ภาคผนวก

การสังเคราะห์และการกำหนดลักษณะเฉพาะของลวดนาโนและทรงกลมไมโครของดีบุกออกไซด์โดย
การระเหยทางความร้อน

SYNTHESIS AND CHARACTERIZATION OF SnO_2 NANOWIRES AND MICROSPHERES BY THERMAL EVAPORATION

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บทคัดย่อ: ในเอกสารการวิจัยนี้, โครงสร้างนาโนทินไดออกไซด์ (SnO_2 nanostructures) ถูกสังเคราะห์ขึ้นโดยกระบวนการไอระเหยทางความร้อนที่อุณหภูมิ 800 °C ภายใต้บรรยากาศไนโตรเจน และออกซิเจน เป็นเวลา 3 ชั่วโมง โดยใช้ผงดีบุกบริสุทธิ์เป็นสารตั้งต้น ผลิตภัณฑ์ที่สังเคราะห์ได้ถูกศึกษาลักษณะบ่งชี้โดย X-rays diffraction (XRD) และกล้องจุลทรรศน์ชนิดส่องกราด (scanning electron microscopy; SEM) ผลจาก XRD แสดงให้เห็นว่าโครงสร้างของผลิตภัณฑ์ที่เตรียมได้เป็นโครงสร้างผลึกแบบ tetragonal โดยมีค่าคงที่ของแลตทิซ a = 0.4718 นาโนเมตร และc = 0.3187 นาโนเมตร ภาพจาก SEM แสดงถึงโครงสร้าง SnO_2 nanowires ที่ยาวประมาณ 10 ไมโครเมตร กว้าง 200 นาโนเมตร ถึง 500 นาโนเมตร เส้นผ่านศูนย์กลางของ SnO_2 microspheres อยู่ในช่วง 10 ไมโครเมตร ถึง 100 ไมโครเมตร

Abstract: In this paper, SnO_2 nanostructures were synthesized by thermal evaporation growth at 800 °C under atmospheric of nitrogen and oxygen gas for 3 hrs. using high pure tin powder as the source materials. The synthesized products were characterized by X-rays diffraction (XRD) and scanning electron microscopy (SEM). XRD patterns indicate that the structure of prepared products are tetragonal in structures with lattice parameters of a = 0.4718 nm and c = 0.3187 nm. SEM images show that SnO_2 nanowires are about tens of micrometers in length, 200 - 500 nm in width. The diameters of SnO_2 microspheres vary from 10 μm. to 100 μm.

Introduction: Tin oxide (SnO_2) is an important and inexpensive semiconductor with a wide band gap (Eg = 3.6 eV, at room temperature), is well known for its potential application in gas sensors, transparent conducting electrodes and solar cells [1-3]. Recently, several researchers have successfully synthesized nanostructures of SnO_2 by thermal evaporation. For example, SnO_2 nanostructures in the forms of nannowires and branched structures were prepared using the active carbon and SnO_2 powder at low temperature (700 °C) [4]. SnO_2 nanostructures form of needle- shaped have fabricated by heating Sn powder in air flow at 900 °C [5]. Li et al. synthesized SnO_2 nanowires by thermal evaporation using a mixture of SnO_2 powder and graphite as the source materials [6]. Some reports indicate that SnO_2 nanobelts were synthesized under some

special conditions [7-8]. In this research, we have been growth of SnO_2 nanowires and SnO_2 microspheres synthesized by thermal evaporation without any catalysts.

Methodology: Our experiment was carried out in a quartz tube furnace. A horizontal quartz tube was located inside the furnace. The high-pure tin powder 1 g was placed on alumina boat, which was loaded to the center of the quartz tube that was inserted in the tube furnace. Then the furnace was heated up to 800 °C from room temperature under a nitrogen gas flow at a rate of 1 L/min, then a flow of oxygen gas rate of 0.5 L/min and kept for 3 hrs. After evaporation, the furnace was cooled down to room temperature, and then we took the sample products from the furnace. The synthesized products were investigated by X-ray diffraction (XRD: Cu Kα_1 radiation) (Philips X'pert MRD) and scanning electron microscopy (SEM).

Results, Discussion and Conclusion: We can observe that the prepared products were very clearly different from initial source materials. The prepared products were characterized by XRD. Figure 1 indicate that the XRD pattern of products, the diffraction peaks of the (110), (101), (200), (111), (210), (211), (220), (022), (310), (112), (301), (202) and (321) planes can be readily indexed to the tetragonal structure of SnO_2, with lattice constants of a = 0.4718 nm, c = 0.3187 nm.

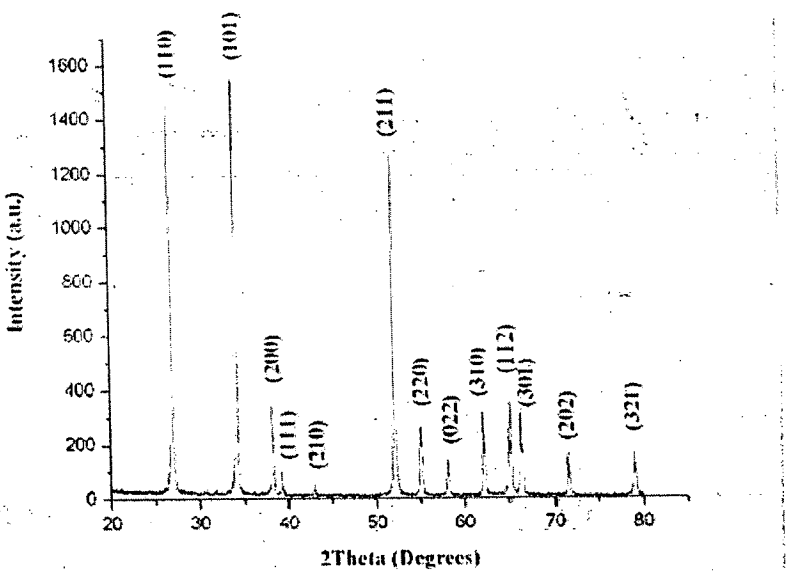

Figure 1. The XRD patterns of the synthesized products

The morphology of the products were investigated by SEM. Figure 2 showed typical SEM images of synthesized products. We can observe in Figure 2a that the diameters of SnO_2 microspheres vary from 10 μm. to 100 μm. Figure 2b indicated that the morphology of SnO_2 nanowires are about tens of micrometers in length, 200 - 500 nm in width. These nanowires will be grown from one microsphere to the other.

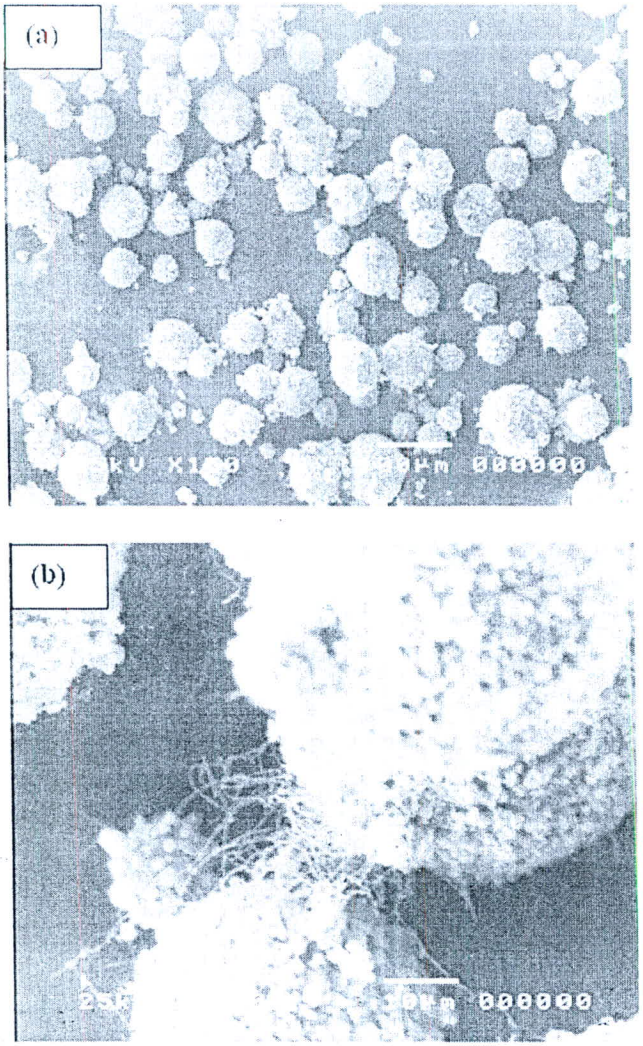

Figure 2 SEM image of the products as (a) SnO_2 microspheres and (b) SnO_2 nanowires form on microspheres

The growth of SnO_2 nanowires is controlled by the vapor – liquid-solid (VLS) mechanism. the following chemical reaction will take place during the thermal evaporation process:

$$2SnO(g) = Sn(l) - SnO_2(s) \quad (1)$$

$$SnO_2(s) = SnO(g) + 1/2\ O_2(g) \quad (2)$$

The temperature was elevated up to the reaction temperature: tin source was continuously evaporated to from tin vapor. Then a large amount of tin vapor was transported to the deposition zone by carrying gas, in which tin atoms combined with oxygen atoms to from tin oxide vapor, as the reaction (1) described. Subsequently, the SnO_2 nanowires grow by precipitation of SnO_2 from the supersaturated droplets, the reaction (2) is reversible [9-11].

