Journal of Ceramic Processing Research. Vol. 6, No. 2, pp. 134~137 (2005)

J O U R N A L O F
Ceramic Processing Research

Parameter dependence of nickel oxide nanoparticles prepared by pulsed-laser ablation

Leszek Zbroniec, Takeshi Sasaki and Naoto Koshizaki*

Nanoarchitectonics Research Center, National Institute of Advanced Industrial Science and Technology, Central 5, 1-1-1 Higashi, Tsukuba, Ibaraki 305-8565, Japan

Nickel oxide nanoparticles were fabricated by a laser ablation technique using the third harmonic of an Nd:YAG laser and sintered NiO targets in an on-axis configuration under argon pressures of 0.67, 1.33, and 2.00 Pa. The effects of the number of irradiating laser pulses, gas pressure, and target-to-substrate (T-S) distance on the average particle size, size distribution, and particle areal density were investigated. The nanoparticles obtained were always crystalline and 2 to 6 nm in diameter, irrespective of the preparation conditions as determined by high-resolution transmission electron microscopic (HRTEM) analysis. The average particle size increased with the number of laser pulses, indicating the particle growth on the substrate. The particle areal density was strongly affected by the target-to-substrate distance. The formation process of the nanoparticles is also discussed.

Key words: Laser ablation, Nickel oxide, Nanoparticle, Pressure, and Target-substrate distance.

Introduction

Many efforts have been made in the research and development of various types of NO_x sensors but still there is a strong demand for reliable and selective NO_x gas sensors for use in atmospheric and exhaust monitoring. Recently, new optical functionality has been developed in CoO/SiO_2 [1] and NiO/SiO_2 [2] nanocomposites that change their optical transmittance by exposure to ambient gases such as NO and CO. These unique optical and/or chemical properties result from the interfacial and/or surface effects between nanoparticles and the matrix. Therefore nanoparticles are a key part to construct such nano-structured functional materials. Among the preparation techniques employed to date, pulsed-laser deposition (PLD) has proven successful for depositing nanoparticles of variety of materials such as semiconductors, glasses, metals and alloys, ceramics and their nanocomposites. Some advantages of PLD over other preparation methods include congruent deposition, ease of operation and control, and low source material consumption. There now exists a considerable amount of literature describing ablation processes and parameters governing the deposition. However, the formation of nanoparticles during laser ablation is still not clearly understood. Since the functionalities in these nanocomposites arise from quantum size and surface/interfacial effects, it is important to reveal the parameters that determine the size and morphology of the nanoparticles so as to control the mean diameter, size distribution and number density of the resulting nanoparticles by adjusting experimental parameters. In this report we focus on finding the optimal ablation conditions for the synthesis of NiO nanoparticles for their potential use for gas sensing nanocomposites.

*Corresponding author:
Tel : +81-29-861-6358
Fax: +81-29-861-6355
E-mail: koshizaki.naoto@aist.go.jp

Experimental

The third harmonic (355 nm) of a Nd:YAG laser was utilized as an ablation source. The pulse energy was 200 mJ and the beam was focused to a 3.5 mm^2 spot size near the outer edges of the target. The repetition rate of the laser was 10 Hz. The target material was a NiO pellet (20 mm diameter × 5 mm thick) prepared by the usual ceramics techniques. The target and substrate were rotated at 20 and 9 rpm during the laser irradiation, and the ablation duration was from 40 to 200 pulses. Substrates used were carbon coated mica, which were placed parallel to the target, i.e. in an on-axis configuration. The distance between the substrate and the target was either 50 or 60 mm. Argon was utilized as a background gas during ablation, and the pressure was set to 0.67, 1.33, and 2.00 Pa. Two to four copper grids were used to sample the deposited films of approximately 1 cm × 1 cm, and 2 to 4 digital images of the most representative portions of the film were recorded for the analysis of the nanoparticles obtained at each ablation condition. The morphology and crystallinity of nanoparticles were examined by the

HRTEM (JEOL, JEM2010) and XRD (Rigaku RAD-C) using CuKα radiation.

