Journal of Materials Science and Engineering B 5 (9-10) (2015) 353-360
doi: 10.17265/2161-6221/2015.9-10.003

Study the Synthesis Parameter of Tin Oxide Nanostructure

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Abstract: In this article, the effect of synthesis parameters on structural properties of SnO_2 nanowire by thermal evaporation process, have been studied. The nanostructures are characterized by scanning electron microscopy, Transmission electron microscopy and X-ray spectroscopy. By X-ray diffraction pattern, synthesized SnO_2 nanowire were found to be crystalline rutile SnO_2. We studied the effect of synthesis parameters such as the deposition temperature, distance variation of the substrate from precursor on the structure of our synthesized nanowires. It was found that their growth was governed by vapor-liquid-solid mechanism (VLS) because of using Sn self catalyst. In this mechanism, the Sn droplet deposited serve as preferred sites for the growth of SnO_2 nanowire.

Key words: Tin oxide NWs, thermal evaporation, synthesis factor.

1. Introduction

Transparent conducting and semiconducting oxide nonmaterial like tin oxide have [1] variety of practical application such as light emitting diode [1], solar cell [2] and sensor [3]. These nanostructures can be grown by various methods such as thermal treatment [6], hydrothermal method [8] and electrochemical deposition [7] and thermal evaporation. We have synthesized tin oxide nanostructure by one of simplest method named as thermal evaporation. In thermal evaporation process, researcher are using most common process name carbothermal reducing process [4, 5] by which we can deposited material at some lower temperature respect to desired melting point of that metal oxide material. In the study of Wu et al. [11] in 2005, the influence of reaction on the temperature of synthesis at 850 $^{\circ}$C elucidated. They also considered the effect of the temperature of synthesis on the reaction time of 1 h on the structure of TiO_2 nanowires [12]. By these consideration, variation in growth parameter, like temperature, gas flow rate and distance of substrate to source, the morphology of deposited nanostructure can be modify. In growth of metal oxide, there is many reported work for metal oxide to carbon (graphite) ratio in was taken in decade years. That's why; researcher had taken most common ratio 1:1 of tin oxide material with graphite powder. Tin oxide, nanostructures using the mixture of the corresponding oxide (tin oxide) material and graphite in 1:1 ratio as the source material. The Effect of the growth temperature and source to precursor distance variation on the morphology and properties of the obtained nanomaterials had been studied.

2. Experiment

A commercial one surface polished n-type Si (100) oriented 50 mm in diameter wafer with resistivity 1-20 Ω·inch and thickness 525 ± 25 μm was used as a substrate and source of silicon for the growth of SnO_2/Si nanostructure. The Si wafer was cut into dimensions of 0.5 inch × 0.5 inch before being cleaned by standard RCA cleaning method. Alumina boat, on which deposition has been taken, cleaned with propanol along with acetone. I have taken SnO_2 powder (99.99% pure) along with graphite fine powder (99.50% pure) in 1:1 ratio as a precursor. Ar gas had taken at constant flow rate of 100 sccm. Prior of heating, pressure inside the furnace keeps on

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atmosphere pressure. Furnace was heated up to 900 °C, 1,000 °C and 1,100 °C to analysis the temperature effect in growth of nanostructure. Deposition was maintained till 1 h. The set up of atmospheric sintering furnace is shown on Fig. 1.

3. Characterization of Nanostructure

A set of five nanostructure samples has been prepared with different growth conditions of tin oxide. Table 1 shows the details of prepared sample.

