负偏置沉积法可控制备 Cu_2O 多孔纳米结构薄膜

周磊¹, 诸一琦², 苏江滨^{1,3*}, 刘阳¹, 郎咸忠¹, 蒋美萍^{1*}, 唐斌¹, 朱贤方³, 曾祥明⁴

1. 常州大学数理学院, 常州 213164;

2. 江苏理工学院电气信息工程学院, 常州 213001;

3. 厦门大学物理系, 中国-澳大利亚功能纳米材料联合实验室, 厦门 361005;

4. 新余学院新能源科学与工程学院, 新余 338004

* 联系人, E-mail: jbsu@cczu.edu.cn; mpjiang@cczu.edu.cn

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摘要 由于具有低成本、无毒、铜源丰富等优点, 以及在气敏传感器、太阳能电池、光催化等领域的潜在应用前景, Cu_2O 薄膜引起了人们的广泛关注. 采用射频平衡磁控溅射镀膜系统, 在薄膜沉积过程中通过施加不同衬底负偏压可控制备了 Cu_2O 多孔纳米结构薄膜. 研究发现, 所得 Cu_2O 薄膜具有灵活可调的孔隙度和纳米构筑单元形貌特征, 并且它们与衬底负偏压的大小密切相关; 薄膜沿衬底法线方向呈柱状生长且具有显著的(111)择优取向; 禁带宽度在2.0~2.35 eV之间可调. 很明显地, 传统的溅射离子轰击、再溅射理论并不适合用来解释上述负偏压效应, 因此在此基础上提出了一种负偏置沉积过程中材料原子或分子在薄膜表面选择性优先沉积机制.

关键词 Cu_2O , 多孔纳米结构薄膜, 平衡磁控溅射, 负偏置沉积

氧化亚铜(Cu_2O)为铜的一价氧化物, 是一种重要的p型过渡金属氧化物半导体材料. 由于具有低成本、无毒、铜源丰富等优点, 以及在气敏传感器^[1,2]、太阳能电池^[3,4]、光催化^[5~7]等领域的潜在应用前景, Cu_2O 薄膜引起了人们的广泛关注. 一般地, 为了提高气敏元件的灵敏度、太阳能电池的光电转换效率或者光催化剂的活性等, 人们习惯于将薄膜制成多孔结构来增加其比表面积. 在现有文献中, Cu_2O 薄膜的制备方法主要有直接氧化法^[8~10]、电化学沉积法^[11~13]和磁控溅射沉积法^[14~17]等, 但是这些方法都没有发现用来制备 Cu_2O 多孔薄膜, 尤其是兼具多孔薄膜特点和纳米构筑单元优异特性的 Cu_2O 多孔纳米结构薄膜^[18,19]. 通常地, 人们更倾向于采用模板法^[20]、溶胶-凝胶法^[21]和脱合金法^[22]等来制备多孔薄膜. 然而, 这些多孔薄膜的常规制备方法都存在这样或那样的

缺点. 比如, 模板法制备的薄膜受模板的限制, 制备方法不灵活, 而且在后期去除模板时易损坏薄膜; 溶胶-凝胶法制备的薄膜收缩率高、附着性差、容易开裂, 而且薄膜中存在有残余的羟基、碳等; 脱合金法更多被用于制备金属多孔薄膜, 而且可能会引入溶液中的杂质等. 因此, 寻找或开发一种新方法克服上述多孔薄膜制备方法中存在的缺点是很有必要的. 我们知道, 磁控溅射沉积法是目前制备高质量薄膜的一种常用方法, 它不会引入其他杂质, 而且还具有设备简单、易于控制、镀膜面积大和附着力强等优点. 事实上, 人们也已经成功利用磁控溅射方法制备了具有多孔结构的金属薄膜和 ZnO 、 TiO_2 等半导体薄膜. 比如, Maslyk 等人^[23]利用直流磁控溅射技术, 通过改变 Ar 和 O_2 的流量值(在 Ar 和 O_2 的流量固定比值为 10:1 的前提下)得到了多孔 Zn/ZnO 薄膜; Agnarsson 等人^[24]

