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Effect of Growth Parameters on SnO_2 Nanowires Growth by Electron Beam Evaporation Method

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Abstract. Tin oxide (SnO_2) nanowires were synthesized via catalyst assisted VLS growth mechanism by the electron beam evaporation method at a growth temperature of 450 ºC. The effects of growth parameters such as evaporation rate of Tin, catalyst film thickness, and different types of substrates on the growth of SnO_2 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 SnO_2 NWs were presented. Nanocomposites such as Zinc oxide - SnO_2, Graphene oxide sheets- SnO_2 and Graphene nanosheets-SnO_2 were able to synthesize at a lower substrate temperature of 450 ºC. These nanocompsoites 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: SnO_2 NWs; VLS growth; Evaporation rate; Different substrates; Graphene.

1. Introduction

Tin oxide (SnO_2) 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]. SnO_2 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 SnO_2 nanocomposites such as Zinc oxide (ZnO)-SnO_2 [14], Graphene nanosheets (GNS)-SnO_2 [15], and Graphene oxide (GO)-SnO_2 [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-SnO_2 and GO-SnO_2 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-SnO_2 nanocomposites were used for increasing the gas sensing response [14], transparent conducting electrodes [20]. Therefore, it is important to study growth of the SnO_2 NWs and SnO_2 nanocomposites.

SnO_2 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 SnO_2 NWs growth by electron beam evaporation (EBE) method for the first time at a low substrate temperature of 450 ºC [24]. Optimum growth temperature and oxygen partial pressure for the SnO_2 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 SnO_2 NWs growth.

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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 ºC, Oxygen partial pressure 4×10^{-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 1×10^{-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 4×10^{-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 ºC, oxygen partial pressure 4×10^{-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.

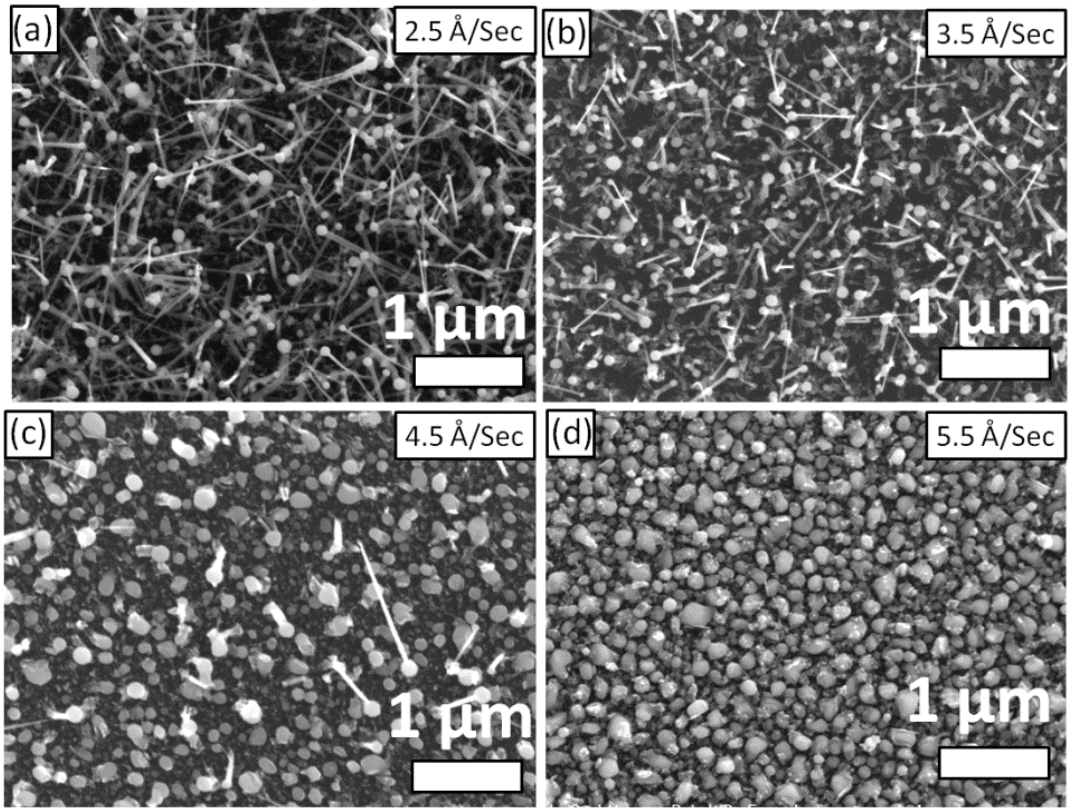

Figure 1. SnO_2 NWs growth on Si substrate at different evaporation rates of Sn (a) 2.5 Å/sec, (b) 3.5 Å/sec, (c) 4.5 Å/sec, (d) 5.5 Å/sec.

