters used in our calculation are given in the Table 1.

Table 1
Material parameters used in the calculation.

Material	V_b (eV) with ZnO	ε_r	m^*
HfO_2	2.2 [26]	25 [26]	$0.11m_e$ [26]
Al_2O_3	2.5 [27]	9 [28]	$0.40m_e$ [28]
AlN	3.29 [26]	8.5 [26]	$0.32m_e$ [26]
SiO_2	4.3 [29]	3.9 [29]	$0.50m_e$ [29]
ZnO	–	8.66 [26]	$0.24m_e$ [26]