Electrophoretic Deposition of In_2O_3 nanoparticles prepared by PLAL in Water

Dr.Khaleel I. Hassoon
Applied Sciences Department, University of Technology/Baghdad.
Email:kihassoun@yahoo.com

Revised on:18/8/2014 & Accepted on: 29/1/2014

ABSTRACT

Indium oxide nanoparticles were prepared in water using Laser Pulsed Ablation technique in Liquid (PLAL). The Nd:YAG laser was used as an ablation source. The nanoparticles are deposited onto Si wafers by direct overcastting method and also glass substrates covered with Indium Tin Oxide (ITO) by electrophoretic deposition (EPD) method. The optical properties for the colloid (nanoparticles in water) are studied with spectrophotometers. UV–vis spectral analysis showed that the solutions have absorption edge at 3 eV and average particle size about 30 nm. In order to estimate the particle size of In_2O_3 in water, the colloidal solutions have been deposited on silicon wafers and imaged by Atomic Force Microscopy (AFM). On the other hand, the Scanning Electron Microscope (SEM) is used to study the topographic nature of of the prepared thin film. The results of the spectrophotometric analysis shows that the average energy gap and average particle size of In_2O_3 nano particles were about 3 eV and about 30 nm; respectively. Interference technique which used to identify the thickness of the films, deposited by electrophoretic deposition, showed that the thickness is about 90 nm. The images of SEM showed that the film, prepared by electrophoretic deposition on ITO substrates, is of porous structure. We observed that the overall process time in this case is much shorter than CVD and PVD.

الترسيب بالانتقال الكهربائي لجسيمات In_2D_3 النانوية المحضرة بطريقة PLAL في الماء

الخلاصة

تم تحضير جسيمات أوكسيد الانديوم النانوية في الماء باستخدام تقنية القشط في السائل باستعمال الليزر النبضي. تم استخدام ليزر النيوديميوم - ياك كمصدر ضوئي قاشط. رسبت الجسيمات النانوية بواسطة طريقة الترسيب المباشر على شرائح سيليكونية وقد رسبت على قواعد زجاجية مغطاة بأوكسيد القصدير المشوب بالانديوم المسماة ITO

https://doi.org/10.30684/etj.33.2B.18
2412-0758/University of Technology-Iraq, Baghdad, Iraq

بواسطة طريقة الانتقال الكهربائي. دُرست الخواص البصرية للمحلول الغروي (الجسيمات النانوية في الماء) بواسطة مقياس الطيف الضوئي وقد رسبت بشكل غشاء رقيق جدا على القواعد الزجاجية. لغرض تقدير خشونة السطح وحجم الجسيمات النانوية رسب المحلول الغروي على شرائح سيليكونية وتصويرها بواسطة مجهر القوة الذرية AFM. من ناحية أخرى صُوّر الغشاء الرقيق لأوكسيد الانديوم بواسطة المجهر الالكتروني الماسح لمعرفة طبيعة سطح الغشاء النانوي المحضر. أظهرت نتائج تحليلات مقياس الطيف الضوئي امتلاك الجسيمات النانوية لمعدل فجوة طاقة بحدود 3 الكترون فولت ومعدل قطر بحدود 30 نانومتر. أظهرت طريقة الليزر أنّ سمك الغشاء المرسب بطريقة الانتقال الكهربائي على قواعد ITO هو بحدود 90 نانومتر. أظهر صور المجهر الالكتروني الماسح أنّ الغشاء المحضر بواسطة الانتقال الكهربائي على قواعد ITO هو ذو تركيب مسامي. لوحظ أن الزمن الكلي في هذه الحالة أقل بكثير من الزمن اللازم للترسيب بتقنية التبخير الحراري في الفراغ أو الترسيب الكيميائي البخاري.

