Study of the Effect of laser Pulses on Synthesis of SnO_2 Nanoparticles by Laser Ablation in Methanol

Dr. Uday M. Nayef
Applied Science Department,University of Technology/ Baghdad
E-mail: unayef@yahoo.com
Ali J. Hadi
Applied Science Department,University of Technology/ Baghdad

Received on:20/10/2013 & Accepted on: 13/5/2014

ABSTRACT

SnO_2 nanoparticles were prepared by laser ablation of tin in methanol at room temperature. The particles were characterized by means of TEM, AFM, FTIR, UV-Visible absorption spectrum and electrical properties. AFM micrographs show that the obtained material is spherical nanoparticles, the size and size distribution of which depends on the experimental conditions.

From FTIR spectrum show the peak absorption of SnO_2NPssuspension at 657 cm^{-1}.

It is found that the band gap energy of SnO_2NPs is higher than that of bulk SnO_2 due to the decreases in the particle size according to the quantum confinement model.

From the *J-V* characteristics Al/SnO_2 NPs/c-Si/Al hetrojunction the values of ideality factor for these devices is greater than unity which can be attributed to the recombination of electrons and holes in the depletion region as well as the tunneling effect depending on both sides of the heterojunction and on the presence of defect states.

Keywords: SnO_2 nanoparticles; Laser ablation; morphology; energy gap; heterojunction.

دراسة تأثير عدد النبضات على تحضير دقائق SnO_2 النانوية بالتشظية بالليزر في الميثانول

الخلاصة

تم تحضير دقائق SnO_2 النانوية بتقنية التشظية بالليزر في الميثانول في درجة حرارة الغرفة. تم تشخيص الدقائق بواسطة المجهر الالكتروني النافذ (TEM) ومجهر القوى الذري (AFM) ومطياف تحت الحمراء (FTIR) وطيف الامتصاص الاشعة الفوق البنفسجية والمرئية والخواص الكهربائية. يظهر المجهر الالكتروني النافذ (TEM) لتوصيف شكل وحجم دقائق ثنائي اوكسيد القصدير النانوية حيث اظهرت معدل قطر يتراوح من 17 الى 37 نانومتر في محلول الميثانول ذو شكل كروي منتظم وكذلك اظهرت نتائج مجهر القوى الذري (AFM) ان الدقائق التي تم الحصول عليها هي دقائق نانوية كروية. ظهر من مطيافالاشعة تحت الحمراء (FTIR) ان قمة امتصاص عوالق دقائق SnO_2 النانوية عند 657 cm^{-1} .

وجد ان فجوة حزمة الطاقة لدقائق SnO_2 النانوية اكبر من SnO_2 في حالتها الحجمية يرجع ذلك الى انخفاض حجم الدقائق وفقا لنموذج الحصر الكمي. من خصائص *J-V* للمفرق الهجين Al/SnO_2NPs/c-Si/Al ان قيم عامل المثالية لهذه النبيطة هو اكبر من الواحد التي يمكن ان تعزى الى اعادة اتحاد الكترون – فجوة في منطقة النضوب فضلا عن تاثير التنفيق اعتمادا على كلا الجانبين للمفرق الهجين وعلى وجود مستويات العيوب.

https://doi.org/10.30684/etj.32.6B.4
2412-0758/University of Technology-Iraq, Baghdad, Iraq

INTRODUCTION

Since the shape, size, and dimensionality of semiconductors are vital parameters for their properties, developing a facile method to prepare important nanomaterials with well-defined structures is of great interest and importance. Crystalline tin oxide, cassiterite structure, is a wide band gap semiconductor (~3.6 eV), It has been widely used for various catalytic applications, gas sensing, transparent conducting electrodes and liquid crystal displays, etc. [1-5].

Laser ablation is a "top-down" approach to fabricate nanoparticleswhere the bulk crystals were broken down to smaller particles by an intense laser beam. Pulse laser ablation in liquid emerged as a reliable alternative to conventional chemical reduction methods for fabricating oxide and noble metal particles [6].

