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Chestnut Bur-Like ZnO Crystals Synthesized by Solar Thermal Evaporation Technique

Min-Sung Kim[1] and Geun-Hyoung Lee[2,*]

[1]*Department of Information & Communication Engineering, Tong-Myong University, 535 Yongdang-dong, Nam-gu, Busan 607-711, Korea*
[2]*Department of Materials & Components Engineering, Dong-Eui University, 995 Eomgwang-no, Busanjin-gu, Busan 614-714, Korea*

Chestnut bur-like zinc oxide crystals were synthesized by the thermal evaporation of zinc sulfide powder without the use of any catalyst. A magnifying lens was used to heat up the zinc sulfide powder. Thermal solar energy was concentrated on the zinc sulfide powder by the magnifying lens. Then the zinc sulfide powder was heated and evaporated within a relatively short time. The zinc sulfide vapor was oxidized in air and the chestnut bur-like zinc oxide crystals were formed. EDX spectrum revealed that the zinc oxide crystals had wurtzite hexagonal structure. A strong green emission was observed in cathodoluminescence spectrum. The thermal evaporation technique using solar energy is one of the techniques to reduce the energy consumption and costs. [doi:10.2320/matertrans.M2012091]

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1. Introduction

The II-VI semiconductor zinc oxide is a promising material for the applications in electronic and optoelectronic devices due to its wide band gap of 3.37 eV and large excitonic binding energy of 60 meV at room temperature. In particular, the wide band gap makes ZnO material a potential candidate for the ultraviolet (UV) light emitting and laser diodes. The large exciton binding energy would allow for efficient room-temperature exciton-based devices to function at a low threshold voltage. UV lasing action has been observed in zinc oxide nanostructures as well as thin films. Thus many studies have been made on the synthesis and application of zinc oxide nanostructures. For synthesizing zinc oxide nanostructures, various methods such as thermal evaporation,[1)] molecular beam epitaxy,[2)] chemical vapor deposition[3)] and pulsed laser deposition[4)] have been used. These methods are generally carried out in vacuum, and so the complicated evacuation system and process are required to use these methods. Therefore studies on the development of simple synthetic method have been attracted considerable attention in recent years. Recently, we have reported a simple synthetic method to synthesize various zinc oxide nanostructures through thermal evaporation and oxidation of metallic zinc source in air.[5–7)]

In this paper, we report a simple method of synthesizing zinc oxide nanostructures through solar thermal evaporation method under air atmosphere. And we also report the successful synthesis of chestnut bur-like zinc oxide nanostructures using this solar thermal evaporation method. Particularly, solar energy, not electricity, was used as the heat source to vaporize zinc source material. This method is very much effective in reducing energy consumption and costs.

2. Experimental Procedure

Zinc sulfide powder (purity, 99.99 mol%) with spherical shape was used as the source material to synthesize zinc oxide crystals. The diameter of the zinc sulfide powder was approximately 4 μm. The zinc sulfide powder was loaded into an alumina crucible. Sunrays were focused directly onto the zinc sulfide powder through a magnifying lens. Then thermal solar energy was concentrated on the zinc sulfide powder. A schematic of the experimental environment is shown in Fig. 1. The diameter and the focal length of the lens were 127 and 100 mm, respectively. The diameter of focal area was about 2 mm. The solar energy heated up a small amount of zinc sulfide powder in the focal area. The temperature was increased rapidly to the melting point of zinc sulfide within a few seconds. Heating the zinc sulfide powder produced zinc sulfide vapor. The zinc sulfide vapor was oxidized in air. The product after the oxidation was collected for characterization. The morphology of the oxidation product was examined by scanning electron microscopy (SEM). Fourier transform infrared spectrometer (FTIR) was used to investigatethe crystal structure of the product. Cathodoluminescence (CL) was measured at room temperature.

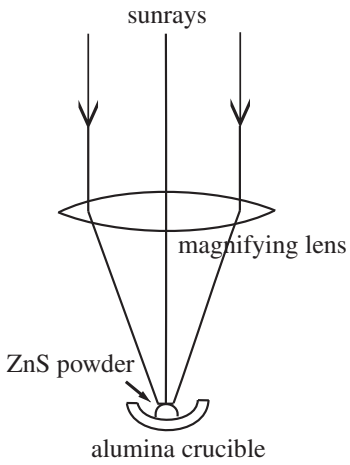

Fig. 1 The schematic of experimental environment.