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_2O_3 NWs [32] in the literature. From the above

and previous studies, growth temperature of 450 °C, oxygen partial pressure of 4×10^{-4}-6×10^{-4} mbar, deposition time of 15 min, Sn evaporation rate ~2.5 Å/sec and 3 nm Au catalyst layer thickness are optimum growth parameters for SnO_2 NWs growth by EBE.

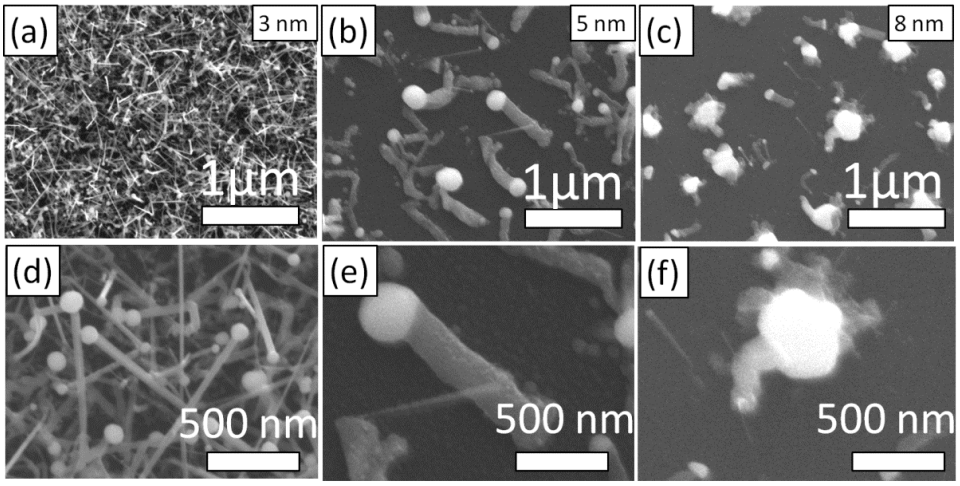

Figure 2. FESEM images of the SnO_2 NWs growth with different gold catalyst layer thickness of (a,d) 3 nm, (b,e) 5 nm, (c,f) 8 nm.

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].

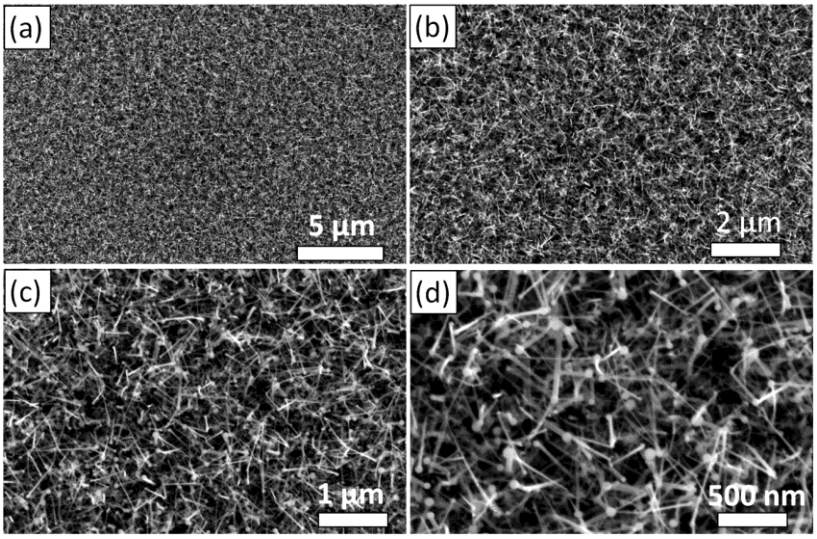

Figure 3. (a)-(d) FESEM images of SnO_2 NWs grown on Si substrate at different magnifications

3.3.2. SnO_2 NWs growth on Stainless steel foil. Figure 4 (a)-(d) shows the FESEM images of the SnO_2 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 SnO_2 NWs compared to the SnO_2 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 SnO_2 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].

