Effect of Growth Parameters on SnO₂ Nanowires Growth by Electron Beam Evaporation Method

R. Rakesh Kumar¹, ², Y. Manjula¹, K. Narasimha Rao²
¹Dept. Of. Physics, School of Technology, GITAM University, Hyderabad-502329
²Dept. Of. Instrumentation and Applied Physics, Indian Institute of Science, Bangalore-560012

Corresponding author: R. Rakesh Kumar  E-mail: rakesh.rajaboina@gmail.com

Abstract. Tin oxide (SnO₂) nanowires were synthesized via catalyst assisted VLS growth mechanism by the electron beam evaporation method at a growth temperature of 450 °C. The effects of growth parameters such as evaporation rate of Tin, catalyst film thickness, and different types of substrates on the growth of SnO₂ nanowires were studied. Nanowires (NWs) growth was completely seized at higher tin evaporation rates due to the inability of the catalyst particle to initiate the NWs growth. Nanowires diameters were able to tune with catalyst film thickness. Nanowires growth was completely absent at higher catalyst film thickness due to agglomeration of the catalyst film. Optimum growth parameters for SnO₂ NWs were presented. Nanocomposites such as Zinc oxide - SnO₂, Graphene oxide sheets- SnO₂ and Graphene nanosheets-SnO₂ were able to synthesize at a lower substrate temperature of 450 °C. These nanocomposites will be useful in enhancing the capacity of Li-ion batteries, the gas sensing response and also useful in increasing the photo catalytic activity.

Keywords: SnO₂ NWs; VLS growth; Evaporation rate; Different substrates; Graphene.

1. Introduction
Tin oxide (SnO₂) is one of the most important nanomaterial for gas sensors [1-2], anodes for Li-ion batteries [3-4], transparent conducting oxide electrodes [5], field emitters [6], and dye-based solar cells [7]. SnO₂ has been synthesized in different forms such as NWs, nanoparticles, nanosheets, nanorods, nanobelts, and nanotubes [6, 8-12]. Among them, NWs are the most promising nanomaterial for many applications [13]. Recently SnO₂ nanocomposites such as Zinc oxide (ZnO)-SnO₂ [14], Graphene nanosheets (GNS)-SnO₂ [15], and Graphene oxide (GO)-SnO₂ [16-18] have attracted much attention due to the improvement in the performance of the gas sensing, storage capacity of Li-ion batteries and photocatalytic activity. GNS-SnO₂ and GO-SnO₂ composites were used for increasing the storage capacity of Li-ion batteries. In addition to the above, growth of these NWs and nanocomposites on conducting substrates such as stainless steel, copper foils also enhance the capacity of Li-ion battery [19], ZnO-SnO₂ nanocomposites were used for increasing the gas sensing response [14], transparent conducting electrodes [20]. Therefore, it is important to study growth of the SnO₂ NWs and SnO₂ nanocomposites.

SnO₂ NWs have been synthesized by a variety of methods such as thermal evaporation [3], chemical vapor deposition [21], pulse laser deposition [22], and hydrothermal growth [23]. Recently our group has explored SnO₂ NWs growth by electron beam evaporation (EBE) method for the first time at a low substrate temperature of 450 °C [24]. Optimum growth temperature and oxygen partial pressure for the SnO₂ NWs were discussed in the previous report [24]. It is also important to study the effect of other deposition parameters such as the evaporation rate of Tin (Sn), gold catalyst film thickness, and different types of substrates on the SnO₂ NWs growth.

¹ R. Rakesh Kumar, Dept. Of. Physics  
E-mail: rakesh.rajaboina@gmail.com.
In the current manuscript, the effects growth parameters were studied on the growth of the SnO$_2$ NWs. SnO$_2$ NWs growth was also studied on different substrates such as Silicon (Si), Stainless steel (SS) foil, GNS coated Si, GO sheets coated Si and ZnO nanorods coated Si.

