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GaN 基半导体异质结构中的应力相关效应

Stress Related Effects of GaN Based Semiconductor Heterostructures

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摘 要

GaN 基半导体作为光电子材料领域极为重要的材料，其异质结构在器件开发领域得到十分广泛的应用，目前，影响其未来发展的有几大关键性难题，本质上都与应力场有关，深受大家关注且亟待解决。本论文通过实验研究和计算模拟，全面深入地考察了 GaN 基半导体异质结构中应力场的相关效应，分析其复杂性质、阐明其物理机制，进而讨论这些效应对 GaN 基半导体电学和光学性质的作用。在基础研究手段上，我们利用金属有机化学汽相外延技术制备 GaN 基异质结构，如侧向外延 GaN 和 AlGaIn/GaN 系统的异质结构；采用包括电子显微镜、俄歇电子能谱、阴极荧光光谱等技术，表征异质结构的各项化学、物理性质。首先提出了电子信息思想和“俄歇谱广义位移”概念，结合以密度泛函理论为基础的第一性原理计算方法，重点开发了微纳米区域的应力场、电学量测量技术，对微观表征技术的发展起重要的推动作用。基于上述手段，我们针对以下几方面关键物理问题进行研究并取得重要结果：

在 GaN 中应力场和发光性质的研究方面，通过对侧向外延 GaN 的应力分布测量，发现双轴应力释放的关键机制和区域，通过对穿透位错的拐弯、攀移等行为的分析发现双轴应力场可转变为纵向应力场，并带来带边发光增强的效应，从而提高了紫外发光强度；同时，集体有序拐弯的位错线所形成的横向位错阵列，对极化场造成密集的碎断作用，减小电子空穴的离化，增加了发光复合几率，进一步促进 GaN 发光效率的提高。

在 GaN/AlGaIn/GaN 异质结构的压电极化效应的研究方面，通过测量界面层区的化学和电学性质，发现 Al 与 Ga 在界面互扩散形成了一定宽度的界面组分缓变层区，在此层区内，因极化效应作用形成了局域的二维电荷薄层。通过对局域电场的测量，重建了异质结能带结构，表明能带弯曲所形成的界面势谷对二维电荷薄层起到限制的作用。通过第一性原理计算 AlGaIn/GaN 异质结构的几何和电子结构，得到极化场作用下的弯曲能带结构，与实验结果很好的吻合，并发现了价带、导带弯曲的不一致性，预测了 AlGaIn/GaN 量子阱的短波发光器件开发的切实可行性。

在应力场控制下的 AlGaIn 体系异质界面相变的研究方面，通过计算发现，在 GaN 基

底层上，薄膜相变存在临界厚度，且高 Al 组分有利于相变的发生；对电子结构的详细分析说明，Al-N 键的共价化及其次近邻键相互作用对从纤锌矿结构到闪锌矿结构的相变起到关键的作用。相变的发生带来极化场效应的减小，从而改变了 AlGa_N 薄膜的电子结构和光电子性质。通过对 AlGa_N/Ga_N 异质结构样品的实验观察发现，界面存在 AlN 偏析薄层并呈现闪锌矿结构相，很好的佐证了理论的预测。另一方面，在 AlN 基底层上的闪锌矿结构相变，则发生于特定的应力场范围内，说明适当的应力场可以有效地控制结构相变。

根据以上对 Ga_N 基半导体异质结构中应力相关的几个最重要问题的精细测试和微观分析，显示了应力相关效应的可控性和有益性，为 Ga_N 基半导体开发应用的进一步发展带来新的希望。

关键词： Ga_N 基半导体、异质结构、电子结构、俄歇电子能谱、应力场、压电极化、相变

Abstract

GaN-based semiconductor has been one of the most important and potential optoelectronic materials, the heterostructure of which plays the dominant role in the fabrication of new functional devices. However, several critical problems that have significantly restricted the further development of its advanced applications are principally related to its stress field. The research in this thesis aimed to provide a thorough insight into the stress-related effects in the GaN-based heterostructures, especially at the nano-scale heterointerface, through both experimental and theoretical studies.

The epitaxial heterostructures, such as epitaxial-lateral-overgrowth (ELO) GaN and AlGaIn/GaN, were prepared by using metal-organic chemical vapor deposition. Advanced characterization techniques, including scanning electron microscopy, Auger electron spectroscopy, cathodoluminescence, etc., were employed for analyzing the chemical and physical properties of the heterostructures. Concepts of “Electron cipher” and “Auger general shift” were proposed for the first time, which led to the establishment of nano-scale measurements for local stress field, electric field, and charges. Upon the framework of the first-principles calculation methods, the construction techniques for modeling heterostructure systems and imposing stress fields were developed. Based on above techniques, following issues have been studied and important approaches were obtained:

1. The stress field and optical properties of ELO-GaN were investigated. The stress distribution on the cross section suggests a mechanism of the release of misfit in-plane stress and the critical release region was determined. The bending of threading dislocations (TDs), the climb movement of dislocation loops, and the jog of stacking faults have been observed and analyzed and the results proved the existence of a longitudinal stress field in the lateral region. Such stress field results in the enhancement effect of band-edge emission efficiency and consequently, improves the ultraviolet luminescence intensity. On the other hand, the horizontal dislocation array introduces the fragmentation effect into the *c*-axial polarization field, which also effectively improves the recombination rate of electron-holes.

