Available online at www.sciencedirect.com

ScienceDirect

Ceramics International 34 (2008) 1081–1083

CERAMICS INTERNATIONAL

www.elsevier.com/locate/ceramint

Study of ZnSe powder mass depleted in temperature field

Minqiang Wang *, Xiao Huo, Jianping Li, Zhonghai Lin, Xi Yao

Electronic Materials Research Laboratory, Key Laboratory of Ministry of Education, Xi'an Jiaotong University, Xi'an 710049, China

Available online 7 October 2007

Abstract

Evaporative crystallization of nano-particles involves a complicated multiphase mass and heat transfer process that is dependent on the crystal size in a temperature field. It becomes more complicated for the crystallization of ZnSe powders using this method because of multiprocesses including sublimation, crystallization, and decomposition. This work reports our preliminary studies on the evaporation process to two different sizes of ZnSe powders. We investigated the influences of crystal size on mass depleted between 200 and 800 °C. On the basis of our experimental data, a model of mass depleted of ZnSe nano- and micro-powder was proposed.

Keywords: Powder; XRD; Thermogravimetry; ZnSe

1. Introduction

ZnSe is an important semiconductor with a typical wide band gap of 2.58 eV which has excellent optical properties for blue light laser diodes, infrared laser diodes, and photoelectron devices [1,2]. ZnSe thin film is an important material of photoconductive and fluorescence devices. As a result, its preparation has been studied extensively. The property of powder mass depleted in temperature field is investigated using flash evaporation method which is simple and inexpensive as compared with some traditional film methods such as molecular beam epitaxy (MBE), sputtering, deposition from binary vapors, etc. There are various film materials that have been obtained by flash evaporation method [3–5]. And the preparation technology and method of superfine particles was well established in recent years [6–10], especially concerning the nano-sized powder [11–15]. Flash evaporation and evaporative crystallization is a complicated multiphase mass and heat transfer process [16]. In a given temperature field, the behaviors of nano-sized powders are complicated since evaporation, sublimation, decomposition and crystallization happen simultaneously, and these properties also have a relationship with the powder size.

In this work, ZnSe powder is chosen as a target material to study the mass depleted in temperature field. There are several methods [17–20] to obtain ZnSe nano-sized powder, while the method reported in this work is simple which can be expanded to industrialize nano-sized powders.

2. Experimental procedure

Zinc and selenium powder with a nominal purity of 99.999% were used as the starting materials. Given amounts of Zn and Se powders with an atomic ratio of 1:1 was added into the hardened steel vial that contains several steel balls. Powders after milling for 10 and 50 h were chosen in this experiment. The 10-h-milled powder was annealed at 400 °C for 1 h. X-ray diffraction curves of the samples were measured using apparatus (Rigaku, RAD) with Cu Kα radiation (1.54065 Å). Three parts of ZnSe powders were used as experimental materials to study the mass depleted in temperature field.

Thermogravimetry (TG) was measured by TGA/SETA851e. These powders were first heated at 100 °C for 30 min to remove the absorbed water. Then the temperature began to increase from 100 to 800 °C in 7 min with an aim to simulate a flash evaporation condition. All powders were protected under nitrogen environment during the TG experiment.

* Corresponding author.
E-mail address: mqwang@mail.xjtu.edu.cn (M. Wang).

0272-8842/$34.00 © 2007 Published by Elsevier Ltd and Techna Group S.r.l.
doi:10.1016/j.ceramint.2007.09.104

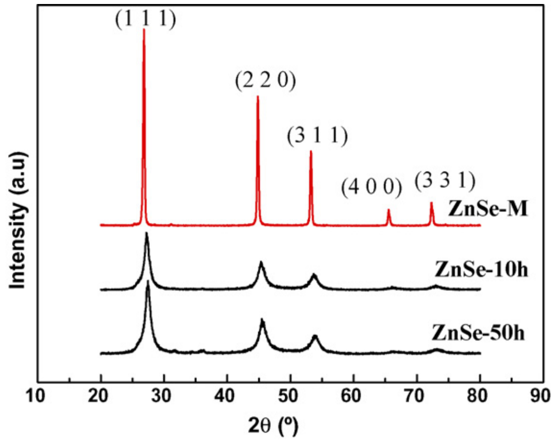

Fig. 1. XRD of three difference mean sizes powder, ZnSe-M is the one that 10-h-milled powder taken an anneal process, ZnSe-10 h and ZnSe-50 h are the powders that have been milled for 10 and 50 h, respectively.

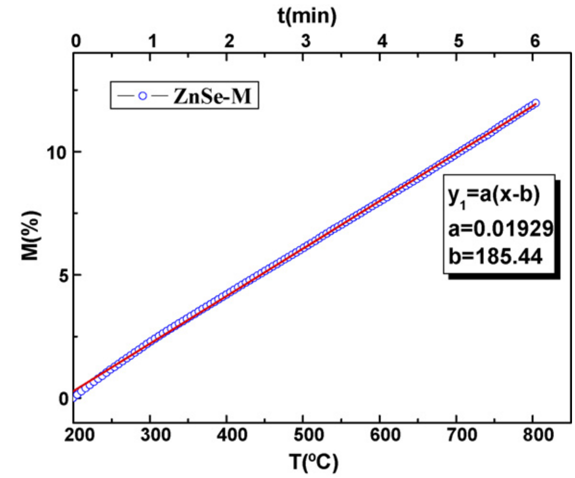

Fig. 2. Mass loss curve (MLC) of micro-sized powder and the simulation.

