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Two photon processes in ZnO quantum dots

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ABSTRACT

The two-photon bound–bound (TPBB) and the two-photon bound-free (TPBF) processes are studied for the electron in the initial 1S state in the conduction band of the ZnO quantum dot (QD) embedded in the HfO_2 and the AlN matrices. The energy and the wave functions of the QD are obtained by using the effective mass approximation with a finite barrier height at the dot-matrix interface. Using the second order perturbation theory results are obtained for the two-photon absorption coefficient and the photoelectric cross section. The photoelectric cross section ratio for the circularly to the linearly polarized photons is also obtained. It is observed that the two-photon processes depend significantly on the polarization of the incident beam, the dot size, and the surrounding matrix. It is found that the electric quadrupole interaction enhance the TPBF photoelectric cross section.

1. Introduction

Semiconductor quantum dots (QDs) have been explored widely for the size tunable nonlinear optical properties. Nonlinear optical (NLO) phenomenon in QDs have technological applications in multiphoton microscopy [1], optoelectronic devices [2], bioimaging [3,4], light up-conversion [5], optical limiter [6]. Reliable theoretical predictions of multiphoton processes in QDs of different materials offer an alternate to choose the material for NLO measurements in order to avoid time consumption and costly synthesis. Such theoretical predictions are necessary and are of immense importance for the practical realization of various applications based on two-photon processes.

In the past two-photon bound–bound (TPBB) excitation process in QDs has been studied [6–15] while theoretical modelling of the two-photon bound-free (TPBF) photoelectric process in the QDs is at its inception. Most of the theoretical studies of TPBB processes have been made for interband transitions ($2\hbar\omega \geq E_g$) with the photon wavelength (energy $\hbar\omega$) lying in the visible region (E_g the band gap energy). However, the study of the two-photon intersublevel (ISL) transitions in the conduction band offers the advantage of photon wavelength lying in the IR region which is extremely useful for optoelectronic devices and biomedical applications.

Compared to the bulk, the QDs have large two-photon absorption cross section in both the visible and the near IR region [16–19]. Some studies on the size dependence of the two-photon absorption in QD have been reported for CdSe [20,21]. Although many authors reported two-photon absorption properties of various QDs [6–22] such studies (theoretical and experimental) are scarce in ZnO QDs for ISL transitions. Some experimental investigations have been performed on

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polycrystalline ZnO, single crystal ZnO, microcrystalline ZnO thin films [23,24]. Recently ZnO has been studied as a promising candidate for biological imaging and tracking device due to its nontoxic nature and NLO properties [3,25–27]. But none of these studies are based on ISL transitions in ZnO QD in the conduction band.

Most of the theoretical investigations on the multiphoton processes associated with the TPBF transitions have been performed for atomic systems using the electric dipole approximation. In the dipole approximation the size of the atom is assumed to be smaller than the wavelength of the incident radiation. In some earlier studies [28–34] it has been found that the higher multipole such as the electric quadrupole plays an important role in the multiphoton ionization process. The study of the TPBF photoelectric process including the effects of dipole and quadrupole interaction offers the possibilities of studying the excited states which may otherwise be forbidden, thus providing spectroscopic information complimentary to that obtained through the inclusion of the dipole interaction only. With the inclusion of the quadrupole effect it becomes possible that the two-photon ionization process occurs either with one dipole and one quadrupole photon or with both quadrupole photons instead of the usual two dipole photons. Experimentally the quadrupole effect has been investigated in atoms by Lambropoulos et al. [29] and Kaminski et al. [35]. Mathur and Co-workers' [32,33] studied the multipole effects in the two-photon ionization of metastable helium which were confirmed experimentally by Haberland et al. [36]. Also the multipole effects in the photoelectron angular distributions for multiphoton ionization of atoms have been predicted experimentally [37–40]. These investigations establish that the maximum value of the ratio for the circularly to the linearly polarization TPBF cross sections $r = \frac{\sigma_c}{\sigma_l}$ is below 1.5. This is in agreement with the theory of Klarssfeld and Maquet [41] where the maximum ratio for N photon ionization is predicted below $\frac{(2N-1)!!}{N!}$.

In this paper we investigate the TPBB and the TPBF processes for the electron in the initial 1S state in the conduction band of the ZnO QD. The TPBB and TPBF processes are described as,

$$2\hbar\omega + D^-(E_i) \rightarrow D^-\left(E_f\right) \qquad \text{(TPBB)}$$

$$2\hbar\omega + D^-(E_i) \rightarrow D + e^-\left(\vec{k}_f\right) \quad \text{(TPBF)}$$

where $D^-(E_i)$ represents a singly charged QD embedded in a dielectric matrix and D represents the neutral QD. E_i and E_f are the initial and the final state energy of the electron, $\hbar\omega$ is the incident photon energy and $\vec{k}_f$ represents the wave vector of the ejected photoelectron. In the TPBB process the absorption of two photons excites the electron from its initial confined state (i) to a higher excited state (f) in the conduction band of the dot. In TPBF process the absorption of the two photons by the electron ejects the electron from its initial confined state (i) in the conduction band of the dot to a free state $\vec{k}_f$ outside the dot.

To investigate the TPBB and TPBF processes we use the second order perturbation theory to obtain the cross sections. We obtain the transition energies of the confined states of singly charged ZnO QD in the conduction band using the effective mass approximation. The confined state energies are found to be in a good agreement with the available experimental data of Germeau et al. [42] (Fig. 2 of Ref. [43]).

We consider the dot surrounding matrices as HfO_2 and AlN. The choice of the HfO_2 matrix is useful owing to its low synthesis temperature, thermal and kinetic stability, high dielectric constant which minimizes the leakage current in devices, and sufficient conduction band offset at the dot matrix interface to act as barrier for electrons [44–46]. The choice of the AlN

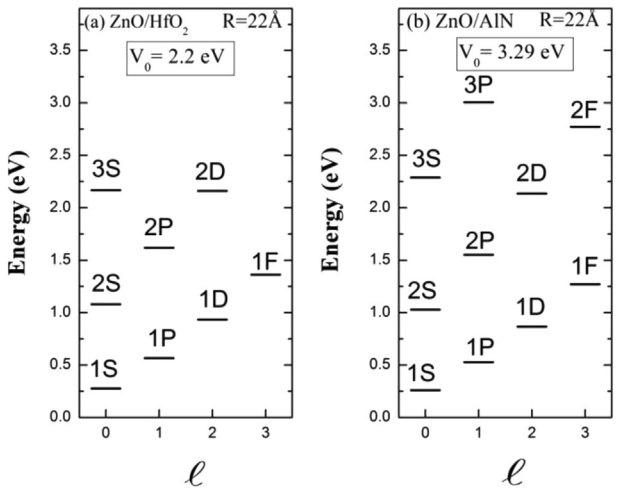

Fig. 1. Confined discrete energy levels in the conduction band of the ZnO QD embedded in the matrices (a) HfO_2; and (b) AlN at dot radius R = 22 Å.