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Synthesis and characterization of jar-like ZnO structures

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A new jar-like ZnO structure was synthesized by heating a mixture of Zn and InI_3 powder with a weight ratio of 4:1 dispersed on Si wafer at 450 °C in air. The diameter of the jar was of the order of 15 µm and the length of 20 µm. The formation of a molten InI_3 drop, coating the drop with Zn powders, oxidation of these Zn grains, decomposition of InI_3 to In and I vapors and the subsequent release of these vapors from the structure are considered important steps in the formation of the observed structures. The necessary elements in forming such structures are analyzed, which can be used as a guide in the design of experiments to synthesize similar structures for different purposes. Such structures are predicted to be able to soak large amount of liquid and release it at low rate, which is a desired property in some applications.

Keywords: *ZnO, synthesis, novel structure, SEM*

1. Introduction

The unique properties of nanomaterials originate from their reduced sizes and unique shapes. Different applications are expected for nanomaterials with different morphologies. For example, wire-like structures are suitable for composite material application to enforce mechanical strength [1] while nanoparticles can be used for drug-delivery [2] and photoluminescence [3]. Therefore, size and morphology control of the nanomaterial are important for the effective application.

Among nanomaterials reported so far, ZnO-based system is promising in many applications and is probably the one with the most versatile morphologies: nanoparticles, nanorods, nanobelts, nanorings, and nanosprings et al have been reported [4]. Recently, in an effort to dope In to ZnO nanostructures [5–9] by heating the mixture of Zn and InI_3 powders, we obtained a jar-like structure, which has never been reported before. The result is presented here and the formation mechanism and potential application are discussed.

2. Experimental

The synthesis was performed in air. A schematic diagram of the instrument is shown in Fig. 1. A quartz tube of 48 mm inner diameter and 450 mm length with one end sealed was inserted to a tube furnace of model F21125 manufactured by H&C thermal systems. The furnace was set at a temperature of 450 °C. The powders of InI_3 and Zn, purchased from Alfa Aesar, were mixed in a weight ratio of 1 to 4. The powders were crushed and ground in a mortar, and dispersed onto a piece of Si wafer of approximately 20×8 mm^2. The dispersion was uneven to ease the characterization. The wafer was then placed in a glass bottle and the whole bottle assembly was inserted into the quartz tube which was

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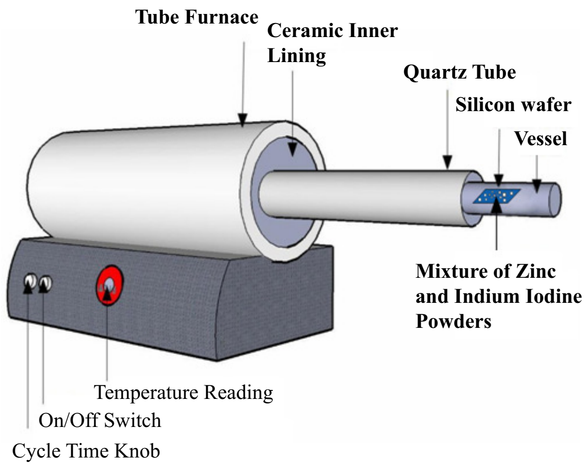


Fig. 1. Schematic diagram of the instrument for synthesis used in the present work.

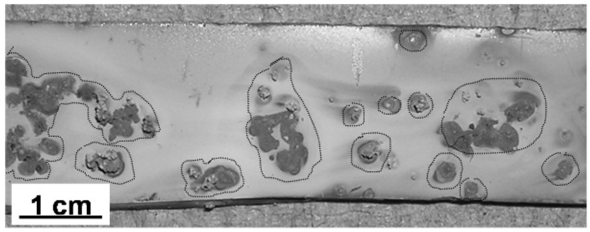


Fig. 2. A typical optical micrograph of the Si wafer after the synthesis experiment. The areas circled with dashed lines represent the areas where raw materials were placed.

in thermal equilibrium of 450 °C with the furnace. Finally, the open end of the quartz tube was covered with aluminum foil to reduce the interchange with fresh air. The furnace was held at this temperature for 20 min. Purple smoke was observed in this period. Then, a hole was punched on the aluminum foil to let fresh air in and the purple smoke out of the tube. The same temperature was maintained for 40 min before the wafer was taken out and examined with a FEI Sirion XL30 scanning electron microscope (SEM). This SEM is equipped with Oxford Inca energy dispersive X-ray spectrometer (EDS) for elemental analysis. The heating process was designed based on previous experimental reports [10] and has been modified by trial and error for the present experiment. Some of the selected structures was cross-sectioned and observed by dual beam focused ion beam (FIB) system of DB237 from FEI.

