The synthesis and optical characterization of well aligned ZnO nanorods using seed layer of Mn_3O_4 nanoparticles

M. ATIF[a,c,*], M. S. ALSALHI[a], K. KHUN[b], M. WILLANDER[b]
[a]*Physics and Astronomy Department, College of Science, King Saud University, Riyadh, Saudi Arabia*
[b]*Physical Electronic and Nanotechnology Division, Department of Science and Technology, Campus Norrköping, Linköping University, SE-60174 Norrköping, Sweden*
[c]*National Institute of Laser and Optronics, Nilore, Islamabad, Pakistan*

In this study, vertically aligned ZnO nanorods were fabricated by hydrothermal growth method using manganese oxide Mn_3O_4 nanoparticles as a seed layer. X- ray diffraction and Raman studies have shown the nano meter size of Mn_3O_4 nanoparticles. ZnO nanorods were characterized by field emission scanning electron microscopy and X-ray diffraction techniques. The prepared ZnO nanorods are highly dense, uniform and verily aligned and possess good crystal quality. Photoluminescence analysis has demonstrated that the ZnO nanorods exhibit deep level emission in green region due to oxygen vacancy related emission and the orange /red region is resulted due to interstitial oxygen defects related emission. This method for the fabrication of well aligned ZnO nanorods can be adapted for the development of optoelectronic devices.

(Received May 25, 2014; accepted July 10, 2014)

Keywords: ZnO nanorods, Well align, Hydrothermal method, Nanoparticles, Photoluminescence, Raman

1. Introduction

Zinc oxide (ZnO) nanostructures are getting more attention among researchers due to their unique properties and future perspective in increasing the performance of optoelectronic and biomedical diagnosing devices. Especially, one dimensional nanostructure has been widely used in several applications such as solar cells [1], gas sensors [2], lasers [3], piezoelectric sensors [4], logic circuits [5]. Several growth methods have been adapted for the growth of these one dimensional nanostructures, but hydrothermal growth approach is more popular due to its simplicity, cheapness and versatility in growing different morphologies on the variety of substrates [6-7]. The use of seed layer prior to the growth of desired morphology is fascinating than the growth pattern and the alignment of nanostructure. Moreover, the presence of seed crystals on the substrate which provide the heterogeneous nucleation and hence the free energy of activation is more lowered as compared to homogeneous nucleation in solution and also gives almost structural match, therefore preferred growth of ZnO with good crystallinity is observed [7]. Due to above fact of heterogeneous nucleation, it is highly desirable to have a well aligned ZnO nanorods or nanowires either of seed layer on a substrate or on selective area of substrate [8-10].

Recently, the researchers are paying more attention towards manganese oxide nanomaterials because of their tremendous applications in the research areas of catalysis, electrochemistry, molecular adsorption, magnetite, and batteries [11-14]. The frequent use of manganese oxides is found in the preparation of eletrode materials [11, 12], catalysts [13, 14], and soft magnetic materials [15]. Various manganese oxides exist such as Mn_2O_3, Mn_3O_4, MnO, Mn_2O_6 etc, but Mn_3O_4 is considered highly efficient catalyst for the oxidation of methane [16] and carbon monoxide [17] as well as for the selective reduction of nitrobenzene [18]. The existence of Mn_3O_4 into different polymorphs is a very useful catalyst in the combustion of the organic substances for the wide range of temperatures 373-773 K [19]. Moreover, Mn_3O_4 is used as initiating material for the synthesis of soft magnetic materials such as manganese zinc ferrite for power supplies applications [20] and the nanometre size of Mn_3O_4 showed enhanced working performance for these applications due to their significant high surface area and decreased size at large extent [21]. Several low temperature methods have been used for the synthesis of nanoscale based Mn_3O_4 magnetic nanoparticles including sol-gel method and controlled oxidation of water suspension of $Mn(OH)_2$ [22,23]. In addition these methods, water-alcohol thermal method and decomposition of acetylcetonate [Mn (acac) 2] in oleylamine at 180 ^{o}C have been employed for the preparation of Mn_3O_4 nanorods and nanoparticles respectively [24, 25]. The precipitation method has remained well known for the synthesis of metal oxides using their salts with hydroxides and finally dehydration is carried out for the produced adduct product.

In this study, we have grown well aligned, highly dense and uniform ZnO nanorods on the gold coated substrate using Mn_3O_4 nanoparticles as seed layer by following the hydrothermal growth technique.

