

# Fine-structured ZnO patterns with sub-micrometer on the ceramic surface fabricated by a replication method

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Fine-structured ZnO patterns with sub-micrometer based on a replication method was fabricated. A replication method was used mixtures of polyvinyl alcohol (PVA) and ZnO nanosized particles in water. The mixtures were then filled in a quartz mold with different pattern sizes and dried at room temperature. After the drying, the PVA and ZnO dried film was detached from the mold. Through burn-out at various sintering temperatures, ZnO patterns with line and space patterns as smalls as sub-micrometer in size were successfully fabricated. The results demonstrated possibilities to produce inorganic materials with various compositions and structures with a facile approach and a simple method.

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## 1. Introduction

The ability to create patterns of arbitrary shape on substrates of varying size and shape has huge potential in a wide range of fields from optoelectronics to biological applications.<sup>1,2)</sup> In particular, the ability to create micrometer and sub-micrometer architecture for functional ceramics is a prerequisite of exploring the rich field of ceramic nanotechnology.<sup>3)</sup>

Numerous studies have been centered on developing novel methods and processes to fabricate fine-structured ceramic patterns. Although several ceramic patterning methods have been developed during the last decades, techniques that can pattern ceramics are very limited.<sup>4-10)</sup> Most commonly used approaches for patterning ceramic surfaces were the hard-lithography techniques, that in many cases are time-consuming, expensive, and low-resolution techniques. This is due in part to the refractory nature of ceramics and the difficulty in etching such materials.<sup>11)</sup> For instance, when ceramic patterns are to be prepared by sputtering, one of top-down methods, it is difficult to avoid etching processes in order to lift off the patterns. This may lead to severe problems such as sidewall redeposition, contamination, and structural damage.<sup>12)</sup>

Furthermore, nanoimprint lithography (NIL) using nanoscale molds, first reported by Chou,<sup>13,14)</sup> is recognized as a promising candidate for nanolithography in the next generation. However, the disadvantage of this technique involves expensive and complex processes. The main reason for the expense of the nanoimprint equipment is that the nanoscale molds need to be hardened by thermal and photonic treatments after imprinting.

On the other hand, by bottom-up methods, difficulties also exist in precisely controlling the shape, size, and relative position of the nanocomponents.<sup>15)</sup> Recently, a sol-gel method was applied for the patterning of TiO<sub>2</sub> and ZnO.<sup>16)</sup> However, this

process required both silicon and polymer molds. Furthermore, the complicated chemical process yielded hazardous wastes. Thus, much simple processes to fabricate patterned ceramics have been awaited.

Therefore, our research group, Kim and Nakayama et al. has recently successfully fabricated on fine-structured patterns with micron-meter of alumina porous material fabricated by a replication method.<sup>17)</sup>

In this study, we attempted to fabricate sub-micron sized fine-structured ZnO patterns on the ceramic surface using simple a method combining, the advantages of the use of polyvinyl alcohol (PVA) polymer material and ZnO nanosized particles, without using expensive equipments and complicated chemical processes. We used PVA as a binder for the formation of ZnO suspensions in aqueous solutions. ZnO nanosized powder was chosen because of its optical and electrical properties, and its high chemical and mechanical stability.<sup>18)</sup> PVA polymer materials offer several advantages, including low toxicity, low cost, high Young's modulus, and solubility in water.<sup>19)</sup> Furthermore PVA has already been widely used as a low cost binder in the commercial production of ceramics.<sup>20)</sup>

## 2. Experimental procedure

The critical steps in our patterning scheme are shown schematically in **Fig. 1**. A quartz mold (10 mm × 10 mm × 0.625 mm), which was fabricated using a conventional electron-beam lithography and a dry etching process, was obtained from a commercial vendor (NTT AT, Co. Ltd., Japan). The mold contained various patterns such as line and space (L&S), with a pattern size ranging from 350 nm to 10 μm. PVA (average degree of polymerization = about 500, Wako Pure Chemical Industries, Co. Ltd., Japan) and ZnO nanoparticles (34 nm; C. I. KASEI, Co. Ltd., Japan) were used as raw materials.

