

Growth and characterization of chemical-vapor-deposited zinc oxide nanorods

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Abstract

ZnO nanorods were grown on Si substrates by metal-organic chemical vapor deposition (CVD). The ZnO nanorods were characterized by scanning electron microscopy, transmission electron microscopy (TEM), and X-ray diffraction. It was found that highly oriented ZnO single-crystalline nanorods were formed only on the substrate coated with a gold film. Without the gold, ZnO was deposited as a continuous film. No Au was observed on top of the ZnO nanorods, implying that the Au plays no role as catalytic metal in vapor–liquid–solid mechanism for formation of ZnO nanorods. In CVD, oriented ZnO nanorods along the *c*-axis were grown as a result of $\langle 111 \rangle$ textured Au. High-resolution TEM shows that the gold layer and ZnO are in orientation relationship of Au $\{111\}$ planes//ZnO (0002) basal planes.

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1. Introduction

ZnO oxide nanostructures such as nanowires/nanorods, nanobelts, and nanodots have been recently received intensive studies, due to their versatile properties in optoelectronics and sensors [1–5]. Most of nanostructured ZnO materials are synthesized in nanowires/nanorods by vapor transport based on vapor–liquid–solid (VLS) growth mechanism using metal as catalyst such as Au and Cu [1,6,7]. However, some studies show that Au is not necessary for nanowire growth. Recently, it has been shown that metal-organic chemical vapor deposition (MOCVD) can also be used to grow well-aligned ZnO nanorods without using any metal catalyst [8–13]. To understand if the role of Au in growth of ZnO nanorods in MOCVD is similar to VLS, we have grown ZnO on top of a Au film coated on Si substrate in this study. Microstructural characterization of X-ray diffraction, scanning electron microscopy, and trans-

mission electron microscopy shows that Au assists the alignment of ZnO nanorods by epitaxial growth, but no VLS mode can be found.

2. Experimental procedure

After the Si(001) wafer in $1 \times 1 \text{ cm}^2$ was coated with a sputtered Au film in 10 nm thickness, it was loaded in a MOCVD reactor. ZnO was deposited using zinc acetylacetonate ($\text{Zn}(\text{C}_5\text{H}_7\text{O}_2)_2$) (99.995% purity) and oxygen gas (99.999% purity) as the zinc and oxygen sources, respectively. The substrate and oxygen gas temperature were all kept at 500 °C. $\text{Zn}(\text{C}_5\text{H}_7\text{O}_2)_2$ was heated to 134 °C before flowing into the reaction chamber through a preheating tube at 170 °C with carriers gas of N_2 (99.999% purity). Both O_2 and N_2 flow rates were set at 500 sccm. The pressure was at 1 atm. Cross-sectional TEM specimen preparation was carried out by conventional method of mechanical grinding and polishing, followed by Ar ion milling.

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3. Results and discussion

The SEM images in Fig. 1 show the morphology of the ZnO after deposition for 60 min and 120 min. It can be seen that there are two different sizes of ZnO for each deposition time. For 60-min deposition (Fig. 1a and b), the smaller size of ZnO nanorods is about 50 nm, while the larger one is about 100–150 nm. For 120-min growth (Fig. 1c and d), the smaller size is in the range of 60–90 nm, and the larger one increases to 250–290 nm. Although there are different sized ZnO, all the ZnO are well aligned in a direction perpendicular to the substrate surface, and the tip of each rod has the same shape in a cone-like form. Interestingly, there is no Au particle at the tip of each ZnO nanorod, implying that no VLS growth occurs for ZnO nanorod formation with Au. The XRD patterns in Fig. 2 only show the ZnO (0002) and Au (111) peaks, indicating that ZnO nanorods are textured along *c*-axis direction which is parallel to Au [111]. The evidence of Au existence shows that Au still remains in the specimens. X-ray energy dispersive spectroscopy in SEM at the interface between ZnO and Si reveals strong Au peaks, consistent with SEM observations in Fig. 1. Further characterization of the interfacial region was carried out by cross-sectional TEM. Fig. 3 shows the bright-field (BF) TEM image with a corresponding selected area diffraction (SAD) pattern obtained from a sample after 30-min deposition. The nanorods exhibit columnar morphology. The SAD shows that the nanorods are oriented along *c*-axis, and each nanorod is of single crystallinity. Above the Si substrate, a thin layer in bright contrast is amorphous

