Fabrication of SnO\textsubscript{2} Q-dot thin films using Ultrasonic Spray Techniques for optoelectronics applications

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Abstract
Synthesis of SnO\textsubscript{2} nanoparticles without using a capping agent is a difficult task with chemical route of synthesis. This paper reports on synthesis of tin oxide (SnO\textsubscript{2}) nanoparticles with dimension in the nano particle regime using simple chemical rout and successfully applied Ultrasonic Spray system to developed thin film on glass substrate again investigated the thickness dependent electrical and optical properties of SnO\textsubscript{2} nano particles. Nano-particle film resistant and optical transmittance showed prominent dependence on film thickness.

Keywords: SnO\textsubscript{2} Nanoparticles, Ultrasonic Spray method

INTRODUCTION
The disclosure of novel materials, procedures, and marvels at the nanoscale and the improvement of new test and hypothetical strategies for inquire about give new chances to the advancement of creative nano frameworks and nanostructure materials. The properties of materials at the nanoscale can be altogether different from those at a bigger scale. At the point for the measurement of a material is diminished from a huge size, the properties continue as before at in the first place, and afterward little changes happen, until at long last when the size dips under 100 nm, emotional changes in properties can happen. In the event that just a single length of a three dimensional nanostructure is of nano measurement, the structure is alluded to as quantum well; if two sides are of nanometer length, the structure is alluded to as quantum wire. A quantum speck has each of the three measurements in the nano run. Furthermore, the three sorts of nanostructures in light of the fact that the adjustments in properties emerge from the quantum-mechanical nature of material science in the area of the ultra-little is related to term quantum.

There are two simultaneous ideologies to fabricate nano structured materials like chalcogenide, metal etc. nano structured. Top-down and bottom up, within the top-down technique, a appropriate beginning fabric is contracted the usage of physical or chemical method, a first-rate downside of the top-down approach is the imperfection of the floor structure. such defects in the surface structure can have a good sized effect on physical houses and surface chemistry of the metallic nano-particles because of the high aspect ratio.

In case of backside-up, or self assembly, refers to the development of a structure atom-by-atom, molecule-by means of-molecule, or cluster-through-cluster. in this method, first of all the nano-established building blocks (ie, nano-debris) are fashioned and, subsequently, assembled into the final material the use of chemical or organic processes for synthesis. a wonderful advantage of the bottom-up method is the improved possibility of acquiring metallic nano-debris with comparatively lesser defects and greater homogeneous chemical compositions.

It is observed that the variety of oxide materials could not be better validated than inside the style of self-assembled nanoscale materials. The wide assortment of electronic and synthetic properties of metal oxides makes them energizing materials for fundamental research and for innovative applications alike. Therefore, Oxides traverse extensive variety of electrical properties from wide band-hole covers to metallic and superconducting. Furthermore, tin dioxide has a place with a class of materials that consolidates of electrical conductivity has high with optical straightforwardness and along these lines constitutes an essential part for optoelectronic applications. It is utilized substance applications oxides as help materials for scattered metal impetuses additionally frequently display chemically action without anyone else.

Concerning tin oxide, for example SnO\textsubscript{2} nanobelts, SnO\textsubscript{2} nanodiskettes, and other nanoscopic materials shape. It is just of the request of 10-100 nm in the cross-area and up to a few millimeters long for the SnO\textsubscript{2} nanobelts have the mass such as rutile structure yet. It’s surfaces are low file mass terminations and along these lines, show comparable properties to single precious stone surfaces. The tin oxide become has a considerable lot of these nanostructures a basic vapor stage transport development is utilized. Consequently, tin oxide is not one of a kind in its self-development of nano-organized materials different oxides additionally develop nanowires (ZnO, In2O3, SiO2, Ga2O3, and GeO2), nanobelts (Ga2O3, In2O3, ZnO, PbO2, CdO, and SnO2), and also nanorods (MgO).It has Large portions of gas detecting properties. Furthermore, their huge surface to volume proportion make them promising materials for all around characterized, profoundly touchy gas sensors.

