

博 士 学 位 论 文

单晶 4H-SiC 衬底光电化学机械抛光 方法与机理研究

Research on Method and Mechanism for Photoelectrochemical
Mechanical Polishing of Monocrystalline 4H-SiC Substrates

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摘 要

单晶 4H-SiC 作为宽禁带半导体材料的核心代表之一,是制备高性能电力电子器件的理想衬底材料,近年来备受关注。与传统的硅(Si)和新兴的氮化镓(GaN)材料相比,4H-SiC 具有出色的高温稳定性和化学稳定性,在航空航天和军事领域等极端服役环境中展现出显著优势。尽管 4H-SiC 具有巨大的应用潜力,但其广泛应用仍面临一些技术和成本挑战。目前,高性能电力电子器件主要在 4H-SiC 衬底的 Si 面上加工制造。采用金刚石磨粒研磨虽可快速实现衬底表面平坦化,但不可避免地引入表面划痕及亚表面损伤,显著影响器件的性能。因此,提升衬底表面质量成为确保器件性能的关键环节。传统化学机械抛光(CMP)技术作为当前实现 4H-SiC 超光滑、无损伤表面的成熟工艺,已在工业生产中广泛应用。然而,由于 4H-SiC 硬度高、化学稳定性强,表面被氧化改性的能力较差,导致 CMP 过程中材料去除率极低,通常 Si 面的材料去除率小于 $0.5\text{ }\mu\text{m/h}$ 。采用 CMP 去除几微米的损伤层需要数十小时,不仅影响产能,而且导致成本居高不下,严重制约了高性能功率半导体器件的发展与应用。鉴于此,单晶 4H-SiC 衬底的高质高效抛光加工成为目前亟待突破的关键瓶颈问题。

针对 4H-SiC 衬底的高质高效抛光加工要求,本文聚焦多能场耦合辅助 CMP 的关键科学问题,提出单晶 4H-SiC 衬底光电化学机械抛光新方法。围绕 4H-SiC 衬底的光电化学氧化特性与机理、原子键合状态演变规律及材料去除机理、光-电-化学等多能场作用协同的光电化学机械抛光技术体系和装置、外加电压调控光电化学机械抛光工艺开展系统的研究,具体研究内容和主要结论如下:

(1) 基于 4H-SiC 的晶体结构与能带理论,系统分析了 4H-SiC/溶液界面的能带结构特征。通过线性扫描伏安法(LSV)、电流密度-时间(j - t)曲线及荧光光谱测试,对比研究 4H-SiC 的电化学氧化和光电化学氧化的特性和行为差异,揭示了 4H-SiC 的低浓度空穴诱导的电化学氧化机制与高浓度空穴主导的光电化学氧化机理。在此基础上,构建了描述 4H-SiC 的电化学和光电化学氧化过程的演化模型。同时,结合反应分子动力学(ReaxFF-MD)模拟,从原子尺度揭示了光电化学氧化反应过程中 4H-SiC 表面与界面的演化机制。实验与模拟结果表明,光电化学氧化的速率远高于电化学氧化,且光电化学氧化对 4H-SiC 衬底表面软化改性具有显著效果,可为后续采用硬度低于 4H-SiC 衬底的软磨粒抛光加工提供基础优势。

(2) 基于构建包含 4H-SiC 衬底、羟基自由基($\cdot\text{OH}$)水溶液与二氧化硅(SiO_2)磨粒的反应分子动力学模型,从微观反应机制出发,研究光电化学机械抛光过程中 4H-SiC 表面的氧化行为及其与机械作用协同去除的动态过程,揭示原子键合状态的演变机制。

研究表明,原子主要以 Si-O、O-Si-O、C-O、O-C-O 及 O-C-Si-O 等形式从表面脱离, Si-OH 与 C-OH 键作为关键中间产物在去除中起过渡作用。其中,外加电压通过增强界面氧化反应活性,提高氧化产物生成效率,主导原子的高效去除;抛光压力则通过增强磨粒接触力和界面摩擦,加速原子键断裂与迁移,显著提高材料去除速率。外加电压与抛光压力的合理匹配可优化氧化程度、摩擦强度与原子去除效率,实现在化学反应与机械载荷间的动态平衡,提升光电化学机械抛光效率。

