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Growth of Vertically Aligned ZnO Nanowires on Iron Oxide Layer

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Abstract. A low cost and substrate-independent method has been established to synthesize vertically aligned ZnO nanowires (NWs) on *iron oxide films* coated silicon substrates via low pressure Chemical Vapor Deposition (CVD) method at 650°C. In this study, Si substrates were dipped into the iron (III) nitrate nonahydrate solution prior to the synthesis process. This oxidized iron film facilitated the growth of highly oriented (002) ZnO seed layer, which allowed subsequent vertically aligned ZnO NWs to be grown on top of it during the synthesis. This approach has provided a good alternative to grow vertically aligned ZnO NWs without the need of considering the epilayer relationship between the ZnO and the material to be used as substrate.

1. Introduction

ZnO NWs have attracted overwhelming research interests due to its wide ranging potential applications such as mechanical actuators and piezoelectric sensors [1], room temperature UV lasers [2], solar cells [3] and vertical surround gate field-effect transistors [4]. Particularly, vertically aligned ZnO NWs can be synthesized by homoepitaxy growth or heteroepitaxy growth. In homoepitaxy growth, highly (002) oriented ZnO film has been used as seeds layer to facilitate the aligned growth of ZnO NWs [5-7]. On the other hand, substrates with a small lattice mismatch between ZnO NWs are needed in the heteroepitaxy growth to provide a good template for vertically aligned ZnO NWs. For example, epitaxy layers which have a small lattice mismatch with ZnO such as SiC (5.5%) [8], GaN (1.9%) [9] and a-sapphire (0.08%) [9], are commonly used to grow vertically aligned ZnO NWs. Despite of these developments to synthesize vertically aligned ZnO NWs, the existing approaches tends to be less versatile and expensive for practical applications. For instance, highly (002) oriented ZnO seeds layers for homeoepitaxy growth are usually prepared by costly and sophisticated vacuum deposition techniques such as Atomic Layer Deposition [5,10], and Metal-Organic Chemical Vapor Deposition [11]. Besides, heteroepitaxy growth of ZnO NWs is limited to insulating or expensive substrates such as SiC and GaN epilayer. Consequently, a low cost and substrate independent approach needs to be established in order to grow vertically aligned ZnO NWs for the fabrication of high performance devices.

In this work, we demonstrated that vertically aligned ZnO NWs could be grown on iron oxide films coated silicon substrates by CVD process. Lattice mismatch between ZnO and substrate is not a critical factor for aligned growth of ZnO NWs in this approach as long as thin iron (III) nitrate nonahydrate film could be coated on the substrate surface. The as-grown ZnO NWs exhibited a strong near band edge emission with a suppressed orange emission in room temperature photoluminescence (PL) measurement, indicating that the NWs were good in crystal quality. Thus, this provides a low cost and substrate independent approach to grow vertically aligned ZnO NWs with good crystal quality for a better device performance.

2. Experiments

Silicon (100) substrates were ultrasonically cleaned in acetone and rinsed with deionized water. One batch of substrates was dipped into 0.01 M iron (III) nitrate nonahydrate solution. The as-coated substrates were dried by heating the substrates to 70~80^{o}C in air. The growth of ZnO NWs was carried out in a horizontal tube reactor by a vapor transport process for 30 minutes. Zn powder (99.99%) was loaded in the middle of tube furnace. The iron (III) nitrate nonahydrate film coated silicon substrates were loaded into a reactor. The furnace was heated up to 650^{o}C under a constant flow of argon gas. When the desired temperature was reached, oxygen gas (5% of total gas flow rate) was flowed into the furnace for 30 min. in order to grow NWs. The pressure during the growth process was kept at 15 torr. The crystalline structure of the iron oxide films and NWs were characterized by a X-ray Diffractometer (Bruker, Cu K_α radiation with wavelength of 1.5406 Å). The morphology of the samples was examined using a scanning electron microscope (SEM, Phillips XL30 ESEM-FEG). The photoluminescence (PL) property of ZnO NWs was characterized using N_2 laser as excitation source (337 nm, pulse rate 20 Hz).

3. Results and discussion

The crystal structures of as-deposited and heat-treated (650^{o}C) iron (III) nitrate nonahydrate film on silicon were studied using XRD measurement. As shown in Fig. 1 (a)(i), the as-deposited film composed of diffraction peaks of FeO, Fe_2O_3 and Fe_3O_4. In contrary, the heat treated film mainly consists of diffraction peaks from Fe_2O_3 as demonstrated in Fig. 1 (a)(ii). This result suggests that the iron (III) nitrate nonahydrate film was likely oxidized to Fe_2O_3 film during the synthesis process. This Fe_2O_3 film was responsible for the vertically aligned growth of ZnO NWs.