Firstly, PVA and ZnO nanoparticles were mixed in water and ball-milled using zirconia balls (diameter of 5 mm) for 24 h. The content of ZnO was in the range of 3–15 wt %, where PVA

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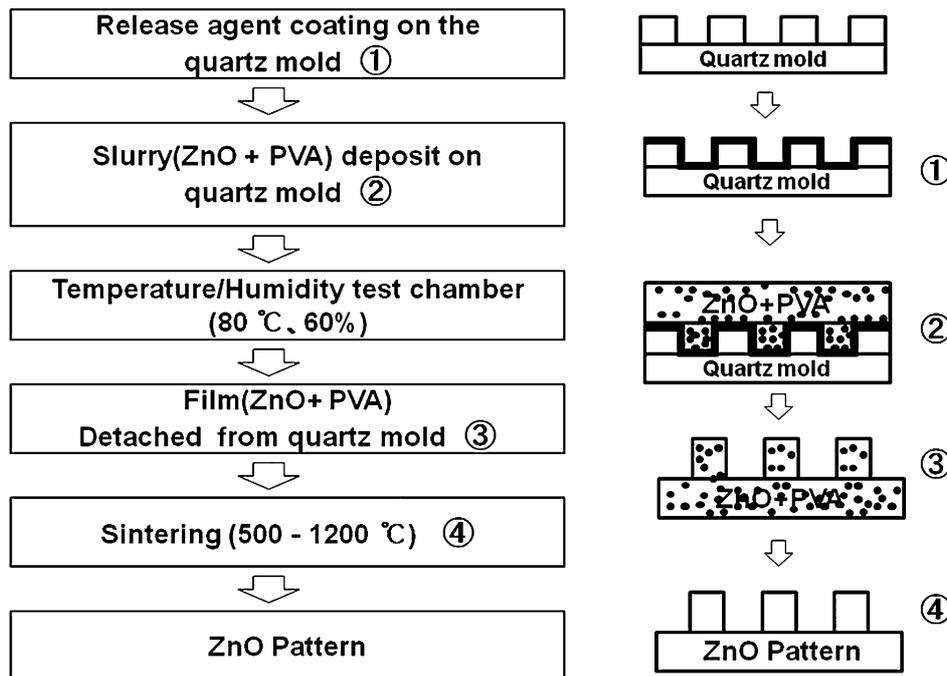


Fig. 1. A schematic drawing of the experimental procedure for the replication process.

content was fixed at 3 wt%. The surface of the quartz mold was coated with a release agent (HD-1100, HARVES Co. Ltd., Japan) to allow the dried film of the PVA–ZnO mixture to be detached from the mold. The PVA–ZnO mixture was then filled to cover the patterned quartz mold and dried. The drying process was carried out in a temperature/humidity test chamber (KCL-2000, EYELA Co. Ltd., Japan) maintained at a temperature of 80°C with the relative humidity of 60% to minimize the distortion of the film. The dried film was then detached from the quartz mold by peeling. The patterned films were sintered at various temperatures ranging from 500 to 1200°C for 1 h in air.

The size and surface morphology of the ZnO patterns were observed using a scanning electron microscope (SEM, JSM-6700F, JEOL, and Japan) and a violet laser scanning microscope (VK-9700, Keyence, Japan) with a capability to measure the height and width.

### 3. Results and discussion

Preliminary work showed that for PVA concentrations greater than 5 wt%, the PVA powder partially remained undissolved in the slurry. For PVA concentrations less than 2 wt%, no ZnO patterns were formed due to low binding strength. Thus, the content of PVA was fixed at 3 wt%.

To optimize the fabrication method, the relative quantities of PVA, ZnO and water were then varied as shown in Table 1. The patterns were partially formed when the ZnO contents were less than 3 wt% or more than 15 wt% owing to the insufficiency of particles connection or binding strength, respectively. Accordingly, optimized ZnO patterns were fabricated with the PVA content of 3 wt% and the ZnO contents of 6–12 wt%.