3. Results and discussion

An optical micrograph of the wafer after evaporation is shown in Fig. 2. The areas where the raw powders were placed stand out from the rest with different contrast and are circled with dashed lines. As shown in Fig. 3a, particles with size ranging from several hundred nm to several µm and a variety of shapes are observed in the areas between the circled ones. The interesting jar-like features are found in the areas circled by the dashed lines. Figs. 3b–3d show some representative examples of the new structures. The diameters of these jars are of the order of 15 µm while their lengths are approximately 20 µm. Most of them have an opening. EDS analysis was performed on both areas to reveal the elemental distribution. Figs. 4(a) and (b) show typical EDS spectra taken from the areas in between and inside the circles of Fig. 2, respectively. The probing areas are approximately 250 $\times$ 400 µm^2, implying that they represent the average of the corresponding areas. The spectra taken from individual jar-like structures show the results similar to that of Fig. 4(b). While an In peak was observed in Fig. 4(a), it is absent in Fig. 4(b). It should be pointed out that, occasionally, In can be found on the surface of jar-like structures, which will be explained later in detail.

Results of an in-depth SEM examination of the jar-like structures are shown in Fig. 5. The structures in both Figs. 5a and 5b consist of multi grains. The grains in the vicinity of the opening seem bigger and have more distinct facets. The structure shown in Fig. 5c is more spherical, has smooth surface, and has no grain boundaries. A fragment, featuring a hexagonal pattern, on the surface of the sphere in Fig. 5c is enlarged and shown in the inlet.

The following model is suggested for the formation of the observed jar-like structures. Some temperatures that are important for the understanding of the model are listed here. InI_3, Zn, and ZnO melt at temperatures of 207 °C, 420 °C, and 1975 °C, respectively. InI_3 decomposes at 300 °C. Upon inserting the assembly described in the experimental

