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Hydrothermal synthesis with controlled nucleation and growth to produce regular structures

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Abstract
Hydrothermal synthesis is a process that combines material synthesis driven by the reaction of aqueous solutions and the crystal growth at elevated temperature and pressure. Various materials and structures have been produced aiming at new sensors or actuators. However, the estimation of the structure or morphology after the synthesis is difficult because the crystal growth proceeds freely after indefinite nucleation. This study proposes an improved hydrothermal process to produce regular structures with controlled nucleation and crystal growth. First example is zinc oxide (ZnO) urchin-like structures. ZnO particles of ϕ100 nm were self-assembled on a substrate with dip coating method. Then, hydrothermal synthesis was carried out using these particles as nuclei. Urchin-like structures were obtained because a particle has all of the facets on the surface. Second example is titanium dioxide (TiO_2) rods vertically aligned on a substrate. In this case, the substrate crystal structure is the key. Fluorine doped tin oxide (FTO) can be used not only for transparent electrode but for the special substrate for hydrothermal synthesis because the lattice constant of FTO is similar with that of TiO_2.

Hydrothermal synthesis, urchin-like structure, nucleus, self-assembly, pillar

1. Introduction

Various regular structures have been produced aiming at functional surfaces or devices. Hydrothermal synthesis is a process that combines material synthesis and the crystal growth. It has been applied to produce regular structures like urchin [1] or pillars [2]. However, the estimation of the structure or morphology after the synthesis is difficult because the crystal growth proceeds randomly after indefinite nucleation. Control of the substrate characteristic will change the nucleation, and thus morphology of the structure.

This study proposes an improved hydrothermal process to produce regular structures with controlled nucleation and crystal growth.

2. Principle

Figure 1 shows the experimental procedure and principles. Material synthesis and crystal growth proceed at elevated temperature and pressure in a chamber as shown on the left side. When the growth proceeds on a substrate the morphology is affected by the substrate characteristic. In this study, particulate nuclei was tried in addition to the crystalized substrate.

On the right side in the figure, two different crystal morphologies are shown. The upper figure shows the case of zinc oxide (ZnO) growth. ZnO has hexagonal crystal structure and crystal grows along c-axis selectively. Particulate nuclei has all of the facets ideally, thus, urchin-like structure can be obtained [1].

The lower figure shows another case of titanium dioxides (TiO_2), which has tetragonal system and grows selectively along c-axis. If the substrate has similar lattice constant, pillars that have crystallography oriented and perpendicular to the substrate can be obtained just same with epitaxial growth [2].

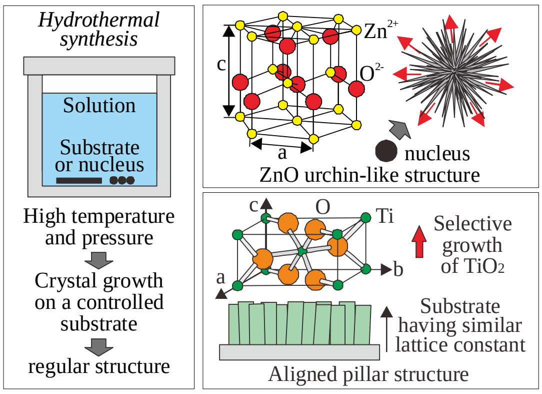

Figure 1. Hydrothermal synthesis to produce regular structures

3. Experimental results

Table 1 shows the experimental conditions for ZnO urchin-like structures and TiO_2 nano-pillars fabrication. ZnO nano-particles were assembled as the nuclei for ZnO urchins on a silicon substrate of 15 mm square which was covered with polydimethylsiloxane (PDMS) layer, while crystalized fluorine tin oxide (FTO) plate (25×30 mm) was prepared for TiO_2 nano-pillars. Reaction conditions were determined referring literatures [1] [2]. The reaction was carried out in a sealed container of 50 mL capacity placed in an oven at the specified temperature.

Table 1 Typical condition of hydrothermal syntheis

ZnO urchin-like strucrure	Substrate, nuclei	Silicon covered with PDMS, ZnO particles (ϕ100 nm)
	Hydrothermal	$Zn(NO_3)_2$ 0.58 g, $C_6H_{12}N_4$ 0.29 g, water 20 mL, 90°C, 9 h
TiO_2 nano-pillar	Substrate (nuclei)	Fluoro Tin Oxide (FTO)

	Hydrothermal	H_2O, HCl, $TiCl_4$, 150°C, 2-12 hrs

3.1. Urchin-like structure from assembled nuclei

Urchin-like structures were produced using the assembled particles as nuclei. The nuclei were assembled with dip coating method [3]. A hydrophilic substrate was dipped and draw-up from an aqueous suspension in which the particles were dispersed. The suspension spread on the substrate and particles assembled without any control due to the meniscus attraction between them as the evaporation of the suspension. In this experiments, the PDMS surface was processed with oxygen plasma to improve the affinity between the particles and the substrate.

Figure 2 shows the schematic and observation results after repeated coatings. The coverage of the particles on the surface at the first coating was limited due to insufficient wettability of the PDMS in spite of oxygen plasma treatment. However, the coverage was improved up to 70% after three times iteration.

