Phosphate-mediated ZnO Nanosheets with a Mosaic Structure

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(Received March 3, 2004; CL-040241)

Seaweed-like ZnO sheets consisting of wurtzite-type nanoplates with a thickness less than 5 nm were grown in an aqueous solution system containing phosphate anions. The platy crystals were formed with specific adsorption of phosphate anions on the (001) plane.

Recently, low-dimensional materials, including nanodots, nanowires, and nanosheets, have been developed to understand their novel physical properties and potential applications to nanotechnologies in the electronic and optoelectronic fields. Semiconductors were mainly focused in the particular forms of nanomaterials because of their optical and electrical properties. Wurtzite-type zinc oxide (ZnO), a wide band gap semiconductor, is well known as a transparent, conducting, piezoelectric material with excellent electrical and optical characteristics. Nanoscale ZnO has been prepared using various methods including vapor-phase and solution-phase processes.[1–4] Nanowires have been previously fabricated by vapor-phase transport processes.[1] Helical nanorods formed from stacking of nanoplates were prepared in an aqueous solution system containing $Zn(NO_3)_2$ and sodium citrate.[2] Stacking nanodisks were also produced by electrodeposition in the presence of organic dyes.[3] These 2-D sheets in single-crystalline form were assembled along the [001] orientation. In the stacked aggregates, however, the (001) surface was not highly accessible to chemical species and physical probes.

Recently, crystalline ZnO films can be directly grown on substrates by heterogeneous nucleation and subsequent crystal growth in aqueous solutions at near-ambient temperature and pressure.[5–13] Manipulation of the microstructure and morphology of ZnO crystals would be achieved by the addition of various coexisting species in the aqueous systems. This paper describes the preparation of free-standing nanosheets consisting of wurtzite ZnO mosaic crystals in an aqueous solution system. The presence of phosphate anions highly restricted the growth of the crystalline phase in the aqueous solution. Finally, seaweed-like nanosheets of ZnO were obtained on a specific substrate. An easy-to-access form of semiconducting nanomaterials is applicable to various fields, including sensors, photochemical cells, and photocatalysts.

On the basis of our previous results,[11] the concentration of the precursors in the solutions was determined for the growth of wurtzite ZnO crystals on a substrate. An aqueous solution containing 0.01 mol/dm^3 zinc sulfate heptahydrate ($ZnSO_4 \cdot 7H_2O$; Kanto Chemical) as a zinc source and 0.3 mol/dm^3 ammonium chloride (NH_4Cl; Junsei Chemical) as a complexing agent was adjusted to pH 11.0 by the addition of 5 mol/dm^3 $NaOH_{(aq)}$. Trisodium phosphate dodecahydrate ($Na_3PO_4 \cdot 12H_2O$; Wako Pure Chemical) was added to the aqueous solution as a modifier of the morphology of the grown crystals. The molar ratio of PO_4/Zn (R_p) in the precursor solution was varied in the range between 0 and 2.0 in order to study the influence of the phosphate anions on the morphology. Glass slides previously coated by a ZnO thin film with a thickness of about 50 nm were used as a substrate to promote heterogeneous nucleation on the surface.[11] The undercoat was prepared by spinning a 2-methoxyehtanol solution with zinc acetate dihydrate ($Zn(CH_3COO)_2 \cdot 2H_2O$; Kanto Chemical) and monoethanolamine ($NH_2CH_2CH_2OH$; Kanto Chemical) and heating at 400 °C for 10 min. The preparation of ZnO crystals was performed in a polystylene vessel maintained at 60 °C for 24 h. The substrate loaded with the products was withdrawn from the precursor solutions, rinsed with purified water, and dried at room temperature.

X-ray diffractometry (XRD) was performed with a Rigaku RAD-C using Cu Kα radiation. Microstructures were observed with a Hitachi S-4700 field-emission scanning electron microscope (FESEM) and a Phillips TECNAI F20 field-emission transmission microscope (FETEM). The composition was estimated by an energy-dispersive X-ray analyzer (EDX) equipped with the transmission microscope. Fourier transform infrared (FTIR) spectra were recorded with a BIO-RAD FTS-60A.