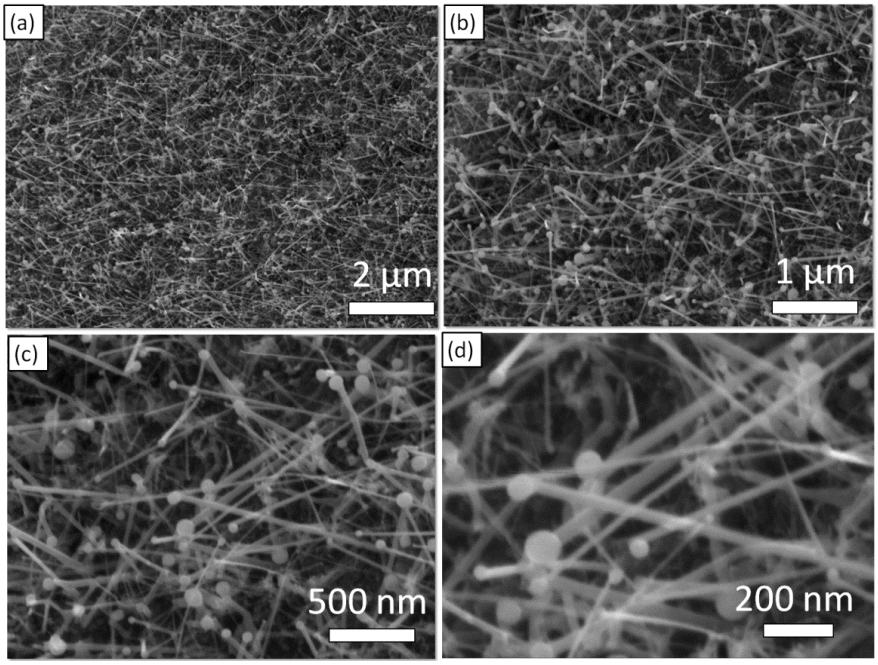

Figure 4. (a)-(d) FESEM images of SnO_2 NWs on SS foil substrate at different magnifications.

3.3.3. SnO_2 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 SnO_2 NWs growth. Figures 5 (c)-(f) show the surface morphology grown SnO_2 NWs on GO sheets at different magnifications respectively. It is also clear from the figure 5 (f), each SnO_2 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 SnO_2 NWs growth on GO edges can be seen clearly in low magnification FESEM images in figure 5 (c)-(d).

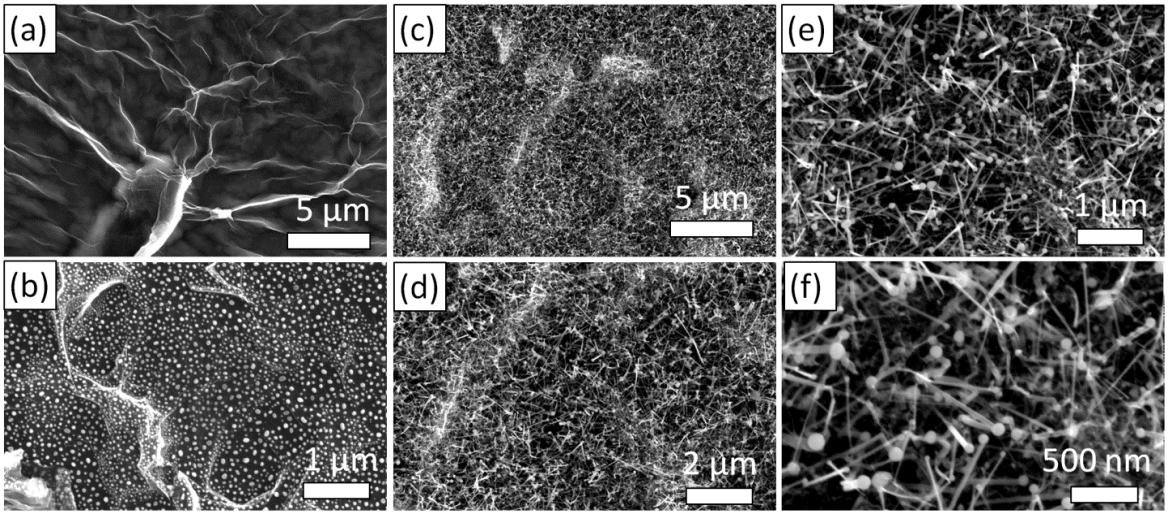

Figure 5. (a) GO sheets on Si substrate (b) formed Au catalyst particles on GO sheets, (c)-(f) FESEM images of SnO_2 NWs on GO sheets at different magnifications.

