New route in the synthesis of Tin(II) oxide micro-sheets and its thermal

by Bambang Yudono

Submission date: 17-Jan-2020 02:42PM (UTC+0700)
Submission ID: 1242994424
File name: n_the_synthesis_of_Tin_II_oxide_micro-sheets_and_its_thermal.pdf (871.82K)
Word count: 2154
Character count: 10867

Materials Letters 211 (2018) 293–295

Contents lists available at ScienceDirect

Materials Letters

journal homepage: www.elsevier.com/locate/mlblue

New route in the synthesis of Tin(II) oxide micro-sheets and its thermal transformation

Adri Huda [a], Chanel T. Handoko [a], Muhammad Djoni Bustan [b], Bambang Yudono [a], Fakhili Gulo [a,*]

[a] Program Studi Ilmu Lingkungan, Program Pascasarjana, Universitas Sriwijaya Jl. Padang Selasa, No. 524, Bukit Besar, Palembang 30139, Sumatera Selatan, Indonesia
[b] Program Studi Teknik Kimia, Fakultas Teknik, Universitas Sriwijaya Jl. Palembang, Prabumulih KM. 32, Indralaya 30662, Sumatera Selatan, Indonesia

ARTICLE INFO

Article history:
Received 6 June 2017
Received in revised form 9 October 2017
Accepted 10 October 2017
Available online 12 October 2017

Keywords:
Hydrothermal-alkaline
Preparation
Transformation
Semiconductor
Tin oxide

ABSTRACT

The micro-sheets tin(II) oxide (SnO) has been synthesized using hydrothermal-alkaline solution at 95 °C (low temperature) under the ambient atmosphere. The as-prepared material showed a romarchite tetragonal structure without impurities. Furthermore, the study of SnO transformation has been carried out by thermal treatment ranging from 400 °C to 700 °C. The result shows that the transformation was a direct oxidation without forming any intermediate phases. The SnO started to oxidize at 400 °C and fully transformed into tin(IV) oxide (SnO_2) at 600 °C. The thermal treatment has also changed the morphology and particle size of SnO from micro-sheets-structure to amorphous-flowerlike nanostructure and shifted the absorption spectra resulting in shorter UV wavelength and higher calculated-band gap.

1. Introduction

Tin oxide is a semiconductor that exists in two forms: tin(II) oxide (SnO) and tin(IV) oxide (SnO_2). Based on literature reviews, tin oxide has an intermediate phase (Sn_xO_{x+1}) which is heterovalent tin(II/IV) oxide [1]. SnO is a p-type semiconductor [2], while SnO_2 is an n-type semiconductor [3]. Both forms of tin oxide have received much attention due to their excellent physicochemical properties, which are suitable to be applied in many sectors [4–7]. However, the SnO suffered from very poor stability because of quick oxidation of Sn^{2+} to Sn^{4+} and it is quite difficult to prepare [8].

Tin oxide has been successfully synthesized by some techniques [8–11]. Among these techniques, the hydrothermal method is the simplest ways to prepare tin oxide by simply water heating and no special equipments needed. A simple $SnCl_2$ precursor has been used to prepare the SnO in some reports [12–14]. However, the dissolving process of the precursor in water is potential to release hydrochloric acid (HCl) that will suppress the SnO_2 forming [13]. The aim of this work is to synthesize the SnO by avoiding the presence of HCl using alkaline solution in the hydrothermal process. Moreover, the study of the transformation of SnO also becomes an interesting issue to clarify the contradictions of the Sn-O phase diagram [12]. This study is also important to understand the transformation of SnO in order to determine its thermal behavior for optimization of the material function.

2. Experimental

The SnO micro-sheets were prepared by the hydrothermal-alkaline solution method. The tin oxide were formed by slowly dissolving $SnCl_2{\cdot}2H_2O$ (1 g, E-Merck), with stirring, in distilled water and heated at 75 °C for 30 min. After the temperature reached, the pH of the solution was adjusted to 11 by slowly dropping 5 M Sodium Hydroxide (NaOH). The mixture was refluxed at 95 °C for 3 h and cooled to room temperatures. The obtained blue-black precipitation was filtered and washed using hot distilled water for several times, follow by final rinses with ethanol. Finally, the precipitation was dried in the oven at 80 °C for 1 h and calcined at 300 °C for 3 h. In order to observe the transformation reaction, the as-prepared SnO was annealed under ambient atmosphere varying from 400 to 700 °C for 3 h.

