2010 2nd International Conference on Mechanical and Electronics Engineering (ICMEE 2010)

Characterization of Responsivity and Quantum Efficiency of TiO_2– Based Photodetectors Doped with Ag Nanoparticles

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***Abstract*—There is a motivation to reduce the thickness of photodetectore to improve the efficiency of extracting excuted carrier. However, reducing the thickness of thin film also reduces the amount of light absorbed. To alleviate this problem we can use light trapping. Ag Nanoparticles with specific diameters are exposed to improve optical characteristics of TiO2-based photodetectors. Optical properties of photodetectors depend on optical properties of nanoparticles. There for photodetectore application we need to identify which of these properties(scattering, absorption) are beneficial and then design suitable nanoparticle to maximize these effect while minimizing unwanted optical properties. Nanoparticles diameter is usually between 5-100nm. If the diameter of nanoparticles is about more than 100nm, light will not be absorbed efficiently, and when it is smaller than 5nm, charge transition through channels fades and scattering is increased. Effect of nanoparticles on absorption coefficient, quantum efficiency, and responsivity of photodetectors based on TiO2 are discussed in this paper.**

***Keywords*—Nanoparticle(NP); Responsivity(R); Absorption coefficient; Quantum Efficiency(QE)**

I. INTRODUCTION

Titanium dioxide (TiO2) is one of the most popular semiconductor materials that can be used in many catalytic applications. Titanium dioxide attracts much attention in recent years because of its unique physical and chemical properties, such as high refractive index, excellent optical transmittance in the visible and near-infrared regions, high dielectric constant and photocatalytic activity[1].

TiO2 has a wide band gap (3 and 3.23 eV for anatase and rutile, respectively). It has been reported that the optical properties of TiO2 can be improved by doping with metal particles (Ag, Au or Cu). 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[1- 3].

The size induced properties of nanoparticles make them suitable for many applications in various areas such as catalysis, optics, and life environments. Silver nanoparticles have many applications, among them antibacterial applications and nanocomposite fabrications are some of the more important applications.

Nanoparticles are made in two steps. In the first step small spherical particles(seed) with average diameter between 5-20 nm are formed with different ratio of silver ion concentration to stabilizer/reductant. In the second step 20-100nm nanoparticle are formed by non iterative seed-mediated growth [4].

Although the influence of size on the bulk material is negligible, size effect of nanoparticles depends on their shape and diameter. The final size depends on seed size and amount of ions to be reduced on their precursor.

II. OPTICAL PROPERTIES OF METAL NANOPARTICLE

The optical properties of metal nanoparticles are sensitive to particle shape, size, composition and the local dielectric environment. For photodetector applications we are interested in controlling the peak resonance wavelength and relative contribution of absorption and scattering to extinction. There for photodetectore application we need to identify which of these properties(scattering, absorption) are beneficial and then design suitable nanoparticle to maximize these effect while minimizing unwanted optical propertiese.

A. Shape

To explore the influence of nanoparticle shape we will investigate the optical properties of various Ag nanoparticle with constant volume. 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. The largest difference occurs between the sphere and pyramid, with~180 nm shift in peak wavelength position. The peak position shift correlates well with an increase in the number of sharp tips as the shape is changed from sphere to pyramid.

B. Size

The optical properties of large and small nanoparticles are completely different. The extinction cross section of three different sizes of silver nanoparticles are shown in Fig. 2. As the silver particles get larger, the scattering portion of the extinction increases. As the size of the silver particles increases, its unique plasmonic signature shifts towards the red region of the visible spectrum.

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C. 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 red shift of the localized surface Plasmon(LSP). The sensitivity of nanoparticles to dielectric environment changes is shown in Fig. 3.

