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Ultrafast microwave-assisted synthesis of various zinc oxide nanostructures

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The conventional hydrothermal process for the synthesis of zinc oxide (ZnO) nanostructures has been a slow process and provides less control in terms of shape, size and nucleation time. Whereas, synthesis through microwave heating takes only a few minutes to produce high quality, ultra-pure zinc oxide nanostructures. In this study, we have presented a protocol to fabricate various ZnO nanostructures (vertically-aligned nanorods, vertically-aligned nanowalls, nano flowers and nanopillars) using a domestic microwave oven. Based upon the process study, variation in diameter and length of vertically aligned ZnO nanorods with growth time has been reported. Uniformly distributed ZnO nanowalls along with ZnO nanoflowers have been fabricated in less than 5 minutes. In addition to this, ZnO nanopillars have been fabricated for the first-time using evaporation and degradation phenomena in themicrowave oven. Furthermore,the ZnO nanorods have been found to exhibit a super hydrophobic behaviour, whereas the ZnO nanowalls, nanoflowers and nanopillars have shown a hydrophobic behaviour. The developed ZnO nanostructures may have been found their applications in the areas of optics, electronics, biomedical, solar cell, sensors and transistors *etc.*

Keywords: Hydrothermal, Microwave heating, Nanostructure, Sol-gel

1 Introduction

Unique optical, chemical, electrical, and piezoelectric properties of ZnO nanostructures have made them an important material for research and development[1–4].They exhibit interesting properties like high catalytic efficiency and strong adsorption ability. The band gap of ~3.37 eV with high excitation binding energy of 60 meV and their hydrophobic nature[5–10]with a contact angle in the range of 120° to 150°makes them suitable for solar cell applications[11–14]. The multiplicity of morphologies is the speciality of ZnO nanosystems forming the basis for their versatile and unrivalled applications, involving biomedical, optical, optoelectronics, magnetism, tera-hertz devices and photocatalysis[3,9,15–19]. Moreover, ZnO nanostructures are widely used in semiconductor devices such as gas sensors, light emitting diodes, field effect transistors, ultraviolet lasers, photodetectors, and piezo-nanogenerator[16,20]. These nanostructures can be synthesised in different morphologies, such as nanorods, nanoplates, nanorose, nanoring, nanocages and films by varying their method of synthesis[20–24]**.** Multiple morphologies having varying properties is the primary reason for the wide variety of applications of these nanostructures[1,3]. Due to their broad range of applications, bulk growth of ZnO nanostructures is required with reduced growth time.However, ZnO nanostructures are grown using processes such as vapour-liquid-solid, metal organic carbon vapour deposition, pulsed laser deposition and thermal evaporationwhich usually require high temperatures ranging from 450°C to 900°C (with high processing time of 3 to 8 hours) and sometimes need a suitable catalyst, which also hinders variety in terms of the choice of the substrate materials[23,25,26].In addition to these processes hydrothermal process is most commonly used process for the growth of ZnO nanostructures. However, the conventionally used hydrothermal process is time-consuming (10 to 20 hours). All these factors contribute tomakethese processes less efficient not just energetically but also economically. Many ZnO nanostructures with one-dimensional (1D) and two-dimensional (2D) morphologies, such as nanorods, nanobelts, nanowalls and nanoflowers, have been synthesized earlier using hydrothermal process. Out of these ZnO nanowalls (NWs) provide a 2D network and larger surface area compared to ZnO nanorods. ZnO nanowalls have considerable application potential in energy-storage devices,field emission devices, and biological sensors[27]. They are novel two-dimensional nanostructures that hold promise for applications that require networks with large surface area, such as solar