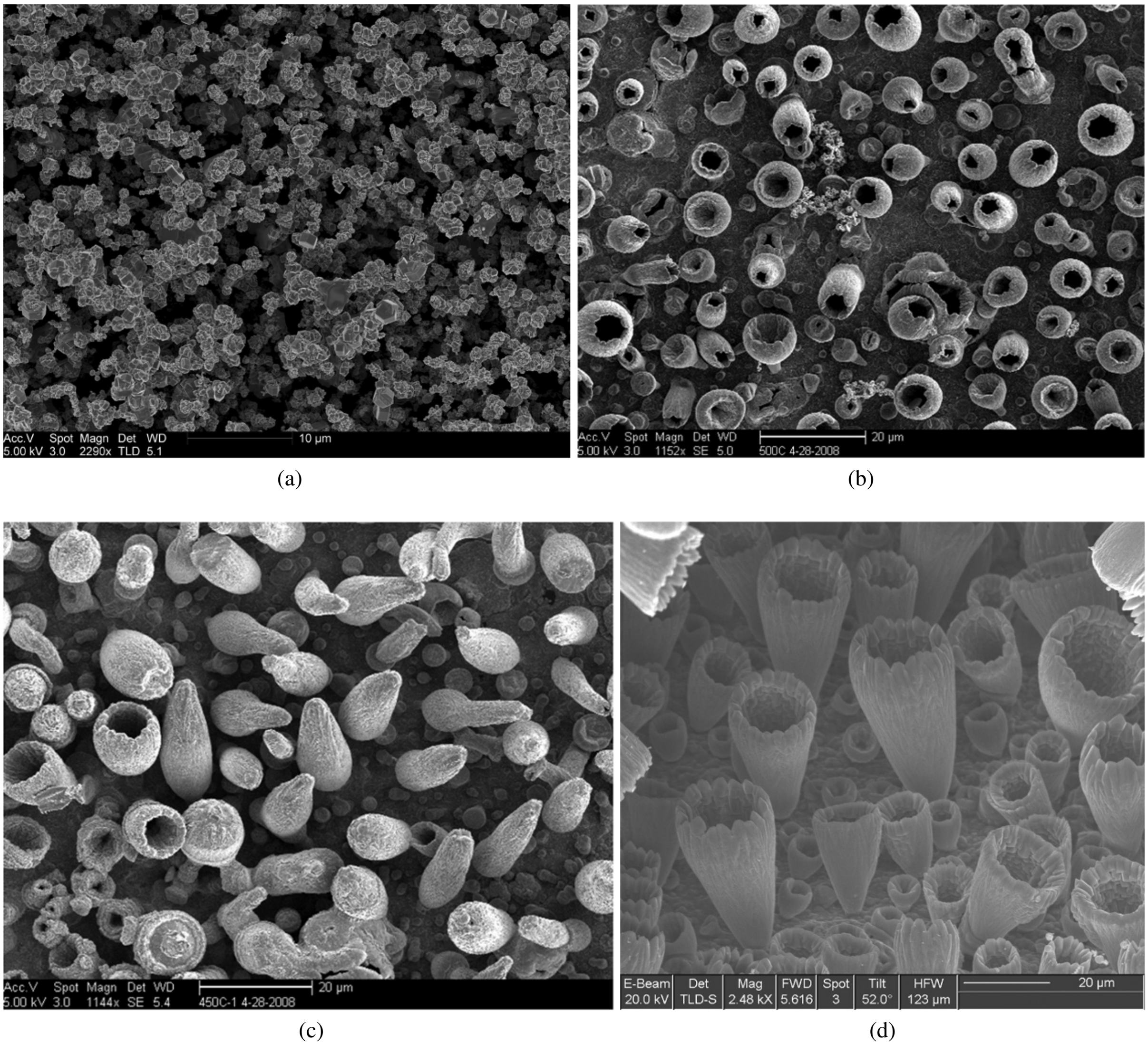


Fig. 3. Representative SEM images showing different structures observed in the present experiment. (a) corresponds to the areas in between the circled areas while (b), (c), and (d) were taken inside the marked area of Fig. 2. Jar-like structures in (b), (c), and (d) are new.

section, the temperature of the InI_3 and Zn mixtures increases rapidly since the furnace/(quartz tube) has been preset at a temperature of 450 °C. At some point, liquid drops of InI_3 form and are coated with Zn powders. As temperature increases further, InI_3 decomposes, forming gas bubble inside the liquid drop. In approximately the same time, the Zn powders on the surface melt and are oxidized, forming a shell structure enclosing the internal materials related to InI_3. As more InI_3 decomposes, the