学校编码：10384　　　　　　　　　　　　　　分类号_____密级_

学　　号：B200429001　　　　　　　　　　　　　　　　　UDC__

厦门大学

博　士　学　位　论　文

碳纳米管的声波传播特性及其在声学微系统中应用的研究

Investigation on Acoustic Properties of Carbon Nanotubes and Its Application in Acoustic Microsystem

张　翊

指导教师姓名：郭隐彪　教授
　　　　　　　郭航　　教授

专 业 名 称：测试计量技术及仪器

论文提交日期：2009 年 11 月

论文答辩时间：2009 年 12 月

学位授予日期：2009 年　　月

答辩委员会主席：________

评　　阅　　人：________

2009 年 11 月

Investigation on Acoustic Properties of Carbon Nanotubes and Its Application in Acoustic Microsystem

A Dissertation Submitted for the Degree of Doctor of Philosophy

By Yi Zhang

Supervised by Prof. Yinbiao Guo & Prof. Hang Guo

Department of Mechanical & Electrical Engineering

Xiamen University

November, 2009

厦门大学学位论文原创性声明

本人呈交的学位论文是本人在导师指导下,独立完成的研究成果。本人在论文写作中参考其他个人或集体已经发表的研究成果，均在文中以适当方式明确标明，并符合法律规范和《厦门大学研究生学术活动规范（试行)》。

另外,该学位论文为(　　　　　　　　　　　　　　)课题(组）的研究成果，获得（　　　　　　　　　　）课题（组）经费或实验室的资助，在（　　　　　　　　　　）实验室完成。(请在以上括号内填写课题或课题组负责人或实验室名称，未有此项声明内容的，可以不作特别声明。)

声明人（签名）:

年　　月　　日

厦门大学学位论文著作权使用声明

本人同意厦门大学根据《中华人民共和国学位条例暂行实施办法》等规定保留和使用此学位论文，并向主管部门或其指定机构送交学位论文（包括纸质版和电子版），允许学位论文进入厦门大学图书馆及其数据库被查阅、借阅。本人同意厦门大学将学位论文加入全国博士、硕士学位论文共建单位数据库进行检索，将学位论文的标题和摘要汇编出版，采用影印、缩印或者其它方式合理复制学位论文。

本学位论文属于：

（　　）1.经厦门大学保密委员会审查核定的保密学位论文，于　　年　　月　　日解密，解密后适用上述授权。

（　　）2.不保密，适用上述授权。

（请在以上相应括号内打“√”或填上相应内容。保密学位论文应是已经厦门大学保密委员会审定过的学位论文，未经厦门大学保密委员会审定的学位论文均为公开学位论文。此声明栏不填写的，默认为公开学位论文，均适用上述授权。）

声明人（签名）：

年　　月　　日

摘 要

碳纳米管具有优异的机械、电学和热学等特性，将碳纳米管集成到微纳机械电子系统(MEMS/NEMS)中，可以用于新型微纳传感器的开发，以提高传感器的灵敏度，缩小体积，降低能耗，从而应用到一些特殊环境中。

研究碳纳米管的物理特性是将之应用到工程实际的前提，本文着重从理论上研究碳纳米管的声波传播特性，在此基础上提出并分析了碳纳米管在声学微系统上的潜在应用。论文主要贡献与具体创新点如下：

(1) 研究碳纳米管中的声波传播特性，建立了碳纳米管中声波传播的解析模型，探讨不同尺寸参数情况下碳纳米管的声波频率，分析结果表明：对于长度为数微米的单壁或双壁碳纳米管，它们能够传播的声波频率在10GHz内，对于工程应用，此频率范围是运用MEMS即微机电技术制造的超声驱动器可以达到的；

(2) 首次提出并阐述了碳纳米管声学桥的这一新概念/方法，即通过共振超声谱方法测量置放在两个微型压电换能器之间的碳纳米管的多个固有频率，确定其物理特性。作为碳纳米管声学桥的理论基础，从理论上分析了碳纳米管声学桥测量碳纳米管材料特性的可行性；在此基础上，研究碳纳米管声学桥作为高精度质量敏感元件和超高真空传感器的潜在应用；

(3) 详细研究了三个方向驱动力作用下碳纳米管尺寸和结构特性、声波模式等参数对声波引起碳纳米管振动特性的影响，结果表明：轴向力作用下的碳纳米管具有在低频率产生振动响应的特性，周向力作用下的临界频率次之，径向力作用的临界频率最高。这为选择碳纳米管声学桥合适的驱动方式提供了理论指导；

(4) 提出锆钛酸铅(PZT)作为压电层的微型体声波换能器机械结构的等效电路模型，运用PSPICE软件研究其整体频率响应特性，通过研究各结构层变化对有效机电耦合系数和器件品质因数的影响，从而确定电极层和氮化硅薄膜层的较优值；