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采用直流磁控溅射技术, 调控沉积温度在500~650℃之间获得了纳米多孔结构的TiO₂薄膜; Yang等人^[25]也利用直流磁控溅射系统成功制备了具有纳米多孔柱状结构的Ti薄膜. 那么, 我们是否也可以利用磁控溅射设备或对其进行针对性改造, 来实现具有纳米结构的Cu₂O多孔薄膜的可控制备呢? 鉴于此, 本文通过大量试验研究, 发现采用射频平衡磁控溅射镀膜系统并施加不同衬底负偏压的方法, 能够用来可控沉积Cu₂O多孔纳米结构薄膜. 而且, 所得Cu₂O薄膜具有灵活可调的孔隙度和纳米构筑单元形貌特征; 它们呈柱状生长且具有显著的(111)择优取向; 禁带宽度在2.0~2.35 eV之间可调. 进一步地, 我们还分析了Cu₂O多孔纳米结构薄膜的形成机制.

1 实验方法

本文制备实验是在JGP500A型高真空平衡磁控溅射镀膜系统中进行的, 以干净的普通玻璃片为衬底, 3 in(1 in=2.54 cm)直径的高纯Cu靶(质量分数99.99%)为靶材, 衬底到靶材的距离约15 cm. 先将腔室真空抽至 5.0×10^{-4} Pa, 然后通入纯度为99.999%、流量为15 sccm(1 sccm表示标况下1 mL/min)的高纯Ar气, 并调节高阀使腔室气压维持在0.1 Pa. 区别于常规做法——通“Ar+O₂”混合气体、采用反应溅射来制备Cu基氧化物薄膜, 本文实验中只通Ar不通O₂, 直接用Ar离子来溅射Cu靶, 沉积Cu₂O薄膜. 关于产物中O成分, 通过计算和对比实验^[26]发现主要来源于实验过程中腔体中残余的氧, 而不是实验完成后样品暴露在空气中发生氧化的情况. 实验时, 调节溅射功率为射频80 W, 先预溅射10 min以除去Cu靶表面可能的氧化层, 然后移开样品挡板沉积90 min, 薄膜厚度约240 nm. 为了研究多孔薄膜制备的可控性, 分别在0, -50, -100, -150和-200 V直流偏压下进行实验. 最后利用场发射扫描电子显微镜(FESEM, ZEISS SUPRA55), 掠入射X射线衍射仪(GIXRD, RIGAKU D/max 2500PC)和紫外可见分光光度计(SHIMADZU UV-2450)对样品作进一步表征与分析.

2 结果和讨论

2.1 微观形貌

图1为不同衬底负偏压下制备得到的Cu₂O薄膜的FESEM照片. 从图中可以看出, 不同负偏压下所

图1 不同衬底负偏压下Cu₂O薄膜的FESEM照片. (a) 0 V; (b) -50 V; (c), (f) -100 V; (d) -150 V; (e) -200 V

Figure 1 FESEM images showing the Cu₂O thin films obtained at different substrate negative bias voltages. (a) 0 V; (b) -50 V; (c), (f) -100 V; (d) -150 V; (e) -200 V

得Cu₂O薄膜都表现出大面积、均匀、表面平整以及多孔的特点, 但是它们微观形貌的细节却不尽相同. 当偏压 $V_s=0$ V时(即不施加衬底偏压), 对应图1(a), 薄膜呈现出相对疏松的“韧带-孔洞”双连续多孔结构, 而且“韧带”大部分为弯曲的纳米绳索状, 长度较短且彼此胶连在一起, 仅部分出现较明显的棱角; 当偏压 $V_s=-50$ V时, 对应图1(b), 薄膜表面出现棱角分明的纳米三棱锥状结构, 边长约50 nm, 彼此间较少胶连, 而且薄膜的孔隙度较高; 当偏压 $V_s=-100$ V时, 对应图1(c), 薄膜显得相对平整、致密, 薄膜中除了具有弯曲的纳米级裂缝以外, 还出现了一些孔径约14~25 nm的圆形纳米孔洞; 当偏压 $V_s=-150$ V时, 对应图1(d), 它与偏压 $V_s=-50$ V的情况相似, 薄膜表面同样出现了许多三棱锥状结构, 只是尺寸稍大, 边长约68 nm; 当偏压 $V_s=-200$ V时, 对应图1(e), 薄膜中许多小颗粒胶连在一起形成大颗粒, 薄膜表面虽然也能看到一些孔洞, 但整体最为致密. 图1(f)进一步给出了衬底偏压 $V_s=-100$ V时薄膜的横截面形貌. 从图中可以看出, Cu₂O薄膜沿衬底法线方向呈柱状结构生长, 而且彼此之间有明显的柱状空隙存在.