pressure of gas bubble increases to such a level that the gases force their way out, leaving an opening on the structure. At this moment, ZnO solid shell is formed, preventing the empty structure from collapsing.

This model was examined and confirmed by further experiment. Toward this goal, we lowered the furnace temperature from 450 °C to 300 °C and repeated the experiment in hope to find the jar-like structures in transition stage. The SEM image which supports the above mentioned model is shown in Fig. 6a. Different stages of the structure formation are observed in this picture: the lower right corner

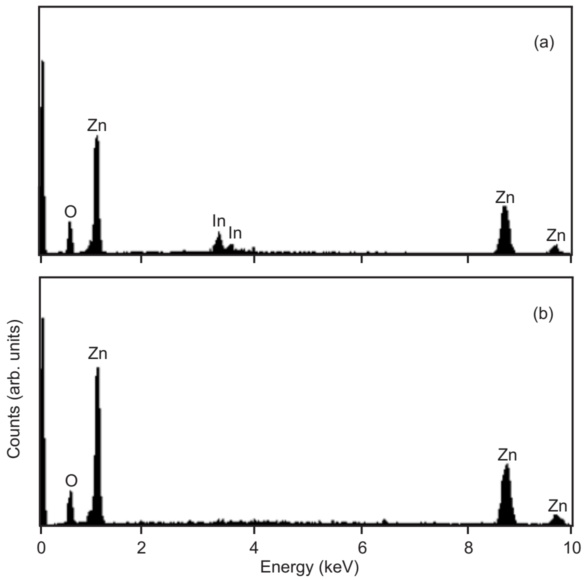


Fig. 4. EDS spectra taken from the areas (a): in between and (b): inside the circled areas of Fig. 2, respectively. An In peak is observed in (a) and is absent in (b).

