

## ARTICLES

## Pattern and Feature Designed Growth of ZnO Nanowire Arrays for Vertical Devices

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An approach is demonstrated for growing aligned ZnO nanowire/nanorod arrays following a predesigned pattern and feature with controlled site, shape, distribution, and orientation. The technique relies on an integration of atomic force microscopy (AFM) nanomachining with catalytically activated vapor–liquid–solid (VLS) growth. The pattern and growth locations are defined by the catalyst distribution created by AFM, and the orientation is determined by the epitaxial growth on a single-crystal substrate. The technique opens a variety of possibilities of using nanowire arrays as sensor arrays, piezoelectric antenna arrays, nanolasers, photonic band gap crystal, biosensors, and field emitters with controlled density, location, shape, and distribution according to a designed pattern and feature.

Recently there has been considerable interest in methods for the fabrication of one-dimensional (1D) ordered nanostructures by the catalytically activated vapor–liquid–solid (VLS) growth process,<sup>1–3</sup> in which the catalyst initiates and guides the growth, and the epitaxial orientation relationship between 1D nanostructures and the substrate leads to the alignment. Among various emerging 1D nanomaterials,<sup>4,5</sup> the ZnO nanostructure,<sup>6</sup> a direct wide band gap (3.37 eV) semiconductor with a large excitation binding energy (60 meV), is one of the most promising functional nanomaterials, exhibiting near-UV emission,<sup>7</sup> optically transparent electrical conductivity, and piezoelectricity.<sup>8</sup> The growth of patterned and aligned 1D ZnO nanostructures<sup>2,3</sup> shows great promise for applications in sensing,<sup>9</sup> room-temperature UV lasers,<sup>10</sup> and field emission.<sup>11</sup> For realizing further nanodevice applications in numerous biotechnology and optoelectronics, it is essential that the periodicity and patterns could be controlled and designed with deliberate control over interfeature distance, positions, shape, and orientation controlled ZnO nanowire/nanorod arrays.

A variety of nanofabrication methods, including focused ion beam patterning,<sup>12</sup> electron-beam lithography,<sup>13</sup> dip-pen nanolithography,<sup>14</sup> and scanning tunneling microscope lithography,<sup>15</sup> have been used to fabricate functional arrays of zero-dimensional (0D) structures with sizes from sub-100 nm to micrometer length scale. Atomic force microscopy (AFM) has been demonstrated as a powerful technique for nanoindentation.<sup>16–18</sup> In this paper, we present a versatile method for fabricating periodic arrays of ZnO nanowire/nanorod using the catalyst pattern created by AFM. The integration of AFM nanomachining technique with the VLS deposition process allows a high degree of control in selectivity, nucleation density, and positioning accuracy. The AFM nanomachining technique is used to pattern 0D catalysts

for fabricating an array of ZnO. The present proof-of-concept experiments have opened up a variety of possibilities of using such arrays as nanolasers, photonic band gap crystals, sensors, piezoelectric antennas, and field emitters.

The nanofabrication process in this paper was accomplished in five steps: (1) the application of an extremely thin layer of photoresist polymer spun onto the surface of a single-crystal Al<sub>2</sub>O<sub>3</sub> substrate (Figure 1a,b); (2) indentation of holes through the polymer following a designed pattern using an AFM tip and exposure of the underlying Al<sub>2</sub>O<sub>3</sub> substrate at defined regions (Figure 1c); (3) sputtering an Au film on the polymer surface (Figure 1d); (4) removal of resist via a solvent rinse and the remainder of catalyst patterns (Figure 1e); and (5) finally, growth of aligned ZnO nanorods on the patterned catalysts (Figure 1f). The details of some major steps are introduced as follows.