In summary, SnO_2 nanowires and SnO_2 microspheres have been successfully synthesized by thermal evaporation growth at 800 °C for 3 hrs, using high pure tin powders as the source materials. The products were characterized by XRD and SEM instrument.

References:

1. Feng Gu , Shu Fen Wang , Chun Feng Song , Meng Kai Lu , Yong Xin Qi , Guang Jun Zhou , Dong Xu , and Duo Rong Yuan. *Chemical Physics Letters*., 2003, 372, 451– 454.
2. Yong-Jun Ma, Feng Zhou, Li Lu, and Ze Zhanga. *Solid State Communications*., 2004, 130, 313–316.
3. Xianghua Kong and Yadong Li, *Sensors and Actuators*., 2005, B 105, 449–453.
4. J.X. Wang, D.F. Liu, X.Q. Yan, H.J. Yuan, L.J. Ci, Z.P. Zhou, Y. Gao, L. Song, L.F. Liu, W.Y. Zhou, G. Wang, and S.S. Xie, *Solid State Communications*., 2004,130, 89–94.
5. Hyoun Woo Kim, and Seung Hyun Shim. *J. Alloys and Compounds*., 2006, 426, 286–289.
6. Lijun Li, Fujian Zong, Xiaodong Cui, Honglei Ma, Xiaohui Wu, Quande Zhang, Yongli Wang, Fan Yang, and Jianzhi Zhao. *Materials Letters*., 2007, 61, 4152–4155.
7. Han Xiangming, Zhang Bing, Guan Shaokang, Liu Jindun, Zhang Xiang, and Chen Rongfeng. *J. Alloys and Compounds*., 2008, 461, L26–L28.
8. Zaiyin Huang and Chunfang Chai. *Materials Letters*., 2007, 61, 5113–5116.
9. J.Q. Hu,Y. Bando, and D. Golberg. *Chemical Physics Letters*., 2003, 372, 758–762.
10. Yiqing Chen, Xuefeng Cui, Kun Zhang, Dengyu Pan, Shuyuan Zhang, Bing Wang, and J.G. Hou. *Chemical Physics Letters*., 2003, 369, 16–20.
11. L.A. Ma, and T.L. Guo. *Materials Letters*., 2009, 63, 295–297.

Keywords: SnO_2 nanostructures, thermal evaporation, nanowires, microspheres.

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Studies on the Preparation and Gas Sensing Properties of SnO_2 Nanostructures at Room Temperature

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Keywords: SnO_2 nanostructures, nanowires, nanoparticles, carbon-assisted, gas-sensing

Abstract. The SnO_2 nanostructures have been synthesized by carbon-assisted growth at 800 °C for 3 hours. Using high pure tin powder as the source materials. The synthesized products were investigated by stereo microscope, X-rays diffraction (XRD) and scanning electron microscopy (SEM). XRD patterns show that the prepared products are tetragonal-structures with the lattice constant a = 0.4718 nm and c = 0.3187 nm. SEM images indicate that SnO_2 nanowires are about tens of micrometers in length, 80-100 nm in width. The diameter of SnO_2 nanoparticles vary from 10 nm to 100 nm. The synthesized products are high sensitivity and fast response time to ethanol gas at room temperature.

Introduction

Tin dioxide (SnO_2) is a very important n-type semiconductor with a wide band gap (Eg = 3.6 eV, at room temperature) and for its potential applications in gas sensors, transparent conducting electrode, transistors and solar cells [1-3]. SnO_2 nanostructures have been successfully synthesized by several methods. Recently, some reports indicate that SnO_2 nanowires have been prepared using the active carbon reaction with the SnO_2 powder at 700 °C under atmosphere of nitrogen [4]. SnO_2 nanobelts have been synthesized by water-assisted using high pure Sn powder growth at 850 °C in atmosphere of argon with flow rate of 20 sccm for 1 hour [5]. Xiangming et al prepared SnO_2 nanobelts by thermal evaporation of Sn foil at 1100 °C under atmospheric pressure, were very sensitivity and response to ethanol gas [6]. One-dimensional SnO_2 needle-shaped nanostructures were prepared by thermal evaporation of pure tin powder at high temperatures, a constant pressure of air and kept flowing at 150 mTorr [7]. SnO_2 nanowires were formed by the CVD method, using pure Sn powder and single-crystal substrates of $LaALO_3$ heated at 900 °C under argon gas with the rate of 30 mL/min and O_2 with flow rate of 50 mL/min for 30 min [8]. Ansari et al performed SnO_2 nanoparticles by so-gel method, were used in thick film to detect low concentration hydrogen gas very sensitively [9]. SnO_2, thick film doped with Pd using for sensor to study the CO-water interaction on its surface [10]. Jain et al reported that SnO_2 thick film LPG gas sensor were effecting from grain size on Ni and Al doping [11]. However, all of the above methods either needed high temperatures or a mixture of catalysts and metal oxides before heating.

In this work, SnO_2 nanoparticles and nanowires were prepared by carbon-assisted growth at 800 °C using high pure tin powder as the source materials. These SnO_2 nanostructures were used for investigating the sensitivity and the response time to ethanol gas at room temperature.

Experimental

Our experiment was carried out in quart tube furnace, a horizontal quart tube was mounted inside the furnace. The mixtures of active carbon powder were prepared from coconut shell [12] and tin powder (99.0 %, Aldrich) with ratio of 1:1 by weight as the starting materials, was placed in alumina boat and the substrates for growth of nanostructures put on the source materials. Si substrates were cleaned with ethanol several times, and then dried in air. The alumina boat was located in the middle of a quartz tube that was inserted in the furnace. The furnace was heated under flowing

nitrogen gas with the rate of 1 L/min when the temperature in the center of tube increase to 800 °C. O_2 gas with flow rate of 0.5 L/min was introduced and kept at this temperature for 3 hours. After the reaction completed, the quartz tube was cooled down to room temperature. The morphologies of the products were investigated by stereo microscope (image analyzer: OLYMPUS, SZX9), scanning electron microscopy (SEM: JEOL 6400) and the crystal structure of the products were characterized by X-ray diffraction (XRD: Cu Kα_1 radiation) (Philips X'pert MRD). The synthesized products were dispersed in the ethanol, the materials decomposes to form nanoparticles and nanowires. The gas sensors were fabricated as follow: SnO_2 nanoparticles were grinded with several drops of distilled water in a ceramic mortar to form a slurry [13]. Then, the slurry was painted onto the glass substrate with a wide of 4 mm and length of 5 mm. SnO_2 nanowires were mixed with PVA (polyvinyl alcohol) [14], to form paste before fabricating the sensor. The nanowires and nanoparticles sensors were calcined at 200 °C for 2 hours. The glass substrate was performed two electrodes using silver paint and Cu wires, the width between electrodes was about 2 mm. The gas sensitivity properties were measured using a test system showed in Fig. 1. Fig. 1a, the sensor was located at each end of the quartz tube. The temperature of the furnace was controlled at 27 °C, then an ethanol gas was flowed into the testing tube by pump with flow rate of air about 5 L/min, while the temperature of heater vary from 40 °C to 70 °C, and the time constant of air-flowing of 10 s. The measuring electric circuit showed in Fig. 1b. The circuit voltage (V_c = 10 V) was supplied across the sensor and the load resistor (R_L = 1 MΩ) was connected in series. The signal voltage across the load was measured using manual method. The resistance of sensor was measured in air and an ethanol gas. The sensitivity (S) of semi- conducting gas sensor is generally defined as $S = (R_{air} - R_{gas})/R_{air}$, where R_{air} and R_{gas} are the resistance of sensor in air and in a test gas [14].

