

Synthesis of colloidal SnO₂:Bi₂O₃ nanoparticles using nanosecond laser ablation under liquid

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To cite this article

Mohammed Jawad Kadhim, Firas Sabeeh Mohammed, Marwa Abdul Muhsien Hassan. Synthesis of Colloidal SnO₂:Bi₂O₃ Nanoparticles Using Nanosecond Laser Ablation under Liquid. *International Journal of Nanoscience and Nanoengineering*. Vol. 1, No. 1, 2014, pp. 12-16.

Abstract

 $SnO_2:Bi_2O_3$ collodial NPs were synthesized by pulsed laser ablation of Sn:Bi target (50%:50%) in double distilled water (DDW) at room temperature. High purity Sn:Bi target (purity of 99.99%) was fixed at bottom of open a plastic cell containing of 2 ml DDW and DDW+ PVP which represent the liquid media. Ablation is carried out with laser operating at 1.064 nm wavelengths at fluence set in the range of 40.5J/cm² and (60 laser pulses). The diffraction peaks in the XRD pattern broadened due to the particles in the sample are too small. The primary particle size calculated by Sherrer formula is about 20 nm. The spherical nanoparticles morphologies were carried out by scan electron microscope (SEM) analysis, exhibits spherical with average size distribution found to be 25 nm.

Keywords

Nanoparticles, SnO₂, PL, Laser Ablation, Bi₂O₃

1. Introduction

Nanostructured SnO₂ particles were prepared using different chemical and physical methods. Its important yield from its wide band gap (3.6 eV) that presents a proper combination of chemical, electronic and optical properties [1]. Because of its unique electrical and catalytic properties, tin oxide has been widely used for various electrochemical and catalytic applications, such as gas sensors for environmental monitoring and catalysts. For these applications, SnO₂ small particle size or large specific surface area is essential to high performance [2]. Bismuth is a semimetal with a rhombohedra structure. The synthesis of bismuth nanoparticles has been recently reported by using a chemical method [3]. Bismuth oxide (Bi₂O₃) is a well known transition metal oxide and it has been intensively studied due to its interesting thermal and electrical transport properties. Moreover, Bi2O3 nanoparticles can offer large surface area and good electrochemical stability. Recently Bi₂O₃ nanoparticles have attracted considerable attention due to their potential applications in electrochemical sensors for sensing zinc, paracetamol and to probe DNA

hybridization [4]. Metal oxides nanoparticles (NPs) have shown their great interest in field of sensing, optoelectronics, catalysis, solar cells and so on due to their unique physical and chemical properties differing from the bulk [5]. Adsorption of a gas on the surface of a metal oxide semiconductor material can bring about a significant change in the electrical resistance of the material. During the conversion, a number of physical and chemical parameters such as film thickness, grain size, intergrain contact, porosity, grain network, phase composition, elemental composition, bulk stoichiometry, surface architecture, type of additives and dopants, etc. are involved in the changes of conductance of the oxide when the film is exposed to a gaseous atmosphere. Among these parameters, growth and adding dopants and additives into the oxide strongly affects the surface properties and structure of the metal oxide gas sensors. Oxides such as SnO₂, WO₃, and ZnO have been considered by many researchers in the field of semiconductor gas sensors. Although pure oxides, individually, are sensitive to a range of gases, they also have their own detection issues such as cross-sensitivity, sensitivity to humidity, shorter life time,

lack of ability to detect a certain gas, higher temperature of reaction and so on. Some additives such as noble transition metals do not participate in the reaction phase, but promote the improvement of sensitivity of the sensor to be strongly sensitive to a certain type of gas, decrease response and recovery times, improve thermal stability of the overall structure and sensor properties, and modify the catalytic reactivity and morphology of deposited films. Small quantities of dopants in oxide forms such as TiO₂, Bi₂O₃, MoO₃, NiO, etc. modify the microstructure, suppress the grain growth, and enhance the porosity of the basic oxide, leading to an increase of film sensitivity toward a certain gas, and reducing the reaction temperature to as low as room temperature. Besides, dopants can promote the speed of reaction in presence of certain gas versus a longer response and recovery time for some other gases. They also can improve sensitivity of the sensor to humidity and eliminate cross-sensitivity [6].

