Effect of *in situ* annealing on structure and optical properties of ZnTe nanoparticles produced by pulsed laser ablation

IOP Publishing Journal of Physics: Conference Series **59** (2007) 716–719
doi:10.1088/1742-6596/59/1/152 Eighth International Conference on Laser Ablation

Effect of *in situ* annealing on structure and optical properties of ZnTe nanoparticles produced by pulsed laser ablation

Takaaki Orii[1,2,3], Makoto Hirasawa[1,2], and Takafumi Seto[1,2],

[1]Research Consortium for Synthetic Nano-Function Materials Project (SYNAF), National Institute of Advanced Industrial Science and Technology (AIST), Central 2, 1-1-1 Umezono, Tsukuba, Ibaraki, 305-8568, Japan

[2]Also at: Advanced Manufacturing Research Institute (AMRI), National Institute of Advanced Industrial Science and Technology (AIST), AIST East, 1-2-1 Namiki, Tsukuba, Ibaraki 305-8564, Japan

[3]Present address: Nanoparticle Characterization Laboratory, Center for Intellectual Property Stratages, RIKEN (The Institute of Physical and Chemical Research), 2-1 Hirosawa, Wako-Shi, Saitama 351-0198, Japan

E-mail: t.orii@riken.jp

Abstract. An improvement in morphology, crystallinity, and optical property of ZnTe nanoparticles produced by pulsed laser ablation (PLA) was achieved by *in situ* annealing. ZnTe nanoparticles produced in argon gas ambience by PLA were annealed in the gas flow at a temperatures T_a ranging from 300 °C to 800 °C and size-selected by a differential mobility analyzer. The bimodal size distribution of the ZnTe nanoparticles changed to unimodal at T_a = 600 °C. In this condition, the shape of the monodispersed ZnTe nanoparticles, classified into around 20 nm, became uniformly spherical and their crystallinity estimated by x-ray diffraction was extremely improved. These improvements by the *in situ* annealing were examined for ZnTe nanoparticles produced from off-stoichiometric target. Although the optical property of ZnTe nanoparticles produced from a zinc rich target was improved, those produced from a tellurium rich target could not be improved. It was found that the effect of *in situ* annealing on optical properties of ZnTe nanoparticles was dependent upon its content.

1. Introduction

Nanoparticles exhibit a variety of properties that differ from those of bulk materials and as such have been of interest to many researchers over the last few decades. Especially, a modification of the electronic states of semiconductor nanoparticles using the quantum confinement effect[1-3] is expected as a hopeful strategy for creating a novel material for optoelectronic devices. Actually, all kinds of nanoparticles, e.g. Cd-chalcogenide, silicon, gold, silver and so on, have been synthesized by various methods and have exhibited size dependent properties[4, 5]. In recent years, synthesis of nanoparticles from more complex materials such as alloys, multinary compounds, and metal-doped semiconductors has been attempted in anticipation of higher or multiple functions. Pulse laser ablation (PLA) is an effective method for producing nanoparticles from such complex materials[6] since it can vaporize a mixture of materials while maintaining the original composition[7]. Various compound

semiconductor nanoparticles have been produced by PLA in inert gas ambience[8]. However, in many cases, semiconductor nanoparticles produced by PLA have not exhibited the desired electronic and optical properties depending on size due to poor morphology and crystallinity.

In this work, we describe a post annealing process (PAP) which provides an improvement in the morphology and crystallinity of size-selected ZnTe nanoparticles produced by PLA. The transition of morphology, crystallinity and optical properties of ZnTe nanoparticles induced by the *in situ* annealing were evaluated by scanning electron microscope (SEM), x-ray diffraction (XRD) and Raman scattering spectroscopy. Moreover, an influence of the atomic content of ZnTe nanoparticle on the effect of PAP was examined by electron probe microanalysis (EPMA). Finally, optical properties of the monodispersed ZnTe nanoparticles treated with PAP were discussed.