The final samples were investigated using X-ray diffractometer (XRD) (Rigaku-Miniflex-600, Cu-Kα target, λ = 1.54187 Å), Fourier Transform Infra-Red (FTIR), Spectrophotometer (IRPrestige-21 Shimadzu), Scanning Electron Microscope (SEM) (JEOL JSM-6510LA), Energy Dispersive X-ray Spectroscopy (EDXS) (JEOL), and UV–Vis Spectrophotometry (Shimadzu-2450).

* Corresponding author.
E-mail address: fgulo@unsri.ac.id (F. Gulo).

https://doi.org/10.1016/j.matlet.2017.10.029
0167-577X/

3. Results and discussions

The containing HCl in sample produced during the dissolving step of precursor has an important role to determine the oxidation state of tin oxide (Reaction (1)). SnO could not be produced, if there is presence HCl in reaction, even in small amount (Reaction (2)) [13]. In the hydrothermal-alkaline solution method, the adding of NaOH would neutralize the formed HCl (Reaction (3)) and substitute Cl^- ions from $Sn_4(OH)_2Cl_6$ to $Sn_4(OH)_6Cl_2$ which easily transform to SnO as the final product (Reaction (4)).

$$4SnCl_{2(s)} + 2H_2O_{(l)} \leftrightarrow Sn_4(OH)_2Cl_{6(aq)} + 2HCl_{(aq)} \quad (1)$$

$$2SnCl_{2(s)} + O_{2(g)} + 2H_2O_{(l)} \leftrightarrow 2SnO_{2(s)} + 4HCl_{(aq)} \quad (2)$$

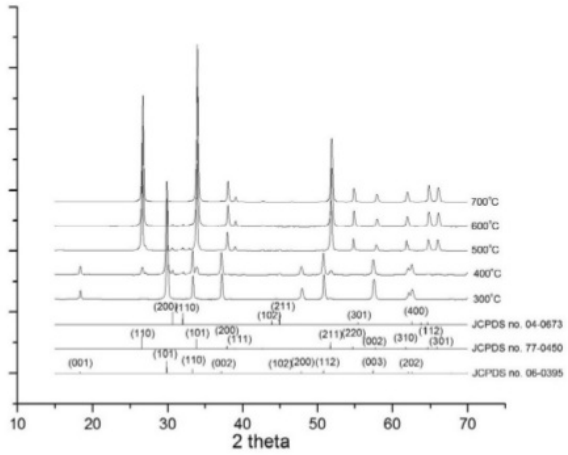

Fig. 1. XRD pattern of as-prepared sample annealed at 300 °C–700 °C.

$$Sn_4(OH)_2Cl_{6(aq)} + 2HCl_{(aq)} + 6NaOH_{(aq)} \rightarrow Sn_4(OH)_6Cl_{2(aq)} + 6NaCl_{(aq)} + 2H_2O_{(l)} \quad (3)$$

$$Sn_4(OH)_6Cl_{2(aq)} + 2NaOH_{(aq)} \rightarrow 4SnO_{(s)} + 2NaCl_{(aq)} + 4H_2O_{(l)} \quad (4)$$

The XRD patterns of these samples are presented in Fig. 1. All diffraction peaks are indexed properly to the pure romarchite tetragonal SnO (JCPDS 06-0395) at 300 °C and show minimum contributions of SnO_2 and Sn. Based on EDS spectrum, the sample is only composed by Sn and O without any impurities detected. It shows that the synthesis technique of hydrothermal alkaline solution successfully produces pure single crystal of SnO by preventing the presence of HCl.

