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博 士 学 位 论 文

铝掺杂氧化锌透明薄膜之制备及其在氮化镓基发光二极管之应用

Investigation of transparent Al-doped ZnO films for high performance GaN-based light emitting diodes

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摘　要

多晶的或无定形的透明导电氧化物(Transparent conducting oxides,简称 TCOs)，由于其独特的光学和电学性能，成为近年来研究的热点。其中，铝掺杂氧化锌（Al-doped ZnO,简称 AZO）因具有低电阻率和高可见光区透过率，成为主要的透明导电氧化物材料之一，加上其原材料丰富，价格低廉且无污染，在光电器件领域有望替代 ITO 成为最理想的透明导电材料。

本文采用射频磁控溅射技术首次在室温下，以 ZnO: Al_2O_3 (98：2 wt%)为靶材，在石英玻璃衬底上制备多晶 AZO 透明导电薄膜。同时应用 X 射线衍射仪（XRD）、原子力显微镜（AFM）、扫面电子显微镜（SEM）、俄歇电子能谱仪（AES）、X 射线光电子能谱仪（XPS）、霍尔效应测试系统以及紫外-可见分光光度计等测试手段，研究了不同射频功率、Ar 气压强、衬底与靶位间距、薄膜厚度以及不同退火条件（包括不同气体氛围和不同温度）对薄膜结构特性、电学性能与光学性能的影响。此外，本文将工艺优化下生长的 AZO 薄膜作为 p-GaN 的透明电极，制备一系列的 AZO/GaN 欧姆接触和 GaN 基发光二极管，研究了 AZO 与 GaN 的欧姆接触性能，并探讨引入不同过度金属层（Ni, Pt, Ag）来降低欧姆接触电阻，提高 GaN 基 LED 性能。所取得的成果如下：

1．本文首次系统地研究了室温下各溅射工艺参数（射频功率、氩气压强、衬底与靶材间距、薄膜厚度）对 AZO 薄膜性质的影响，生长的 AZO 薄膜为六角纤维锌矿结构，呈 c 轴择优取向，对薄膜的组分分析表明薄膜符合化学剂量比（Zn：O≈1：1）。由于薄膜在室温下沉积，薄膜结构相对疏松，晶粒边界上有少数 O 原子的吸附。同时在 300W 射频功率、0.4Pa Ar 气压强（流量为 30sccm）和 7.0cm 靶位与衬底间距条件时，得到最低电阻率为 $2.88\times10^{-4}\Omega\cdot cm$、可见光区透射率 90%以上的 500nm AZO 薄膜。

2．AZO 薄膜在 N_2 氛围中退火后，薄膜的电阻率增大，载流子浓度降低，其电学性能退化程度随退火温度的升高而增大。经 N_2 氛围中 500 度退火后，薄膜电阻率升至 $2.09\times10^{-2}\Omega\cdot cm$，相应的载流子浓度和霍耳迁移率分别降为 $8.04\times10^{19}cm^{-3}$ 和 $3.71cm^2/Vs$。而当退火温度升高到 700 度时，薄膜电阻率大于 $1\times10^{5}\Omega\cdot cm$，同时 Burstein-Moss 效应消失，光学带隙变小至 3.34eV。其主要原因是样品经高温退火后，AZO 薄膜里的 O 与掺杂 Al 集合，使得 Al 掺杂载流子浓度和迁移率迅速降低，导致电学性能变差。

3．在退火气体 N_2 中加入约 4%的 H_2，能够让 Al 被氧化的程度得到抑制，AZO 薄膜电阻率退化程度变小。在含 H_2 氛围中 500 度退火时，薄膜电阻率只稍微升高至 $8.65\times10^{-}$

$^{4}\Omega\cdot cm$，相应的载流子浓度和霍耳迁移率变化不大，分别降为 $5.73\times10^{20}cm^{-3}$ 和 $12.6cm^{2}/Vs$。这是由于 H 的还原性质，使得 Al 被氧化的几率降低，Al 有效掺杂得到保护。但经 600 度退火后，由于室温薄膜比较疏松，AZO 薄膜里的 O 被 H 还原，使得薄膜变薄。薄膜700 度退火后，AZO 薄膜里的 O 完全被 H 还原，剩余的 Zn 在高温下蒸发，AZO 薄膜消失。

4．采用电子束蒸发在石英衬底上先沉积一薄的金属层（Ni, Pt, Ag），接着再采用磁控溅射沉积 AZO 薄膜，形成 metal/AZO 双层薄膜，研究不同金属及不同厚度对双层薄膜电阻和透过率的变化关系。研究发现在过渡金属薄层沉积的 AZO 薄膜的结晶性变差，电阻率变大。不过，制备的双层薄膜 2nm Ni/250nm AZO 的方块电阻为 21.0Ω/□，可见光区平均透过率为 76.5%，依然适合作为 GaN 基 LED 的透明电极。

5．在国内首次采用磁控溅射 AZO 薄膜在 p-GaN 表面制备欧姆接触，研究发现因溅射出来的高能粒子损伤 p-GaN 表层活性，无法形成线性的 AZO/GaN 欧姆接触。在 p-GaN 和 AZO 之间用电子束蒸发生长三种不同金属（5nm Ni, Ag, Pt）过渡层，其接触性能得到显著改善，且改善的程度随金属层的厚度增加而增大，在无退火情况下，本文获得的比接触电阻率分别为：5.01×10^{-3}，5.74×10^{-3}，$3.90\times10^{-3}\ \Omega\cdot cm^{2}$。此外，同时制备了一系列的 AZO 电极的蓝光和近紫外-紫光 GaN 基 LED，获得 500nmAZO 电极、5nmNi/250nmAZO 电极、5nmAg/250nmAZO 电极、5nmPt/250nmAZO 电极蓝光 LED 在 20mA 下，正向电压分别是 $V_{f（AZO）}$=5.12V；$V_{f（Ni/AZO）}$=3.20V；$V_{f（Ag/AZO）}$=3.40V；$V_{fPt/AZO}$=3.05V；各 LED 其轴向出光光强依次为 40.4，32.3，28.7，29.4mcd。其中，本文国际上首次引入的 Ag, Pt 两种过渡薄层作为电极制备 LED，其中 Pt/AZO 电极 GaN 基 LED 的正向电压仅 3.05V。

