Optical Characteristics of ZnO – Based Photodetectors Doped with Au Nanoparticles

S. Mohammadnejad[1], S. G. Samani[2], and E. Rahimi[3]
Nanoptronics Research Center, School of Electrical Engineering,
Iran University of Science and Technology, Tehran, Iran
[1]shahramm@iust.ac.ir, [2]s_ghatreh@yahoo.com, [3]erahimi@iust.ac.ir

***Abstract*—Zinc oxide as a primary material for ultraviolet detectors has shown to have a very high ratio of photo current to dark current which makes it suitable for photodetectors. Au Nanoparticles with specific diameters are exposed to improve optical characteristics of ZnO-based photodetectors. They have a high absorption coefficient, so charge transition is increased and photo current will be amplified as a result. Optical properties of photodetectors depend on nanoparticles characteristic. For photodetectore application we need to identify which of optical properties (scattering, absorption) are beneficial and then design suitable nanoparticle to maximize these effect while minimizing unwanted optical properties. Effect of Nanoparticles on optical parameters of photodetectors based on ZnO is discussed in this paper.**

Keywords—nanoparticle(NP); dark current; absorption coefficient; quantum efficiency

I. INTRODUCTION

Nanoparticles of metals have recently become the focus of research because of their unique properties, which are different from those of bulk materials. These properties depend on the size, shape and differences in the environments of nanoparticles. Although the influence of size on the bulk material is negligible, optical properties of nanoparticles depends on their shape and diameter. The size induced properties of nanoparticles make them suitable for many applications in various areas such as catalysis, optics, and life environments [1].

Photovoltaic process consists of two phases: 1- Absorption of photon and electron-hole pair. 2- Charges are transferred to external contact. In the first stage, we need device to have appropriate and optimal thickness in order to absorb photons. It is necessary to have a diffusion length larger than thickness size in stage two [2]. Therefore, there is a relationship between absorption coefficient and optical properties of semiconductor materials. Nanoparticles increase the effective path length of light and ratio of area to volume and act as optical traps [3].

The large area to volume ratio increases the carrier life time and reduces the carrier transit time. Total transfer and generated charges are increased and as a result, photo current is amplified. When the detector channel is filled by NP, problems of surface defects are still remained. Deep traps in the NP increases the rise time transition charges because first transition charges fill traps then a photo current reaches its maximum value [4].

II. *NANOPARTICLE* CHARACTRISTIC

A. Optical properties

The optical properties of nanoparticle are determined by localized surface plasmon resonance (LSPR). When, we refer to a surface Plasmon resonance that gives bright colors. The LSPR depends on the size, shape and differences in the environments of nanoparticles.

1) Shape: To explore the influence of nanoparticle shape we will investigate the optical properties of various Au nanoparticle with constant volume. The LSPR depends strongly on shape. The effect of metal nanoparticle shape has been investigated by simulation based on finit-diffrence time domain (FDTD). Extinction cross section is shown in Fig. 1.

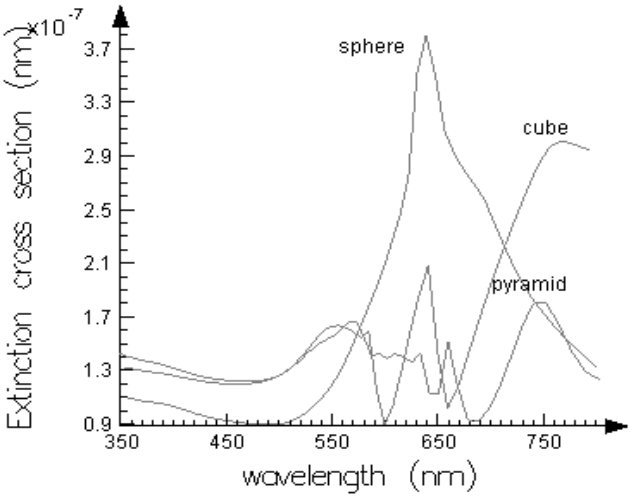

Figure 1. FDTD Extinction simulation of Au nanoparticle with same volume

2) Size: The optical properties of large and small nanoparticles are completely different. The extinction cross section of three different sizes of gold nanoparticles are shown in Fig. 2. As the gold particles get larger, the scattering portion of the extinction increases.

