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Fine-structured oxide ceramics from a novel replication method

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ABSTRACT

Fine-structured oxide ceramics sintered bodies with sub-micrometer scales were fabricated by a replication method from mixed slurry of polyvinyl alcohol (PVA) and nanosized ceramic particles in water. By using this replication method and burn-out at various sintering temperatures, fine-structured line and space patterns with sizes as small as 300 nm were fabricated on surfaces of TiO_2 and ZnO. The mechanism of pattern deformation was investigated and a general expression to predict the minimum pattern size was proposed based on the relationship between pattern size and grain size. The results demonstrated the feasibility of using this simple method to produce sintered oxide ceramic materials with various compositions and structures.

1. Introduction

The ability to fabricate high precision micro- to nanoscale structures in a wide variety of materials is of crucial importance for the advancement of microtechnology, nanotechnology and nanoscience [1–3]. For example, developing micrometer and submicrometer architecture for functional ceramics is expected to promote the industrialization of ceramic nanotechnology. Numerous methods to fabricate fine-structured ceramic patterns have been developed, but they need to be improved more for practical applications [4–10].

Most of the common approaches to patterning ceramic surfaces are top-down hard-lithography techniques, which are usually time-consuming, expensive, and achieve low resolution, partly because of the refractory characteristics of ceramics; it is difficult to etch [11]. For instance, when ceramics patterns are prepared by sputtering, one of top-down methods, etching processes are necessary for lifting off the patterns. This may lead to severe problems such as sidewall redeposition, contamination, and structural damage [12].

Nanoimprint lithography (NIL) using nanoscale molds, first reported by Chou [13,14], is a promising candidate for nanolithography in the next generation. However, this technique has the disadvantage that it involves expensive and complex processes. The main reason for the high cost of the nanoimprint equipment is that the nanoscale molds must be hardened by thermal or photonic treatments after imprinting.

Bottom-up methods also encounter difficulties in precisely controlling the shape, size, and relative position of the nanocomponents [15]. Recently, a sol–gel method was applied to the patterning of TiO_2 and ZnO [16], but this process requires both silicon and polymer molds. Furthermore, the complicated chemical process produces hazardous wastes. Thus, a simple process to fabricate patterned ceramics is necessary.

This paper presents a simple method to fabricate submicron-sized, fine-structured ceramic patterns on a ceramic sintering body (Fig. 1). The proposed method is based on NIL, but requires only a mold, ceramic powder slurry and a furnace. The slurry consists of polyvinyl alcohol (PVA) polymer material, nanosized oxide ceramic particles and water, and therefore does not require expensive equipment or complicated chemical processes. Two types of powders of oxide nanosized ceramic were used. TiO_2 nanopowder [17] was chosen because of representative function ceramics as photocatalyst material. ZnO nanopowder [18] was also used, because it is a well-known semiconducting ceramic with a wide band gap of ~3.37 eV and a large exciton binding energy of ~60 meV at room temperature. PVA was used as a binder for the formation of oxide ceramic suspensions in aqueous solution. PVA polymer materials offer several advantages, including low toxicity, low cost, high Young's modulus, and solubility in water [19]. PVA is

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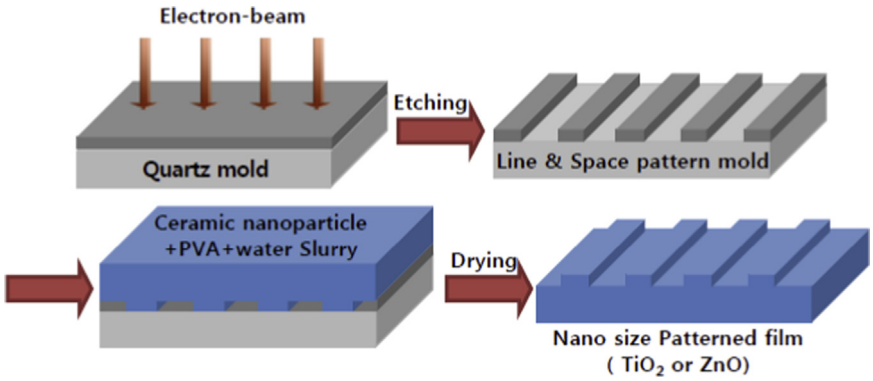

Fig. 1. The schematic diagram of overall experiment process.

Table 1
Optimization of the mixing ratios of the oxide ceramic slurry.

Sample number	PVA (wt%)	Ceramic powder (wt%)	H_2O (wt%)	Remark
1	3	3	94	Partial film formation
2	**3**	**6**	**91**	**Formation of the film**
3	**3**	**9**	**88**	
4	**3**	**12**	**85**	
5	3	15	82	Partial film formation

widely used in commercial production of ceramics [20].