Nanostructure obtained by synthesis was subjected to characterization by XRD (X-ray diffraction), SEM (Scanning electron microscopy), TEM (Transmission electron microscopy) and UV-Vis reflection spectra. Crystal structure can be understood by X-ray diffraction peaks which clearly shown tetragonal structure of tin oxide. The crystallite size (t) was calculated from the FWHM (Full width at half maximum) of the maximum intense diffraction peak of the XRD pattern by using the Debye-Scherrer formula [9] given by:

$$t = 0.9\,\lambda/\beta\cos\theta \quad (1)$$

where, λ is the wavelength of the X-rays used, β is the FWHM, θ is the Bragg angle, and t is the average crystallite size. From above equation, crystalline size of SnO_2 nanostructure have been found 51 nm, 91 nm and 269 nm for substrate at 50 mm, 75 mm and 25 mm respectively at 1,100 °C as probability of precipitation of SnO vapour in Sn metal droplet is higher as we far from precursor. Again 1693 nm and 4 nm for 1,000 °C and 900 °C respectively at 50 mm from source, it is only due to desired melting temperature at near to 1,100 °C. Fig. 2 shows the XRD patterns of the tin oxide nanostructure at variety in synthesis parameter. The products are crystalline and the diffraction peaks can be indexed as the tetragonal rutile structure, which is consistent with the reported data (JCPDS).

Now surface morphology was investigated by SEM and SEM image shows the growth of tin oxide nanostructure on Si substrate. Observed diameter of nanostructure on substrate at 25 mm, 50 mm and 75 mm were 450 nm, 250 nm and 50 nm respectively and length of nanowire was found approximately several microns. Again diameter at substrate at different deposition temperature 1,000 °C was 400 nm with length approximately several microns. Substrate at 900 °C was not supported due to very low vaporising temperature for SnO respect to desired temperature. The diameter of nanowire corresponding to varying synthesis parameter is shown in Fig. 3.

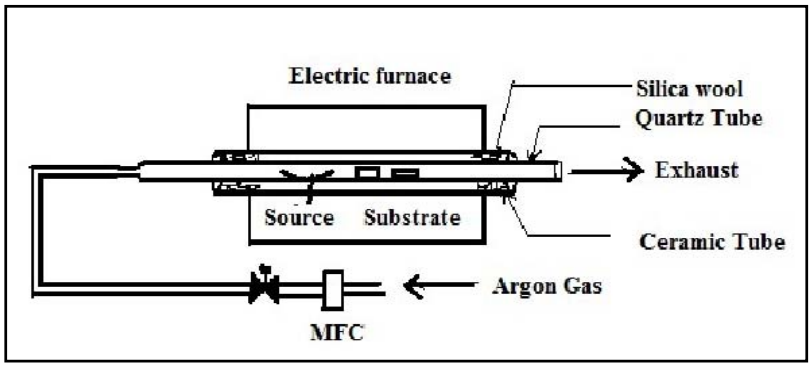


Fig. 1 Schematic diagram of thermal evaporation chamber.

Table 1 Nomenclature of SnO_2 samples when substrate placed at "atm" pressure.

Sample details	Aberrations as referred in text
25 mm from source at 1,100 °C, 100 sccm	Sn1
50 mm from source at 1,100 °C, 100 sccm	Sn2
75 mm from source at 1,100 °C, 100 sccm	Sn3
50 mm from source at 1,000 °C, 100 sccm	Sn4
50 mm from source at 900 °C, 100 sccm	Sn5

