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Growth of Flower Like Zno Nanostructures: The Influence of Substrate

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Abstract:

The present report highlights the development of ZnO flowers with diverse structural organization and the influence of the morphology on the luminescence response. Flower like morphology of ZnO comprising of nanorods and nanosheets have been developed using simple chemical technique. The obtained nanostructures have been characterized by scanning electron microscopy, while energy dispersive X-ray characteristics have been exploited to obtain information about chemical composition. It has been found that the quality of the substrate dictates the formation of nanorod or nanosheet for the development of flower like morphologies. The growth process of the flower like structure has been discussed with appropriate growth mechanism and scheme. Finally, it has been found that the structural arrangements highly influence the optical emission from the two types of flowers. The ZnO flowers with nanorod as structural unit is found to be promising for optoelectronic application, while flowers composed of nanosheets may be efficient for photocatalytic or gas sensing applications.

Keywords **—ZnO, nanorods, nanosheets, photoluminescence**

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I. INTRODUCTION

In today's modern life, most of the electronic appliances largely rely on the light emitting and detecting components. The rapid technological development has enabled to fabricate quality light emitting diodes (LEDs) and photodetectors that exhibit superior performance in various areas of display, imaging, optical communication etc [1-3]. Although most of the fields have attained a high level of advancement, there is a continual quest for achieving better devices in terms of speed, selectivity, efficiency as well as flexibility. In this context, the scientific community has exhibited keen interest in exploring Zinc oxide (ZnO) based nanostructures owing to their promising attributes towards electronic and optoelectronic devices [3-5]. ZnO is a wide band gap material (~ 3.37eV) and exhibits high exciton binding energy (~ 60 meV) at 300 K. The presence of wide band gap bestows the material strong ultraviolet light emission characteristics. Further the existence of various native defects like zinc/oxygen vacancies or any anti-sites leads to the emission of light in the visible region of the electromagnetic spectrum [4,5]. The tunable defect related emission makes the system technologically feasible for various optoelectronic applications. Further the existence in variety of nanostructures like nanowires, nanorods, nanoneedles, nanoshells, nanourchin and nanoflower, makes the system technologically important for various application [6-8].

With the development of various synthesis techniques, it has been possible to synthesis quality nanostructures with diverse morphology. It is quite important to obtain an insight of the growth mechanism as such information can be beneficial to tune the morphology as well as the property. Amongst various fabrication methods, the aqueous solution growth technique is established to be an efficient and inexpensive route to obtain quality nanostructures of ZnO [9]. Here the present work reports on the fabrication of ZnO flower like structures of different compositional units using the aqueous solution growth technique. Two different types of ZnO flowers constituting nanorods and nanopetals/nanosheets have been synthesized by simply varying the substrate such as glass and aluminum. It has been found that the attachment and arrangement of the ZnO nuclei on the substrate determines the morphological variation. Finally the influence of the structural organization of the flowers on the light emission characteristics of ZnO has been discussed elaborately.

II. EXPERIMETAL

Synthesis: In a typical synthesis process, glass and Aluminum (Al) substrates (5 cm x 2 cm) were immersed in an equimolar solution of zinc nitrate hexahydrate [$Zn(NO_3)_2.6H_2O$] and hexamethylenetetramine [HMT, $(CH_2)6N_4$] in ~ 100 mL of deionized water kept under constant stirring for at 60 oC 5 hr. After the completion of the desired growth time, the substrates were taken out from the aqueous solution and washed with deionized water. The final product was obtained upon drying the samples at hot air oven for 1 hr at 80^{o}C. The ZnO grown on glass and Al substrates were labeled as ZnG and ZnAl for further study.

Characterization: The as synthesized samples were studied using Scanning electron microscopy (SEM), while energy dispersive X-ray spectroscopy (EDS) was performed to analyze the chemical constituents of the samples. The luminescence characteristics have been analyzed by photoluminescence spectroscopy.

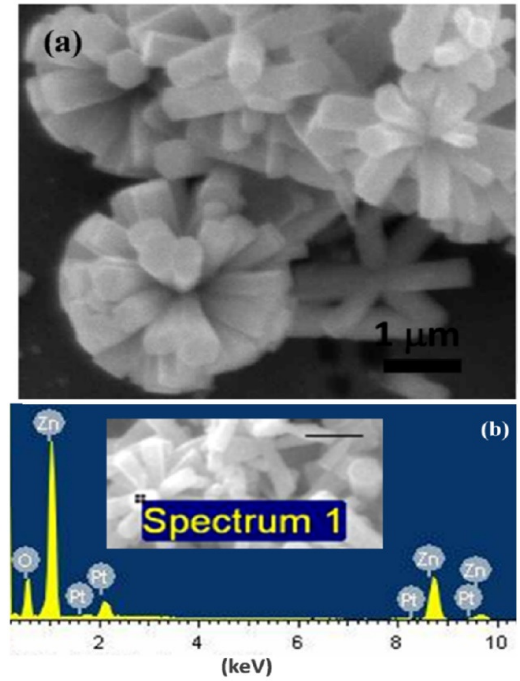

Figure 1: (a) SEM image of flowers obtained in ZnG sample, (b) EDS spectrum of the ZnO flowers. Inset of (b) represents the EDS capturing position.