2. Experimental

To fabricate submicron-sized patterns, TiO_2 nanoparticles (anatase 80%, 36 nm; C. I. KASEI, Co. Ltd., Japan) and ZnO nanoparticles (34 nm; C. I. KASEI, Co. Ltd., Japan) were used as starting materials. PVA (average degree of polymerization ~500, Wako Pure Chemical Industries, Co. Ltd., Japan) was added as a binder. A quartz mold (10 mm × 10 mm × 0.625 mm), which was fabricated using conventional electron-beam lithography and a dry etching process, was obtained from a commercial vendor (NTT advance technology, Co. Ltd., Japan). The mold contained line and space (L&S) patterns, the line size 350 nm and the space size 1 μm, with a height of 350 nm.

PVA and oxide ceramic nanoparticles were mixed in water and ball-milled using zirconia balls (5 mm in diameter) for 24 h. The content of oxide ceramic nanoparticles was in the range of 3–15 wt%, with PVA content [PVA] fixed at 3 wt%, based on results of preliminary experiments in which slurries with [PVA] > 5 wt% did not disperse all powder, and slurries with [PVA] < 2 wt% had low binding strength and therefore did not form oxide ceramic patterns. The surface of the mold was coated with a release agent (HD-1100, HARVES Co. Ltd., Japan) to allow the dried film of the PVA–oxide ceramic slurry to be detached from the mold. The PVA–oxide ceramic slurry was then filled to cover the patterned mold and dried in a temperature/humidity test chamber (KCL-2000, EYELA Co. Ltd., Japan) at 80 °C and 60% relative humidity to minimize distortion of the film. The dried film was peeled from the mold. The patterned films were sintered at various temperatures ranging from 500 to 1500 °C for 1 h in air.

The size and surface morphology of the oxide ceramic patterns were observed using a scanning electron microscope (SEM, JSM-6700F, JEOL, and Japan), a digital microscope (VHX-1000, Keyence, and Japan) and a violet-laser scanning microscope (VK-9700, Keyence, and Japan) with a capability to measure the height and width.

3. Results and discussion

To optimize the fabrication method, the relative quantities of PVA, oxide ceramic materials and water were systematically varied (Table 1). The patterns were partially formed when the contents of oxide ceramic materials were less than 3 wt% or more than 15 wt%, owing to insufficient particle connection and binding strength, respectively. Accordingly, optimized oxide ceramic patterns were fabricated with the PVA of 3 wt% and the oxide ceramic materials of 6–12 wt%.

Sintering temperature T_{sin} affected the TiO_2 patterns produced using the quartz mold (Fig. 2). At 500 °C, parallel and evenly spaced patterns were produced. The patterns of the quartz molds with aspect ratios < 1 and with L&S appearance were successfully reproduced on the TiO_2 samples. At 1000 °C, the lines began to bend and to become wavy, and grain growth took place. At

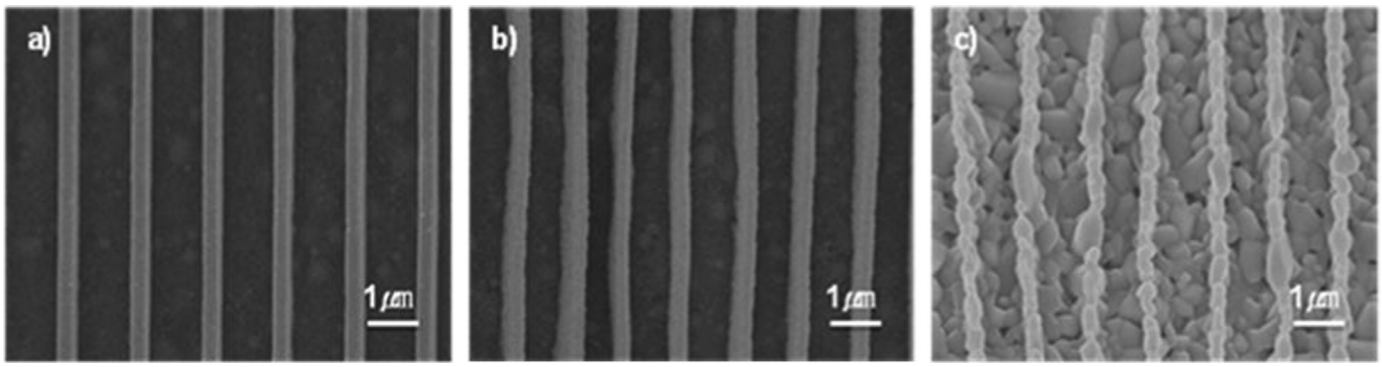

Fig. 2. SEM images of fine-structured TiO_2 patterns with submicron-size (a) after drying, and sintered at (b) 500 °C and (c) 1000 °C.