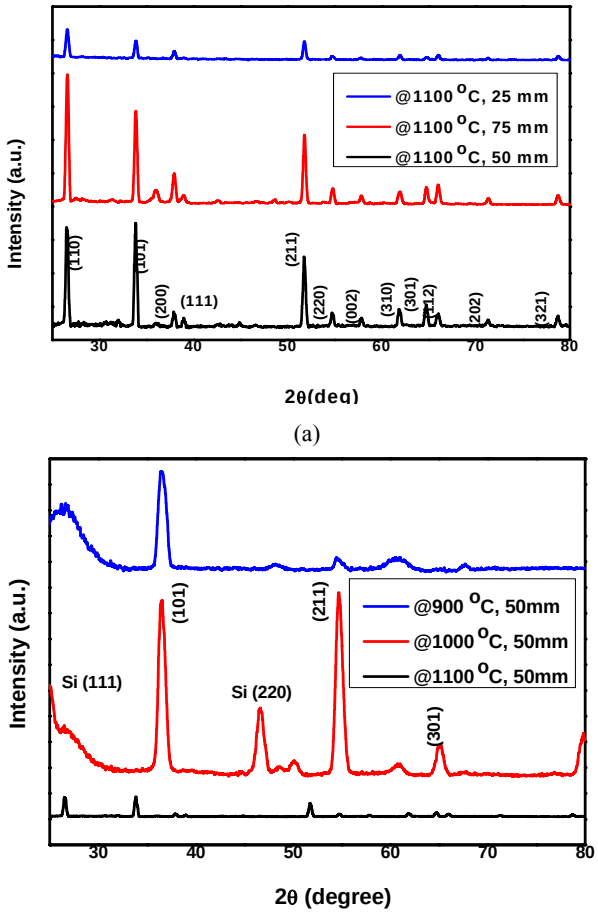


Fig. 2 XRD image of tin oxide nanostructure at variation in: (a) distance between source to substrate shows tetragonal structure and (b) synthesis temperature shows tetragonal structure.

Now as we know that melting temperature of SnO_2 powder is 1,630 °C, but after carbothermal process, it can be reduced till 1,100 °C so we can see that possible growth of nanostructure at 1,100 °C. Now VLS growth mechanism for growth of nanostructure can understand by TEM image shown in Fig. 4. Schmatic diagram of growth of nanowire have been shown in Fig. 5.

From the theory of thermal physics or thermodynamically it was clear that high pressure can cause reduction in melting temperature of the material. So pressure inside the quartz tube was an important parameter but by physics atmospheric pressure. A model has been discussed for all kind of growth condition inside thermal evaporation chamber is shown in Fig. 6. Table 3 shows combine study along result observed by varying various parameters for growth of tin oxide nanostructure.

Discussion can carried out some more explanation towards justification for above experiment.

We can now solve for the velocity of the SnO molecules at any temperature by formula:

