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Zn_2SiO_4 and SnO_2 nanowires synthesized by thermal ramping technique

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ABSTRACT

In this report, nanowires of Zn_2SiO_4 and SnO_2 have been successfully synthesized using a simple novel method namely thermal ramping technique. The technique applies thermal ramping of the sample to a temperature of 900 ^oC using carbothermal reduction method. This technique requires no carrier gas. Elemental analysis and crystal structure were evaluated using Field Emission Scanning Electron Microscopy (FESEM) , Energy Dispersive X-ray (EDX) and X-ray Diffraction(XRD) analysis. Nanowires of SnO_2 and Zn_2SiO_4 with diameter ranging from 15-25 nm were observed. The effect of Au thickness in synthesizing Zn_2SiO_4 is also discussed.

Key words: Thermal Ramping, Carbothermal Technique, SnO_2 Nanowires

INTRODUCTION

Nanowires has gained a lot of attention in various applications **(**Thong, Loan, and Hien 2010, Zang et al, 2011, Peng et al, 2009**)** due to its unique physical and electronic structural. Since then, various method have been studied and developed in synthesizing nanowires (Duraja, Mansorov, and Tokmolden 2009, Korotcenkov et al, 2010, Chen et al, 2009**)**. Carbothemal technique is one of the simplest techniques used to synthesize nanowires. Nanowires of SnO_2 for example, have been synthesized using this method and used in numerous gas sensing research. Reports have proved its suitability for gas sensing applications. However there could be more research in enhancing both the selectivity and sensitivity of the sensor. Apart from SnO_2, there have been several researches (Xu et al, 2003, Li et al, 2010, An et al, 2010) on Zn_2SiO_4 and its possible role in future nanotechnology. It is said that its magnitude of absorption coefficient, reflectivity, refractive index and extinction coefficient are suitable for antireflection coating applications (Karazhanov et al, 2009). In this report the synthesis technique is based on the modified carbothermal technique. Carbothermal technique is chosen due to its capability to vaporize a material at lower temperature. Gold catalyst used induces the nanowires growth by vapor-liquid-solid (VLS) mechanism. The introduction of ramping elements to the conventional technique has successfully emulated the suitable and required atmosphere for the growth of the nanowires. The new technique developed has proven to be simple, reliable and cheap, without incorporating too many parameters such as pressure of the deposition chamber, source to substrate distance and the flow rate of the carrier gas, which are indispensable in the conventional carbothermal technique

EXPERIMENTAL PROCEDURE

Silicon substrates were cleaned in ethanol and treated with ultrasonic bath, etched in 65 vol. % HNO_3 aqueous solution prior to the experiment. Then the substrates were coated with Au, 10 nm and 25 nm in thickness respectively. ZnO powder (99.5% purity) and carbon powder (99.5 % purity) with molar ratio of 1:2 were used as the source material and thoroughly mixed. The source material and substrate were later loaded into the same porcelain boat and placed in the middle of an alumina tube. The tube is 2.0 inches of external diameter, 1.85 inches of internal diameter and 24 inches length. The alumina tube was

put inside the furnace horizontally. The sample was heated according to Fig. 1 ramping pattern.

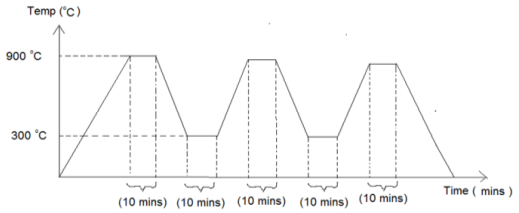


Figure 1. Ramping pattern of the temperature applied during the heating process

As for synthesizing SnO_2 nanowires, the whole procedures were then repeated using SnO_2 as the precursor material. Electron Microscopy (FESEM), Energy Dispersive X-ray (EDX) and X-ray Diffraction (XRD) were used to analyse the morphology, elemental component and crystal structure of the nanostructures.