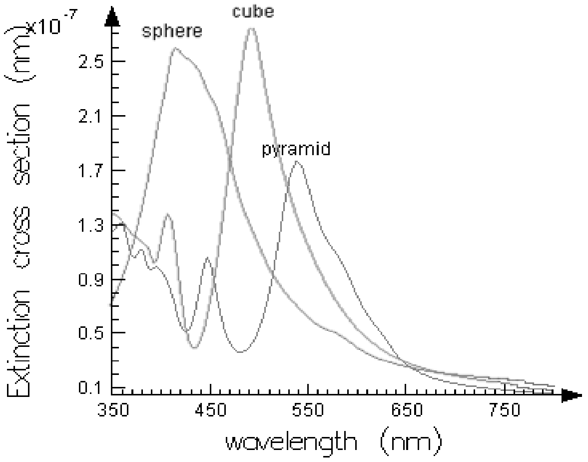

Figure 1. FDTD Extinction simulation of Ag nanoparticle with same volume

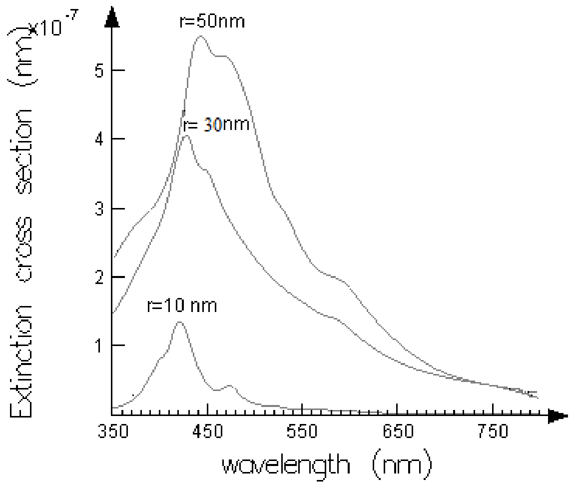

Figure2. The extinction cross section of three different sizes of silver nanoparticles

III. PHOTODETECTOR BASED ON TiO2

TiO_2 thin films were prepared by sol-gel method and were then used to fabricate photodetectors. Solar-blind UV photodetectors have attracted much consideration because of civil and military applications in astronomy, biology, flame sensors, and environmental monitoring [5, 6]. The most common UV detectors currently in use are made from widebandgap inorganic semiconductors such as GaN, ZnO and TiO2.

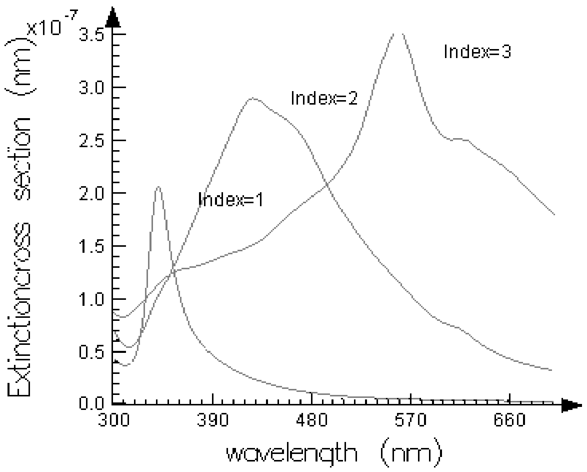

Figure 3. Extinction of Ag nanoparticle as a function of surrounding dielectric environment

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. 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. 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 [7]. 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. Responsivity(R) of a detector 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 light, 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 the equation (1):

$$R = \frac{\eta\lambda(\mu m)}{1.24} \qquad (1)$$

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

$$\eta = \eta_i\left(1 - e^{-\alpha l}\right) \quad (2)$$

α denotes the absorption coefficient, l is the length of active area and η_i is interal quantum efficiency. Absorption coefficient can be determined by equation (3):

$$Q_{abs} = \frac{\alpha}{\pi a^2} \quad (3)$$

Where Q_{abs} is absorption efficiency and a is the radius of the sphere.

As it is clear from the equation (2); 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

For simulation of optical properties of thin film and photodetector, we use Bohren and Huffman equations [8]. Absorption efficiency, Quantum Efficiency (QE) and Responsivity(R) for wavelengths $\lambda = 350(m = 0.08 + 0.48i), 500(m = 0.05 + 1.22i), 700nm(m = 0.06 + 1.92i)$ and l=50nm are shown in Fig. 4, 5 and 6, Where $m = n + ik$ is the refractive index of the sphere relative to the ambient medium, $x=ka$ is the size parameter, a is the radius of the sphere, $k = 2\pi/\lambda$ is the wave number, and λ is the wavelength.

Simulation result shows that the mentioned parameters are not appropriate for some diameter of nanoparticles. Absorption efficiency is maximum for nanoparticles with small radius. This additional absorption improved in 500～700nm spectral region. The quantum efficiency and responsivity curves, indicates that after doping of Ag onto TiO2, the QE and R are maximum in $\lambda = 500$ nm. 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.

Optical properties of TiO2 doped with Ag nanoparticle for $\lambda = 500nm$ are shown in Fig.7, where Q_{ext} is exciting efficiency, Q_{sca} is scattering efficiency and Q_{abs} is absorption efficiency that mentioned above. Simulation result shows that for $x > 0.5$, $a > 45$ nm, scattering is increased and absorption is decreased.