2. Experimental details
2.1. Growth of SnO$_2$ NWs
The experimental setup of EBE and growth procedure used for Au-catalyzed SnO$_2$ NWs can be found in the earlier report [24]. Optimum growth parameters such as growth temperature 450 °C, Oxygen partial pressure 4x10$^{-4}$ mbar were considered directly for the present study from the earlier study [24]. Initially, 3nm gold catalyst film was coated onto the different substrates namely Si, SS foil, GNS coated Si, GO sheets coated Si and ZnO nanorods coated Si. Graphene oxide sheets were prepared from graphite powder according to the modified Hummer’s method [25]. The obtained sheets were suspended in distilled water and spin coated several times onto a Si substrate to get dense sheets on the substrate. Similarly, Graphene nanosheets were prepared by plasma enhanced chemical vapor deposition (PECVD) [26]. Growth procedure of GNS by PECVD is available in the literature [26]. ZnO nanorods were grown on Si by hydrothermal method and the growth details can be found in our earlier report [27]. Au- coated (~ 3 nm) substrates were kept 20 cm above from Sn source material in the deposition chamber and evacuated to a vacuum level of 1x10$^{-5}$ mbar. Nanowires growth was carried out similar to the previous report [24]. Nanowires growth was carried out for 15 min growth duration at substrate temperature of 450 °C and at 4x10$^{-4}$ mbar oxygen partial pressure with different Sn evaporation rates and also with different catalyst thickness coated Si substrates. Finally, NWs growth was carried on different substrates mentioned above at optimum growth conditions to study the effect of different substrates on the SnO$_2$ NWs growth.

2.2. Characterization of SnO$_2$ NWs
Morphology, chemical composition of the obtained thin films were characterized by field emission scanning electron microscopy (FESEM) (FEI, SIRION), equipped with energy dispersive x-ray spectroscopy (EDS).

3. Results and discussion
3.1. Effect of Sn evaporation rate
SnO$_2$ NWs growth was carried out at different evaporation rates of Sn by keeping growth temperature 450 °C, oxygen partial pressure 4x10$^{-4}$ mbar constant. The thickness of the films was maintained constant for all the evaporation rates of Sn. Figure 1(a)-(d) shows the top view of deposited SnO$_2$ films on the Si substrates at different Sn evaporation rates of 2.5, 3.5, 4.5 and 5.5 Å/sec, respectively. Optimum SnO$_2$ NWs growth is observed for Sn evaporation rate of 2.5 Å/sec and below. As the evaporation rate increased to 3.5 Å/sec, the density of NWs is decreased as shown in figure 1(b). Very few NWs and almost all the surface covered with Sn-Au alloy particles were observed on the substrate upon increasing of evaporation rates to 4.5 Å/sec and is shown in figure 1(c). The complete absence of NWs growth was observed at higher evaporation rates of 5.5 Å/sec and beyond.
Figure 1. SnO$_2$ NWs growth on Si substrate at different evaporation rates of Sn (a) 2.5 Å/sec, (b) 3.5 Å/sec, (c) 4.5 Å/sec, (d) 5.5 Å/sec.

Growth behaviour of SnO$_2$ NWs with the increase in Sn evaporation rate can be explained by considering the incubation time for the NWs growth [28-29]. Incubation time is defined as the time required for the catalyst particle to form alloy and supersaturation before NWs growth starts. As evaporation rate was increased from 2.5 to 3.5 Å/sec, some of the catalyst particles were failed to initiate the NWs growth results in the poor density of NWs on the substrate like as shown in figure 1(b). If the arrival rate of evaporated Sn atoms is too high, Sn atoms cannot participate in NWs growth and growth leads to uncatalyzed deposition or thin film deposition over the substrate like as shown in figures 1 (c) - (d). All the catalyst particles were failed to initiate the NWs growth at higher evaporation rates of 5.5 Å/sec and beyond results in the complete absence of NWs growth. This trend of SnO$_2$ NWs growth with the evaporation rate of the growth material is well supported in literature for Silicon, Germanium NWs growth by e-beam evaporation [30].