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*Corresponding author (E-mail: prabhat@iitrpr.ac.in) cells and gas sensors. Within the past decade, the first studies of nanowalls have been reported in a variety of materials systems, and proof-of-concept gas sensors, nanogenerators, and photoconductors based on nanowalls have been recently demonstrated. Among all of the inorganic materials utilized in electronic devices, ZnO is particularly promising for its fast electron transport. ZnO may also be grown in a diversity of nanoscale architectures, which is critical for bulk heterojunction solar cells, as the varying distances between nanoscale features may be tuned to match energy carrier diffusion lengths[28].Nanowalls may be grown by techniques similar to one dimensional nanorods, a class of related but distinct nanostructures. Notably, the growth of ZnO nanowalls and nanorods may coexist during a single growth, for example, nanowalls may form a network between nanorods and have been observed to be taller near nanorods, which suggests the sharing of collected precursors between these two nanostructures. Moreover, nanowire growth has also been observed to occur after nanowall formation at nanowall junctions, potentially due to precursor atom clustering. The morphological evolution of nanorods into nanowalls further implies regimes of preferred growth of these one and twodimensional architectures[28]. Another important three dimensional (3D) fluffy nanostructure of ZnO is nanoflowers which possesses many useful properties. This characteristic is primarily attributed to their large specific surface area and their performance in preventing aggregation of single nanomaterials together with each other in the periodof reaction that improves the photodegradation efficiency of pollutants. To date, fluffy-like 3D ZnO nanoflowers have been obtained viaindependent methods, such as a facile aqueous solution route, aone-step solvothermal method and direct sonochemical synthesis. However, there has not been much research on complex methods, suchas ultrasonic assisted hydrothermal methods for the synthesis of 3D-fluffy ZnO nanoflower[29].

Recently several processesfor ultra-fast growth of ZnO nanorods have been reported by many researchers, howeverthe synthesis processes of ZnO in terms of controlling size, structure and morphology are found to befind in conflicts with each other[23-28]. Out of the wide variety of morphologies that can be synthesised by varying process parameters, the present work reports the fabrication of four major morphologies namely nanorods, nanowalls, nanoflower, and nanopillars using an ultra-fast microwave assisted growth process. Moreover, wettability behaviour of fabricated ZnO nanostructures with water is also investigated.

2 Materials and Methods

For the growth of different ZnO nanostructures, an aqueous solution of zinc salts namely zinc nitrate hexahydrate ($ZnNO_3.6H_2O$) - 25 mM and hexamine ($(CH_2)_6N_4$) - 12.5 mM as precursor material is prepared in deionised water. Zinc acetate dihydrate ($ZnCH_3(COO)_2.2H_2O$) along with monoethanolamine (MEA) is used for the seed layer. Ammonium hydroxide (NH_4OH) is used in the growth process of ZnO nanowalls whereas, ammonia (NH_3) in the growth of ZnO nanoflowers. Microwave oven (Model: MP9889FCR, LG, Korea) is used for fabrication of ZnO nanostructures. The basic setup used for the growth of various zinc oxide nanostructures using microwave oven is shown in Fig. 1.

Surface morphology of prepared ZnO nanostructures is observed using scanning electron microscopy (SEM) [Jeol 6610LV, Japan]. To confirm the element composition of ZnO nanostructures, energy dispersive spectroscopy (EDS) [Oxford INC A.X, United Kingdom] and XRD (Panalytical X, peart Pro, MPD system, United Kingdom) with an X-ray source of Cu (1.54Å) is used. In addition to this, the contact angle study is performed using a contact angle goniometer (First Ten Angstroms, USA).

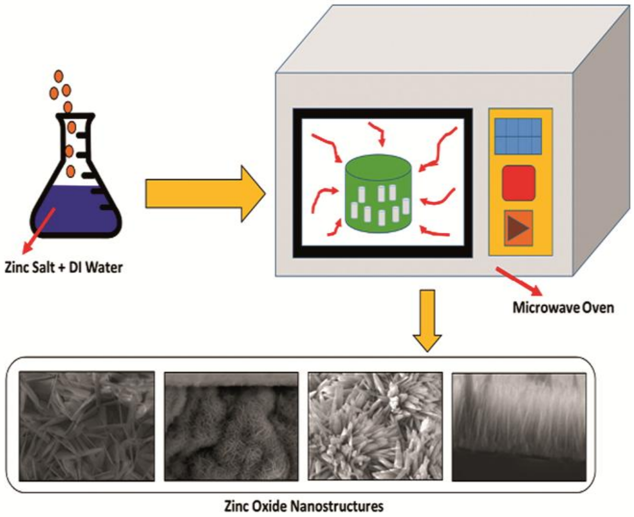

Fig. 1 — Schematic for growth of various zinc oxide nanostructures rods in microwave oven at 900 W.

