Density-controlled growth of aligned ZnO nanowire arrays by seedless chemical approach on smooth surfaces

Sheng Xu, Changshi Lao, Benjamin Weintraub, and Zhong Lin Wang[a)]
School of Materials Science and Engineering, Georgia Institute of Technology,
Atlanta, Georgia 30332-0245

A novel ZnO seedless chemical approach for density-controlled growth of ZnO nanowire (NW) arrays has been developed. The density of ZnO NWs is controlled by changing the precursor concentration. Effects of both growth temperature and growth time are also investigated. By this novel synthesis technique, ZnO NW arrays can grow on any substrate (polymer, glass, semiconductor, metal, and more) as long as the surface is smooth. This technique represents a new, low-cost, time-efficient, and scalable method for fabricating ZnO NW arrays for applications in field emission, vertical field effect transistor arrays, nanogenerators, and nanopiezotronics.

I. INTRODUCTION

ZnO nanorod and nanowire (NW) arrays have been extensively studied over the past several years for their potential applications in fabricating electronic, optoelectronic, electrochemical, and electromechanical devices, such as solar cells,[1] ultraviolet (UV) lasers,[2] piezo-nanogenerators,[3,4] light-emitting diodes,[5] and field-emission devices.[6] For many of these applications, it is crucial to synthesize well-aligned NW arrays. A variety of methods have been reported for fabricating arrays of aligned NWs, including vapor phase transport,[7,8] metal-organic chemical vapor deposition (MOCVD),[9,10] and hydrothermal synthesis.[11,12] However, vapor-phase transport and MOCVD usually require single-crystal substrates and high operation temperature, which are expensive and not compatible with organic substrates for applications in flexible and wearable electronics. Hydrothermal synthesis is a good alternative approach from this purpose, but it usually employs ZnO seeds in the forms of thin films or nanoparticles[13–15] or requires an external electrical field to promote the growth of ZnO nanostructures.[16,17] In such a case, nanowhiskers would grow densely on the entire substrate with large variation in orientation, which may not meet the needs for nano-generators,[3,4] because it requires well-aligned and well-separated NWs.[18,19] Density-controlled synthesis of oriented arrays of one-dimensional ZnO NWs or nanorods has been achieved by nanosphere lithography,[7,20] photo-lithography[21–23] and electron-beam lithography,[24,25]

which are expensive, time consuming, and usually used for small-scale experiments.

In this work, we report a chemical approach for achieving density-controlled growth of aligned ZnO NWs arrays without using ZnO seeds, as shown in Fig. 1. By adjusting the precursor concentration, the density of ZnO NW arrays could be controlled within one order of magnitude (number of ZnO NWs per 100 μm^2) with one NW growing from one spot site. This novel synthesis technique does not require ZnO seeds or external electrical field, and it can be carried out at low temperatures and large scale on any substrate, regardless of whether it is crystalline or amorphous.