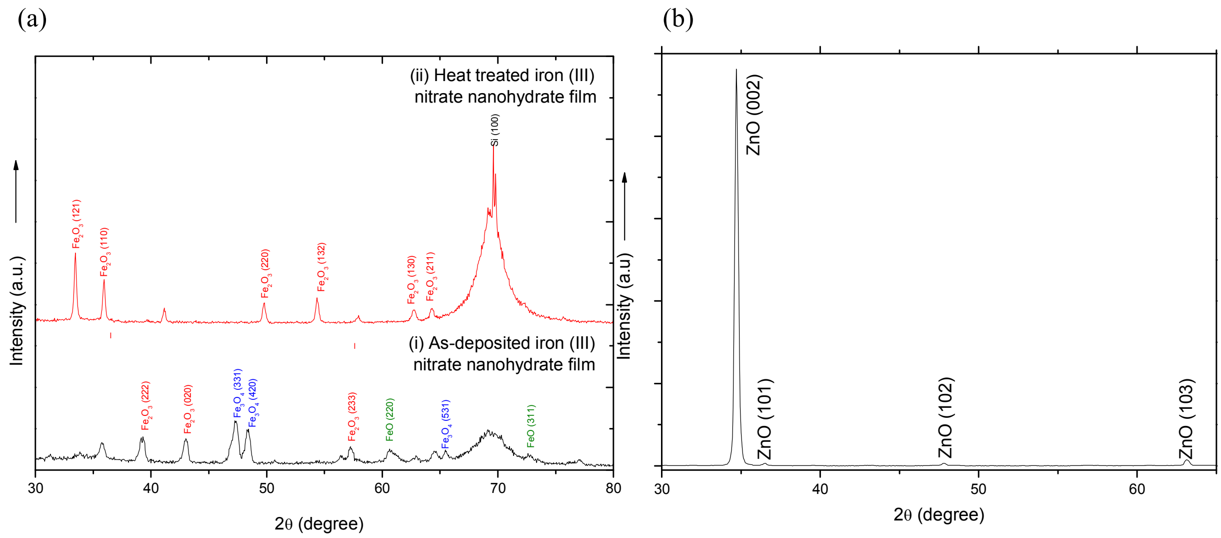

Fig. 1. XRD patterns of (a)(i) as-deposited iron nonahydrate films, (a)(ii) heat-treated iron nonahydrate films on silicon substrate; and (b) ZnO NWs grown on Fe_2O_3 film deposited silicon surface.

Fig. 1 (b) shows the XRD result of ZnO NWs grown on the Fe_2O_3 film. A very strong (002) diffraction peak indicated that a preferential growth of ZnO NWs in [0001]. This has been verified by the reasonably vertically aligned growth of ZnO NWs as shown in Fig. 2 (a) and (b). The NWs show uniform diameter throughout the length, ranging from 30 to 135 nm. The length of the NWs was 0.8 to 1.1 μm. No alloy nanoparticle is observed at the tips of the NWs as shown in Fig. 2 (c). The EDX analysis [Fig. 2 (d)] indicates that the specimen composed of Fe element besides Zn and O elements.

Theoretically, the CVD grown ZnO layer with random crystal orientation should be grown on top of the Fe_2O_3 film prior to the growth of ZnO NWs [5, 12]. This is attributed to the large lattice mismatch between Fe_2O_3 (a = 5.420 Å) and ZnO (a = 3.249 Å). However, an unexpected outcome has been observed. The as-deposited iron (III) nitrate nonahydrate film was oxidized to Fe_2O_3 film during the synthesis process as illustrated in Fig. 3 (a). The Fe_2O_3 film facilitated the growth of highly (002) oriented CVD grown ZnO layer [Fig. 3 (b)]. This allowed homeoepitaxy growth of vertically aligned of ZnO NWs from the highly (002) oriented CVD grown ZnO layer as displayed in Fig. 3 (c). Further study is required to unravel the formation of (002) oriented ZnO layer by Fe_2O_3 film. The growth of ZnO NWs from Fe_2O_3 film was followed the Vapor-Solid (VS) mechanism since (i) no foreign catalyst was used, (ii) no alloy nanocluster was observed at the tip of ZnO NWs and (iii) the melting point of the iron oxide (i.e. 1370 ^oC to 1565^oC, depends on the types of iron oxide) is higher than the synthesis temperature, i.e. 650 ^oC. Therefore, growth of ZnO NWs in this case is unlikely governed by the Vapor-Liquid-Solid (VLS) mechanism.

