学校编码：10384　　分类号＿＿＿＿密级＿＿＿＿

学　　号：20520060153207　　UDC＿＿＿＿＿＿＿＿＿＿＿＿

厦门大学

博　士　学　位　论　文

熔融先驱体法制备连续 SiC 自由薄膜及其结构与发光特性研究

Synthesis, Microstructure and Photoluminescence Properties of Continuous Freestanding Silicon Carbide Films by Melt Spinning of Precursor

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论文提交日期：2010 年 8 月

论文答辩时间：2010 年 8 月

学位授予日期：2010 年　　月

答辩委员会主席：＿＿＿＿＿＿

评　　阅　　人：＿＿＿＿＿＿

2010 年 8 月

Synthesis, Microstructure and Photoluminescence Properties of Continuous Freestanding Silicon Carbide Films by Melt Spinning of Precursor

A Dissertation Submitted to the Graduate School in Partial Fulfillment of

the Requirements for the Degree of

Doctor Philosophy

By

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August, 2010

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摘　要

SiC作为第三代宽带隙半导体材料因具有禁带宽度大、热导率高、耐高温、抗辐射、机械强度大和化学稳定性好等特性而成为制作高温、高频、大功率和极端条件下半导体器件的理想材料，已广泛应用于微机电系统(MEMS)、短波光电子器件及发光二极管等领域。由于制备SiC体单晶困难且昂贵，SiC薄膜的异质外延生长显得尤为重要，但目前外延生长SiC薄膜均借助基材进行沉积，存在晶格和热膨胀系数失配等问题，导致界面处存在因应力失配而引起的大量缺陷，使其发光效率降低，使用寿命缩短。因此，有必要寻求无界面缺陷的SiC薄膜制备工艺与方法。此外，SiC薄膜是较好的蓝光发射材料，但其属于间接跃迁半导体，发光效率较低是制约其在发光器件中应用的主要障碍，虽然已发现多孔、无定形、纳米及掺杂改性的SiC能提高其发光效率，也用量子限制效应、表面模型与缺陷态模型等来解释其发光机理，但对于SiC薄膜材料发光性能的提高及其发光机制的考察尚显不足，仍需进一步深入研究与探索。

本文基于先驱体熔融纺膜法的技术，以聚碳硅烷(PCS)和聚铝碳硅烷(PACS)为原料，通过自行设计的喷膜装置熔融纺出连续PCS、PACS自由薄膜，并对其不熔化预处理与高温裂解制得系列连续SiC自由薄膜，结合微观结构及光谱学分析对其进行了发光特性与发光机理研究，深入研究了交联条件、掺杂、烧结条件及退火温度等工艺对薄膜理化性能和微结构演变的影响及其关键控制因素，阐明了薄膜形成的微观机制及发光机理。研究结果为新型强光发射SiC薄膜的质量控制和组分、微结构的创新设计提供了依据，为其在蓝色发光器件、紫外光敏器件及MEMS等高技术领域的应用提供了有效的技术支撑。主要研究内容及结果如下：

1、合成了不同异质元素的先驱体，发现其在360-450 nm范围有较强的蓝紫光发射特性。其中，PACS的发光强度最大，含镝PCS次之，并探明了先驱体的发光机理；采用自制喷膜装置与先驱体熔融纺膜法技术制备出了新型连续SiC自由薄膜，具有成本低、工艺简单，可工程化及结构功能一体化等特点。薄膜具有厚度与成分可控、可避免晶格和热膨胀系数失配问题。波长375 nm激发下，在410-450 nm范围有较强的蓝光发射。

2、研究了不熔化预处理及高温裂解对薄膜发光特性的影响机制，并考察了样品的界面微结构演变和发光机制。结果表明：(1) 交联时间越长，氧含量越高，

SiO*x*C*y*和游离碳增加，β-SiC晶粒减小；(2) 薄膜在410-450 nm范围内有较强的蓝光发射，1200 ℃烧结的薄膜随交联时间增加，发光强度增大；而1300 ℃样品其发光强度相对下降；(3) 412 nm与435 nm附近的发光峰为界面富含的氧空位和双氧空位缺陷态构成发光中心，电子在β-SiC晶粒中受到受激发后，价带被激发到导带，与空穴形成电子-空穴对隧穿到晶体表面驰豫到带尾，而被氧空位缺陷态俘获，发生辐射复合而产生了蓝光发射。(4) 由于量子表面效应与缺陷态共同作用，交联10 h于1150 ℃烧结的薄膜发光强度较高。随着温度升高，由于SiO_xC_y高温分解在薄膜本体内留下较多缺陷，导致更多非辐射中心，发光强度明显减弱，甚至猝灭。

3、评价了连续 SiC 自由薄膜在高温环境下稳定性能以及微观结构演变。(1) 建立了一套连续 SiC 自由薄膜高温环境模拟气氛处理系统；(2) 建立了 Ar-Si-C-O-H 数据库并进行热力学计算，证明薄膜在高温环境中主要存在惰性氧化；(3) 连续 SiC 自由薄膜独特的性质可在表面形成一层连续的 SiO_2 氧化层。随着退火温度的升高，薄膜的抗氧化和发光特性略有降低，薄膜中无定型 SiO*x*C*y* 减少，β-SiC 晶粒长大及游离碳增多，薄膜表面硬度与电阻率下降；(4) 建立了 SiC 薄膜在空气与水氧环境下的高温氧化动力学模型，并对其热氧化工艺进行优化。