Zn_2SiO_4 NANOWIRES

Figure 2 shows the FESEM images of the Zn_2SiO_4 nanowires. From the images, the length can be approximated to be 2 – 3 um whereas the diameter ranges from 15 - 25 nm (refer Fig. 2c). The growth of the Zn_2SiO_4 nanowires does not follow any proper pattern. However, there is significant effect to the density of the nanowires when using different thickness of gold catalyst (refer to Fig 2a and 2b). The increase in the gold thickness results in low density of Zn_2SiO_4 nanowires.

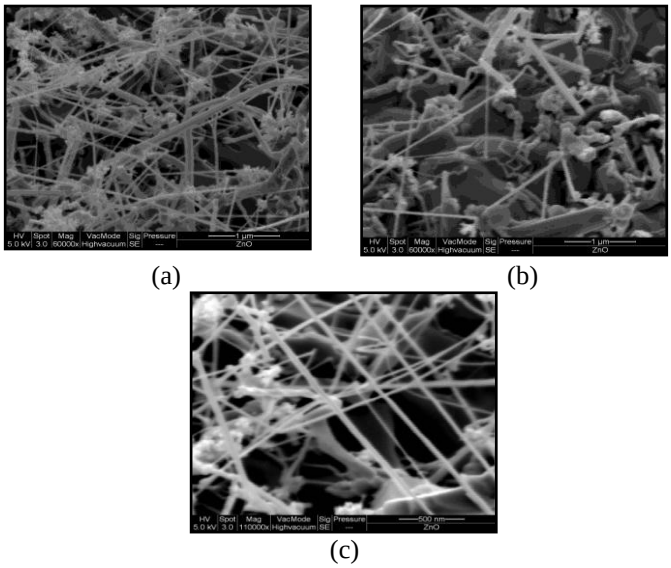


Figure 2. FESEM images of Zn_2SiO_4 nanowires prepared with different Au coating thickness: (a) 10nm (b) 25 nm and (c) 10 nm (different magnification)

XRD spectrum of the nanowires is indicated in Fig. 3 with its strong peaks are labelled. XRD results indicate that these peaks can be indexed to Zn_2SiO_4 compound. The lattice constants are a = b = 13.948 Å and c = 9.315 Å which corresponds to rhombohedral structure.

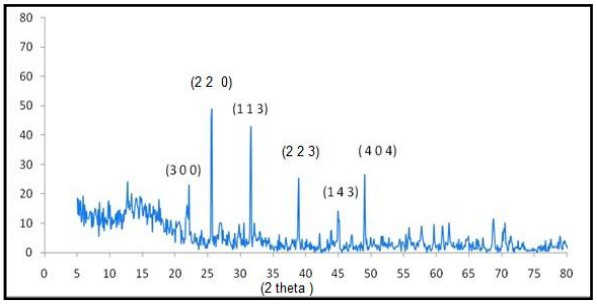


Figure 3. XRD pattern of synthesized Zn_2SiO_4 nanowires

In this experiment, carbon was used as a reduction agent to lower the vaporizing temperature of ZnO. Au catalyst was used to induce the growth of the nanowires by Vapor-Liquid-Solid (VLS) mechanism.

$$ZnO + C \rightarrow Zn + CO \quad (1)$$

The formation of Zn_2SiO_4 can be explained as follow. As the temperature is ramped up to 900 ^oC, ZnO decomposes to Zn and CO. Vapors of Zn fills inside the alumina tube. Some of the vapor will escape through the cap at both end of the tube. Instead of using carrier gas to transport these vapors to the substrate (substrates and ZnO powder are placed in the same porcelain boat), the temperature is ramped down or cooled down to force the vapors to lose its kinetic energy. The vapors will then get condensed on the Au-coated substrate before being oxidised back to ZnO by the O in the surrounding. These ZnO droplets are then react with Si-O from the substrate(oxidised Si melted surface) and together with Au they form $ZnO/SiO_2/Au$ alloy. The process of forming $ZnO/SiO_2/Au$ alloy recurs as the temperature is ramped up and down for the second and third time. Due to the high temperature during the ramp up process, the alloy will quickly combine to form Zn_2SiO_4 (Wang, H.Q et al, 2007**)**. There is another possibility that instead of $ZnO/SiO_2/Au$ alloy formation, Zn/Si/Au alloy is formed. This alloy droplets will then get oxidised by the O in the surrounding to directly form Zn_2SiO_4 (Wang, X., Summers, C.J. and Wang, Z.L., 2004).