Based on observed XRD patterns, the transformation process begins at 400 °C when thermally activated oxygen stimulates the nucleation of SnO_2 [12]. The increasing of temperature above 400 °C enhances the peak intensity of cassiterite tetragonal SnO_2 (JCPDS 77-0450) and Sn tetragonal (JCPDS 04-0637), while the intensity of SnO slowly decreases caused by oxidation (Reaction (5)) [12,15]. There is no intermediate phase peak appeared during the thermal treatment indicated the direct oxidation. However, the tetragonal peaks of Sn disappear as temperature reaching 500–700 °C. It indicates that there is a further oxidation of Sn particles occured (Reaction (6)).

$$2SnO_{(s)} \leftrightarrow SnO_{2(s)} + Sn_{(l)} \quad (5)$$

$$Sn_{(l)} + O_{2(g)} \leftrightarrow SnO_{2(s)} \quad (6)$$

Fig. 2 shows the morphology structure of micro-sheets. The morphology changes also show that the oxidation of SnO occurs during thermal treatment. SnO has three-dimensional (3D) microspheres which assemble into dense micro-sheet sub unit (Fig. 2a). The thickness of micro-sheets varies from 0.100 μm to 0.700 μm (Fig. 2b) which is 0.3536 ± 0.158 μm in average. The minimum and maximum thicknesses are 0.144 μm and 0.629 μm

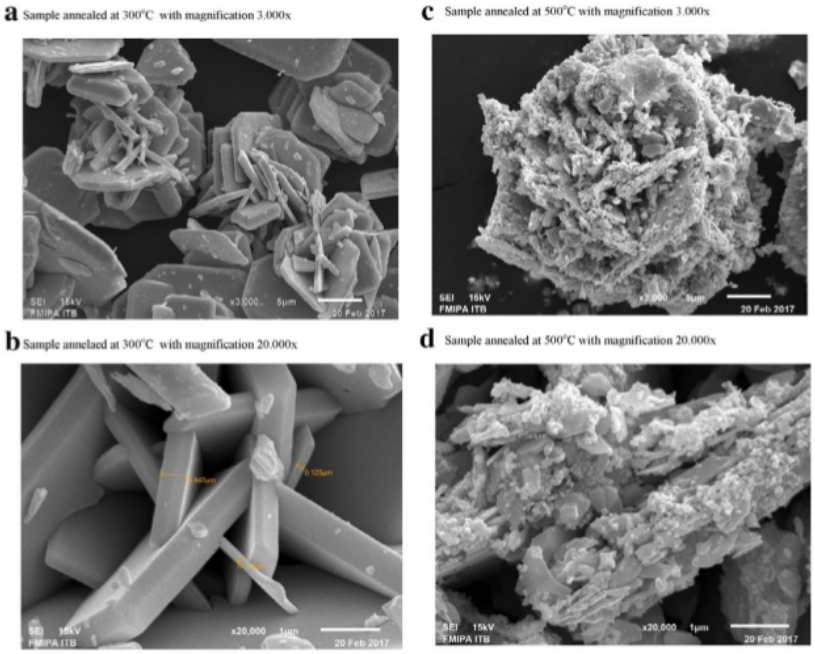

Fig. 2. SEM images of the sample (a and b) annealed at 300 °C with magnification 3.000× and 20.000× respectively; the sample (c and d) annealed at 500 °C with magnification 3.000× and 20.000× respectively.

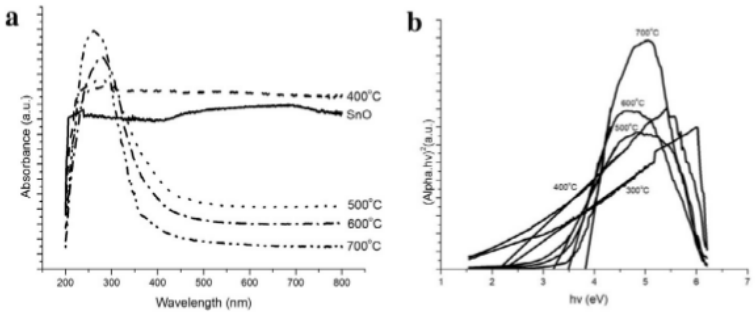

Fig. 3. (a). UV–visible absorption spectra and (b) direct band gap of the sample in several temperatures.

