

Growth Mechanism of SnO₂ Nanomaterials Derived From Backscattered Electron Image and EDX Observations

Ronald de los Reyes, Gil Nonato C. Santos

Abstract—SnO₂ nanomaterials were synthesized using the unseeded, non-catalytic horizontal vapor phase growth (HVPG) deposition. The sample was synthesized at a growth temperature of 1200°C and growth time of 6 hours. The resulting nanostructures ranges from nanowires, nanorods to nanobelts as confirmed by JEOL JSM 5310-SEM. Backscattered electron image observations show that nanobelts has less intense brightness compared to nanorod and nanowire images. This suggests that the nanobelts are of lighter composition. Using energy dispersive X-ray (EDX) analysis, it was confirmed that the nanobelts are oxygen deficient, being made up of SnO while the nanorods and nanowires are made of the more common SnO₂. From these findings, a growth mechanism was proposed detailing the transition of the SnO₂ nanostructures from the powder SnO₂ source material.

Index Terms—growth mechanism, SnO₂ nanomaterials, backscattered electron image, EDX, HVPG

1 INTRODUCTION

Synthesis of nanomaterials with controlled morphology, size and crystal structure is a key step towards nanotechnological applications. Recently it has been shown that the horizontal vapor phase growth (HVPG) deposition is successful in synthesizing nanostructured SnO₂ [1,2,3]. SnO₂ is an n-type wide band gap semiconductor with rutile crystal structure. It is a key functional material for optoelectronic devices, gas sensors [4], barrier layer for solar cells [5], anode material for lithium-based batteries [6] and liquid crystal displays. By understanding the growth mechanism by which nanomaterials are formed in HVPG, it may be possible to device ways in the future on how to control or alter the growth kinetics of the SnO₂ nanomaterial.

In this work, SnO₂ nanomaterials were grown via HVPG and investigated using scanning electron microscopy (SEM). During SEM analysis, the electrons bombarding the sample interact with the sample in different ways. Signals are emitted from all points in the sample, which carry out a distinct information depending on the origin of the signal. Three common signals that can be obtained are (1) secondary electrons (2) backscattered electrons and (3) X-rays.

Secondary electrons are outer shell electrons dislodged by energetic incident electrons and are produced by energy loss of deflected electrons. These signals originate from the nanometer layer of the sample and are obtained to give topographical observations and morphological information of the sample.

Backscattered electrons are produced by interactions between incident electrons and the sample's atomic nuclei. The intensity of the signal has a direct dependence on the mass

number Z or the atomic number of the element comprising the sample as shown by figure 1. A backscattered electron image (BEI) of a specimen can give contrast depending on the mean atomic number of the constituent elements and is used to discriminate compositional information of the material.

Lastly, X-rays are produced by elastic collisions between primary electron beams and atoms approximately 1000 nm to a few microns deep with in the specimen. During irradiation of the sample by incident electrons, inner shell electrons of the specimen atom are ejected, leaving vacancies in the original position. To fill the vacancies, outer shell electrons are transferred to fill up the vacancies and their excess energy is emitted as an X-ray. Since the energies of the individual shell electrons are determined by the type of elements, the X-rays generated by the electron transfer are characteristic of the elements. This is the characteristic X-rays of the element. The X-rays are used to identify the elements present on the sample.

2 EXPERIMENTAL SECTION

High Purity (99.99%) Merck SnO₂ powder, of 35 mg mass was loaded into a closed-end quartz tube. The closed end quartz tube is then connected to the THERMIONICS High Vacuum System to lower the pressure inside the tube to approximately 10⁻⁶torr. An appropriate mixture of oxygen gas and LPG is then used to seal the remaining open end of the tube. The tube was sectioned into three zones namely: zone 1, where the SnO₂ powder is located; zone 2, which is the middle portion of the tube and zone 3, which is the opposite end of zone 1. A typical set-up of the quartz-tube and furnace set-up is shown in figure 1.