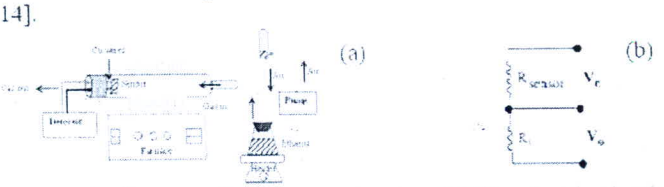

Figure 1. (a) Schematic diagram of measurement system (b) The electric circuit of gas sensor (V_c: circuit voltage; V_o: signal voltage and R_L: load resistor).

Results and Discussion

After the furnace had cooled down to room temperature, the Si substrate was taken from the alumina boat. We can saw the white color of products on Si substrate very clearly under naked eyes observation. The products were investigated by image analyzer, XRD and SEM instruments. Fig. 2a, the image analyzers indicate that white layer products formed on the Si wafer and inner wall of alumina boat. The structures of prepared products were characterized by XRD. Fig. 2b shows a typical XRD pattern of the products on the substrate. The main diffraction peak in the patterns can be indexed to the SnO_2 tetragonal structure, with lattice constants of a = 0.4718 nm, c = 0.3187 nm.

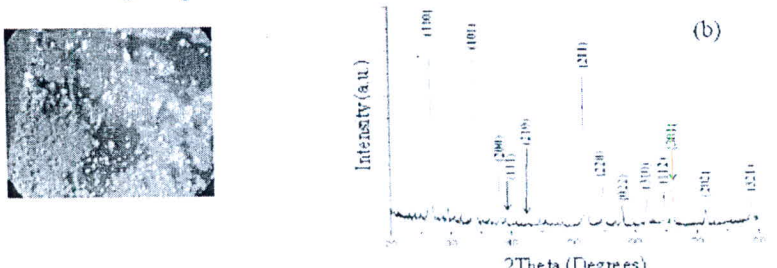

Figure 2. The images of products as (a) the stereo microscope showed the picture of the products on the Si substrate after cooling down to room temperature and (b) the XRD patterns of the products.

The diffractions are well in agreement with JCPDS file No. 41-1445. The morphologies of synthesized products were investigated by SEM showed in Fig. 3a-3c. Fig. 3a. showed the low-magnification SEM image of SnO_2 nanostructures, nanoparticles and nanowires. Fig. 3b-3c shows a high-magnification SEM images, the diameter of SnO_2 nanoparticles vary from 10 nm to100 nm and the typical SnO_2 nanowires with the length of wires about tens of micrometers, 80-100 nm in width. There are two well-accepted mechanisms for the growth of one-dimensional nanostructures, the vapor-liquid-solid (VLS) and the vapor-solid (VS) processes. The VLS growth is a catalyst-assisted process, in which the catalyst particle acts as liquid forming agent [3,4]. The most observing sign of the VLS mechanism, there is droplet observed at end of the prepared products.

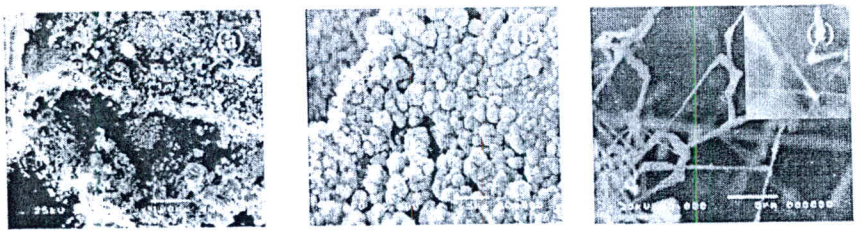

Figure 3. SEM images of the products. (a) low-magnification. (b) and (c) high-magnification.

In this figure, SEM images indicate that there are some particles on the nanowires tip as the growth mechanism. During the thermal evaporation process, the following chemical reactions will happen by 3 reactions. (1) $Sn(s) - C(s) + O_2(g) = SnO(g) - CO(g)$. (2) $2SnO(g) = Sn(l) + SnO_2(s)$ and (3) $SnO_2(s) = SnO(g) + 1/2\ O_2(g)$. These processes were explained by previously reports [3,4,15]. The synthesized products were assembled into sensor for measuring their electric conductance. Fig. 4a. showed the changes in sensitivity of the prepared SnO_2 nanostructures after a sensor was exposed to methanol gas and ethanol gas with various concentrations, and with flow rate of air about 5 L/min, while the temperature of heater vary from 40 °C to 70 °C. We can found that SnO_2 nanoparticles and SnO_2 nanowires had relatively high sensitivity to methanol gas. SnO_2 nanoparticles had higher sensitivity to methanol gas, compared with SnO_2 nanowires, and the sensitivity of gas sensors to methanol gas was higher than the atmosphere of ethanol gas.

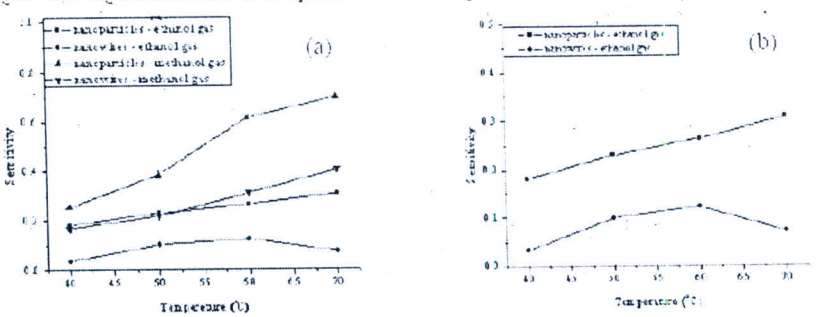

Figure 4. Sensitivities of products (a) to various temperature of ethanol and methanol gases, and (b) sensitivities of differential SnO_2 nanostructures in ethanol gas concentation at room temperature.

However, the response time of nanostructures to ethanol gas was faster than to methanol gas at room temperature. Here, response time was defined as the time needed for a sensor to attain the 90 % of maximum change in resistance after the contact of test gas with sensor surface [16]. Fig. 4b, shows the relationship between the sensitivity of SnO_2 nanostructures and temperature of ethanol from 40°C to 70°C, the sensitivity of sensors increased from 0.18 to 0.31 for SnO_2 nanoparticles and increased from 0.03 to 0.12 for SnO_2 nanowires, then it slightly decreased to 0.07. According to previous reports [16-18], the sensitivity of gas sensor depended on the ease of

diffusion of gas molecules inside the sensor. Higher surface area could enhance the interaction between SnO_2 surface and gas molecules. These results were evident that SnO_2 nanoparticles had better gas sensor practice than SnO_2 nanowires at room temperature and the sensitivity gradually increases with increasing temperatures of test gas. The sensor exhibited sensitivity and fast response time of about 10 - 12 s when the testing ethanol gas was flowed.

Conclusion

The synthesis of SnO_2 nanowires and SnO_2 nanoparticles have been successfully synthesized by carbon-assisted growth at 800 °C for 3 hours, using high pure tin powders as the source materials. The image analyzer, XRD and SEM instruments were studied. The prepared products were tetragonal-structures with the lattice constant a = 0.4718 nm and c = 0.3187 nm. SnO_2 nanowires are about tens of micrometers in length, 80-100 nm in width. The diameter of SnO_2 nanoparticles vary from 10 nm to100 nm. The synthesized products. SnO_2 nanostructured are high sensitivity and fast response time to ethanol at room temperature.

