

2011-02-28

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Recommended Citation

Peng-zeng LU, Su LI, Jin-qian JIA, Zhen-hai LIANG. Electrochemical Deposition of Zinc Oxide Crystal Whiskers[J]. *Journal of Electrochemistry*, 2011 , 17(1): Article 18.

DOI: 10.61558/2993-074X.2823

Available at: <https://jelectrochem.xmu.edu.cn/journal/vol17/iss1/18>

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电化学法沉积氧化锌晶须

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摘要: 应用阳极氧化法沉积氧化锌(ZnO)松针状晶须, SEM和XRD观察、表征样品形貌与结构. 结果表明, 电沉积氧化锌晶须直径为20~50 nm、长度200~300 nm、长径比10~15, 纯度高, 结晶度好, 属六方晶系纤锌矿(JCPDS 36-1451). 循环伏安法研究了该氧化锌结晶过程, 并考察了电解液的锌酸盐 $[Zn(OH)_4]^{2-}$ 浓度和基底表面氧化膜对晶须生成的影响.

关键词: 电化学; 氧化锌; 晶须; 螺旋位错

中图分类号: O611.4

文献标识码: A

氧化锌(ZnO)具有3.37 eV的禁带宽度, 其激子束缚能高达60 meV^[1], 是一种重要的宽禁带、直接带隙的半导体功能材料. 氧化锌晶须更以其完整的晶体结构, 独特的纳米效应在光电催化^[2-3]、紫外激光发射^[4-5]、杀菌^[6]和增强复合材料^[7]等具备优越的特性, 引起广大研究者的浓厚兴趣.

氧化锌晶须为立体四针状单晶体, 日本松下已于1989年成功研制. 目前, 氧化锌晶须的制备主要有化学气相沉积^[8-9]、金属氧化物化学气相沉积^[10]、碳热还原^[11-12]和水热合成^[13]等方法, 但都不同程度地存在着实验条件苛刻、工艺复杂、反应时间长等不足. 电化学合成条件温和, 过程可控, 本文采用一步电化学氧化法沉积松针状氧化锌晶须, 以期为其他金属氧化物晶须的制备提供新方法.

1 实验部分

1.1 仪器及材料

HB171500SL-5A型直流稳定电源, H1650-W型台式离心机, HJ-4型磁力搅拌器, 锌片(纯度99%), 其余试剂均为分析纯, 实验水为二次蒸馏水.

1.2 氧化锌晶须制备

1) 电解液

将11.55 g $Zn(NO_3)_2$ 和8.97 g KOH分别溶于

40 mL水配成 $Zn(NO_3)_2$ 溶液和KOH溶液. 尔后, 把 $Zn(NO_3)_2$ 溶液缓慢加入KOH溶液, 搅拌至混合均匀, 得饱和 $[Zn(OH)_4]^{2-}$ 溶液. 再将溶液离心5 min, 倾出上部清液过滤即得无色透明电解液.

2) 电沉积

将1 cm × 5 cm的锌片在无水乙醇中超声清洗10 min, 除去表面油污, 去离子水冲洗晾干. 以上述饱和 $[Zn(OH)_4]^{2-}$ 溶液为电解液、锌片为阳极、石墨作阴极, 磁子搅拌并通电1 h, 电流密度0.3 mA/cm², 制成ZnO样品.

1.3 氧化锌晶须的检测表征

使用JSM-6700F型场发射扫描电镜(日本FE-SEM)观察以上制备的ZnO晶须表面形貌. D/max 2500型X射线衍射仪(日本理学公司XRD)表征该晶须物相及结构, 辐射源: $CuK\alpha$, $\lambda = 0.151178$ nm, 循环伏安性测试使用含EC-Lab软件控制的Vmp3 Multi Potentiostat型恒电位仪(美国Princeton), 三电极体系锌片为研究电极(1 cm × 5 cm)、铂丝为辅助电极、饱和甘汞(SCE)作参比电极, 扫描速率: 50 mV/s.