3 Results and Discussion

3.1 Synthesis of Vertically Aligned ZnO Nanorods

Vertically aligned ZnO nanorodsare synthesized using both hydrothermal and microwave methods. For the growth of ZnO nanorods, p-type Si wafers are cleaned using 20 min ultra-sonication in acetone followed by ethanol and dried under nitrogen gas. A seed layer is prepared by mixing 0.75 mM zinc acetate dihydrate in ethanol and spin coated on the cleaned Si wafers at 3000 rpm at a spin time of 2 minutes. The coating procedure is repeated five times to ensure proper and uniform coating of the seed layer, which is subsequently annealed at 500 °C in vacuum for 30 minutes.The prepared Si wafershaving seed layer of thickness 150 nm are placed in an autoclave upside down in the growth solution. The autoclave is kept in a furnaceat 130°C for 22 hours. The sample is taken out, rinsed in deionised water and dried using nitrogen. Surface morphology of the prepared vertically-aligned ZnO nanorods using this hydrothermal process is shown in Fig. 2a.

For microwave synthesis of vertically-aligned ZnO nanorods, the annealed silicon substrate is placed upside down in the growth solution in the microwave oven in a glass beaker, instead of Teflon autoclave used for the hydrothermal process. The synthesised vertically-aligned ZnO nanorods, having a diameter of 120 nm and a length of 900 nm could be developed in 2 min at 900 W, which are shown in Fig. 2b. Moreover, the ZnO nanorods fabricated on Si wafer in the microwave oven are found to have adiameter, which is one-tenth of that produced by the hydrothermalmethod. Growth rate increases with increase in microwave power; at higher power growth, theprocessing time decreases significantly and results in a fast axial growth saturation, which has also been observed by Mahpeykar *et al.*[30].It could be observed that fabricating vertically-aligned ZnO nanorods in a microwave oven is an ultra-fast process with easy control on size and density of ZnO nanorods. Heteronucleationis observed in the microwave-fabricated ZnO nanostructure as they properly utilise the precursor material. Whereas, in conventional hydrothermal process, homonucleation leads to wastage of precursor materials causing settlement of ZnO nanorods at the bottom of the vessel. A comparison of processing times to develop ZnO vertically aligned nanorods by various reported processes/techniques vis-à-vis the presented microwave processis shown in Table 1, which clearly indicates that the present method is the fastest route.