respectively. In thermal treatment, SnO that has polygon-type morphology (Fig. 2a) would obtain the amount of energy to diffuse oxygen to the surface and start to tilt forming the micro-flower structure [10,12,15]. By increasing the temperature, the micro-flower structure would further transform to the amorphous-flower-like nanostructure corresponded to SnO_2 structure transformation (Fig. 2c). Furthermore, this morphology change has an effect on the thickness of sheets, decreasing from 0.036 μm (36 nm) to 0.085 μm (85 nm) (Fig. 2d). It may also be interesting that the thermal treatment could control the nucleation process and crystal morphology of tin oxide.

The transformation of SnO is also confirmed using FTIR and UV–vis spectrophotometer. Through FTIR, the transformation could be observed by peak shifting from 400 cm^{-1} to 700 cm^{-1} as the asymmetric vibration fingerprint of Sn-O-Sn [16]. At ~501 cm^{-1}, the appeared peak could be assumed as the vibration peak of Sn-O as it has previously been reported by Campo et al. in which the vibration peak appears at 520 cm^{-1} [12]. The increasing of annealing temperature also slightly shifts the peaks from 501 cm^{-1}, 609 cm^{-1}, 624 cm^{-1}, and 623 cm^{-1} due to the transformation of Sn-O to be Sn-O_2 [17,18].

UV–Vis spectrophotometer proves the transformation of the micro-sheets by analyzing the changes of adsorption spectrum. At 300 °C and 400 °C, the absorption spectra of the sample have a flat pattern both in UV and Vis wavelength which confirms as SnO [19]. Furthermore, the absorption properties of the sample could be explained further by calculating the band gap using Tauc plot method [20]:

$$\alpha h\nu = A(h\nu - Eg)^n$$

where α is the optical absorption coefficient, hν is the photon energy, Eg is the band gap, A is constant, and n is equal to 1/2 and 2 for direct and indirect transition, respectively.

The direct band gap is approximately 2.20–2.10 eV, while the indirect band gap could not be determined due to its narrow band gap. The narrow band gap should form a flat pattern both in UV and Vis wavelength [19]. When the annealing temperatures increase to 500 °C, 600 °C, and 700 °C, there are changes of the maximum wavelength becoming shorter wavelength. It is also proven by calculating the band gap with *Eg* values of 3.[illegible], 3.50, and 3.80 eV (Fig. 3d). The wide bandgap confirms that SnO_2 is an n-type wide band gap (~3.6 eV) semiconductor [21].

Based on the above results, the transformation reaction of as-prepared SnO is a direct oxidation without forming the intermediate phases. Tin(II) oxide directly transforms to tin(IV) oxide after reaching energy during thermal treatments. It is necessary to understand the transformation process of tin oxide to control the phase changes for the future applications.

4. Conclusion

In summary, the pure tin(II) oxide was successfully prepared by using a new route hydrothermal-alkaline solution technique at pH 11 and a low-temperature of 95 °C. The as-prepared material has a single crystal of SnO without any impurities. It starts to oxidize at 400 °C and fully transforms to SnO_2 at 600 °C. The transformation of SnO is a direct oxidation without forming the intermediate phase of tin oxide. The transformation affects the morphology, particle size, and absorption characteristics of SnO.

Acknowledgement

This work was financially supported by PMDSU program of Kemenristekdikti. The authors thank *Balai Riset dan Standarisasi Industri Palembang* for supporting facilities.