In the absence of phosphate ions, hexagonal rods of wurtzite ZnO with a diameter of $\approx$50 nm were grown with a preferred orientation on a substrate (Figure 1a). The *c* axis of the rods was arranged perpendicularly to the substrate. The morphology of ZnO crystals was drastically changed by the addition of phosphate ions into the precursor solution. When the molar ratio R_p in the precursor solution was 0.1, the presence of phosphate ions increased the diameter of the hexagonal rods and decreased the height (Figure 1). The variation means that the anions adsorbed on the (001) surface restricted the growth along the [001] direction. A seaweed-like platy morphology was obtained when the R_p ranged between 0.2 and 1.0 (Figure 2). This noncrystallographic form was constituted of curved thin sheets with a thickness below 5 nm. Figure 3 shows TEM images of a flake of the ZnO nanosheets. We observed hexagonal habits on a flake (a) and a patchwork of small crystallites with the lattice image of the (100) plane in the flakes (b). These micrographs reveals the curved sheets were a mosaic of wurtzite-type ZnO crystallites, of which the *c* axis was perpendicular to the surface.

The elemental analysis by EDX indicated that the ZnO nanosheets contained a large amount of phosphate ($P/Zn \approx 0.8$ in mol) although the exact content was not determined because of a loss during the washing process. The presence of phosphate in the products was confirmed by the appearance of broad absorption bands ranging between 850 and 1150 cm^{-1} assignable to the P–O stretching vibrations in the IR spectra. The specific interaction of phosphate ions was theoretically elucidated with the Partial Charge Model (PCM),[14,15] which predicts the complexation behavior of inorganic anions with Zn^{2+} on the basis of the electronegativity equalization principle. These results suggest that phosphate ions were selectively adsorbed on the (001) surface consisting of Zn^{2+} and restricted the growth of regular

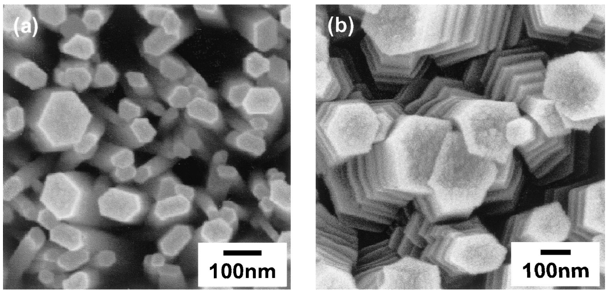

Figure 1. SEM images of hexagonal rods of wurtzite ZnO crystals grown in a solution without (a) and with a small amount of phosphate ions ($R_p = 0.1$) (b).

hexagonal habits originating from the wurtzite structure. Then, the height of the hexagonal rods decreased with the specific adsorption. The ultimate suppression of the crystal growth along the [001] direction induced the formation of nanosheets with a mosaic structure. The wavy morphology is attributable to the flexibility of the patchwork of the mosaic with phosphate as a glue. The phosphate mainly existed on the surface of the ZnO sheets because the XRD peaks due to the wurtzite structure were not shifted. Although the prohibition of the regular growth of ZnO crystals was already demonstrated by the presence of organic dyes and citrate,[2,3] the morphological evolution of the crystals with the coexistence of phosphate ions was relatively remarkable. Condensation of the adsorbed phosphates on the surface may promote the strong inhibition of the crystal growth. The optical band gap of the ZnO sheets was estimated to be ca. 3.2 eV using diffuse reflectance spectroscopy with a JASCO V-550. It suggests that the nanosheets have the normal electronic structure of a wurtzite ZnO crystal regardless of the presence of phosphate. Since the seaweed-like free-standing sheets were grown perpendicularly to the substrate, a high accessibility is achieved for various kinds of molecules and ions. Thus, this novel type of nanoscale morphology for semiconducting materials would be utilized in electrochemical applications such as sensors and photoelectrodes.

