Computational analysis on the emission of ZnO nanowires and coreshell CdSe/ZnS quantum dots deposited on different substrates

[1]S.Farid, [1]M. Purahmad, [1,2,3]M. A. Stroscio* and [1,3]M. Dutta
[1]Dept. of Electrical and Computer Engineering, [2]Dept. of BioEngineering, [3]Dept. of Physics
University of Illinois at Chicago,
Chicago, IL 60607, USA
*stroscio@uic.edu

***Abstract*—Computational analysis on the emission properties of ZnO nano wires (NWs) and coreshell quantum dots (QDs) have been made by considering the effects of scattering mechanism of the incident field and the total electric field from the surface of varied substrates. Simulation results indicate that the substrate (GaAs) having the highest emission intensity showed maximum light scattering from its surface while ITO that has the least emission intensity results in minimum rate of energy that is transferred per unit area. The simulation results proved that emission intensities spectrum is dependent on the type of substrate being used as well as the scattering of light from the surface of substrates and is independent on the type of material being deposited as well as the total electric field from the surface of substrate.**

Keywords-component; Nano wires; Core shell quantum dots; Poynting vector; Vapor liquid solid (VLS); photoluminiscence (PL) spectra

I. INTRODUCTION

Coreshell type quantum dots have received much attention due to their ability to improve the photoluminescence quantum yields by passivating surface nonradiative recombination sites [1]. By capping the nanocrystalline materials (CdSe) with a wider band gap shell (ZnS) not only increases the luminescence efficiencies but also helps in increasing the photostablility of core shell QDs due to its broad absorption and narrow emission spectra. In addition to this, they have a photoluminescence (PL) spectra that is tunable by the QD core diameter that results in exciton confinement within the QD core [2]. These quantum dots (QDs), nanowires (NWs) and nanostructures due to their unique optical properties have been extensively studied by the research community these days.

In particular, zincoxide (ZnO) nanowires have received great interest among 1D-nanostructures, such as semiconducting nanowires [3], carbon nanotubes [4] , and nanobelts [5] due to their multifunctionality and being a well known piezoelectric material [6]. ZnO being a II-VI compound semiconductor with a wide direct band gap (3.37 eV) and large exciton binding energy (60 meV) is a promising candidate for optoelectronic devices. ZnO NWs have shown many applications in the areas of biosensors, optoelectronics, resonators, nanolasers and electric nanogenerators [7-11].

In spite of all the applications of core shell quantum dots and ZnO nano wires, little research has been done on the effects of substrates on the optical properties of these devices. Substrates play an important role in determining the properties of optoelectronic devices. Photoluminescence emission intensities vary significantly for materials deposited on transparent or non-transparent substrates. The detailed analysis on the photoluminescence (PL) emission spectra of CdSe/ZnS coreshell quantum dots (QD) and as grown ZnO nanowires (NWs) has been discussed in one of our previous studies [12]. In this work, we have developed a computational model by taking into account the Poynting vector that represents the directional energy flux density based on the effects of scattered field and total electric field from the surface of different transparent and non-transparent substrates by considering the light scattering mechanism as a function of distance from the substrate surface after depositing ZnO nanowires and coreshell quantum dots.

II. NUMERICAL MODEL

Light scattering is a powerful tool for measuring the material characterization as it carries information about the microstructure of the material. However this information is very tedious to extract as it involves parameters to determine the reflectance of a layer of light scattering materials as a function of the optical constants of the material. A careful investigation is needed in order to determine the dependence of the substrate on the surface, types of deposited materials as well as on the design of the stack.

In this work, scattering of light from normal and parallel plane waves is considered by determining the directional energy flux density. In order to represent the directional energy flux density of an electromagnetic field from the surface of substrate, Poynting vector S is used which is represented as

$$S = E * H$$

Where E being the electric field and H represents the magnetic field. This Poynting vector S is related to the poynting vector theorem which relates the conservation of energy density u and states as

$$\frac{\partial u}{\partial t} + \nabla . s = -J . E$$

Where J represents the current density, and E the electric field. The electromagnetic energy density u is represented as

$$u = ½ (E^*D + B * H)$$

where D being the electric displacement field and B represents the magnetic flux density.

These factors took into account the net electromagnetic energy flow into a small volume as well as the work done by free electrical currents that are not necessarily converted into electromagnetic energy. This computational analysis was carried to see the influence of scatterings as well as reflections of the incident field and the total field from the surface of substrates.