II. EXPERIMENTAL DETAILS

In this work, we chose Si (100) and flexible Kapton polymer as the substrates. For simplicity of description, we use Si substrate to describe the experimental procedure and to illustrate the effects of various experimental parameters on the growth. A piece of Si (100) wafer substrate was cleaned by a standard cleaning progress. First, the wafer was ultrasonicated consecutively in acetone, ethanol, IPA (isopropyl alcohol), and de-ionized water each for 10 min; then it was blown dry with nitrogen gas and baked on a hotplate at 200 °C for 5 min to eliminate any adsorbed moisture. Then a 50-nm-thick layer of Au was deposited on top of the Si wafer by magnetron plasma sputtering. This was expected to act as an "intermediate-layer" to assist the growth. Between the Si wafer and Au layer, 20 nm Ti was deposited as an adhesion layer to buffer the large lattice mismatch between Si(100) surface with native oxide on and Au(111) surface and to improve the interface bonding. Then the substrate was annealed at 300 °C for 1 h. The next step
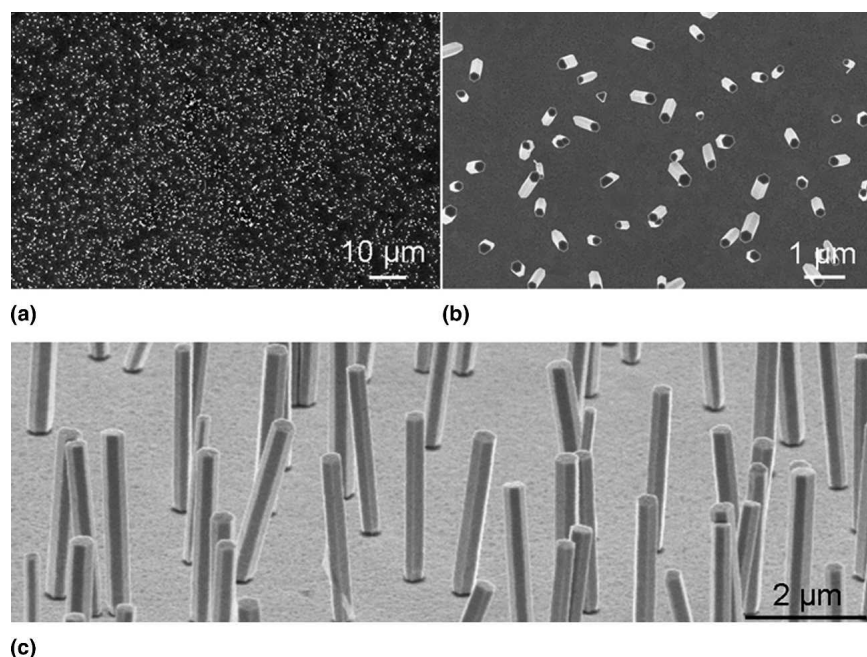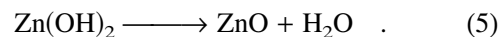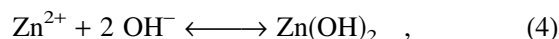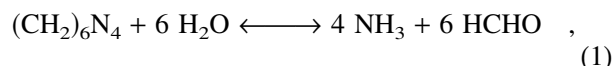
FIG. 1. A general view of as grown ZnO nanowire arrays at 5 mM, growing 24 h at 70 °C: (a) top view, (b) enlarged top view, and (c) with a 60° tilt.

was to prepare the nutrient solution. The nutrient solution was composed of a 1:1 ratio of zinc nitrate and hexamethylenetetramine (HMTA). Both of the chemicals were reagent grade from Fluka (St. Louis, MO). The substrate was put face down at the top of the nutrient solution surface. Because of surface tension, the substrate could float at the top of the solution surface. Growth of ZnO NWs was conducted in a mechanical convection oven (model Yamato DKN400, Santa Clara, CA). The products were examined at 5 kV using a LEO 1530 scanning electron microscope (SEM).

III. RESULTS AND DISCUSSION

The annealing process helps the as-deposited Au layer form a uniform crystalline thin layer on the surface of Si substrate, which is critical in the oriented growth of aligned ZnO NWs. The chemistry of the growth is well documented.[26–29] Zinc nitrate salt provides Zn^{2+} ions required for building up the ZnO NWs. Water molecules in the solution provide O^{2-} ions. Even though the exact function of HMTA during the ZnO NW growth is still unclear, it is believed to act as a weak base, which would slowly hydrolyze in the water solution and gradually produce OH^-. This is critical in the synthesis process because, if the HMTA hydrolyzes too fast and produces a lot of OH^- in a short period of time, the Zn^{2+} ions in solution will precipitate out quickly due to the high pH environment. Therefore, Zn^{2+} would contribute little to the ZnO-NW-oriented growth and eventually result in fast consumption of the nutrient and prohibit further growth of ZnO NWs.

$$(CH_2)_6N_4 + 6\ H_2O \longleftrightarrow 4\ NH_3 + 6\ HCHO \quad , \tag{1}$$

$$NH_3 + H_2O \longleftrightarrow NH_3 \cdot H_2O \quad , \tag{2}$$

$$NH_3 \cdot H_2O \longleftrightarrow NH_4^+ + OH^- \quad , \tag{3}$$

$$Zn^{2+} + 2\ OH^- \longleftrightarrow Zn(OH)_2 \quad , \tag{4}$$

$$Zn(OH)_2 \longrightarrow ZnO + H_2O \quad . \tag{5}$$

The growth process of ZnO NWs can be controlled through the five chemical reactions listed above. All of these reactions are in equilibrium and can be controlled by adjusting the reaction parameters, such as precursor concentration, growth temperature, and growth time, to push the reaction equilibrium forward or backward. In general, precursor concentration determines the NW density. Growth time and temperature control the ZnO NW morphology and aspect ratio. In the following parts, the growth mechanism of ZnO NW arrays is elucidated with detailed analysis from our experimental results.