4、从原料的合成阶段引入 Al 掺杂改性，制备了连续 SiC(Al)自由薄膜，并对其结构与发光特性进行了研究。利用微观结构观察与光谱学表征相结合阐明了含 Al 相在薄膜的作用、状态和存在位置。结果表明：(1) 薄膜具有近化学计量比，含有 β-SiC 晶粒、α-SiC 晶粒、碳簇以及少量的氧和铝；(2) Al 作为烧结助剂，对改善薄膜结构致密度，控制晶粒长大的作用十分明显。但其作用受交联时间、烧结温度和晶粒尺寸等因素的影响；(3) 交联 3 h 并于 1800 ℃烧成薄膜具有较高的致密度和较强的发光特性，在室温下表现出了 380-500 nm 宽谱带发光，其 420 nm 处的发光峰可归因于 β-SiC 位错与层错的缺陷工程以及 α-SiC 晶格的缺陷，而 440 nm 处则源于晶体界面、游离碳和多孔存在；(4) 氧主要以 Al_4O_4C 相存在，铝以 Al_4SiC_4 与 Al_4O_4C 两相形式存在，在高温条件下均能抑制薄膜中晶粒长大的作用。结合结构分析与热力学计算结果并最终建立了连续 SiC(Al)自由薄膜的结构模型。

关键词：先驱体法; 熔融纺膜; 连续 SiC 自由薄膜; 连续 SiC(Al)自由膜; 光致发光

Abstract

Silicon carbide (SiC) films exhibit several advantages such as wide band gap, good radiation resistance, high thermal conductivity, superior mechanical strength and chemical inertness. These unique properties endow SiC films with great potential for applications in the power microelectromechanical systems (MEMS) in harsh environments, high-temperature electronic and optoelectronic devices applications (light emitting diodes). The heteroepitaxy of the SiC films is very important since high quality SiC wafer is expensive and hardly to be achieved. However, the performance of the heteroepitaxial SiC films is often dependent on the film/substrate interaction due to the mismatches of thermal expansion coefficient and lattice constant at the interface. And residual strain accumulated at the interface can lead to warping problems. Therefore, there has been a considerable amount of interest in the development of alternative technique for producing SiC films which may avoid the significant difference of the thermal expansion coefficients between SiC and substrate.

SiC films are also explored as one of the most outstanding blue luminescent materials, but they can not emit light efficiently enough at room temperature due to their indirect band gaps. Recently, amorphous SiC, porous crystalline SiC, nanometer SiC and doped SiC have been reported to improve the blue luminescent efficiency and stability. Several models have been proposed to explain the luminescence, such as quantum confinement, surface states and defect states. However, the luminescent efficiency is still too low to be used in actual devices, and the origin of the observed light emission was not clear. Thus, further experimental and theoretical investigations were needed to address this issue.

In this thesis, a novel technique based on melt spinning of precursor was introduced to produce continuous freestanding SiC films. The Polycarbosilane (PCS) and Polyaluminocarbosilane (PACS) precursors were deaerated, melt spun, crosslinked and pyrolyzed at high temperature in order to convert the initial precursors into freestanding SiC films. The photoluminescence (PL) properties and mechanism of samples were demonstrated through their microstructure and spectroscopy analysis. Effects of oxidation time, doping, sintering and annealing temperatures on the physicochemical properties and microstructural evolution of the SiC films were further investigated. Much of analysis and discussion will then reveal the factors related to the PL properties and microstructural evolution of the films. The obtained results would

help to explore the SiC blue-emitting mechanisms and facilitate the application of SiC films in advanced optoelectronic devices, MEMS and such complex shaped-materials. The main subjects and results are summarized as follows:

1. PCS and doped PCS precursors were prepared using a one-pot method. The PL spectrum of precursors showed a wide luminescence band from 360 nm to 450 nm, and the origin of PL was also investigated. Comparing PL spectra of different samples, it was revealed that the PL intensity from the PACS was larger than that from the PCS and Dy-PCS. The dense and continuous freestanding SiC films were first synthesized using the novel technique of melt spinning of PCS precursor. An equipment consisted of spinneret, mandril, tank, seal cover and seal groove was successfully set up for melt spinning. In comparison with heteroepitaxy process, the freestanding films could avoid mismatches of thermal expansion coefficient and lattice constant at the interface between SiC coatings and substrate. The thickness of the films ranged from 8 μm to 190 μm depending on the spout size of spinneret mouth and spinning speed. The PL spectra of films appeared in the visible light range and had a broad spectra feature with two blue peaks at 416 nm and 435 nm under 375 nm excitation of a Xe lamp.

2. Effects of curing time and pyrolysis temperature on the PL properties of SiC films were demonstrated. The interface structural evolution and PL mechanism were also examized. The results and conclusions were as follows: (1) By increasing the curing time, the oxygen, SiO_xC_y and free carbon content enhanced as the size of β-SiC grains decreased. (2) The PL spectra showed two strong blue emissions at 416 nm and 435 nm, which were unchanged neither with oxygen content nor with β-SiC crystallite size. The PL intensity enhanced with increasing curing time when sintered at 1200 °C. However, a reversed trend was identified after the films were sintered at 1300 °C. (3) Spectroscopy and microscopy studies provided the evidences that photoexcitation occurred in the β-SiC nano-crystals cores, while photoexcited electrons and holes in the β-SiC nano-crystals transferred into the oxygen mono- and di-vacancy defect centers from SiO_xC_y surrounding the β-SiC nano-crystals and radiatively recombine there. (4) The higher PL intensity of samples cured for 10 h and sintered at 1150 °C was attributed to quantum surface effect and defect states. But too many flaws caused by the decomposition of SiO_xC_y at elevated temperature. And the flaw content increased with the rise of sintering temperature, more complex quenching defects and therefore nonradiative recombination were formed. The PL efficiency declined, evidently.