3) Dielectric environment: The optical properties of metal nanoparticles are strongly sensitive to dielectric environment which is useful for tuning their optical properties. An increase of refractive index of medium surrounding a nanoparticle result in a wavelength shift of

the localized surface Plasmon. The sensitivity of nanoparticles to dielectric environment changes is shown in Fig. 3.

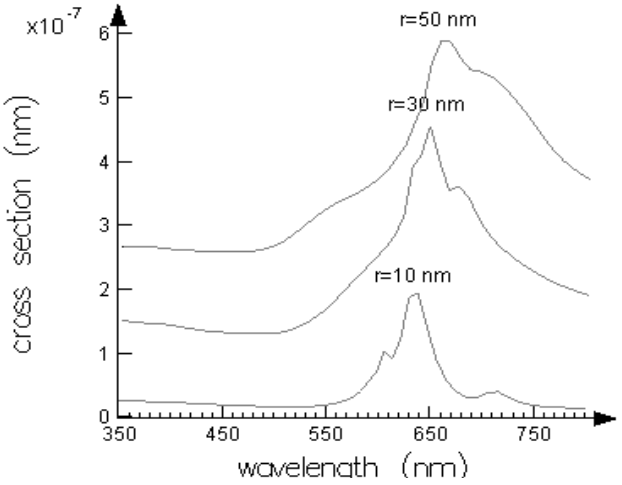

Figure2. The extinction cross section of three different sizes of Au nanoparticles. (background index=3)

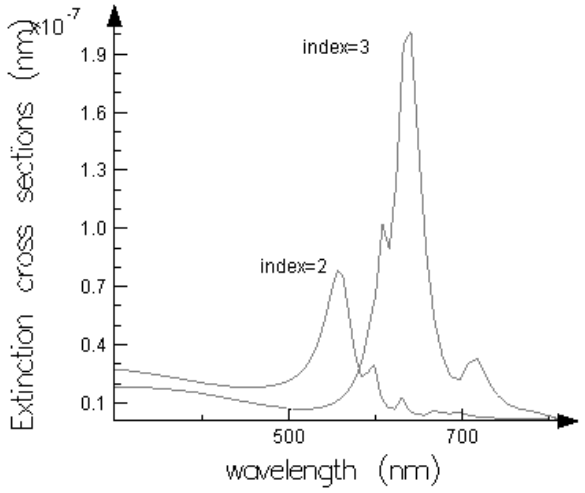

Figure 3. Extinction of Au nanoparticle as a function of surrounding dielectric environment

B. *Electrical characteristic*

The dielectric function $\varepsilon(\omega)$ of metals is written as $\varepsilon = \varepsilon_1 + i\varepsilon_2$, where ε_1 and ε_2 are the real and imaginary parts of metal dielectric function. When the size of particle becomes comparable to or smaller than the electron mean effective free path, the electron mean effective free path is smaller than that in the bulk material. The Drude dielectric function is used for free electrons and given by [5]:

$$\varepsilon_{Drude}(\omega) = 1 - \frac{\omega_p^2}{\omega^2 + i\Gamma\omega} \tag{1}$$

$$\omega_p = \sqrt{\frac{ne^2}{m_e\varepsilon_0}} \tag{2}$$

$$\Gamma = \Gamma_{\text{bulk}} + \frac{A\upsilon_F}{a} \tag{3}$$

Where ω_p is plasma frequency, Γ is the damping constant in the Drude dielectric function, n is the electron density of free electron, m_e is effective mass, A is particle shape parameter and is taken as 1 for a spherical particle, a is nanoparticle radius and υ_F is Fermi velocity. The parameters are used: $\omega_p = 13.8 \times 10^{15} s^{-1}$, $\Gamma_{\text{bulk}} = 1.075 \times 10^{14} \text{s}^{-1}$, $\upsilon_F = 1.39 \times 10^6 \text{ m/s}$ for a spherical Au particle but the free electrons is lower for Au. Fig.4 shows that the real and imaginary parts of Drude dielectric function for $\lambda = 400nm$. In materials, the contributions of free and interband electrons to $\varepsilon(\omega)$ can be separated:

$$\varepsilon(\omega) = \varepsilon_{bulk}(\omega) + \frac{\omega_p^2}{\omega^2 + i\Gamma_{\text{bulk}}\omega} - \frac{\omega_p^2}{\omega^2 + i\Gamma\omega} \tag{4}$$

Where $\varepsilon_{\text{bulk}}(\omega)$ is the contribution of the interband electron. Fig.5 shows that the real and imaginary parts of dielectric function for $\lambda = 400nm$. When a small nanoparticle is irradiated by light and the nanoparticle size is much smaller than the wavelength of light, the electric field of the light is constant, and so the interaction of light with the nanoparticle can be analyzed in the quasi static approximation (QSA) with the neglect of electrodynamics. In order to extend the electrostatic behavior to larger nanoparticles in which the electrostatic approximation gradually fails, the modified long wavelength approximation (MLWA) is employed in our calculation to include the pertubative correction to the electrostatic approximation [5].