Results and Discussion

Irradiation duration and ambient gas pressure

All the NiO nanoparticles deposited were crystalline, independent of the preparation conditions. Figure 1a shows a HRTEM image of the particles obtained after ablation with 80 laser pulses at 0.67 Pa and 200 mJ/pulse. The electron diffraction pattern in the inset clearly shows the diffraction rings. Lattice planes with a spacing $d = 1.97$ Å, which corresponds to the NiO (012) planes, can be seen on the enlarged image of the particle marked by the window "A". XRD peaks in Figure 1b confirmed the NiO phase. The crystallite size calculated from the X-ray spectra from the (012) peak broadening was 3.8 nm which was in very good agreement with TEM measurements of 3.7 nm. The particle size distribution was usually of log-normal type and a typical example is shown in Fig. 1c. The particles were single crystalline at the lowest number of 40 and 80 pulses, but some bicrystal particles were also observed at around 120 pulses (Fig. 1d).

Ablation experiments, unless otherwise indicated, were performed with the target-to-substrate distance set to 50 mm. It was found that the average particle size was almost the same at the same number of laser pulses and gradually increased with the number of laser pulses at 0.67, 1.33, and 2.00 Pa, as depicted in Fig. 2a. This strongly suggests that the particle size is determined after landing of ejected species onto the substrate. There is relatively little contribution from nanoparticle growth in the ambient.

It is worth mentioning that even though the structure of the deposited particle-aggregated films might look quite similar under the TEM it is speculated here that the deposition at higher pressure leads to a more porous and looser structure. Recently we tested NiO based gas sensors and found that the sensitivity of the sensors was the same at both 0.67 and 80.0 Pa but the sensors fabricated at 80.0 Pa had a much faster response to a change in the environment, i.e. they were faster both in sensing the gas and in recovering [3]. This property indicates that the gas can penetrate the sensors more easily in the film prepared at higher pressure. The sensors, however, were fabricated using much longer ablation times than the particles fabricated in the present study. In ablation at 80.0 Pa the ejected atoms experience substantial cooling via multiple collisions and therefore the impact energy of the atoms/clusters upon the substrate becomes lowered. In effect, compactness of the nanoparticle aggregated film deposited at 80.0 Pa was also lower than that of the film deposited at 0.67 Pa.

As seen in Fig. 2b, the areal density of particles

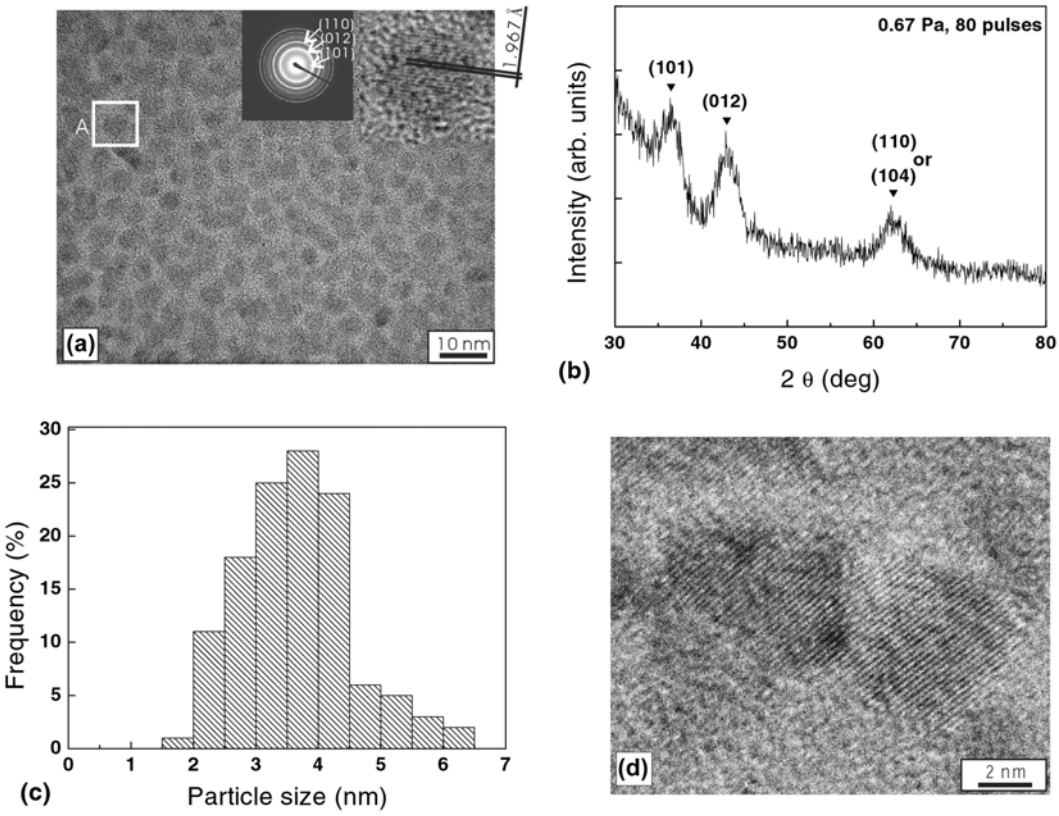

Fig. 1. (a) HRTEM image, (b) XRD pattern, and (c) the size distribution of the NiO nanoparticles synthesized with 80 pulses at 0.67 Pa Ar pressure and 200 mJ pulse energy. (d) HRTEM image of a bicrystal NiO particle formed with 120 pulses at 0.67 Pa and 200 mJ/pulse.