References

[1] Y. He, D. Li, J. Chen, Y. Shao, J. Xian, X. Zheng, P. Wang, RSC Adv. 4 (2014) 1266–1269.
[2] T. Yang, J. Zhao, X. Li, X. Gao, C. Xue, Y. Wu, R. Tai, Mater. Lett. 139 (2015) 39–41.
[3] G. Sun, F. Qi, S. Zhang, Y. Li, Y. Wang, J. Cao, H. Bala, X. Wang, T. Jia, Z. Zhang, J. Alloys Compd. 617 (2014) 192–199.
[4] Y. Hu, K. Xu, L. Kong, H. Jiang, L. Zhang, C. Li, Chem. Eng. J. 242 (2014) 220–225.
[5] M. Forster, Energy 29 (2004) 789–799.
[6] J. Safaei-Ghomi, H. Shahbazi-Alavi, E. Heidari-Baghbahadorani, RSC Adv. 4 (2014) 50668–50677.
[7] W. Xia, H. Wang, X. Zeng, J. Han, J. Zhu, M. Zhou, S. Wu, CrystEngComm 16 (2014) 6841.
[8] P.H. Suman, A.A. Felix, H.L. Tuller, J.A. Varela, M.O. Orlandi, Sens., Actuators B: Chem. 208 (2015) 122–127.
[9] H. Uchiyama, S. Nakanishi, H. Kozuka, J. Solid State Chem. 217 (2014) 87–91.
[10] M.Z. Iqbal, F. Wang, T. Feng, H. Zhao, M.Y. Rafique, Rafi ud Din, M.H. Farooq, Q. ul ain Javed, D.F. Khan, Mater. Res. Bull. 47 (2012) 3902–3907.
[11] K.-C. Kim, D.H. Lee, S. Maeng, Mater. Lett. 86 (2012) 119–121.
[12] C.M. Campo, J.E. Rodríguez, A.E. Ramírez, Heliyon 2 (2016) e00112.
[13] H.-T. Fang, X. Sun, L.-H. Qian, D.-W. Wang, F. Li, Y. Chu, F.-P. Wang, H.-M. Cheng, J. Phys. Chem. C 112 (2008) 5790–5794.
[14] G. Sun, F. Qi, Y. Li, N. Wu, J. Cao, S. Zhang, X. Wang, G. Yi, H. Bala, Z. Zhang, Mater. Lett. 118 (2014) 69–71.
[15] D. Leng, L. Wu, H. Jiang, Y. Zhao, J. Zhang, W. Li, L. Feng, Int. J. Photoenergy (2012) 1–6.
[16] S. Das, S. Kar, S. Chaudhuri, J. Appl. Phys. 99 (2006) 114303.
[17] K. Santhi, C. Rani, S. Karuppuchamy, J. Alloys Compd. 662 (2016) 102–107.
[18] P. Patil, R. Kawar, T. Seth, D. Amalnerkar, P. Chigare, Ceram. Int. 29 (2003) 725–734.
[19] Y. Ogo, H. Hiramatsu, K. Nomura, H. Yanagi, T. Kamiya, M. Hirano, H. Hosono, Appl. Phys. Lett. 93 (2008) 32113.
[20] K. Wongsaprom, R. Bomphotsawatkun, E. Swatsitang, Appl. Phys. A 114 (2014) 373–379.
[21] M. Aziz, S.S. Abbas, W.R.W. Baharom, Mater. Lett. 91 (2013) 31–34.

New route in the synthesis of Tin(II) oxide micro-sheets and its thermal

ORIGINALITY REPORT

12%	8%	6%	11%
SIMILARITY INDEX	INTERNET SOURCES	PUBLICATIONS	STUDENT PAPERS

PRIMARY SOURCES

1	pms.unsri.ac.id Internet Source	1%
2	Masoomeh Siminghad, Shabnam Sheshmani, Ashraf Sadat Shahvelayati. "Application, optimisation and kinetic studies of SnO micro-square in photoinduced decolourisation of Acid Orange 7 and Acid Orange 10 under visible light irradiation", International Journal of Environmental Analytical Chemistry, 2019 Publication	1%
3	Submitted to Jawaharlal Nehru Technological University Student Paper	1%
4	oa.upm.es Internet Source	1%
5	Submitted to Xiamen University Student Paper	1%
6	Submitted to University College London Student Paper	1%

7	jlsuboptimal.unsri.ac.id Internet Source	1%
8	Submitted to SASTRA University Student Paper	1%
9	escholarship.org Internet Source	1%
10	link.springer.com Internet Source	1%
11	www.intechopen.com Internet Source	1%
12	Submitted to Cornell University Student Paper	1%

Exclude quotes	On	Exclude matches	< 1%
Exclude bibliography	On		