(5) 利用溶胶-凝胶(Sol-gel)方法生长PZT薄膜，并分别在溅射了钛或铂/钛薄膜的硅衬底上旋涂生长PZT薄膜，采用MEMS微加工工艺，开发了可用于测试用Sol-gel法生长的PZT薄膜的铁电特性的工艺流程，并对所制备的PZT薄膜的铁电

特性进行测试。结果表明，在进行400ºC热处理、650ºC退火的条件下制备出的PZT薄膜，其铁电特性较优。基于这些结果，使用Sol-gel法生长的PZT薄膜可以应用于碳纳米管声学桥的MEMS驱动器的制造中；

(6) 首次利用静电纺丝工艺实现了PZT纳米纤维桥式结构的搭建，并研究所添加的聚醋酸乙烯酯(PVA)浓度、施加的电压、辅助电场及喷射针头孔径等工艺参数对实验结果的影响。PZT微桥的实现为下一步碳纳米管声学桥整体系统的制造奠定了基础。

本文所做的工作为今后继续研究基于碳纳米管的声学微系统，实现其应用，具有积极的意义。

关键词：碳纳米管；声学特性；声学微系统；静电纺丝

Abstract

Since the discovery of carbon nanotubes (CNTs), more and more efforts are being made to integrate carbon nanotubes into micro and nanoelectromechanical systems (MEMS/NEMS), due to the fact that CNTs have small size, low density, high stiffness and strength, as well as excellent electronic properties. Previous studies of the mechanical properties of CNTs concentrated on their static properties for lack of the available detailed experimental data and computational power limitations. Very few studies on acoustic properties of CNTs have been conducted.

In this dissertation, we study the acoustic wave propagation in carbon nanotubes, with a target of building up the guidance for carbon nanotube based nano acoustic devices in various engineering applications. The main contents of my works are summarized as following:

(1) The continuum elastic model is used to study the acoustic wave propagation in single-walled, double-walled carbon nanotube and carbon nanotube-polymer composite. And then the influence of structural parameters of carbon nanotubes on their acoustic resonant frequency is investigated. The results show that: if the length of the carbon nanotube is longer than several microns, the frequency of its fundamental acoustic mode can be within a 10GHz range, which is obtainable by using MEMS-based thin film ultrasonic transducers;

(2) A new method/concept for the investigation of physical properties of carbon nanotube is then firstly presented, which is called carbon nanotube acoustic bridge. It is using resonant ultrasound spectroscopy (RUS) to obtain the eigenfrequencies of the carbon nanotube that is slightly clamped between two micro ultrasonic transducers. Then we derive the relationship between the structural parameters of carbon nanotube and the quality factor of its vibration modes. Based on these, three potential applications of carbon nanotube acoustic bridge are established: it is used as a powerful tool to study the material properties of various kinds of carbon

nanotubes; it is proved to own a sensitivity of 10^{-20}g/Hz to an extremely small change of mass, which enables it used as a mass-changing detector with high sensitivity; with the derived relationship between the shift of its resonance frequencies and the pressure where the carbon nanotube acoustic bridge is, it can used as a vacuum sensor for ultrahigh vacuum;

(3) The effects of three driving forces on vibration of carbon nanotubes with different dimensional and structural properties and different acoustic wave modes from a shell model are studied. It is concluded that the value of critical frequency of carbon nanotube is lowest driven by axial force, secondly driven by circumferential force, the highest if by radial force. The results would help to choosing an appropriate driving mode for carbon nanotube acoustic bridge;

(4) A new equivalent circuit model of micro film bulk acoustic wave transducer with PZT piezoelectric layer is also set up to study its frequency response. The PSPICE software is employed to study the effect of the structural parameters on the resonant frequency, quality factor and effective coupling coefficient of the transducer. Based on this, the structural parameters of the electrode layer and silicon nitride layer are optimized to obtain improved performance for the transducer;

(5) The PZT thin films are successfully spun on silicon substrate, which is coated with Ti or Pt/Ti thin films, by using the sol-gel method. A MEMS process for the PZT thin film structure used in the measurement of their ferroelectric properties is developed, and then the polarization electric hysteresis is measured by using a Sawyer Tower circuit. The results show that the ferroelectric properties of PZT thin films prepared by the sol-gel method with heat treatment at 400℃ and annealing treatment at 650℃ can have very good performance. All of these results show that PZT thin films with a Pt/Ti layer on silicon substrate prepared by using the sol-gel method in our study can be applied to develop the PZT-based MEMS transducer for carbon nanotube acoustic bridge;

(6) A micro bridge structure with PZT nanofibers is firstly realized by using electrospinning process. The effects of PVA concentration, applied voltage, additional electric field and the inner diameter of the capillary tip on the experimental results are

studied in details. The PZT micro bridge is first step for realizing the whole carbon nanotube acoustic bridge system.

All these work will provide some guidance to the future research and exert a positive effect on the realization and applications of carbon nanotube materials on acoustic microsystem.

Keywords: Carbon nanotube; acoustic properties; microsystem application; electrospinning process

目 录

Table of Contents