corresponds to the initial stage of the formation, while the central and left upper areas correspond to the stages before and after the formation of the openings, respectively. One of the structures in the central part of Fig. 6a is observed in high magnification and is shown in Fig. 6b. Its cross sectional view prepared by FIB is shown in Fig. 6c. It should be pointed out that Fig. 6c is tilted by 52° relative to Fig. 6c to have a better view of the inner structure. The core is obviously empty in Fig. 6c, though there is no obvious opening on the structure surface as can be seen in Fig. 6b.

Different behaviors of In, I, and Zn vapors also play a role in the formation of the observed jar-like structures. The In and I vapors as a product of InI_3 decomposition drift away from their source: I corresponds to the observed purple smoke which escapes from the furnace completely after the aluminum cover is punched while In combines with oxygen and lands on the Si substrate. The partial pressure of Zn is predicted to be much lower because of the low temperature of the furnace compared to the boiling temperature of Zn. Its ease to combine with oxygen in air implies a short drifting distance. The combined effect implies that In has much higher

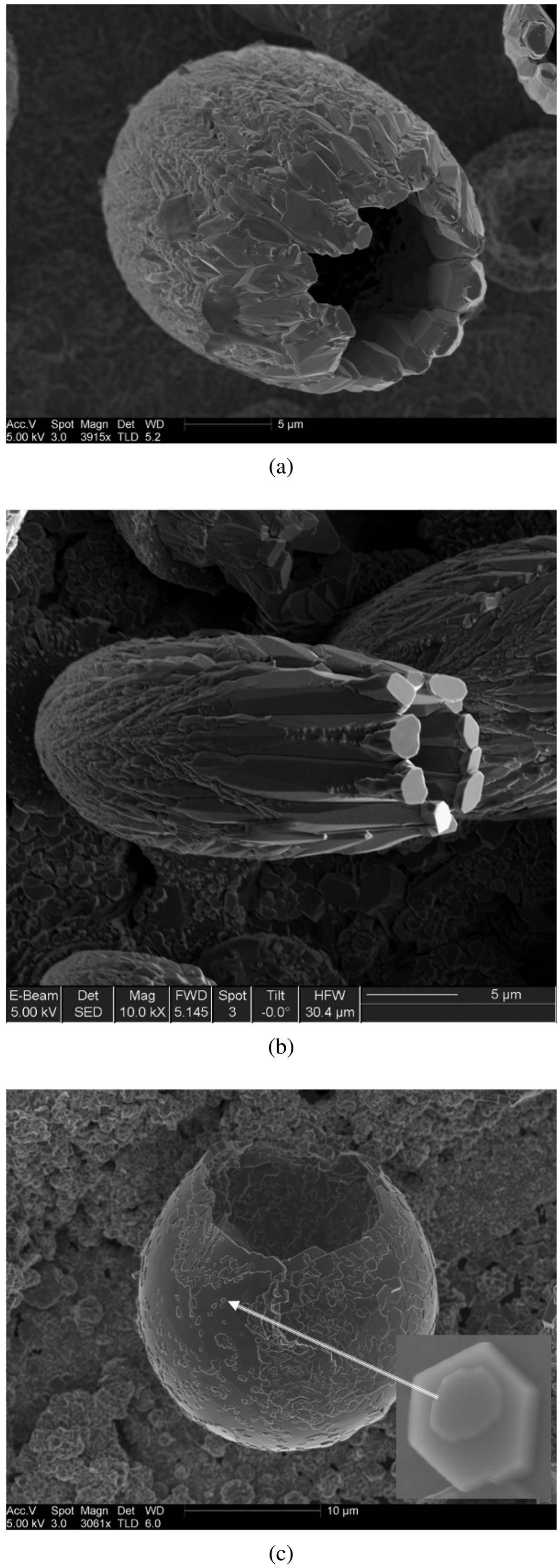
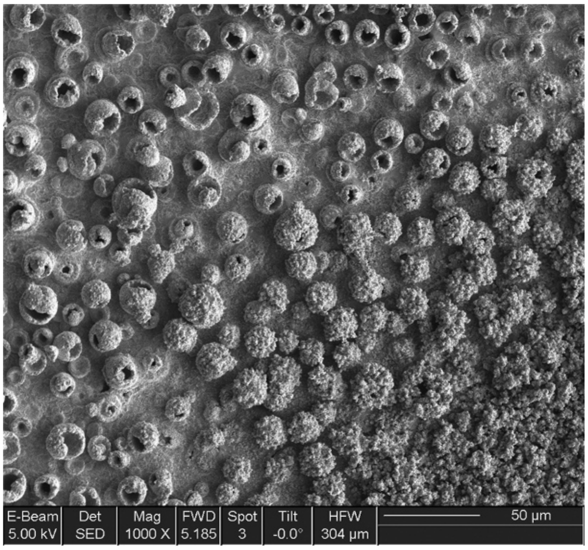
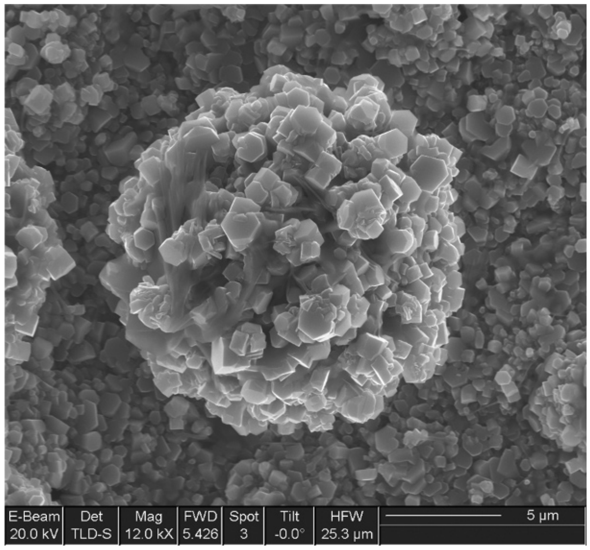