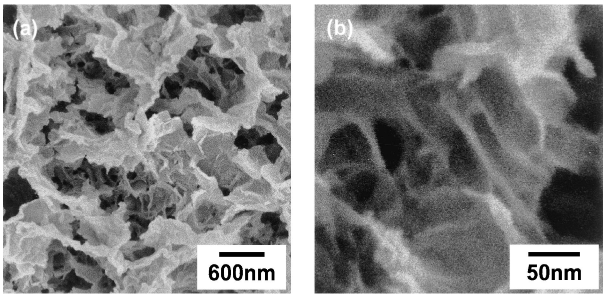

Figure 2. SEM images of seaweed-like sheets of wurtzite ZnO crystals grown in a solution with $R_p = 0.2$–1.0; low magnification (a) and high magnification (b).

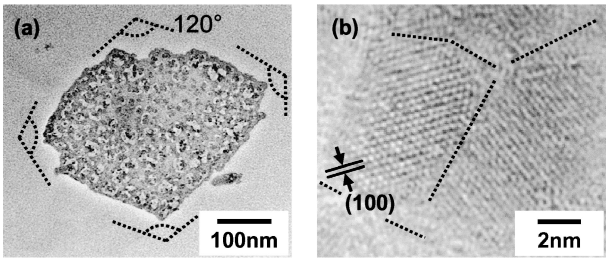

Figure 3. TEM images of a part of seaweed-like sheets of wurtzite ZnO crystals grown in a solution with $R_p = 1.0$.

In conclusion, we successfully prepared a free-standing nanosheet form of wurtzite ZnO crystal using a strong inhibiting effect of phosphate ions on the growth of the (001) surface. Nanosheets with a uniform thickness less than 5 nm exhibited a phosphate-mediated mosaic texture consisting of platy subunits.

This work was supported by Grant-in-Aid for Scientific Research (No. 15560587) and 21st Century COE program "KEIO Life Conjugate Chemistry" from the Ministry of Education, Culture, Sports, Science and Technology, Japan.

References

1 M. H. Huang, Y. Wu, H. Feick, N. Tran, E. Weber, and P. Yang, *Adv. Mater.*, **13**, 113 (2001).
2 Z. R. Tian, J. A. Voigt, J. Liu, B. Mckenzie, and M. J. Mcdermott, *J. Am. Chem. Soc.*, **124**, 12954 (2002).
3 T. Yoshida, M. Tochimoto, D. Schlettwein, D. Wöhrle, T. Sugiura, and H. Minoura, *Chem. Mater.*, **11**, 2657 (1999).
4 J. Zhang, L. Sun, C. Liao, and C. Yan, *Chem. Commun.*, **2002**, 262.
5 T. Saeed and P. O'Brien, *Thin Solid Films*, **271**, 35 (1995).
6 P. O'Brien, T. Saeed, and J. Knowles, *J. Mater. Chem.*, **6**, 1135 (1996).
7 K. Ito and K. Nakamura, *Thin Solid Films*, **286**, 35 (1996).
8 M. Izaki and T. Omi, *J. Electrochem. Soc.*, **144**, L3 (1997).
9 M. Izaki and J. Katayama, *J. Electrochem. Soc.*, **147**, 210 (2000).
10 D. S. Boyle, K. Govender, and P. O'Brien, *Chem. Commun.*, **2002**, 80.
11 S. Yamabi and H. Imai, *J. Mater. Chem.*, **12**, 3773 (2002).
12 L. Vayssieres, K. Keis, A. Hagfeldt, and S. E. Lindquist, *Chem. Mater.*, **13**, 4396 (2001).
13 M. Öner, J. Norwig, W. H. Meyer, and G. Wegner, *Chem. Mater.*, **10**, 460 (1988).
14 J. Livage, M. Henry, and C. Sanchez, *Prog. Solid State Chem.*, **18**, 259 (1988).
15 M. Henry, J. P. Jolivet, and J. Livage, *Struct. Bonding (Berlin)*, **77**, 153 (1992).

Published on the web (Advance View) May 29, 2004; DOI 10.1246/cl.2004.768