INTRODUCTION

In the last decade, there has been a great interest in deposition of ultra thin films from the nanoparticles (NPs) because of their promising applications in solar cells, gas sensors and optical photodetectors [1]. Plenty of techniques were used for the generation of nanoparticles. The most common techniques are vapor phase transport (VPT) [2], chemical vapor deposition (CVD) [3], diode sputtering (DS) [4], and Molecular Beam Epitaxi (MBE) [5]. However most of these techniques are still costly, and generally require a costly vacuum chamber for the precise control of atmospheric conditions and temperature [2, 7]. In the last decades, Pulsed laser ablation in liquid (PLAL) used for the generation of nanoparticles has been reported as an alternative technique for the controlled fabrication of various nanoparticles of noble metals, oxides and semiconductors [6]. PLAL facilitates the production of crystallized nanoparticles in a single step procedure without subsequent heat-treatment. Pure colloidal solutions can be formed without the formation of by-products. However, many of these solutions that contain nanoparticles are usually suffering from aggregation and agglomeration. Fortunately, some chemicals called surfactants could be added to the liquids in order to prevent aggregation and to control the size distribution.

In Pulsed Laser Ablation in Liquid (PLAL), the irradiances are about (10^9-10^{10} W/cm^2) which sufficient to generate plasma at the interface between the metallic target and the liquid. This process leads to generation a shock wave that induces plasma with high pressure and temperature. The transient pressure in front of the plasma plume can push the metallic species such as ions, atoms and clusters into the expanded plasma–liquid interfacial region [2, 5, 6]. Recent research interest in nanoscience and nanotechnology has focused on discovering facile techniques to manipulate materials that historically have shown to be difficult to handle because of their size [**7**]. The electrophoretic deposition (EPD) is one of the promising techniques to deposite TiO_2 and ZnO films that frequently used for dye sensitize solar cells [8]. In addition to its simplicity, the main advantages of EPD are site-selectivity, dense packing of the nanomaterials, size-scalability of the film, and marked control over the deposition thickness of the film [7].

In this work, we studied the optical properties of In_2O_3 nanoparticles in water. The resulting nanoparticles have been deposited on silicon substrates using overcastting and

EPD methods. We observed that the overall process time in this case is much shorter than CVD and PVD.

Experimental

Our experimental setup for PLAL is presented elsewhere [8, 9, 10]. The laser is Nd-Yag which purchased from HUAFEI company. The laser parameters are: wavelength 1064 nm, maximum energy 1000 mJ per pulse, pulse width 10 ns, repetition rate 10 Hz, effective beam diameter 5 mm. In our experiment we chose from the laser an energy of 700 mJ per pulse. One pellet from In was used as target immersed in deionized water (DW). The metallic targets are immersed in open cells (cuvettes). After completion of each ablation experiment, the solutions were transferred to a vial and stored for subsequent analysis. No measurable loss of liquid volume during the course of our experiments was observed. In this work, no surfactant is used. To decrease the effect of agglomeration, the deposition process is conducted immediately after the preparation of nanoparticles. In order to conduct the transmittance measurements, one of the cells containing the pure deionized water is kept as a reference and the other one containing deionized water solution containing In_2O_3 nanoparticles. The optical properties were conducted with a Spectrophotometer (SCHMATZU). After that, the nanoparticles were deposited on the surface of silicon wafers using direct overcastting method with and without heating. The overcastting method, means placing a small drop of the obtained solutions onto the surface of the substrate then allowing it to dry with/without heating. The surface topography of In_2O_3 nanoparticles deposited on Si wafers was measured with AFM and the topography of In_2O_3 nano thin film deposited by electrophoretic deposition by SEM. Silicon samples for AFM were prepared by placing a small drop of the obtained solutions onto the surface of the silicon samples and then allowing it to dry while In_2O_3 samples for SEM analysis were prepared by electrophoretic deposition.

Results and Discussion

The formation of Indium Oxide Nanoparticles (IONPs) cystallites was confirmed by X-ray diffraction (XRD) in an earlier work [11]. The transmittance of In_2O_3 nanoparticles prepared by PLAL in is presented in Figure 1.