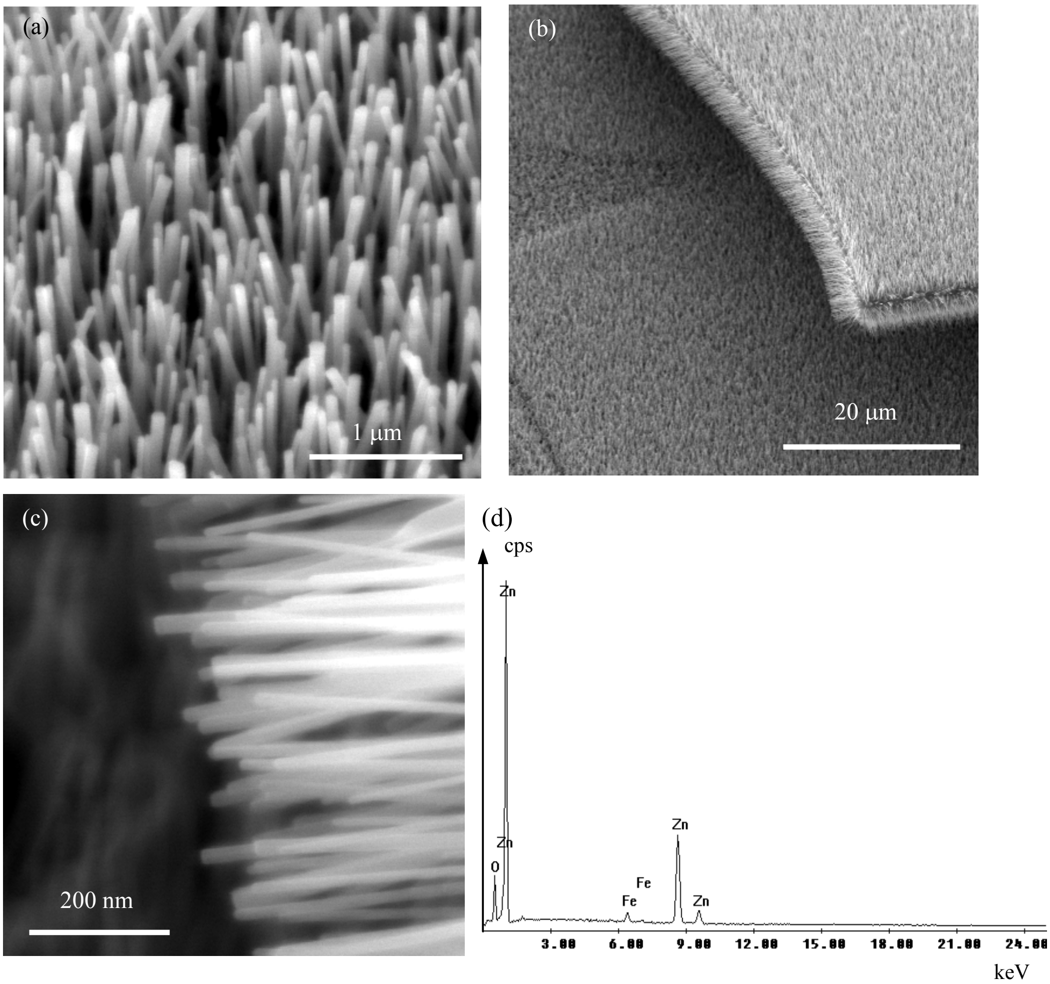

Fig. 2. (a-b) SEM images of ZnO NWs. (c) A high-magnification SEM image showing no nanoparticle at the tips of the NWs, and (d) EDS spectrum of ZnO NWs grown on Fe_2O_3 film deposited silicon substrate.