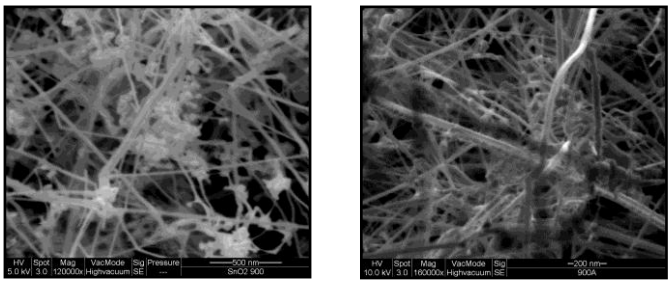
$$2\,ZnO + SiO_2 \rightarrow Zn_2SiO_4 \quad (2)$$

We assume the Au has been left out without forming any bond with Zn or Si since there is no Au-Zn or Au-Si intermetallic compound detected by XRD analysis. Continuous supply of Zn vapors results in the supersaturation of the alloy and thus crystallisation takes place. The crystallisation then acts as the nucleation sites and initiates the growth of the Zn_2SiO_4 nanowires. The thickness of Au-catalyst could affect the nanowires density by indirect controlling the supersaturating level of the $ZnO/SiO_2/Si$ or Zn/Si/Au alloy. Since the nanowires starts to grow only when the alloy supersaturates,

thus the thinner the Au layer, the faster the alloy droplets will get supersaturated. This way, the growth of the nanowires can be initiated faster. Although no detail studies of Au-catalyst role in the formation of Zn_2SiO_4 nanowires is carried out, we believe that it is sufficient to roughly procure the idea of how the Au layer plays it role.

SnO_2 NANOWIRES

FESEM images of the SnO_2 nanowires grown on silicon substrate are shown in Fig. 4. As in the case of SnO_2 nanowires, Fig. 4(a) shows that the nanowires formed also do not follow any proper alignment or pattern. The diameter of the nanowires ranges from 15-25 nm and the length extends to few micrometers.



(a) (b)

Figure 4. SnO_2 nanowires at different magnification and different spot. (a) 120 000 x and (b) 160 000 x

We used energy dispersed x-ray spectroscopy (EDX) to analyse the elemental components of the nanowires. Fig. 5 shows the elemental components of the SnO_2 nanowires. The result shows that the nanowires composed of Sn, O, Si and Au elements with weight percentage 36.99 %, 46.67 %, 15.66 % and 0.68 % respectively. The present of Si and Au elements come from the Si substrate and gold catalyst used respectively.
The XRD results indicate several peaks correspond to SnO_2 crystal planes which can be indexed to tetragonal rutile structure of SnO_2 with lattice constant a= b = 4.738 Å and c = 3.187 Å.

