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Soft-solution route to various ZnO nanoplate arrays†

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Abstract

Three different ZnO nanoplate arrays on Si-wafer were successfully synthesized at 95 °C from ZnO nanoparticles with modified surface by citrate anion. Shape, size, density, and orientation of the resulting nanoplates were dramatically changed by the nucleus seed concentration, which was controlled through different coating processes on the substrate.

New metals and semiconductors with unusual morphologies due to their characteristic growth patterns often exhibit significant changes in their magnetic, electronic, and optical properties.^{1–4} Therefore, many attempts have been made to manipulate the morphology of inorganic materials, which is currently considered as a new research area in chemistry, physics, and material sciences.^{1–4} Zinc oxide (ZnO) semiconductor has been studied extensively among various metal oxides since it has a direct wide bandgap ($\Delta E_g = 3.37$ eV) and large exciton binding energy (60 meV), both of which are important for practical applications as ultraviolet (UV) lasers,^{5,6} photochemical sensors,⁷ solar cells,^{8,9} catalysts,^{10,11} cell imaging probes,¹² and so on. Typically, ZnO crystals with a hexagonal rod shape elongated along the *c*-axis are conventionally achieved due to a large anisotropic growth rate

of the individual facet, $V_{[0001]} \gg V_{[01\bar{1}0]} > V_{[000\bar{1}]}$.^{13–17} Therefore, a large family of ZnO nanostructures based on nanorods has been synthesized.^{14–17} However, the diameter of the polar surface of ZnO nanorods is continuously reduced by increasing the length due to the intrinsic growth habit. Polar surfaces play a central role not only as a reflecting mirror for UV lasing action but also as active sites for photocatalytic reaction.^{5,10} Actually, we found that the photocatalytic activity was enhanced upon increasing the polar surface area of the ZnO crystals.¹⁰ Moreover, Capasso *et al.* reported that the lasing action was not observed from ZnO nanorods with diameters below 150 nm in spite of having a cavity length of a few tens of μm .¹⁸ On the basis of nanoplates having an increasing polar surface, therefore, new opto-electronic nanodevices could overcome the limit of the ZnO nanorod building blocks. Such ZnO nanoplates could be achieved by growth rate control through negatively charged citrate anion adsorption on the Zn^{2+} -terminated (0001) surface of the nucleus seed.^{10,19,20}

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In this study, we describe a soft-solution route to three different nanoplate arrays on Si-wafer, which allows us to fabricate opto-electronic nanodevices with low production cost from the ZnO seed nanoparticles. To achieve this goal, ZnO nanoparticles as the seed crystal were chemically modified by citrate anions. Shape, size, density, and orientation of the ZnO nanoplates on the substrate were dramatically changed by the nanoparticle coating procedure. Namely, the concentration of the nucleus seed could allow us to fine control the ZnO nanoplate array. Among them, a nanoflower array based on nanoplates is the first to be reported to the best of our knowledge, although flower-like ZnO nanostructures based on nanorods have been frequently reported so far.^{21–23} In addition, the polar surface area was remarkably enhanced in nanowall arrays with numerous empty spaces, which were created by random orientation of the nanoplates along the *c*-axis. In multistacked nanoplate arrays, the vacant spaces observed in the nanowall arrays were filled by overgrowth of the nanoplates.

A p-type Si (100) wafer as a substrate was cleaned with acetone in an ultrasonic bath, and etched with piranha solution (3 : 1 mixture of concentrated H₂SO₄ and 30% H₂O₂) at room temperature for 30 min. The 0.01 M ZnO colloid starting precursor was prepared in ethanol (99.5% (v/v)) following a previously reported procedure.⁵ For the growth of nanoflower arrays, the resulting 10 μM nucleus seed was dispersed on Si-wafer by a spraying method using an air atomizing nozzle. In addition, for the growth of nanowall arrays and multistacked nanoplate arrays, the seed nanoparticles were dip-coated onto the substrate once and three times through a withdrawal speed of 4.2 cm/min. For the solvent evaporation, the seed coated substrates were heated at 100 °C for 30 min. Nutrient solutions for all nanoplate arrays were prepared from 100mL of 0.1 M Zn(OAc)₂ and 10 mL of 0.17 mM sodium citrate aqueous solution. Teflon-lined autoclaves, including the ZnO nanoparticles dispersed on Si-wafer and stock solution, were maintained at 95 °C for 6 h in a conventional furnace. Finally, the product on the Si-wafer was washed with deionized H₂O (18.2 MΩ) several times to remove any of the residual salts. Morphologies of the resulting products were observed using a field emission scanning electron microscope (FE-SEM, HITACHI, S-4300) and high resolution transmission electron microscope (HR-TEM, JEOL, JEM-3000F) with 300 kV accelerating voltage.