2. Material and methods

Manganese chloride tetra hydrate, ethanol, zinc nitrate hex hydrate, and hexamethylenetetramine were purchased from sigma Aldrich Sweden. All other chemical used were of analytical grade.

2.1. The synthesis of Mn_3O_4 nanoparticles

In a typical procedure for the preparation of Mn_3O_4, 5grams of $MnCl_2.4H_2O$ were dissolved in100 ml distilled water and then vigorously stirred for 10 min. Afterwards, the solution was transferred into a 60-mL Teflon-lined stainless-steel autoclave, sealed, and maintained at 180 ^oC for 12 h. And then, the autoclave was allowed to cool to room temperature naturally. Finally, the brown precipitates were centrifuged and washed with distilled water and ethanol several times and dried under vacuum at 60 ^oC for 4 h. The as-prepared precipitates were calcinated at 300 ^oC for 5 h in order to complete conversion of manganese hydroxide to Mn_3O_4 nanoparticles.

2.2. The Preparation of seed solution of prepared magnetic nanoparticles for the growth of ZnO nanorods

The seed solution of Mn_3O_4 nanoparticles was prepared in 100 mM hydrochloric acid. Different concentrations of Mn_3O_4 nanoparticles were optimised for the growth of well aligned ZnO nanorods, but we used 85 mg of nanoparticles in 5 ml of hydrochloric acid and a homogeneous seed solution was obtained in sonicated bath.

2.3. The fabrication of ZnO nanorods on the gold coated glass substrate and their characterisation

ZnO nanorods were fabricated on the gold coated glass substrate using seed layer of Mn_3O_4 nanoparticles by hydrothermal growth approach. The method of growth was followed according to work [26].

The nanostructures of ZnO were characterised by FESEM, EDX, XRD techniques and the optical study was carried out by photoluminescence technique.

3. Results and discussion

3.1. The crystalline study of as obtained Mn_3O_4 nanoparticles

The X-ray diffraction (XRD) study of as prepared Mn_3O_4 nanoparticles by precipitation method is shown in Fig. 1(a). The diffraction peaks appeared in the graph can be indexed to the tetragonal structure of Mn_3O_4 nanoparticles which are according to the (JCPDS card NO: 24-0734). Moreover, the XRD study was supported by the Raman study for defining the crystalline structure of as prepared Mn_3O_4 nanoparticles. All the appeared Raman peaks revealed the crystalline hausmannite structure of Mn_3O_4 nanoparticles [27] as shown in Fig. 1(b). Both studies have demonstrated the single crystalline nature of Mn_3O_4 nanoparticles.

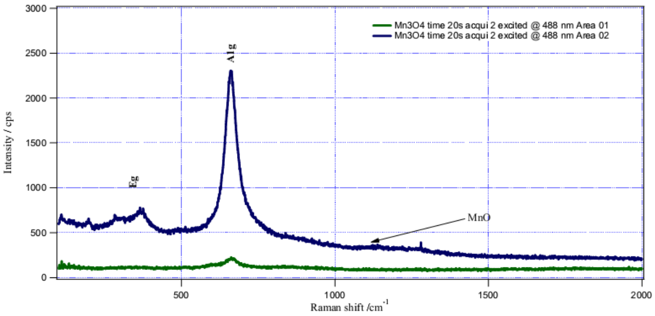

Fig 1. The Raman spectrum of Mn_3O_4 nanoparticles.

3.2. The morphological study of ZnO nanorods synthesised with seed layer of Mn_3O_4 nanoparticles

SEM was used to investigate the morphology of Mn_3O_4 seeded ZnO nanorods. Fig. 2 (a) shows the top view image of ZnO nanorods and it can be observed that the nanorods are highly dense, uniform and vertically oriented on the gold coated glass substrate. Beside the top view, cross sectional image of ZnO nanorods is shown in Fig. 2 (b) and it is clearly shown that the Mn_3O_4 nanoparticles provide highly sound nucleation for the growth of well aligned ZnO nanorods. This could be due to magnetic behaviour of two different inorganic materials at nanoscale and in doing so better orientation is observed.