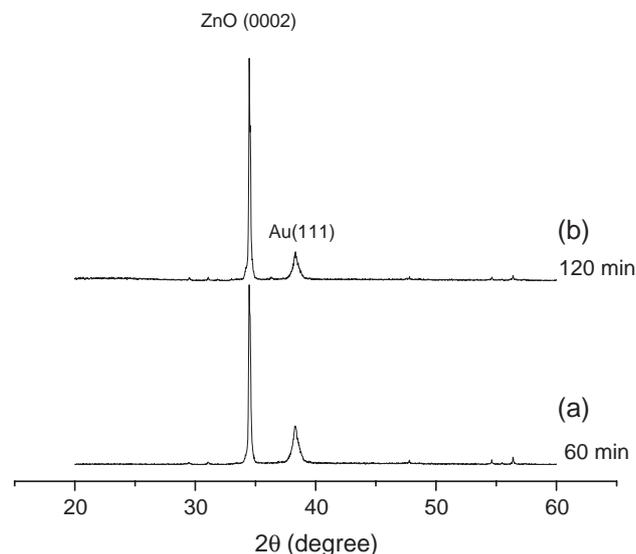


Fig. 2. XRD patterns of (a) 60 min and (b) 120 min.

SiO₂ which is native oxide of Si. Between the SiO₂ and ZnO, there is a dark contrast layer which is identified by EDS as the Au film (Fig. 3b). The Si and O peaks arise from the SiO₂ layer due to the beam broadening effect of the electron probe in a size about 20 nm. The Cu peaks were caused by the Cu grid of the TEM specimen. High-resolution TEM in Fig. 3c reveals that ZnO (0002) and Au (111) lattice fringes are parallel to each other. No interlayer formation can be observed between Au and ZnO. The spacing of the lattice fringes of Au also shows that no Si exists in the film which support our interpretation of EDS

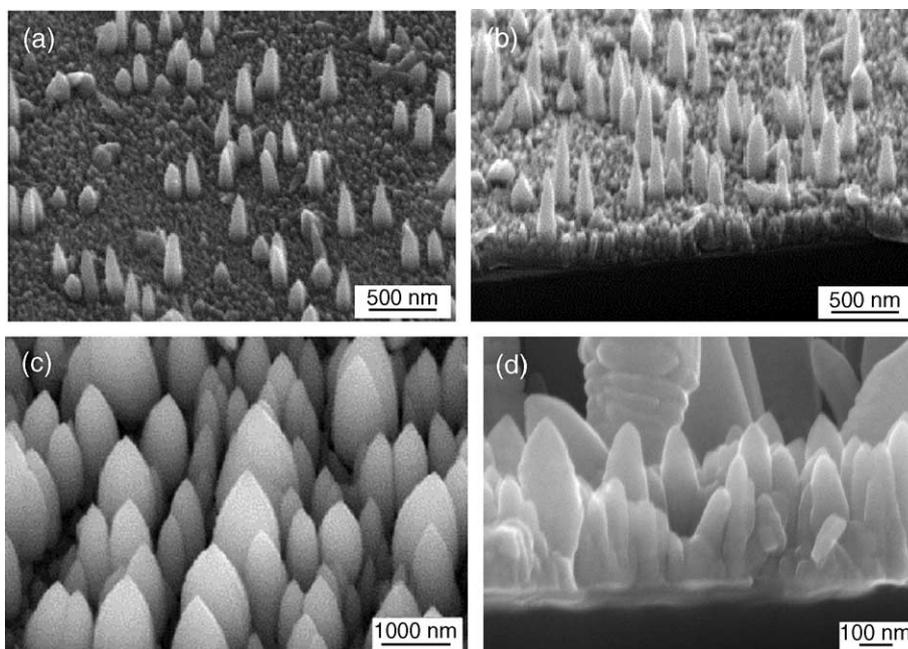


Fig. 1. SEM images showing the morphology of (a) and (b) ZnO for 60 min and (c) and (d) for 120 min. (a) and (c) are top view, and (b) and (d) are tilt view.