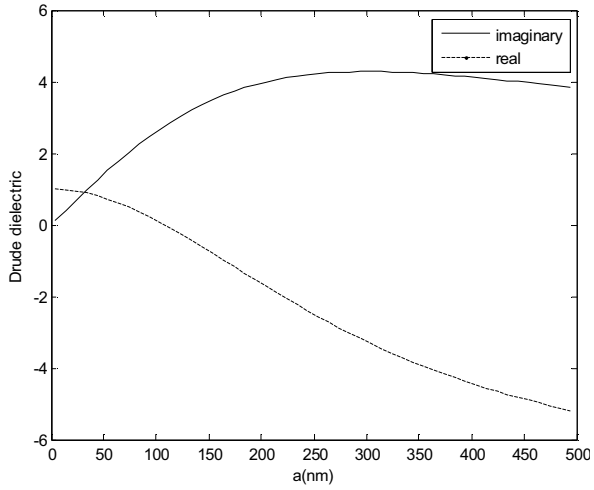

Figure 4. The real and imaginary parts of Drude dielectric function for $\lambda = 400nm$.

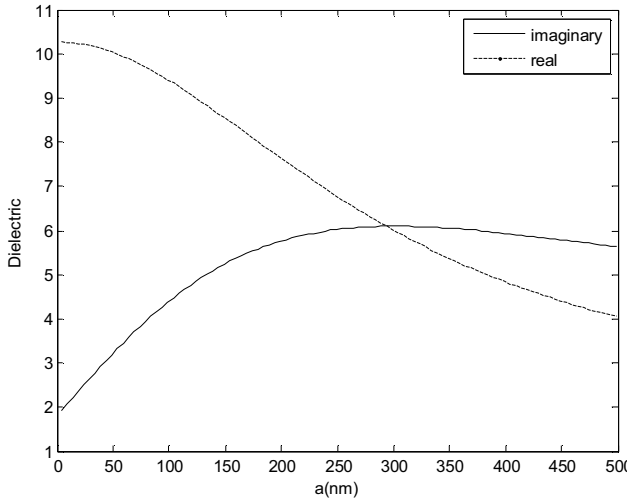

Figure 5. The real and imaginary parts of dielectric function for $\lambda = 400nm$.

The electrodynamic correction of MLWA can be determined by:

$$P = \alpha(E + E_{rad}) \tag{5}$$

$$\alpha = 4\pi a^3 \left(\frac{\frac{\varepsilon}{\varepsilon_m}-1}{\frac{\varepsilon}{\varepsilon_m}+2}\right) \tag{6}$$

$$E_{rad} = \frac{2}{3}ik^3P + \frac{k^2}{a}P \tag{7}$$

Where α is the particle polarizability, E is electric field, P is induced polarization and ε_m is the dielectric of the embedding medium. When, $\varepsilon = -2\varepsilon_m$ the nanoparticle polarizability will become very large. This is known as surface Plasmon resonance. At the surface Plasmon resonance can well exceed the geometrical of particle. In such a case a substrate covered with density of particles could completely absorb and scatter the incident light. For light trapping it is important that scattering is more efficient than absorption [6].

When the nanoparticle size increases, dynamic depolarization occurs and conduction electrons across the particle no longer move in stage. This leads to a reduction in the depolarization field at the centre of the particle [6]. As a result, there is a reduced restoring force and therefore a red-shift in the particle resonance.

III. Photodetector based on ZnO

Direct band gap detectors have high quantum efficiency which makes them appropriate for UV detectors. Furthermore, a wide band-gap material decreases dark current and also leads to bulk absorption of photons rather than surface absorption.

