Fabrication of the finestructured alumina materials with nanoimprint method

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Nanoimprint lithography (NIL), is recognized as one of the candidates for next generation nanolithography. Usually nanoimprint equipment is highly expensive because the nano-scale mold needs to be hardened with thermal and photonic treatment after casting. In this study, we attempted to fabricate finestructured alumina materials without using highly expensive equipment. This method is based on the idea that poly vinyl alcohol (PVA) is simply detached from silicon mold by peeling. The experiment process used PVA and alumina nano-size particle, mixed in water solution. The mixed solution was then put into a micro-scale Si-mold and hardened at room temperature. After hardening the PVA and alumina nano-size particle mixed solution was detached from the micro-scale Si-mold. Throughout burn-out and low-temperature sintering, we confirmed the fabrication of finestructured micrometer-size alumina with nano-size pores.

1. Introduction

Nanoimprint lithography (NIL), which is recognized as one of the candidates for next generation nanolithography, was first reported by Chou.1,2) However nanoimprint lithography includes expensive and complex processes. Usually nanoimprint equipment is highly expensive because the nano-scale mold needs hardening with thermal and photonic treatments after casting. Recently, several polymer materials have been applied in most types of usual NIL as the template materials, including polydimethyl siloxane (PDMS), polymethyl methacrylate (PMMA), polyurethane (PU), and polyvinylalcohol (PVA).3) Particularly, the nanoimprint application using PVA polymer materials with following advantages has been numerous concentrations. First of all, PVA has been proposed as a nanoimprint template for a high resolution and low cost, a high Young’s modulus, due to its solubility in water.4) For instance, a conventional lift-off process using polymethyl methacrylate (PMMA) uses acetone as solvent, while a lift-off process using PVA uses water as a solvent. Also PVA has desirable properties for printing, including a high Young’s modulus of 1.9 GPa, compared to 1.8 MPa for polydimethylsiloxane (PDMS), which is important for minimizing distortions.5)–9) In this study, we attempted to fabricate finestructured alumina materials without using highly expensive nanoimprint equipment. We used a simple method by combining the advantages of usual nanoimprint method and PVA polymer material. This method is based on the idea that PVA is simply detached from silicon mold by peeling.

2. Experimental

Figure 1 shows the schematic process of this experiment. Si mold (25 mm × 25 mm × 1 mm) was chosen from a commercial product (Kyodo International, Co., Ltd., Japan), which was fabricated by conventional electron-beam lithography and by a dry etching process. Si mold have patterns such as space & line, dot, hole and pattern size ranging 0.5, 1, 2 μm. PVA (Average MW = 500, Wako Pure Chemical Industries, Co., Ltd., Japan) and alumina nano particles (TM–300D, γ-alumina, 10 nm; Taimei Kagaku, Co., Ltd.) were used for raw materials.

Firstly, PVA and alumina nano particles were mixed in water solution and ball-milled with zirconia ball (about 5 mm, 12 h). The surface of Si mold was coated with a fluorine-contained release agent (HD–1100, Harces fluorine chemical, Japan) to
detach the PVA/alumina complex from Si-mold. Then, the PVA/alumina complex was put into the patterned silicon mold and dried. The dry process was carried out by temperature/humidity test chamber (KCL–2000, EYELA Co., Ltd.) to minimize distortion of PVA/alumina complex film in condition of temperature (80°C) and humidity (60%). The dried PVA/Alumina complex was detached from the silicon mold by peeling. The patterned complex was sintered at various sintering temperatures ranging from 1000 to 1500°C. Usually, the PVA burns out during sintering around 500°C.

Size and surface of alumina patterns was observed using scanning electron microscope (SEM, JSM–6700F, JEOL Ltd.) Phase identification was carried out by X-ray diffraction (XRD, RINT 2500, Rigaku, Co.) analysis.

### 3. Results and discussion

It is observed that using various Si mold patterns, such as; dot, hole, line & space types, and pattern sizes ranging from 0.5 μm to 2 μm, imprinted porous alumina patterns, in accordance with those of Si molds, were fabricated. Followed by sintering, the most porous alumina patterns were shrunk in size (SEM image in Fig. 2). In the case of Si mold pattern having 0.5 μm in size, sub-micron sized porous alumina pattern, down-to about 0.3 μm in size, was formed.

To optimize the fabrication method of the finestructured alumina materials, the amounts of PVA, alumina and water were changed as showed just as Table 1. In case, PVA amounts exceed 5 wt%, PVA starts to educe. While the amount of PVA goes down lower than 2 wt%, the alumina pattern was not formed owing to the decrease of binding strength. When the amount of alumina powder was less than 6 wt% or more than 12 wt% of total amount, the patterns were not fabricated. The optimized alumina patterns were fabricated with 5 wt% of PVA and 6–12 wt% of alumina powder.

Table 1. Improvement Percentages of the Chemical Composition of the Alumina Slurry

<table>
<thead>
<tr>
<th></th>
<th>PVA</th>
<th>Al₂O₃</th>
<th>H₂O</th>
<th>Remark</th>
</tr>
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<tbody>
<tr>
<td>1</td>
<td>2 wt%</td>
<td>6 wt%</td>
<td>92 wt%</td>
<td>Formation</td>
</tr>
<tr>
<td>2</td>
<td>2 wt%</td>
<td>12 wt%</td>
<td>86 wt%</td>
<td>of film</td>
</tr>
<tr>
<td>3</td>
<td>2 wt%</td>
<td>6 wt%</td>
<td>92 wt%</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>2 wt%</td>
<td>12 wt%</td>
<td>86 wt%</td>
<td></td>
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</tr>
<tr>
<td>6</td>
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</tr>
<tr>
<td>7</td>
<td>5 wt%</td>
<td>18 wt%</td>
<td>77 wt%</td>
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</table>

Figure 3 shows surface SEM images of alumina pattern after sintering. PVA is removed by evaporation from around 500°C resulting in the formation of pores. The pore size and porosity is dependent on the amount of PVA present and sintering temperature. The porosity and surface area of the various patterned alumina could be controlled with a processing control such as sintering temperature (100°C–1500°C).

In case of alumina nano powder, phase transition of alpha phase from gamma phase was confirmed with XRD patterns of alumina. After sintering, the pattern shrinks down to 16–31% (Fig. 4). Shrinking rate of sintered alumina patterns was increased according to the elevation of sintering temperature. For this shrinking mechanism, the use of micron size Si mold can lead a sub-micron alumina patterns after the occurrence of shrinking.
4. Conclusions

We confirmed the fabrication of finestructured alumina with nano-size pores using a simple process. Porosity and shrinkage of alumina patterns could be determined by controlling the sintering temperature, and the shrinkage control facilitated the fabrication of sub-micron alumina pattern in spite of the use of micron size Si mold. In addition, surface area of the patterned alumina materials could be controlled by simple sintering temperature control. We believe that the proposed process to fabricate ceramic finestructured patterning has merits in the simple process and low production cost, therefore it can be applied in the various field. It is considered that the submicron-patterned alumina with nanoporous structure is likely to be widely applied on not only catalyst support but also super water repellent and heat-proof material because of high surface area.

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References