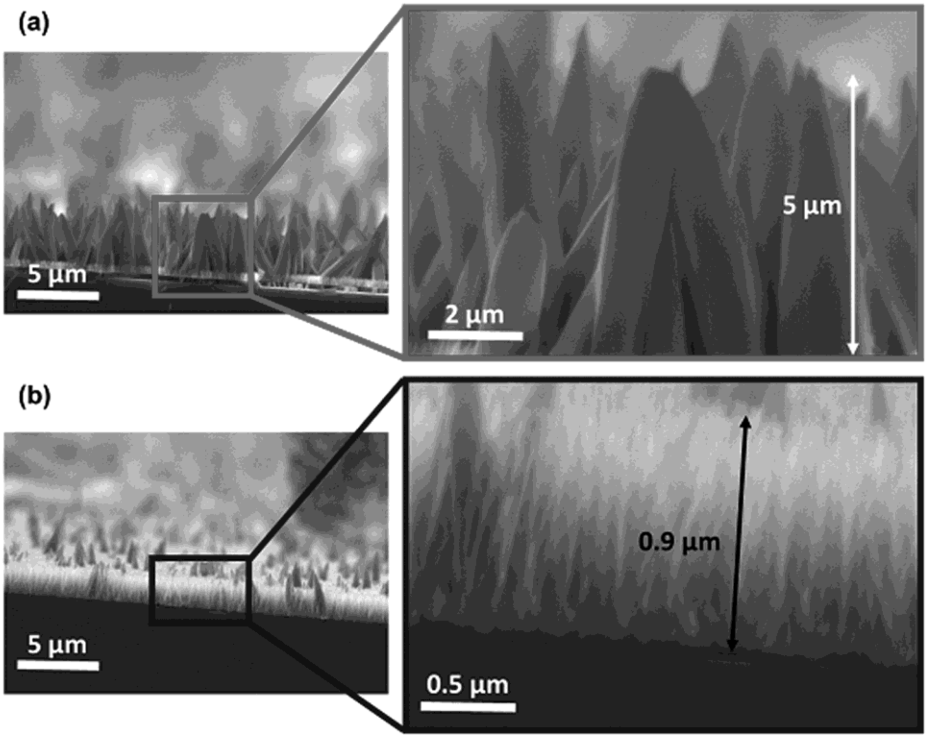

Fig. 2 — SEM images of vertically-aligned ZnO nanorods fabricated using (a) Hydrothermal process at 130 °C for 22 h and (b) Ultra-fast microwave oven at 900 W for 2 min.

Table 1 — A comparison of vertically aligned ZnO nanorods synthesized by various methods.

Ref.	Method	Zn source	Catalyst	Temp (°C)	Substrate	Time (min)	Diameter (nm)	Power (W)
30	Microwave	$Zn(NO_3)_2{\cdot}6H_2O$	ZnO (seed)	--	Glass	10	--	850
43	Microwave	$Zn(NO_3)_2{\cdot}6H_2O$	PVA–$Zn(OH)_2$	90	GaN	120	80–170	--
43	Microwave	$Zn(NO_3)_2{\cdot}6H_2O$	PVA–$Zn(OH)_2$	90	sapphire	120	30 to 90	--
43	Microwave	$Zn(NO_3)_2{\cdot}6H_2O$	PVA–$Zn(OH)_2$	90	Glass	120	40 to 100	--
43	Microwave	$Zn(NO_3)_2{\cdot}6H_2O$	PVA–$Zn(OH)_2$	90	quartz	120	30 to 90	--
44	Microwave	$Zn(NO_3)_2{\cdot}6H_2O$	ZnO (seed)	140	--	20	60–80	600
45	Hydrothermal	$Zn(NO_3)_2$	ZnO (seed)	95	Glass	240	800	--
46	Microwave Plasma-Assisted	Zn powder	--	25	Glass	7	319	800
47	CVD	(CH3)2Zn.N (C2H5)3	--	800	sapphire	15	250	--
48	Thermal Evaporation	Zn powder	Cu	650	Glass	30	350	--
49	Sol-gel	Zn(CH3COO)2	ZnO (seed)	500	Glass	60	125	--
Present Work Microwave		$ZnNO_3.6H_2O$	Zinc acetate dihydrate	--	Silicon	2	120	900

Variation in diameter and length of ZnO nanorods for the hydrothermal and the microwave processesis shown in Fig. 3, which indicates a variation of 0.5 µm to 2 µm in diameter with growth timeduring the hydrothermal process, whereas the corresponding variation for the microwave process is the range of 0.06 µm-0.18 µm. It is found that the length scale is 5-times and diameter scale is 10-times smaller in the microwave process compared to that in the hydrothermal process. ZnO nanorods synthesis by microwave oven takes only 2 minutes compared to the method like precipitation method which takes 60 minutes[31]. Moreover, microwave synthesis of ZnO nanorods present in this study is way faster than conventional process like hydrothermal, micro-emulsion and sol-gel which takes more than 20 h[32–34].