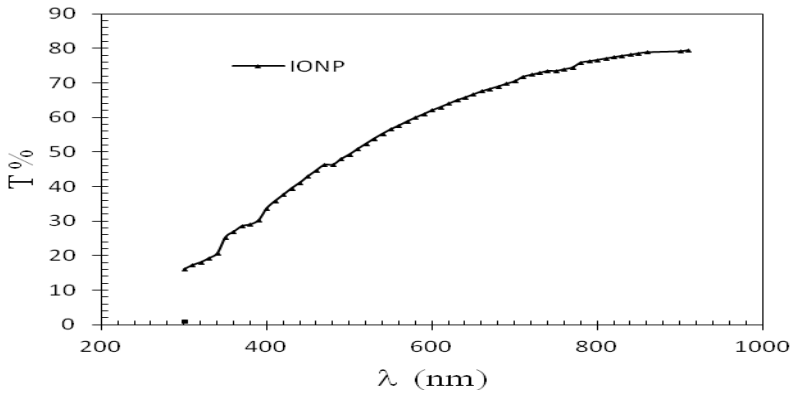


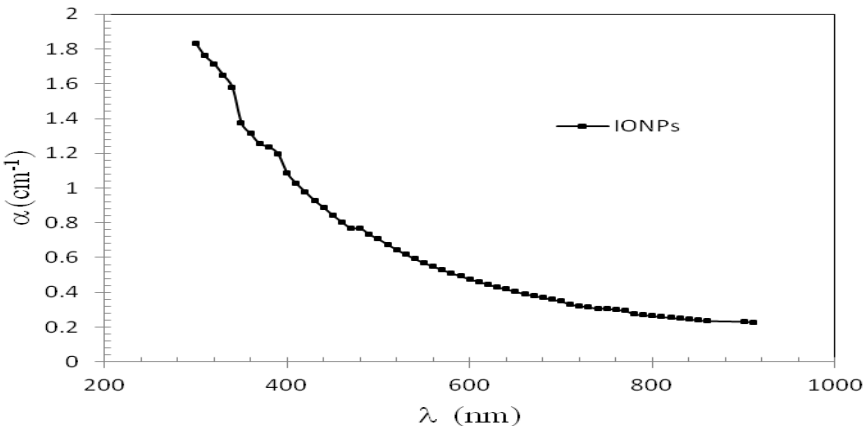
Figure (1): Transmittance of IONP in DW prepared by PLAL using Nd-Yag laser with energy 400 mJ.

IONPs has approximately the same spectral behaviour in the visible range. From the transmittance data $T(\lambda)$ as a function of the wavelength λ, the absorption coefficient $\alpha(\lambda)$ of the nanoparticles was determined using the well-known relation [12]:

$$\alpha(\lambda) = \ln(1/t)/T(\lambda) \quad \ldots(1)$$

Where

(t) are the cuvette thickness. The values of absorption coefficient as a function of wavelength is shown in Figure 2.



Figure(2): Absorption coefficient of IONPs in water prepared by PLAL using Nd-Yag laser with energy 400 mJ.

In general, the values of absorption coefficient for nanoparticles are very low compared with their values for the same constituents in the bulk. This is because of the low yield of NPs prepared by PLAL. Using the concept of matrix element and the Fermi golden rule, the relationship between the absorption coefficient and the energy gap is given by [12]:

$$(\alpha h\nu)^2 = A(h\nu - E_g) \quad \ldots (2)$$

where

A is constant. E_g is the direct band gap of the semiconductor. To evaluate the optical band gap (E_g) of the nanoparticles, we have plotted $(\alpha h\nu)^2$ versus the photon energy. Figure 3 shown for a direct gap, a plot of $(\alpha h\nu)^2$ versus photon energy should yield a straight line that crosses the photon energy axis at the band gap. The optical energy gap of nanostructured In_2O_3 is found to be 3 eV. Using Brus equation above with the result of

the energy gap concluded from the optical properties, this equation gives an average size of In_2O_3 nanoparticle about 30 nm.