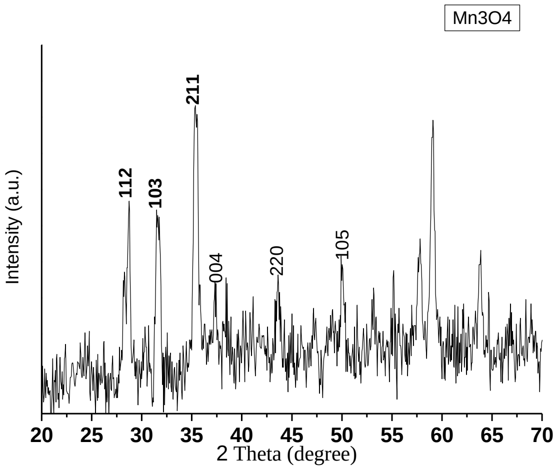

Fig. 2. The XRD pattern of Mn_3O_4 nanoparticle.

ZnO is polar crystalline material in which positive charge is carried by Zn and the negative charge on O [28]. Number of elementary reactions involved in the growth process of hydrothermal technique has been proposed [28, 29]. The strongly motivated growth mechanism for a single crystal synthesis is known as Ostwald ripening pathway [29]. It is naturally acceptable that large crystal formation is taking place first, then followed by small crystal growth and also the formation of large crystals is thermodynamically spontaneous due to energy difference between large crystal arrays and small crystals which is according to the Gibbs-Thomson law [30]. The chemical reactions involved in the synthesis of ZnO nanostructures using zinc nitrate and HMT can be designed as below. The most important is the role of HMT which generates the OH^{-1}ions in reaction bath and finally theses hydroxide ions result a product which is called ZnO. Firstly, zinc nitrate and HMT are decomposed at the desired temperature and simultaneously the amount of OH^{-1} ions and Zn^{2+} ions is increased.

$$Zn(NO_3)_2 \rightarrow Zn^{2+} + 2NO_3^{-1} \tag{1}$$

$$(CH_2)_6N_4 + 6H_2O \rightarrow 6CHO + 4NH_3 \tag{2}$$

$$NH_4OH \rightarrow NH_3 + H_2O \tag{3}$$

$$Zn^{2+} + 4NH_3 \rightarrow [Zn(NH_3)_4]^{2+} \tag{4}$$

$$Zn(OH)_2 \rightarrow ZnO + H_2O \tag{5}$$

The presence of colloidal phase of $Zn(OH)_2$ in reaction solution which has the tendency to work as part time nuclei for the formation of nanorod morphology. However, the Zn $(OH)_2$ phase start to be soluble with increasing growth temperature. Moreover, when the concentration of Zn^{2+} and OH^{-1} exceeds to a critical level of ZnO super saturation, then small ZnO particles automatically start to form in the complex medium of reaction bath [31-32]. Fig. 3 shows an XRD analysis of ZnO nanorods using seed layer of Mn_3O_4 nanoparticles. The observed intense 002 peak is evident for the better alignment of ZnO nanorods and preferred orientation in the c-axis direction by using seed stuff of Mn_3O_4 nanoparticles. Other appeared diffraction patterns include for crystal planes such as 100, 101, 102, 103, 112 and 004 and also one peak is observed for the gold coating on the glass substrate.

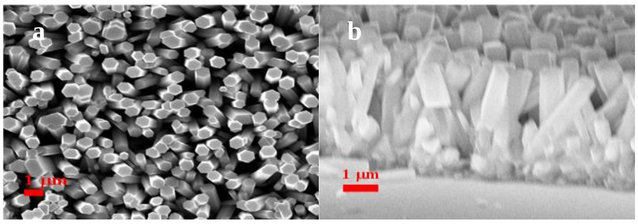

Fig. 3(a, b) The top view and b. cross section SEM image of ZnO nanorods grown with Mn_3O_4 seed.

3.3. Photoluminescence study of ZnO nanorods prepared with seed layer of Mn_3O_4 nanoparticles

The room temperature PL study of ZnO nanorods deposited on the gold coated glass substrate using the seed layer of Mn_3O_4 nanoparticles is shown in Fig. 4. PL emission of the ZnO nanorods can be seen in the near band emission in the UV region and the visible emission can also be observed due to the structural defects incorporation in the bulk of ZnO. The near band emission in UV region can be observed at 381 nm and the green emission peak is centred at 528 nm and orange/red emission band is measured at 683 nm. The high intensity of green and orange/red emission peaks could be assigned to higher number of defect states in the ZnO nanorods prepared with seed layer of Mn_3O_4 nanoparticles. The green emission band peak can be related to oxygen defects states and the orange/red emission corresponds to interstitial defects in the ZnO nanorods [33]. PL study suggests that the fabricated ZnO nanorods exhibited good crystal quality with relatively more defect states compared to zinc acetate seed layer.