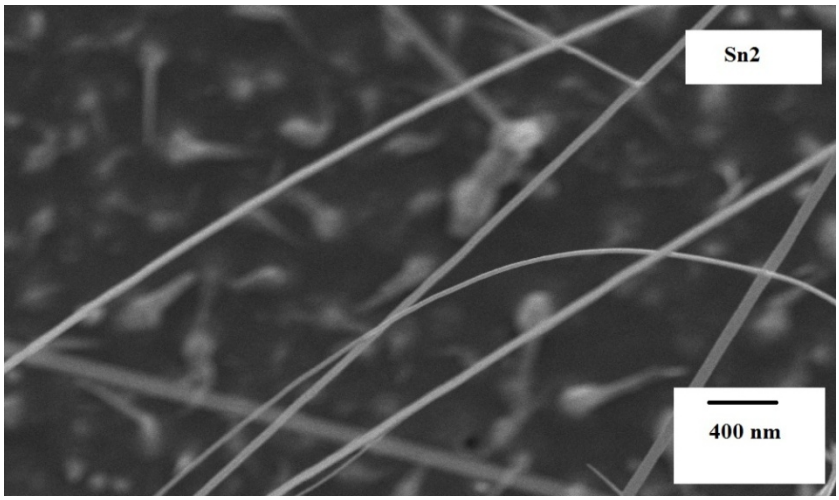
$$(1/2)\, mv^2 = (3/2)\, kT \quad (2)$$

$$mv^2 = 3\, kT$$

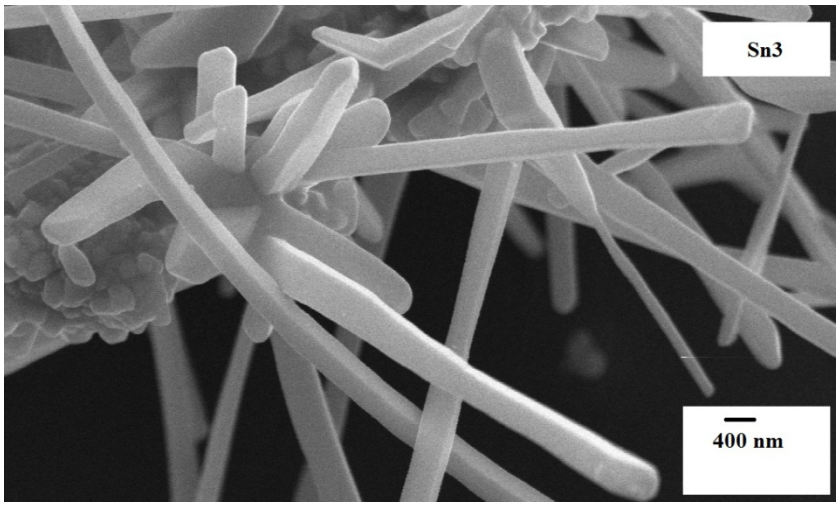
$$v^2 = 3\, kT/m \quad (3)$$

where, m is mass, v is velocity, k is Boltzmann's constant, and T is the temperature in Kelvin. Now calculated root means square velocity of SnO vapour at 1100 °C is 50.417 cm/s from above equation. T rue mass flow of Ar gas can be calculated from Standard cubic centimetres per minute (sccm) by equation.

$$m = (mP/nRT)\, Q \quad (4)$$



(a)



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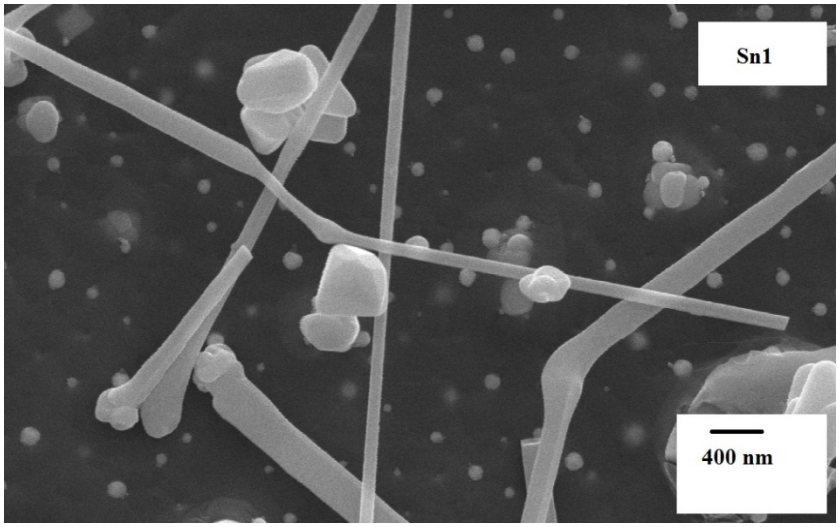

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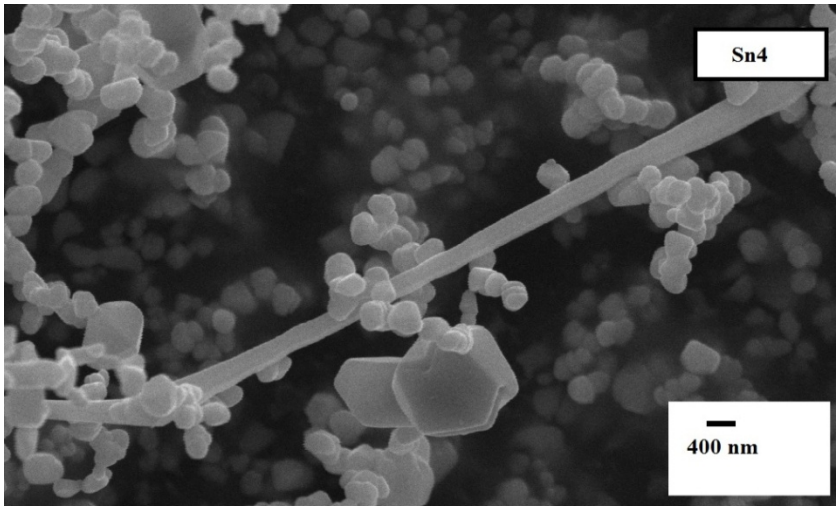