3.2 Synthesis of Vertically-Aligned ZnO Nanowalls

A p-type silicon wafer is cleaned with acetone in the ultrasonic bath for 15 min followed by rinsing the sample thoroughly with deionised water and drying using nitrogen. A 10 ml solution is prepared by homogeneous mixing of 5 mM zinc acetate dehydrate in acetone at room temperature for theseed layer. The thin seed layer is coated on the silicon wafer using a spin coatingat an rpm of 3000 for 30 sec followed by UV curing for 90 second, The seed layer coating is deposited five times to ensure proper and uniform coating. The growth solution of ZnO nanowalls contains additional 0.8 mM ammonium hydroxide NH_4OH with 25 mMzinc nitrate hexahydrate and

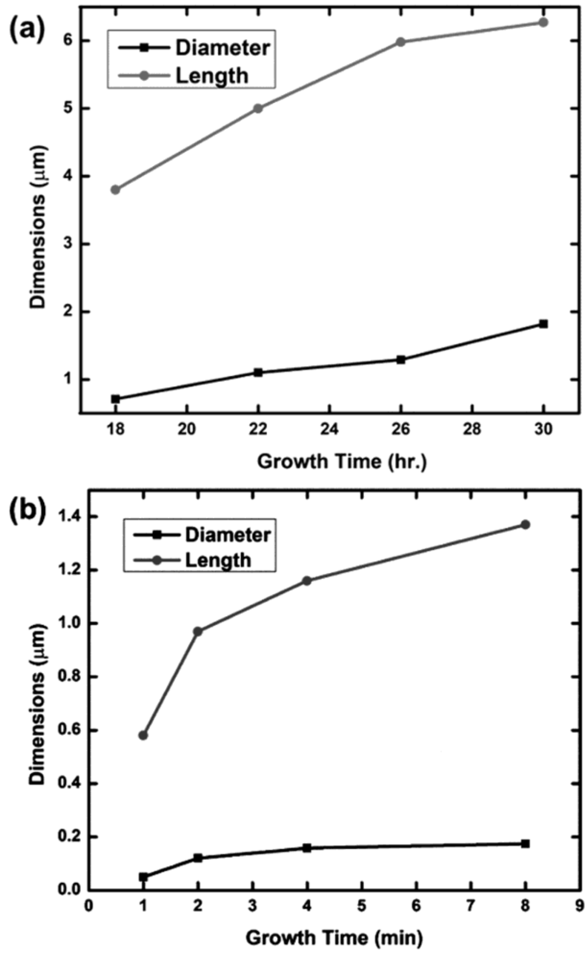

Fig. 3 — Variation of diameter and length of ZnO nanorods with growth time for (a) Hydrothermal process and (b) Microwave process at 900 W.

12.5 mMhexamine in deionised water. The seeded substrate is placed upside down in a glass beaker containing the growth solution. In this way, ultra-fast ZnO nanowalls are grown using the microwave oven operating at a power of 900 W in only 2 min, against a reported time of 30 min for the conventional hydrothermal process or 40 min for the CVD process[35,36]. Fabricated ZnO nanowalls are vertically-aligned as shown in Fig. 4a and 4c. All the nanowalls are seen to be inter-connected with an average length of nanowall as 4 µm and awidth of 800 nm (Fig. 4b) compare to ZnO nanowalls are fabricated due to defect-selection processes, sincezinc oxide nanorods are etched away by the presence of excessive OH^- ions due to ammonium hydroxide in the growth solution. The chemical reactions expected to drive the formation of ZnO nanowalls is as follows[37]:

$$(CH_2)_6N_4 + 6H_2O \rightarrow 6HCHO + 4NH_3 \quad \dots (1)$$

$$NH_3 + H_2O \leftrightarrow NH_4^+ + HO^- \quad \dots (2)$$

$$Zn(NO_3)_2 \rightarrow Zn^{2+} + 2NO_3^- \quad \dots (3)$$

$$Zn^{2+} + 2HO^- \leftrightarrow ZnO(s) + H_2O \quad \dots (4)$$

$$Zn^{2+} + 2HO^- \leftrightarrow Zn(OH)_2 \quad \dots (5)$$

$$Zn(OH)_2 \leftrightarrow ZnO + H_2O \quad \dots (6)$$

3.3 Synthesis of ZnO Nanoflowers

For the fabrication of ZnO nanoflowers,the sample preparation is done similar to that for the ZnO nanowalls. The only difference is in the growth solution, where ammonium hydroxide NH_4OH is replaced by 10 to 15 drops of ammonia with 25 mM zinc nitrate hexahydrate and 12.5 mM hexamine in deionised water. Ammonia (NH_3) is one of the important constituents playing dual role serving as a complexing agent forming $[Zn(NH_3)_4]^{2+}$ with zinc ions along with maintaining the pH of the solution. ZnO nanoflowers are synthesised using the microwave for 5 min at 900 W compared to the conventional sol-gel and hydrothermal process which takes more than 10 hours[38,39]. Figure 5 shows closely packed ZnO nanoflowers with an average length of 3.2 µm and width of 1.6 µm for each petal.

