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ZnO 纳米薄膜磁控溅射制备及其紫外光电探测器研制

Deposition of ZnO nano-film by rf magnetron sputtering and fabrication of ultraviolet photodetector

黄　波

指导教师姓名：　吴　孙　桃　教授

郭　东　辉　教授

专　业　名　称：　凝　聚　态　物　理

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By

Bo Huang

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中文摘要

随着信息社会的发展，人们对光电产品的需求与日俱增，促使了光电产业的高速增长。如同集成电路产业对硅材料的依赖一样，高速增长的光电产业促进人们寻找更为合适的半导体光电材料。在目前所研究的第三代宽禁带半导体材料中，ZnO由于具有优良的综合性能，而被人们普遍看好，被认为是很有前途的第三代半导体材料，使其成为近年来国际上半导体光电材料的研究热点。目前质量较高的ZnO薄膜和纳米薄膜一般需要用MOCVD或MBE等较昂贵的设备在蓝宝石基底上生长，这限制了它的潜在应用。

本论文的主要工作是研究如何利用简便的磁控溅射技术在SiO_2/Si衬底和石英玻璃上生长高质量的ZnO纳米薄膜；研制ZnO纳米薄膜紫外光电探测器，研究器件的制作工艺技术，以及器件和材料的光电性能。本论文的研究，对利用简便的磁控溅射技术生长高质量的ZnO纳米薄膜，对实现ZnO纳米薄膜在光电器件的大规模商业应用，具有重要的意义。本论文的主要研究内容及结果：

采用射频磁控溅射在SiO_2/Si和石英玻璃上制备出晶粒大小、晶粒取向以及晶粒特性等可以调控的ZnO纳米多晶薄膜。在不同的溅射气压、溅射功率、氩氧比等工艺参数条件下分别进行制备，对部分制备后的样品进行不同温度的通氮气、氧气或氩气退火处理。通过XRD、SEM、光致发光谱(PL)、透射谱和反射谱的测试分析，研究制备溅射工艺条件、退火处理条件与ZnO纳米薄膜的晶粒取向、大小、表面形貌、光学特性等的关系。根据测试与分析结果，优化制备工艺参数，制备出C轴高度择优取向的颗粒大小均匀、致密等结构优良的ZnO纳米多晶薄膜。

从ZnO六方晶系的弹性本构关系出发，推导出XRD测量时涉及到的晶体坐标系、样品坐标系和实验坐标系下样品的应力与应变关系，得到了适用于Bragg-Brentano模式和Seemann-Bohlin模式的XRD测量的应力与应变关系式。以此为基础，研究了不同工艺条件下、不同衬底上和不同退火条件下制备的ZnO薄膜的应力变化，以及薄膜应力对薄膜的光学特性的影响，探讨了磁控溅射制备薄膜的生长模型。

从测量得到的薄膜透射谱，利用非线性优化技术计算得到薄膜的光学常数和

薄膜厚度等参数。利用光致发光谱和反射/透射谱的测量，研究ZnO薄膜的光学性质。从实验和理论上研究颗粒度大小不同、退火前后和不同退火处理条件下的ZnO纳米薄膜光学性质的差异。

制作出良好的Ag/ZnO Schottky接触和Al/ZnO Ohmic接触。采用Ag作为接触电极，制成了具有良好Schottky特性的光电二极管。在SiO_2/Si衬底上制作金属-半导体-金属 (MSM）结构的Ag/ZnO/Ag Schottky紫外光电探测器 (PD)。研究了探测器的I-V、C-V和光谱响应特性以及材料的光电性能。通过反复流片、测试分析和改进，研制出的响应峰值大约在370nm附近，具有良好紫外响应的紫外光电探测器。