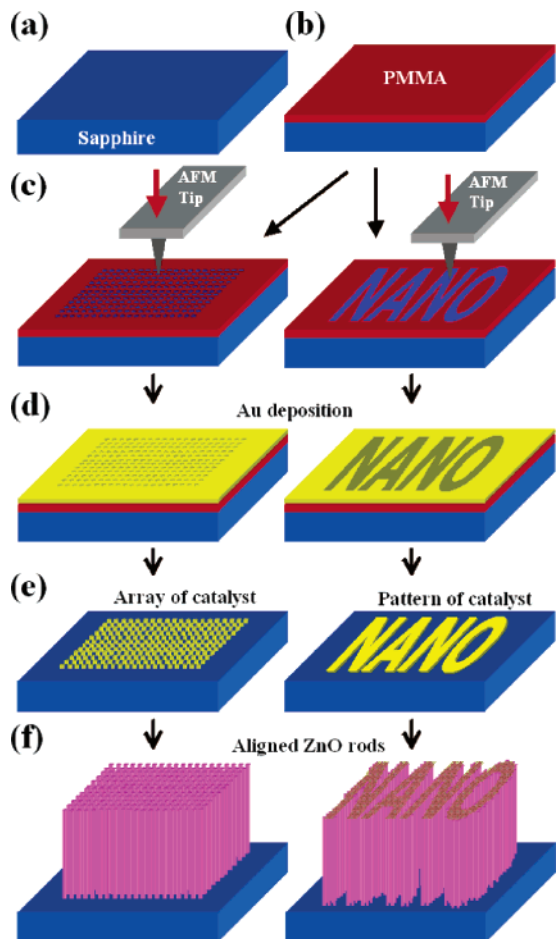
**Preparation of Patterned Catalyst.** An AFM nanomachining technique was used to fabricate the patterned Au nanodots, which served as the catalyst for growing nanorods. A 1.25 wt % poly(methyl methacrylate) (PMMA, molecular mass 96 500 g) solution was spin-coated onto a single-crystal Al<sub>2</sub>O<sub>3</sub>(11 $\bar{2}$ 0) substrate. The substrate is chosen to grow ZnO nanorods epitaxially on its top for achieving an aligned array.<sup>2</sup> After a 30-min soft baking at 150 °C, the PMMA film was produced and also free of pinholes. A commercial AFM (Smena-B, NT-MDT, Russia) and rectangular silicon probes (NSC15, Mikro-Masch, Russia) with a tip radius of 10 nm and a spring constant of 32.5 N/m were employed for the experiment. The AFM was operated in the intermittent-contact mode for imaging. Each indentation was realized by moving the scanner and tip in the vertical (*z*-axis) direction toward the sample. A desired pattern was created by locating the tip on designated positions controlled by computer.

By moving the AFM tip vertically for a distance of 180 nm, which corresponded to an indentation force of 3.8  $\mu$ N, a nanohole array was generated in the PMMA film utilizing AFM

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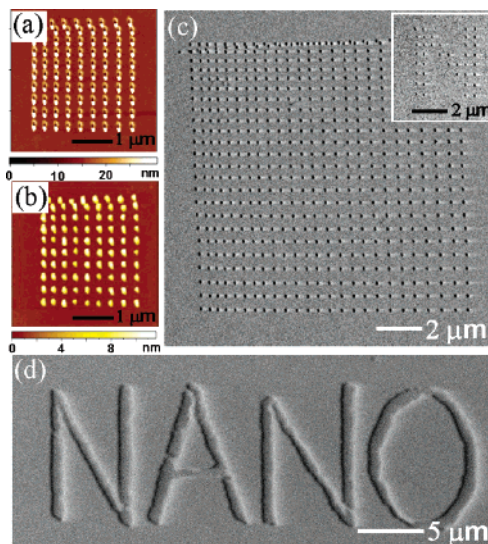
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**Figure 1.** Schematic diagrams of selective ZnO nanorod growth on patterned catalyst array via AFM nanolithography: (a) an  $\text{Al}_2\text{O}_3(11\bar{2}0)$  substrate is spin-coated with (b) a thin PMMA resist layer; (c) pattern and feature are created by utilizing an AFM tip operated in vector (left image) and bitmap (right image) scanning mode, respectively; (d) Au films are deposited onto the exposed  $\text{Al}_2\text{O}_3$  surface and PMMA films via sputtering; (e) once the resist is completely removed with a solvent rinse, a patterned catalyst is achieved; (f) arrayed or patterned, well-aligned ZnO nanorods are obtained after applying catalytically activated vapor phase transport and the condensation deposition process.

operated in a vector scan mode. This was proven to be sufficient to displace the soft polymer resist, thereby exposing the surface of sapphire (Figure 2a). After coating a 10 nm thick Au film and etching away the PMMA, an Au nanodot array with a smallest dot size of 70 nm and a period of 250 nm was fabricated (Figure 2b). Figure 2c shows the SEM image of a resultant  $25 \times 25$  gold nanodot array (inset: SEM image of a gold nanodot pattern “N”). Inset in Figure 2c shows an SEM image of a pattern “N”, consisting of Au dots, indicating the simplicity of the method for generating an array of catalyst nanodots with precise control of positions and spacing.