The fundamental absorption is related to band gap energy. The relation between absorption coefficient and band gap energy is given by equation (4):

$$\sqrt{\alpha v h} = B(hv - E_g) \quad (4)$$

Where h is planck's constant, v is the frequency of the incident photon, E_g is band gap energy and B is the optical density of states. B can be determined from specific absorption coefficient. By using of equation(4), we can see relation between band gap energy and nanoparticles radius in Fig. 8. The band gap energy is determined for $\lambda = 350, 500$ and 700nm. As shown in Fig. 8, E_g decrease slowly and become nearly constant for $a > 30nm$ at $\lambda = 350$nm, decrease rapidly for $a < 30nm$ at $\lambda = 500$nm and then increase slowly. E_g is zero for $a = 70nm$ at $\lambda = 700$nm, it means that TiO2 will change to conductor.

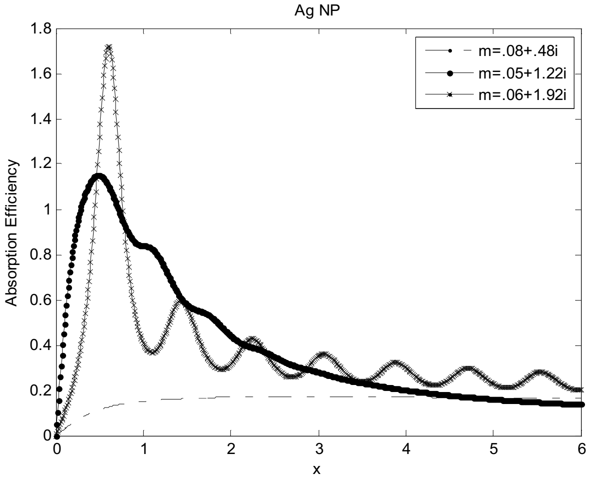

Figure 4. The influence of nanoparticle radius on absorption efficiency for $\lambda = 350, 500$ and 700nm

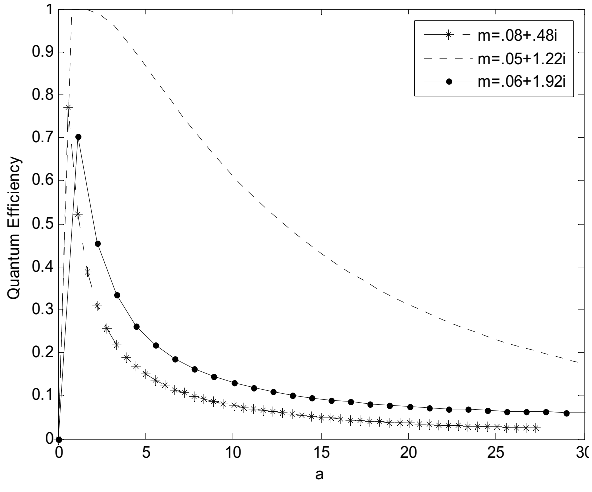

Figure 5. The influence of nanoparticle radius on quantum efficiency for $\lambda = 350, 500$ and 700nm

V. CONCLUSION

Ag 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 Responsivity depends on photon absorption coefficient. An increase in the absorption coefficient was achieved using nanoparticles.

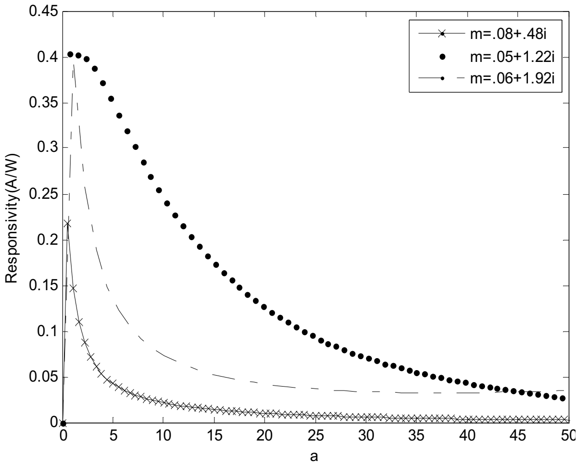

Figure 6. The influence of nanoparticle radius on Responsivity for $\lambda = 350, 500$ and 700nm

