Heteroepitaxial Chemical Bath Deposition of Ultra-High Density ZnO Nanorod Arrays on Au films and Au Periodic Templates

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Abstract
We demonstrated an ultra-high density (~100 µm²) heteroepitaxial ZnO nanorod arrays on Au films / Si (111) substrates by chemical bath deposition (CBD). We also developed two different Au periodic templates to realize periodic ZnO nanorod arrays.

1. Introduction
In recent years, many social infrastructures such as highways and thermal power plants are aged and have risks of sudden breakdown. Ultrasonic testing is commonly used to detect cracks in those structures. Currently, ultrasonic testing is generally conducted under room temperature, and PbZrₓTi₁₋ₓO₃ (PZT) is mainly used as the piezoelectric material for the contact probe. However, the piezoelectricity of PZT disappears above the Curie temperature (350°C). Therefore, we cannot inspect the high-temperature parts of thermal power plants, factories, etc.

We focused on zinc oxide (ZnO), a cheap, non-toxic material that retains piezoelectricity at high temperatures and has good processability. Furthermore, nanorod (NR) shape of piezoelectric ZnO crystals has anomalous large fracture strain up to ~10% when NR diameter is reduced to around 100 nm or less [1,2]. Thus, NR-shaped piezoelectric material is expected to have improved the piezoelectric response. In order to achieve large piezoelectric response in ultrasonic contact probe, ZnO NR arrays need to have ultrahigh areal density exceeding 100 µm², which has NR interspaces less than 100 nm.

Here we show a ultra-high density (~100 µm²) heteroepitaxial ZnO nanorod arrays on Au films / Si(111) substrates by chemical bath deposition (CBD). We also developed an ultra-high density periodic template for vertically aligned and hexagonal prismatic heteroepitaxial ZnO NR arrays on Au thin films. To create the template uniformly over a large area at a low cost, we use a trigonally close-packed monolayer array of polystyrene nanospheres (PS-NSs) to develop two different Au periodic template.

2. Experimental

CBD of ZnO NR arrays on Au thin-film

In this work, Si(111) wafer were cut into pieces. First, the Si(111) substrate was ultrasonically cleaned in acetone and then ethanol, both for 5 minutes. After that, it was cleaned in de-ionized water (DI water) for 1 minute. Then, Si(111) substrate was soaked in 47% and 3% hydrogen fluoride (HF) aqueous solution to remove surface oxide film both for 1 minute and then cleaned with DI water twice, both for 1 min. The Si(111) substrate was dried using nitrogen gas gun. Next, Au thin-film was deposited on top of the Si(111) substrate by a vacuum deposition at room temperature. Then, 200 mL of precursor aqueous solution of zinc nitrate hexahydrate and hexamethylenetetramine is prepared at a molar ratio of 1:1. Finally, the wafers were put face down into the precursor solution and sealed in a container. CBD takes place in this container placed in an electric furnace set to 85.0°C for 3.5 hours. After the sample was rinsed with DI water and dried, the samples were observed using Hitachi S-4300 FE-SEM. Our CBD method is detailed in ref. [3].

UV Lithography Template

Au thin-film was deposited on Si(111) substrate as detailed “CBD of ZnO NR arrays on Au thin-film”. The Au thin-film surface was cleaned in the organic solvent and subsequent UV-O₂ treatment. Poly Methyl Methacrylate (PMMA) solution was then spin-coated on the substrate surface. Next, the substrate was floated in DI water upside down and then treated with UV-O₂ process for hydrophilization. Water dispersion of monodispersed PS-NSs (diameters = 262 nm) is spin-coated onto PMMA film / Au thin-film / Si (111) substrate, which forms trigonal close-packed PS-NS array. Next, the PS-NS array on PMMA thin film was exposed to UV light for several minutes. Therein, PS-NSs are expected to work as optical lense to focus UV light onto underlying PMMA layer. Finally, the sample was developed to remove the PS-NS and PMMA layer locally exposed to UV light. The samples were observed by SEM at 1 kV.