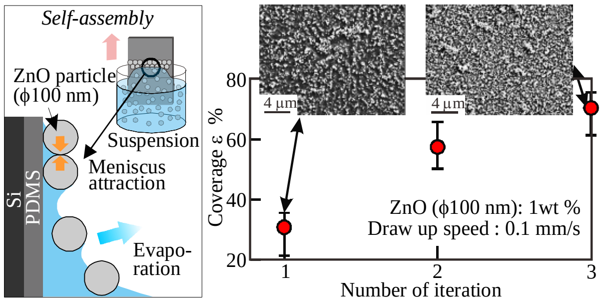

Figure 2. Dip-coating of ZnO particles as nuclei of crystal growth

Figure 3 shows the fabrication results of ZnO urchin-like structure showing the effect of reaction time. It can be seen from the scanning electron microscope (SEM) photos that urchin-like structures were successfully produced. The mean diameter of the urchins increased linearly with the reaction time. It was found that pitch between the urchins also increased with reaction time, which means that small urchins got together to produce larger urchins or coalesced.

These structures have wide surface area, thus applicable to gas sensor because ZnO has semiconductor properties and reacts with gas molecules. It was found that sensitivity was improved comparing with particle structure sensor. Assembled urchins can keep electrical contact between them under deflection of the sensor structure, thus, flexible and wearable sensor will become possible.

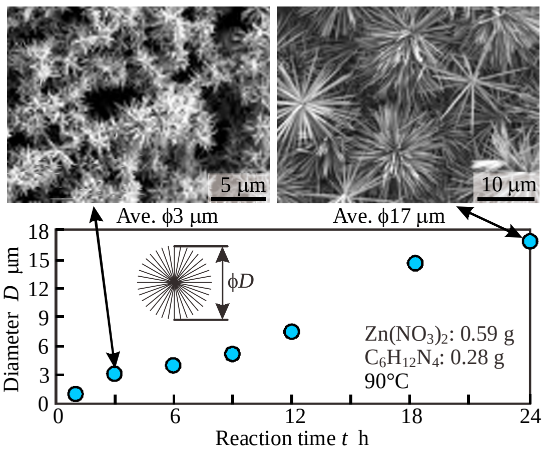

Figure 3. Effect of reaction time on urchin-like structure size

3.2. Nano-pillar on a controlled substrate

Figure 4 shows the results of TiO_2 nano-pillar fabrication showing the effect of reaction time on the morphology. Two SEM photos from top and inclined views are shown together with schematics for each reaction time. It is found that nano-pillars oriented perpendicular to the substrate were produced before six hours reaction. However, after longer reaction, urchin-like structures were observed on the top of pillars. On an amorphous glass substrate pillars were obtained but the direction was random. It was concluded from these results that parallel nano-pillars can be produced with the limitation of the height up to 4 µm.

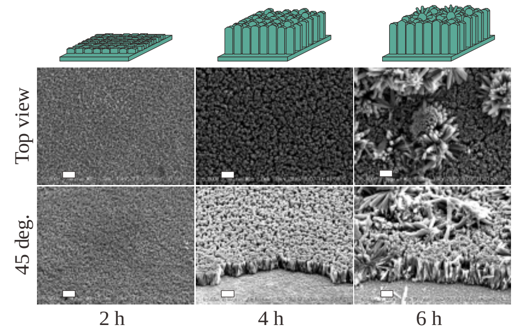

Figure 4. SEM images and schematics of TiO_2 structures showing the effect of synthesis time. Scale bar 2 µm.

Figure 5 shows the height distribution and Abbott's bearing curve of the pillars based on the measurement of white light interferometry. The height distributed over 0.75 µm, while it distributed over 15 µm under worse conditions though the results is not shown. Thus, top surface of the pillars is considered as flat and smooth.

TiO_2 has photocatalyst property and the contact angle decreased from 32 degrees to 5 degrees or less after irradiation of ultraviolet (UV) light of 68 J/cm^2. The superhydrophilicity was confirmed. Aiming at self-cleaning function, the smoothness of the surface becomes important because rough surface often causes pinning of the droplet and increases the sliding angle.

TiO_2 can be made into $BaTiO_3$ by applying additional hydrothermal process. Regular and crystallography oriented TiO_2 structure will be preferable in such a process. Thus, thin and flexible piezoelectric actuator is also expected because smooth surface will keep good electrical contact with electrode.

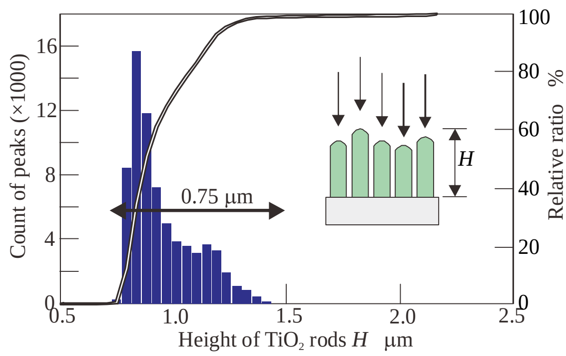

Figure 5. Height distribution of TiO_2 nano-rods

4. Conclusions

Two examples of hydrothermal synthesis, ZnO urchin-like structure and TiO_2 pillars, were described showing the importance of nucleation and growth control.

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