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.

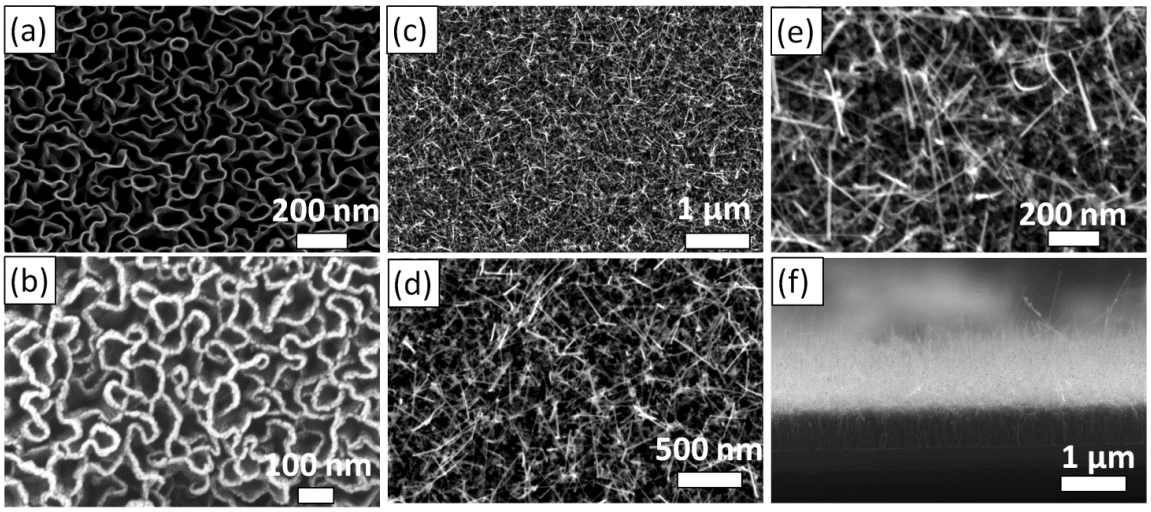

Figure 6. (a) GNS on Si substrate (b) formed Au catalyst particles on GNS, (c)-(e) FESEM images of SnO_2 NWs on GNS sheets at different magnifications, (f) cross section view of SnO_2 NWs on GNS.

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].

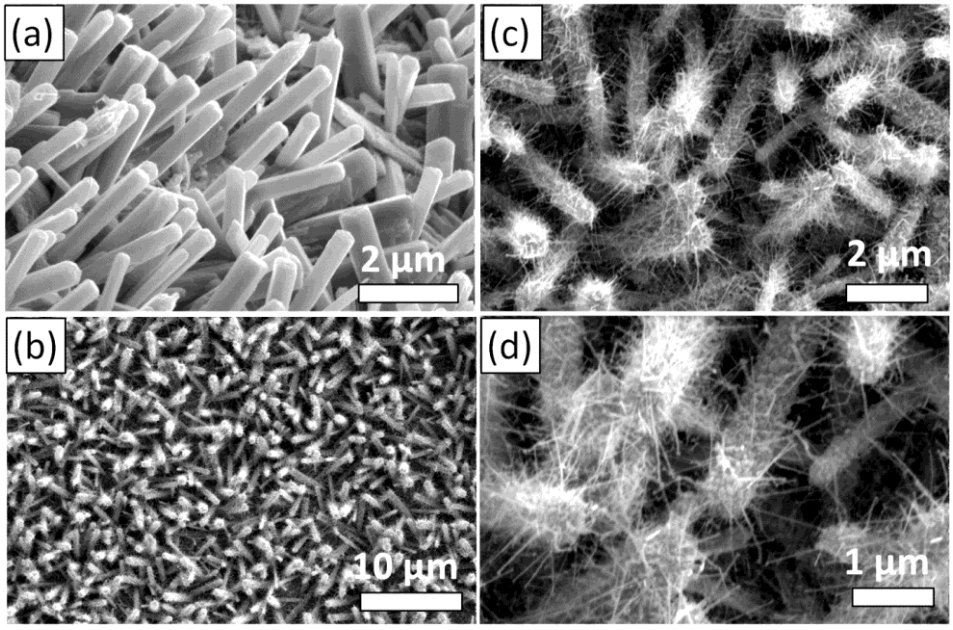

Figure 7. (a) ZnO nanorods on Si substrate (b)-(d) FESEM images of SnO_2 NWs on ZnO nanorods at different magnifications.