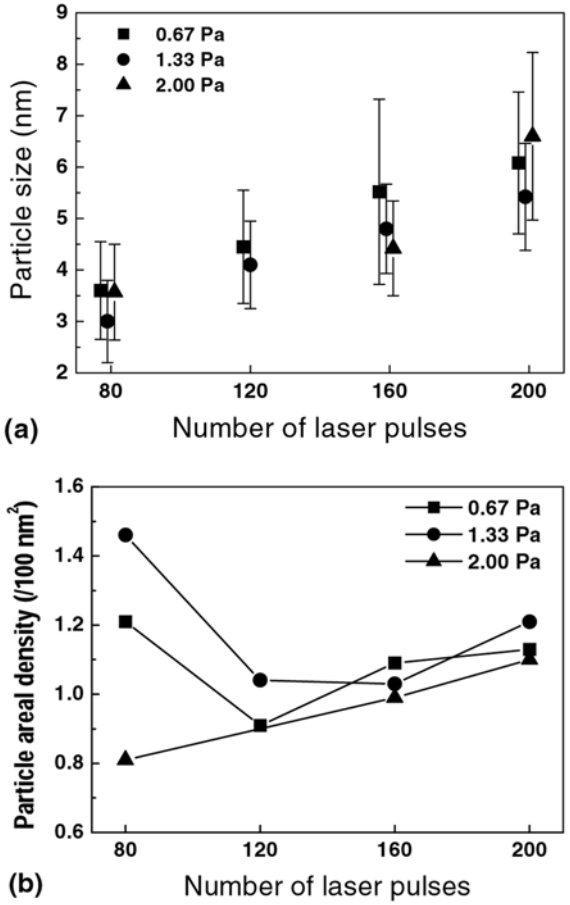

Fig. 2. (a) Dependence of the average NiO nanoparticle size (the bars show standard deviations) on the number of laser pulses at various pressures for irradiation. (b) Dependence of nanoparticle areal number density on the number of pulses at various pressures.

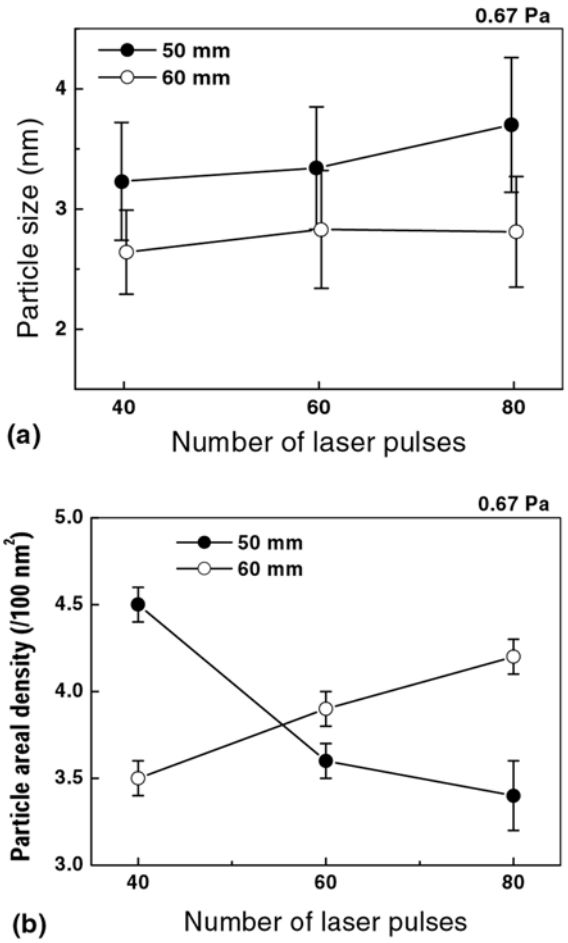

Fig. 3. Average particle size as a function of number of pulses for two different target-to-substrate distances at 0.67 Pa (a). (b) Nanoparticle areal density as a function of number of pulses for two different target-to-substrate distances at 0.67 Pa.