Band-gap energy of ZnO is 3.3eV. When, it is doped with metals like Cd and Mg, band-gap energy changes to a range of 2.8 to 4.8 [7]. ZnO has some advantages over other common semiconductors like GaN. The first advantage is the availability of a natural substrate for it. The second is that alloy system of $Mg_xZn_{1-x}O$ is more adapted than $Al_xGa_{1-x}N$. This becomes important when we try to form an active device layer far from the surface in a hetero structure. These two properties make ZnO to have less defects than GaN and so dark current in ZnO is smaller than GaN[8, 9]. Responsivity of a detector(R) consists of two steps: 1- Quick process because of electron-hole Generation. 2- Oxygen chemical absorption. Oxide on the material surface is formed; a layer of electron-hole pair is formed that reduce the conductance. When the detector is exposed on UV, generated holes move on the surface and negative charges are neutralized by oxidation process, so the electrons are gathered at anode, electrical conductivity and light absorption is increased, responsivity can be determined by equation(1):

$$R = \frac{\eta\lambda}{1.24} \tag{8}$$

Where R is responsivity, λ is the wavelength and η is quantum efficiency that expresses as:

$$\eta\alpha(1 - e^{-\sigma a}) \tag{9}$$

σ denotes the absorption coefficient and a is the length of active area. As it is clear from the equation; by increasing absorption coefficient, quantum efficiency will be increased too. As a result, responsivity is improved too. It should be noted that the increase in the length of active area, with more quantum efficiency but increases the response time.

IV. SIMULATION

Following equations for simulation has been used [10]:

$$a_n = \frac{m^2\Psi_n(mx)[x\Psi_n(x)]' - \mu\Psi_n(mx)[mx\Psi_n(mx)]'}{m^2\Psi_n(mx)[xh_n^1(x)]' - \mu h_n^1(x)[mx\Psi_n(mx)]'} \tag{10}$$

$$b_n = \frac{\mu\Psi_n(Nx)[x\Psi_n(x)]' - \Psi_n(Nx)[Nx\Psi_n(Nx)]'}{\mu\Psi_n(Nx)[xh_n^1(x)]' - h_n^1(x)[Nx\Psi_n(Nx)]'} \tag{11}$$

Where m = n + ik is the refractive index of the sphere relative to the ambient medium, $x=ka$ is the size parameter, a the radius of the sphere, $k = 2\pi/\lambda$ is the wave number, and λ the wavelength, μ is the ratio of the magnetic permeability of the sphere to the magnetic permeability of the ambient medium that is usually equal to 1. ψ_n and $h_n^1(u) = \psi_n(u) + iy_n(u)$ are spherical Bessel functions. Efficiency (Q) and the absorption coefficient (σ_{abs}) leads to the following equation:

$$Q_{ext} = Q_{sca} + Q_{abs} \text{ or } \sigma_{ext} = \sigma_{sca} + \sigma_{abs} \tag{12}$$

$$Q_{sca} = \frac{2}{x^2}\sum_{n=1}^{\infty}(2n+1)(|a_n|^2 + |b_n|^2) \tag{13}$$

$$Q_{ext} = \frac{2}{x^2}\sum_{n=1}^{\infty}(2n+1)Re(a_n + b_n) \tag{14}$$

$$Q_i = \frac{\sigma_i}{\pi a^2} \quad (15)$$

The Simulation results for wavelengths $\lambda = 400, 500$ and 600 nm are shown in Fig.6, Fig.7 and Fig.8. Simulation result shows that the absorption efficiency is not appropriate for some diameter of nanoparticles. Absorption efficiency is maximum for nanoparticles with radius a = 52nm, a = 47nm and a = 25nm in the wavelength of λ = 400nm, λ = 500nm and λ = 600nm respectively. Since the nanoparticles act as a light trap and increase carrier life time, rate of generation and transition of carriers will be increased; recombination rate of electron – hole pairs mitigated, so the dark current, noise beats (recombination from electron - hole), thermal noise (due to random motion charges) decline.