2.2 晶体结构

图2(a)中的GIXRD谱图显示了不同衬底负偏压

图2 (网络版彩色)(a) Cu_2O 薄膜的GIXRD衍射谱图; (b) Cu_2O (111) 衍射峰强度和晶粒尺寸随衬底负偏压的变化关系图

Figure 2 (Color online) (a) GIXRD patterns of the Cu_2O thin films; (b) diffraction peak intensities and grain sizes of Cu_2O (111) against the substrate negative bias voltages

下 Cu_2O 多孔纳米结构薄膜的晶体结构. 通过与标准卡片比对, 发现该谱图中的衍射峰位与 Cu_2O 标准卡片(卡片号: JCPDS-34-1354)的衍射峰位完全吻合, 而且谱图中没有发现有任何其他杂质峰如Cu和CuO等, 这就说明了这些样品均为纯的 Cu_2O 薄膜, 偏压并没有改变产物的化学成分. 从图中还可以看出, 所有的 Cu_2O 薄膜都表现出很强的(111)择优取向, 而在其他晶向如(110), (200), (220)和(311)的衍射峰强度都很弱, 几乎可以忽略. 由于实验中采用的是平面外GIXRD, 它测量的是与样品表面近平行的晶面, 这就说明了在薄膜的生长方向上 Cu_2O 晶粒的取向几乎一致, 都是(111)方向. 特别地, 我们对 Cu_2O (111)晶向的衍射峰强度和晶粒尺寸分别随衬底负偏压的变化关系作了进一步研究, 如图2(b)所示. 研究发现, 随着衬底负偏压的增加, (111)晶向的衍射峰强度整体上呈“W”状走势, 从0~-100 V先减小后增大, 从-100 V再到-200 V同样先减小后增大; 利用谢乐公

式计算得到, 随着衬底负偏压的增加, Cu_2O (111)的晶粒尺寸呈现先增大后减小的趋势, 并在 $V_s = -50$ V时达到最大值. 值得注意的是, 此时(111)晶向的衍射峰强度却处于一个极小值, 这可能是因为薄膜中(111)晶粒数目较少的缘故. 综上表明了衬底偏压对于衍射峰强度和晶粒尺寸的影响都不是线性关系, 可能有两个或两个以上的因素(比如2.4小节中的机制I和机制II)在共同作用、相互竞争的结果.

2.3 光学性质

图3首先给出了不同衬底负偏压下 Cu_2O 多孔纳米结构薄膜样品的 $(Ah\nu)^2-h\nu$ 曲线, 其中, A 为薄膜的吸光度, $h\nu$ 为入射光子的能量. 然后作 $(Ah\nu)^2-h\nu$ 曲线中线性部分的切线, 延长线交于 $h\nu$ 轴, 它们的交点即为相应的禁带宽度值 E_g . 从图中可以看出, 在衬底偏压 $V_s = 0, -100$ 和 -200 V时, 禁带宽度值均为2.0 eV, 而在衬底偏压 $V_s = -50$ 和 -150 V时, 禁带宽度值则均为2.35 eV. 这与 Cu_2O 块体材料的禁带宽度值2.17 eV均有一定程度的偏离, 表明了可以通过控制衬底负偏压的大小来得到不同禁带宽度值的 Cu_2O 多孔薄膜. 但是, 必须注意到的是, 并不是不同偏压下得到的 Cu_2O 多孔薄膜的禁带宽度值就不同. 从上面的分析可以发现, 在偏压 $V_s = -50$ 和 -150 V时, Cu_2O 薄膜的结晶程度是相对较差的, 同时薄膜表面都出现了棱角分明的纳米三棱锥状结构, 这两点可能都会影响到薄膜的禁带宽度. 这是因为, 半导体薄膜的禁带宽度除了与半导体的能带结构有关, 同时还会受到一些因素如量子尺寸或纳尺寸效应, 掺杂和缺陷的影响. 对于本文的 Cu_2O 多孔薄膜来说, 首先, 对于不同的