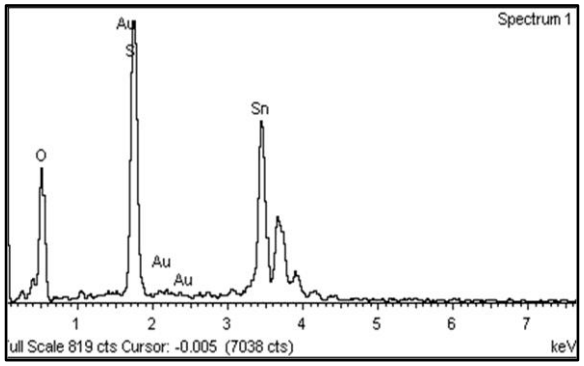


Figure 5. EDX profile of SnO_2 nanowires

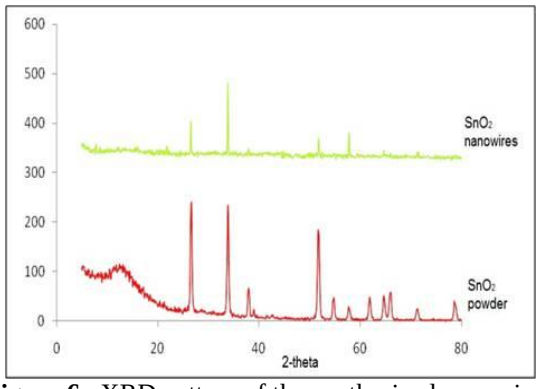


Figure 6. XRD pattern of the synthesized nanowires

The presence of the droplets at the nanowires (observe from the FESEM images) suggests that the growth of the SnO_2 nanowires follows general vapour-liquid-solid (VLS) mechanism (Dayeh, S.A., Yu, E.T. and Wang, D., 2007).
In carbothermal reaction, the SnO_2 is first reduced by carbon according to the following chemical reaction (Wang, B. et al, 2009):

$$SnO_2\,(s) + C\,(s) \rightarrow SnO(g) + CO(g) \quad (3)$$

Since the vapour of SnO(g) produced is metastable, it will decompose to Sn and SnO_2 when the temperature is ramped down (Messing et al, 2009) :

$$2\,SnO\,(g) \rightarrow SnO_2\,(s) + Sn\,(g) \quad (4)$$

Thus, the formation of the nanowires can be explained by the reaction of the vapour with the Au catalyst on the surface of the substrate. At high temperature, Au thin film forms liquid spherical particles on the Si substrate. The particles will then act as adsorption sites for the Sn vapour to deposit. This creates Au and Sn mixture or Au/Sn alloy particle (Salehi, Janfeshan and Sadmezhaad, 2009).
Later, these alloys provide energetically preferred sites for the adsorption of SnO vapour (Wang, J.X. et al, 2004). The vapour at the surface of alloy then reacts with traces of O_2 in surrounding to form SnO_2 before diffuses into the alloy droplets. The continuous deposition and diffusion (through repetition of ramping up and down) make the alloy supersaturated and crystallisation of SnO_2 will then create solid/liquid interfaces of alloy and SnO_2 crystal. The nucleation starts and the SnO_2 growth occur.

CONCLUSION

In this experiment, the SnO_2 and Zn_2SiO_4 nanowires with diameter ranging from 15-25 nm have been successfully synthesized by thermal ramping technique. The nanowires however do not follow any growth pattern. Both nanowires formation are governed by VLS mechanism which is induced by the usage of the Au catalyst. Apart from catalyst role, the different in the Au thickness does also contribute in the densification of the nanowires. Lowering the thickness of Au

has resulted in the denser nanowires and vice versa. The thermal ramping technique has proven to successfully create the same reaction atmosphere as other techniques do to synthesize nanowires. The technique omits several parameters which are usually indispensable in the conventional carbothermal technique such as material to substrate distance, carrier gas and its flow rate. Incorporating the ramping in temperature has proven to be a successful substitute for the omitted parameters and thus simplified the process.

REFRENCES

An, J-S., Noh, J.H., Cho, I-S., Roh, H-S., Kim, J.Y., Han, H.S. and Hong, K.S. Tailoring the Morphology and Structure of Nanosized Zn2SiO4: Mn2+ Phosphors Using the Hydrothermal Method and Their Luminescence Properties, J. Phys. Chem. C 2010, 114, 10330–10335.

Chen, Z.W., Jiao, Z., Wu, M.H., Shek, C.H., Wu, C.M.L. and Lai, J.K.L., Bulk-quantity synthesis and electrical properties of SnO2 nanowires prepared by pulsed delivery, *Materials Chemistry and Physics*(2009), Vol 115, 2-3, pp 660-663.