3. Results and discussion

X-ray diffraction patterns of the samples (Fig. 1) indicated that the milled ZnSe powder crystallized in a sphalerite structure with no traces of other byproducts. The samples were pure ZnSe except for a minor amount of ZnO in 50-h-milled powder, which did not influence the mass depleted property of ZnSe. Table 1 shows the mean sizes estimated by XRD curve. XRD patterns of the first two powders demonstrate the mean size of powder is at nanoscale and that of the last one is at micron level. Although, the data showed in Table 1 cannot give precise powder size, these data can be used to compare the sizes of powder. It is clear that the particle of 50-h-milled powder is smaller than 10-h-milled powder, and the particle of annealed powder is much bigger than the others. In Fig. 2, the curve is of annealed powder which is named ZnSe-M; the mass loss curve (MLC) is linear, which demonstrates there is only one process of evaporation; the powder is steady enough in this temperature field. The simulation expression is given in the inset, in which the parameter (a) is related to flash evaporation velocity and (b) is related to the initiation temperature of analysis. Figs. 3 and 4 show the MLC of 10-h-milled powder and 50-h-milled powder. And these two curves can be analyzed to two different rules. The linear loss is caused by evaporation, while the nonlinear loss is caused by decomposition and crystallization. The nonlinear loss of 10-h-milled powder only appeared between 450 and 600 °C, while that of 50-h-milled powder appeared between 400 and 550 °C Comparing these two mass loss curves relative to two different mean size nano-powders showed in Figs. 3 and 4, the linear mass depleted is weaken and the nonlinear mass depleted is scaled up in Fig. 4. The nonlinear

Table 1
Mean sizes of the three powder calculated by XRD

Samples	Mean size (nm)
ZnSe-M	453.54
ZnSe-10 h	96.1
ZnSe-50 h	88.3

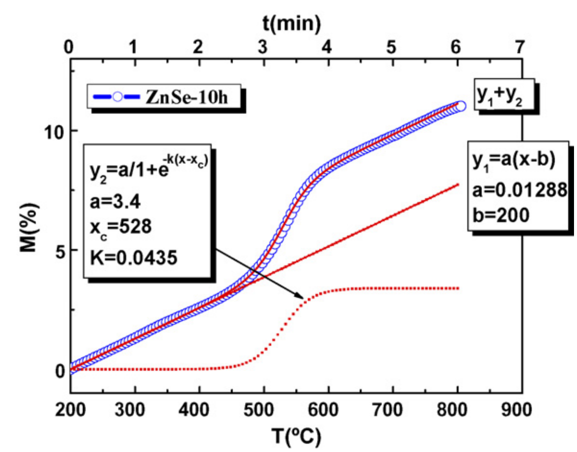

Fig. 3. Mass loss curve (MLC) of 10-h-milled powder and the simulation.

mass loss of 10-h-milled powder is 28% in the whole loss, and that of 50-h-milled powder is 60.7%. Math simulations of these two curves shared the same expression except for the parameters (a), (K) and (X_c). The parameters in math simulation expression have different physical meanings: (a) is the mass

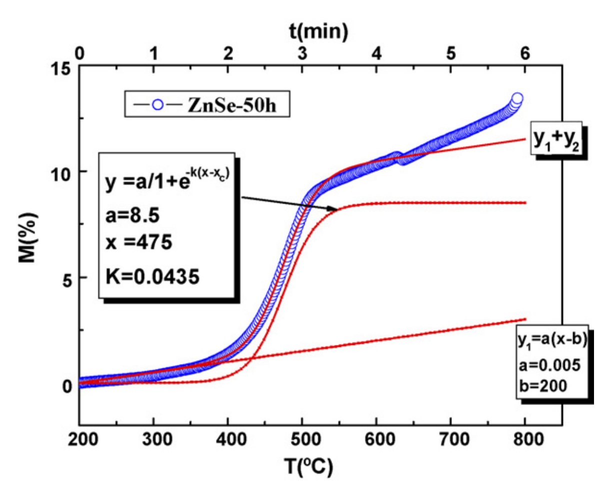

Fig. 4. Mass loss curve (MLC) of 50-h-milled powder and the simulation.

depleted of nonlinear loss. (K) is the parameter of temperature velocity, because the condition of TG experiments are the same, (K) is also the same for two curves. (X_c) is the center temperature of the nonlinear process, which shows the nonlinear mass loss shift towards low-temperature area compared 50-h-milled powder with 10-h-milled powder. It is the evidence that the mean size of the powder has relationship with the flash evaporation property. Nano-sized powder has a lower decomposition and crystallization temperature.