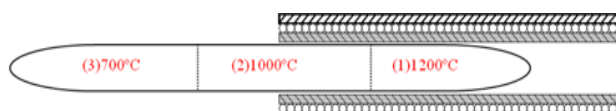


Figure 1: Cut-away view of the horizontal tube furnace-quartz

- Ronald de los Reyes, Master of Science in Physics, Lecturer, De La Salle University-Manila, Philippines. E-mail: delosreyes.ronald@gmail.com
- Gil Nonato C. Santos, Doctor of Philosophy in Materials Science, Professor, De La Salle University-Manila, Philippines. E-mail: santosg@dlsu.edu.ph

tube set up. Shown are the different zones and the corresponding temperature.

The tube was then loaded into the Thermolyne horizontal tube furnace with zone 1, completely inside the furnace. A temperature gradient was created by letting Zone 2 be at the opening and zone 3 completely outside the furnace. The temperature gradient across the length of the tube is monitored by a type-K thermocouple. The tube's zone 1 was heated at 1200°C for 6 hours and allowed to cool down overnight. During annealing, zone 2 has a temperature of 1000°C and zone 3 is at 700°C. The tube is then broken into fragments, with fluffy white products observed in the inner walls of the tube.

Surface and elemental analysis were performed using JEOL 5310 scanning electron microscope (SEM) and Oxford ISIS energy dispersive X-ray (EDX) system respectively. Images were obtained using the secondary electron and backscattered electron signals to obtain topographical and compositional information between observed nanostructures of SnO₂. These observations were then related with the EDX results.

3 RESULTS AND DISCUSSION

Figure 2 shows a typical quartz tube fragment with the SnO₂ deposit present in its inner walls. It can be observed that the SnO₂ source material, which was initially confined only at one end, has been dispersed through out the length of the quartz tube.



Figure 2: Quartz tube fragment showing the deposited SnO₂ nanomaterial in the inner walls

Figure 3 shows SEM images of the structures that were formed. Common structures observed are nanorods, nanowires, nanobelts, and nanoparticles. Most of the nanomaterials are found in zone 2. Nucleation tips are observed in the nanorods as shown in figure 4a. This suggests that the one dimensional structures, the nanorods and nanowires have undergone vapor-liquid-solid (VLS) transition.

Figure 4 shows the backscattered electron image (BEI) of the SnO₂ nanomaterials. From this figure, three sites are defined as follows: site 1, corresponding to the belt structure; site 2, corresponding to the rod structure; and site 3 corresponding to the background or the SiO₂ substrate. There is a noticeable difference in brightness among the three sites, especially between the rod and belt structure. This observation suggests that the belt is lighter in composition compared to the rod. The rod structure is also the brightest in the BEI, indicating that it is heavier in composition compared to any other portion in the

sample.

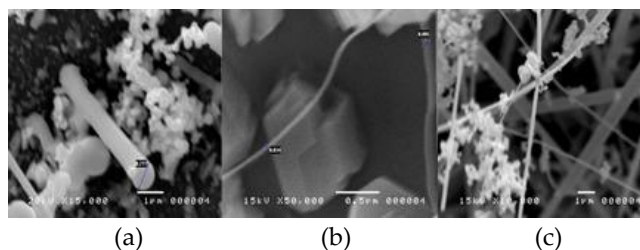


Figure 3, from Left to Right: (a) SnO₂ nanorod exhibiting the presence of a nucleation tip (b) SnO₂ nanowires (c) SnO₂ nanobelts and nanowires, with some nanoparticles

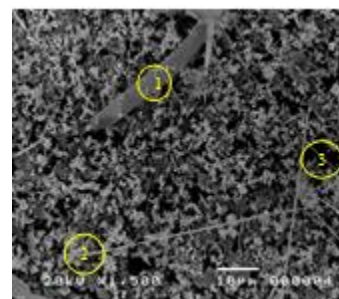


Figure 4: Backscattered electron image (BEI) of the sample showing three different sites: (1) gray area, corresponding to the belt structure; (2) bright area corresponding to the rod structure; (3) dark area corresponding to the background SiO₂ substrate

Figure 5a-5c shows the EDX spectra for figure 5's sites 1, 2 and 3 respectively. The observed Si-peak is attributed to the quartz tube (SiO₂) substrate. Table 1 on the other hand shows the atomic and element percentage composition for the 3 detected elements namely O, Sn and Si. From the percentage composition (Element %) results, a calculation can be performed to remove the oxygen contribution of SiO₂, and extract the stoichiometric composition of SnO₂. For site 1, the molar ratio is 4 O: 1 Si: 2 Sn. Removing the SiO₂ contribution gives a 1:1 Sn to O ratio. This indicates that the belt structure is made up of SnO.