2. Experiments

The monodispersed ZnTe nanoparticles were produced by PLA of ZnTe targets in an Ar background gas. The basic concept of the experimental setup has been reported previously[9]. It is composed of a laser ablation chamber, an electric furnace, a differential mobility analyzer (DMA) and a deposition chamber. The second-harmonic of an Nd: YAG laser (λ = 532 nm, pulse energy: 20 mJ, pulse duration: 7 ns, repetition rate: 20 Hz) was focused on the ZnTe target rotated at 2 rpm. The ZnTe targets were compacted by compression of a micron-sized powder with varying Zn:Te stoichiometry. The ratios of Zn to Te were prepared into 6:4 and 4:6 by blending Zn powder or Te power with ZnTe powder. Nanoparticles formed in the ablation chamber were transferred with the Ar gas flow, and passed through a quartz tube heated by the furnace for the PAP. The PAP acted to improve the morphology of agglomerate species of primary particles and the crystallinity of the primary particles. The temperature was controlled from room temperature (RT: 25 °C) to 800 °C. Then, the annealed nanoparticles were introduced into the DMA for size classification. Since a part of the primary particles generated by PLA has an electric charge, the DMA can analyze the size of the nanoparticles without an additional ionizer. The flow rates of Ar gas introduced into the ablation chamber and Ar sheathe gas in the DMA were adjusted by mass flow controllers at 0.2 slpm (standard liter / min) and 1.0 slpm, respectively. In this gas flow condition, the pressure of Ar gas in the ablation chamber was 1.3 kPa and the residence time of nanoparticles in the PAP was approximately 1 sec. The size-selected ZnTe nanoparticles were deposited on Si substrates.

The geometric particle size and morphology of size-selected ZnTe nanoparticle deposited film was observed by SEM (JEOL, JSM-6700F). The content of the deposited films was evaluated by EPMA: (HITACHI S-3500N). XRD pattern was measured using Cu Ka x-ray source (Rigaku RINT2000). Raman scattering spectra were measured using a triple-pass polychromator system (Jasco TRS600) equipped with a charge-coupled device. The excitation light was the 514.5 nm line of an Ar^+ laser.

3. Results and Discussion

It is well known that the size distribution of the primary particles, such as clusters and nanocrystals, generated by PLA in gas ambience is mainly dependent on the gas pressure[10]. And the primary particles aggregate and compose small agglomerate species. The size distribution of the agglomerate species generated by PLA of the stoichiometric ZnTe target in Ar background gas was measured by the DMA equipped with ion collector and electrometer. Figure 1 shows changes in size distribution of ZnTe nanoparticles with annealing temperature T_a. The size distribution at T_a = 300 °C was broad and bimodal with two peaks at approximately 15 and 22 nm. In general, the major component at the smaller size is considered the primary particles and the other is attributed to the agglomerate species. The peak of the agglomerate species decreased its larger size component at T_a = 500 °C and exhibited an obvious peak at about 22 nm. When T_a increased to 600 °C, the peak of the agglomerate species deflated and the peak in primary particles shifted slightly to a smaller size. This change of size distribution depending on T_a is explained by a decrease in the mobility-equivalent diameter due to the sintering and crystallization of the agglomerate and amorphous species. Therefore, the improvement of the morphology and the crystallinity of ZnTe nanoparticles suspended in gas flow occurs at about

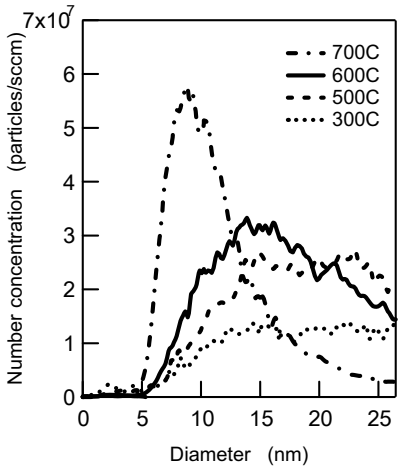

Figure 1. Size distributions of the ZnTe nanoparticles produced by PLA of stoichiometric ZnTe targets with various annealing temperature.