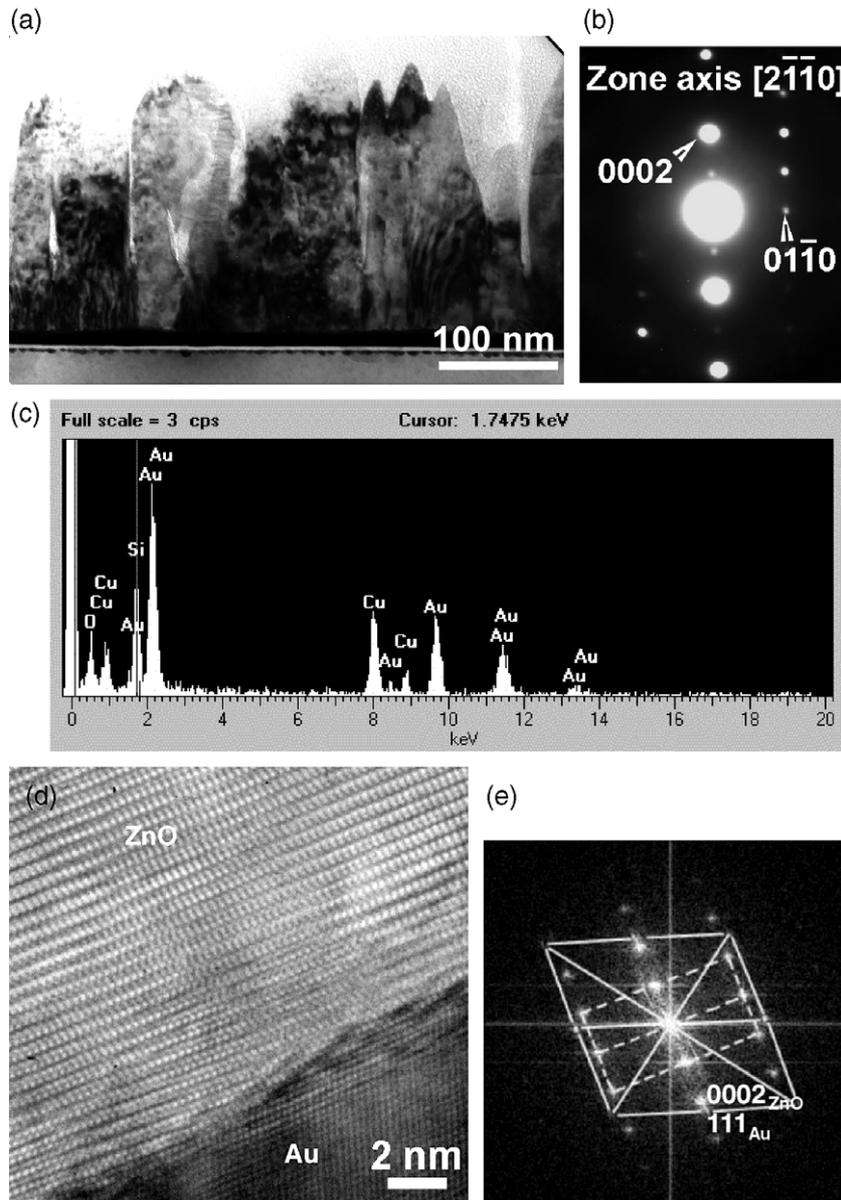


Fig. 3. (a) TEM micrograph in cross-section view showing the microstructure of ZnO with Au after 60 min deposition. (b) SAD pattern of ZnO nanorod. (c) EDS from the Au film. (d) High-resolution TEM from the interfacial region around ZnO and Au showing lattice fringes of ZnO (0002)//Au (111). (e) FFT pattern of (d) showing the orientation relationship of ZnO with Au.

result. From fast-Fourier transform in Fig. 3d, we can deduce the orientation relationship of ZnO and Au to be $[2\bar{1}\bar{1}0]_{\text{ZnO}}//[01\bar{1}]_{\text{Au}}$ and $(0002)_{\text{ZnO}}//(111)_{\text{Au}}$, consistent with XRD results. Fig. 4 is the BF TEM image from a sample deposited for 120 min. It can be seen that the Au film exists between SiO_2 and ZnO, which is also confirmed by EDS. The two different sized ZnO nanorods can also be seen. The tilted nanorods and those in horizontal position are caused by TEM specimen preparation. It can be observed that the larger nanorods are directly grown on the Au film as well. Thus, the growth rate of larger nanorods is much faster than that of smaller ones. As both kinds of

nanorods have similar morphology and crystalline characteristics, the actual reason for the different growth rate at the moment is not known.