From the HR-TEM study, the ZnO seed nanoparticles were found to be quasi-spherical with a homogeneous diameter of 4 nm as shown in Fig. 1(a). For the ZnO nanoparticles coated by the spraying method, the nanoplates with flower-like shape were grown on a large area of the Si-wafer after autoclaving (Fig. 1(b)). A further high-magnification image shown in Fig. 1(c) showed ZnO nanoflowers with six petal-like edges having a uniform diameter of 6 μm, and having the appearance of a “white magnolia” flower. In addition, a butterfly-like ZnO crystal, which seems to consist of nanoplates grown perpendicularly to the substrate, was also reproducibly observed near the nanoflowers, as shown in Fig. 1(c). Different orientations of the ZnO nanoplates might be induced by the random orientation of the seed particles dispersed on Si-wafer. From this butterfly-like ZnO crystal, we found that the thickness of the nanoplates was approximately 50 nm as shown in Fig. 1(d). One interesting observation was that the one-dimensional nanostructure (marked with a white arrow), which seems to be generated by connecting nanoplates with a diameter of 50–500 nm, were grown around the ZnO nanoflower like the slender roots of a real flower as shown in Fig. 1(d). Such a one-dimensional nanostructure with connecting nanoplates observed from the center of the ZnO nanoflower is shown in the inset of Fig. 1(c).

According to Bendall *et al.*, secondary growth of hexagonal ZnO nanorods under citrate solution could lead to a laminar structure.²⁴ In addition, they suggested that the secondary growth only occurs from the (0001) plane of the well aligned ZnO nanorods because the random orientation of the ZnO nanorods could interrupt the initial growth of large base

plates.²⁴ The present root-like structure could be explained by secondary growth of the ZnO nanoflower. Namely, flower- and butterfly-like ZnO nanostructures were initially grown from the nucleus seed and then the root-like structure was generated by secondary growth of the ZnO nanoflower. Despite the random orientation of the flower-like and butterfly-like structures, their large (0001) surface area could facilitate secondary growth.

Fig. 2(a) shows the HR-TEM image and selected area diffraction (SAED) pattern of the top surface of the ZnO nanoflower corresponding to the (0001) plane of a typical ZnO crystal. For the top surface of the butterfly-like structure, Fig. 2(b) shows that the nanoflowers were

grown along the $\begin{bmatrix} 01 & \bar{1} & 0 \end{bmatrix}$ zone-axis and enclosed by the (0001) and $\pm \begin{bmatrix} \bar{2} & 110 \end{bmatrix}$ planes. The observed distance of 5.2 Å between the lattice planes corresponds to the 5.21 Å between the (0001) planes of a ZnO crystal. This result clearly indicated that the ZnO nanoflowers were preferentially grown along the nonpolar facets due to the modified growth habit.

In the case of the one time dip-coated nanoparticles, most of the ZnO nanoplates were grown perpendicularly to the substrate as shown in Fig. 3(a) and (b). Thickness of the nanoplates was approximately 10 nm, which is similar to that of the nanoflowers due to the same growth condition.