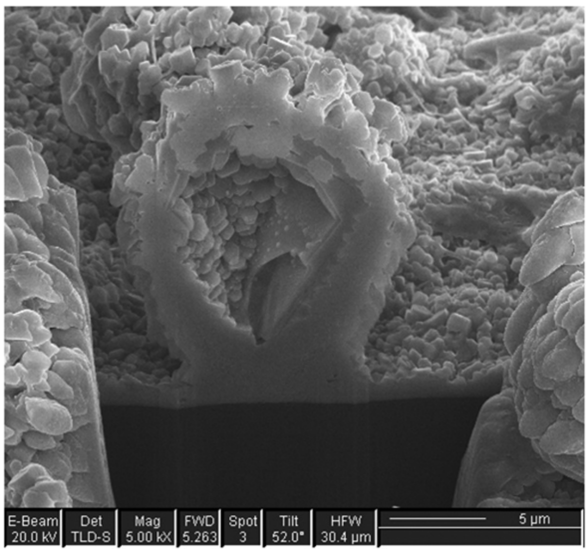
Fig. 5. SEM images of typical jar-like structures.



(a)



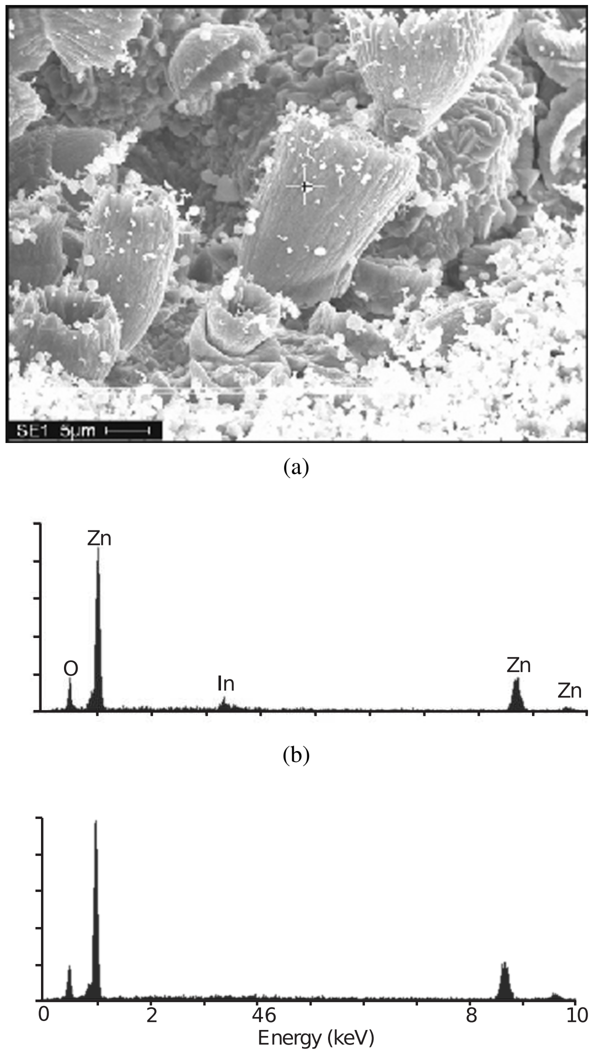
(b)



(c)

Fig. 6. SEM images of structures observed when furnace temperature was set at 300 °C. Jar-like structures in different formation stages were observed in (a). An enlarged image of the structure is shown in (b). The same structure, cross-sectioned by FIB and the SEM image taken at a tilt angle of 52° is shown in (c).

probability to drift to the original empty area and deposit there compared to Zn. This is evidenced by the EDS spectra shown in Fig. 4, where an increased In to Zn ratio is observed in the spectrum of Fig. 4(a) taken from the original empty area compared to that of Fig. 4(b) from the jar-like structures. Occasionally, exceptions are observed, an example of which is shown in Fig. 7. The jar-like structure shown in the SEM image of Fig. 7a is featured by the bright dots on its surface. An EDS spectrum with electron beam positioned on the bright dot is shown in Fig. 7b. As a comparison, an EDS spectrum taken when electron beam is beyond the bright dots is shown in Fig. 7c. Increased intensity of In



(a)

(b)

(c)

Fig. 7. An example showing the occasional deposition of In_2O_3 on the jar-like ZnO structure. The corresponding locations of (b) and (c) EDS spectra are marked with arrows on the SEM image of (a). An increased In peak height in (b) indicates that the bright dots are of In_2O_3.

peak in Fig. 7b is obvious. We consider these bright dots in Fig. 7a as the In_2O_3 deposits after the formation of ZnO jar-like structures. There is another feature that may be considered to be related to the drifting and oxidation of Zn vapor. As can be seen in Fig. 5a and 5b, the grain size around the opening of the structure tends to be bigger as compared to the bottom and these grains seem to have well defined facets. This is explained as follows. Zn vapors formed inside the jar are able to drift to the opening because of the lack of air inside. Once such vapor is exposed to air around the opening, it combines with oxygen and deposits on the pre-existing ZnO grains around the rim, resulting in bigger grain sizes as compared to others. This vapor-solid process tend to cause crystal growth in a selected orientation, which is considered as the reason for the more distinct facets.