A. Concentration

The density of ZnO NWs on the substrate could be controlled by the initial concentration of the zinc salt and HMTA. To explore the relationship between the precursor concentration and the density of the ZnO NW arrays, a series of experiments was performed by varying the precursor concentration but keeping the ratio constant between the zinc salt and HMTA. Experimental results show that the density of the NW arrays is closely related

to the precursor concentration. Detailed analysis of the measured data is shown in Fig. 2 (line with filled circle data points). From 0.1 to 5 mM, the ZnO NWs density, defined as number of NWs per 100 μm^2, increases dramatically, possibly for the following reasons. Zinc chemical potential inside the solution body increases with zinc concentration. To balance the increased zinc chemical potential in solution, more nucleation sites on the substrate surface will be generated, and therefore, the density of ZnO NWs will increase. When the zinc concentration is further increased, the density of ZnO NWs remains approximately steady with a slight tendency to decrease. The steady/saturated density may be understood from the nucleation and growth process. The NW density is decided by the number of nuclei formed at the beginning of the growth, which continue to grow and form nanorods (shorter NWs). The arrival of more ions on the substrate may not initiate new nuclei at a later stage because of two possible reasons. One, with consideration of the critical size required for a nucleus to grow into a crystal, no new nanorods would form if the sizes of the nuclei were smaller than the critical size. Second, due to the existence of the first group of grown nanorods, the newly arrived ions on the substrate have a higher probability of reaching the existing NWs than the newly formed nuclei. Thus, the size of the nuclei may not exceed the critical size, and they will eventually dissolve into the solution body. In such cases, a continuous increase in solution concentration may not increase the density of the NWs when its density is larger than the saturation density. This also explains why the grown NWs in our experiments have fairly uniform height. Even though the density of the ZnO NW remains steady at high precursor concentration level, the surface coverage percentage increases slightly due to the lateral

growth of the NWs (Fig. 2, line with filled triangle data points).

B. Growth time

Wurtzite ZnO has polar surfaces, such as (0001) and (000$\bar{1}$), and non-polar surfaces such as {01$\bar{1}$0} and {2$\bar{1}$$\bar{1}$0}. At different growth stages, including at the beginning, middle, and end, the polar surfaces' axial growth is found to have a different relative growth rate from that of non-polar surfaces lateral growth. At the beginning growth period (from the start to around half an hour), lateral growth seems to be more significant than axial growth [Fig. 3(a)]. When the growth time exceeds half of an hour, the width of ZnO NWs is almost independent of time, indicating little lateral growth [Fig. 3(b)]. This indicates that, at the beginning growth stage, lateral growth is more significant than axial growth. In the middle growth stage, from half an hour to around 6 h, axial growth is dominant. At the final growth stage, from 6 to 48 h in our experiments, lateral growth and axial growth seem to be equally significant, as can be seen from Figs. 3(b) and 3(c). In this period, ZnO NWs length is almost doubled. At the same time, ZnO NWs width is also doubled. The aspect ratio remains nearly constant.

Our previous study indicates that the Zn-terminated (0001) surface is much more catalytically active than the O-terminated (000$\bar{1}$) surface for the growth of NWs. For the aligned array, we believe that all of the NWs have their positive c axis pointing upward, which means that the (0001) surface is at the growth front. This characteristic results in the alignment of polarity and piezoelectric affect of all the NWs.