In addition to various dot patterns, we have also demonstrated the fabrication of catalytic nanostructures utilizing the AFM nanomachining operated in bitmap scan mode. Compared with the vector scan operation, the bitmap scan operation allows the AFM tip to provide access to arbitrary complex customized scan profiles due to less pill-up of PMMA. Figure 2d illustrates the letters “NANO”, consisting of continuous Au nanostructures, by utilizing Au deposition on a series of resist furrows produced in bitmap scan mode. The realization of this pattern demonstrates the ability of this technique to cope with complex design.



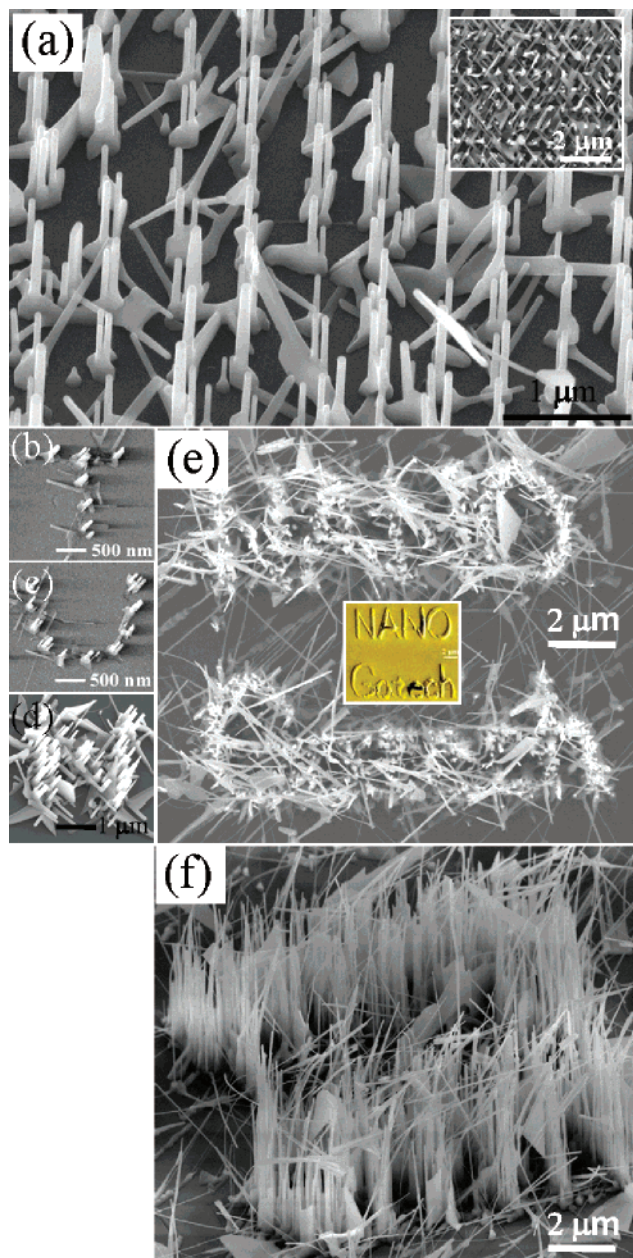
**Figure 2.** AFM images of (a) a nanohole array on PMMA and (b) the corresponding gold nanodot arrays after lift-off. (c) SEM image of the resultant  $25 \times 25$  gold nanodot array (inset: SEM image of a gold nanodot pattern “N”). (d) The letters “NANO” consisting of continuous Au nanostructures.

Au films were then sputtered on the top of the PMMA. The samples were then soaked in acetone to remove the PMMA and dried with nitrogen.