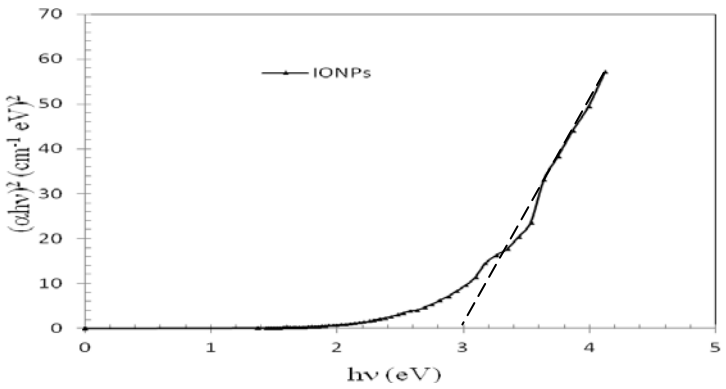


Figure 3: $(\alpha h\nu)^2$ versus $h\nu$ for IONPs in DW.

When the particles becomes in the range of nano-scale, the solution of Schrodinger equation for a particle in a box gives an energy gap which inversely proportional to the square of the particle size d. This well-known phenomenon is called quantum confinement and the energy gap takes the form [13]:

$$E_g = \frac{\pi^2 \hbar^2}{2md^2}, \quad \ldots (3)$$

where

m is the mass of the particle in vacuum, $\hbar = h/2\pi$, h is Planck constant.

Brus [14] has derived another formula which is more accurate for a semiconducting quantum well:

$$E_g = E_g^{bulk} + \frac{\pi^2 \hbar^2}{2\mu d^2} - \frac{1.8e^2}{4\pi\varepsilon\varepsilon_0 d} - \frac{\pi^2 \mu}{(4\pi\varepsilon\varepsilon_0 d)^2} \quad \ldots (4)$$

Using where $m_e = 0.3m_0$, $m_e = 0.45m_0$, and is the effective mass of the semiconductor which is given by $\mu = \frac{m_e m_h}{m_e + m_h} = 0.18m_0$. This equation can be solved by Matlab using trial and error method to estimate the average particle size of the naoparticle from the value of the energy gap concluded from Figure 3 above [15]. Using the above mentioned method, the particle size of the nanoparticles is turn out to be about 30 nm.

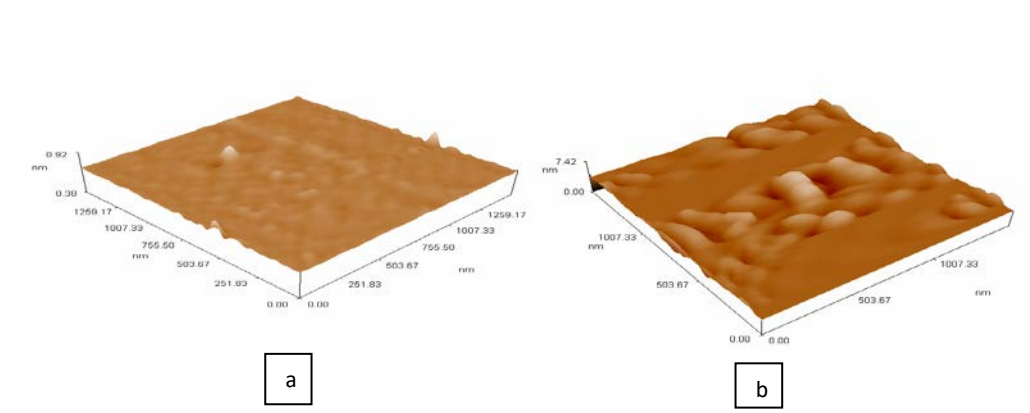


Figure (4): 3D of AFM images for (a) the surface of Si substrate before deposition of In_2O_3 nanparticles . S_a (roughness average) = 0.0075 nm, S_q (root mean square) = 0.0115 nm (b) after the deposition of In_2O_3 NPs by direct overcastting method onto hot Si substrates S_a = 0.307nm, S_a = 0.519 nm.