2. Method Work

Q-switched Nd/YAG laser system type HUAFEI providing pulses of 1064 nm and 532 nm(frequency doubled) wavelength with maximum energy per pulse of 1000 mJ, pulse width of 10 ns, repetition rate of 10 Hz and effective beam diameter of 5 mm, was used for laser ablation. The laser is applied with a lens with 110 mm focal length is used to achieve high laser fluence. SnO₂:Bi₂O₃ collodial NPs were synthesized by pulsed laser ablation of Sn:Bi target (50%:50%) in double distilled water (DDW) at room temperature. High purity Sn:Bi target (purity of 99.99%) was fixed at bottom of open a plastic cell containing of 2 ml DDW and DDW+PVP which represent the liquid media. Ablation is carried out with laser operating at 1.064 nm wavelengths at fluence set in the range of 40.5J/cm² and (60 laser pulses). The laser beam was focused on the Sn:Bi target using convex lens of 11 cm focal length to produce sufficient laser fluence for the ablation. The typical laser beam diameter on the target was varied in the range of 3 mm in diameter by changing the distance between the focusing lens and the Sn:Bi target. The position of metal plate was continuously translated mechanically using a controlled motor. The colloidal solution vibrated for 10 min by ultrasonic vibrator in order to get homogeneity for the product. The spot size of the laser beam on the surface of the metal plate of 0.6 mm in radius (r). The laser fluence (F) was 40.5 J/cm^2 where:

$$F = \frac{Pulse \; energy}{A} \& A = 2\pi r^2 \tag{1}$$

The pulse energy was 915.624 mJ/cm².

PVP liquid solutions are construction by adding 0.3 gm of pure PVP powder to 10 ml of DDW. The deposition process for one drop of collodial nanoparticles was hold on quartz substrate by using thermal deposition process for the purpose drying samples then hold the samples measurements as show in figure (1).



Figure 1. Thermal deposition process.

3. Results and Discussion

To clarify the crystalline structure, an XRD pattern of the as-prepared $\text{SnO}_2:\text{Bi}_2\text{O}_3$ colloidal NPs (Figure 2). The diffraction peaks at around 34 and 27.9° are assigned to SnO_2 (101) and α -Bi₂O₃ (121). No diffraction peaks due to metallic Sn, Bi or other tin oxides an bismuth oxides were discerned. The diffraction peaks in the XRD pattern broadened due to the particles in the sample are too small. The primary particle size calculated by Sherrer formula is about 20 nm.



Figure 2. SEM image of SnO_2 : Bi_2O_3 colliodal NPs supertion preperd by drop drying on quartz substrate using laser ablation unde water+PVP solution.

Atomic force microscopy (AFM) was used to examine SnO₂:Bi₂O₃ colloidal nanoparticles, pore diameter, depth and roughness surface for each sample. The increase in surface roughness of the oxides leads to a increase in the efficiency for sensing properties, therefore, it is very important to investigate the surface morphology of the SnO₂:Bi₂O₃ colloidal nanoparticles. surface The morphology of SnO₂:Bi₂O₃ colloidal nanoparticles as observed from the AFM micrographs proves that the grains are uniformly distributed for 2D and 3D views with individual grains extending upwards as shown in figure (3) (a) (b). The surface of the $SnO_2:Bi_2O_3$ colloidal nanoparticles were characterized using AFM micrographs. It shows a change in roughness of the oxide surface with calcined temperature. It is known that the increase in surface roughness may cause deterioration of the electrical and optical properties. However, these differences in mean