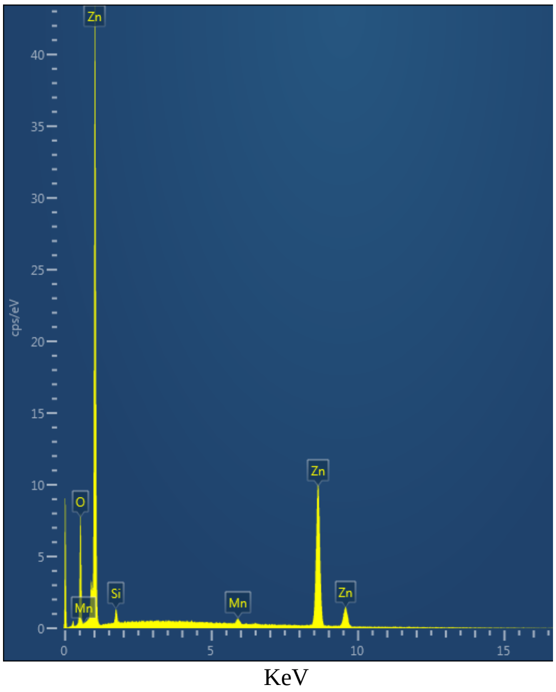

Fig. 4. The EDX for ZnO nanorods grown with Mn_3O_4 seed.

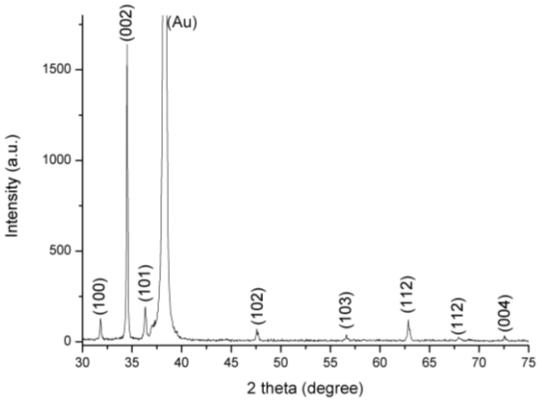

Fig. 5. The XRD pattern of ZnO nanorods.

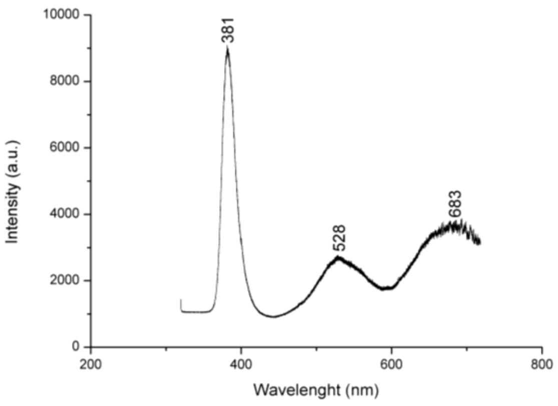

Fig. 6. The photoluminescence study of ZnO nanorods grown with Mn_3O_4 seed.

4. Conclusion

This work describes the synthesis of ZnO nanorods using seed layer of Mn_3O_4 nanoparticles by hydrothermal growth method. The use of manganese oxide nanoparticles provided a good platform as a nucleation for the growth of well aligned ZnO nanorods. The structural characterisation has shown that the ZnO nanorods are perpendicularly oriented to substrate, highly dense, uniform on the substrate and exhibits good crystal quality. Photoluminescence study has revealed that the ZnO nanorods are enriched with oxygen vacancy and interstitial defects. The approach towards to control of alignment of ZnO nanorods may be useful in improving the performance optoelectronic devices based on ZnO nanorods.

Acknowledgement

This project was supported by King Saud University, Deanship of Scientific Research, College of Science Research Center.