Figure 4 (a) and (b) respectively shows the AFM images before and after the deposition of In_2O_3 nanoparticles on Si wafers by direct overcastting method. The films revealed good adhesion with the substrates. The three dimensional image of AFM gives an indication for the surface roughness and the particle size which a function for the particle size specially for one layer of the deposited NPs. The roughness of Si wafer before the deposition of In_2O_3 was 0.0075 nm and after the deposition of the nanoparticles it became 0.307 nm. The In_2O_3 NPs are also deposited on ITO substrates and Si wafers using the EPD method. Figure 5 shows a simple diagram revealing the EPD method. The figure demonstrates a cuvette containing stainless steel and ITO electrodes and ethanol as an electrophoretic liquid. The applied dc voltage and deposition time were 20 V and 15 min. respectively.

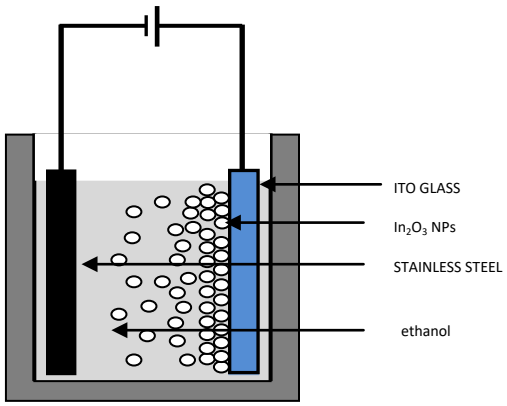


Figure (5) Schematic diagram of the EPD. In_2O_3 NPs is deposited on the anode (ITO) substrate. The NPs are already prepared by PLAL.

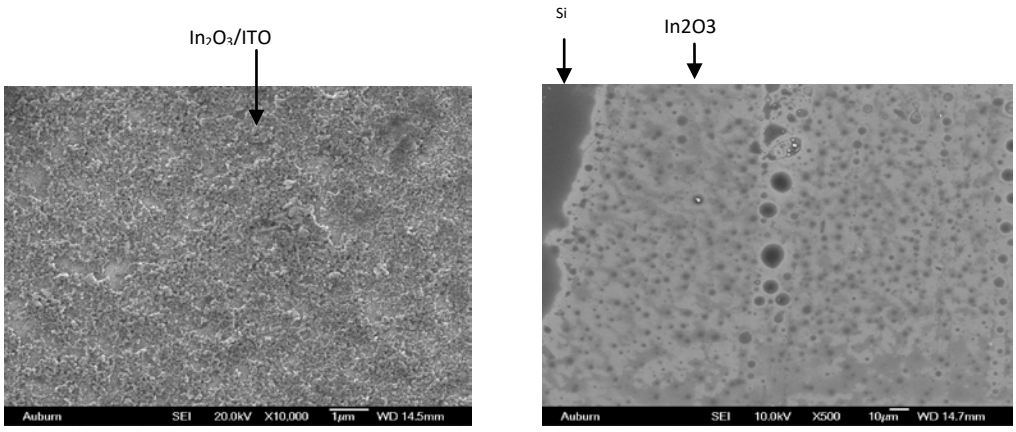


Figure (6): SEM images for (a) In_2O_3 ultra thin film deposited electrophoretically onto ITO substrate. (b) In_2O_3 ultra thin film deposited electrophoretically onto Si wafer.

A lot of features can be studied for In_2O_3 films prepared by EPD from In_2O_3 NPs already prepared by PLAL. The porosity is the most distinctive feature of the film. Figure 6 (b) is an SEM image for In_2O_3 thin film deposited on Si wafer by EPD. This film also revealed good adhesion with Si wafer but it contains a lot of voids. The average thickness of those thin films is about 90 nm as measured by laser fringes method. In spite of having porous structure, the films showed good adhesion with the Si and ITO substrates. It is worthwhile to mention that the porosity of the thin film is an important feature in some devices such as thin film sensors and solar cells.