Pulse laser ablation of a solid target in liquid media is becoming an increasingly popular approach for controlled synthesis of noble metal and metal oxide nanoparticles. It is a chemically simple, allowing safe and stable handling of the colloids, due to reduced by-product formation, simpler starting materials and there is no need for a catalyst [7].
Three main steps contribute in laser ablation synthesis method and formation of nanoparticles from a target immersed in liquid. Only in a short period of time, typically about a few microseconds, all these steps take place and nanoparticles are synthesizedas ablated particles go through the plume induced by laser ablation in liquid in which the temperature and pressure are very high, nanoparticles with new optical, electrical and mechanical properties can be expected to be fabricated [8-9].Well crystallized nanoparticles can easily be obtained in one–step procedure without subsequent heat-treatments [10]. Nanoparticles are well known that optical and electrical properties are strongly dependent on the size and shape of nanoparticles Therefore, control of size and shape is very important for tuning its properties over a wide range. Hence, from the fundamentals and practical aspects, studying the effects of synthesis parameters on the physical properties is very important and can lead to the size and shape selective applications [11-12].

Experimental

SnO_2 nanoparticles were produced by the laser ablation of a tin target of 99.8% purity from (Fluke co.) placed in a continar glass containing 1.5 ml of methanol. The tin target was irradiated vertically by a Q-switched Nd:YAG laser pulses at 1064 nm. The morphology properties of nanoparticles suspension such as particle shape and size were identified also byatomic force microscopy (AFM) (CSPM-AA3000). The absorbance of the prepared solution was examined using a spectrophotometer (Lambda 750, Perkin Elmer). Chemical composition of SnO_2 has been measured by Fourier Transform Infrared (FTIR) (Burker Tensor 27). The electrical properties of SnO_2 NPs layers based device (Al/SnO_2 NPs/c-Si/Al) were studied for *I-V* and *C-V* measurements.

Results and discussion

Figure (1) Shows TEM images of colloidal SnO_2 NP_S at different laser energies. The average particles sizes of nanoparticles were calculated to have of 37 and 17 nm at laser energy 200 and 600 mJ respectively. The NPs in liquids have an almost perfect spherical

shape and shown in images agglomerated,some presented chains of welded particles. It also displays the size of particles dependency on laser energy.