2 结果与讨论

2.1 SEM分析

图1示出电沉积氧化锌晶须(a. 50000倍和b. 100000倍)的SEM照片. 可以看出晶须排列致密,

呈松针状结构;直径为 20 ~ 50 nm,长度 200 ~ 300 nm,长径比在 10 ~ 15 之间,符合晶须标准(长径比 5 ~ 1000,直径 20 nm ~ 100 μm)^[14].

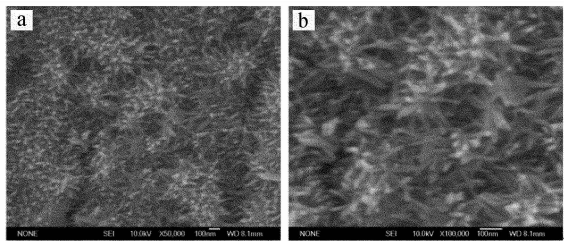


图 1 电沉积氧化锌晶须

Fig. 1 SEM images of the electrodeposited ZnO crystal whiskers
a. ×50000, b. ×100000

2.2 XRD 分析

图 2 是氧化锌晶须的 XRD 谱图,从图可见在 2θ 31.7°、34.4°、36.3°、56.6°和 77.1°分别显示表征氧化锌(ZnO)的(100)、(002)、(101)、(110)和(202)晶面的衍射峰,其他峰属锌基底的衍射峰.与标准图谱对照,该氧化锌晶须为六方晶系纤锌矿 ZnO(JCPDS 36-1451)^[15].其于 31.7°、34.4°和 36.3°出现的衍射峰窄而高,尤以 36.3°峰为最高.说明样品结晶度较高,晶须优先沿(101)晶面方向生长,无杂质峰,产物纯度极高.

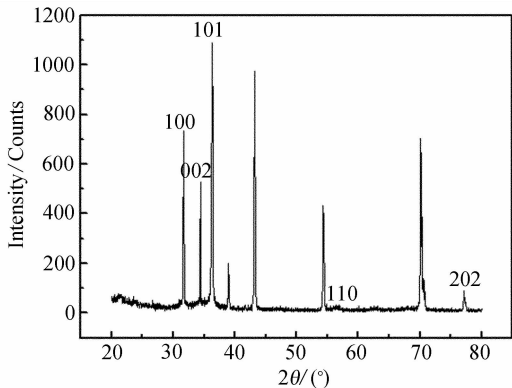


图 2 电沉积氧化锌晶须的 XRD 谱图

Fig. 2 Typical XRD pattern of the electrodeposited ZnO crystal whiskers

2.3 氧化锌晶须的生长机理初探

图 3 示出在饱和锌酸盐 [Zn(OH)₄]²⁻ 溶液中氧化锌晶须的循环伏安曲线.从图可看出,在 -1.15 V 附近呈现金属锌的氧化峰,表明阳极锌

在碱溶液中被氧化成了 [Zn(OH)₄]²⁻,该反应的标准电位 φ^θ([Zn(OH)₄]²⁻/Zn) = -1.215 V.但实际的氧化峰电位正移,此乃阳极析氧及浓差极化产生的过电位,图中无 [Zn(OH)₄]²⁻ 离子的还原峰,可知该反应不可逆.

实验发现,电沉积时阳极(锌片)周围有微量气泡逸出.一段时间后,表面生成灰色产物,阴极产生大量气泡,并有少量的灰白色沉淀聚积于底部.对应的电化学反应如下:

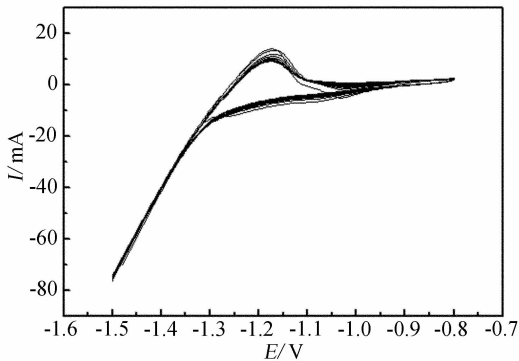
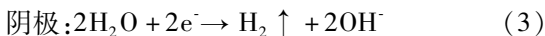
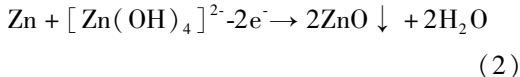
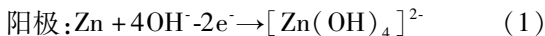


图 3 饱和锌酸盐 [Zn(OH)₄]²⁻ 电解液中氧化锌晶须的循环伏安曲线

Fig. 3 CV curves of the synthesizing zinc oxide whiskers in the saturated [Zn(OH)₄]²⁻ solution scan rate: 50 mV/s

以下考虑影响晶须生长的两方面因素:

1) 锌酸盐 [Zn(OH)₄]²⁻ 浓度

实验表明当电解液不含 [Zn(OH)₄]²⁻ 或其浓度较低时,阳极(锌片)氧化而无灰色物质沉积产生.这可能是由于 [Zn(OH)₄]²⁻ 浓度尚未达到生成 ZnO 稳定常数的浓度,氧化生成的 [Zn(OH)₄]²⁻ 未能在锌电极表面沉积就扩散入溶液中.显然,该锌酸盐的浓度在晶须生长过程中起着决定性作用^[16].

2) 锌表面的氧化膜

氧化之前,如先去除锌片表面的氧化膜,锌电极就不能生成晶须.从微观动力学考虑,锌表面氧化膜可为晶须的成长提供晶种.据 F. C. Frank^[17] 晶须螺旋位错生长理论,即在溶液-锌片界面处,表

面一定量原氧化锌晶种为晶体的成长提供了一个成核台阶,在近似饱和的 $[\text{Zn}(\text{OH})_4]^{2-}$ 溶液中,活化的 Zn 原子不断向台阶处扩散,只有到达台阶转折处的生长基元(活化 Zn 原子),才能和 $[\text{Zn}(\text{OH})_4]^{2-}$ 结合成为晶相分子.由于各晶面能级的不同,晶相分子在扩散中有所侧重,晶体生长可择优取向^[18],并在台阶处生成螺旋位错,此时,晶体也绕着位错的轴线螺旋延伸直至成点,最终生成氧化锌晶须.

3 结 论

应用阳极氧化法在新配置的锌酸盐溶液中于 0.3 mA/cm^2 电流密度下,可沉积松针状氧化锌晶须(直径:20~50 nm,长度:200~300 nm,长径比:10~15),其属六方晶系纤锌矿(JCPDS 36-1451).电解液锌酸盐 $[\text{Zn}(\text{OH})_4]^{2-}$ 浓度对氧化锌晶须的生成起决定作用,Zn 表面氧化膜为晶须的成长提供了晶种,氧化锌晶须的生成符合 V-L-S 体系的螺旋位错机理.

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Abstract: Pine needle ZnO crystal whiskers were electrodeposited by anodization of zinc foil. The crystal whiskers were characterized by scanning electron microscopy (SEM) and X-ray diffraction (XRD) spectroscopy. The results show that the lengths and diameters of ZnO crystal whiskers are 200 ~ 300 nm and 20 ~ 50 nm, respectively, with the ratio of the length to diameter ranging from 10 ~ 15. The whiskers belong to wurtzite ZnO (JCPDS 36-1451) with good crystallinity and high purity. The crystallization behavior of ZnO was studied by cyclic voltammetry. The effects of the surface oxide layer at the zinc substrates and the $[\text{Zn}(\text{OH})_4]^{2-}$ concentration of the aqueous electrolyte on the formation of zinc oxide whiskers were investigated.

Key words: electrochemistry; zinc oxide; crystal whisker; screw dislocation