2. The piezoelectric polarization field in GaN/AlGa_N/GaN heterostructure was examined. By elemental profiling, a considerably wide gradient interface region was formed due to the inter-diffusions of Al and Ga. Two dimensional sheet charges in the gradient heterointerface region were observed, demonstrating the effect of polarization. The energy band structure is rebuilt via local electric field detections and the potential well at the interface formed with the curvature of bands gives rise to the confinement of the polarization charges. Simulation of GaN/AlGa_N band structure was consistent with the experimental results. In particular, the band structure in the quantum well exhibits a different degree of bending between the valence band and conduction band. The flat valence band in the well predicts the feasibility of the fabrication of AlGa_N/GaN quantum-well-based short wavelength optical devices.
3. The wurtzite-to-zinc blende phase transition of AlGa_N thin films upon GaN and AlN basal layers were investigated. On GaN basal layers, it was found that the structural transition depends on the critical thickness of AlGa_N film and higher Al mole fraction favors the phase transition. Detailed analysis reveals that the second-nearest-neighbor interaction and the tendency towards covalency of Al-N bonds play the key role for the phase transition. The structural transition will effectively reduce the polarization electric field in AlGa_N film and consequently, influence the optoelectronic properties. On AlN basal layers, a preferable stress range was found for the formation of zinc blende phase. This fact demonstrates that we can intentionally control the phase transition in optional AlGa_N films by adjusting the stress field.

Above all, the approaches in the intersectional investigations on GaN-based heterostructures have led to important microcosmic knowledge and understandings to those crucial problems and have demonstrated the controllability and serviceability of the stress-related effects. This work provides new prospects for the future developments of nitride semiconductors.

Key words: GaN-based semiconductor, heterostructure, electronic structure, Auger electron spectroscopy, stress field, piezoelectric polarization, phase transition.

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第一章 序 论

1.1 GaN 基半导体研究的根本性问题

电子科技的发展与大众的生活已息息相关,不论是电或者光都是现代生活中万万不可缺少的要素,而光电子器件开发和应用的最重要基础则建立于半导体材料的研究。硅(Si)和砷化镓(GaAs)曾经是影响最深远、最具代表性的半导体材料,有着十分广泛的实际应用,但其最根本的缺陷——窄禁带(Si 约 1.1 eV、GaAs 约 1.4 eV)或者间接带隙(Si),成为它们继续发展不可逾越的屏障。禁带窄,则使其应用只能局限在长波长且十分狭窄的光谱范围;同时,价带中的电子很容易因热激发或离化进入导带,无法适应高温、高功率的应用需求^[1];至于间接带隙,则根本无法有效发光。于是,宽禁带的直接带半导体材料便脱颖而出,成为研究和应用的主角。

在宽禁带直接带半导体中,又以 GaN 基半导体最具开发潜力和发展前景,它凭借着宽广的带隙[0.7 eV (InN)、3.5 eV (GaN)、6.2 eV (AlN)]^[1]和优越的性能(热稳定、化学稳定、高导热等)^[2, 3],已经成为近年来光电子材料和器件研究的重点。GaN 最早于 1940 年由 Juza 和 Hahn 利用 NH₃ 通过加热的 Ga 金属反应制得^[4],而后一直到了 1969 年 Maruska 等人才开始采用 CVD 技术在蓝宝石衬底上异质外延大面积 GaN 晶体^[5],该外延技术的框架仍被沿用至今。之后的整个 70 年代,人们不断地致力于实现 GaN 基短波长发光器件的开发,虽然基于 M-i-n 结构从蓝光到黄光的发光二极管(LED)也曾被制造出来^[6, 7],但由于深为大量的位错密度(10^{11} cm^{-2})和困难的 *p* 型电导所苦,大功率的器件迟迟不能实现。这种困顿和沉寂一直延续到 80 年中后期,Akasaki 等人意外地发现电子束激发 GaN:Mg 材料可以使之表现为 *p* 型电导^[8],Amano 等人在 GaN 外延生长中引入低温缓冲层有效降低缺陷密度^[9],以此为契机,GaN 材料和器件的研究很快得到迅速的进步,并引起大家的广泛关注和极大的重视。不久之后,基于 *p* 型电导的进一步开发^[10]和缺陷密度经侧向外延技术处理的进一步降低^[11]。在 1995 年,利用 InGaN/GaN 超晶格结构,高亮度、长寿命的可见光(特别是蓝光)LED 器件制造成功^[12, 13],并投入工业生产和市场应用。至此,全面的 GaN 基半导体光电子技术研究的局面就此打开,各类相关光电子器件不断得到开发,性能也不断提高。

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