A flower-like structure is observedas the petals are seen growing fromcommon stems throughout the micrograph. Addition of ammonia in growth solution leads to increase in pH of the solution from 7 to 12, which supplies additional OH^- ions for the reaction. Therefore, the growth of ZnO nanoflowers is mainly due to two factors, that is, availability of excessive OH^-ions and high temperature owing to increase in heating time.

3.4 Synthesis of ZnO Nanopillars

A p-type silicon wafer is cleaned as mentioned in the section related to the synthesis of vertically-aligned ZnO nanowalls. For the seed layer, 0.75 mM of zinc acetate dihydrate is uniformly mixed in

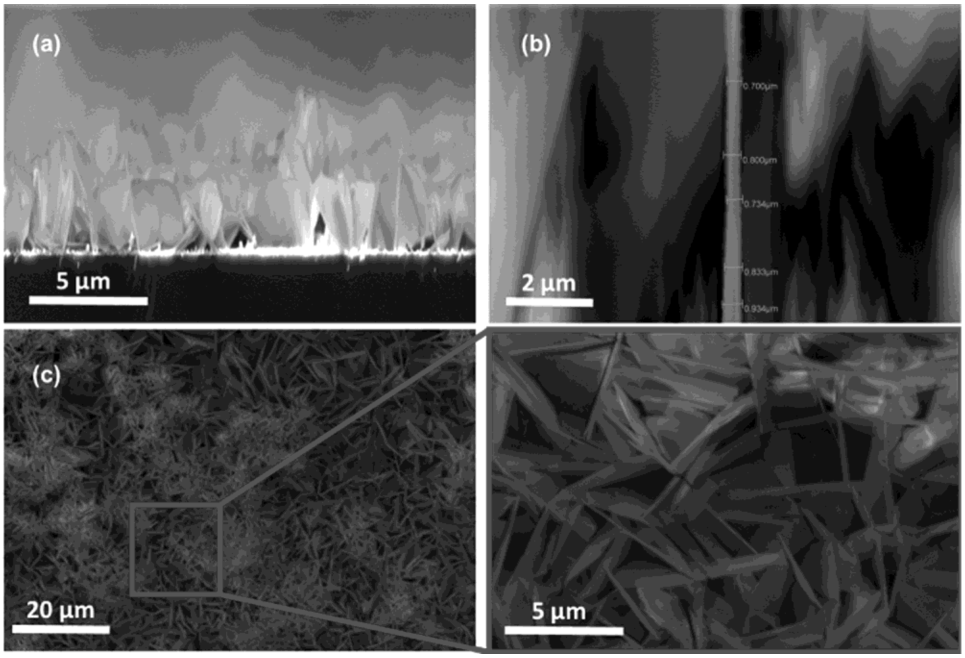

Fig. 4 —SEM image of (a) Side view of fabricated ZnO nanowalls, (b) ZnO nanowalls with an average length of 4 µm and width of 800 nm and (c) Top view of fabricated ZnO nanowalls using a microwave oven at 900 W for 2 min.

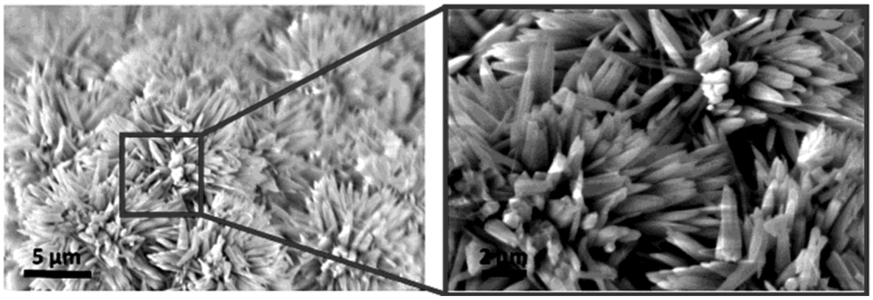

Fig. 5 — SEM image of fabricated ZnO nanoflowers with an average length of 3.2 µm and a width of 1.6 µm using a microwave oven at 900 W for 5 min.