关键词：铝掺杂氧化锌；射频磁控溅射；氮化镓基发光二极管

ABSTRACT

Recently, a great deal of interest has been fueled in the development of polycrystalline or amorphous transparent conducting oxide (TCO) semiconductors used for practical thin-film transparent electrode applications, due to their excellent electrical and optical properties. Aluminum-doped zinc oxide (AZO) thin films, which are the most important TCO, with low resistivity and high transparency in visible range are promising as alternatives to ITO for thin-film transparent electrode applications, since AZO source materials are inexpensive and non-toxic.

Using a zinc oxide target doped with Al_2O_3 (2 wt%.), transparent conductive Al-doped zinc oxide (AZO) films with highly (002)-preferred orientation were deposited on quartz substrates at room temperature by RF magnetron sputtering in this paper. Optimization of deposition parameters were based on RF power, Ar pressure in the vacuum chamber, film thickness, and distance between the target and substrate. The structural, electrical, and optical properties of the AZO thin films with and without annealing were investigated by XRD, AFM, SEM, XPS, AES, Hall measurement, and optical transmission spectroscopy etc. Moreover, a series of p-GaN Ohmic contact and GaN-based light emitting diodes with AZO and AZO/Ni, Pt, Ag transparent electrodes have been fabricated. The electrical and optical properties of the devices have been investigated. The important results were obtained as follows:

1． The crystal structure of the AZO films is hexagonal wurtzite and shows the typical c-axis crystallographic orientation. The films are loose, due to deposition at low temperature. All samples are almost stoichiometric with the little O atoms chemisorbed at the grain boundary. The 500 nm-thickness AZO films with an electrical resistivity as low as 2.88×10^{-4} Ω· cm and an average optical transmission of 90.4 % in the visible range were obtained at RF power of 300 W, Ar flow rate of 30 sccm, and target distance of 7 cm.

2． After conventional thermal annealing in N_2 atmosphere for 20min at 400°C~700°C, the resistivity of the film gets worse with increase of annealing temperature and reached 2.09×10^{-2}Ω·cm at 500°C, while the Hall mobility and the carrier concentration decreased to 3.71 cm^2/Vs and 8.04×10^{19} cm^{-3} respectively. As annealing at 700 °C, the film became an insulator, then the B-M effect disappeared and optical band-gap reduced. That implies Al in the films was combined by O after annealing, leading to the decrease of Hall mobility and carrier concentration.

3． After conventional thermal annealing in N_2/H_2 atmosphere for 20min at 500°C, the resistivity of AZO film slightly increased to 8.65×10^{-4} Ω· cm, while the Hall mobility and the carrier concentration also slightly decreased to 12.6 cm^2/Vs and 5.73×10^{20} cm^{-3} respectively. The main reason for non-influence after annealing is that O atoms in the film were deoxidized by H, and the Al ions were avoided being oxidation by O. However, as annealing at 600°C, as a result of more O atoms was combined by H, the AZO films became thin. As annealing at 700°C, all O atoms in the AZO films were reacted by H, and remains Zn in the substrate, while Zn evaporates at more than 500°C temperature ambient.

4． A layer of metal (Ni, Ag, or Pt) was deposited by e-beam evaporation techniques onto the surface of quartz substrates, coated with AZO (Al-doped ZnO), to form metal/AZO double film structures, using RF manetron sputtering. The electrical and optical properties of Ni, Pt, Ag/AZO double film structures were studied. The deposition of AZO films on the surface of a metal layer resulted in the limitation of crystal quality with a slight reduction of their optical transmittance. However, the sheet resistivity and the average transmittance in the visible range of 2nm Ni/250nm AZO double films is 21.0 Ω/□ and 76.5% respectively, which is still suitable as transparent electrode for GaN-based LEDs.

5． AZO transparent contacts to p-GaN have been fabricated in this paper. The contact with single AZO layer shows non-line I-V characteristics, due to the damage of p-GaN layer by high energy sputtering ion. However, it was found that deposition of thin metal films (Ni, Ag, and Pt) by evaporation before sputtering AZO films will improve the I-V characteristics. The specific contact resistance without any annealing was determined to be 5.01×10^{-3}, 5.74×10^{-3}, and $3.90\times10^{-3}\Omega\bullet cm^2$ for 5nm Ni/AZO, 5nm Ag/AZO, and 5nm Pt/AZO layer contacts respectively. In additional, a series of GaN based LEDs with transparent AZO as ohmic p-contact have been designed and fabricated. The forward voltages (V_f) measured at 20 mA were equal to 5.12, 3.20, 3.40, and 3.05 V for the 500nm AZO, 5nm Ni/250nm AZO, 5nm Ag/250nm AZO, and 5nm Pt/250nm AZO blue LED, respectively. And the light intensity of these LEDs was 40.4, 32.3, 28.7, and 29.4 mcd respectively.

Key words: Al-doped ZnO (AZO), RF magnetron sputtering, GaN based light emitting diodes.

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