掺杂氧化铪基薄膜铁电性能的研究进展*

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摘　　要：铁电薄膜的研究多集中于钙钛矿结构材料，然而，这些传统的铁电材料存在与硅Si兼容性差、含铅而污染环境、物理厚度大、电阻低、带隙小等问题。不同的掺杂剂，如Si、Zr、Al、Y、Gd、Sr和La可以在HfO_2薄膜中诱导铁电或反铁电性，使其剩余极化率达到45 μC·cm^{-2}，矫顽力（1~2 MV·cm^{-1}）比传统铁电薄膜大约1个数量级。同时，HfO_2薄膜厚度可以非常薄（低于10 nm），并具有很大的带隙（约5 eV）。这些优于传统铁电材料的特质可以克服包括铁电场效应晶体管和三维电容传统铁电材料等在薄膜存储器应用中的障碍。除此之外，反铁电薄膜的热电耦合性将有望用于能量收集、存储、固态冷却和红外传感器等多种应用中。HfO_2掺杂薄膜可以通过不同的沉积技术如ALD、溅射和CSD来制备，其中ALD技术沉积的薄膜优势更加明显。本文综述了近年来掺杂HfO_2薄膜材料铁电性和反铁电性的研究进展，详细介绍了不同掺杂元素、薄膜厚度、晶粒尺寸、电极、退火及应力等对薄膜铁电性的影响。

关 键 词：原子层沉积；氧化铪薄膜；掺杂；铁电性；极化

中图分类号：TB34　　**文献标识码：**A　　**文章编号：**1002-0322（2024）01-0010-11

doi：10.13385/j.cnki.vacuum.2024.01.02

Research Progress on Ferroelectric Properties of Hafnium Oxide Doped Thin Films

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Abstract: Most studies on ferroelectric thin films are focused on perovskite structural materials. However, these traditional ferroelectric materials have a variety of problems, such as poor compatibility with Si, environmental pollution caused by Pb, large physical thickness, low resistance, and small band gap. Different dopants such as Si, Zr, Al, Y, Gd, Sr and La can induce ferroelectric or antiferroelectric properties in HfO_2 films, resulting in residual polari stion up to 45 μC·cm^{-2} and coercivity (1~2 MV·cm^{-1}) approximately one order of magnitude greater than that of conventional ferroelectric films. At the same time, the thickness of HfO_2 films can be very thin (below 10 nm) and the band gap is large (~ 5 eV). These advantages over traditional ferroelectric materials can overcome the obstacles of traditional ferroelectric materials including ferroelectric field effect transistors and 3D capacitors in thin film memory applications. In addition, the electrical and thermal coupling of antiferroelectric films holds promise for a variety of applications, such as energy harvesting/storage, solid state cooling, and infrared sensors. HfO_2 doped thin films can be deposited by different deposition techniques, such as ALD, sputtering and CSD, and ALD has more obvious advantages in film deposition. In this paper, the recent progress of ferroelectric and antiferroelectric properties in HfO_2 doped thin films is reviewed. The effects of different doping elements, film thickness, grain size, electrode, annealing, and stress on the ferroelectric properties of HfO_2 thin films are described in detail.

Key words: ALD; HfO_2 thin film; doping; ferroelectric; polarization

20世纪20年代初，Valasek在罗息盐上首次发现并报道了铁电性，并对其进行了广泛的研究[1-4]。铁电（FE）材料有两个剩余极化状态（$\pm P_r$），即使在去除电偏置后，这两个剩余极化状态的内存应用可以是“0”和“1”的状态[3-4]，可应用于包括微电机械系统（MEMS）、射频识别（RFID）芯片和半

收稿日期：2023-02-17

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* **基金项目：**2021年上海交通大学决策咨询重点课题（No.JCZXSJA-04）。