(3) 围绕 4H-SiC 衬底的光电化学机械抛光加工原理,建立抛光工具与 4H-SiC 衬底之间的相对运动模型,系统分析通孔分布形式与转速比对衬底表面光照均匀性的影响规律。基于 COMSOL 模拟研究了不同电场施加结构对衬底表面电场分布的调控作用。结合工艺需求,对抛光液组分进行优化设计,确保其同时具备良好的透光性、导电性与机械去除能力。研究结果表明,采用叶序状通孔分布形式可确保 4H-SiC 衬底表面的光照均匀性;通孔式真空导电吸盘可确保电场均匀施加,显著抑制了局部电场集中与表面电场不均匀衰减现象。优化后的抛光液组成为粒径 35 nm、质量分数 5 wt% 的胶体 SiO₂ 与 0.1 M 的 K₂SO₄ 电解液。基于以上关键参数,构建了一套集成紫外光辐照系统、电化学控制系统、抛光液滴加系统的光电化学机械抛光装置,所构建的工艺体系和装置满足 4H-SiC 衬底表面的均匀加工。

(4) 为了实现 4H-SiC 衬底的高质高效抛光,提出外加电压调控光电化学机械抛光工艺的策略。在光电化学氧化机理的基础上建立 4H-SiC 的光电化学氧化速率预测模型,阐明外加电压与氧化速率的关系,揭示不同外加电压下 4H-SiC 的光电化学氧化特性。进一步开展不同外加电压下光电化学机械抛光试验,并建立基于多因素耦合机制的机械去除能力预测模型,阐明表面氧化速率和机械去除能力的关系,并通过光电化学机械抛光试验验证工艺的可行性。研究结果表明,在 9V 电压下,光电化学机械抛光材料去除率可达 4.2 $\mu\text{m}/\text{h}$,是传统化学机械抛光效率的 8 倍。在 5V 电压下进行光电化学机械抛光获得了光滑无损伤表面 ($S_a=0.13\text{ nm}$),满足器件制造要求。

关键词: 单晶 4H-SiC; 光电化学机械抛光; 表面改性; 材料去除; 表面质量

ABSTRACT

Monocrystalline 4H-SiC, as a representative wide bandgap semiconductor material, is regarded as an ideal substrate for the fabrication of high-performance power electronic devices and has garnered significant attention in recent years. Compared with traditional silicon (Si) and the emerging gallium nitride (GaN), 4H-SiC exhibits exceptional thermal and chemical stability, giving it notable advantages in extreme operating environments such as aerospace and military applications. Despite its substantial application potential, the widespread deployment of 4H-SiC remains hindered by several technical and cost-related challenges. At present, high-performance power devices are predominantly fabricated on the Si-face of 4H-SiC substrates. While diamond abrasive lapping can rapidly achieve surface planarization, it inevitably introduces surface scratches and subsurface damage, which significantly degrade device performance. Therefore, enhancing the surface quality of the substrate has become a key prerequisite for ensuring optimal device functionality. Chemical mechanical polishing (CMP) remains the most mature and widely adopted technique for achieving ultrasmooth, damage-free surfaces on 4H-SiC substrates. However, due to the high hardness and strong chemical stability of 4H-SiC, its surface exhibits limited susceptibility to oxidative modification, which leads to an extremely low material removal rate during the CMP process. The material removal rate on the Si face is typically less than 0.5 $\mu\text{m/h}$. Consequently, removing several microns of the damage layer using CMP can take dozens of hours, severely limiting throughput and driving up processing costs. This issue restricts the development and industrial application of high-performance power semiconductor devices. In this context, achieving high-quality and high-efficiency polishing of single-crystal 4H-SiC substrates has become a critical bottleneck that urgently requires breakthrough solutions.

To reconcile the dual demands of high-efficiency and high-quality polishing of 4H-SiC substrates with the requirement for producing ultrasmooth, damage-free surfaces, this work focuses on the key scientific issues associated with multi-field-coupled assisted CMP and proposes a novel photoelectrochemical mechanical polishing (PECMP) method for single-crystal 4H-SiC. Systematic investigations are conducted on the photoelectrochemical oxidation characteristics and mechanisms of 4H-SiC, the construction of a PECMP system and apparatus integrating synergistic photo-electro-chemical multi-field effects, the underlying material removal mechanisms and the evolution of atomic bonding states, as well as the influence of electric field intensity on the PECMP process. The specific research content and main conclusions are summarized as follows:

(1) Based on the crystal structure and band theory of 4H-SiC, the band structure characteristics at the 4H-SiC/solution interface were systematically analyzed. Through linear

sweep voltammetry (LSV), current density-time (j - t) measurements, and fluorescence spectroscopy, a comparative study was conducted on the characteristics and behaviors of electrochemical oxidation and photoelectrochemical oxidation of 4H-SiC. The results reveal distinct mechanisms: electrochemical oxidation is driven by low-concentration hole injection, while photoelectrochemical oxidation is dominated by high-concentration photogenerated holes. On this basis, an evolution model describing the electrochemical and photoelectrochemical oxidation processes of 4H-SiC was established. Furthermore, by employing reactive force field molecular dynamics (ReaxFF-MD) simulations, the interfacial evolution mechanisms during photoelectrochemical oxidation were elucidated at the atomic scale. Both experimental and simulation results demonstrate that the photoelectrochemical oxidation rate is significantly higher than that of electrochemical oxidation. Moreover, photoelectrochemical oxidation effectively softens and modifies the surface of the 4H-SiC substrate, providing a favorable foundation for subsequent polishing with soft abrasives that have a hardness lower than that of 4H-SiC.

(2) Based on a reactive molecular dynamics model incorporating a 4H-SiC substrate, an $\cdot\text{OH}$ aqueous solution, and SiO_2 abrasives, this study investigates the oxidation behavior of the 4H-SiC surface and the dynamic process of synergistic material removal via chemical and mechanical actions during PECMP, from the perspective of microscopic reaction mechanisms. The evolution of atomic bonding states during the removal process is also elucidated. The results show that atoms are primarily removed from the surface in the form of Si-O, O-Si-O, C-O, O-C-O, and O-C-Si-O bonds. Si-OH and C-OH bonds serve as critical intermediate species that facilitate the transition and detachment of atoms. The electric field plays a dominant role by enhancing interfacial oxidation activity and promoting the generation of oxidation products, thereby accelerating atomic removal. Polishing pressure, on the other hand, strengthens abrasive/surface contact and interfacial friction, promoting bond breaking and atomic migration, which significantly increases the material removal rate. A rational combination of electric field intensity and polishing pressure optimizes the oxidation degree, frictional strength, and atomic removal efficiency, achieving a dynamic balance between chemical reactions and mechanical loads. This synergy is key to enhancing the overall efficiency of the PECMP process.

(3) Focusing on the PECMP principles for 4H-SiC, a relative motion model between the polishing tool and the 4H-SiC substrate was established. The effects of through-hole distribution patterns and rotational speed ratios on surface illumination uniformity were systematically analyzed. Using COMSOL simulations, the influence of different electric field application structures on the electric field distribution across the substrate surface was investigated. In accordance with process requirements, the polishing slurry composition was optimized to ensure high optical transmittance, electrical conductivity, and effective

mechanical removal capability. The results indicate that a phyllotactic through-hole distribution ensures uniform light exposure across the 4H-SiC substrate surface. A through-hole vacuum conductive chuck enables uniform application of the electric field, significantly mitigating localized field concentration and uneven field attenuation. The optimized polishing slurry consists of colloidal SiO₂ particles with a diameter of 35 nm at a mass concentration of 5 wt%, combined with a K₂SO₄ electrolyte of 0.1 M. Based on these key parameters, an integrated PECMP system was developed, comprising a UV irradiation module, an electrochemical control unit, and a polishing slurry dispensing system. The constructed process system and apparatus effectively enable uniform surface processing of 4H-SiC substrates.

(4) To achieve high-quality and efficient polishing of 4H-SiC substrates, a strategy for controlling the PECMP process through electric field intensity is proposed. Based on the principles of photoelectrochemical oxidation, a predictive model for the photoelectrochemical oxidation rate of 4H-SiC is developed to elucidate the relationship between electric field intensity and oxidation rate, and to reveal the photoelectrochemical oxidation characteristics of 4H-SiC under different electric field intensities. Further experiments on PECMP under varying electric field intensities are conducted, and a predictive model for mechanical removal capacity based on a multi-factor coupling mechanism is established. This model clarifies the relationship between surface oxidation rate and mechanical removal capacity, and the feasibility of the process is validated through PECMP experiments. The results indicate that at an applied voltage of 9V, the material removal rate during PECMP can reach 4.2 $\mu\text{m}/\text{h}$, which is 8 times the efficiency of traditional chemical mechanical polishing. PECMP conducted at 5V achieved a smooth, damage-free surface ($S_a = 0.13 \text{ nm}$), meeting the requirements for device fabrication.

Key Words : Monocrystalline 4H-SiC; Photoelectrochemical mechanical polishing; Surface modification; Material removal; Surface quality