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约束刻蚀剂层技术用于 GaAs 表面的三维微加工和 Cu 表面平坦化的研究

The Study of Applying CELT to Three Dimensional Micromachining of GaAs and the Planarization of Cu Interconnections

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The Study of Applying CELT to Three Dimensional Micromachining of GaAs and the Planarization of Cu Interconnections

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摘要

微机电系统、微光学系统、微芯片系统等领域的发展促进了微/纳米加工技术的发展与完善。微/纳米加工技术是当今微系统制造领域研究的热点和核心，是人类探索微纳米世界的必不可少的工具。1992 年厦门大学田昭武院士提出的约束刻蚀剂层技术（Confined Etchant Layer Techinique，简称 CELT）是一种具有距离敏感性的化学刻蚀技术，不仅能批量加工出复杂的三维微结构，而且工艺简单，适用的材料非常广泛。CELT 在实验和理论方面发展了十余年，成功应用于对金属、半导体和绝缘体等材料的微加工。本论文完善和发展了半导体材料 GaAs 的 CELT 加工技术，并将 CELT 初步应用于超大规模集成电路 Cu 互连线结构的平坦化研究中。

论文主要分为四个章节，第一章综述了微/纳米加工技术以及超大规模集成电路 Cu 互连线结构平坦化技术的发展现状，介绍了现有微/纳米加工技术以及超大规模集成电路 Cu 互连线结构平坦化技术的主要特点，分析了现有微/纳米加工技术以及超大规模集成电路 Cu 互连线结构平坦化技术的局限性，提出了本论文的主要设想和研究思路。第二章介绍了论文研究中所涉及的实验技术和表征手段。第三章论述了 CELT 用于 GaAs 表面的电化学微加工的研究结果。选用 HBr/L-胱氨酸/H_2SO_4 为刻蚀体系，研究刻蚀体系中各组分的浓度比例、GaAs 类型、模板微结构对 GaAs 刻蚀加工过程的影响。第四章论述了超大规模集成电路 Cu 互连线结构平坦化的 CELT 刻蚀体系的初步研究。通过筛选，确定 Br^- 为前驱刻蚀物种，L-胱氨酸为约束剂，利用 Pt 微圆柱电极在 Cu 片表面进行刻蚀加工实验，对所选的刻蚀体系进行优化，随后用 Pt 单晶电极和 PMMA/Ti/Pt 片状电极对 Cu 片进行表面平坦化。尝试在带有凹槽结构的 Si 片上溅射一层 Cr 层作为导电层，在 Si/Cr 上电化学沉积 Cu，用 CELT 技术对其进行表面平坦化。

本论文工作的主要成果有如下两点：

1．研究了刻蚀体系中各组分的浓度比例、GaAs的类型、GaAs的阳极腐蚀、模板微结构对CELT于GaAs刻蚀加工过程的影响。实验所选用的刻蚀体系为HBr/L-胱氨酸/H_2SO_4，利用PMMA/Ti/Pt微半球阵列电极研究刻蚀体系中各组分

的浓度比例对GaAs刻蚀加工过程的影响；利用PMMA/Ti/Pt微半球阵列电极，研究了GaAs类型对GaAs刻蚀加工过程的影响；利用PMMA/Ti/Pt微半球阵列电极和PMMA/Ti/Pt微透镜阵列电极研究模板微结构对GaAs刻蚀加工过程的影响；研究了不同类型GaAs在不同的刻蚀体系中的阳极腐蚀，并用XPS数据和EDX数据分析了不同类型GaAs在不同的刻蚀体系中的阳极腐蚀后产物。

2．初步研究了CELT用于超大规模集成电路Cu互连线结构的表面平坦化。通过对刻蚀体系的筛选，确定Br^-为前驱刻蚀物种，L-胱氨酸为捕捉剂，利用Pt 微圆柱电极在Cu片表面进行表面平坦化实验，对所选的刻蚀体系进行优化，随后在优化体系中用Pt单晶电极和PMMA/Ti/Pt片状电极对Cu片进行表面平坦化。尝试在带有凹槽结构的Si片上溅射一层Cr层作为导电层，在Si/Cr上电化学沉积Cu，用CELT技术对其进行表面平坦化。

关键词：约束刻蚀剂层技术； GaAs； Cu互连线结构； 表面平坦化

Abstract

With the development of the microelectromechanical systems (MEMS), micro-optics and microchips, microfabrication technology has been developed and improved. Now, the micro-fabrication technology has become the hotspot of the research and the score of the MEMS, which is an indispensable tool to explore the micro-nano world. The Confined Etchant Layer Technology (CELT) is a potential method to fabricate complex 3D microstructures, which is proposed by Prof. Zhao-Wu Tian et al., at Xiamen University in 1992. CELT is a kind of distance sensitivity, low cost, mask chemical etching process. CELT has been applied to fabricate complex 3D microstructures on the metal, semiconductor, and also insulator. Here, the thesis focuses on the application of CELT to the 3D microstructure microfabrication on GaAs and planarization of Cu interconnection in ultra large scale integrated circuit (ULSI).