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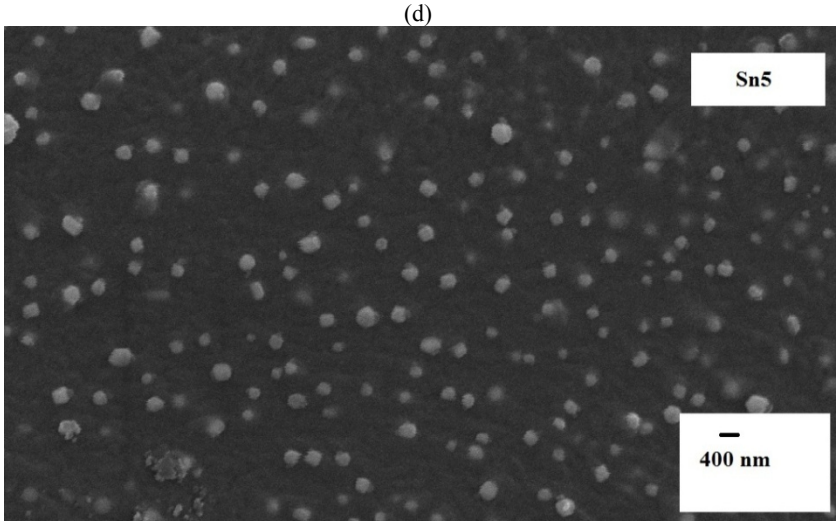

(e)

Fig. 3 SEM image of tin oxide nanostructure shows diameter approx: (a) 50 nm at 1,100 °C, 50 mm and 100 sccm flow rate; (b) 200 nm to 300 nm at 1,100 °C, 75 mm and 100 sccm flow rate; (c) 400 nm to 600 nm at 1,100 °C, 25 mm and 100 sccm flow rate: (d) 400 nm at 1,000 °C, 50 mm and 100 sccm flow rate; (e) at 900 °C, 50 mm and 100 sccm flow rate.

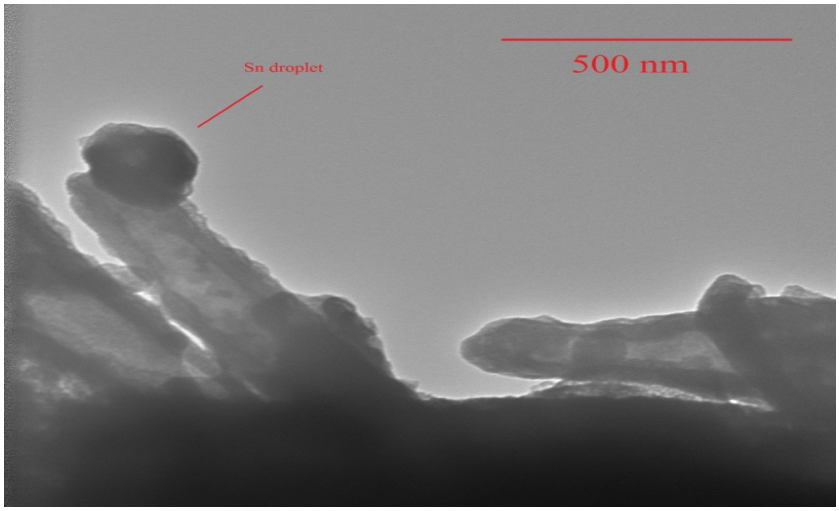

Fig. 4 TEM image shows VLS growth of self catalyse Sn droplet on the tip of nanostructure observed at 1,100 °C at 50 mm from source.

Table 2 Synthesis condition and morphology of SnO_2 nanowire at "atm" pressure.