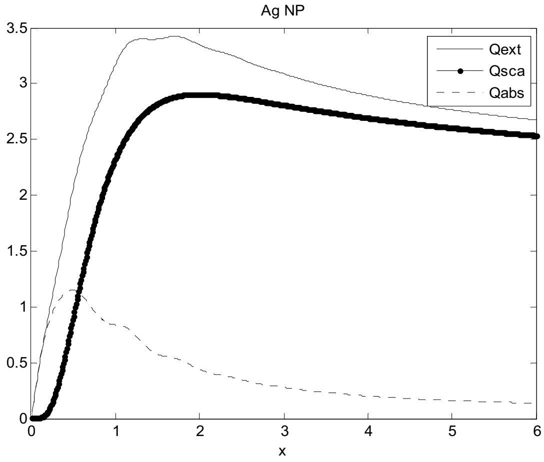

Figure 7. Optical properties of TiO2 doped with Ag nanoparticle for $\lambda = 500nm$

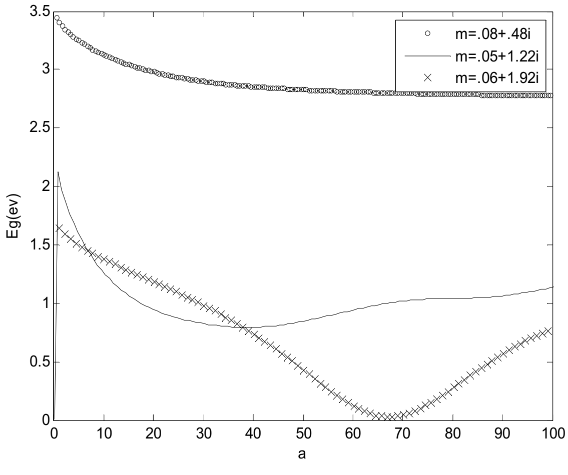

Figure 8. Band gap energy as a function of nanoparticles radius for $\lambda = 350, 500$ and 700nm

Optical properties of photodetector was found to be related to nanoparticle and the optical properties of metal nanoparticles are sensitive to particle shape, size, composition and the local dielectric environment. 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 propertiese. The largest difference extinction occurs between the sphere and pyramid nanoparticles, with~180 nm shift in peak wavelength position. As the silver particles get larger, the scattering portion of the extinction increases and plasmonic signature shifts towards the red region of the visible spectrum. 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.

The band gap energy depends on nanoparticles radius and it is nearly unchanged for $\lambda \cong 300$. Absorption coefficient improved after doping of Ag onto TiO2 in λ =500~700nm so E_g is decreased for small radius.

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] Kominami H, Murakami S, Kato J, Kera Y and Ohtani B, “Correlation between some physical properties of titanium dioxide particles and their photocatalytic activity for some probe reactions in aqueous systems, ” J. Phys. Chem. B**106** 10501–7, 2002.

[3] Tapan K. Sau, Anjali Pal, N.R. Jana, Z.L. Wang4 and Tarasankar Pal, Chemistry Department, Panjab University, Chandigarh, India; Department of Civil Engineering, IIT,Kharagpur, India; University of South Carolina, Columbia, SC, USA; Georgia Institute of Technology, Atlanta, GA, USA; Department of Chemistry, Indian Institute of Technology, “ Size controlled synthesis of gold nanoparticles using photochemically prepared seed particles,” Journal of Nanoparticle Research 3: 257–261, 2001.

[4] E. Monroy, F. Omnes and F. Calle, “Wide-bandgap semiconductor ultraviolet photodetectors,”Semicond. Sci. technol, R33, 2003.

[5] Yangang Han, Gang Wu, Mang Wang, Hongzheng Chen, “Hybrid ultraviolet photodetectors with high photosensitivity based on TiO2 nanorods array and polyfluorene, ” Department of Polymer Science and Engineering, Key Laboratory of Macromolecule Synthesis and Functionalization of Ministry of Education, State Key Lab of Silicon Materials Zhejiang university,2009.

[6] W. H. QI, M. P. WANG, Y. C. SU, “ Size effect on the lattice parameters of nanoparticles,”Department of Material Science and Engineering, Central South University, Changsha, 410083, Hunan,People’s Republic of China877– 878,2002.

[7] JIANG Zhiliang ,FENG Zhongwei , LI Tingsheng , LI Fang, ZHONG Fuxin , XIE Jiyun & YI Xianghui,“ Resonance scattering spectroscopy of gold nanoparticle,” Institute of New Technology and Material, Guangxi Normal University，Guilin 541004, China,2000.

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