

雾化学气相外延法异质外延 Ga_2O_3 薄膜的生长特性谢佳慧¹, 穆文祥¹, 李竹程¹, 李光清¹, 李 阳¹, 贾志泰^{1,2}, 陶绪堂¹

(1. 山东大学, 晶体材料国家重点实验室, 新一代半导体材料研究院, 晶体材料研究院, 济南 250100;

2. 山东省工业技术研究院, 济南 250100)

摘 要: 氧化镓各晶相的应用广泛, 亚稳相只能通过外延的手段获得。选择合适的生长方法和提高异质外延水平仍是学术界一直探讨的问题。采用雾化学气相沉积(Mist-CVD)法在蓝宝石衬底上异质外延生长了氧化镓薄膜, 通过优化工艺条件实现了物相调控, 系统研究了外延膜的结晶质量、组分和表面形貌, 以及生长速率变化规律。同时, 探究了 Mist-CVD 生长系统中, Ga_2O_3 外延膜的晶体成核及晶相控制机理。在原有 $\alpha\text{-Ga}_2\text{O}_3$ 生长工艺的基础上, 制备了 α/ε 混相薄膜、 $\varepsilon\text{-Ga}_2\text{O}_3$ 纯相薄膜, 呈三维岛状生长模式。在 $\varepsilon\text{-Ga}_2\text{O}_3$ 纯相薄膜的基础上, 随着氧气流量的增加, 结晶质量先稳定后下降, 生长速率先增加后降低, 最高达到 $3\mu\text{m/h}$ 。通过退火, 获得了 $\beta\text{-Ga}_2\text{O}_3$ 纯相薄膜, 表面粗糙度由 10.80 nm 降低至 5.42 nm 。在利用 Mist-CVD 法进行不同晶相外延调控及其生长机理研究方面具有一定借鉴意义。

关键词: 氧化镓; 异质外延; 雾化学气相沉积法; 蓝宝石衬底

中图分类号: O782+7 文献标志码: A 文章编号: 0454-5648(2024)02-0373-08

网络出版时间: 2023-12-05



随着现代社会能源、信息、军事等领域对低损耗、大功率、高性能电力电子器件的需求不断提高, 宽禁带半导体凭借其优异的材料特性成为目前研究的热点。宽禁带半导体材料因其禁带宽度大、化学稳定性好且耐高温, 受到学术界的普遍重视和广泛研究。其中, 氧化镓作为一种新兴的半导体材料, 因禁带宽度大($4.8\sim 5.3\text{ eV}$)^[1-2], 使其具有超高击穿场强^[3]、超大 Baliga 优值^[4]和短的紫外截止边^[5], 可以很好地应用在高耐压、大功率、低损耗功率器件以及深紫外光电器件中。氧化镓常见的有 5 种晶相, 其中 $\beta\text{-Ga}_2\text{O}_3$ 为高温稳定相($\geq 870\text{ }^\circ\text{C}$)^[6], α 、 ε 、 γ 和 δ 相为亚稳相^[7]。

外延技术是制备器件的基础, 而且氧化镓亚稳相的制备只能通过外延的手段进行。目前 Ga_2O_3 外延常用方法为分子束外延(MBE), 金属有机物化学气相外延(MOCVD), 卤化物气相外延(HVPE)和雾化学气相外延(Mist-CVD)。其中, Mist-CVD 方法无需真空系统, 安全经济、操作简单且可控性强, 已