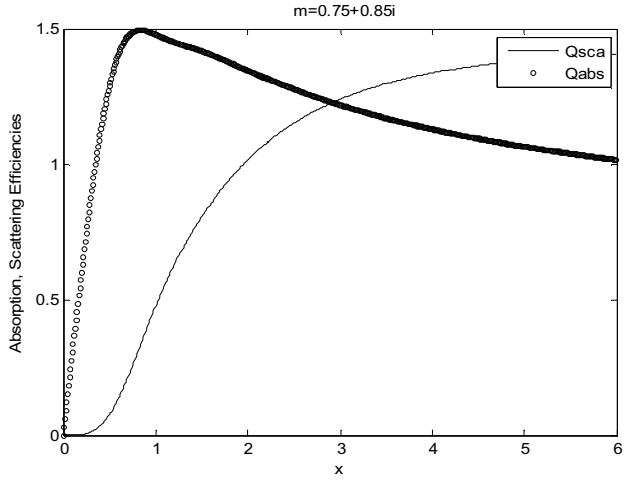

Figure 6. Absorption and scattering efficiency in exchange for λ = 400nm

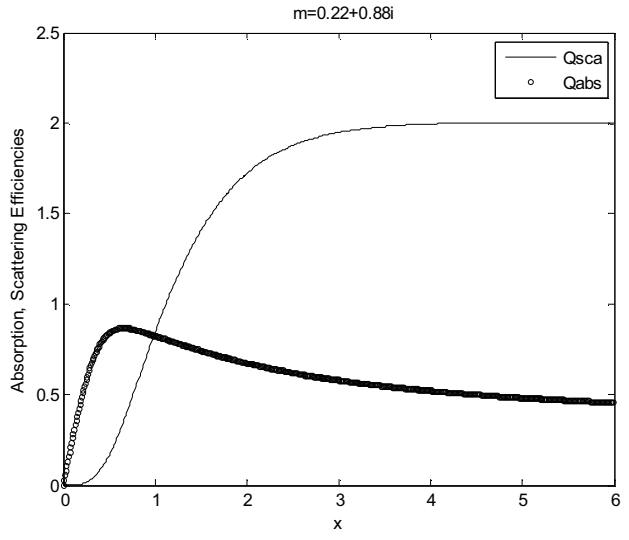

Figure 7. Absorption and scattering efficiency in exchange for λ = 500nm

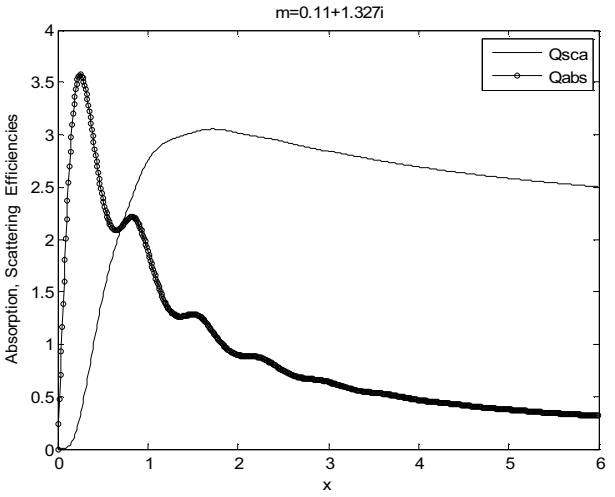

Figure 8. Absorption and scattering efficiency in exchange for λ = 600nm

To indicate the influence of each parameter n, k on the absorption efficiency and help to select appropriate materials, we do simulate for different values per m=1+i, 1+4i, 1+8i, 4+i, 8+i. Simulation results are shown in Fig.9 and Fig.10. According to Fig.9 any part of the larger imaginary and real part does not change then the efficient absorption declines strongly. Fig.10 shows that the real part variations less effect on the absorption efficiency.

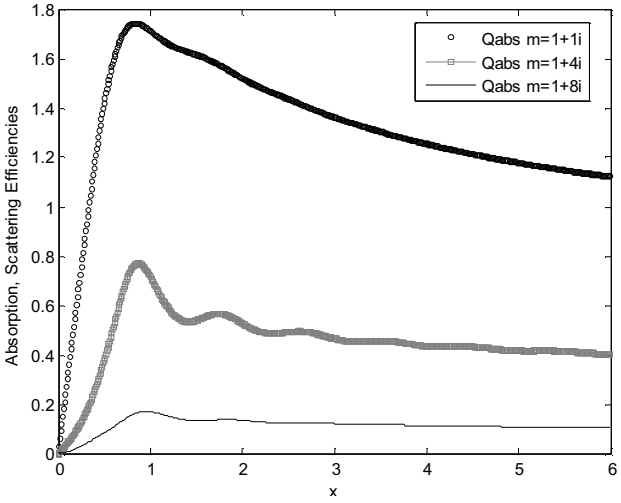

Figure 9. The quantum efficiency for fixed n.

V. CONCLUSION

Au nanoparticles have high absorption coefficient, so the charges depict very high transition. That's why optical current increase, dark current, recombination electron - hole and noise decrease. Quantum efficiency and response depends on photon absorption coefficient. An increase in the absorption coefficient was achieved using nanoparticles.