*Corresponding author, E-mail: ghl@deu.ac.kr

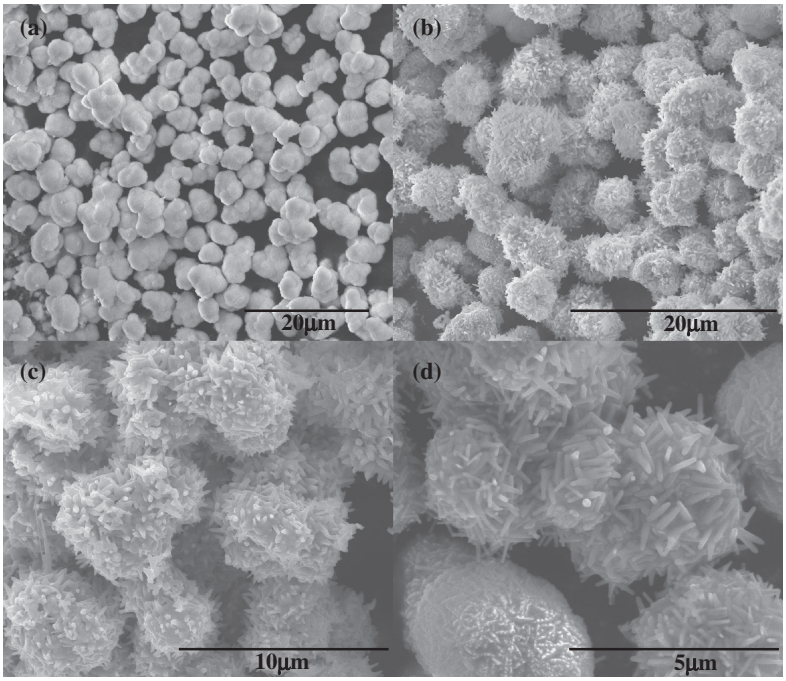

Fig. 2 SEM images of (a) zinc sulfide source powder and (b), (c), (d) the as-prepared product.

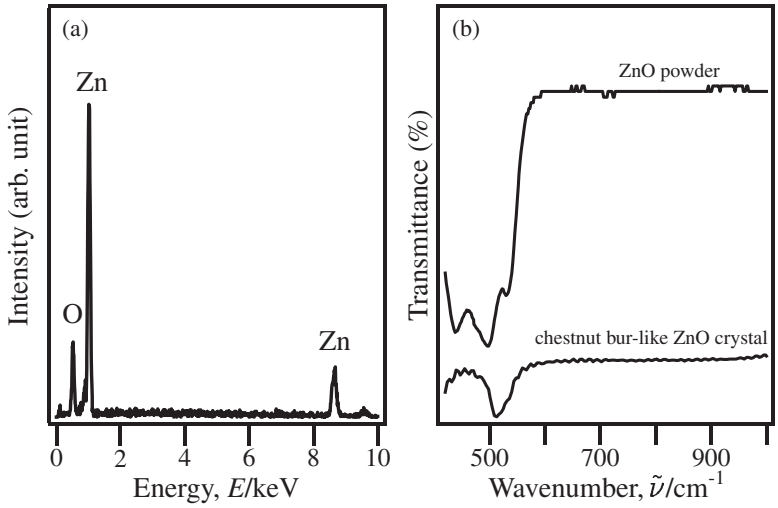

Fig. 3 EDX and FTIR spectra of the as-prepared product.

3. Results and Discussion

The morphology of the as-prepared product was observed by SEM. Figure 2 shows SEM images of zinc sulfide source powder and the as-prepared product. Figure 1(a) shows the SEM image of the zinc sulfide source powder. Parts b, c and d of Fig. 1 show the SEM image of the as-prepared product with different magnifications. The zinc sulfide powder has spherical shape and an average diameter of 4 μm. As shown in Fig. 1(b), the as-prepared product consists of particles with a chestnut bur-like structure with a diameter in the range of 3–5 μm. Each chestnut bur-like particle is composed of numerous nanorods protruding from the center. The nanorods have diameters of 100–200 nm and lengths of 1–2 μm.

Figure 3 represents (a) the EDX and (b) FTIR spectrum of the as-prepared product. For comparison, FTIR spectrum was also measured for commercial zinc oxide powder (purity, 99.99 mol%). EDX analysis reveals that the product is composed of zinc and oxygen elements. Any other impurities including sulfur were not detected in the EDX spectrum, which indicates the product is zinc oxide material with high purity. The FTIR spectrum was acquired in the range of 40000–100000 m^{-1}. In the FTIR spectrum of commercial zinc oxide powder, the absorption bands are observed around wave numbers of 46000, 50000 and 53500 m^{-1}. The absorption peaks at 43000, 46400, 50000 and 53500 m^{-1} have been usually observed for zinc oxide particles.[8–10] Meanwhile, a strong absorption band at 52000 m^{-1} is observed in the FTIR spectrum of the chestnut-bur like zinc oxide crystals. It has been reported that the band at 52000 m^{-1} is correlated to zinc oxide nanorods with wurtzite hexagonal structure.[11,12] Consequently, it is suggested that

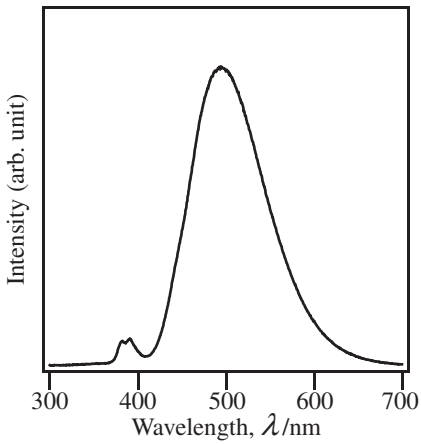

Fig. 4 Room temperature CL spectrum of the chestnut bur-like zinc oxide crystals.

the band at 52000 m^{-1} was attributed to the zinc oxide nanorods on the chestnut-bur like zinc oxide crystals.