经广泛应用于 $\alpha\text{-Ga}_2\text{O}_3$ 外延膜的制备^[8-10], 表现出此方法在氧化镓亚稳相生长方面的应用潜力。

$\beta\text{-Ga}_2\text{O}_3$ 可以通过同质外延生长, 但是衬底价格昂贵, 制备成本高; 异质外延也在同步发展, 其最主要的挑战是克服晶格失配带来的缺陷问题。通常, $\beta\text{-Ga}_2\text{O}_3/\alpha\text{-Al}_2\text{O}_3$ 的 $(\bar{2}01)$ 面的摇摆曲线半高宽超过 0.5° ^[11], 由失配引发的晶格缺陷会导致掺杂困难, 迁移率降低。同时, 由于氧化镓存在多种亚稳相, 所以杂相是困扰氧化镓外延亟需解决的重要问题。 $\alpha\text{-Ga}_2\text{O}_3$ 是六方晶系, 由于与蓝宝石衬底晶格匹配良好(失配度约为 3.54%)^[8], 已经可以通过各种方法生长出高质量(约为 60 arcsec)^[12], 低位错密度(约为 10^6 cm^{-2})^[13], 生长速率快(约为 $10\mu\text{m/h}$)^[14]的外延膜。但是, $\alpha\text{-Ga}_2\text{O}_3$ 中易存在杂相, 形成晶界^[15], 难以支撑器件的稳定应用。 $\varepsilon\text{-Ga}_2\text{O}_3$ 是正交晶系, 与 6H-SiC 和蓝宝石衬底的晶格失配分别为 3.3% ^[16], 4.1% ^[17]。Yao 等利用 HVPE 在蓝宝石衬底上生长 $\varepsilon\text{-Ga}_2\text{O}_3$, 生长速度为 41.7 nm/min ^[18], Chen 等采用 MOCVD 生长

收稿日期: 2023-06-29。 修订日期: 2023-08-24。

基金项目: 国家自然科学基金(51932004, 52002219)。

第一作者: 谢佳慧(1999—), 女, 硕士研究生。

通信作者: 穆文祥(1989—), 男, 博士, 副教授;

李 阳(1990—), 女, 博士, 副研究员;

陶绪堂(1962—), 男, 博士, 教授。

Received date: 2023-06-29. Revised date: 2023-08-24.

First author: XIE Jiahui (1999—), female, Master Candidate.

E-mail: 202114051@mail.sdu.edu.cn

Correspondent author: MU Wenxiang (1989—), male, Ph.D., Associate Professor.

LI Yang (1990—), female, Ph.D., Associate Professor.

TAO Xutang (1962—), male, Ph.D., Professor.

E-mail: mwx@sdu.edu.cn; yangli@sdu.edu.cn; txt@sdu.edu.cn

ϵ - Ga_2O_3 薄膜, 半高宽为 0.20° ^[19]。但目前 ϵ - Ga_2O_3 薄膜的研究相对较少, 外延生长方面还存在大量空白。综上所述, 氧化镓各晶相的异质外延水平仍需进一步提高, 比如生长过程中仍然存在混相问题, 导致晶相调控困难; 成核机理方面, 缺乏过程性的具体研究和解释说明等。

本工作通过自主研发设计的立式雾化化学气相沉积外延炉, 探索了 Ga_2O_3 各晶相在蓝宝石衬底上最为合适的生长区间。分别探究了氧化镓晶相调控、结晶质量、生长速率与生长工艺参数之间的关系, 以及退火对表面形貌的优化。为了更好地表征实验现象和结果, 从微观上分析了薄膜的成核机理以及 Mist-CVD 的前驱体雾滴运动规律, 从宏观上加以各种测试结果进行验证表征, 以期获得晶相可控、结晶质量好、生长速率快的 Ga_2O_3 纯相薄膜。

1 实验

1.1 薄膜生长

采用 Mist-CVD 方法异质外延 Ga_2O_3 薄膜, 所用设备为立式雾化化学气相沉积外延炉, 所用衬底为 2 英寸商用蓝宝石衬底。采用乙酰丙酮镓 $[\text{Ga}(\text{acac})_3]$ 水溶液作为 Ga 和 O 的前驱体, 浓度为 0.05 mol/L , $1.5\% \text{ HCl}$ 作为助溶剂。采用高纯 Ar (99.999%) 作为载气, Ar 流量和生长压力分别为 2 250 mL/min 和 101.325 kPa , O_2 作为稀释气体。在 $600\sim 750^\circ\text{C}$ 的生长温度、 $225\sim 600 \text{ mL/min}$ 的 O_2 流量范围内对生长参数进行调节, 生长时间为 1 h 。