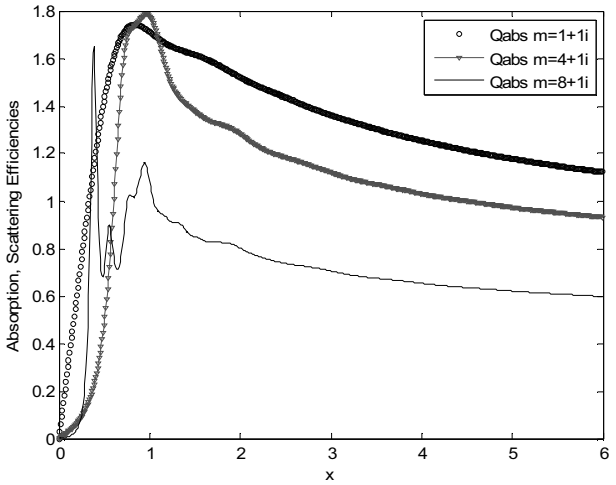

Figure 10. The quantum efficiency for fixed k.

Optical properties of photodetector was found to be related to nanoparticle diameters.

Nanoparticles diameter are usually 5-100nm. If the diameter of nanoparticles are more than this values, light will not be absorbed efficiently, and smaller than this values charge transition through channels becomes less and scattering is increased. In addition to nanoparticle diameter must be attention to n, k parameters.

The free electrons are lower for Au, leading to surface Plasmon resonance in the visible. The resonance frequency can be tuned by varying the dielectric constant and nanoparticle diameter. When a small nanoparticle is irradiated by light and the nanoparticle size is much smaller than the wavelength of light, the electric field of the light is constant and can be neglected of electrodynamic.

When the particle size increases, dynamic depolarization occurs and conduction electrons across the particle no longer move in stage. This leads to a reduction in the depolarization field at the centre of the particle.

REFRENCES

[1] R.M.TILAKI, A.IRAJIZAD, S.M.MAHDAVI, "stability, size and optical properties of silver nanoparticles prepared by laser ablation in different carrier media, "Appl.Phys.A 84, 215-219.2006.

[2] Eliza Hutter and Janos H. Fendler," Size quantized formation and self-assembly of gold encased silver nanoparticles,"Center for Advanced Materials Processing, Clarkson University, Potsdam, NY 13699-5814, USA,2002.

[3] P. Matheu, S. H. Lim, D. Derkacs, C. Mcpheeters, E. T. Yu, "Metal and dielectric nanoparticle scattering for improved optical absorption in photovoltaic devices," applied physics,2008.

[4] Jin Hyung Jun, Hojun Seong, Kyoungah Cho, Byung-Moo Moon, Sangsig Kim, "Ultraviolet photodetectors based on ZnO nanoparticles," Department of Electrical Engineering and Institute for Nano Science, Korea University, Seoul 136-701, Republic of Korea , 2009.

[5] Huimin Su, Yingshun Li2, Xiao-Yuan Li2 and Kam Sing Wong," Optical and electrical properties of Au nanoparticles in two-dimensional networks an effective cluster model," Department of Physics, the Hong Kong University of Science and Technology, Clear Water Bay, Hong Kong SAR,P. R. China.2 Department of Chemistry, the Hong Kong University of Science and Technology, Clear Water Bay, Hong Kong SAR, P. R. China, Otics Express 22223(2009).

[6] G. Xu, M. Tazawa, P. Jin, S. Nakao, and K. Yoshimura, "Wavelength tuning of surface plasmon resonance using dielectric layers on silver island films," Appl. Phys. Lett. 82, 3811-3813 (2003).

[7] Y.-N. He, C.-C. Zhu, J.-W. Zhang, "The study on mechanism of ultraviolet laser emission at room temperature from nanocrystal thin ZnO films grown on sapphire substrate by L-MBE," Microelectron. J. 35 (4) (2004) 389–392.

[8] Tian Z R R, Voigt J A, Liu J, et al., "Complex and oriented ZnO nanostructures,".Nat Mater, 2003, 2: 821

[9] V. Gupta, R. Menon, and K. Sreenivas," Enhanced Ultraviolet Photo-Response of Nanostructure Zinc Oxide (ZnO) Thin Film Irradiated With Pulsed Laser," Department of Physics & Astrophysics University of Delhi, Delhi 110007, INDIA, 2008.

[10] C. F. bohren, D. R Huffman, "Absorption and Scattering of Light by Small particles", Wiley. 2004.