Simulation was carried out by considering the square shaped substrate obstacle that is in exposure to the incident plane wave of frequency 325nm. The same excitation wavelength was used for our experimental work to excite the four different substrates as silicon (Si), gallium arsenide (GaAs), glass and indium tin oxide (ITO) coated glass. The scattering wave can be thought of as reflections from all angels from the surface of substrate while reflection coefficient of a normal polarized and a parallel polarized plane waves can be expressed as followings

$$\Gamma_{\perp} = \frac{\cos\theta i - \sqrt{(\varepsilon_{2r}/\varepsilon_{1r}) - \sin^2\theta i}}{\cos\theta i + \sqrt{(\varepsilon_{2r}/\varepsilon_{1r}) - \sin^2\theta i}}$$

$$\Gamma_{\parallel} = \frac{-\cos\theta i + (\varepsilon_{1r}/\varepsilon_{2r})\sqrt{(\varepsilon_{2r}/\varepsilon_{1r}) - \sin^2\theta i}}{\cos\theta i + (\varepsilon_{1r}/\varepsilon_{2r})\sqrt{(\varepsilon_{2r}/\varepsilon_{1r}) - \sin^2\theta i}}$$

The reflection coefficient is dependent on the material of the substrate, the incident angle θi [13] and reflections from the normal and parallel polarized plane waves. The scattering of light from substrate surfaces and absorption coefficients of the material determine the amount of radiations absorbed, emitted, and scattered. As indicated in fig.1, the distance traveled before the light is absorbed or is scattered is dependent on the inverse of the scattering and absorption coefficients.

III. RESULTS AND DISCUSSIONS

The energy flux density of the scattered field and the total field of different substrates against the z position from the surface of substrate are shown in fig. 1 and fig. 2. Simulation results agreed with our numerical model that indicates an inverse relation of the scattered field with the increased distance from obstacle. The variations in intensities for the scattered light has been verified with the experimental results of a previous study as shown in fig.3 which indicates that the emission intensity for the non transparent GaAs substrate has the highest PL intensity while it is least for the transparent objects like ITO coated glass. The results as indicated in fig. 1 shows that the energy flux density of the scattered field from the surface of GaAs has the maximum Poynting field value and glass the least that matches our numerical and experimental data.

The experimental data was obtained from the samples having ZnO nanowires grown on the surface of same substrates that are used for our numerical model. These experiments have been done at room temperature using both transparent and non transparent coated and uncoated substrates. ZnO nanowires have been grown by VLS growth method. The details of the experimental work has been explained in another study of our [12]. The results indicates that the PL intensity of the grown rods on GaAs substrate shows the highest PL intensity order while the ITO coated glass showing the lowest PL intensity which matches our simulation results indicating that the PL intensity order is dependent on the scattering field from the surface of substrate. For more investigation into the problem, the experiment was repeated by replacing the as grown ZnO NWs with the coreshell quantum dots. The results indicate the same intensity order with different emission wavelength for the coreshell dots (not shown here).

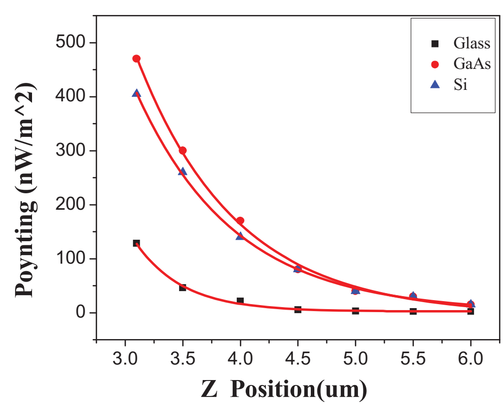

Fig. 1 Energy flux density of the scattered field versus z-position distance from the surface of substrate

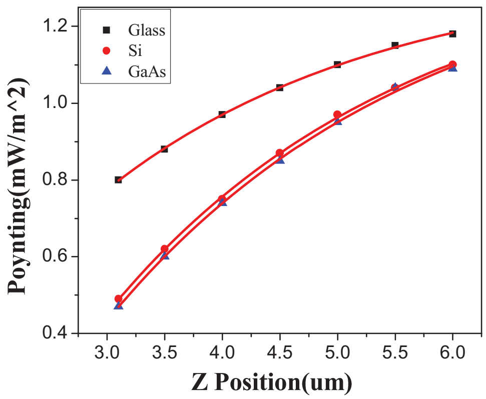

Fig. 2. Energy flux density of total field versus position from the surface of substrates.

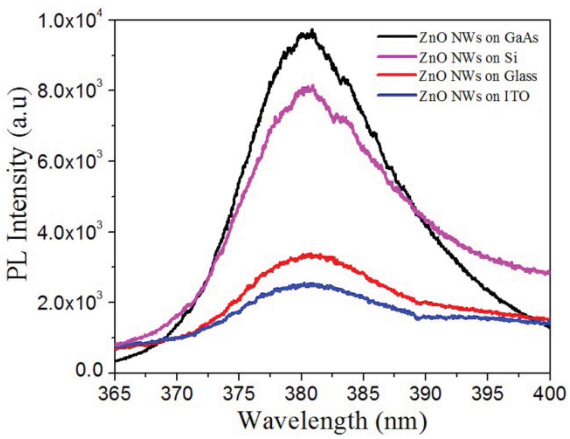

Fig. 3. Photoluminescence spectra of ZnO nanowires on different substrates (graph labeled from top to bottom order)

In order to find the relation of the energy flux density of the total field versus the position from the surface of substrates, simulation was carried out to plot the poynting vector values of the total electric field against the z position from substrate as shown in fig. 2.The results indicate a contrast to our results for the scattered field and the experimental data. Thus the comparisons of simulation results shown in fig. 1 and fig. 2 demonstrate that the intensity of scattered field at the surface indicate the PL intensity order rather than the total field.

