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Heteroepitaxial Chemical Bath Deposition of Ultra-High Density ZnO Nanorod Arrays on Au thin-films: Impacts of Au thin-film crystallinity and Periodic Template

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Abstract

We demonstrate ultra-high areal density (~100 μm^{-2}) ZnO nanorod (NR) arrays which are grown hetero-epitaxially on Au (111) thin-films / Si (111) substrates under low-temperature processes (< 100°C). We further investigate how the crystallinity of Au thin-film impacts on the growth of ZnO NR array. We also demonstrate ZnO NR arrays with improved NR periodicity and NR diameter uniformity by selective growth on Au thin-films using PMMA films template with trigonal hole 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 performed at room temperature using $PbZr_xTi_{1-x}O_3$ (PZT) ultrasonic contact probe, due to its excellent piezoelectric properties at room temperature. However, since PZT loses its piezoelectricity above its Curie temperature (350°C), we need high-temperature piezoelectric materials for ultrasonic testing of thermal power plants, factories, etc.

We focus on zinc oxide (ZnO), which is a non-toxic, cheap, and processable material that retains piezoelectricity up to its melting point (1975°C). Furthermore, piezoelectric ZnO crystal gains anomalous large fracture strain up to ~10% when it has a NR shape with NR diameter less than 100 nm [1,2]. Thus, piezoelectric ZnO NR array is expected to have greater piezoelectric response than its thin-film counterpart. In order to achieve large piezoelectric response in ultrasonic contact probe, ZnO NR arrays need to have ultra-high areal density exceeding 100 μm^{-2}, in which the NR interspace is less than 100 nm.

Here we demonstrate ultra-high density (~100 μm^{-2}) heteroepitaxial ZnO NR arrays on Au (111) thin-films / Si (111) substrates by chemical bath deposition (CBD). We further study how the crystallinity of Au thin-film impacts on the growth of ZnO NR array by x-ray diffraction (XRD) and SEM-electron backscatter diffraction (EBSD). We also demonstrate ZnO NR arrays with improved NR periodicity and NR diameter uniformity by selective growth on Au thin-film using PMMA film templates with trigonal hole arrays (NS-UVL template), which are fabricated by UV photolithography of PMMA films covered with a trigonally close-packed monolayers of polystyrene nanospheres (PS-NSs).

2. Experimental

Vacuum Deposition of Au thin-film on Si (111) substrate

A Si (111) wafer is cut into 5 × 4 mm^2 pieces. First, the Si (111) substrate is cleaned ultrasonically in acetone and in ethanol and then rinsed in deionized (DI) water. Then, the substrate is soaked in hydrofluoric (HF) acid to remove its surface oxide layer and then rinsed with DI water. The substrate is dried using nitrogen gas. Next, Au thin-film was deposited onto the substrate in vacuum at room temperature.

CBD of ZnO NR arrays on Au thin-film [3]

200 mL of equimolar precursor aqueous solution of zinc nitrate hexahydrate and hexamethylenetetramine is prepared in a container. The substrates are put face down into the precursor solution and sealed in a container, which is then placed in an oven set at 85.0°C for 3.5 hours to initiate CBD. After the growth, the samples are rinsed with DI water and dried.

NS-UVL Template

4% anisole solution of poly-methyl methacrylate (PMMA) is spin-coated onto the surface of Au thin-film / Si (111) substrate, which then proceeds UV-O_3 treatment for its hydrophilization. Then, suspension water of mono-dispersed PS-NSs (diameter D_{PS} = 262 nm) is spin-coated onto the substrate, which forms trigonally close-packed monolayer of PS-NSs on PMMA film. Next, the substrate is exposed to UV light, where PS-NSs are expected to work as near-field optics to illuminate underlying PMMA film by localized UV light. The substrate is ultrasonicated in a 1:3 solution of MIBK and IPA to remove PS-NSs and to develop PMMA film after UV exposure. Finally, the substrate undergoes plasma cleaning (PC) using a mixed gas of Ar + O_2 to remove PMMA residue on Au film in trigonally arrayed holes.

Characterization

The samples are characterized using FE-SEM (Hitachi S-4300), XRD (Rigaku SmartLab), and SEM-EBSD (JEOL JSM-IT800SHL with TSL Solutions OIM Analysis ver.8).

3. Results and Discussion

CBD of ZnO NR on Au thin-film / Si (111) substrate

Figure 1 shows plan-view SEM image of ZnO NR array grown on Au thin-film / Si (111) substrate in precursor aqueous solution of 50 mM, which evidences vertical growths of hexagonal columnar ZnO NRs with perfect alignment in both axial and basal orientations. XRD and SEM-EBSD analyses of this ZnO NR array suggest heteroepitaxial relationships: ZnO (0001) NRs // Au (111) thin-film // Si (111) substrate. Figure 1 also demonstrate ZnO NR array has diameter of D_{NR} = 51 ± 15 nm and ultra-high areal density of N_{NR} = 100 µm^{-2}, indicating that the average ZnO NR interspace is 100 nm.