III. RESULTS AND DISCUSSION

The formation of flower like nanostructure of ZnO in the ZnG sample is evident from the SEM image Figure 1(a). It can be observed that the flowers are composed of nanorod like structures which are directed radially outward. The average size of a flower is ~ 3-4 nm, while the average length and diameter of the constituting nanorods varies in the range from 1.2-1.5 nm and 300-500 nm respectively. To verify the formation of ZnO, EDS has been performed and is presented in Figure 1(b). The spectrum has been captured on the tip of a nanorod constituting the flower as shown in the inset of Figure 1(b).The presence of Zn and O can be clearly observed in the EDS spectrum and thus confirms the formation of ZnO. The additional peak due to Pt arises from the Pt-coating deposited on the sample to avoid charging effect during SEM imaging.

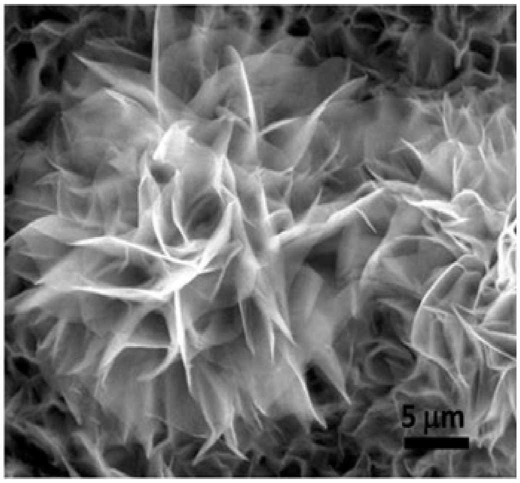

Figure 2: SEM image of ZnAL flowers

On the contrary in the ZnAl sample, the ZnO flower is found to be composed of nanosheet like structures resembling the petals of the flowers Figure 2. The average size of a flower is found to be ~ 25 nm, while the thickness of the two-dimensional petals varies from 60-80 nm. The morphological variation of the two types of flowers obtained in ZnG and ZnAl samples, indicates the variation in growth mechanism originated from the diverse nature of the substrates.

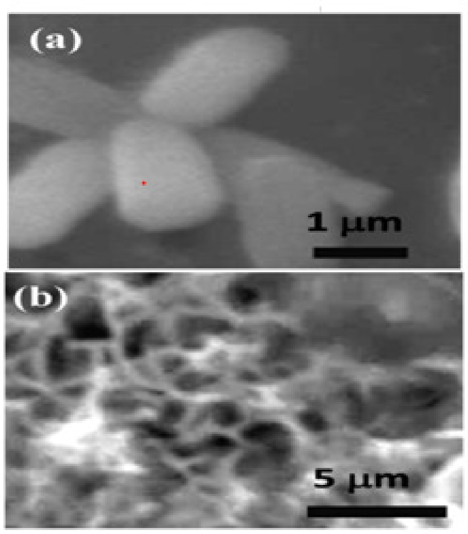

Figure 3: SEM image of (a) ZnG and (b) ZnAl samples at an intermediate stage of the reaction

In order to obtain an insight of the diverse growth mechanism, the SEM images of the samples at an intermediate stage of the reaction has been analyzed. In Figure 3(a), it is evident that multiple numbers of nanorods originate from a single point for ZnG sample. Thus, it can be assumed that the nanorods originate from a single source of nucleation and with the progress of the reaction the complete growth ofthe nanorods leads to the self-organized rod-based flower like structure.

On the other hand for ZnAl sample, the formation of sheet like two-dimensional features of ZnO can be observed at an intermediate stage (Figure 3(b)). Thus it is expected that the growth of the sheet like nanostructure with all possible orientations leads to the formation of self-organized petal based flower structure

Now the diverse structural organization is originated from the nature of the two substrates. Since the reaction process is identical in the two cases, the formation of ZnO nuclei as a reaction of zinc nitrate and HMT as shown below.