From the crystallographic viewpoint, the ZnO nanoplates were elongated along the *a*- and *b*-axes, but the *c*-axis of the nanoplates was randomly orientated. Consequently, numerous empty spaces were naturally created by surrounding the nanoplates as a wall. Compared to the hexagonal nanorod array, the polar surface area could be remarkably enhanced by this nanowall structure due to the unique shape and orientation. It has been previously reported that Zn²⁺ defects could be naturally created in the (0001) surface to reduce the macroscopic dipole moment generated between two polar facets.²⁵ Consequently, coordinatively unsaturated zinc and oxygen atoms frequently exist on the polar surfaces.²⁵ It also suggests that the present ZnO nanowall array could facilitate the redox reaction of organic and inorganic molecules based on our previous study on photocatalytic effect of the nanoplates.¹⁰ Moreover, the ZnO nanoplates have a unique UV-lasing property with whispering-gallery-mode-like enhanced emission, which is important for the reduction of threshold power density.²⁰ It is worthwhile to note here that a broad green- and yellow-emission around 510 nm and 590 nm was not observed in the photoluminescence (PL) spectrum of the ZnO nanowall array (see the Supporting Information†). In addition, the full width at half maximum (FWHM) of the UV emission of the ZnO nanowall array is 1.8 times as narrow as that of the ZnO nanorod array. Therefore, we expect that the ZnO nanowall array is a more suitable structure for opto-electronic nanodevices than the ZnO nanorod array. On the other hand, the ZnO nanoparticles were densely grown as multistacked nanoplates by three times dip-coating procedure as shown in Fig. 3(c) and (d). A high concentration of the seeds coated on the Si-substrate could induce the growth of the multistacked nanoplates. Therefore, the vacant spaces observed from the nanowall array disappeared by overgrowth of the nanoplates. The thickness of the nanowalls was increased by decreasing the concentration of citrate solution from 0.17 to 0.08mM because a low concentration of citrate ions did not effectively protect the growth rate along the [0001] direction of the nucleus seed, as is well documented by Cao *et al.* (see the Supporting Information†).²⁶

Fig. 4 shows X-ray diffraction (XRD) patterns of the above three different nanoplate arrays. As shown in Fig. 4(a), strong (00*l*) peaks were observed from the ZnO nanoflower array due to their preferred orientation along the *c*-axis. Additionally, weak (*hkl*) peaks also appeared owing to butterfly-like and slender-like nanostructures. For the ZnO nanowall array (Fig. 4(b)) and multistacked nanoplate arrays (Fig. 4(c)), the (00*l*) peaks almost disappeared but the (*hkl*) peaks were strongly enhanced by the nanoplate growth along the *a*- and *b*-axes.

This result was highly consistent with the above microscopic results. Moreover, it suggests that the nanoplate orientation could be controlled by the concentration of the nucleus seed on the substrate.

Scheme 1 illustrates that the density of the nucleus seeds coated on the substrate could adjust the shape, orientation, and density of the ZnO nanoplates.

Fig. 5(a) shows the FE-SEM images of pineapple-like ZnO rings, which were obtained from the mother solution after autoclaving. The pineapple ZnO rings have a diameter of 7 μm and a thickness of 500 nm as shown in Fig. 5(b) and (c). Such a ring formation could be induced by dissolving the polar surfaces due to the weak acidic condition ($\text{pH} = 6.5$) of the mother solution. For the Si-substrate without the nucleus seed, only amorphous crystals were observed on the substrate and the pineapple ZnO crystals were produced from the mother solution (see the Supporting Information†).

In conclusion, the citrate anion can be used as a blocking agent to modify the characteristic growth pattern of ZnO crystals. In addition, size, shape, density, and orientation of the ZnO nanoplates can be controlled by changing the concentration of the coated nanoparticles. Consequently nanoflower, nanowall, and multistacked nanoplate arrays were successfully designed through a soft-solution procedure. Such nanoplate arrays can be used to explore new nanodevices with a large polar surface area. Moreover, the mild fabrication process and the use of Si-wafer could remarkably curtail the production cost and could accelerate the practical application of ZnO nanoplate arrays as new opto-electronic nanodevices.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

Acknowledgments

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Fig. 1. (a) HR-TEM image of ZnO nanoparticles. (b) Low- and (c) high-magnification FE-SEM images of ZnO nanoflowers on Si-wafer. (d) FE-SEM image of 1-D nanostructures attached to nanoflower.

Fig. 2. HR-TEM images and SAED patterns of (a) the top surface and (b) the cross-section of a ZnO nanoflower.

Fig. 3. Low- and high-magnification FE-SEM images of (a, b) ZnO nanowalls and (c, d) multistacked nanoplate arrays.

Fig. 4. XRD patterns of (a) ZnO nanoflower, (b) nanowall, and (c) multistacked nanoplate arrays on Si (100) substrate (*).

Fig. 5.
(a) Low- and (b, c) high-magnification FE-SEM images of the product obtained from the mother solution after autoclaving.

Scheme 1.

Variation of shape, orientation, and density of ZnO nanoplates upon coating the nucleus seed.