For site 2, it is shown that the elements have molar ratios of 30 O: 1 Si: 8 Sn. Removing the SiO₂ contribution leaves a 1:7 Sn to O ratio. The corresponding rod structure therefore has excess oxygen compared with the usual Sn to O ratio of 1:2 or SnO₂, which explains why it appears bright in the BEI.

For the percentage composition of site 3, the resulting molar ratios of the elements are 20 O: 24 Si: 3 Sn. No oxygen atom will be left to pair with the Sn atom, after removing the SiO₂ contribution. It is therefore identified that dark areas in the backscattered electron image is mostly SiO₂ in composition with isolated Sn metal. This also explains why site 3 appears to be dark in the BEI because SiO₂ is lighter than SnO₂.

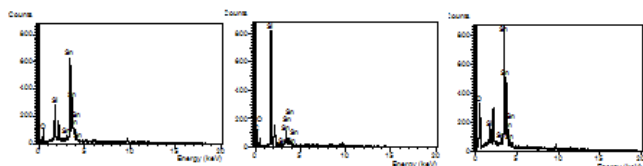
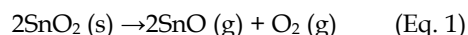


Figure 5 from Left to Right: (a) EDX spectrum for site 1 (b) EDX Spectrum for site 2 (c) EDX spectrum for site 3

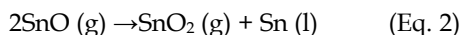
Table 1: Element and Atomic Percentage composition from the EDX results for sites 1, 2 and 3

Element	Site 1 (belt)		Site 2 (rod)		Site 3 (SiO ₂)	
	Element %	Atom ic %	Element %	Atom ic %	Element %	Atom ic %
O K	17.98	55.34	33.18	77.10	24.07	43.08
Si K	7.94	13.92	1.96	2.59	49.60	50.56
Sn L	74.08	30.74	64.86	20.31	26.33	6.35
Total	100%	100%	100%	100%	100%	100%

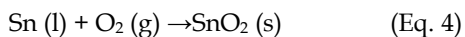
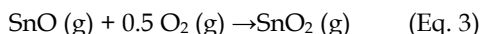
At this point, it is interesting to look at what happened to the SnO₂ powders inside the quartz tube during the growth process. As the quartz tube is heated at 1200°C, the SnO₂ powders initially located at zone 1 of the quartz tube sublimes to vapor phase. During this process, decomposition of SnO₂ would have occurred given by the equation:



The SnO vapors are then transported, towards the cooler regions of the quartz tube aided by the thermal gradient along the length of the tube. The O₂ in reaction 1 would have acted as a carrier gas for the SnO. Although SnO is relatively stable, it can spontaneously undergo the following disproportionation reaction [7], almost simultaneously with the first



The vapor SnO would condense first to liquid state in zone 2 together with the liquid Sn metal. The Sn metal may act as a catalyst in this process and give way for the formation of SnO₂ nanowires, and nanorods. After an initial period of nucleation and incubation, a crystallite will commonly develop into a three-dimensional object with well-defined low index crystallographic faces. The growth process eventually terminates when the temperature is below the melting point of about 1000°C, corresponding to zone 2 temperature. Another possible process that may lead to the formation of nanowires is the re-oxidation reactions:



Considering these two equations, it is evident that O₂ preferably reacts with liquid Sn rather than with the SnO vapors. Going back to the EDX result of site (3) of figure 5, the existence of isolated Sn metal has been determined. This indicates that the concentration of O₂ is limited in the present equip-

ment although a small leak is possible. As shown earlier from the backscattered electron image, the nanoparticles and nanorods correspond to the bright field and EDX analysis shows that it is oxygen rich, therefore it must be made up of SnO₂. The presence of nucleation tips in the SEM images of the nanorods also suggests that the Vapor-Liquid-Solid (VLS) mechanism is responsible for the formation of the rods and other 1D structure. In addition, it can be said that reaction (2) may not always happen. For cases that the SnO vapor is stable, it may undergo deposition following the vapor-liquid-solid (VLS) or vapor-solid (VS) transition. From the backscattered electron image and EDX analysis, it was shown that the nanobelts are made up of SnO. Since there is no evidence of nucleation tips for the nanobelt structure as shown by the SEM images, it is safe to assume that the VS mechanism is responsible for the formation of the nanobelts.

4 CONCLUSION

SnO₂ nanomaterials were synthesized using horizontal vapor phase growth deposition without a catalyst or a seed. The resulting nanostructures range from nanorods, nanowires, nanobelts and nanoparticles as confirmed by the SEM images. Backscattered electron images of the structures were obtained and related with the EDX results. It has been observed that the resulting nanobelts are oxygen deficient, made up of SnO while the nanorods and nanowires are made up of SnO₂. With the knowledge of the composition of the source material, and the resulting nanostructure, a growth mechanism is for the formation of tin oxide nanostructures.

The results suggest that during crystal growth, the SnO₂ source powder initially located in zone 1, sublimes to vapor phase and was transported to cooler regions in the quartz tube. The SnO₂ undergoes dissociation to SnO and O₂ with the O₂ acting as a carrier gas for SnO and aided by the thermal gradient. Some of the SnO will undergo disproportionation reaction to form SnO₂ and Sn. This results to the formation of nanowires and nanobelts. The process proceeds via Vapor-Liquid-Solid (VLS) transition, as shown by the nucleation tips found on the nanorods. On the other hand, some SnO that won't undergo disproportionation reaction will be deposited directly as SnO. There are no evidences of a nucleation similar to those of nanorods for the nanobelts and it is suggested that nanobelt formation undergoes Vapor-Solid (VS) transition. Energy dispersive X-ray analysis and backscatterd electron images of the nanomaterials confirm that the nanowires and nanorods are oxygen rich which suggest that it is composed of SnO₂. On the other hand, it is found that nanobelts are oxygen deficient, which suggest that it is made of SnO. The substrate's EDX analysis confirms that is mostly made up of SiO₂ and there are isolated Sn metal deposited to it.

ACKNOWLEDGMENT

This work was supported in part by a grant from the Department of Science and Technology-Science Education Institute, Philippines.

REFERENCES

- (1) VT Ngo, GNC Santos, RV Quiroga and A Salvador, "Synthesis of Tin Oxide Nanomaterial Using the Vacuum Deposition Technique" in Proc. of the 25th SamahangPisikangPilipinas, Los Banos, Laguna, Philippines: 20; 2007.
- (2) S Sowl, A Co, V Ngo, GNC Santos, R Pobre, RV Quiroga and A Salvador, "Beaklike SnO₂ Nanorods with Fluorescence and Photoluminescence Properties", in Proc of the 25th SamahangPisikangPilipinas, Los Banos, Laguna, Philippines, 16, 2007.
- (3) GNC Santos, V Ngo, PM Ong, R De Los Reyes, and RV Quiroga, "Growth, Structure Evolution and Thermal Properties of SnO₂ Nanomaterial" in Proc. Of the 25th SamahangPisikangPilipinas, Los Banos, Laguna, Philippines: 20; 2007.
- (4) OK Varghese, LK Malhotra. Sensors Actuators B53: 19; 1998.
- (5) S Ferrere, A Zaban , BA Gregg. J PhysChem 101: 4490; 1997 .
- (6) J Zhu, Z Lu, ST Aruna, D Aurbac, AGedanken. ChemMater 12(9): 2557; 2000.
- (7) MS Moreno, G Punte, G Rigotti, RC Mercader, AD Weisz, MA Blesa, "Kinetic study of the disproportionation of tin monoxide" Solid State Ionics, 144, 81-86;2001.