Acknowledgments

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References

[1] A. Rosental, A. Tarre, A. Gerst, J. Sundqvist, A. Harsta, A. Aidla, J. Aarik, V. Sammelselg and T. Uustare: Sens. Actuators, B Vol. 93 (2003), p. 552
[2] F. Gu, S.F. Wang, M.K. Lu, Y.X. Qi, G.J. Zhou, D. Xu and D.R. Yuan: Opt. Mater. Vol. 25 (2004), p. 59
[3] C. Zheng, Y. Chu, Y. Dong, Y. Zhan and G. Wang: Mater. Lett. Vol. 59 (2005), p. 2018
[4] J.X. Wang, D.F. Liu, X.Q. Yan, H.J. Yuan, L.J. Ci, Z.P. Zhou, Y. Gao, L. Song, L.F. Liu, W.Y. Zhou, G. Wang and S.S. Xie: Solid State Commun. Vol. 130 (2004), p. 89
[5] Z. Huang and C. Chai: Mater. Lett. Vol. 61 (2007), p. 5113
[6] H. Xiangming, Z. Bing, G. Shaokang, L. Jindun, Z. Xiang and C. Rongfeng: J. Alloys. Comp. Vol. 461 (2008), p. L26
[7] H.W. Kim and S.H. Shim: J. Alloys. Comp. Vol 426 (2006), p. 286
[8] Y-J. Ma, F. Zhou, L. Lu and Z. Zhang: Solid State Commun. Vol. 130 (2004), p. 313
[9] S.G. Ansari, P. Boroojerdian, S.R. Sainkar, R.N. Karekar, R.C. Aiyer and S.K. Kulkarni: J. Phys. Chem. Vol. 64 (2003), p. 1037
[10] J. Kappler, A. Tomescu, N. Barsan and U. Weimar: Thin Solid Films. Vol. 391 (2001), p. 186
[11] K. Jain, R.P. Pant and S.T. Lakshmikumar: Sens. Actuators, B Vol. 113 (2006), p. 823.
[12] P. Chumninok, P. Kasian, P. Limsuwan, U. Tipparach, S. Samran, L. Chow and S. Pukird: Adv. Mater. Res. Vol. 55 (2008), p. 637
[13] J. Zhang, S.Wang, Y. Wang, M. Xu, H. Xia, S. Zhang, W. Huang, X. Guo and S. Wu: Sens. Actuators, B Vol. 139 (2009), p. 369
[14] A.V. Kadu, S.V. Jagtap and G.N. Chaudhari: Curr. Appl. Phys. Vol. 9 (2009), p. 1246
[15] Y. Chen, X. Cui, K. Zhang, D. Pan, S. Zhang, B. Wang and J.G. Hou: Chem. Lett. Vol. 369 (2003), p. 16
[16] L. Xi, D. Qian, X. Tang and C. Chen: Mater. Chem. Phys. Vol. 108 (2008), p. 232
[17] A. Chaturvedi, V.N. Mishra, R. Dwivedi and S.K. Srivastava: J. Micr. Vol. 30 (1999), p. 259
[18] H. Wang, J. Liang, H. Fan, B. Xi, M. Zhang, S. Xiong, Y. Zhu and Y. Qian: J. Solid State Chem. Vol. 181 (2008), p. 122

การควบคุมเวลาที่ใช้ในการสังเคราะห์เส้นลวดนาโนคอปเปอร์ออกไซด์จากแผ่นทองแดง

TIME CONTROLLING ON SYNTHESIZATION OF CUO NANOWIRES PREPARED FROM CU PLATE

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บทคัดย่อ: โครงสร้างเส้นลวดนาโนคอปเปอร์ออกไซด์ถูกสังเคราะห์โดยวิธีไอระเหยทางความร้อน โดยใช้แผ่นทองแดงในอากาศที่อุณหภูมิ 500 °C เป็นเวลา 15, 20 และ 24 ชั่วโมง โครงสร้างนาโนคอปเปอร์ออกไซด์ ถูกศึกษาคุณสมบัติและลักษณะบ่งชี้โดย โดยเทคนิคการเลี้ยวเบนของรังสีเอกซ์ (XRD) และกล้องจุลทรรศน์อิเล็กตรอนแบบส่องกราด (SEM) ผลจาก XRD แสดงโครงสร้างผลึกของ CuO และ Cu_2O ลักษณะทางกายภาพ และเงื่อนไขการเกิดของเส้นลวดนาโนคอปเปอร์ออกไซด์ถูกศึกษาโดย SEM ความยาวของเส้นลวดนาโนจะขึ้นอยู่กับเวลา เส้นผ่านศูนย์ของเส้นลวดนาโนคอปเปอร์ออกไซด์มีค่าประมาณ 10 นาโนเมตร ถึง 80 นาโนเมตร และความยาวหลาย 10 ไมโครเมตร

Abstract: CuO nanowires were synthesized by thermal evaporation method using Cu metal plate in air at temperature of 500 °C for 15, 20 and 24 hrs. The CuO nanostructures were characterized by X-ray diffraction (XRD) and scanning electron microscope (SEM). XRD patterns showed the bicrystal nanostructures of CuO and Cu_2O. The morphology and growth condition of CuO nanowires were studied by SEM and length of CuO nanowires depended on time. The diameter of CuO nanowires vary from 10 nm to 80 nm and length of several 10 micrometers.

Introduction: Copper oxide (CuO) has many interesting properties. It is p-type semiconductor with a narrow band gap (1.2 eV), and has a monoclinic crystal structure, and a wide rang of application in gas-sensors, magnetic strong media, solar-energy, electronics, catalysis, batteries, semiconductor, varistors [1-4]. CuO nanostructure can be synthesized by using various techniques. CuO nanowires were synthesized by thermal evaporation in oxygen ambient using Cu foils at the temperature from 300°C to 900°C [4]. Which prepared in air using Cu plate, were annealed at 400° C for 24 hrs in air [5] and. CuO nanorods can be synthesized by thermal decomposition of CuC_2O_4 chemical reaction between $Cu(CH_3COO)_2.HO_2$ and $H_2C_2O_4.HO_2$ nonyl phenyl ether (9)/(5)(NP-9/5) and NaCl flux [6].The ethanol sensing properties of CuO nanowires prepared by oxidation reaction of copper plate, was annealed at 600°C in air [7]. In this paper, CuO nanowires synthesized by thermal evaporation at 500°C in air using Cu plate.

Methodology: A 1cm × 1cm of Cu plate was rinsed by acetone and de-ionized by water several time. After it has been dried by an air gun. to place in alumina boat. the Cu plate was loaded into the middle of the tube furnace. and heated at 500°C for 15, 20 and 24 hrs in air. After evaporation, the furnace was cooled down to room temperature. Copper nanowires were contained in the black ash-like top layer formed on the Cu substrate. The CuO nanostructures were characterized by x-ray diffraction (XRD). while the morphology and growth condition of CuO nanowires were studied by scanning electron microscope (SEM).

Results, Discussion and Conclusion: The products were synthesized in air at 500°C for 15, 20 and 24 hrs. Figure 1 showed the XRD pattern of the heat treatment on the black -ash like top layer. They indicated that CuO and Cu_2O phases (JCPDS 05-0661) are both found after thermal evaporation. Figure 2 shows morphologies of the product prepared with different evaporation times at 500°C. Most of nanowires look like that they have the same diameter. We can observe the evaporation time has been affect to the length of the nanowires. The length of nanowires depended on more evaporation time. For 15, 20 and 24 hrs, the lengths of nanowires are 7, 10 and 16 μm respectively.

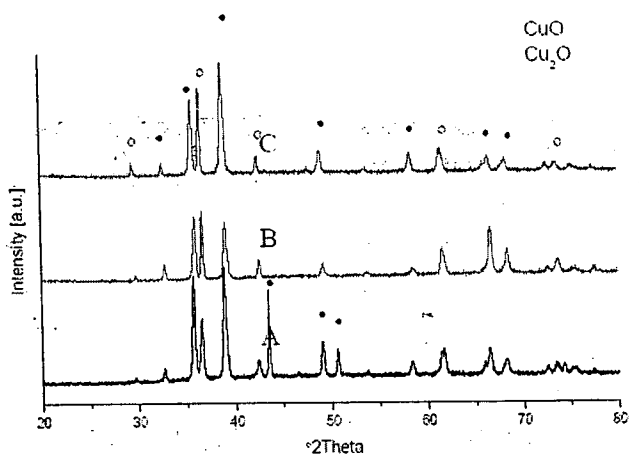

Figure1. XRD pattern of the blacktop layer of products, showed CuO and Cu_2O crystal structures.