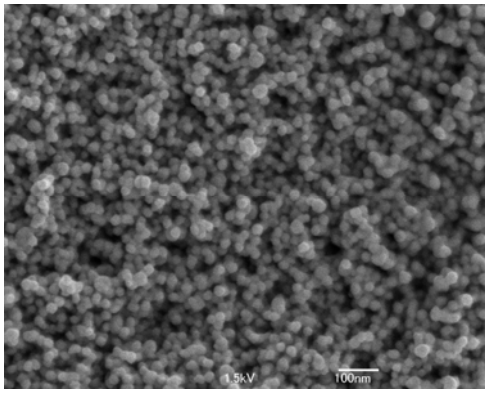

Figure 2. SEM image of monodispersed ZnTe nanoparticles classified as 20 nm by DMA.

T_a = 600 °C. When T_a was increased to 700 °C, the peak drastically shifted to smaller size (8 nm). We believed that the ZnTe nanoparticles vaporized at T_a = 700 °C in the furnace, and then the nanoparticles formed again from the vapor at the downstream region.

Figure 2 shows a typical SEM image of the ZnTe nanoparticles classified as 20 nm. The nanoparticles were produced from the stoichiometric target (Zn:Te = 5:5) and annealed at 600 °C. It reveals that the size-selected ZnTe nanoparticles were spherical and of uniform size. When the value of T_a was not sufficiently high, many coalescent species composed of smaller particles and clustesr were observed.

Figure 3 shows the annealing temperature dependence of XRD pattern of the ZnTe nanoparticles produced from the Zn rich target (Zn:Te = 6:4) and classified as 15 nm. Although the diffraction patterns of the nanoparticles annealed at a temperature lower than 500 °C were broad, all diffraction patterns indicated the zinc-blende structure and no peaks corresponding to metallic zinc. The XRD peak narrowed gradually with an increase in the annealing temperature. Especially, the peak width narrowed drastically at T_a = 600 °C. We simulated the XRD pattern using the Scherrer formula assuming that the ZnTe nanoparticles have a monodispersed size distribution at 15 nm and ideal crystallinity. In comparison with the simulated curve, the crystallinity of ZnTe nanoparticles annealed at T_a = 600 °C was extremely high. A similar annealing temperature dependence of the XRD pattern was observed for ZnTe nanoparticles produced from the stoichiometric target. This annealing temperature dependence of XRD pattern coincides with the above mentioned annealing temperature dependence of the size distribution. We confirmed the content of ZnTe particles with the EPMA. According to the results, the Zn to Te ratio of ZnTe particles without annealing was almost conserved in that of the target. However, the excess zinc content decreased rapidly with an increase in the annealing temperature and reached the stoichiometric ratio at T_a = 300 °C. Therefore, the change of XRD pattern with increasing temperature from 300 °C to 600 °C corresponds to the crystallinity improvement of stoichiometric ZnTe nanoparticles. It was found that the crystallization of ZnTe nanoparticles (15 nm) suspended in gas flow proceeds at temperatures higher than 500 °C and the crystallinity was improved to nearly single crystalline quality by annealing at T_a = 600 °C within 1 sec.

Figure 4 shows Raman spectra of ZnTe nanoparticles produced from the three targets (Zn:Te = 6:4, 5:5, 4:6). The nanoparticles were annealed at T_a = 600 °C and classified into 10 nm. Many sharp peaks were observed for the ZnTe nanoparticles produced from the Zn rich target and the stoichiometric one. These Raman shifts of 206, 411, 618, and 822 cm^{-1} corresponds to fundamental LO phonon mode and