The morphology of the structures shown in Figs. 5a and 5b is different from that in Fig. 5c. We believe that this is a result of slightly different formation processes. It is assumed that the structures as observed in Figs. 5a and 5b go through a state when the Zn grains on the surface of the structure are partially solid, partially melted, and partially oxidized. All these phases are confined in a space close to the original Zn grain and the melt from different grains does not connect. Because of the simultaneous reaction of phase transformation on all Zn grains, each original Zn grain corresponds to at least one ZnO grain, resulting in polycrystalline ZnO structures on the shell. This explains the observed rough surface. On the other hand, in the process of forming the structure shown in Fig. 5c, Zn melt from different grains is connected and mass exchange occurs between different Zn grains. The end result of this process is a shell of Zn melt with a smooth surface and uniform thickness. The oxidation started at some locations progresses to the entire drop, transforming the liquid shell to a single crystal ZnO shell. The existence of a complete shell of Zn melt on the top of the InI_3 liquid drop is the key to understanding the spherical morphology, uniform thickness, and single crystal structure. The hexagonal facet shown in the inlet of Fig. 5c indicates that the surface of the sphere is parallel to (0 0 1) ZnO crystal plane.

It has been reported that ZnO nanorods can bundle together, forming multi-petals structures [11]. These multi-petals are different from the present jar-like structure in Figs. 5a and 5b since they do not form the hollow structure. The multi-petals structure is believed to be a result of post synthesis interaction between nanorods while the present one is a result of the growth process.

This report demonstrates the possibility and the ruling factors in forming jar-like structures. The function of InI_3 is to provide a liquid drop which is coated with Zn powders. In other words the liquid serves as a mold in forming the jar-like structure. The temperature and atmosphere must be suitable so as the coated Zn powders could transform into solid ZnO shell before the liquid transforms to other form. The liquid must vaporize once the hard ZnO shell is formed in order to obtain hollow structures. Though the end product of the present experiment is not pure jar-like structures, it is possible to obtain pure jar-like ZnO structures by improving experimental design based on the principle outlined here.

The present unique ZnO structure is expected to show improved performance in some applications. Due to the jar-like structure, one possible usage is to hold liquid and to release it at a reduced rate. For example, water can be filled to the jar by soaking the powder of jar-like structures in water. When such powders are brought out of water, the powders will keep the releasing water for extended period because the water is enclosed inside the small void of the jar. The rate can be adjusted by varying the size of the jar and such controlled release is desired in some applications, such as cosmetics.

4. Conclusion

Jar-like structure of 15 μm diameter and 20 μm long was obtained by heating a mixture of ZnO and InI_3 powder in a weight ratio of 4:1. It is suggested that melting of InI_3, coating of the liquid drop with Zn powders, decomposition of InI_3 to In and I vapors, and melting and oxidation of Zn surface are all processes involved in the formation of the observed structures. The key for the formation of this structure is the fact that the melting and oxidation of Zn on the surface occur approximately at the same time as InI_3 decomposes to gas and is released from the structure. The idea can be extended to other systems to obtain the hollow structures. The unique jar-like structures are expected to show improved performance in the applications such as retaining and releasing liquid/vapor in a controlled way.

Acknowledgements

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References

[1] SHAFFER M.S.P., WINDLE A.H., *Adv. Mater.*, 11 (1999), 937.
[2] LABHASETWAR V., SONG C., LEVY R.J., *Adv. Drug Delivery Rev.*, 24 (1997), 63.
[3] GUO L., YANG S., YANG C., YU P., WANG J., GE W., WONG G.K.L., *Appl. Phys. Lett.*, 76 (2000), 2901.
[4] WANG Z.L., *J. Phys.: Condens. Matter.*, 16 (2004), R829.
[5] JIE J., WANG G., HAN X., YU Q., LIAO Y., LI G., HOU J.G., *Chem. Phys. Lett.*, 387 (2004), 466.
[6] BAE S.Y., NA C.W., KANG J.H., PARK J.J., *Phys. Chem.*, B109 (2004), 2526.
[7] XU L., SU Y., CHEN Y., XIAO H., ZHU L., ZHOU Q., LI S., *J. Phys. Chem.*, B110 (2006), 6637.
[8] QI J., ZHANG Y., HUANG Y., LIAO Q., LIU J., *Appl. Phys. Lett.*, 89 (2006), 252115.
[9] KONG X.Y., DING Y., YANG R., WANG Z.L., *Science*, 303 (2004), 1348.
[10] XU C., RHO K., CHUN J., KIM D.E., *Appl. Phys. Lett.*, 87 (2005), 253104.
[11] ZHAO B., CHEN H., *Mater. Lett.*, 61 (2007), 4890.

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