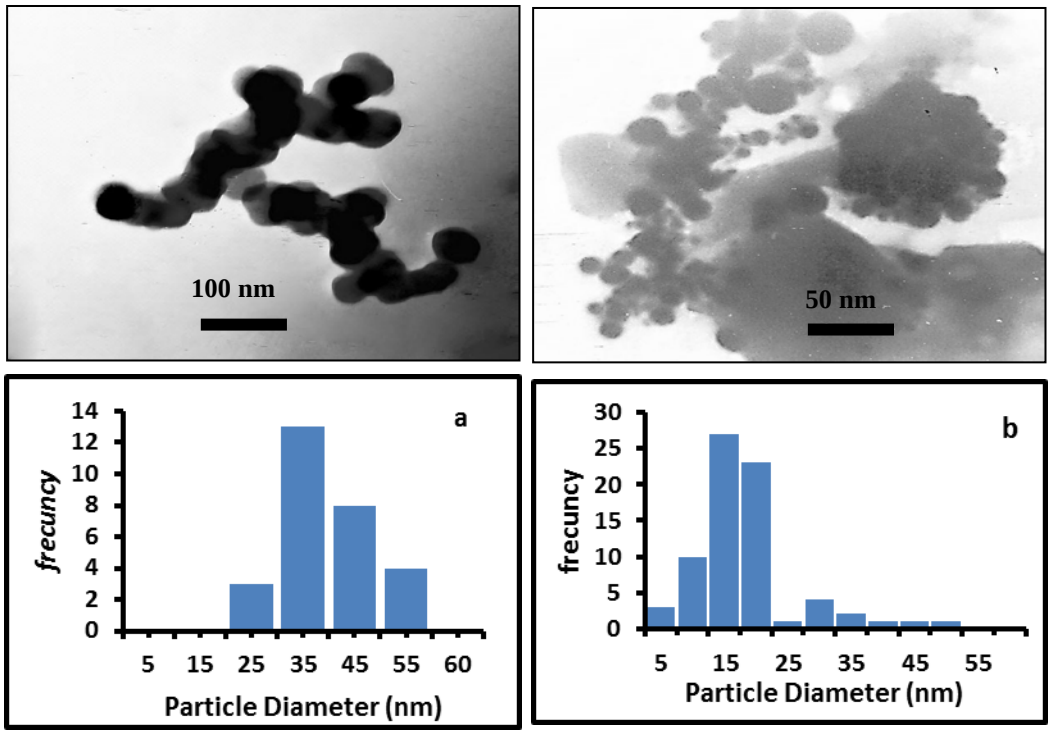


Figure (1): TEM micrographs of SnO_2 NPs prepared with pulse laser energy of (a) 200 mJ (b) 600 mJ

Figure (2) Shows the AFM images show that SnO_2 nanoparticles has semi-spherical shapes and from graphical (2D and 3D) we see that the number and particles distribution increases with increasing in number of pulses.FromFigure (2) an increase in number of pulses, the size diameter of the prepared nanoparticles decreases. Actually, with increase in number of pulses, more number of nanoparticles is produced and these nanoparticles accumulate near the laser spot; when the number of produced nanoparticles becomes sufficiently large, they shield the incident laser radiation. Hence the value of the incident laser intensity reaching the solid target is decreased, which causes no further increase in the number of nanoparticles. However, further incidence of the laser light causes fragmentation of the nanoparticles produced in the earlier steps and leads to the reduction of size of the nanoparticles produced with longer values of laser pulses duration [13-14].