**Growth of Patterned ZnO Arrays.** The growth is governed by catalytically activated vapor phase transport and condensation deposition process, i.e., the VLS process. Using the patterned catalyst, ZnO nanorods were grown by a VLS process in a two-zone vacuum furnace in a reasonable temperature gradient. ZnO powder (Cerac Incorporated, 99.995%) and graphite powder (Cartina, 99.8%) were mixed in 1:2 molar ratio, which was used to lower the growth temperature. The source materials were then ground together and loaded into an alumina boat that was placed at the center of the high-temperature zone in an alumina tube. A single-crystal  $\text{Al}_2\text{O}_3(11\bar{2}0)$  substrate with the Au pattern was placed at the center of the low-temperature zone 30 cm away from the source downstream. After being evacuated by a rotary pump to a pressure of  $1 \times 10^{-3}$  Torr, the horizontal furnace was heated from room temperature at a heating rate of  $5 \text{ }^\circ\text{C}/\text{min}$  to  $1100 \text{ }^\circ\text{C}$  at the source and  $800 \text{ }^\circ\text{C}$  at the substrates for 90 min with constant flowing  $\text{O}_2$  gas (5 sccm) and Ar gas (25 sccm), then cooled to room temperature. The grown structure was analyzed by scanning electron microscopy (SEM) (LEO 1530) and transmission electron microscopy (JEOL 4000EX).

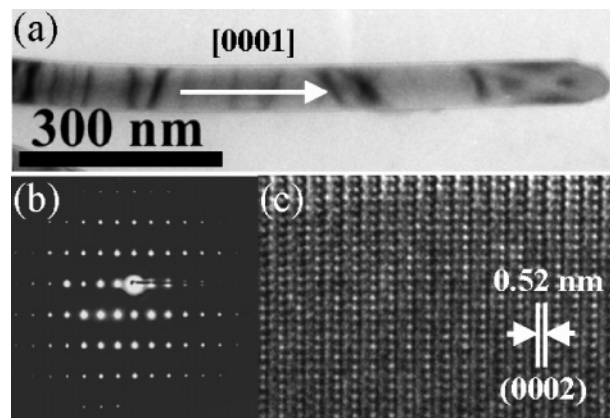
Results of the grown ZnO nanorods are shown in Figure 3. Figure 3a shows a  $25^\circ$ -tilted view of the aligned ZnO nanorod arrays over the region of gold nanodot arrays. The inset in Figure 3a shows that each white spot represents one ZnO nanorod oriented perpendicular to the sapphire substrate. It is clear that the positions of nanorods in the arrays correspond well to the distribution of the Au nanodots shown in Figure 2c. A periodicity in locations of the nanorods is apparent. Among the vertically aligned ZnO nanorods, some nanorods that grew sideways were also observed,<sup>2</sup> which may be due to the rough polished surface of the substrate. A recent study has shown that growth on flat GaN or AlN thin film does not produce side branched nanorods.<sup>10</sup> Figure 3b–d shows the nanorods distributed in the dot matrix forms of capital letters “T”, “U”, and “N”.

Complex patterns of ZnO arrays were also obtained on the Au-patterned substrates created by AFM nanomachining operated in bitmap scan mode, indicating clearly the arrangement

