研究通讯

采用高分子自组装ZnO纳米线及其形成机理

贺英 $*^{I}$, 王均安 2 , 桑文斌 3 , 吴若峰 I , 颜莉莉 I , 方云英 3

(1上海大学材料与工程学院高分子材料系 上海 200072)

(²上海大学材料研究所 上海 200072)

(3上海大学材料与工程学院电子信息材料系 上海 200072)

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摘要 介绍了一种能在各种晶面的硅衬底上制备垂直于衬底取向生长的ZnO纳米线阵列的新方法. 该法采用高分子络合和低温氧化烧结反应, 以聚乙烯醇(PVA)

高分子材料作为自组装络合载体来控制晶体成核和生长. 首先通过PVA侧链上均匀分布的极性基团羟基(—OH) 与锌盐溶液中的 Zn^{2+} 离子发生络合作用, 然后滴加氨水调节络合溶液pH值为8.5±0.1, 使络离子 Zn^{2+} 转变为Zn (OH)₂,再将硅片浸入此溶液中, 从而在硅衬底表面得到较均匀的 $Zn(OH)_2$ 纳米点, 随后在125 \mathbb{C} 左右 $Zn(OH)_2$ 纳米点通过热分解转化为ZnO纳米点, 其后在420 \mathbb{C}

烧结过程中衬底上的ZnO纳米点在PVA高分子网络骨架对其直径的限域下逐渐取向生长成ZnO纳米线,并且烧结初期PVA碳化形成的碳通过碳热还原ZnO为Zn,

再在氧气氛中氧化为ZnO的方式在纳米线顶端形成了催化活性点,促进了纳米线顶端ZnO的吸收. 烧结后碳逐渐氧化被完全去除.采用场发射扫描电镜(FE-SEM)、透射电镜(TEM, HR-TEM)和X射线衍射(XRD) 对纳米线的分析结果表明,ZnO纳米线在硅衬底上分布均匀,具有六方纤锌矿结构,并且大多沿[0001] 方向择优取向生长,直径为20~80 nm,长度可从0.5至几微米.

提出了聚合物控制ZnO结晶和形貌的网络骨架限域模型以解释纳米线的生长行为.

关键词 <u>ZnO纳米线</u> <u>自组装</u> <u>高分子诱导</u> <u>定向生长</u> <u>配位络合</u> 分类号

ZnO Nanowire Self-assembling Generated via Polymer and the Formation Mechanism

 $\mbox{HE Ying} \mbox{1, WANG Jun-An$}^{2}, \mbox{SANG Wen-Bin$}^{3}, \mbox{WU Ruo-Feng} \mbox{1, YAN Li-Li$}^{1}, \mbox{FANG Yun-Ying} \mbox{3}$

(¹ Department of Polymer Materials, School of Materials Science and Engineering, Shanghai University, Shanghai 200072)

(2 Institute of Materials, Shanghai University, Shanghai 200072)

(³ Department of Electronic Information Materials, School of Materials Science and Engineering, Shanghai University, Shanghai 200072)

Abstract A novel process was reported for preparing zinc oxide (ZnO) nanowires almost vertically well-aligned on various planes of silicon substrates by using polyvinyl alcohol (PVA) as self-assembling complex polymer to control nucleation and crystal growth via polymer complexation and low-temperature oxidizing-sintering. Highly regular Zn(OH)₂

nanodots on the Si substrate were first synthesized via complexing the homogeneous polar hydroxy groups —OH on PVA side-chains with Zn^{2+} ions in zinc salt solution when the pH value of the solution was adjusted to 8.5 ± 0.1 by addition of a concentrated aqueous ammonia. Then the synthesized $Zn(OH)_2$ nanodots decomposed into ZnO nanodots at about 125~% by thermal hydrolysis. Subsequently the ZnO nanodots grew gradually up into the well-oriented ZnO nanowires on the substrate at sintering temperature of 420~%. In the early stage of sintering, the carbonized PVA grid backbones were formed, which confined the ZnO nanowire's diameter and enhanced the absorption of ZnO at the tips of nanowires. At the presence of carbonized PVA, part of ZnO reduced to Zn through carbothermal reduction and in oxygen Zn was further oxidized to ZnO, forming the catalytically active site at the tips of nanowires. All the polymers were removed after sintering. The analytical results of FE-SEM, TEM, HR-TEM and XRD indicated that the ZnO nanowires are evenly distributed on Si substrate and possess a hexagonal wurtzite structure with preferred orientation along the [0001] direction of ZnO, and their diameter varies from 20 to 80 nm and the length from 0.5 to several μ m. A polymer-controlled crystallization and morphogenesis by polymer grid backbone localization model was proposed to explain the growth behavior of ZnO nanowires.

Key words ZnO nanowire self-assembling polymer induced oriented growth coordinate complexation

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