Dayeh, S.A., Yu, E.T. and Wang, D., III-V Nanowire Growth Mechanism: V/III, Ratio and Temperature Effects, *Nano Lett.*(2007), 7, 8, pp. 2486-2490.

Duraja, E-S.M., Mansorov, Z.A. and Tokmolden, S., Synthesis, characterization and photoluminescence of tin oxide nanoribbons and nanowires, Physica B : Condensed Matter (2009), 404, 21, pp.3952-3956.

Karazhanov, S.Z., Ravindran, P., Fjellvåg, H. and Svensson, B.G., Electronic Structure and Optical properties of $ZnSiO_3$ and Zn_2SiO_4, J. Appl. Phys**.** 106, 123701 (2009).

Korotcenkov, G.K., Cho, B.K., Nazarov, M., Noh, D.Y. and Kolesnikova, E.V., Cathodoluminescence studies of un-doped and (Cu, Fe, and Co)-doped tin dioxide films deposited by spray pyrolysis, Current Applied Physics(2010), Vol 10, 4, pp. 1123-1131.

Li, C., Bando, Y., Dierre, B., Sekiguchi, T., Huang, Y., Lin, J. and Dmitri, Effect of Size-Dependent Thermal Instability on Synthesis of Zn2SiO4-SiO*x* Core–Shell Nanotube Arrays and Their Cathodoluminescence Properties, Golberg Nanoscale Res Lett (2010) 5:773–780.

Messing, M.E., Hillerich, K., Johansson, J., Deppert, K., Dick, K.A., The use of gold for fabrication of nanowire structures, Gold Bull *42*(2009), 3, pp. 172-181.

Peng, K-Q., Wang, X., Wu, X-L., Lee, S.T., Platinum Nanoparticle Decorated Silicon Nanowires for Efficient Solar Energy Conversion, Nano Letters 2009 9 (11), 3704-3709.

Salehi, M., Janfeshan, B., and Sadrnezhaad, S.K., Growth Of Tin Oxide Nanotubes By Aerial Carbothermal Evaporation applied Physics A: Materials Science & Processing Volume 97, Number 2, 361-364.

Wang, B., Yang, Y.H., Wang, C.X. and Yang, G.W., Chem. Phys. Lett. 407, 347 (2005).

Wang, H. Q., Wang, G.Z., Jia, L.C., Tang, C. J. and Li, G. H. Catalyst Synthesis of Silicon-Based Zn2SiO4-SiO*x* Heterostructure Nanowires, J. Phys. Chem. C 2007, 111, 14307-14311.

Wang, J.X., Liu, D.F., Yan, X.Q., Yuan, H.J., Ci, L.J., Zhou, Z.P., Gao, Y., Song, L., Liu, L.F., Zhou, W.F., Wang G. and Xie, S.S., Growth of SnO_2 nanowires with uniform branched structures, Solid State Communications 130 (2004) 89–94.

Wang, X., Summers, C.J. and Wang, Z.L., Mesoporous Single Crystal ZnO Nanowires Epitaxially Sheathed With Zn2SiO4, Adv. Mater. 2004, 16, No. 14 July 19.

Xu, X., PeiWang, ZeminQi, HaiMing, Xu, J., Liu, H., Shi, C., Lu, G., and Ge, W., Formation mechanism of $Zn2SiO_4$ crystal and amorphous SiO2 in ZnO/Si system, J. Phys.: Condens. Matter 15 (2003) L607–L613.

Zhang, X., Jie, J., Wang, Z., Wu, C., Wang, L., Peng, Q., Yu, Y., Jiang, P., and Xie, C.,Surface induced negative photoconductivity in p-type ZnSe : Bi nanowires and their nano-optoelectronic applications, J. Mater. Chem., 2011, 21, 6736-6741.

Thong, L.V., Loan, L.T.N., Hieu, N.V., Comparative study of gas sensor performance of SnO2 nanowires and their hierarchical nanostructures, Sensors and Actuators B: Chemical, Volume 150, Issue 1, 21 September 2010, Pages 112-119.