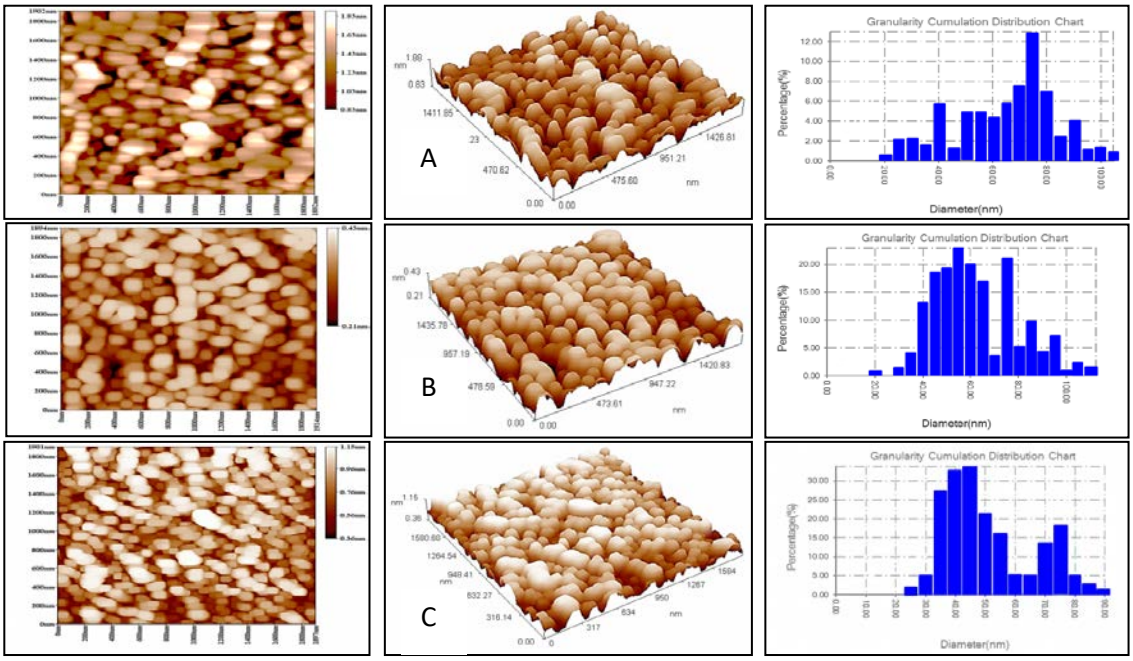


Figure (2): 2D and 3D AFM images of SnO_2NPsprepared with differentnumber of pulses of (A) 60 (B) 90 and (C) 120 pulses.

Table (1): Results of The AFM images morphology characteristics with of SnO_2 NPs

Laser pulses	Avg. diameter (nm)	Ave. Roughness (nm)	RMS (nm)
60	70.56	0.203	0.246
90	57.21	0.0393	0.0467
120	40.74	0.153	0.181

Figure(3) Shows the FTIR spectrum of SnO_2NPssuspensions, where we observed a broad peak centered at 3358 cm^{-1} corresponding to O–H stretching, the appearance of sharp peaks at 3000-2800 cm^{-1} region for C–H stretching.Also the same anti-symmetric vibrations of Sn–O are formed, the peak absorption of SnO_2NPssuspension at 657 cm^{-1}.

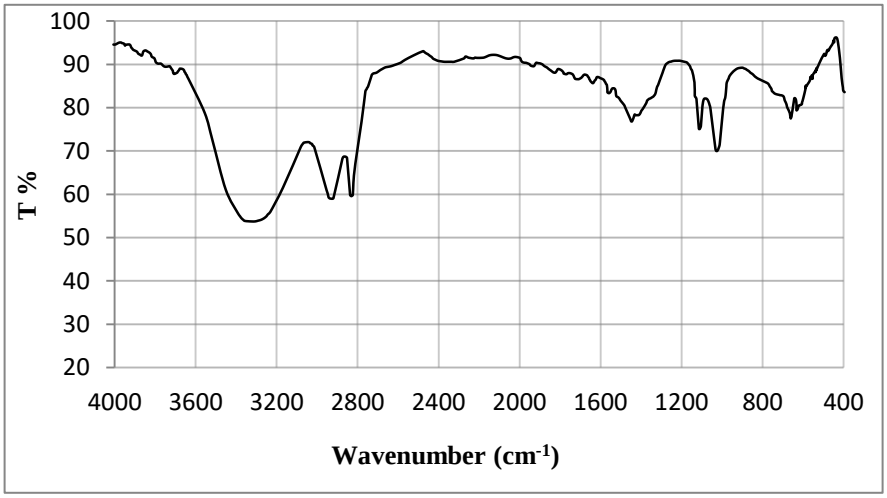
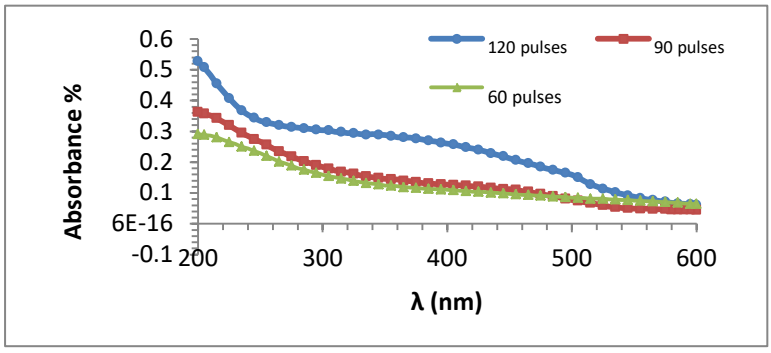


Figure (3): FTIR spectrum of SnO_2NPssuspensions in methanol at 600 mJ and No. of pulses 120.