Tin oxide (SnO\textsubscript{2} mineral form ‘cassiterite’) is the inorganic semiconductor usually regarded as an oxygen-deficient n-type semiconductor having rutile structure, which possesses six coordinate tin atoms and the three coordinate oxygen atoms. [1-2].

Because of versatile properties like Intrinsic carrier High mobility, n-type semiconductor with wide energy band gap of SnO\textsubscript{2} ~3.65 eV it have been used in many application such as transparent conductive films, gassensors, lithium-ion batteries.
Furthermore solar cells electrochemical applications, electrode materials for Li-ion batteries, catalysts for redox reactions and gas sensors solid-state gas sensors for environmental monitoring of CO, H₂, and NO.

EXPERIMENTAL

Chemical Used
Tin(IV) chloride (SnCl₄) Sigma Aldrich (98%), Methanol Merck Millipore (99%), Acetone Merck Millipore (99.5%), 2-propanol Merck Millipore (99.5%), Liquor Ammonia (95%)
All chemicals were used without further purification.

Fabrication of SnO₂ Nanoparticles

A step by step cleaning of apparatus used for the synthesis by using soap solution, double distilled water, Acetone, 2-propanol with 7 minute bath sonication. 0.5M solution of Tin (IV) chloride (SnCl₄) were prepare in water with continuous stirring using magnetic stirrer for about 10-15 min. Liquor ammonia were added drop wise in the solution up to the pH of solution become ~8-9. Then solution was kept at 70°C uniform temperature in the paraffin oil bath for 2 hours. After 2 hours reaction separation and purification of product were carried by centrifugation at 5000 rpm for 8 minute and sonication for 5 minute about 3-4 times with methanol and then acetone after that storage of the yield by drying in vacuum oven about 110°C temperature for 60 minute. To removal of Tin hydroxide phase the powder were annealed at 200°C for 3 hours on hot plate.

Reaction Mechanism

\[ \text{NH}_3 + \text{H}_2\text{O} \rightarrow \text{NH}_4^+ + \text{OH}^- \]
\[ \text{SnCl}_4^+ + \text{NH}_3 + \text{H}_2\text{O} \rightarrow \text{Sn}^{2+} + \text{Cl}^- + \text{OH}^- + \text{H}^+ \]
\[ \text{Sn}^{2+} + 2\text{OH}^- \rightarrow \text{Sn(OH)}_2 \]
\[ \text{SnCl}_4 + \text{NH}_3 + \text{H}_2\text{O} \rightarrow \text{Sn(OH)}_2 \text{ Heating} \rightarrow \text{SnO}_2 \]

Fabrication of Thin film using Ultrasonic spray system

Figure 1 shows the Schematic Diagram of Ultrasonic Spray method. The ultrasonic nozzle was operated at 120 kHz. The 5 mg/ml SnO₂ solution in methanol were sprayed with 1 sec ON and 3 sec OFF spray time. The nozzle was held at 12.5 cm from the substrate, while the substrate was kept on hot plate at 50°C. The solution was feeded using syringe pump with flow rate 10 ml/hr. Nitrogen with flow rate 15 litres per minute (lpm) was used as carrier gas for controlling and shaping the spray precisely. The SnO₂ films were prepared for different number of cycles VIZ. 30, 50, 75 and 100.

Table 1: Film deposition parameters

<table>
<thead>
<tr>
<th>Sr. No.</th>
<th>Substrate Temperature °C</th>
<th>Number of cycles</th>
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<tbody>
<tr>
<td>1</td>
<td>50</td>
<td>30</td>
</tr>
<tr>
<td>2</td>
<td>50</td>
<td>50</td>
</tr>
<tr>
<td>3</td>
<td>50</td>
<td>75</td>
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<td>4</td>
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RESULT AND DISCUSSION

Synthesized SnO₂ Nanoparticles were characterized by following characterizing techniques for several confirmations. X-ray powder diffraction (XRD) was carried out using D8 advance Bruker diffractometer with incident source wavelength λ=1.54Å. Field Effect-Scanning Electron Microscopy (FE-SEM) images for the powder sample were taken using Hitachi S4822, ultrafine imaging magnification 50000X to 100000X with Bruker Energy Dispersive X-ray (EDAX) attachment. The Absorption spectra were obtained using UV-VIS spectrophotometer (Shimadzu UV 1600). Current–voltage (I–V) measurement was performed using Keithley 2611A Source measure meter under 100 mW/cm².

