博 士 学 位 论 文

类金刚石薄膜光电性质研究与 MSM 光电器件探索

Study on Optoelectronic Properties and MSM Devices of Diamond-Like Carbon Thin Films

程　翔

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摘　要

本文对金刚石和类金刚石（DLC）薄膜的半导体特性参数和光电性质进行评述。采用射频等离子体增强型化学气相沉积方法生长各种 DLC 薄膜，在对所生长的 DLC 薄膜结构表征的基础上，详细研究了其光电性质。研制了以 DLC 薄膜为有源层的 MSM 光电探测器，并对其 I-V 特性、光谱响应、C-V 特性进行详细测量和分析。最后总结本文的工作，并对将来的工作提出建议，同时展望了 DLC 薄膜在光电方面的应用前景。

在深圳纳诺材料技术研究所的大力帮助下，成功生长了不同光学带隙的各种 DLC 薄膜。采用 AES、Raman 谱、XPS 和 FT-IR 谱等方法对所生长的 DLC 薄膜进行结构表征，发现改变射频电压等工艺条件可以有效控制 DLC 薄膜中 sp^2C 和 sp^3C 的比例，从而改变了 DLC 薄膜材料的各种性能。

通过对 DLC 薄膜的紫外透射谱测量，发现随着生长条件的不同，样品的光学带隙在 1.0~3.8eV 范围内发生变化，采用非晶碳薄膜的两相模型对薄膜的能带结构进行了阐述。在确认 TiN/DLC 为欧姆接触后，测量了 DLC 薄膜的直流电导随温度的变化规律，发现三个温区的主要导电机制各不相同，具有典型的非晶态材料电导特征。并由此计算出 DLC 薄膜的扩展态和定域态的电子迁移率。分析 DLC 薄膜不同温度下的光致发光（PL）特性，对发光机理作了初步探索。对掺氨和掺氮的 DLC 样品，进行了 AES、电化学 C-V、直流电导和 PL 测量。得到 DLC：N 样品电子浓度的纵向分布，以及 N 对 DLC 薄膜带隙结构的影响，比较非掺和掺 N 的 DLC 薄膜的 PL 性能，讨论了掺 N 后发光中心的变化。

用所生长的两批 DLC 薄膜为有源层，成功研制了 MSM 结构的光电探测器。对器件的 I-V 特性、C-V 特性和光谱响应进行详细的测量和分析。两

批光电探测器的探测主峰分别为 450nm 和 550nm，在 325nm 的激光辐照下光响应度分别为 3mA/W 和 0.26mA/W。经过测量分析得到了 Ti、Al、Au 和 Ag 等金属和 DLC 薄膜接触时的接触内建势和肖特基势垒高度数据。

本工作的创新点在于：用实验证实了 RF-PECVD 方法可以成功地控制 DLC 薄膜的光学带隙；成功地对 DLC 薄膜进行高浓度 n 型掺杂，并采用电化学 C-V 测量了电子的纵向分布；发现 TiN 薄膜和 DLC 薄膜可以形成良好的欧姆接触；测量 Ti、Al、Au、Ag 和 DLC 薄膜的接触势垒高度；成功研制了以 DLC 薄膜为有源层的 MSM 光电探测器；用两相模型和非晶态能带理论对 DLC 薄膜的直流变温电导特性作全面解释。

关键词：DLC 薄膜；光电性质；MSM 器件

ABSTRACT

The semi-conductor characteristic parameters and optoelectronic properties of diamond and diamond-like carbon (DLC) were expounded in this work. Series of DLC thin films were grown by RF-PECVD, and the optoelectronic properties of DLC thin films were investigated based on the characterization. DLC based MSM photoelectron detectors were then successfully fabricated and their characteristics of devices such as current-voltage, spectral response, capacitance-voltage, were also measured and thoroughly studied. Finally presented in this thesis were the summary of our research, some suggestion for the future work and the prospects of the application of DLC thin films in optoelectronic techniques.

With the great assist of Shenzhen Institute of Nano Materials, we successfully grew DLC thin films with different optical bands. The films were characterized by Auger Electron Spectroscopy (AES), Raman spectroscopy, X-ray Photoelectron Spectroscopy (XPS) and Fourier Transform Infrared (FT-IR) Spectroscopy. It is found that we can effectively control the ratio of sp^2C and sp^3C and then change the properties of DLC thin films by altering the growth conditions such as RF voltage.

By measuring the ultraviolet transmission spectroscopy we determined the optical bands of the sample at the range of 1.0-3.8eV. The band structure of the thin films was then discussed based on the two-phase model of the amorphous carbon. After a detailed analysis of Ohm contact between TiN and DLC thin films, the DC conductivity of DLC thin films varied by temperature was measured and it is found that the main conducting principles at three different temperature ranges were different, which shows the typical conductivity property of noncrystalline materials. And subsequently, the electron mobility in extended states and localized states of DLC films were calculated respectively. Photoluminescence characteristics of the DLC samples were studied at varied temperatures and the mechanism of photoluminescence were also discussed. The DLC samples with doping of NH_3 and N were characterized by AES, electrochemistry C-V, DC conductivity and PL. The distribution of electron density of DLC:N thin films was analyzed and also the effect of the dopant N on the DLC band gap. By comparing the photoluminescence performance of non-doping with that of N-doping, the change of photoluminescence centers by the doping of N was discussed.

DLC based MSM photoelectron detector was fabricated with our two batches of DLC films. Current-voltage, spectral response, capacitance-voltage, were thoroughly measured and analyzed. The spectral response peaks are found to be at 450 nm and 550nm respectively and the absolute response reached 3mA/W and 0.26mA/W respectively at 325nm. Based on measurement and analysis, the contact inner potential and Schottky barrier between the metals Ti, Al, Au, Ag and DLC thin films were also obtained.

The innovative points of the work are: the control of the optical band gaps of the thin films during the growth by RF-PECVD was successfully utilized, n-type doping was achieved, and then the longitudinal distribution of electron density was measured; good ohm contact between TiN and DLC thin films was found, and then Schottky barrier between the metals Ti, Al, Au, Ag and DLC thin films were determined; DLC-based MSM photodetectors were successfully fabricated; The property of DC conductivity of DLC thin films was interpreted with two-phase model and noncrystalline band theory.

Key words: DLC thin films; optoelectronic properties; MSM devices.

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