synthesized at 2.00 Pa increased almost linearly with number of pulses whereas it exhibited a minimum at 120-160 pulses for particles synthesized at 0.67 and 1.33 Pa. A rapid decrease in the areal particle density after ablation at 0.67 and 1.33 Pa might possibly be due to continual growth of particles as bicrystals at around 120 pulses. A big difference in particle number density was observed for the higher pressure of 2.00 Pa, but only for the short ablation time. Since the particle size at 2.00 Pa was almost the same as that at 0.67 Pa at a longer ablation time, the substantial difference in the areal particle density at 80 pulses could suggest that the higher ambient pressure might affect the collision processes in the ambient leading to an energy reduction of landing atoms/clusters on the substrate due to deflection and/or larger cluster growth.

Target-to-substrate distance

The effect of target-to-substrate (T-S) distance on the average particle size was investigated by a different set of experiments. We found some discrepancies especially in the areal number density of particles. This is probably caused by the effective fluence change at the target surface due to the optical setting difference of the laser beam line. However, the trends in this series of experiments revealed interesting results. Figure 3a indicates that the shorter distance produced larger nanoparticles at an ambient pressure of 0.67 Pa. Recent research indicates that 0.67-2.00 Pa ambient pressure used in the present experiment is too low to provide a collision frequency sufficient for nanoparticle formation in the PLD plume and suppress the energy after landing [4]. Therefore nanoparticles would grow via rapid surface diffusion [5]. If the particles formed in the plume, the longer T-S distance would produce larger particles due to a longer residing time and more collisions, which directly contribute to the nanoparticle growth [6]. Recent work on the synthesis of Fe_2O_3 by PLD [7] concluded that an Ar pressure below 13.3 Pa was too low to preserve good crystallinity of Fe_2O_3 at an off-axis position between the target and substrate. However, with an on-axis configuration in this case, at relatively higher pressure like 80.0 Pa, nanoparticle growth on the substrates might make a large contribution. This is quite reasonable since an off-axis

configuration requires trajectory deflection of species to land on the substrate.

Different T-S distances also resulted in interesting behavior of particle areal density versus number of laser pulses, as shown in Figure 3b. A shorter T-S distance produced a monotonically decreasing number density with increasing ablation time, whereas the longer T-S distance resulted in its gradual increase. In the shorter T-S distance case, particles have sufficient energy even after landing, resulting in an areal density decrease due to the coalescence of nanoparticles. On the other hand, when the T-S distance becomes larger, particles after landing do not have enough energy to move around, leading to the increase in the areal density.

Summary

Nickel oxide nanoparticles were fabricated by laser-ablating sintered NiO targets in an on-axis configuration under argon pressures of 0.67, 1.33, and 2.00 Pa. The nanoparticles obtained 2 to 6 nm in diameter were always crystalline as determined by high-resolution transmission electron microscopic (HRTEM) analysis. The number of irradiating laser pulses, gas pressure, and target-to-substrate (T-S) distance affected the average particle size, size distribution, and particle areal density. The average particle size increased with the number of laser pulses, indicating particle growth on the substrate. The particle areal density change with the number of laser pulses was due to the difference in the contribution of surface particle growth induced by the target-to-substrate distance.

References

1. N. Koshizaki, K. Yasumoto, and T. Sasaki, Sensors and Actuators B 66 (2000) 122-124.
2. A. Martucci, M. Pasquale, M. Guglielmi, M. Post, and J.C. Pivin, J. Am. Ceram. Soc. 86 (2003) 1638-1640.
3. L. Zbroniec, A. Martucci, T. Sasaki, and N. Koshizaki, Appl. Phys. A 79 (2004) 1303-1305.
4. D.B. Geohegan, A.A. Puretzky, G. Duscher, and S.J. Pennycook, Appl. Phys. Lett. 72 (1998) 2987-2989.
5. G. Medeiros-Ribeiro, A.M. Bratkovski, T.I. Kamins, D.A.A. Ohlberg, and R.S. Williams, Science 279 (1998) 353-355.
6. A. Matsunawa, S. Katayama, A. Susuki, and T. Ariyasu, Trans. J. Welding Res. Inc. 15 (1986) 61.
7. L. Zbroniec, T. Sasaki, and N. Koshizaki, Appl. Phys. A 79 (2004) 1783-1787.