Figure (4), presents an optical absorption spectra of the samples prepared in methanol solvent. When an increase in laser energy results in an increase in the absorbance spectra intensity, while the peak position remaining practically constant. This enhancement in intensity can be explained by the increase in the concentration of SnO_2NPs formed in solution during the ablation processthese results are confirms with other researches [15-17]. When increase in number of laser pulses Figure (4a) results in an increase in absorption peak intensity. It is clear that more nanoparticles could be generated in higher number of laser pulses. Actually, with increase in laser pulses, more number of nanoparticles is produced and these nanoparticles accumulate near the laser spot; when the number of produced nanoparticles becomes sufficiently large, they shield the incident laser radiation [18].



Figure(4): Optical absorption as a function of wavelength for SnO_2 NPs prepared at differentnumber of pulses.

From Figure (5) and Table (2), give values of the energy band of all the prepared samples is higher than that of bulk SnO_2 (3.6 eV) and the band gap energy increases for the samples prepared with larger value of laser pulses. This attributed to the decreases in the particle size with increasing laser pulses. This behavior can be explained by the quantum confinement model [19].

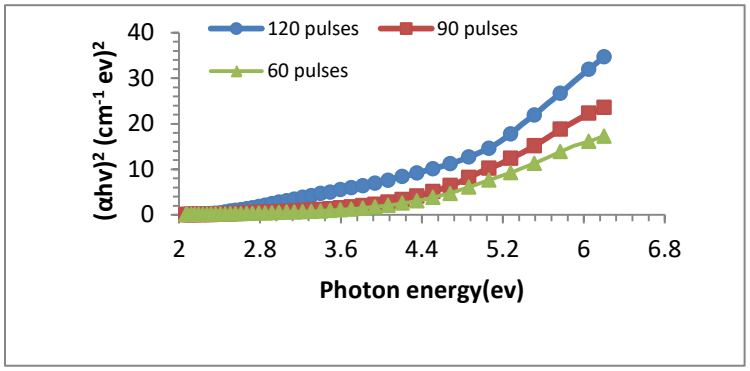


Figure (5): The $(\alpha h\upsilon)^2$ versus $h\upsilon$ plots for SnO_2 NPs prepared at different laser number of pulses

Table (2): Values of optical band gap as function of laser number pulses for SnO_2 NPs.

No. of pluses	Laser energy (mJ)	E_g (eV)
60	**600**	4.16
90		4.2
120		4.26

Figure (6) shows the forward bias current can be divided into two distinct regions; the first one represents recombination current while the second represents the tunneling current. At 0.3 volt , the forward current increases exponentially because the bias voltage exceeds the potential barrier. This bias voltage gives the electrons energy to overcome the barrier height and flow that is called diffusion current. The values of ideality factor for these devices is greater than unityequal to 5.758 which can be attributed to the recombination of electrons and holes in the depletion region as well as the tunneling effect depending on both sides of the heterojunction and on the presence of defect state

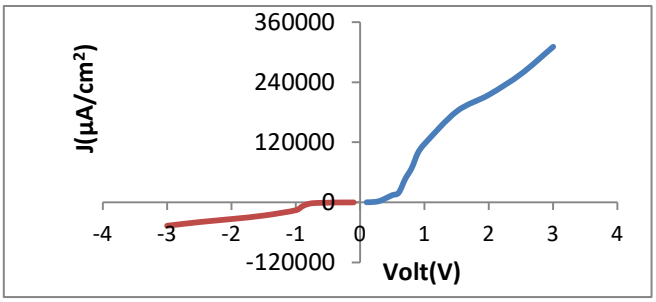


Figure (6): *J-V* characteristics under dark for SnO_2NPs/c-Si heterojunction at 600 mJ 120 pulse.