本论文的主要创新性工作有：利用射频磁控溅射制备出C轴择优取向、颗粒均匀、致密的ZnO纳米晶柱薄膜；详细推导出XRD测量涉及的应力和应变关系，研究了ZnO纳米薄膜应力和光学特性的关系；利用非线性优化技术得到磁控溅射制备的ZnO纳米薄膜在较宽波长范围内的折射率和吸收系数；根据具体的工艺流程，结合氧等离子体处理工艺对薄膜进行表面处理，有效地降低了Ag/ZnO Schottky二极管的漏电流；探索出一整套 Ag-ZnO-Ag MSM 光电探测器的制作工艺，开发出能实现200nm/100nm厚Ag/Au电极制作的单步反剥离工艺；通过在器件表面覆盖钝化层，提高光电探测器的响应速度。

关键词：ZnO纳米薄膜；磁控溅射；XRD；透射/反射谱；MSM光电探测器

Abstract

With the rapid development of information society, the demand for the opto-electrical products is becoming increasingly fierce and the growing consumer market has been promoting the development of the opto-electrical industry. As silicone material for the IC industry, more suitable opto-electrical materials are needed to develop for the opto-electrical industry. In the familiar third generation semiconduction materials, ZnO is viewed to be a competitive material and has attracted more and more attention in the area of opto-electrical semiconductor material, due to its remarkable properties. At present, high quality ZnO films are grown on sapphire using expensive MOCVD or MBE, which will limit the potential application of ZnO for its high price products.

In this dissertation, ZnO nano-films were deposited on SiO_2/Si and quartz glass substrates using rf magnetron sputtering and ultraviolet photodetectors were prepared on the ZnO nano-films. The opto-electrical characteristics of the films and the ultraviolet photodetectors have been studied. The purpose of this dissertation is to prepare high quality ZnO films using convenience rf magnetron and develop ZnO based photodetectors. The main works are summarized as follow:

The ZnO nano-films are deposited on SiO_2/Si and quartz glass substrates by rf magnetron sputtering. The grain size, orientation and characteristics of the ZnO nano-films can be adjusted by varying the ratio of Ar and O_2, the rf power and the pressure. Some samples have been annealed in N_2, O_2 and Ar at different temperatures. The crystal structures and surface morphologies of the samples were investigated by XRD, AFM and SEM. The optical characteristic of the films were studied by photo luminescence, reflectance and transmission spectroscopy. The relation between the sputtering and annealed parameters and the properties of ZnO films has been studied. In the end, high quality ZnO nano-films with c-axis orientation have been deposited under optimization parameters.

In order to analyze the stress of the ZnO films, the basic equation of stress analysis has been deduced from the relation between stress and strain in three different coordinate systems which are used during the XRD analysis. The relation between stress within the film and the sputtering and annealed parameters has been studied. The influence of the stress on optical properties of the ZnO films has been investigated. According to the result, a grow model of the ZnO film has been discussed.

Optical absorption coefficient and the refractive index have been determined by unconstrained formulation of the nonlinear programming using transmissivity data only. The differences of the PL spectroscopy and other optical properties within different samples have been studied.

Using Ag as contact metal, good Schottky diodes have been developed on annealed ZnO films. Current-voltage characteristics of these devices have been analyzed. Ultraviolet metal-semiconductor-metal (MSM) photodetectors (PD) were fabricated by using Ag as Schottky contact metal. The I-V, C-V and photoresponsivity characteristics of the MSM-PD have been investigated. The photoresponsivity of the MSM-PD is much higher in the ultraviolet range than in the long wave range. The photoresponsivity of the MSM-PD exhibits a maximum value at around 370nm.

The innovative points of the study are: high orientation ZnO nano-films were deposited using convenience rf magnetron sputtering; the basic equation of stress analysis have been deduced from the relation between stress and strain, and the relation between film stress and its optical properties has been studied; The optical absorption coefficient and the refractive index have been determined using unconstrained formulation of the nonlinear programming; A surface treatment in plasma of O_2 has been developed to reducing the dark current of the Schottky diode; Ag-ZnO-Ag MSM-PD has been successfully fabricated. A lift-off process has been developed that can be used to achieve a 200nm/100nm thick Ag/Au electrode; The photoresponsivity speed of the MSM-PD can be improved by covering with a passive film.

Key Word: ZnO nano-films; Magnetron sputtering; XRD; Reflectance/Transmission spectroscopy; MSM-PD

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