There are four parts in this thesis. Chapter Ⅰ introduces the developments and characteristics of the main microfabrication techniques for 3D microstructures and 2D planarization, and proposed the main tasks of thesis. In Chapter Ⅱ, the experimental details, including reagent, instruments, operations and characterizations, are presented. In Chapter Ⅲ, CELT is applied to the electrochemical micromachining on different types of GaAs (*p* type, *n* type, intrinsic). The cyclic voltammograms were obtained by using bromine as the etchant generated on the mold electrode while L-cystine as the scavenger. The array of concave microstructures was fabricated on different types of GaAs surface by CELT using a mold with an array of convex hemispheres. Several factors have been studied including concentration ratio between the etchant precursor and the scavenger, types of GaAs, and anodic oxidation during the process of CELT. In Chapter Ⅳ, the application of CELT to the planarization Cu interconnection has been studied. The cyclic voltammograms were obtained by employing bromine as etchant generated on the mold while L-cystine as an efficient scavenger.

The main results are shown as follows:

1. CELT has been applied to the electrochemical micromachining on different types of GaAs substrate, including *p*-GaAs, *n*-GaAs, and intrinsic GaAs. Several factors, including concentration ratio between the etchant precursor and the scavenger, types of GaAs, the microstructures of the mold, and anodic oxidation during the process of CELT, have been studied. Br_2 was electrogenerated at the surface of the mold and used as the etchant for GaAs; L-cystine was chosen as a scavenger. Hence, the etchant was confined very close to the surface of mold and the etchant layer would keep the shape of the mold. the surface of GaAs workpiece was etched gradually when it approached into the confined etchant layer. The resolution of the fabricated microstructures depended strongly on the concentration ratio of L-cystine to Br^-. The thickness of the confined etchant layer is adjustable. Consequently, the composition of the electrolyte can be optimized for better etching precision. The array of concave microstructures was fabricated on different types of GaAs substrate by using a mold with an array of convex hemispheres. Furthermore, the influence of concentration ratio between the etchant and the scavenger on the quality of microfabrication was investigated. The influence of the microstructures of the mold has been studied in the same solution, using the molds with an array of convex hemispheres and an array of complex microlens respectively. The influence of anodic oxidation had been studied in different etching solution. At the same time, XPS and EDX were used to analysis the production after anodic oxidation, which were in harmonious accordance with the CELT results.

2. The application of CELT to the Cu interconnection has been studied primarily. According to the principle of CELT, the etching solution should normally include a precursor of an etchant and a scavenger. Here, the HBr was chosen as the precursor to electrogenerate the etchant Br_2 at the surface of the electrode, while L-cystine was used as the scavenger to the etchant Br_2. Hence, the etching solution is composed of HBr/L-cystine /H_2SO_4. A well-defined, polished Pt microcylindrical electrode with a diameter 250 μm was employed to examine the size of the etched spots deviating from the real diameter of the microelectrode with different concentration ratio between the L-cystine and HBr. The results showed that the

micromachining resolution could reach into the submicrometer precision when the concentration ratio between the scavenger and the precursor was appropriate. After that, the electrode with a smooth surface was applied to planarize the copper surface. Electrochemical deposition of copper on the Si with the trench microstructures was used to substitute for copper sheet.

Key words: Confined Etchant Layer Technique; GaAs; Cu Interconnection; surface planarizaton.

第一章 绪论

§1.1 微机电系统的简介

微机电系统（MEMS, Micro Electro Mechanic System）是一种先进的制造技术平台。它是以半导体制造技术为基础发展起来的，利用现代微/纳米加工技术将微传感器、微执行器，微电子、微能源以及控制线路等微型功能单元集成在一个芯片上，使其具有光、电子、机械、数据获取和分析等功能的完整智能化微型系统[1-11]，涉及微电子、材料、力学、化学、机械学诸多学科领域及其交叉，也促进了微尺度下的力、电、光、磁、声、表面等物理学分支的发展。

MEMS 技术几乎可以应用于所有的行业领域，而它与其他技术结合，往往会产生一种新型的 MEMS 器件。正因为如此，MEMS 器件的种类极为繁杂。根据目前的研究情况，除了进行信号处理的集成电路部件以外，微机电系统内部包含的单元主要有以下几大类：

(1)微传感器[14-30]：微传感器种类很多，主要包括机械类、磁学类、热学类、化学类、生物学类等等，每一类中又包含有很多种。例如机械类中又包括力学、力矩、加速度、速度、角速度(陀螺)、位置、流量传感器等，化学类中又包括气体成分、湿度、PH 值和离子浓度传感器等。

(2)微执行器[31-38]：微执行器主要包括微马达、微齿轮、微泵、微阀门、微机械开关、微喷射器、微扬声器、微动平台等。

(3)微型构件：三维微型构件主要包括微膜、微梁、微探针、微齿轮、微弹簧、微腔、微沟道、微锥体、微轴、微连杆等。

(4)微光学器件：这是一种利用 MEMS 技术制作的光学元件及器件。目前制备出的微光学器件主要有微镜阵列、微光扫描器、微光阀、微斩光器、微干涉仪、微光开关、微变焦透镜、微外腔激光器、光编码器等。

(5)真空微电子器件：它是微电子技术、MEMS 技术和真空电子学发展的产物，是一种采用已有的微细加工工艺在芯片上制造的集成化微型真空电子管或真空集成电路。它主要由场致发射阵列阴极、阳极、两电极之间的绝缘层和真空微腔组成。