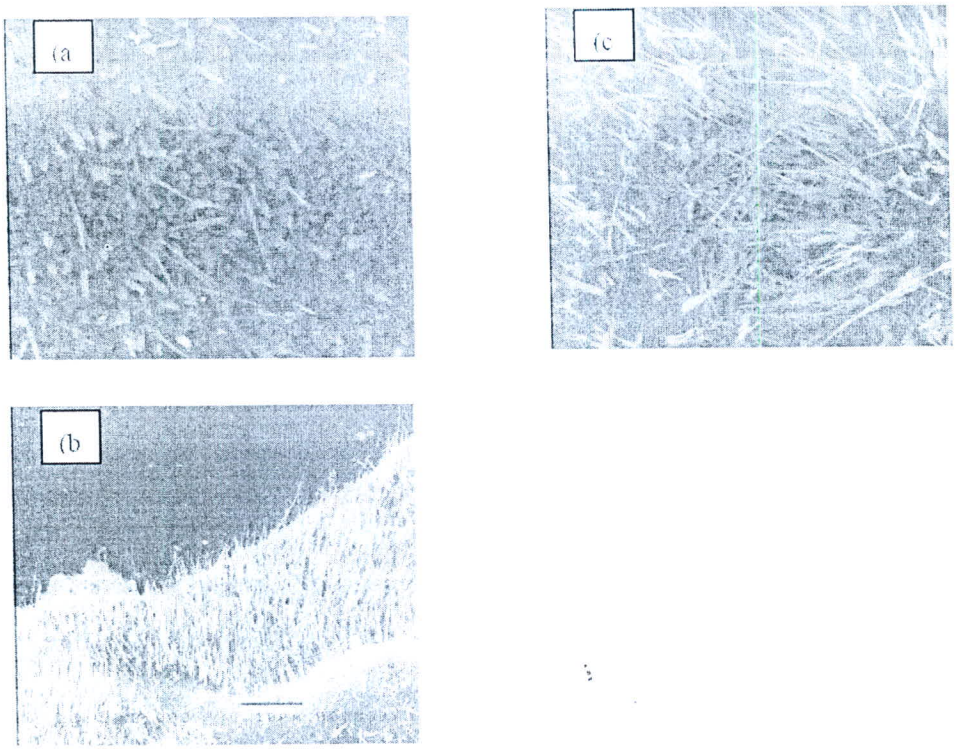

Figure2. SEM image of the nano materials black ash – like top layer in air for (a) 15 hrs (b) 20 hrs (c) 24 hrs

The SEM images show the nanowires structures synthesized on Cu substrate. The diameter of CuO nanowires vary from 10 nm to 80 nm and their lengths are several 10 micrometers

In summary, CuO nanowires have been synthesized by thermal evaporation at 500 °C for 15, 20 and 24 hrs in air. The structures were characterized by XRD and SEM instruments. The diameter of CuO nanowires vary from 10 nm to 80 nm and their lengths are several 10 micrometers. The growth condition and length of CuO nanowires depended on time.

References:

[1] W.Wang, Z.Liu,Y.Liu, C.Xu, C.Zheng, G. Wang. *Applied. Phyics. A*, 2003 76,417-420

[2] C.H. Xu , C.H. Woo a, S.Q. Shi b, *Chemical Physics Letters* 2004, 399, 62–66

[3] W. Wang, Y. Zhu, G. Cheng, Yue-Hong Huang , Materials Letters 2006, 60, 609–612

[4] L.S. Huanga, S.G. Yanga, T. Lia, B.X. Gua, Y.W. Dua, Y.N. Lub, S.Z. Shib, *Journal of Crystal Growth* 2004, 260, 130–135

[5] T. Yu , X. Zhao , Z.X. Shen , Y.H.Wu , W. H. Su, *Journal of Crystal Growth* 2004, 268, 590-595

[6] C. Xu, Yingkai Liu, G. Xu, G. Wang, *Materials Research Bulletin* 2002, 37. 2365-2372

[7] P. Raksa , A. Gardchareon , T. Chairuangsri , P. Mangkorntong , N. Mangkorntong , S. Choopun, *Ceramics International* 2009, 35, 649–652

Keywords: CuO, nanowires, thermal evaporation, nanostructures.

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Gas Sensing Properties of CuO Nanostructures Synthesized by Thermal Evaporation of Copper Metal Plate

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Keywords: Copper oxide, nanowires, thermal evaporation, gas sensitive properties

Abstract. CuO nanostructures were synthesized by thermal evaporation method. Using Cu metal plate at temperature of 400°C for 24 hrs in one atmosphere of oxygen and studied structural and gas sensing properties. The CuO nanostructured were investigated by the stereo microscope (image analyzer), X-ray diffraction, scanning electron microscope. The diameter of CuO nanowires vary from 10 nm to 50 nm and length of several 10 micrometers. The sensitivity of CuO nanostructures and response were performed at room temperature for ethanol and CO_2 sensor.

Introduction

Copper oxide (CuO) is a p-type semiconductor with a narrow band gap (1.2 eV). It is very important industrial materials and using for wide range of applications in gas sensor, magnetic strong media, solar-energy, electronics, catalysis, batteries, semiconductor and varistors [1,4-9]. Recently, CuO nanostructures can be prepared various techniques such as thermal evaporation [2], thermal decomposition [1-4], oxidation reaction and sol-gel [5]. CuO nanorods were synthesized in the circumstances of various molten salts precursor and heat treatment temperatures [1-2]. CuO nanorods with diameters of 5-15 nm and lengths of up to 400 nm were prepared by a simple wet-chemical process [6]. The formation of CuO nanowires were synthesized on copper foils oxidized in wet air at temperatures of 300 - 800 °C [7] and in atmosphere of oxygen at temperatures from 300 °C to 900 °C [8]. The paper reported that CuO nanowires prepared by an oxidation reaction of copper plate heat at 600°C in normal atmosphere, the synthesized products can be studied for ethanol sensor [5]. The CuO powders mixed with $BiTiO_3$ powders were pressed into disks heat at 773 K for 5 hrs, these products were studied CO_2 gas sensor [9]. Crystalline CuO was prepared by heating copper (II) oxide to 900°C for 4 hrs, grounding and then it was pressed into pellets form, these formations were investigated pollution gas sensor, their response for CO and NO_2 [10]. In our paper, we synthesized CuO nanowires by thermal evaporation process. The synthesized products were characterized and studied for ethanol and CO_2 sensors.

Experimental

Copper metal plate size 1cm×1cm was first cleaned by acetone, followed by rinsing with de-ionized water several time and drying by air gun. It was put in alumina boat, and then loaded into the middle of the tube furnace.The furnace was heated at 400°C for 24 hrs in one atmosphere of oxygen with flow rate 2 L/min. After heat treatment, the furnace was cooled drown to room temperature. The black layer on the substrate was peeled for characterization and investigating to ethanol and CO_2 gas sensor. The synthesized products were characterized by the stereo microscope (image analyzer, OLYMPUS, SZX9), X-ray diffraction (XRD: Cu Kα_1 radiation) (Philips X'pert MRD), scanningelectron microscope (SEM) (JEOL 6400). The peeled substrate was performed two electrods using silver paint and copper wires for studying gas sensor. The gas sensing properties were studied at room temperature. The system of gas sensing properties was shown in Fig. 1. Fig. 1a, the sensor was placed at each end of the quartz tube. The electronic circuit of sensor was applied the circuit voltage (V_C) 10 V, acrossed the sensor and the load resistor (R_L = 1 MΩ). The signal

voltage, out put (V_O) was obserbed with time-various 5, 10, 15, 20, 25, 30, 35s while the CO_2 gas or ethanol gas was flowed rate around 5 L/min. The sensitivity, S, of semiconducting gas sensor is generally defined as $S = R_g / R_a$, where R_a and R_g are the resistance of gas sensor in air and gas, respectively [11].

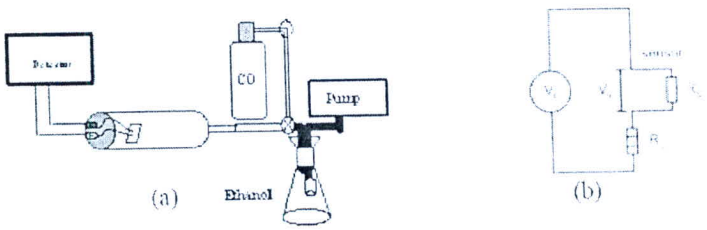


Figure 1. The schematic of measuring electric circuit for gas sensor, (a), and (b) CO_2 and ethanol sensor.

Results and Discussion

When the temperature was cooled down to room temperature, nationally. The copper metal plate was taken from the furnace. We can observed that somethings were occured on the substrate ceatlly different from starting plate. The oxidation reaction is as follow two steps (1) $4Cu + O_2 = 2Cu_2O$ and (2) $2Cu_2O - O_2 = 4CuO$. These proceses were discussed by previous researches [5,6]. Fig. 2. image analyzer showed the formed layer, black ash-like. This black layer was carefully peeled for studying the stuctural and characterization.