3.2. Effect of catalyst layer thickness
Figures 2 (a,d), (b,e) and (c,f) show the FESEM images of the SnO$_2$ films grown at a growth temperature of 450°C and Oxygen partial pressure of 4×10$^{-4}$ mbar with different Au catalyst layer thickness of 3, 5, and 8 nm respectively. Morphology changed from NWs to nanorods and then nanorods to micro whiskers as the catalyst layer thickness is increasing. Micro whiskers and very small diameter NWs were observed at 8 nm catalyst layer thickness as shown in figure 2(c). As the catalyst layer thickness increased, agglomeration of the catalyst film led to large catalyst particles on the substrate. The higher thickness of catalyst layer (>8 nm) led to large agglomeration of the catalyst film and this large agglomeration of the catalyst film failed to initiate the nucleation for nanowire growth and resulting in complete absence of NWs growth. Similar growth behavior with catalyst layer thickness was observed for ZnO NWs [31], and β-Ga$_2$O$_3$ NWs [32] in the literature. From the above
and previous studies, growth temperature of 450 °C, oxygen partial pressure of $4 \times 10^{-4} - 6 \times 10^{-4}$ mbar, deposition time of 15 min, Sn evaporation rate $\sim 2.5 \text{ Å/sec}$ and 3 nm Au catalyst layer thickness are optimum growth parameters for SnO$_2$ NWs growth by EBE.

![Figure 2](image)

**Figure 2.** FESEM images of the SnO$_2$ NWs growth with different gold catalyst layer thickness of (a,d) 3 nm, (b,e) 5 nm, (c,f) 8 nm.

### 3.3. Effect of different substrates
To study the effect of different substrates, SnO$_2$ NWs growth was performed on the different substrates namely Si, SS foil, GO sheets coated on Si, GNS coated on Si, and ZnO nanorods coated Si at optimum growth conditions.

#### 3.3.1. SnO$_2$ NWs growth on Si
Figure 3 (a)-(d) shows FESEM images of the SnO$_2$ NWs grown on Si substrate at different magnifications. Each nanowire has a catalyst particle at their ends confirming the Au-catalyzed VLS growth of SnO$_2$ NWs. Detailed characterization of SnO$_2$ NWs grown on Si substrate was already reported in the previous report [24].

![Figure 3](image)

**Figure 3.** (a)-(d) FESEM images of SnO$_2$ NWs grown on Si substrate at different magnifications
3.3.2. SnO₂ NWs growth on Stainless steel foil. Figure 4 (a)-(d) shows the FESEM images of the SnO₂ NWs grown on SS substrate at different magnifications. Each nanowire has gold catalyst particle at its end confirming that the growth proceeded via Au-assisted VLS mechanism and it can be seen clearly in figure 4(d). Uniform NWs growth was observed throughout the substrate. The rough surface nature of the SS substrate affected the alignment of the SnO₂ NWs compared to the SnO₂ NWs grown on well polished Si. There is no change in the lengths and diameters of the NWs and also the density of the NWs compare to the SnO₂ NWs grown on Si substrate. This brings additional advantages in Li-ion batteries such as better connectivity between NWs and the current collector, better accommodation of the strain of Li-alloying/dealloying, easy electron transport by 1D nanowire character and no need of using any conductive additives and cohesive polymer binder [3].