The data indicates that our simulation results for the scattered field are in agreement with the experimental data showing the dependency of emission spectra on the scattered field from the surface of the substrate. This argument can be extended for the case of metals as well as in the case of ITO-coated glass substrate we have used. It is well known the metals bring the material absorption loss into the cavity [14], so the absorption of light for the case of ITO-coated glass substrate will be maximum resulting in minimum emission intensity as proved from experimental data. Hence, the PL intensity of those quantum dot and ZnO NWs deposited on the ITO-coated glass is even lower than glass substrate.

IV. Conclusions

In summary, the effects of scattered field and the total field from the surface of different substrates on the PL intensity of ZnO NWs and CdSe/ZnS coreshell quantum dots have been studied. The numerical modeling and the simulation results indicate that the substrates having the maximum scattered field have the strongest emission intensity which is in agreement with the experimental data obtained. Also it is concluded that the PL intensity is not a function of the total electric field from the surface of substrate and the type of material being deposited.

References

[1] B. O. Dabbousi, J. Rodriguez-Viejo, F. V. Mikulec, J. R. Heine, H. Mattoussi, R. Ober,K. F. Jensen,and M. G. Bawendi, "(CdSe)ZnS core-shell quantum dots: synthesis and characterization of a size series of highly luminescent nanocrystallites", J. Phys. Chem, vol.101, 1997 , pp 9463–9475.

[2] Grieve, K., Mulvaney, P., & Grieser, F.,"Synthesis and electronic properties of semiconductor nanoparticles/quantum dots",Current Opinion in Colloid and Interface Science,vol. 5, 168, 2000.

[3] T. Kuo, C. Lin, C. Kuo, and M. H. Huang, "Growth of ultralong ZnO nanowires on silicon substrates by vapor transport and their use as recyclable photocatalysts", Chem. Mater.,vol. 19, 2007 , pp 5143–5147.

[4] C. J. Hu, Y. H. Lin, C. W. Tang, M. Y. Tsai, W.K. Hsu, H. F. Kuo, "ZnO-Coated carbon nanotubes: flexible piezoelectric generators", Advanced Materials, vol. 23, 2011, pages 2941–2945.

[5] H. S. Bhatti, D. Kumar, A. Gupta, R. Sharma, K. Singh, P. Sharma, "Synthesis and characterization of Mn doped ZnO nanobelts", J. Optoelectronics and Advanced Materials, vol. 8 ,2006, pp. 860 - 862 .

[6] J. Goldberger, D. J. Sirbuly, M. Law, P. Yang, "ZnO nano transistors", J. Phys. Chem. B,vol.109, 2005, pp 9–14.

[7] M. Willander , O. Nur , Q. X. Zhao , L. L. Yang , M. Lorenz , B. Q. Cao ,J. Z. Pérez , C. Czekalla , G. Zimmermann , M. Grundmann , A. Bakin , A. Behrends , M. Al-Suleiman , A. El-Shaer , A. C. Mofor , B. Postels , A. Waag , N. Boukos , A. Travlos , H. S. Kwack , J. Guinard , D. L. S. Dang , "Zinc oxide nanorod based photonic devices: recent progress in growth, light emitting diodes and lasers," Nanotechnology ,vol.20, 2009 , pp. 332001 .

[8] S. Al-Hilli , A. Öst , P. Strålfors , M. Willander ," ZnO nanorods as an intracellular sensor for pH measurements", J. Appl. Phys. , vol. 102 , 2007 ,pp. 084304 .

[9] X. D. Bai , P. X. Gao , Z. L. Wang , E. G. Wang ," Dual-mode mechanical resonance of individual ZnO nanobelts", Appl. Phys. Lett. , vol.82 ,2003 , pp. 4806 .

[10] Z. L. Wang , J. H. Song ," Piezoelectric nanogenerators based on zinc oxide nanowire arrays", Science , vol.312 ,2006, pp. 242 .

[11] Q. X. Zhao , P. Klason , M. Willander , P. J. Bergman , W. L. Jiang , J. H. Yang , "Synthesis and characterization of ZnO nanostructures grown on Si substrates",Phys. Scr. ,vol.2006 ,2006

[12] M.Purahmed,S.Farid,M.A.Stroscio,M.Dutta," Influence of substrates on the optical characteristics of ZnO nanowires and coreshell CdSe/ZnS quantum dots," unpublished.

[13] U. S. Inan, A. S. Inan, Electromagnetic waves, ISBN 0-201-36179-5, 1999 .

[14] C Adrianni,S Chang, "Metal coated zinc oxide nanocavities", IEEE Journal of quantum electronics,vol.47, 2011,pp.245-251