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 4×10^{-4}-6×10^{-4} mbar, deposition time of 15 min, Sn evaporation rate ~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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References

[1] Kolmakov A, Klenov D O, Lilach Y, Stemmer S and Moskovits M 2005 Nano. Lett. **5(4)** 667
[2] Sysoev V V, Goschnick J, Schneider T, Strelcov E and Kolmakov A 2007 Nano. Lett. 7(10) 3182
[3] Ko Y D, Kang J G, Park J G, Lee S and Kim D W 2009 Nanotechnology **20** 455701
[4] Meduri P, Pendyala C, Kumar V, Sumanasekera G U and Sunkara M K 2009 Nano. Lett. 9(2) 612
[5] Wan Q, Dattoli E N and Lu W 2007 Appl. Phys. Lett. **90** 222107
[6] Deng K, Lu H, Shi Z, Liu Q and Li L 2013 ACS Appl. Mater. Interfaces **5 (16)** 7845
[7] Gubbala S, Chakrapani V, Kumar V and Sunkara M K 2008 Adv. Funct. Mater. **18** 2411
[8] Vidhu V K and Philip D 2015 Mater. Char. **101** 97
[9] Wang C, Zhou Y, Ge M, Xu X, Zhang Z and Jiang J Z 2010 J. Am. Chem. Soc. **132** 46
[10] Xi G and Ye J 2010 Inorg.Chem. **49** 2302
[11] Li L 2013 Mater. Lett. **98** 146
[12] Wang J, Du N, Zhang H, Yu J and Yang D 2011 J. Phy. Chem. C **115** 11302
[13] Pan J, Shen H and Mathur S 2012 J. Nanotech. **2012** 1
[14] Wang L, Li J, Wang Y, Yu K,, Tang X, Zhang Y, Wang S and Wei C 2016 Sci. Rep. **6** 35079
[15] Yang X, He Y S, Liao X Z, Chen J, Wallace G G and Ma Z F 2010 ECS Transactions **28(30)** 151
[16] Tang L, Nguyen V H, Lee Y R, Kim J and Shim J J 2015 Synth. Met. **201** 54
[17] Zhu X, Zhu Y, Murali S, Stoller M D and Ruoff R S 2011 J. Pow. Sour. **196** 6473
[18] Singh A, Sharma A, Tomar M and Gupta V 2017 Sens. Actuat. B **245** 590
[19] Cui L F, Yang Y, Hsu C M and Cui Y 2009 Nano. Lett. **9** 3370
[20] Giusti G, Consonni V, Puyoo E and Bellet D 2014 ACS Appl. Mater. Interfaces **6(16)** 14096
[21] Thabethe B S, Malgas G F, Motaung D E, Malwela T and Arendse C J 2013 J. Nanomater. **2013** 1
[22] Bazargan S and Leung K T 2012 J. Phys. Che. C **116(9)** 5427
[23] Lupan O, Chow L, Chai G, Schulte A, Park S and Heinrich H 2009 Mater. Sci. Eng. B **157** 101
[24] Kumar R R, Rao K N, Rajanna K and Phani A R 2013 Mater. Res. Bull. **48** 1545
[25] Hummers W S and Offeman R E 1958 J. Am. Chem. Soc. **80** 1339
[26] Thomas R and Rao G M 2015 RSC. Adv. **5** 84927
[27] Gaddam V, Kumar R R, Parmar M, Nayak M M and Rajanna K 2015 RSC. Adv. **5** 89985
[28] Irrera A, Pecora E F and Priolo F 2009 Nanotechology **20** 135601
[29] Consonni V, Trampert A, Geelhaar L and Riechert H 2011 Appl. Phys. Lett. **99** 033102
[30] Artoni P, Pecora E F, Irrera A and Priolo F 2011 Nanoscale. Res. Lett. **6** 162
[31] Wang X, Song J, Summers C J, Ryou J H, Li P, Dupuis R D and Wang Z L 2006 J. Phys. Chem. **110** 7720
[32] Choi K H, Cho K K, Cho G B, Ahn H J and Kim K W 2009 J. Crys. Growth. **311** 1195