55.50nn

35.50nn

25.50n

15.50

5.50nm

roughness have a significant influence on optical properties of the films considered in this study. These results, together with the XRD analysis, clearly indicate that the crystallinity is influenced by the nature of structural material. This is in good agreement with other results. Figure (3) show the surface morphology (AFM image) of SnO₂:Bi₂O₃ colloidal nanoparticles suspension prepared using drop drying on quartz substrate at temperature 70 °C, it's clearly obvious the plasma is intense enough to achieve its long life time and high temperature in such a conditions, the space asymmetry of distributions is no longer predominant because the plume region is filled with a high density of species, Here the influence of aligned media will be much slighter [1]. Several small bright spherical shaped SnO₂: Bi₂O₃ nanoparticles are more closely anchored throughout the film surface and the AFM results show uniform distributed of the Nanoparticles on the substrate, as shown in the following figure (3). The averge grain size found to be about 30 nm while the roughness average value about (0.787 and 5.71) nm, the difference in particle size and surface roughness related to the the uniform growth and distrubution of SnO2:Bi2O3 nanoparticle on substrate surface at higher tempreture. This could be ascribed to the large surface area and highly porous surface morphology of SnO2:Bi2O3 nanoparticles. Polyvinylpyrrolidone PVP $(C_6H_9NO)_x$ aqueous solution is a

typical polymer (M.W.5000) that is used extensively as a stabilizing agent of metal colloids. In addition, PVP will also interact with ablated matter (atoms, clusters, and droplets) produced by laser ablation and prevent their aggregation, it is expected that PVP will affect on the particle size [7] as shown in figure (3) (b).

The AFM technique uses a laterally moving tip, while the cantilever reflects the sample's topography, or the Z measurements. Even though the tip is very sharp, it is impossible to gather the information from the underside of specimen. The spherical particle will be viewed as a bump by the Atomic Force Microscope. To correct the AFM image for this effect some deconvolution techniques are used. In conclusion, the AFM and SEM images are complementing each other. Surface morphologies obtained through Scanning Electron Microscope (SEM) study carried out by (Hitachi FE-SEM model S-4160, Japan) in the University of Tehran at 16 kV of SnO₂:Bi₂O₃ nanopartical. The spherical nanoparticles morphologies were carried out by scan electron microscope (SEM) analysis as shown in figure (4) exhibits spherical with average size distribution found to be 25 nm. SEM analysis. Spherical morphology with a highly porous, foam-like structure can be observed.



size:6520 00nm X 6520 00nm an Square) Skewness) (Root Mo. k(Surface Skewno. u(Surface Kurtosis) 5.0 Peak) 50.9 [nm] Sht) 48.7 -0.28

Hybrid Parameters (Mean Summit Curvature) -0.0206[1/nm] 0.296 [1/nm] Iq(Root Mean Square Slope) Ir(Surface Area Ratio) 3.92

Functional Parame Sbi(Surface Bearing Index) 0.427 Sci(Core Fluid Retention Index) 1.33 Svi(Valley Fluid Retention Index) 0.1 Spk(Reduced Summit Height) 8.75 ore Roughness Depth) 11.6 [nm] 11.9 [nm]

CSPM Imager Surface Roughness Analysis

Spatial Parameters: Sds(Density of Summits) 612 [1/um2] Fractal Dimension 3





Figure 3. AFM image of SnO_2 : Bi_2O_3 colliodal NPs supertion preperd by drop drying on quartz substrate using laser ablation under (a) water and (b) water+PVP solution.



Figure 4. SEM image of SnO_2 :Bi₂O₃ colliodal NPs supertion preperd by drop drying on quartz substrate using laser ablation unde water+PVP solution.

4. Conclusions

Metal oxides $SnO_2:Bi_2O_3$ nanoparticales were construction using pulsed laser ablation of Sn:Bi target (50%:50%) in double distilled water (DDW) and water (DDW+PVP) at room temperature. Several small bright spherical shaped $SnO_2: Bi_2O_3$ nanoparticles are more closely anchored throughout the film surface and the AFM results show uniform distributed of the Nanoparticles on the substrate. The primary particle size calculated by Sherrer formula is about 20 nm. The averge grain size found to be about 30 nm while the roughness average value about (0.787 and 5.71) nm, the difference in particle size and surface roughness related to the the uniform growth and distrubution of SnO₂:Bi2O3 nanoparticle on substrate surface at higher tempreture. The spherical nanoparticles morphologies were carried out by scan electron microscope (SEM) analysis, exhibits spherical with average size distribution found to be 25 nm.

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