We prepared six different samples with different concentrations of PMMA and UV exposure times, as summarized in Table 1 shows the experimental conditions (concentrations of PMMA and the time of exposure to UV light) of the sample.

Table 1 Experimental Conditions

<table>
<thead>
<tr>
<th>No.</th>
<th>PMMA solution concentration</th>
<th>UV exposure time</th>
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<tbody>
<tr>
<td>1</td>
<td>2%</td>
<td>5 min</td>
</tr>
<tr>
<td>2</td>
<td>2%</td>
<td>30 min</td>
</tr>
<tr>
<td>3</td>
<td>2%</td>
<td>45 min</td>
</tr>
<tr>
<td>4</td>
<td>4%</td>
<td>5 min</td>
</tr>
<tr>
<td>5</td>
<td>4%</td>
<td>15 min</td>
</tr>
<tr>
<td>6</td>
<td>4%</td>
<td>30 min</td>
</tr>
</tbody>
</table>

Au Dots Template

First, the Si(111) substrate was cleaned in organic solvent...
and then in HF aqueous solution in the same manner as “CBD of ZnO NR arrays on Au thin-film” and then cleaned by UV-O₃ treatment. Second, Water dispersion of monodispersed PS-NSs (diameters = 262 nm) was spin-coated on the wafer, and PS-NSs were arrayed on the sample. After that, Au layer was deposited onto the trigonally close-packed monolayer PS-NS array / Si(111) substrate by a vacuum deposition at room temperature. Then, the sample was ultrasonically cleaned in Methyl Isobutyl Ketone (MIBK) for 5 minutes to remove the PS-NSs. The samples were observed using SEM at 10 kV.

3. Results and Discussion

ZnO NR’s CBD method

Figure 1 shows plan view SEM image of <0001>-oriented hexagonal columnar ZnO NR array grown vertically on Au thin-film / Si (111) substrate with (5 mm)² size, showing hexagonal ZnO(0001) NR top-planes. Figure 1 demonstrated ZnO NR array with ultra-high areal density (~100 µm²), indicating that the average distance between ZnO NR was ~100 nm. Figure 1 also evidenced that all ZnO NRs are perfectly aligned in both axial orientation and in-plane rotation, suggesting fully heteroepitaxial structure: ZnO(0001) NR // Au(111) thin-film // Si(111) substrate.

Therefore sample No.5 in Fig.2(a), 4% PMMA solution and UV light expose for 15min, is best as UV lithography template. While the interspace of neighboring PMMA holes are around 260 nm equivalent to PS-NS diameter, however, PMMA holes are non-uniform in diameters ranging from 120 nm to 250 nm, which needs to be improved. This non-uniformity of PMMA hole size is not accountable by conventional ray optics, in which we expect uniform PMMA hole size due to PS-NS lens effect. Rather, this non-uniformity could be attributed to non-uniform intensity of near-field UV light under each PS-NS which is sensitive to the presence of nanometric gap between each PS-NS and underlying PMMA film.

Au Dots Template

In this experiment, we use PS-NSs as a mask for vacuum deposition. Thus, Au is deposited only at the space between PS-NSs. Figure 2(b) shows the honeycomb pattern of triangular Au dots (white contrast). Si substrate surface is exposed in circular black contrast where the PS-NSs were present as masks. About 40% of the substrate surface has Au dots in honeycomb pattern due to coverage of mono-layered PS-NSs. While other area has either Au dots deposited in a trigonal pattern due to bi-layered PS-NSs or no pattern due to multi-layered PS-NSs.

4. Conclusions

We demonstrated an ultra-high density (~100 µm²) of perfectly-aligned heteroepitaxial ZnO(0001) NR arrays on Au(111) films / Si(111) substrates by chemical bath deposition (CBD). We also developed two different periodic growth templates to realize periodic ZnO nanorod arrays, trigonal UV lithography template and honeycomb Au dots template. Combination of such periodic growth template with CBD will further increase areal density and uniformity of NR diameters, which is essential to improve performance and lifetime of ZnO NR array-based piezoelectric devices such as ultrasonic contact probe.

References