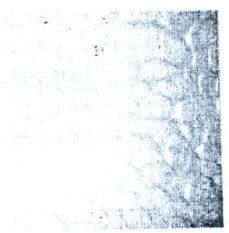
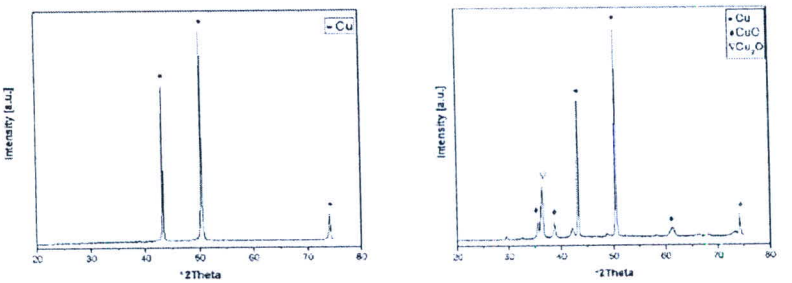


Figure 2. Stereo microscope image of the formed products on copper metal plate in one atmosphere of oxygen.

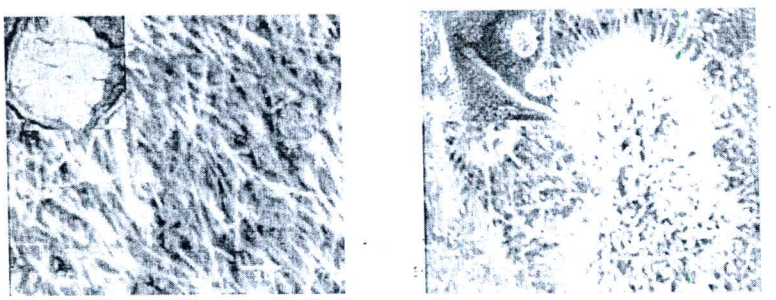
The crystal structure and phase composition were investigated by X-ray diffraction (XRD). The measurements were carried out with a Philips X'pert diffractometer (Cu$k\alpha$; λ=1.540562; Cuka1 filter; 40kv, 35mA), a scanning step of 0.02°. Fig. 3. presented the XRD patterns of the synthesized products. The peak of CuO and Cu_2O phases, (JCPDS 05-0661) are found in this Fig. 3. and CuO-structures were single crystal monoclinic. We can observe the Cu phase in Fig. 3a, before heated treatment. CuO and Cu_2O phase were found in Fig. 3b, after heated treatment and oxidation processes. The morphologies of CuO nanostructures were shown in Fig. 4. SEM images showed the nanostructures materials on black ash–like top layer, the wire-like structures. The diameter of CuO nanowires vary from 10 nm to 50 nm and length of several 10 micrometers. SEM instrument was scanned two areas on peeled substrate. We found different morphologies showed in Fig. 4a, the compact of nanowires and 4b, the clusters of nanowires. We studied the response of gas sensivity using equation $S = R_g / R_a$, where R_a and R_g are the resistance of gas sensor in air and gas, respectively. Fig. 5a shows the resistance of CuO nanostructures sensor to an ethanol and CO_2 gas, operating at room temperature. In atmosphere of normal air, we observed that the measured output voltage and calculated resistances were still steady. When ethanol vapor or CO_2 gas was injected into the quarzt tube. For ethanol gas, the resistances were increasing during rang of time 5-35 s, but under CO_2 gas, the resistances were decreasing at 15 s and 35 s. We can observed that the

time-injection has been affect to the sensitivity of the CuO nanostructures. Fig. 5b presents typical



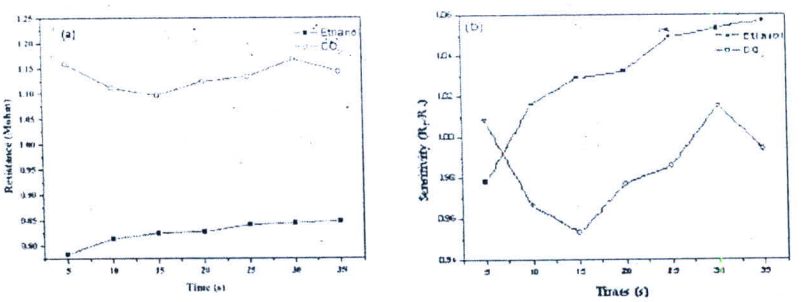
(a) (b)

Figure 3. XRD patterns of (a) copper plate before heat treatment, and (b) the black-ash top layer of copper plate after heat treatment.



(a) (b)

Figure 4. SEM image of the synthesized products under one atmosphere of oxygen. (a) compact nanowires, and (b) cluster of nanowires.



(a) (b)

Figure 5. (a) The resistance of the CuO nanowires sensor at an ethanol and CO_2 gas. (b) The sensitivity of the CuO nanowires sensor at an ethanol and CO_2 gas.

variation in sensitivity of the CuO nanowires sensor to an ethanol or CO_2 gas, operating at room temperature. It is found that the sensitivity of nanostructures depended on more time inject for concentration of ethanol gas. The sensitivity was increasing compared with an increasing time of the detected ethanol gas. The sensitivity of CuO nanowires was decreasing at 15 s and 35 s under CO_2 gas, and increasing during 5-35 s in atmosphere of ethanol gas.

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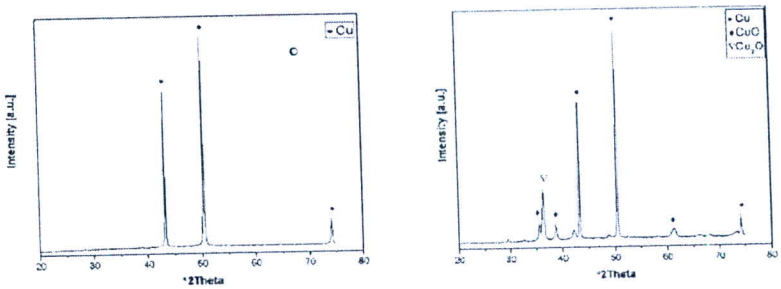

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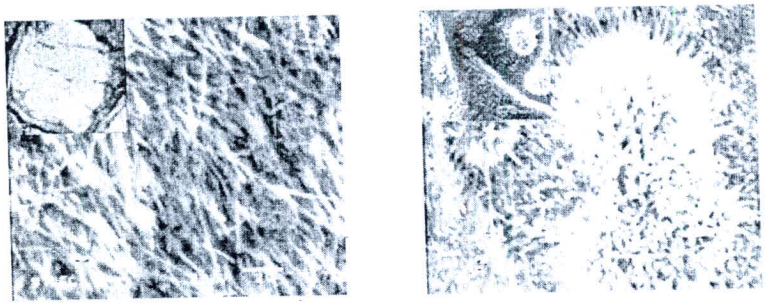

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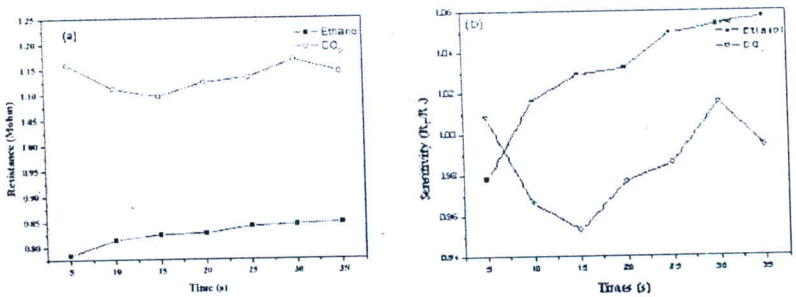

(a) (b)

Figure 5. (a) The resistance of the CuO nanowires sensor at an ethanol and CO_2 gas. (b) The sensitivity of the CuO nanowires sensor at an ethanol and CO_2 gas.

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Conclusion

In summary, CuO nanowires have been synthesized by thermal evaporation at 400 °C under atmosphere of oxygen. The structures characterized by the stereo microscope (image analyzer), X-ray diffraction and scanning electron microscope. The diameter of CuO nanowires very from 10 nm to 50 nm and lengths several 10 micrometers. The results showed the high sensitivity and response of CuO nanowires were performed at room temperature for ethanol and CO_2 gas sensor.