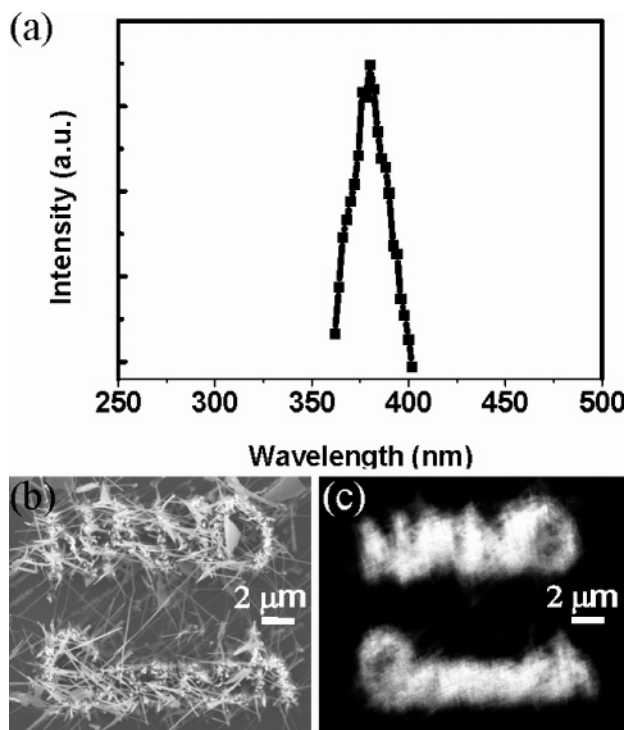


**Figure 3.** (a) A 25°-tilted-view SEM image of the patterned ZnO nanorod arrays (inset: a top-view SEM image of ZnO nanorod arrays). (b, c, d) The capital letters “T”, “U”, and “N” consisting of well-aligned ZnO nanorods. (e) Complex patterns of ZnO arrays: “NANO Gatech” viewed from the top. The inset is an SEM image of the original Au patterns. (f) Side view of the grown ZnO arrays: “NANO Gatech”.

of the well-aligned growth of ZnO nanorods. The inset in Figure 3e is the original gold pattern: the letters “NANO Gatech” for catalyzing ZnO nanorod growth. Figure 3e is the result of the growth, indicating clearly the arrangement of the well-aligned growth of the ZnO nanorods by using AFM nanolithography. Figure 3f exhibits a 25°-tilted view of the same region as that of Figure 3e. Although the result is not as perfect as we would like it to be, possibly due to the diffusion of gold at high growth temperature, it is still possible to create such a pattern. In comparison to the growth of ZnO nanorods by using the patterns generated by monolayer self-assembly of nanosphere (physical growth)<sup>2</sup> and self-assembled molecular monolayer (chemical growth),<sup>3</sup> the potential of the present technique is promising for applications in feature designed nanodevices.



**Figure 4.** (a) TEM image of a single ZnO nanorod and (b) corresponding selected area electron diffraction pattern. (c) HRTEM image of the ZnO nanorod.



**Figure 5.** (a) The CL spectrum recorded from (b) the area of patterned ZnO nanorod arrays and (c) the corresponding CL mapping of part b.

The structure of the ZnO nanorods has been characterized by TEM. Figure 4a shows a typical TEM image of a single ZnO nanorod with a diameter of ~50 nm. The corresponding selected area electron diffraction (SAED) confirms that the phase of the nanorods is hexagonal wurtzite-structured ZnO (Figure 4b). Figure 4c is a high-resolution TEM (HRTEM) image of a nanorod, depicting that the ZnO nanorod is single-crystal and free of dislocations. The growth direction of the ZnO nanorod is [0001].

**Cathodoluminescence (CL) Characterization of Patterned ZnO Nanorod Arrays.** CL is a great technique for characterizing the optical property of nanostructures in relation to their size, shape, and distribution. Since CL uses an electron beam for excitation, it is feasible to excite only one or a group of nanorods. The CL spectra were acquired in the SEM that was equipped with an electron probe microanalyzer (Shimadzu EPMA-1500). CL spectra were accumulated in a single shot mode within an exposure time of 2 nm/s. The room temperature

CL spectrum of the patterned ZnO nanorod arrays is shown in Figure 5a. A peak centered at 380 nm was observed corresponding to the near band edge peak that is responsible for the recombination of free excitons of ZnO. Figure 5b is the plane-view SEM image of patterned ZnO nanorod arrays (the same as Figure 3e), from where the CL signals were acquired. Figure 5c is the corresponding luminescence mapping by selecting the CL peak located at 380 nm, using a 20 nm wide window. Bright areas in the image revealed the luminescence sites, which coincide with the positions of ZnO nanorod arrays. The luminescent letters "NANO Gatech" were observed.

In summary, utilizing the AFM nanomachining technique, together with catalytically activated vapor phase transport and the condensation deposition process, a variety of patterned and featured ZnO nanowire arrays have been grown. The grown pattern and feature are designed by the dotted catalyst prepared by using AFM tip indentation with controlled location, density, and geometrical shape. The vertical orientation of the nanorods is achieved by the epitaxial growth on a single-crystal substrate, which can be sapphire, GaN, and AlN. The technique allows a control over the location, shape, orientation, and density of the grown nanorod arrays. The cathodoluminescence of the nanorods patterned "NANO Gatech" feature illustrates the possible applications of the grown nanostructures for optical applications. The technique demonstrated here is promising for fabricating vertically arrayed devices with designed feature and pattern for future applications in optoelectronics, sensing, field-emission, piezoelectric antenna devices, and biotechnology.

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