C. Temperature

Temperature is an important factor in maintaining a high aspect ratio of the hexagonal prism shape of ZnO NWs. In our experiments, 70 °C is found to be the optimum temperature for obtaining a high aspect ratio and well-defined hexagonal prism shape of the ZnO NWs [Fig. 4(b)]. When the temperature is reduced, for example to 60 °C [Fig. 4(c)], the aspect ratio becomes smaller than that at 70 °C. The aspect ratio of the ZnO NWs is determined by the relative growth rate of the polar surfaces and non-polar surfaces. This means that the relative growth rate of polar surface to non-polar surface at low temperatures is smaller than that at high temperatures. By increasing the temperature for example to 95 °C, pyramid-shaped ZnO nanorods were grown [Fig. 4(a)]. The temperature-dependent growth behavior may also be understood from the basic theory of crystal nucleation and growth. When the temperature is low, the mobility and the diffusion length of the ions on the substrate are rather limited, which prohibit the ions to diffuse
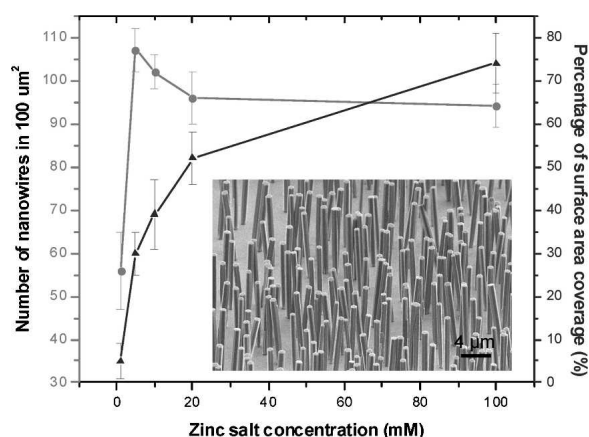

FIG. 2. Density varied with concentration: Plot of ZnO nanowire density in a 100 μm^2 area (line with filled circle data points) and plot of area percentage covered by ZnO nanowires (line with filled triangle data points). Each data point was obtained from 4 different areas. Inset is a typical image of ZnO nanowires grown at 5 mM.
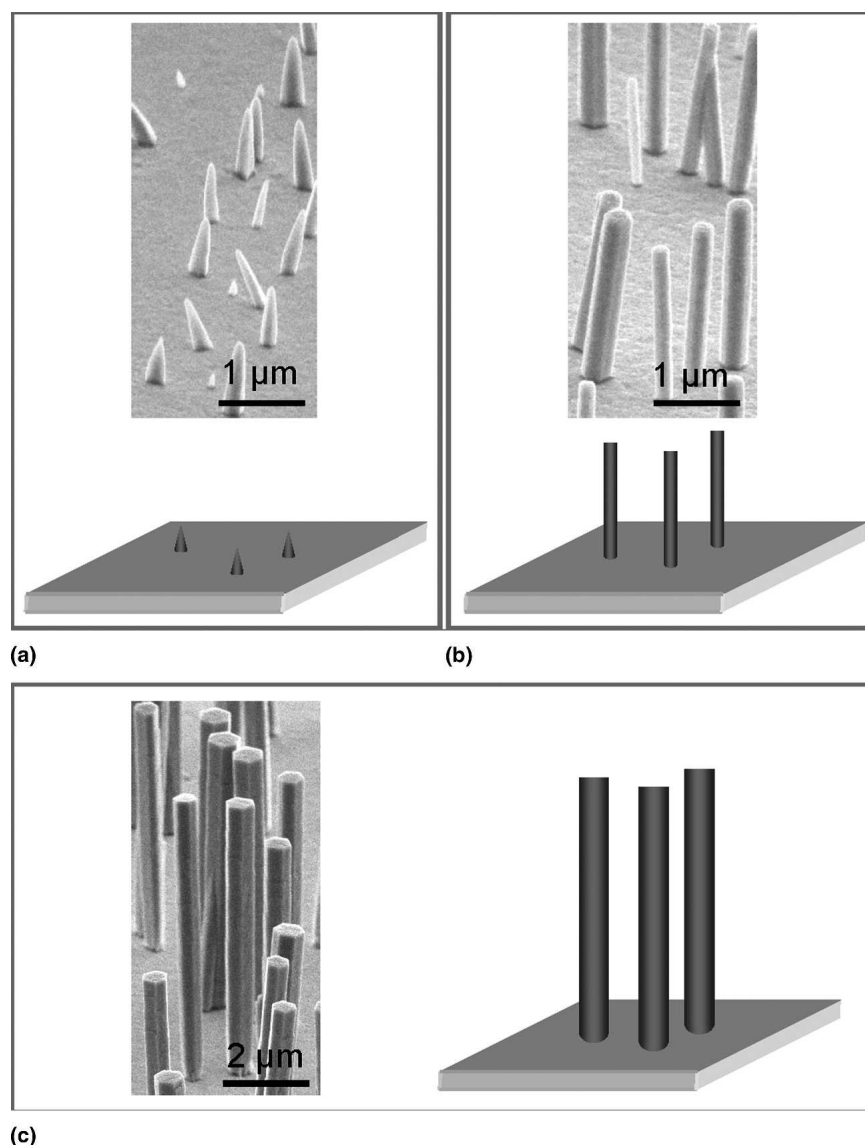
FIG. 3. Time-dependent of ZnO nanowire morphology evolution: (a) 0.5 h, (b) 6 h, and (c) 48 h.