![Figure 4](image)

**Figure 4.** (a)-(d) FESEM images of SnO₂ NWs on SS foil substrate at different magnifications.

3.3.3. SnO₂ NWs growth on GO coated Si. Figure 5(a) shows the surface morphology of GO sheets on the Si substrate after several spin coatings. The Au catalyst particles formed on the GO sheets after annealing the Au catalyst film at 450 °C under high vacuum is shown in figure 5 (b). Catalyst particles were uniformly distributed on GO sheets including sheet edges. These catalyst particles further promote the SnO₂ NWs growth. Figures 5 (c)-(f) show the surface morphology grown SnO₂ NWs on GO sheets at different magnifications respectively. It is also clear from the figure 5 (f), each SnO₂ nanowire has a gold catalyst at its end confirming that the growth proceeded via Au-assisted VLS mechanism. Nanowires growth was observed throughout the GO oxide sheets including edges also. The SnO₂ NWs growth on GO edges can be seen clearly in low magnification FESEM images in figure 5 (c)-(d).
Figure 5. (a) GO sheets on Si substrate (b) formed Au catalyst particles on GO sheets, (c)-(f) FESEM images of SnO$_2$ NWs on GO sheets at different magnifications.

3.3.4. SnO$_2$ NWs growth on GNS coated Si. Figure 6 (a) shows the synthesized GNS on the Si substrate in top view. Figure 6 (b) shows The Au catalyst particles formed on the GNS after annealing the gold catalyst film on GNS sheets at 450 °C. Catalyst particles are mostly distributed on the top surface of GNS sheets like as shown in figure 5 (b). Since the thickness of GNS is small and formed catalyst particle size also same order as the thickness of GNS. Surface morphology of SnO$_2$ NWs grown on GNS at different magnifications is shown in figures 6 (c)-(e). Cross-sectional view of SnO$_2$ NWs can be seen clearly in figure 6 (f). SnO$_2$ NWs, GNS and Si substrate are clearly seen in the cross-sectional view and most of the SnO$_2$ NWs are grown vertical on the GNS sheets like as observed on Si substrate. The diameters of the NWs are small compared to the NWs grown on other substrates. Change in the diameters of the NWs is mainly due to the thickness of the GNS.

Figure 6. (a) GNS on Si substrate (b) formed Au catalyst particles on GNS, (c)-(e) FESEM images of SnO$_2$ NWs on GNS sheets at different magnifications, (f) cross section view of SnO$_2$ NWs on GNS.

3.3.5. SnO$_2$ NWs growth on ZnO nanorods. Surface morphology of the ZnO nanorods grown on Si substrate is shown in figure 7(a) in the tilted view. Detailed characterization of ZnO nanorods can be found in the previous report [27]. Figure 7(b)-(d) shows the surface morphology of the SnO$_2$ NWs on
ZnO nanorods at different magnifications. Uniform NWs growth was observed all over the nanorods and NWs growth was also observed all sides of the ZnO nanorods. The diameters of the NWs are small compared to the NWs grown on other substrates like Si and GO coated Si. NWs growth proceeded via Au-catalyzed VLS growth and this can be evidenced in figure 7 (d). This ZnO-SnO$_2$ nanocomposite will be useful in enhancing the gas sensing property [14].

![Figure 7](image)

**Figure 7.** (a) ZnO nanorods on Si substrate (b)-(d) FESEM images of SnO$_2$ NWs on ZnO nanorods at different magnifications.

4. Conclusions

In summary, the effects of growth parameters on the growth of SnO$_2$ NWs were studied. The studies revealed that lower evaporation rates of tin and smaller catalyst film thickness were more favourable for SnO$_2$ NWs growth. Change in the NWs diameters and alignment of NWs were observed when NWs growth was conducted on different substrates. It was concluded that SnO$_2$ NWs growth slightly depends on the type of substrate used. It was found that the growth temperature of 450 °C, oxygen partial pressure of $4 \times 10^{-4}$-$6 \times 10^{-4}$ mbar, deposition time of 15 min, Sn evaporation rate $\sim$2.5 Å/sec and 3 nm Au catalyst layer thickness were optimum growth parameters for SnO$_2$ NWs growth by EBE. The prepared nanocomposites may find applications in high capacity Li-ion batteries, room temperature gas and chemical sensors and also transparent conducting electrodes.

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