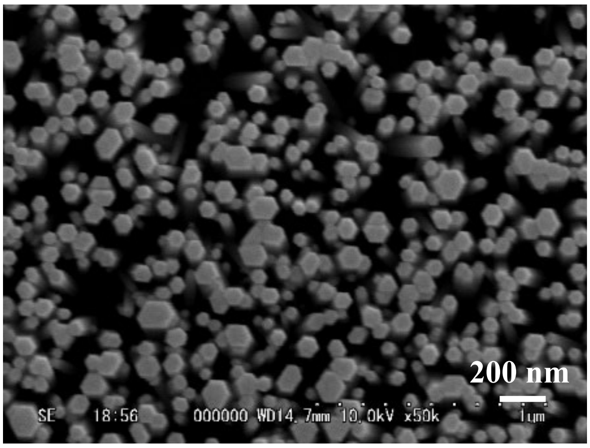

Fig.1 Hetero-epitaxial ZnO NR arrays at ultra-high density.

Fabrication of NS-UVL Template

Figure 2 shows SEM image of the trigonally close-packed hole array in PMMA film. The interspace of neighboring PMMA holes are around 262 nm, equivalent to PS-NS diameter. However, diameters of PMMA holes are not uniform: D_w = 145.6 ± 31.2 nm, which needs to be improved. This non-uniform PMMA hole diameter is not accountable by conventional ray-optics through PS-NS lens, in which we expect uniform PMMA hole size. Rather, this non-uniformity can be attributed to non-uniform intensity of near-field UV light under each PS-NS which is sensitive to the unintentional nanometric gap between each PS-NS and underlying PMMA film.

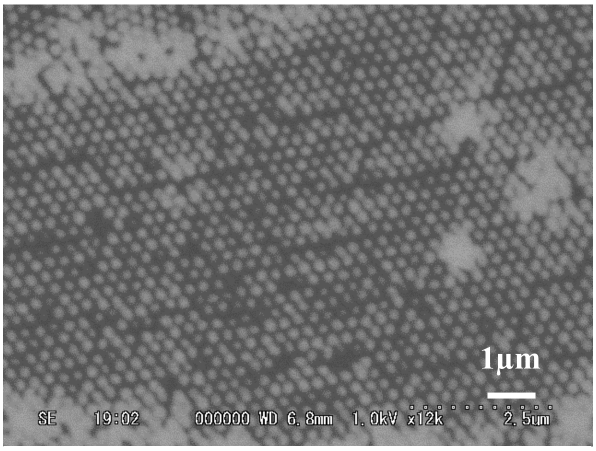

Fig.2 NS-UVL template with trigonal PMMA hole array.

ZnO NR array growth using NS-UVL template

Figure 3 shows a plan-view SEM image of ZnO NR arrays grown onto NS-UVL template area of the substrate in precursor aqueous solution of 100 mM, where ZnO NR has diameter D_{NR} = 177.4 ± 28.4 nm. In contrast, ZnO NRs grown outside of NS-UVL template (grown directly onto Au thin-film) has diameter of D_{NR} = 700 ~ 800 nm. This difference in diameter indicates that NS-UVL template inhibits lateral growths on {1-100} side-planes at initial stage. Note that the D_{NR} on NS-UVL template is slightly larger than its PMMA hole diameter D_w. This is attributed to lateral overgrowth of ZnO NR around PMMA hole (growth window).

Importantly, NR array on NS-UVL template (Fig. 3) has better D_{NR} uniformity and better lateral periodicity than the NR array on bare Au thin-film (Fig. 2). The D_{NR} in Fig. 3 has standard deviations of 21.4% while the D_{NR} in Fig. 2 has that of 29.4%. Also, ZnO NRs align more periodically in Fig.3 than in Fig. 2. This demonstrates that NS-UVL template is promising approach to improve the D_{NR} uniformity and lateral periodicity of ZnO NR array.

To enhance nano-mechanical strengthening of our ZnO NR arrays for piezoelectric applications, we will focus on further increase of NR areal density using NS-UVL template with higher PMMA hole density as well as the improvements in the D_{NR} uniformity and lateral alignment.

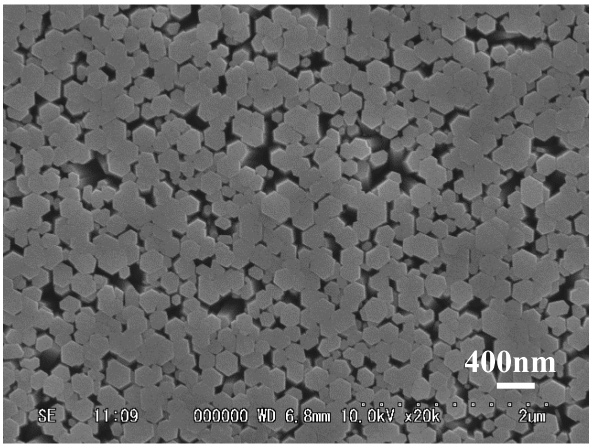

Fig.3 ZnO NR array grown onto NS-UVL template.

4. Conclusions

We demonstrate ZnO nanorod (NR) arrays which are grown vertically on Au thin-films / Si (111) substrates at ultra-high areal density (~100 µm^{-2}) under low-temperature processes (< 100°C). XRD and EBSD studies reveal their heteroepitaxial relationships: ZnO (0001) NRs // Au (111) thin-film // Si (111) substrate. We also investigate how the crystallinity of Au thin-film impacts on the growth of ZnO NR array. Using PMMA films template with trigonal hole arrays, we also demonstrate ZnO NR arrays with improved NR periodicity and NR diameter uniformity by selective growth on Au thin-films.

References

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