Furnace centre temperature (°C)	Carrier gas flow (sccm)	Deposition time (h)	Distance from source (inch)	Diameter of nanowire (nm)	Length of nanowire (μm)
1,100 °C	100	1	1	450	10
1,100 °C	100	1	2	50	30
1,100 °C	100	1	3	250	20
1,000 °C	100	1	2	400	22
900 °C	100	1	2	-	-

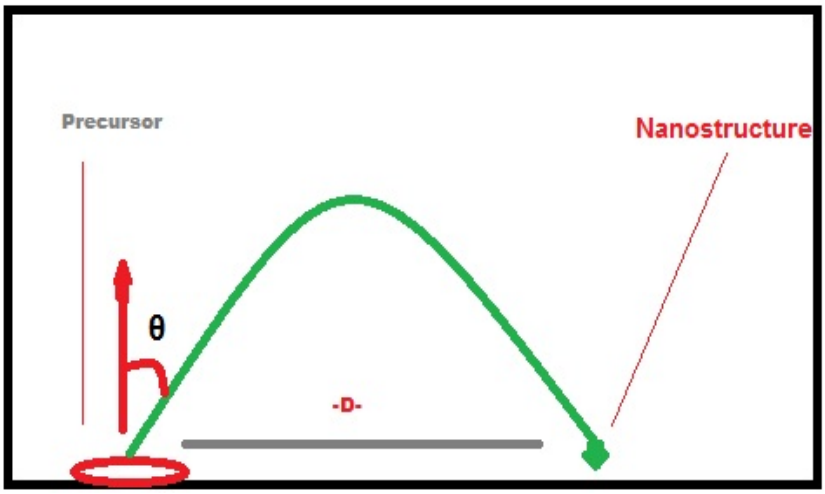

Fig. 5 Schematic diagram of projectile motion of SnO vapour.

