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3D patterning of ZnO nanostructures

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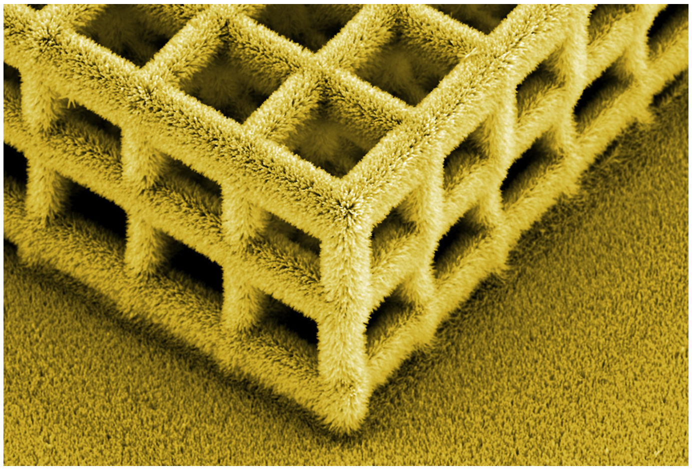

Zinc oxide (ZnO) nanostructures such as nanoparticles, nanowires, nanorods, etc. have been the subject of intense research in recent years. ZnO nanorods (NRs) are potentially ideal for applications such as gas sensors, nanolasers, transparent electrodes in solar cells, as well as in photoelectrochemical cells for water splitting, hydrogen generation, and phototocatalysis.

For the growth of organized ZnO NRs structures, a variety of chemical and physical approaches have been developed, such as Chemical Vapor Deposition, Thermal Evaporation, and Aqueous Chemical Growth. The selective area growth of well-aligned ZnO NRs has also been investigated for the realization of more sophisticated devices, where the control of material pattern and placement is of high importance. The growth of patterned ZnO NRs has been demonstrated with different methods (micro-contact printing, ink jet printing, laser interference lithography etc.) in all cases, however, ZnO nanostructure patterning has been performed on flat surfaces (Si wafers, flexible organic films), while the 3D microstructuring of ZnO NRs has not been achieved yet.

We show that complex fully 3D ZnO aligned NRs structures [1] can be assembled in micrometer scale by combining a laser technique (Multi-Photon Lithography, MPL) [2] and a low temperature hydrothermal growth, seeded by zinc (Zn) layer deposited by Pulsed Laser Deposition (PLD) [3]. The structure that appears on the cover of this issue of *Materials Today* has been made using this method. The first step is to direct ''write'' the 3D scaffold that serves as substrate for the ZnO NRs arrays deposition, using MPL of an organic–inorganic hybrid material. MPL is a laser-based additive manufacturing technique, which allows the fabrication of fully 3D microstructures with ultra-high resolution. It is based on the phenomenon of multiphoton absorption. The beam of an ultrafast laser is tightly focused into the volume of a transparent, photopolymerizable resin, causing the material to absorb more than one photon, and photopolymerize locally. Moving the laser beam inside the material, 3D structures are directly ''written''; all that is needed afterwards is to remove the unexposed, unpolymerized resin, by immersing the sample into an appropriate solvent. Afterwards, the scaffold is covered with a thin film of Zn, applying the PLD [3] technique. This is a laser-based thin film deposition method: the beam of a high-power laser is focused onto the surface of a target of the material to be deposited (Zn in our case), placed inside a vacuum chamber, in ultra-high vacuum conditions. The plume of the ejected material, accompanying laser ablation of the target, deposits uniformly on the surface of the 3D structures placed parallel to the target, to form a thin film. Following hydrothermal growth of zinc nitrate hexahydrate ($Zn(NO_3)_2$), vertically aligned ZnO NRs are grown to the regions where the zinc layer was initially deposited.

This 3D ZnO NRs patterning method is simple to execute, low cost, easy to scale up, and also can be used to grow the nanostructures on non-flat surfaces. In addition, it is possible to control the morphology, geometry and properties of the nanorods by

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varying the different growth conditions (temperature, growth time, precursor concentration, and growth solution pH value). Last but not least, the hydrothermal growth can be easily modified to incorporate more chemical elements and grow doped ZnO nanorods. The size and the density of the nanorods, along with their composition, can be modified to meet different applications [4,5]. In fact, this technology does not even have to be limited to zinc or ZnO. An infinite number of metals, oxides, polymers, even biomaterials can be processed by PLD; it should be therefore possible make 3D nanostructures coated with almost any coating required.

One disadvantage of this method is the slow speed and high cost of the MPL. However, it is the only available technology allowing the direct printing of such complex 3D structures with sub-micron resolution. Given the unique technology capabilities, there is a lot of concentrated research trying to improve its productivity by either developing faster photoinitiators, or holographic MPL, and it is expected that it will progress soon from the laboratory to the factory floor.

In fact, if freeform structures are not needed, MPL is not necessary for the fabrication of 3D structures. Another technique which could provide 3D periodic high-resolution polymeric structures is interference lithography [6]. This way, 3D high-resolution periodic structures could be made using only one (or a few) pulses of light; then PLD and ACG could be used to further functionalize the structures with zinc and ZnO.

When it comes to applications, the most obvious one is water splitting. Pure, doped, and functionalized ZnO nanorods and branched nanorods have been employed as catalysts for water splitting. The preparation of the nanorods has been mostly on conductive flat surfaces; the growth recipes could be easily modified so these nanorods are grown on 3D structures, increasing many-fold the active surface area, and therefore the efficiency of the procedure.

Another obvious application is sensing. ZnO oxide nanorods have been extensively studied as humidity, ethanol and gas sensors; [7] going from 2D to 3D and increasing the active area, will increase the performance of the sensor.

To conclude, we have developed a new method for the fabrication of 3D micro-structured arrays of ZnO nanorods, based on a direct laser technology, a laser deposition technique and a low-temperature hydrothermal method. This method can be modified for the deposition of other materials and for different ZnO and doped ZnO geometries, with potential applications in a variety of fields. Our 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.

Further reading

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