References

[1] M. Law, L. E. Greene, J. C. Johnson, R. Saykally, P. D. Yang, Nature Mater. **4**, 455 (2005).
[2] Q. Wan, Q. H. Li, Y. J. Chen, T. H. Wang, X. L. He, J. P. Li, C. L. Lin, Appl. Phys. Lett. **84**, 3654 (2004).
[3] M. H. Huang, S. Mao, H. Feick, H. Q. Yan, Y. Y. Wu, H. Kind, E. Weber, R. Russo, P. D. Yang, Science **292**, 1897 (2001).
[4] Z. L. Wang, J. H. Song, Science **312**, 242 (2006).
[5] W. Park, J. S. Kim, G. C. Yi, H. J. Lee, Adv. Mater. **17**, 1393 (2005).
[6] R. B. Peterson, C. L. Fields, B. A. Gregg, Langmuir **20**, 511 (2004).
[7] L. E. Greene, M. Law, J. Goldberger, F. Kim, J. C. Johnson, Y.F. Zhang, R. J. Saykally, P. D. Yang, Angew. Chem. Int. Ed. **42**, 3031 (2003).
[8] W. D. Zhang, Nanotechnology **17**, 1036 (2006).
[9] Y. Tak, K. Yong, J. Phys. Chem. **B109**, 19263 (2005).
[10] Y. W. Koh, M. Lin, C. K. Tan, Y. L. Foo, K. P. Loh, Chem. B **108**, 11419 (2004).
[11] A. E. Fischer, K. A. Pettigrew, D. R. Rolison, R. M. Stroud, J. W. Long, Nano. Lett. **7**, 281 (2007).
[12] Y. Zeheng, Z. Yuancheng, Z. Weixin, W. Xue, Q. Yitai, W. Xiaogang, Y. Shihe, J Solid State Chem. **179**, 679 (2006).
[13] J. B. Fei, Y. Cui, X. H. Yan, W. Qi, Y. Yang, K. W. Wang, Q. He, J. B. Li, Adv. Mater. **20**, 452 (2008).
[14] Z. Y. Yuan, Z. L. Zhang, G. H. Du, T. Z. Ren, B. L. Su, Chem. Phys. Lett. **378**, 349 (2003).
[15] M. Kang, E. D. Park, J. M. Kim, J. E. Yie, Appl. Catal. A **327**, 261 (2007).
[16] G. D. Moggridge, T. Rayment, R. M. Lambert, J. Catal. **134**, 242 (1992).
[17] E. R. Stobhe, B. A. D. Boer, J. W. Deus, Catal. Today **47**, 161 (1999).
[18] W. M. Wang, Y. N. Yang, J. Y. Zhang, Appl. Catal. A **133**, 81 (1995).
[19] M. Baldi, E. Finocchio, F. Milella, G. Busca, Appl. Catal. B **16**, 43 (1998).
[20] Z. W. Chen, S. Y. Zhang, S. Tan, J. Wang, S. Z. Jin, Appl. Phys. A **78**, 581 (2004).
[21] A. Vazquez-Olmos, R. Redon, G. Rodriguez-Gattorno, M. E. Mata-Zamora, F. Morales-Leal, A. L. Fernandez-Osorio, J. M. Saniger, J Colloid Interface Sci. **291**, 175 (2005).
[22] E. Mendelovici, A. Sagarzazu, Thermochim. Acta **133**, 93 (1988).
[23] O. Bricker, Am. Mineral. **50**, 1296 (1965).
[24] B. Yang, H. Hu, C. Li, X. Yang, Q. Li, Y. Qian, Chem. Lett. **33**, 804 (2004).
[25] W. S. Seo, H. H. Jo, K. Lee, B. Kim, S. J. Oh, J. T. Park, Angew. Chem. Ind. Ed. **43**, 1115 (2004).
[26] Z. H. Ibupoto, S. M. U. Ali, C. O. Chey, K. Khun, O. Nur, M. Willander, J. Appl. Phys. **110**, 104702 (2011).
[27] F. Buciuman, F. Patcas, R. Craciun, D. R. T. Zahn, Phys. Chem. Chem. Phys. **1**, 185 (1999).
[28] H. Zhang, D. Yang, Y. J. Yi, X. Y. Ma, J. Xu, D. L. Que, J. Phys. Chem. B **108**, 3955 (2004).
[29] O. Krichershy, J. Stavan, Phys. Rev. Lett. **70**, 1473 (1993).
[30] J. W. Mullin, Crystallization, third ed, Butterworth/Heinemann, Oxford, 1997, p. 1436.
[31] L. G. Sillen, A. E. Martell, Stability constants of metal–ion complexes, The Chemical Society, Burlington House, London, 1964.
[32] D. Polsongkram, P. Chamninok, S. Pukird, L. Chow, O. Lupan, G. Chai, H. Khallaf, S. Park, A. Schulte, Physica B **403**, 3713 (2008).
[33] C. H. Ahn, Y. Y. Kim, D. C. Kim, S. K. Mohanta, H. K. Cho, J. Appl. Phys. **105**, 013502 (2009).

---

[*] Corresponding author: atifhull@gmail.com