X-ray Diffraction (XRD)

X-ray diffraction spectra for the given sample of SnO₂ Nanoparticles shows all the peak indexed at 20° =25.28°, 32.87°, 50.72°, 51.83°, 62.75° & 78.35° for corresponding
planes [110], [101], [211], [220], [221], and [400] respectively which reflected to indexed JCPDS card data number 41-1445 for tetragonal crystal structure and having lattice parameter a=b = 4.38, c = 3.187.

**Figure 2:** X-ray diffraction spectra for the given sample of SnO$_2$ Nanoparticles

**Energy Dispersive X-ray (EDX)**

EDX analysis gives acceptable elemental constitution for Sn:O as shown in figure. The given sample shows 37.29 and 60.78 (1:2) atomic percent for Sn and O which confirm that sample contains SnO$_2$ pure phase. Incorporation impurity atom C is due to use of carbon tape during SEM.

**Figure 3:** Energy Dispersive X-ray Spectra for SnO$_2$ Nanoparticles

**Scanning Electron Microscopy (SEM)**

Scanning Electron Microscopy study of the sample shows that the SnO$_2$ nanopartical with average partical size ~ 14 nm is form and having sperical morphology in aggregated form. Aggregation is due to high surface energy of the nanosized partilces.

**Figure 4:** Field Effect Scanning Electron Microscopical image of SnO$_2$ nanoparticles.

**UV –visible spectroscopy**

Optical study of SnO$_2$ nanopartical using UV visible spectroscopy, which shows sharp peak at UV region having direct band gap at ~3.7 ev calculated using Tauc plot which is plotted with photon energy versus (αhν)$^2$ for direct band gap determination. Where, α-absorption coefficient of SnO$_2$ and hν photon energy for corresponding wavelength.

**Figure 5** (a) UV visible spectra, (b) Tauc plot for direct band gap calculation
Effect of Thickness on Optical properties of the SnO$_2$ Film deposited by Ultrasonic Spray Technique

The UV-Visible optical spectra show the optical transmittance values vary with thickness.

For the lower number of cycles i.e. 30, 50 & 75, as the number of cycles the transmittance decreases with increase in number of cycles it may be due to the surface photon scattering phenomenon which creates optical resistive barrier. Due to smoother film for 100 number of cycles transmittance increases.

![Figure 6. UV-Visible transmittance spectra](image)

Current voltage characteristics

1. Current Voltage Characteristics of the film

Effect of Thickness on Electrical properties of the SnO$_2$ Film deposited by Ultrasonic Spray Technique

From IV Characteristic of the film it is clear that, as we increase the no of cycles the thickness of the film increases so that conductivity also increases.

![Figure 7. Current voltage characteristics of SnO$_2$ Film](image)

CONCLUSION

Synthesis of the SnO$_2$ nanoparticles was successfully done using simple chemical reaction method. Tin (II) chloride (SnCl$_4$) and Water (H$_2$O) were taken as tin and oxygen sources respectively. Morphological study by SEM gives the SnO$_2$ nanoparticles with average particle size 14 nm is formed. Elemental study gives acceptable constitution that is SnO$_2$ with atomic ratio 1:2 which conforms that sample contain SnO$_2$ pure phase from EDX spectra. XRD again confirm tetragonal crystal structure for the given sample of SnO$_2$ Nanoparticles, which reflected may be to indexed JCPDS card data number 41-1445. Optical study for the SnO$_2$ Nanoparticle gives the direct optical transition at ~3.7eV due to its high band gap value it can be useful for window layer of the visible optoelectronic devices.

Optical study for fabricated SnO$_2$ films at different number of cycles i.e. 30, 50 & 75, as the number of cycles concluded that, the transmittance decreases with increase in number of cycles it may be due to the surface photon scattering phenomenon which creates optical resistive barrier. Due to smoother film for 100 number of cycles transmittance increases.

REFERENCES