图3 (网络版彩色)不同衬底负偏压下 Cu_2O 薄膜的 $(Ah\nu)^2-h\nu$ 曲线及禁带宽度

Figure 3 (Color online) $(Ah\nu)^2-h\nu$ curves of the Cu_2O thin films obtained at different substrate negative bias voltage and their band gaps

结晶程度,薄膜的缺陷对禁带宽度的影响就会不同;其次,对于不同形貌,薄膜构筑单元的纳尺寸效应也就不同.从这个层次上讲,上述实验结果是可以理解的,尽管具体的影响机制目前尚不清楚.

2.4 偏压机制

通过上述分析,我们发现施加不同衬底负偏压后,所得 Cu_2O 薄膜的形貌、结构和光学性能或多或少都发生了变化.一般地,人们在研究衬底负偏压下磁控溅射沉积薄膜的作用机制时,更多考虑的是溅射 Ar 离子在负偏压电场加速牵引下对薄膜的轰击和再溅射作用^[27],即当偏压较小时, Ar 离子在负偏压电场的加速下轰击正在沉积的薄膜表面,它们所携带的能量仅仅满足材料原子或分子在衬底表面进行扩散、迁移所需的能量,从而薄膜致密性较好,薄膜与衬底的黏附性更好,薄膜质量更高,此为溅射离子的轰击作用;而当偏压过大时,加速入射过来的 Ar 离子携带的能量很高,会将已经沉积到衬底上的薄膜材料再次部分甚至完全溅射掉,从而导致薄膜表面的粗糙度增加,同时薄膜变薄,此为溅射离子的再溅射作用.然而,上述 Ar 离子的轰击和再溅射作用机制显然不适用于本文的情况.这是因为, Ar 离子对薄膜的轰击和再溅射作用更多地出现在非平衡磁控溅射过程中,而本文使用的是平衡磁控溅射镀膜方式.相对于非平衡磁控溅射,平衡磁控溅射由于磁场线几乎完全被束缚在靶材附近,即使加上衬底负偏压, Ar 离子的主要活动范围还是集中在靶材位置附近,很少有 Ar 离子能够挣脱磁场的束缚,运动到远处的衬底(本文靶材到衬底的距离为15 cm)并对正在沉积的薄膜进行轰击或再溅射.另外,从图1的FESEM照片也可以看出,偏压较小时薄膜表面呈现出各种多孔结构,并没有因为 Ar 离子的轰击作用导致薄膜的致密度随偏压增大呈现线性增加,而偏压较大时薄膜表面仍然保持得相对平整,也没有出现再溅射过程常见的表面粗糙化现象.这从侧面进一步说明了非平衡磁控溅射机制并不适用于本文平衡磁控溅射过程.

我们知道,在外加静电场的作用下,导体会发生静电感应,导体中的自由电子将进行重新分配.类似地,半导体中的自由载流子如电子和空穴在外电场作用下也将进行重新分配.它们分配的依据都是高斯定理.一般地,在表面曲率越大的地方或者物体的尖端处,电荷越容易发生聚集,相应的电场强度也就

越大.当给衬底施加一个偏压电场后,正在沉积的导体或半导体薄膜都将发生静电感应,从而薄膜表面出现大量的感应电荷.由于微观尺度下的薄膜表面是凹凸不平的,根据尖端集电效应,这些感应电荷将主要聚集在薄膜表面尖端处或颗粒表面,从而薄膜表面的电场可以看作是一个个点电荷电场的叠加.这种微观尺度下的尖端集电现象将伴随着薄膜的整个偏置沉积过程,并通过电荷间相互作用影响甚至决定薄膜的最终形貌和结构.