Figure 2 shows the scanning electron micrographs of ZnO samples sintered from after drying to 1000°C following the replication of quartz mold. ZnO patterns with sub-micrometers were successfully replicated on the surface of ZnO with L&S appearance. Furthermore, continuous patterns were showed at 500°C, but discontinuous patterns were showed at 1000°C. At 1200°C, ZnO patterns with sub-micrometer were observed due to

Table 1. Optimization of the mixing ratios of the ZnO slurry

Sample number	PVA (wt %)	ZnO (wt %)	H <sub>2</sub> O (wt %)	Remark
1	3	3	94	Partial film formation
2	3	6	91	Formation of film
3	3	9	88	
4	3	12	85	
5	3	15	82	Partial film formation

effect of sintering behavior and grain growth. Although the patterns were successfully transferred, the patterned ZnO samples were found to shrink in size following the sintering process.

The amount of shrinkage rate was estimated by using a violet laser scanning microscope. Figure 3 shows the surface morphology and 3D surface morphology of ZnO sample with pattern sizes of 350 nm to 1 μm. Shrinkage rate of the patterned ZnO sample replicated using a quartz mold is shown in Fig. 4. Width and height of patterns were showed homogeneous shrinkage rate. Following the sintering process, the patterns were found to shrink by as much as 9–48%. Shrinkage was found to increase with increasing the sintering temperature. The shrinkage effect can be a technique to produce the submicron-sized ZnO patterns from a micron-sized quartz mold.

Enlarged scanning electron micrographs of sintered ZnO at 500–1200°C are shown in Fig. 5. From 500 to 1000°C, ZnO sample with pores was showed. At 1200°C, densified surface was observed. Pore and grain sizes were gradually increased with increasing temperature. The grain size  $d$  (nm) and standard deviation of ZnO are plotted as a function of sintering temperature (Fig. 6). At the highest sintering temperature of 1200°C, the ZnO grains show a wide grain size distribution from sub-micron to micro size.

An exothermic burning process of the PVA occurs in the range of 150–450°C and sintering behavior resulting in the formation

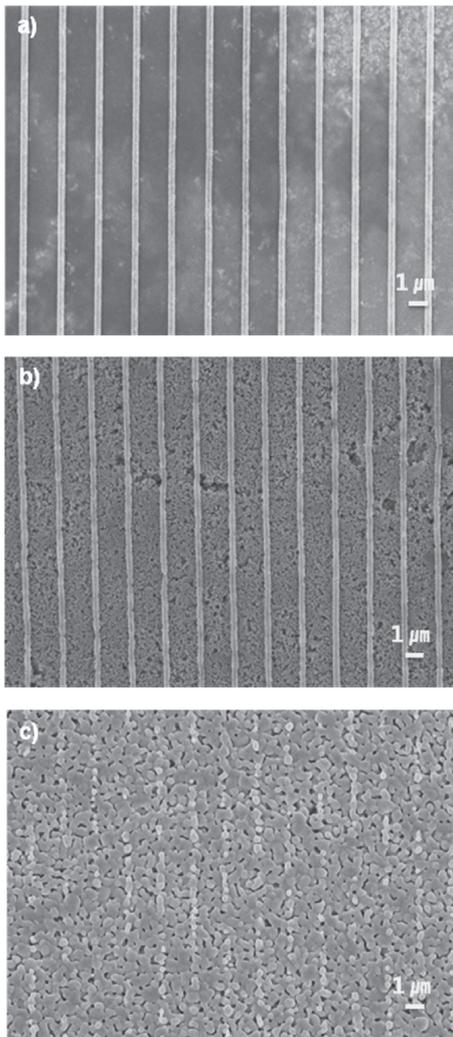


Fig. 2. Scanning electron micrographs of sub-micron ZnO patterns with L&S sintered at a) after drying, b) 500°C, c) 1000°C.