$$C_6H_{12}N_4 + 4H_2O \rightarrow C_6H_{12}N_4H_4^+ + 4OH^-$$

$$[Zn(C_6H_{12}N_4)]^{2+} + 4OH^- \rightarrow Zn(OH)_4^{2-} + C_6H_{12}N_4$$

$$Zn(OH)_4^{2-} \rightarrow Zn^{2+} + 4OH^-$$

$$Zn^{2+} + 2OH^- \rightarrow ZnO + H_2O \quad \text{or}$$

$$Zn^{2+} + 2OH^- \rightarrow Zn(OH)_2 \rightarrow ZnO + H_2O$$

However, the attachment of these ZnO nuclei will be different on glass and aluminium substrates and is summarized in the scheme of Figure 4.Owing to the hydrophobicity of glass substrates very few ZnO nuclei can get attached on the surface and hence the formation of continuous layer is not expected rather cluster of nuclei can be formed. Although the nuclei in a cluster are branched together, they are oriented at different angles in outward fashion. Now it is established that in ZnO unit cell, the growth along [0001] direction is faster than other directions and thus leads to the formation of one dimensional nanorod like structures [4]. Hence in the present case, the differently oriented nuclei will trigger the growth of nanorods which are directed radially outward in different directions leading to the development of rod based flower like structure (Figure 4(a)). On the other hand, the attachment of ZnO nuclei Al substrate is expected to be slightly better than that of glass substrate. It is quite obvious that common metallic Al substrates contain an AlOx layer on the top surface due to oxidation at normal atmosphere. The presence of such oxide layer can offer several dangling bonds for the nuclei to get attached on the surface. However, the non-uniformity of the AlOx layer leads to the uneven coverage of ZnO nuclei on the surface. It is anticipated that one dimensional channel like network of ZnO nuclei are formed

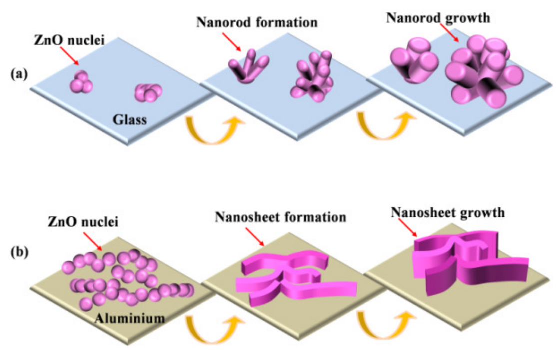

Figure 3: Scheme of the growth mechanism of

(a) ZnG and (b) ZnAl

(Figure 4(b)). With the progress in reaction time the vertical growth of the channel like network leads to formation of sheet like feature as observed in the SEM image of Figure 3(b). Finally, the excess growth of the differently oriented sheets leads to the formation of petal like structures resulting in the evolution of flower like structural organization.

The room temperature PL characteristics of the samples under an excitation of 300 nm are presented in Figure 5. As can be observed in the PL emission of ZnG sample dominates over ZnAl sample. The dominance of PL emission ZnO nanorod system over nanowall is in consistence with previous report of Tang and co-workers [10]. The emission spectrum of ZnG exhibits a broad emission in the visible region with a peak at ~ 440 nm. The absence of near band edge emission indicates the presence of defect related radiative emission. The broad emission spectrum is originated from the Zn or O related vacancy and

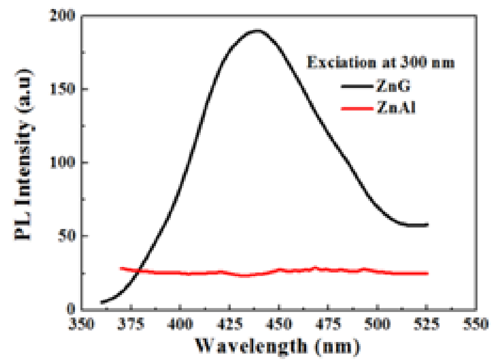

Figure 5: Room temperature PL spectra of the ZnO flowers under 300 nm excitation

interstitial defects. On the other hand the absence of PL emission peak for ZnAl sample is originated from its structural arrangement. As the two dimensionally extended petals can reabsorb the lights which are being emitted from the petals situated at the opposite side. Hence the event of self-absorption of light in the petal based flower like structure can be considered as the main reason for the poor luminescence feature. Thus the nanorod based ZnO flowers with excellent emission property can be ideal candidates for optoelectronic application. Whereas petal based ZnO flowers can provide larger surface area for surface adsorption and hence can lead to photocatalysis or gas sensing like application.

IV. CONCLUSIONS

ZnO flower like structures with different structural units such nanorods and nanosheets have been using simple chemical route. The diverse structural organization of the flowers is found to be originated from the use of two different substrates like glass and aluminium. It has been proposed that the variation in attachment and organization of the ZnO nuclei on the two types of substrates lead to the development of the nanorods and nanosheet based flowers. Further, it has been demonstrated that the diverse structural arrangement of the ZnO flowers can influence the light emission characteristics. In depth study and further optimization of the process may lead to the development of ZnO flowers which can form the basis of futuristic technological applications.

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