4. Conclusions

The mean size of powder has an effect on the property of TG in flash evaporation temperature field. The mass loss curve is different between micro-sized powder and nano-sized powder; there is only linear loss curve of micro-sized powder, and the curve of nano-sized powder is added by two different rules. The center temperature of nonlinear loss is related to the mean size of powder. Compared 50-h-milled powder with 10-h-milled powder, there is a shift of 50 °C towards lower temperatures. The mass loss curve has been simulated and the linear and nonlinear curves are fitted to obey an expression of $a(x - b)$ and $a/1+e^{-k(x - X_c)}$.

Acknowledgements

This work was supported by the Ministry of Sciences and Technology of China through 973-project under grant 2002CB613305, the Science and Technology Developing Project of Shaanxi Province (2006K06-G15) and Xi'an Science and Technology Developing Project (GG5040).

References

[1] K. Katayama, H. Yao, F. Nakanishi, et al., Lasing characteristics of low threshold ZnSe-based blue/green laser diodes grown on conductive ZnSe substrates, Appl. Phys. Lett. 73 (1998) 102–104.

[2] M.Q. Wang, Y.P. Wang, X. Yao, et al., In-situ growth and spectrum characterization of ZnSe nanocrystals in silica gel-glasses, Chin. Sci. Bull. 49 (2004) 747–750.

[3] A. Bayramov, H. Najafov, A. Kato, et al., Feasibility of TFEL application of Ce-doped $CaGa_2S_4$ and $SrGa_2S_4$ films prepared by flash evaporation method, J. Phys. Chem. Solids 64 (2003) 1821–1824.

[4] P. Malar, S. Kasiviswanathan, Characterization of stepwise flash evaporated $CuIn_3Se_5$ films, Solar Energy Mater. Solar Cells 85 (2005) 521–533.

[5] M. Rusu, P. Gashin, A. Simashkevich, Interface characterisation of ZnSe/$CuGaSe_2$ heterojunction, Solar Energy 72 (2002) 235–241.

[6] X. Li, H. Liu, J.Y. Wang, et al., Preparation of YAG: Nd nano-sized powder by co-precipitation method, Mater. Sci. Eng. A 379 (2004) 347–350.

[7] Y. Li, J.P. Zhao, B. Wang, Low temperature preparation of nanocrystalline $Sr_{0.5}Ba_{0.5}Nb_2O_6$ powders using an aqueous organic gel route, Mater. Res. Bull. 39 (2004) 365–374.

[8] T. Ko, D.K. Hwang, Preparation of nanocrystalline lead zirconate powder by homogeneous precipitation using hydrogen peroxide and urea, Mater. Lett. 57 (2003) 2472–2479.

[9] C.L. Chen, W.C.J. Wei, Sintering behavior and mechanical properties of nano-sized Cr_3C_2/Al_2O_3 composites prepared by MOCVI process, J. Eur. Ceram. Soc. 22 (2002) 2883–2892.

[10] K.K. Rao, T. Banu, M. Vithal, et al., Preparation and characterization of bulk and nano particles of $La_2Zr_2O_7$ and $Nd_2Zr_2O_7$ by sol–gel method, Mater. Lett. 54 (2002) 205–210.

[11] Y.Q. Wu, G.X. Lu, S.B. Li, Study of preparation and photocatalytic activity of nanosized WO_3 powder, Acta Chim. Sinica 62 (2004) 1134–1138.

[12] C.F. Chen, Z.G. Chen, Preparation of the nano sized Al_2O_3 powder, Rare Metal Mater. Eng. 31 (2002) 12–15.

[13] B.R. Li, X.H. Wang, M.Y. Yan, L.T. Li, Preparation and characterization of nano-TiO_2 powder, Mater. Chem. Phys. 78 (2003) 184–188.

[14] X.F. Zhou, D.B. Chu, C.J. Lin, Anodic dissolution of spongy titanium in ethanol solution for preparation of nano-sized TiO_2 powder, Electrochim. Acta 47 (2002) 2769–2773.

[15] X.F. Qian, J. Yin, J.C. Huang, et al., The preparation and characterization of PVA/Ag_2S nanocomposite, Mater. Chem. Phys. 68 (2001) 95–97.

[16] P.Y. Zheng, J.S. Yu, S.P. Zhang, et al., Study of heat and mass transfer patterns in evaporative crystallization systems, Sci. Technol. Eng. 6 (2006) 1002–1007.

[17] J. Che, X. Yao, H.Q. Jian, M.Q. Wang, Application and preparation of ZnSe nanometer powder by reduction process, Ceram. Int. 30 (2004) 1935–1938.

[18] H.Y. Li, W.Q. Jie, K.W. Xu, Growth of ZnSe single crystals from Zn–Se–$Zn(NH_4)3Cl_5$ system, J. Cryst. Growth 279 (2005) 5–12.

[19] X.F. Fei, G.Y. Shan, X.G. Kong, et al., Preparation of CdSe/ZnSe core-shell nanocrystal in one-step reaction, Chem. Res. Chin. Univ. 21 (2005) 728–733.

[20] H.Y. Xie, J.G. Liang, Y. Liu, et al., Preparation and characterization of overcoated II–VI quantum dots, J. Nanosci. Nanotechnol. 5 (2005) 880–886.