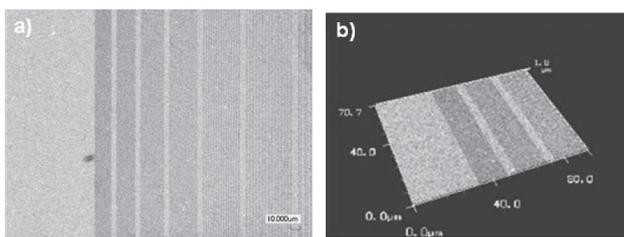


Fig. 3. Surface morphology and 3D surface morphology of sintered ZnO patterns.

of pores took place.<sup>21)</sup> The pore size and the porosity depend on the PVA content and the sintering temperature. It is expected that pore size and shape may be changed by increasing the sintering temperature in the present samples. Thus, it is likely that microstructure in the patterned ZnO can be controlled by adjusting parameters such as the sintering temperature and PVA content.

The size distribution of the ZnO patterns was observed using a scanning electron microscope. **Figure 7** shows the size distribution of ZnO grains sintered at 500–1000°C. The dashed lines show the fitted gaussian distribution curves to the experimental results and  $\sigma$  means standard deviation of gaussian distribution.

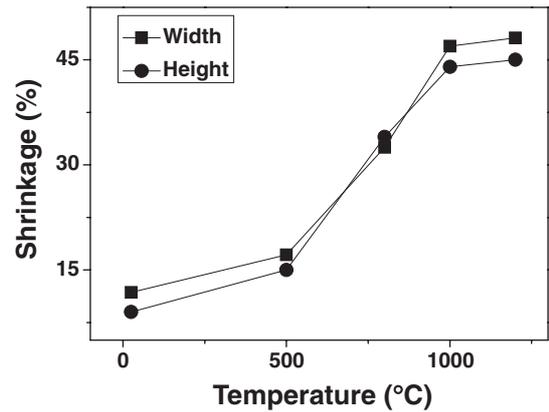


Fig. 4. Shrinkage rate of fine structure in sintered ZnO as a function of the sintering temperature.

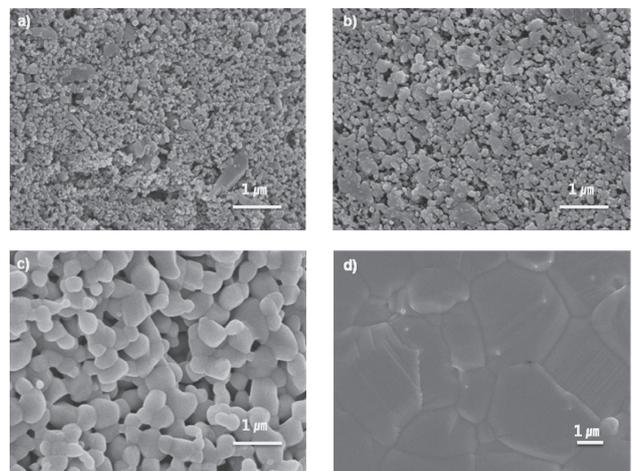


Fig. 5. Scanning electron micrographs of the ZnO patterns sintered at a) 500°C, b) 800°C, c) 1000°C and d) 1200°C.

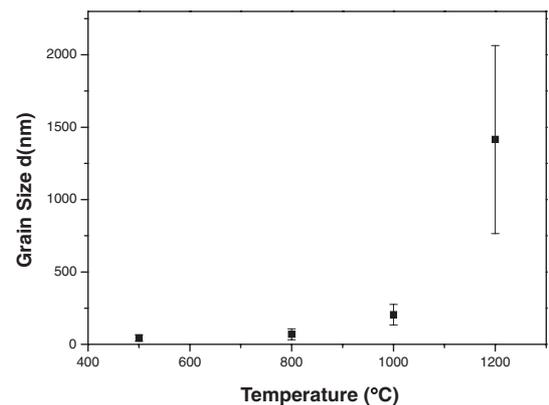


Fig. 6. Grain size  $d$  (nm) of ZnO plotted as a function of sintering temperature.