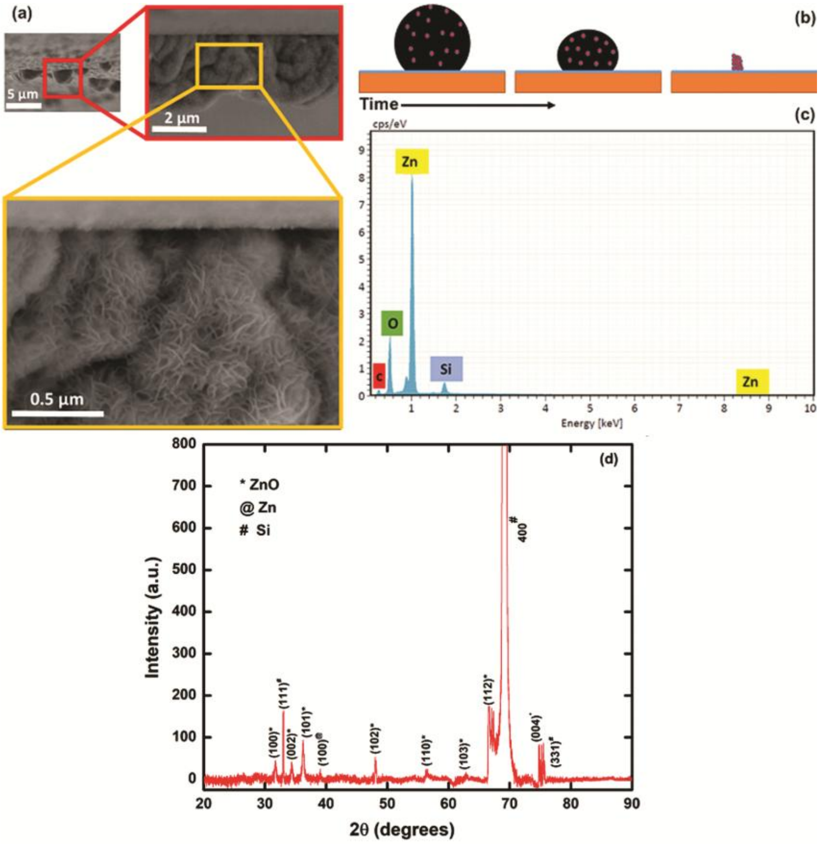

Fig. 6 — (a) SEM image of fabricated ZnO nanopillars with nanowires having an average pillar height of 3 µm and a diameter of 3.5 µm using a microwave oven at 900 W for 8 min, (b) Schematic of evaporation of seed solution droplet, (c) EDS of ZnO nanopillars with nanowires and (d) XRD of ZnO nanopillars with nanowires.