Figure (7) Shows *C-V* characteristics under reverse bias for Al/SnO_2/c-Si/Al at various laser energy at 600 mJ/pulse with 120 pulses. Notice that the capacitance is inversely proportional to the bias voltage for prepared samples, due to the expansion of depletion layer with the built–in potential. The depletion layer capacitance refers to the increment in charge per unit area to the incremental change of the applied voltage. This property gives an indication about the behavior of the charge transition from the donor to the acceptor region, which was found to be "abrupt" in one sample and this is confirmed when the relation between $1/C^2$and reverse bias is a straight line. The built in potential V_{bi} can be distinguished from the plot of $1/C^2 = 0$ versus V obtained from the intersect of the $f(V)=1/C^2$plot with x-axis.

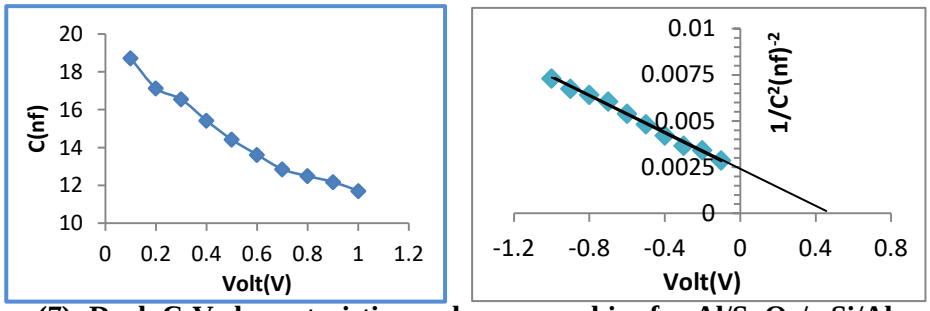


Figure (7): Dark C-V characteristics under reverse bias for Al/SnO_2/c-Si/Al sandwich structure at different laser energy.

Table (4): The value of effective charge carrier, width of depletion layer and built up potential of SnO_2 NPs/c-Si.

Laser energy (mJ)	No. of pulses	N_d (cm^{-3})	W (μm)	V_{bi} (Volt)
600	120	5.34×10^{21}	8.7	0.48

Conclusions

SnO_2 nanoparticles are prepared by laser ablation in methanol from morphology properties show is spherical nanoparticles, the size and size distribution of which depends on the experimental conditions. From FTIR Anti-symmetric vibrations of Sn–O are formed, the peak absorption of SnO_2NPssuspension at 657 cm^{-1}. It is found that the band gap energy of SnO_2NPs is higher than that of bulk SnO_2 due to the decreases in the particle size according to the quantum confinement model.

The Al/SnO_2/c-Si/Al heterojunction has good linearity but with poor photovoltaic characteristics due to charge carriers recombination.

References

[1] S. Gnanam, V. Rajendran, "Luminescence PropertiesofEg-Assisted SnO2 Nanoparticlesby Sol-Gel Process", Digest Journal of Nanomaterials and Biostructures Vol. 5, No 3, July-September 2010, p. 699-704

[2]D. B. Almeida, E. Rodriguez1, R. S. Moreira1, S.Agouram3, L. C. Barbosa1, E. Jimenez, C. L. Cesar "Thiol capped colloidal CdTe quantum dots synthesized using laser ablation"**.** Nanophotonic Materials VI, Vol.7393. 8 pages, 2009.

[3] D. Leng, L. Wu, H. Jiang, Y. Zhao, J. Zhang,W. Li, L. Feng "Preparation and Properties of SnO_2 Film Deposited by Magnetron Sputtering", Journal of Photo-energy, Vol. 2012, 6 pages, 2012.

[4]M. Bagheri-Mohagheghi, N. Shahtahmasebi, M.R. Alinejad, A. Youssefi, M. Shokooh-Saremid "The effect of the post-annealing temperature on the nano-structure and energy band gap of SnO_2 semiconducting oxide nano-particles synthesized by polymerizing–complexing sol–gel method", Journal of Physics B: Condensed Matter, Vol. 403, No. 13-16, pp. 2431–2437, 2008.