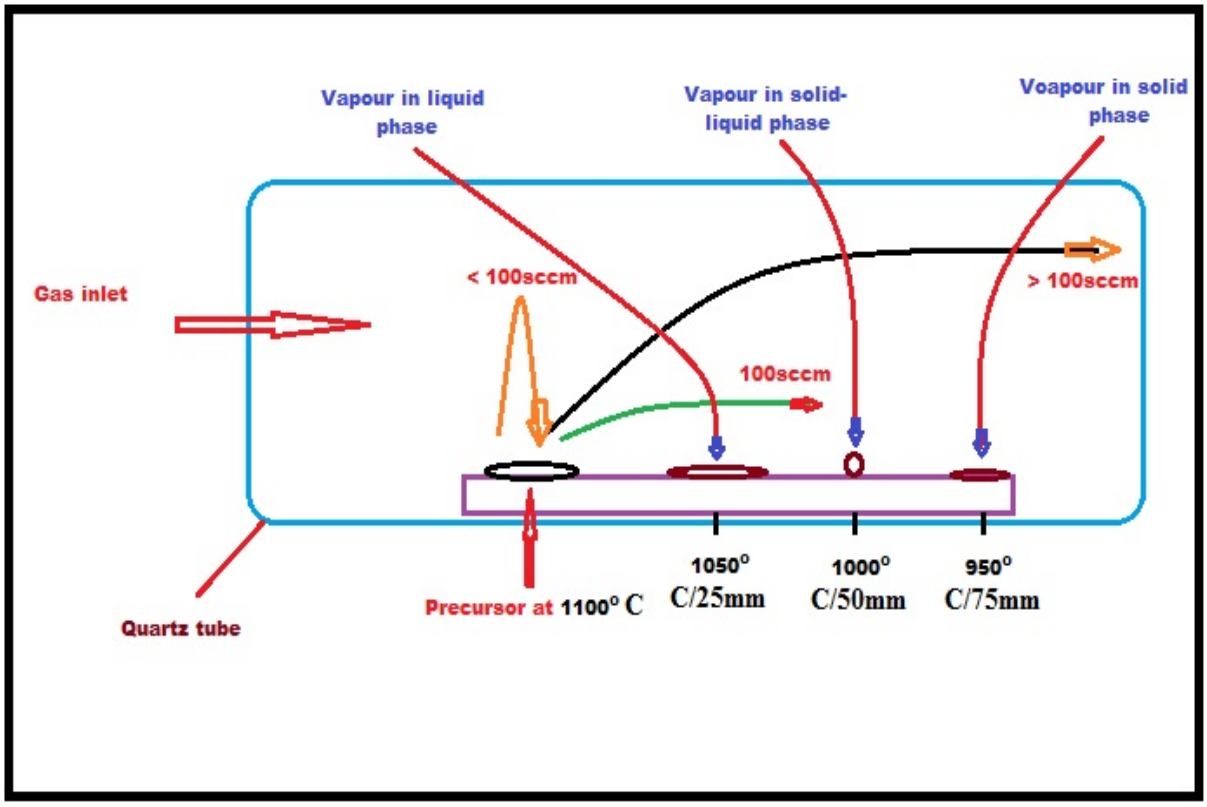

Fig. 6 Growth model of tin oxide nanostructure by varying synthesis parameter.

Table 3 Outcome by varying synthesis parameters in the growth of tin oxide nanostructure.

Sample name	Experimental observation
SnO_2 placed 25 mm from source at 1,100 °C, 100 sccm (Sn1)	Nanostructure observe with much high diameter was not helpful gas sensing application
SnO_2 placed 50 mm from source at 1,100 °C, 100 sccm (Sn2)	Nanostructure observe with narrow diameter (high aspect ratio) was suitable gas sensing application
SnO_2 placed 75 mm from source at 1,100 °C, 100 sccm (Sn3)	Nanotube observe with much diameter was not helpful gas sensing application
SnO_2 placed 50 mm from source at 1,000 °C, 100 sccm (Sn4)	Nanoparticles were observed.
SnO_2 placed 50 mm from source at 900 °C, 100 sccm (Sn5)	Particle have dimension of microns
SnO_2 placed 50 mm from source at 1,100 °C, 200 sccm (Sn6)	Nothing was observed

where, P = Pressure, V = Volume (cm^3), n = Number of moles of gas R = Gas constant (0.0821) (L·atm/mol·K) or 82.1 (cm^3·atm/mol·K), T = Absolute temperature in Kelvin (K), m = Mass in grams (g), m = Mass flow (g/min), m = Mass flow (g/min), and Q = Volumetric flow at standard conditions (SCCM). From these equations we can calculate mass flow of Ar gas from sccm scale which is equal to 0.000591 gram/sec at 100 sccm and 0.001182 grame/s at 200 sccm concentration rate of the gas respectively, inside the thermal evaporation chamber. Now again Maximum Projectile Range expression for projectile range using the formula:

$$D = v^2 / g \cdot \sin(2\theta) \quad (5)$$

Let the projectile start with a speed of v, and angle θ with the horizontal surface. After some time t, it strikes the ground at a distance of D. The value of D gives the range of the projectile motion. Fig. 6 shows schematic diagram of projectile motion of SnO vapour. Now, if suppose that mass flow of Ar gas as a velocity component and taken an resultant with SnO vapour velocity component at 100 sccm concentration of gas by choosing that SnO vapour starts projectile motion with an angle 45°.

D was calculated approximate 5.09 cm from the precursor which is nearly satisfactory equal to our observation. If, the projectile angle can be taken as 30 °C and 80 °C (approximately assumed) when the concentration of gas was taken 200 sccm and 80 sccm respectively then D was approximately 7.68 cm and 2.8 cm respectively, from precursor which again good agreement with result.

4. Conclusions

The outcome of this study is that there are certain parameters for the synthesis and growth of nanostructures inside the thermal evaporation chamber at which the nanostructures can nucleate and grow. It has been observed that the most favorable place for the enhanced growth inside the thermal evaporation chamber is about 50 mm from precursor when the precursor temperature of 1,100 °C in case of tin oxide) and 100 sccm Argon gas flow rate. In our experiment, it has been observed that substrate kept at 50mm from precursor is the most suitable place for perfect nucleation. Gas flow rate also influence significantly and at higher flow rate , more than 100 sccm, the gas flow causes condensation of vapour on substrate before start precipitation, so no nucleation of nanostructures.

Acknowledgement

We acknowledge the financial support from CSIR grant 086(0954)/09/EMR-I.

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