At 500°C, most of ZnO grains are showed in a size range of 30–100 nm and particles with more 150 nm size were also observed. As the temperature increases, both the grain size and size distribution range increase greatly. If grain size is larger than pattern size, pattern could not form. At 1200°C, with grain distribution of micron-sized, ZnO sample could not observation of submicron-sized patterns.

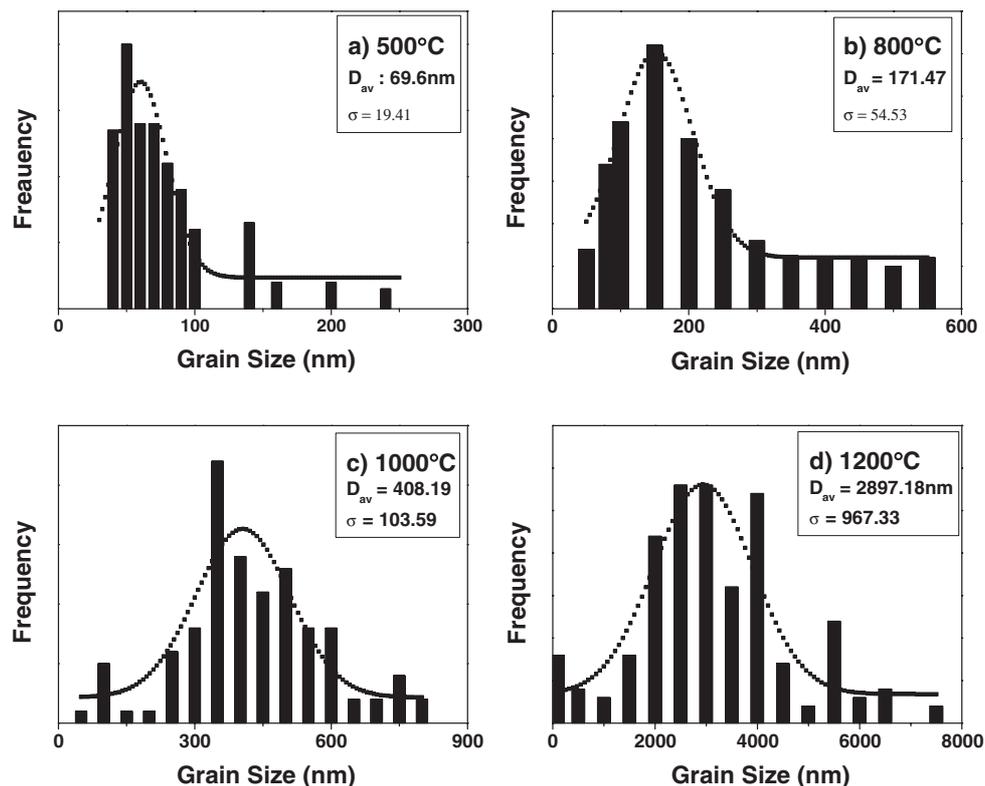


Fig. 7. Particle size distribution of ZnO grains sintered at a) 500°C, b) 800°C, c) 1000°C and d) 1200°C.

In the present research, it was found that heat-treatment of replicated PVA–ZnO mixtures using quartz molds enabled us to fabricate submicron-sized ZnO samples. It is also expected that using this method, various products including catalysts, super-water-repellent, heatproof materials, and microelectronics can be fabricated in a simple process.

#### 4. Conclusions

Submicron-sized ZnO patterns were successfully fabricated by a simple process using PVA–ZnO mixtures and a quartz mold. The shrinkage in the sintering was found to be used as a technique to fabricate submicron-sized patterns from micron-sized quartz molds. This versatile technique seems to offer the advantages of simplicity and low production cost, and it is capable of facilitating the design of complex patterns involving many applications ranging from catalysts, super-water-repellent, heatproof materials, and microelectronics. The replication method used is rather generic and we expect that a large number of different ceramics can be patterned by using this process.

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