Then, let infer the growth mechanism of the chestnut bur-like zinc oxidecrystals. First, zinc sulfide spheres are oxidized by oxygen in air and thin zinc oxide layer is formed naturally on their surface. Next, the cleavages, which provide nucleation sites for the growth of zinc oxide nanorods, are formed on the sphere surface due to a lattice mismatch between zinc sulfide and zinc oxide. Then zinc sulfide vapor, which is diffused out to the zinc oxide surface from zinc sulfide core through the cleavages in the zinc oxide layer, reacts with oxygen in air and zinc oxide nanorods are grown from the zinc oxide surface via vapor-solid mechanism. Then sulfur diffuses away from the zinc oxide surface as sulfur dioxide. This is very similar to the growth mechanism of chestnut bur-like zinc oxide structures proposed by Gui *et al.*[13)]

Figure 4 shows the room temperature CL spectrum of the chestnut bur-like zinc oxide crystals, measured with a typical electron beam of 15 keV. The spectrum exhibits a strong green emission peak at 510 nm and a weak UV emission peak at 380 nm. It is well known that the UV emission called near band edge emission is originated due to a recombination of free-excitons, and the origination of the green emission is due to the recombination of a photogenerated hole with an electron belonging to the oxygen vacancy.[14,15)] Huang *et al.* proposed that strong green emission peak was observed from zinc oxide nanowires because of great fraction of surface and sub-surface oxygen vacancy, which was caused by the high surface-to-volume ratio of nanowires.[16)]

On the other hand, in our previous experiments, the morphology of the zinc oxide crystals was mainly dependent on the light-gathering power of the lens rather than atmosphere conditions such as temperature and humidity, whereas the luminescence property of the zinc oxide crystals depended on the type of source material.

4. Conclusions

A novel chestnut bur-like zinc oxide crystal was prepared by a simple thermal evaporation method using solar energy as heat source. The method is simpler, low energy consumption and low cost process in comparison to the conventional thermal evaporation. In addition, the synthetic method using solar energy would be a green technology to reduce environmental pollution. On the other hand, the chestnut bur-like zinc oxide crystal was composed of numerous nanorods with sharp tips protruding from the spherical core. The chestnut-like zinc oxide crystals have potential for applications in chemical sensors with high sensitivity and field emitter with high performance due to their large surface area and sharp tip morphology.

REFERENCES

1) N. K. Park, G. B. Han, J. D. Lee, S. O. Ryu, T. J. Lee, W. C. Chang and C. H. Chang: Curr. Appl. Phys. **6** (2006) 176–181.
2) Y. W. Heo, V. Varadarajan, M. Kaufman, K. Kim, D. P. Norton, F. Ren and P. H. Fleming: Appl. Phys. Lett. **81** (2002) 3046–3048.
3) W. Lee, M. C. Jeong and J. M. Myoung: Acta Mater. **52** (2004) 3949–3957.
4) Z. W. Liu and C. K. Ong: Mater. Lett. **61** (2007) 3329–3333.
5) G. H. Lee and J. H. Song: Appl. Surf. Sci. **256** (2010) 2837–2840.
6) G. H. Lee and M. S. Kim: Mater. Trans. **50** (2009) 2121–2123.
7) G. H. Lee and C. Allen: J. Ceram. Soc. Jpn. **117** (2009) 111–114.
8) L. Wu, Y. Wu and W. LÜ: Physica E **28** (2005) 76–82.
9) M. Salavati-Niasari, F. Davar and M. Mazaheri: Mater. Lett. **62** (2008) 1890–1892.
10) B. Ranjan, M. Kailasnath, N. Kumar, P. Radhakrishnan, S. Achari and V. P. N. Nampoori: AIP Conf. Rroc. **1147** (2009) 287–296.
11) R. Wahab, S. G. Ansari, Y. S. Kim, H. K. Seo, G. S. Kim, G. Khang and H. S. Shin: Mater. Res. Bull. **42** (2007) 1640–1648.
12) L. Wu, Y. Wu, Y. Shi and H. Wei: Rare Metals **25** (2006) 68–73.
13) Y. Gui, C. Xie, Q. Zhang, M. Hu, J. Yu and Z. Weng: J. Cryst. Growth **289** (2006) 663–669.
14) X. Wang, J. Song and Z. L. Wang: Chem. Phys. Lett. **424** (2006) 86–90.
15) J. Q. Hu, Y. Bando, J. H. Zhan, Y. B. Li and T. Sekiguchi: Appl. Phys. Lett. **83** (2003) 4414–4416.
16) M. H. Huang, Y. Wu, H. Ferick, N. Tran, E. Weber and P. Yang: Adv. Mater. **13** (2001) 113–116.