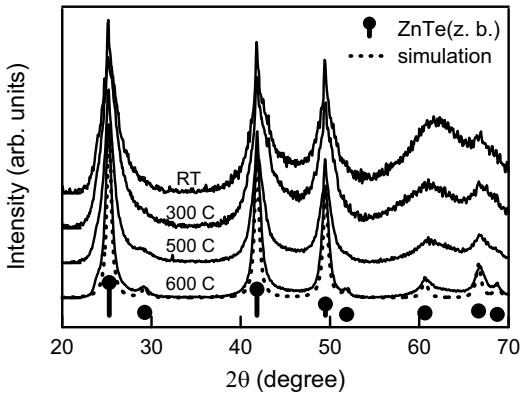

Figure 3. Annealing temperature dependence of XRD patterns of the ZnTe nanoparticles produced by PLA of Zn richi target (Zn:Te = 6:4). The dotted line indicates the simulated XRD curve based on the Scherre formula.

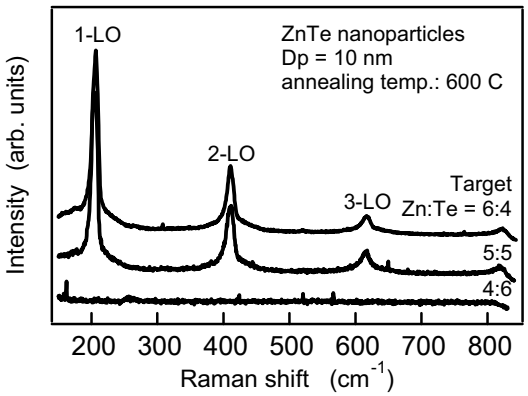

Figure 4. Raman scattering spectra of the ZnTe nanoparticles produced from the three targets (Zn:Te = 6:4, 5:5, 4:6). The nanoparticles were annealed at T_a = 600 °C and classified into 10 nm.

its harmonic series of bulk ZnTe, respectively. However, the ZnTe nanoparticles produced from the Te rich target did not show any Raman peaks. According to the results of the EPMA for the ZnTe nanoparticles produced from the Te rich target, the Te rich content was conserved even if PAP was carried out at T_a = 800 °C. It appears that existence of a Te rich phase, which is stable at high temperature in the ZnTe nanoparticles, prevents the *in situ* annealing from improving the stoichiometry and the optical properties of Te rich ZnTe nanoparticles.

In summary, the effect of PAP on the morphology, crystallinity, and optical property of ZnTe nanoparticles produced by PLA was dependent upon its atomic content. The optical property of the stoichiometric and zinc rich ZnTe nanoparticles was improved successfully by the *in situ* annealing at T_a = 600 °C. However, tellurium rich ZnTe nanoparticles maintained their non-stoichiometric content at T_a = 800 °C and did not show any improvement in the optical property after PAP.

Acknowledgments

This work was partially supported by the New Energy and Industrial Technology Development Organization (NEDO) under the Nanotechnology Materials Program.

References

[1] Brus L E 1983 *J. Chem. Phys.* **79** 5566-71
[2] Ekimov A I, Efros Al L and Onushchenko A A 1985 *Solid State Commun.* **56** 921-4
[3] Kayanuma Y 1988 Phys. Rev. B 38 9797-805
[4] Murray CB, Norris D J and Bawendi M G 1993 *J. Am. Chem. Soc.* **109** 5649-55
[5] Orii T, Hirasawa M and Seto T 2003 *Appl. Phys. Lett.* **83** 3395-7
[6] Tanabe H and Kawai T 1997 *Appl. Phys. Lett.* **70** 321-3
[7] Orii T, Seto T and Hirasawa M 2004 *J Vac.Sci Technol.* A **22** 2096-100
[8] *For example*, Lowndes D H, Rouleau C M, Thundat T G, Duscher G, Kenik E A, Pennycook S J 1999 J Matrerials Research **14** 359-70
[9] Ganeev R A, Ryasnyansky A I, Tugushev R I and Usmanov T 2003 J. Optics A **5** 409-17
[10] Hirasawa M, Seto T and Aya N 2001 J. Nanosci. Nanotech. **1** 381-3
[11] Yoshida T, Takeyama S, Yamada Y and Mutoh K 1996 *Appl. Phys. Lett.* **68** 1772-4