如图4(a)所示,在衬底点电荷电场的作用下,入射过来的 Cu 原子(部分 Cu 原子到达衬底后才发生氧化)或 Cu_2O 分子将受到来自两个方面的作用力:一是金属 Cu 原子或半导体 Cu_2O 分子发生极化导致其正负电荷中心出现一定程度的分离,从而受到衬底上不均匀点电荷电场牵引力的加速作用(机制I);二是由于同种电荷之间相互排斥,沉积到尖端并带上同种负电荷的 Cu 原子或 Cu_2O 分子受到周围同种点电荷电场的排斥、束缚作用(机制II).对于前者,点电荷电场在诱导入射过来的 Cu 原子或 Cu_2O 分子在尖端上选择性优先沉积的同时,将提供给它们额外的动能,从而促进 Cu 原子或 Cu_2O 分子在薄膜表面进行更充分的扩散、迁移;对于后者,周围点电荷电场的束缚作用将阻碍 Cu 原子或 Cu_2O 分子在不同尖端之间或薄膜表面进行扩散、迁移.必须指出的是,尖端集电作用存在于薄膜的整个偏置沉积过程中,如图4(b)所示,它将诱导薄膜沿衬底法线方向呈柱状生长,同时在减少体系能量的驱动下表现出显著的 Cu_2O (111)择优取向.只不过机制I和II的作用力效果是相互矛盾的,机制I会使得柱状结构间的空隙变小、变少,机制II则会使得柱状结构间的空隙变大、变多,因此在不同偏压下它们对薄膜最终形貌和结构的贡献会有所不同:(1)当 $V_s=0$ V时,由于没有负偏压的作用, Cu

图4 (网络版彩色)薄膜负偏置沉积柱状生长示意图.(a)尖端集电效应;(b)柱状生长

Figure 4 (Color online) Schematic illustrations showing the columnar growth of thin films by negative bias deposition. (a) Tip charging effect; (b) columnar growth

原子或 Cu_2O 分子没有足够的能量保证在衬底上进行有效地扩散与迁移,也无法在薄膜表面尖端处进行选择优先沉积,导致 Cu_2O 薄膜表面呈现随机取向的“韧带-孔洞”双连续多孔结构;(2)当 $V_s=-50$ 和 -150 V时,机制II起主要作用,Cu原子或 Cu_2O 分子在点电荷电场的束缚下呈柱状生长的同时,相邻柱状结构之间因带同种电荷而相互排斥,最终 Cu_2O 薄膜表面形成纳米三棱锥状结构,彼此之间胶连较少,薄膜孔隙度增加;(3)当 $V_s=-100$ 和 -200 V时,机制I的贡献大于机制II,沉积到薄膜表面尖端处的Cu原子或 Cu_2O 分子将进一步沿着薄膜表面向四周进行一定程度的扩散,从而薄膜表面颗粒胶连更多,薄膜更致密。

3 结论

本文采用射频平衡磁控溅射镀膜系统,在薄膜沉积过程中通过施加不同衬底负偏压制备了 Cu_2O 多孔纳米结构薄膜.研究发现,所得 Cu_2O 薄膜具有灵活可调的孔隙度和纳米构筑单元形貌特征,并且它们与衬底负偏压的大小密切相关;薄膜沿衬底法线方向呈柱状生长且具有显著的(111)择优取向;禁带宽度在2.0和2.35 eV之间可调.更为重要的是,传统的溅射离子轰击、再溅射理论并不适合用来解释上述负偏压效应,本文在此基础上提出了一种材料原子或分子在薄膜表面选择性优先沉积机制.