Acknowledgments

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References

[1] C.W. Wang, Z. Liu,Y. Liu, C. Xu, C. Zheng and G. Wang: Appl. Phys. A Vol. 76 (2003), p. 417
[2] W. Jisen, Y. Jinkai, S. Jinquan and B. Ying: Mater. Des. Vol. 25 (2004), p. 625
[3] C. Xu, Y. Liu, G. Xu and G. Wang: Mater. Res. Bulletin Vol. 37 (2002), p. 2365
[4] M.S. Niasari and F. Davar: Mater. Lett. Vol. 63 (2009), p. 441
[5] P. Raksa, A. Gardchareon, T. Chairuangsri, P. Mangkorntong, N. Mangkorntong and S. Choopun: Ceram. Inter. Vol. 35 (2009), p. 649
[6] C.H. Xu , C.H. Woo, S.Q. Shi: Chem. Phys. Lett. Vol. 399 (2004), p. 62
[7] L.S. Huanga, S.G. Yanga, T. Lia, B.X. Gua, Y.W. Dua, Y.N. Lub and S.Z. Shib: J. Cryst. Growth. Vol.260 (2004), p. 130
[8] W. Wang, Y. Zhu, G. Cheng and Y.H. Huang: Mater. Lett. Vol. 60 (2006), p. 609
[9] B. Liao, Q. Wei, K. Wang and Y. Liu: Sens. Actuators. B Vol. 80 (2001), p. 208
[10] A. Cruccolini, R. Narducci and R. Palombari: Sens. Actuators. B Vol. 98 (2004), p. 227
[11] A.V. Kadu, S.V. Jagtap and G.N. Chaudhari: Curr. Appl. Phys. Vol. 9 (2009), p. 1246

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Synthesis and Gas Sensing Properties of SnO_2-CuO Nanocomposites

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Keywords: CuO-SnO_2 Nanocomposite, gas sensors, sensitivity, nanorods.

Abstract. SnO_2-CuO nanocomposites have been synthesized with the simple co-precipitation method for gas sensing properties. Sn and CuO powder were the starting materials. The synthesized products were investigated by X-ray diffraction (XRD) and scanning electron microscopy (SEM). The results show that SnO_2-CuO nanocomposites have a tetragonal and monoclinic structure, respectively. SEM images verify that the some microballs are up to 10 μm and nanorods have a diameter range from 10-100 nm, while length ranges a few micrometers. The nanocomposite products were highly sensitivity to CO_2 gas at room temperature.

Introduction

Nanomaterials have attracted the attention of the scientific community worldwide, especially one-dimension (1D) semiconductor nanomaterials. This is because of their promising potential in extensive applications such as semiconductors. SnO_2, a typical n-type semiconductor, has a wide band gap (Eg = 3.65 eV at 300 K). SnO_2 is an important functional material, which has been extensively used in gas sensor, optoelectronic, transistor and solar cells [1-6]. CuO, a typical p-type semiconductor with a narrow band gap (Eg = 1.2 eV at 300 K) is widely used in catalysts, gas sensor, thermoelectric materials [7-10]. We know that introducing another material to the synthesis of composites is an effective way to improve the physical and chemical properties. Some materials, such as SnO_2, ZnO, ZrO_2, TiO_2, In_2O_3 and CuO are introduced to enhance gas sensing property [11-12]. The fundamental sensing mechanism of metal oxide based gas sensors relies on a charge in electrical conductivity. This conductivity is due to the interaction process between the surface structures of reactive chemical species O^-, O^{2-}, H^+ and OH^- and the gas molecules to be detected [13-14]. Many methods have been developed to prepare such nanostructures, such as vapor-liquid-solid (VLS) growth [15-18] and solution-liquid-solid (SLS) method [19-21]. The previous paper reported how SnO_2-CuO nanocomposites were synthesized by impregnating SnO_2 nanowires with $CuCl_2$ solution at 1000 °C for 1 h with trace amounts of O_2 introduced into furnace. Thereafter the product was submerged in a $CuCl_2$ solution (1 wt%). After air-drying, the sample was heated to 900 °C and kept for 6 h in an air atmosphere [11]. In the simple co-precipitation method, $SnCl_4 \cdot 5H_2O$ and $CuSO_4 \cdot 5H_2O$ are mixed together in distilled water as starting materials. The solution obtained is continuously stirred at 80 °C while an NaOH solution is added at a rate of 0.02 ml/s until complete precipitation (solution pH value above 11). After continuously stirring for another 2 h, the precipitate is filtered and washed thoroughly with distilled water. Finally, the precipitate is dried at 105 °C, for 2 h and calcined at 600 °C for 2 h to obtain CuO-SnO_2 nanocomposites [22].

In this work, SnO_2-CuO nanocomposites have been synthesized by simple co-precipitation method. The nanocomposites are to be used for their gas sensing properties. Sn and CuO powder are the starting materials. The gas sensitivity properties were measured in the room temperature by using ethanol gas, CO_2 gas, and a mixture of the two gasses.

Experiments

Synthesis of SnO_2-CuO nanocomposites

SnO_2-CuO nanocomposites have been synthesized by a simple co-precipitation method. Tin powder (99.0%, Aldrich) and copper oxide powder, with ratio of 1:0.1 by weight, are mixed together in distilled water as the source materials. The obtained solution is continuously stirred at 80 oC while a NaOH solution is added until complete precipitation (solution pH value above 11). After continuous stirring for another 2 h, the precipitate is filtered and cleaned with distilled water several times. Finally, the precipitate is dried at 105 °C for 2 h and calcined at 600 °C for 2 h in normal air. The furnace was cooled down to room temperature through free heat convection. The morphologies of the prepared products were investigated with scanning electron microscopy (SEM; JEOL 6400) and the crystal structure of the products were characterized by X-Ray Diffraction (XRD; Cu □1 radiation) (Philips x' pert MRD).

Preparation of gas sensors

The gas sensors were fabricated by using SnO_2-CuO nanocomposites powder and Polyethylene glycol (PEG) with ratio of 60%: 40% by weight. The two are mixed at 50 °C into slurry before fabricating the sensors [23]. The slurry was painted onto a glass substrate with a size of 1 cm². The nanocompósite products were calcined at 150 °C for 2 hours. The two electrodes are made of copperplate on glass substrate. The distances between the electrodes are around 2 mm. The gas sensing properties were measured at room temperature using ethanol gas, CO_2 gas, and a mixture of the two gasses. The sensitivity, S, of semiconducting gas sensor is generally defined as:

$$S = R_a/R_g$$

Where R_a is the resistance of the sensor in atmospheric air, and R_g is the resistance in the presence of reducing gas [24-26].

Results and Discussion

The morphology of SnO_2-CuO nanocomposite were investigated by SEM as shown in Fig. 1. The high-magnification SEM image of Fig. 1(a), showed that the SnO_2-CuO nanocomposites had some clusters formed as nanorods with a diameter ranging from 10 nm to 100 nm and a length of afew micrometers. Fig. 1(b) shows some microballs with a diameter of about 10 μm.

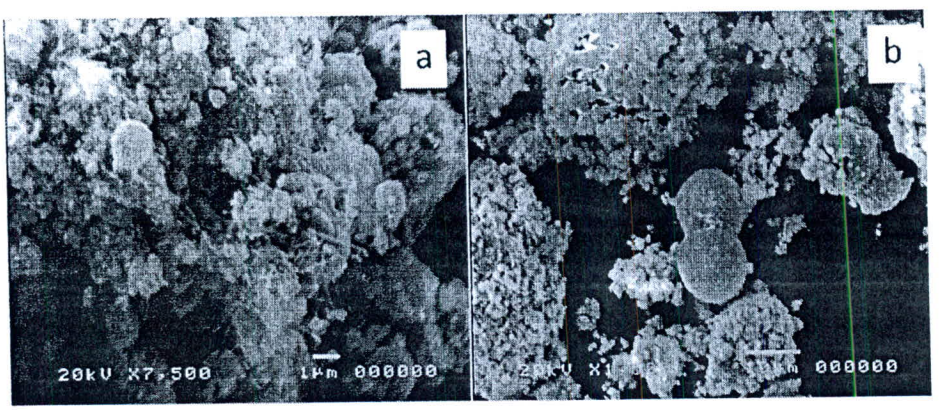

Fig. 1(a)-(b), SEM images of SnO2-CuO nanocomposite

The XRD pattern of SnO_2-CuO nanocomposite is shown in Fig. 2. All of the diffraction peaks were in good agreement with tetragonal phase of SnO_2 (JCPDS No. 41-1445). This revealed that there were many planes of the prepared products corresponding to SnO_2 crystal planes of (110), (101), (200), (211), (220), (002), (310), (112), (202) and (321) respectively and monoclinic CuO (JCPDS No. 05-0661), corresponding to CuO crystal planes of (-111), (111) and (-311) respectively. Percentage weight function of SnO_2: CuO are 95.09%: 5.01% respectively.