Using a simple electrophoretic deposition method, this work revealed that In_2O_3 NPs can be deposited on glass and silicon wafers without the need of using any catalyst.
This may open the door for the possibility of using EPD technique as a cheap and simple method for preparation of ultra thin films. Up to our Knowledge, this is the first time of using In_2O_3 NPs prepared by PLAL for Electrophoretic deposition. Almost all the previous methods of EPD were using ultrafine or nano powders in liquids [16].

Conclusion

In_2O_3 nanoparticles are synthesized in deionized water using high power PLAL technique. The characterization by UV–vis absorption spectrum showed that there was a blue shift in the absorption edge which indicates the quantum confinement property of nanoparticles. The band gap of the synthesized nanoparticles in water is about 3 eV which is greater than the bulk indium dioxide. The In_2O_3 nanoparticles prepared by PLAL are successfully deposited as thin films onto silicon and ITO glass substrates. These nano thin films showed good adhesion with the substrates with porous structure.

We think that this simple, inexpensive and easy technique will find promising applications in optoelectronic devices technology.

Acknowledgment

The author (s) is / are grateful to Dr. A. K. Ali at University of Technology / Iraq and Dr. Z. Y. Cheng/Department of Materials Engineering / University of Auburn / USA for their helps in imaging by SEM equipment.

REFERENCES

[1] Z. Yan, B. Chrisey, Journal of Photochemistry and Photobiology C: Photochemistry Reviews, **13**, 204 (2012).

[2] R. Sugavaneshwar and K. Nanda, Appl. Phy. Let. **104**, 222104 (2014)

[3] H. Sheng, S. Muthukumar, N. W. Emanetoglu, and Y. Lu Appl. Phy. LET. 80, 12, 25 (2002).

[4] L. C. Chen' , S. C. Liu, Solid-State Electronics **50**, Issues 7–8, 1355 (2006).

[5] N. Preissler , O. Bierwagen, A. Ramu, and J. S. Speck, Pys. Rev. B **88**, 085305 (2013)

[6] R. Eason, "Pulsed Laser Deposition of Thin Films Applications-LED Growth of Functional Materials," Wiely-Interscience, (2007).

[7] G. Yang, "Laser Ablation in Liquids, Principles Applications in the Preparation of Nanomaterials," PAN Stanford Publication (2012).

[8] J. Liu, D. Wu, and S. Zeng, J. Mater. Process. Tech. **209,** 3943 (2009).

[9] A. K. Ali and Dayah N. Raouf , "Preparation of Silver Nanoparticles by Pulsed Laser Ablation in Liquid Medium," Eng. & Tech. Journal , **29,** No. 15, 3058 (2011),University of Technology, Baghdad, Iraq.

[10] A. K. Ali, "One-step Synthesis of Copper Oxide Nanoparticles Using Pulsed Laser Ablation in Water: Influence of Laser Wavelength on Optical Properties," Eng. & Tech. Journal , **31,** Part (B) , No. 7, 895-902 (2013), University of Technology, Baghdad, Iraq.

[11] R. A. Ismail, A. K. Ali, M. M. Ismail, K. I. Hassoon Appl. Nanosci., **1**, 45 (2011).

[12] M. Fox, "Optical Properties of Solids", 2nd edition, Oxford Press (2010).

[13] D. J. Griffiths, *Introduction to Quantum Mechanics* Pearson Education International. Second Edition (2005).

[14] L. E. Brus, J. Chem, Phys. **80** (9), 4403 (1984).

[15] M.A. Gondal, Q.A. Drmosh, T.A. Saleh, Applied Surface Science **256**, 7067 (2010).

[16] J. H. Dickerson and A. R. Boccaccini, "Electrophoretic Deposition of Nanomaterials", Springer (2012).