[5] A. Ayeshamariam, C.Sanjeeviraja, R. P. Samy"Synthesis, Structural and Optical Characterizations of SnO_2 Nanoparticles", Journal on Photonics and Spintronics, Vol. 2, No. 2, 2013.

[6] S.R.J. Pearce, S.J. Henley, F. Claeyssens, P.W. May, K.R. Hallam, J.A. Smith, K.N. Rosser "Production of nanocrystalline diamond by laser ablation at the solidy liquid interface", Diamond and Related Materials, Vol. 13, No. 4–8, pp. 661–665, 2004.

[7] G. Bajaj, R. K. Soni "Synthesis of composite gold/tin-oxide nanoparticles by nano-soldering", Journal of Nanoparticle Research, Vol. 12, No. 7, pp. 2597–2603, 2010.

[8] T. Nishi, A. Takeichi, H. Azuma, N. Suzuki, T. Hioki, T. Motohiro "Fabrication of Palladium Nanoparticles by Laser Ablation in Liquid", JLMN-Journal of Laser Micro/Nanoengineering Vol. 5, No. 3, pp.192-196, 2010.

[9] A. Baladi, R. S. Mamoory "Investigation of different liquid media and ablation times on pulsed laser ablation synthesis of aluminum nanoparticles", Applied Surface Science Vol. 256, No. 24, pp.7559–7564,2010.

[10] R. Kuladeep, K. S. Alee, L. Jyothi, D. N. Rao "Synthesis, characterization and nonlinear optical properties of laser-induced Au colloidal nanoparticles", Advanced Materials Letters, Vol. 4, No. 6, pp. 482-487, 2013.

[11] R. M. Tilaki, A. Irajizad, S. M. Mahdavi, "The effect of liquid environment on size and aggregation of gold nanoparticles prepared by pulsed laser ablation", Journal of Nanoparticle Research, Vol. 9, No. 5, pp. 853-860, 2007.
[12] K. K. Kim, D. Kim, S. K. Kim, S. M. Park, J. K. Song, "Formation of ZnO nanoparticles by laser ablation in neat water", Chemical Physics Letters, Vol. 511, No. 1-3 , pp. 116–120, 2011.
[13] H. S. Desarkar, P. Kumbhakar, A.K. Mitra "Optical properties of tin oxide nanoparticles prepared by laser ablation in water: Influence of laser ablation time duration and laser fluence", Materials Characterization, Vol. 73, pp. 158–165, 2012.
[14] M. A. Gondal, Q. A. Drmosh, T.A. Saleh "Preparation and characterization of SnO_2 nanoparticles using high power pulsed laser", Applied Surface Science, Vol. 256, No. 23, pp. 7067–7070, 2010.
[15] A.F.M.Y. Haider , S. Sengupta, K.M. Abedin, A. I. Talukder, "Fabrication of gold nanoparticles in water by laser ablation technique and their characterization", Applied Physics A, Vol. 105, No. 2, pp. 487-495, 2011.
[16] B. G. Rasheed, M. A. Ibrahem, "Optical Properties of Silicon Nanoparticles Produced by Nd:YAG Laser Ablation", Iraqi Journal of Applied Physics, Vol. 4, No. 4, pp. 19-23, 2011.
[17] H. S. Desarkar, P. Kumbhakar, A.K. Mitra "Optical properties of tin oxide nanoparticles prepared by laser ablation in water: Influence of laser ablation time duration and laser fluence", Materials Characterization, Vol. 73, pp. 158–165, 2012.
[18] H. S. Desarkar, P. Kumbhakar, A. K. Mitra, "Effect of ablation time and laser fluence on the optical properties of copper nano colloids prepared by laser ablation technique", Applied Nanoscience, Vol. 2, No. 3, pp. 285-291, 2012.
[19] V. Švrček, D. Mariotti, and M. Kondo, "Ambient-stable blue luminescent silicon nanocrystals prepared by nanosecond-pulsed laser ablation in water", 19 January (2009) Vol. 17, No. 2 / Optics Express 520.