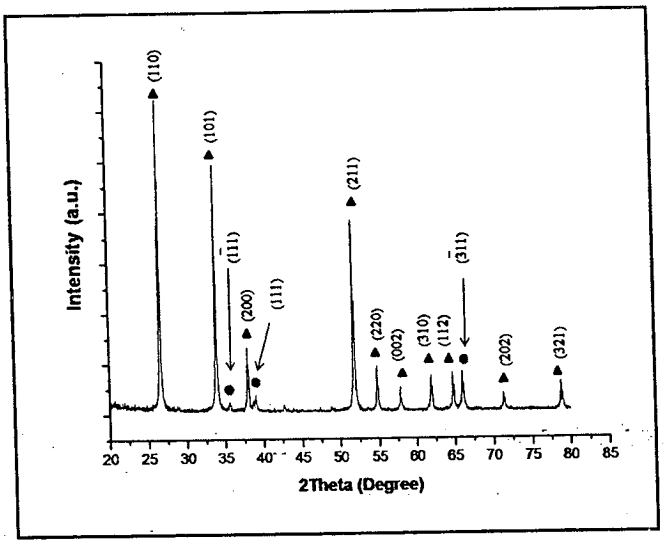

Fig. 2, the XRD pattern of SnO_2-CuO nanocomposite.

The synthesized products were fabricated into sensor for measuring their electrical conductance. Fig. 3, shows changes in sensitivity of the products after the sensors were exposed to ethanol gas, CO_2 gas, and a mixture of the two gasses. The exposure was at a flow rate of approximately 5 L/min at the room temperature. SnO_2-CuO nanocomposite had a higher sensitivity to the pure CO_2 gas over the pure ethanol or the two gas mixture.

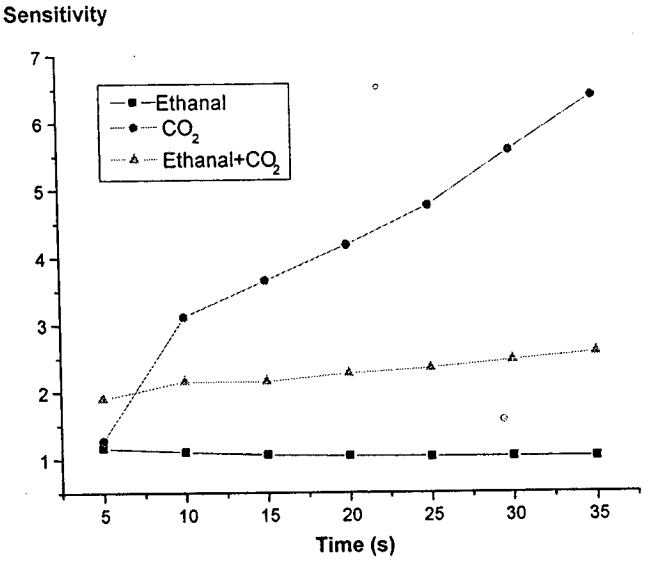

Fig. 3 Sensitivity of SnO_2-CuO nanocomposite of ethanol gas, CO_2 gas, and mixing ethanol with CO_2 gas at the room temperature.

Conclusion

The preparation of SnO_2-CuO nanocomposites has been successfully synthesized by the simple co-precipitation method. These nanaocomposites have shown to have good gas sensing properties. Sn and CuO powder are used as starting materials. The synthesized products were quantified by X-ray diffraction (XRD) and scanning electron microscopy (SEM). The results show that SnO_2-CuO nanocomposites have a tetragonal and monoclinic structure, respectively. SEM images verify that the some microballs have a size of 10 μm and nanorods have a diameter range from 10-100 nm, with length ranging a few micrometers. The gas sensing products are highly sensitivity to CO_2 gas at room temperature.

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References

[1] K. Noipa and S. Pukird: Adv. Mater. Res. Vol. 93-94 (2010), p. 227

[2] M.R. Yang, S.Y. Chu and R.C. Chang: Sens. Actuators. B Vol. 122 (2007), p. 269

[3] L. Xi, D. Qian, X. Tang and C. Chen: Mater. Chem. Phys. Vol. 108 (2008), p. 235

[4] L.V. Thong, L.T. Loan and N.V. Hieu: Sens. Actuators. B Vol. 150 (2005), p. 115

[5] L. Li, F. Zong, X. Cui, H. Ma, X. Wu, Q. Zhang, Y. Wang and J. Zhao: Mater. Let. Vol. 61 (2007), p. 4155

[6] K. Jain, R.P. Pant and S.T. Lakshmikumar: Sens. Actuators. B Vol. 113

(2006), p. 823

[7] T. Yu, X. Zhao, Z.X. Shen, Y.H. Wu and W. H. Su: J. Crystal Growth, Vol. 268 (2004), p. 590

[8] K. Yu, Y. Zhang, L. Luo, H. Geng and Z. Zhu: Mater. Let. Vol. 59 (2005), p. 3525

[9] L. Sun, Z. Zhang, Z. Wang, Z. Wu and H. Dang: Met. Res. Bull Vol. 40 (2005), p. 1204

[10] C. Zhu, C. Chen, L. Hao, Y. Hu and Z. Chen: J. Crystal Growth, Vol. 263 (2004), p. 473

[11] W. Zhou and M. Tan: Optik Vol. 123 (2012), p. 2171

[12] K.Y. Donga, J.K. Choib, I.S. Hwangb, J.W. Leec, B.H. Kanga, D.J. Hama, J.H. Leeb and B.K.Ju: Sens. Actuators. B Vol. 157 (2011), p. 154

[13] X. Kong and Y. Li: Sens. Actuators. B Vol. 150 (2005), p. 449

[14] J. Zhang, S. Wang, Y. Wang, M. Xu, H. Xia, S. Zhang, W. Huang, X. Guo and S. Wu: Sens. Actuators. B Vol. 139(2009), p. 369

[15] J.X. Wang, D.F. Liu, X.Q. Yan, H.J. Yuan, L.J. Ci, Z.P. Zhou, Y. Gao, L. Song, L.F. Liu, W.Y. Zhou, G. Wang and S.S. Xie : Solid State Commun. Vol. 130 (2004), p. 89

[16] Y. Zhag, K. Yu, G. Li, D. Peng, Q. Zhang, F. Xu, W. Bai, S. Ouyang and Z. Zhu : Mater. Lett. Vol. 60 (2006), p. 3109

[17] J.K. Jain, X.L. Chen, W.J. Wang, L. Dai and Y.P. Xu: Appl. Phys. A Vol. 76 (2003), p. 291

[18] C. Zheng, Y. Chu, Y. Dong, Y. Zhan and G. Wang : Mater. Lett. Vol. 59 (2005), p. 2018

[19] L. Yue, G.Y. Qun, T.R. Qin, C. Ping,L. Yong and S.W. Jie: Chinese Sci. Bull. Vol 55 (2010), p.581

[20] W. Wang, Z. Liu, Y. Liu, C. Xu, C. Zheng and G.Wang: Appl. Phys. A Vol. 76 (2003), p. 417

[21] A.S. Ethiraj and D. J. Kang: Nano. Res. Lett. Vol.7:70 (2012), p. 1-5

[22] X.J. Zheng , Y.J. Wei, L.F. Wei, B. Xie and M.B. Wei: Inter. J. Hydro Energy Vol. 35 (2010), p. 11709

[23] H. Wang, J. Liang, H Fan, B. Xi, M. Zhang, S. Xiong, Y. Zhu and Y. Qian : J. Solid State Chem. Vol. 181 (2008), p. 123

[24] J. Liu, X. Huang, G. Ye, W. Lui, Z. Jiao, W. Chao, Z. Zhou and Z. Yu: Sensors Vol. 3 (2003), p. 111

[25] J.C. Sohn, S.E. Kim, Z.W. Kim and Y.S. Yu: Transaction on Electrical and Electronic Mat.Vol. 10 (2009), p. 136

[26] A. Chowdhuri, A. Gupta and K. Sreeivas: Rev. Adv. Mater. Sci. Vol. 4 (2003), p. 76