around, and therefore large size nuclei are formed. Thus, the NW density is low. At high temperature, the mobility and diffusion length of the ions are large enough to reach the sites of the firstly grown NWs, thus, no new nuclei are formed because the precursor ions have higher affinity to the already-formed seeds than they do to bare substrate, resulting in a lower density of NWs on the substrate. At an optimum temperature, such as 70 °C, the mobility of the ions is moderate and their diffusion length is within a small range in the vicinity of the substrate; thus the accumulation of ions at local regions results in high density of NWs. However, their size is small because of the conservation of total ions that are able to migrate to near the substrate.

As discussed previously, HMTA functions as a slowly decomposing weak base, which maintains the weak basic environment in the solution and successively provides Zn^{2+} ions with OH^- ions. From reaction (1), we find that 7 mol reactant produce 10 mol product. Thus, if the reaction temperature were increased, reaction (1) would move forward by virtue of entropy increase, which means that HMTA would decompose more quickly at a high temperature than it would at a low temperature. That is to say, at the beginning, HMTA has already decomposed to a relatively large degree and has produced enough OH^-, resulting in a sufficient and thorough growth of ZnO. Therefore, the base of our ZnO nanorods is thicker than it is at lower temperature. Furthermore, both the axial and lateral growth rates are greatly increased at higher temperature. As time goes by, the supply of Zn^{2+} is limited in the reaction container and gradually becomes exhausted, which leads to the formation of
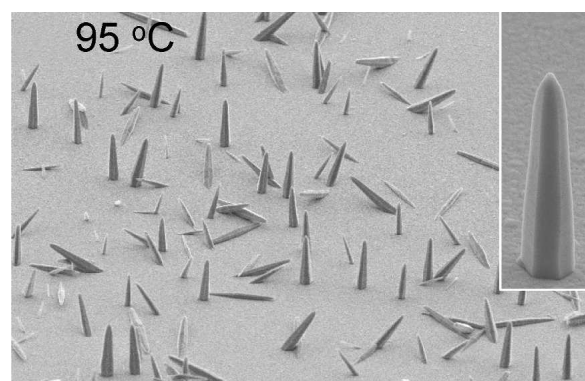
(a)
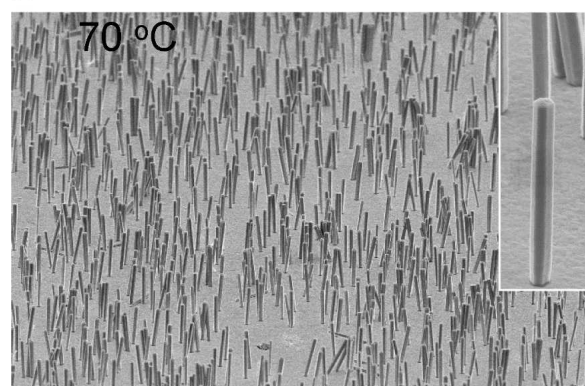
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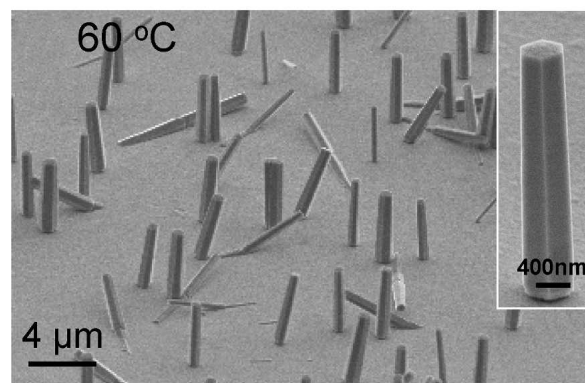
(c)

FIG. 4. ZnO nanowires grown at different temperatures: 60° tilt degree view of ZnO nanowires synthesized at (a) 95 °C, (b) 70 °C, and (c) 60 °C. The three images are recorded at the same magnification, and the three inset images are at the same magnification.

incomplete shape of the NWs (pyramids or tapped nanorods).