2-methoxyethonal at 60 °C. Monoethanolamine (MEA) is added drop wise to obtain a clear solution. The prepared seed layer is spin-coated at 3000 rpm for 30 sec on the cleanedsilicon wafer followed by UV curing for 90 sec.Annealing of seed layered silicon wafer is carried out at 400 °C for 1 h and contact angle of 97° is maintained before the growth of ZnO nanostructure. Growth solution is prepared as described in materials and methods section. Annealed substrateis placed in a glass beaker containing the growth solution with the coated side facing the bottom of the beaker. The beaker is then inserted in the microwave oven at 900 W for 8 min. The substrate is taken out of the microwavewhen all of the growth solution is consumed. SEM analysis confirms the formation of nanopillars as shown in Fig. 6a. A natural process of evaporation and degradation is observed where three phase contact line (TLC) starts to shrink to the centre. During the evaporation from a hydrophobic surface, counter-flow leads to the formation of nanopillars by bringing the suspended particles of seed layer at the centre of evaporating droplet as shown in Fig. 6b.Since there are no such particles present in the seed layer, so accumulating crystal cells are responsible for TCL pinning. During evaporation high concentration of zinc acetate starts reaching to the crystal base due to the deformation of the air-liquid interface. The presence of zinc oxide nanostructure is being confirmed using energy dispersive spectroscopy and X-ray diffraction, which shows the presence of zinc and oxygen on thesilicon wafer (Fig. 6c and 6d).A typical coffee ring effect is observed during our microwave oven process, similar to that observed by several other researchers[40–42]. It is noteworthy to mention that using microwave synthesis the nanopillars are fabricated in less than 10 minutes at low growth temperature whereas in conventional processes where the time for fabricating nanopillars is more than 2 hours with large number of complex fabrication steps[41]. During our process, coffee rings of a minimum diameter of 3.5 µm, against an earlier reported value of 8 µm by Wu et al[40].It is pertinent to mention that the proposed process could yield a smallest of any artificial coffee-ring structure reported in the open literature.

With the synthesis of these ZnO nanopillars, the possibility of a lab on chip with millions of small nano-biosensor is now very realistic to carry out chemical and biological analysis on a single device.

3.5 Wettability Study of Various ZnO Nanostructures

The contact angle for the synthesised ZnO nanostructures has been evaluated usingthe contact angle goniometer. It is observed that the contact angle varies with the features on the silicon surface having different morphologies. The contact angle for the ZnO nanorods synthesised by the microwave technique is found to be maximum (156°) in comparison to that for the other ZnO nanostructures as shown in Fig. 7. It is to be noted that the ZnO nanorods are ultrafast fabricated superhydrophobic material among all the fabricated nanostructures presented in the current work. Whereas, nanowalls having a contact angle of 103°, nanoflowers with a contact angle of 135°and nanopillars having a contact angle of 115°are hydrophobic in nature.

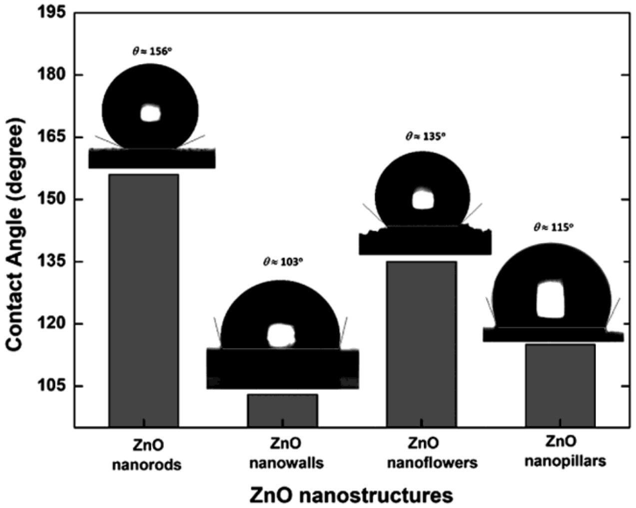

Fig. 7 — Contact angle study of fabricated ZnO nanostructures using microwave oven.

4 Conclusions

In summary, different ZnO nanostructures are being synthesised using a domestic microwave oven. Time for achieving crystallisation temperature during the synthesisof various ZnO nanostructures is reduced to less than 10 minutes at 900 W. Vertically aligned ZnO nanorods, having length in the range of 0.59-1.37 µm with an average diameter of 0.18 µm, are synthesised. Moreover, uniformly distributed vertically-aligned ZnO nanowalls shows an average length of 4 µm and a width of 800 nm on the Si substrate. ZnO nanoflowers having an average length of 3.2 µm and a width of 1.6 µm for each of its petalare fabricatedin less than 5 minutes using microwave power. Whereas, for the first-time, ZnO nanopillars with millions of nanowires are synthesised in 8 minutes.In addition to this,contact angle study shows that the fabricated ZnO nanostructures are hydrophobic in nature. In particular, the contact angle of ZnO nanorods is found to be more than 150°, which signifies that the fabricated ZnO nanorods are superhydrophobic in nature.

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