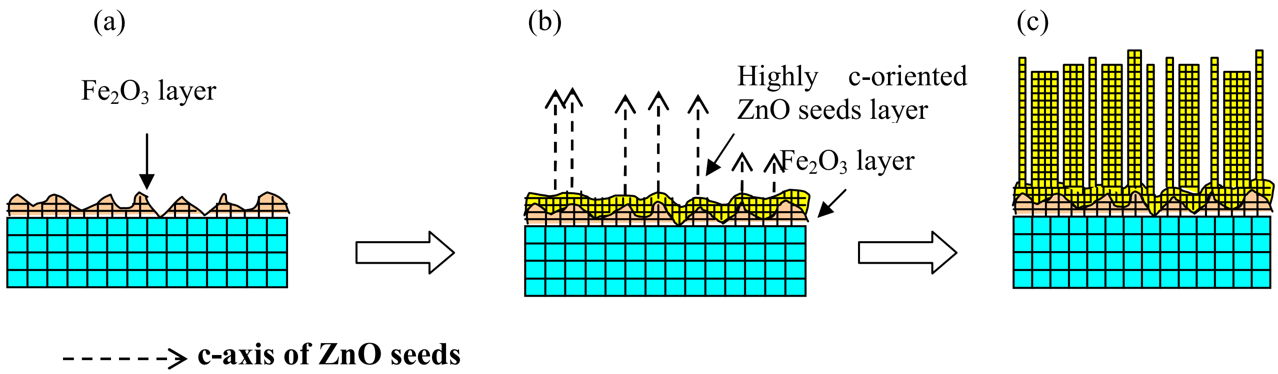

Fig. 3. Growth process of vertically aligned ZnO NWs on Fe_2O_3 coated Si substrate. (a) Formation of Fe_2O_3 layer while ramping up the temperature of the reactor to 650°C, (b) Deposition of highly (002) textured ZnO seeds layer, and (c) Subsequent growth of vertically aligned ZnO NWs from the ZnO seeds layer by CVD.

4. Conclusions

Fe_2O_3 layer played a crucial role to facilitate the growth of highly (002) texture ZnO seeds layer during CVD synthesis process. Formation of highly oriented (002) ZnO seeds layer allowed homeoepitaxy growth of vertically aligned ZnO NWs. The synthesis temperature (650°C) was simply too low to melt the Fe_2O_3 layer and to form Fe alloy droplets which was needed for VLS growth. Thus, the growth of ZnO NWs was likely governed by VS mechanism. Such substrate independent novel approach would meet the much needed requirement for the cost-effective synthesis of vertically aligned ZnO NWs.

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REFERENCES

[1] X. Bai, E.G. Wang, P.X. Gao and Z.L. Wang: Nano Lett. Vol. 3 (2003), p. 1147.
[2] M.H. Huang, S. Mao, H. Feik, H. Yan, Y. Wu, H. Kind, E. Weber, R. Russo and P. Yang: Science Vol. 292 (2001), p 1897.
[3] M. Law, L.E. Greene, J.C. Johnson, R. Saykally and P. Yang: Nat. Mater. Vol. 4 (2005) p. 455.
[4] H.T. Ng, J. Han, T. Yamada, P. Nguyen, Y.P. Chen and M. Meyyappan: Nano Lett. Vol. 4 (2004), p. 1247.
[5] S.Y. Pung, K.L. Choy, X. Hou and C. Shan: Nanotechnology Vol. 19 (2008), p. 435609.
[6] L.S. Wang, X.Z. Zhang, S.Q. Zhao, G.Y. Zhou, Y.L. Zhou and J.J. Qi: Appl. Phys. Lett. Vol. 86 (2005), p. 024108.
[7] S.Y. Pung, K.L. Choy, E.A. Vinogradov, N.N. Novikova and V.A. Yakovlev: J. Cryst. Growth Vol. 312 (2010), p. 2220.
[8] Z. Fan and J.G. Lu: Appl. Phys. Lett. Vol. 86 (2005), p. 123510.
[9] H.J. Fan, F. Fleischer, W. Lee, K. Nielsch, R. Scholz, M. Zacharias, U. Gosele, A. Dadgar and A. Krost: Superlattice Microst. Vol. 36 (2004), p. 95.
[10] G. Sberveglieri: Sens. Actuator B Vol. 23 (1995), p. 103.
[11] J.F. Conley, L. Stecker and Y. Ono: Nanotechnology Vol. 16 (2005), p. 292.
[12] S.Y. Pung, K.L. Choy, X. Hou and C. Shan, in: Crystal Growth: Theory, Mechanisms and Morphology, edited by N.A. Mancuso, Nova publisher (2011) (ISBN: 978-1-61324-529-3), in-press.

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