As discussed above, the concentration controls the nucleation density, growth time controls the aspect ratio, and temperature controls the morphology as well as aspect ratio. By adjusting those three parameters, we can obtain high aspect ratio ZnO NWs, as shown in Fig. 5.

D. Substrate

In the experiments, the effect of different substrates on the controlled growth of aligned ZnO NW arrays was
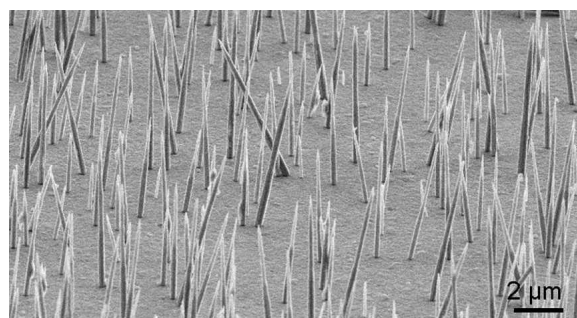

FIG. 5. ZnO nanowires grown at 5 mM, 80 °C for 48 h.

investigated. The results show that the substrate substances have little influence on the growth of ZnO NW arrays as long as the substrates were treated with a standard fabricating procedure as described previously. Growth results on different substrates are shown in Fig. 6. ZnO NW arrays could grow not only on single crystal Si wafers [Fig. 6(a)], but also on amorphous flexible polymer substrates [Fig. 6(b)]. The basic requirement for the aligned growth is that the substrate is smooth.
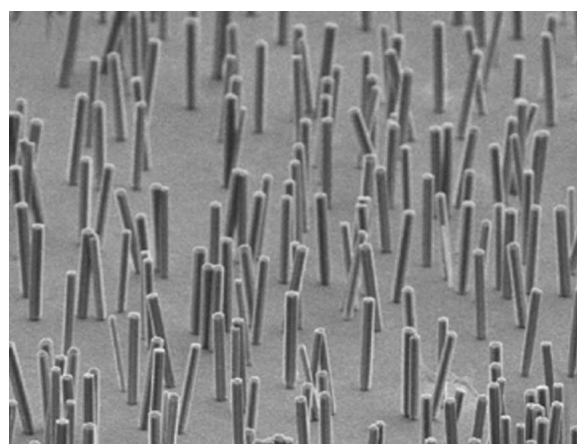
(a)
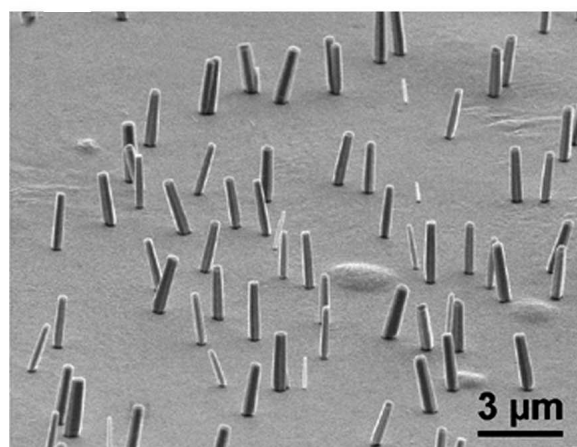
(b)

FIG. 6. ZnO nanowires grown on (a) stiff Si wafer and (b) flexible Kapton polymer substrate, which are at the same magnification.

IV. CONCLUSIONS

Using a novel chemical approach, density-controlled, vertically aligned ZnO NW arrays were successfully synthesized by varying the zinc precursor concentration. The density of ZnO NWs increases with zinc concentration at low concentration level and decreases with zinc concentration at high concentration level. The growth process could be divided into three stages, as controlled by growth kinetics. The first stage is characterized by lateral growth, the second is dominated by axial growth, and the third is described as proportional growth. Growth temperature affects the aspect ratio and morphology of the NWs. The optimum growth temperature was found to be 70 °C. Temperature lower than 70 °C would decrease the NWs' aspect ratio, and temperature higher than that would result in pyramid-like ZnO nanorods. The synthesis has no special requirements for substrate as long as its surface is locally flat. The technique illustrated here is a low-cost, time-efficient, and scalable method for fabricating ZnO NW arrays on any substrate for various applications.

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