Without any Au on the substrate, the morphology of ZnO deposited in the same MOCVD condition is shown in Fig. 5a and b for 60 and 120 min deposition. A continuous film of ZnO is observed without apparent nanorods formed. The surface is relatively smooth in comparison with that on Au. The XRD pattern from 120 min deposition in Fig. 4c shows that there are two ZnO peaks corresponding to (0002) and $(1\bar{1}02)$ reflections, suggesting the ZnO is not strongly textured in *c*-axis orientation.

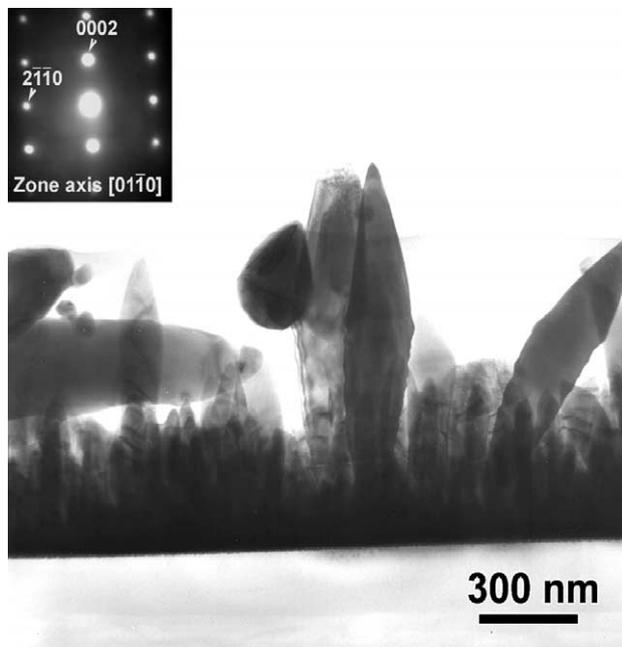


Fig. 4. Cross-sectional TEM micrograph of ZnO after 120 min deposition.

From the above results, it is clear that Au has assisted in the formation of oriented nanorods in MOCVD growth, and the Au plays no role as catalyst in the VLS growth mode. The explanation can be reasoned as follows. It is well known that the sputtered Au on Si substrate has a texture in

$\langle 111 \rangle$. During the first stage of MOCVD deposition, the Au film might further develop into strong $\langle 111 \rangle$ texture. In VLS mode, it has been suggested that Zn metal vapor may dissolve into the solid Au to form liquid alloy. In MOCVD, the Zn precursor might decompose into ZnO and other carbon-containing molecules such as CO, CO₂, and C_xH_yO_z [14]. As there is no chemical reaction between ZnO and Au, ZnO vapor species are adsorbed on the Au surface to form nuclei. Hence, no liquid Au–Zn alloy would form. The Au (111) surface energy is about 0.9 J/m² [15], smaller than that of ZnO *c*-plane (3.4 J/m²) [16]. Thus, the high surface energy of ZnO will promote three-dimensional island growth, which favors the columnar structure along *c*-axis orientation. As a result, the nanorods can be formed.

4. Conclusion

In summary, the Au effect on the growth of ZnO nanorods in MOCVD has been studied. It is found that well-aligned ZnO nanorods are grown along the *c*-axis direction due the (111) Au film. No catalyst role in VLS growth mode for Au can be observed.