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Summary for “负偏置沉积法可控制备 Cu_2O 多孔纳米结构薄膜”

Controllable fabrication of Cu_2O porous nanostructured films by negative bias deposition method

ZHOU Lei¹, ZHU YiQi², SU JiangBin^{1,3*}, LIU Yang¹, LANG XianZhong¹, JIANG MeiPing^{1*}, TANG Bin¹, ZHU XianFang³ & ZENG XiangMing⁴

¹ School of Mathematics and Physics, Changzhou University, Changzhou 213164, China;

² College of Electrical and Communication Engineering, Jiangsu University of Technology, Changzhou 213001, China;

³ China-Australia Joint Laboratory for Functional Nanomaterials, Physics Department, Xiamen University, Xiamen 361005, China;

⁴ School of New Energy Science and Engineering, Xinyu University, Xinyu 338004, China

* Corresponding authors, E-mail: jbsu@cczu.edu.cn; mpjiang@cczu.edu.cn

As one of the most common two kinds of copper oxides, cuprous oxide (Cu_2O) is an important p-type transition metal oxide semiconductor material. Due to the advantages of low-cost, non-toxicity and abundant copper sources and the potential applications in the fields of gas sensors, solar cells and photocatalysts, thin films of Cu_2O have attracted great interest of researchers. To enhance the performances of the above Cu_2O -based surface-sensitive devices and materials, the researchers tend to prepare Cu_2O thin films of porous or even nanoporous structures. However, there is still no effective method available for the controllable fabrication of Cu_2O porous nanostructured films (or porous nanostructure-films, short for PNFs), which owns not only the common features of porous thin films but also the unique properties of nanosize building units. By using a radio-frequency balanced magnetron sputtering (MS) deposition system, in this paper, Cu_2O PNFs were prepared on clean glass slides by applying different negative bias voltage during film deposition. After the preparation, a field-emission scanning electron microscope (FESEM), a grazing-incidence X-ray diffractometer (GIXRD) and an ultraviolet-visible (UV-Vis) spectrophotometer were applied subsequently for the detailed characterizations of surface morphology, texture and optical property respectively. It was observed that the as-prepared Cu_2O PNFs exhibited flexible porosities and nanosize building units, which were greatly dependent on the substrate negative bias voltage. In particular, when the substrate bias voltage was kept at -50 or -150 V, the as-prepared Cu_2O PNFs both demonstrated intriguing triangular pyramid-like nanostructures with distinct edges and corners on the porous film surface. Further, the side view FESEM images and the out-of-plane GIXRD spectra demonstrated a columnar growth of the Cu_2O PNFs with a notable preferential orientation of (111). The optical testing results showed that the band gap of the Cu_2O PNFs obtained at different negative bias voltages was tunable between 2.0 and 2.35 eV, which demonstrated a little red or blue shift relative to that of bulk Cu_2O (2.17 eV). It is expected that the traditional ion bombardment and re-sputtering theories are not suitable for the explanation of the above bias voltage effects. This is because the traditional ion bombardment and re-sputtering theories were proposed to account for the bias deposition in an unbalanced magnetron sputtering (MS) system rather than the present balanced MS system. Further, the experimentally observed non-linearly changed density or porosity of the Cu_2O PNFs with the bias voltage at relatively low values and the common even surface at relatively high values confirmed this viewpoint. Based on the above findings and analysis, a selectively preferential deposition of material atoms or molecules on the film surface during the negative bias deposition was proposed. That is, when the substrate is negatively biased, the tip-charging effect of electrons would occur on the nanoscale rough surface of the substrate or the depositing film. The resulting electric field near the substrate or film surface is non-uniform and could be regarded as an assembly of many electric fields of particle or tip charges. As a consequence, the sputtered atoms or molecules would be acted by two kinds of Coulomb forces: one is the attractive force originating from the electric fields of the closest particles or tips when traveling near the substrate, and the other is the repulsive force coming from the surrounding particles or tips with the same kind of charges after depositing on one particle or tip. For the former force, it would lead to a preferential deposition of sputtered atoms or molecules on the particles or tips and meanwhile provide an additional kinetic energy for the deposited atoms or molecules to migrate or diffuse around; for the later force, the constraint effect of the surrounding electric fields of particle or tip charges would hinder the migration or diffusion of deposited atoms or molecules on the film surface. It is thus expected that the tip charging effect would lead to a columnar growth of films, and the contradictory of the above two forces would influence or even determine the final surface morphology of films which depends on the value of substrate bias voltage.

Cu_2O , porous nanostructured films, balanced magnetron sputtering, negative bias deposition

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