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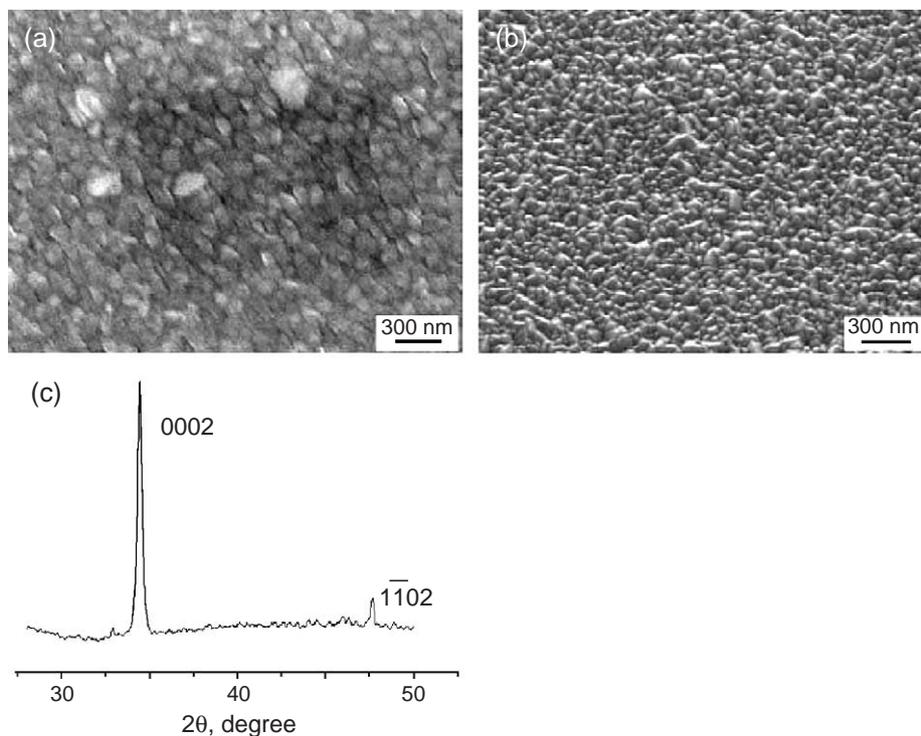


Fig. 5. (a) SEM image and (b) XRD pattern from ZnO deposited on Si without Au.

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References

- [1] M.H. Huang, Y. Wu, H. Feick, N. Tran, P. Yang, *Adv. Mater.* 13 (2001) 113.
- [2] M.H. Huang, S. Mao, H. Feick, H. Yan, Y. Wu, H. Kind, E. Weber, R. Russo, P. Yang, *Science* 292 (2001) 1897.
- [3] Z.W. Pan, Z.R. Dai, Z.L. Wang, *Science* 291 (2001) 1947.
- [4] E.A. Meulenkaamp, *J. Phys. Chem., B* 102 (1998) 5566.
- [5] Z.L. Wang, *Mater. Today* (2004) 26, (June issue).
- [6] S.Y. Li, P. Lin, C.Y. Lee, T.Y. Tseng, *J. Appl. Phys.* 95 (2004) 3711.
- [7] S.Y. Li, P. Lin, C.Y. Lee, T.Y. Tseng, *J. Cryst. Growth* 247 (2003) 357.
- [8] J.J. Wu, S.C. Liu, *Adv. Mater.* 14 (2002) 215.
- [9] W. Lee, M.C. Jeong, J.M. Myoung, *Acta Mater.* 52 (2004) 3949.
- [10] M.C. Jeong, B.Y. Oh, W. Lee, J.-M. Myoun, *J. Cryst. Growth* 268 (2004) 149.
- [11] M. Satoh, N. Tanaka, Y. Ueda, S. Ohshio, H. Saitoh, *Jpn. J. Appl. Phys.* 38 (1999) L586.
- [12] W.I. Park, D.H. Kim, S.-W. Jung, Gyu-Chul Yi, *Appl. Phys. Lett.* 80 (2002) 4232.
- [13] B.P. Zhang, N.T. Binh, Y. Segawa, Y. Kashiwaba, K. Haga, *Appl. Phys. Lett.* 84 (2004) 586.
- [14] S.M. Smith, H.B. Schlegel, *Chem. Mater.* 15 (2003) 162.
- [15] J.M. Zhang, F. Maa, K.W. Xu, *Appl. Surf. Sci.* 229 (2004) 34.
- [16] G. Kresse, O. Dulub, U. Diebold, *Phys. Rev., B* 68 (2003) 245409.