1.2 样品表征

采用 D8-ADVANCE 型 X 射线衍射仪(XRD)测定晶体结构和取向, 分析衍射峰的半高宽(FWHM)和结晶质量。采用 ESCALAB-250 型 X 射线光电子能谱仪(XPS)测定了外延层表面的元素组成和含量。此外, 通过 S-4800 型扫描电子显微镜(SEM)观察了 Ga_2O_3 外延层的 SEM 横截面照片和厚度。利用 ICON 型原子力显微镜(AFM)表征了 Ga_2O_3 外延层的 AFM 图像和表面粗糙度均方根(RMS)。采用 LAMBDA-950 型紫外-可见分光光度计(UV-Vis)表征样品的透过度并计算禁带宽度。

2 结果与讨论

2.1 沉积温度对 Ga_2O_3 薄膜晶相的调控

Ga_2O_3 各晶相的存在温度区间不同, 其热稳定性由高到低依次为 β 、 ϵ 、 α ^[20]; 与(0006)面蓝宝石衬底的失配度也不尽相同, 分别为 6.6% ^[21]、 4.1% ^[17]

和 3.54% ^[8], 而晶格匹配会在一定程度上诱导相关晶相的生成; 这些原因共同导致不同晶相生长条件复杂。前期, 本课题组已经在低温范围($500\sim 580^\circ\text{C}$)下成功实现了高质量 α - Ga_2O_3 外延膜的快速生长^[22]。首先在 $600\sim 750^\circ\text{C}$ 的温度区间内探索了氧化镓外延膜的晶体结构。如图 1a 所示, 在 $600\sim 700^\circ\text{C}$ 会有 α 、 ϵ 混合相的存在, 并且薄膜衍射峰较弱, 无明显的择优取向。这是因为 α 相与 c 面蓝宝石衬底的晶格匹配程度较高, 在低温下更容易诱导其在蓝宝石衬底上生长, 并在晶格失配应变下稳定存在。

在 750°C 生长出 ϵ 纯相, 有明显的择优取向, 通过 Scherrer 公式(1)^[23]:

$$D = k\lambda / \beta \cos \theta \quad (1)$$

其中: D 为晶粒的平均直径大小; k 为 Scherrer 常数, 0.89 ; λ 为仪器采用的 X 射线波长; β 为衍射峰的半高宽度; θ 为衍射角。计算出其晶粒尺寸为 $40\sim 50 \text{ nm}$ 。图 1a 显示 ϵ - Ga_2O_3 的(002)面峰值是 19.16° , (004)为 38.94° , (006)为 69.06° 。如图 1b 所示, 将 2 英寸外延片进行分区测试, 结果显示, 在整个衬底范围内均为 ϵ - Ga_2O_3 纯相。随着生长温度的升高, 衬底与外延膜界面间的失配应变释放^[13], 原子获得能量在表面迁移, 克服晶格限制, 形成更高温度下稳定存在的亚稳相 ϵ - Ga_2O_3 。因当前外延炉设备最高设定温度为 750°C 的限制, 未探索更高温度下的氧化镓晶相, 在更高的生长温度下, 预计会获得 β - Ga_2O_3 纯相薄膜。

通过对生长的 ϵ - Ga_2O_3 薄膜表面进行 XPS 测定, 由图 2a 全谱中发现 198.2 eV 处有微量 Cl 掺入到薄膜中。同时从图 2b 的 XPS 的 Ga 3d 能谱中看出, 只有 Ga^{3+} 的存在。这是因为乙酰丙酮镓主要以 $\text{Ga}(\text{acac})_3$ 的水合物形式存在^[24], 即使前驱体溶液中存在少量其他形式的 Ga 离子化合物, 也对薄膜影响不大。同时前驱体溶液中 Cl^- 的存在^[25], 促进了 Ga^{3+} 与氧离子的结合, 即反应(2), 提高了薄膜纯度。



图 2c 的 O 1s 能谱表明, 作为氧空位缺陷的非晶格氧 O II 含量较少, 晶格氧 O I 含量占据主导地位。

2.2 氧气流量对 Ga_2O_3 薄膜结晶质量和生长速率的调控

Ga_2O_3 薄膜中的氧来自于前驱体溶液中的水分子^[24], 氧气在 Mist-CVD 的生长过程中, 作为稀释气体参与到整个工艺过程中, 但是它的作用远不止

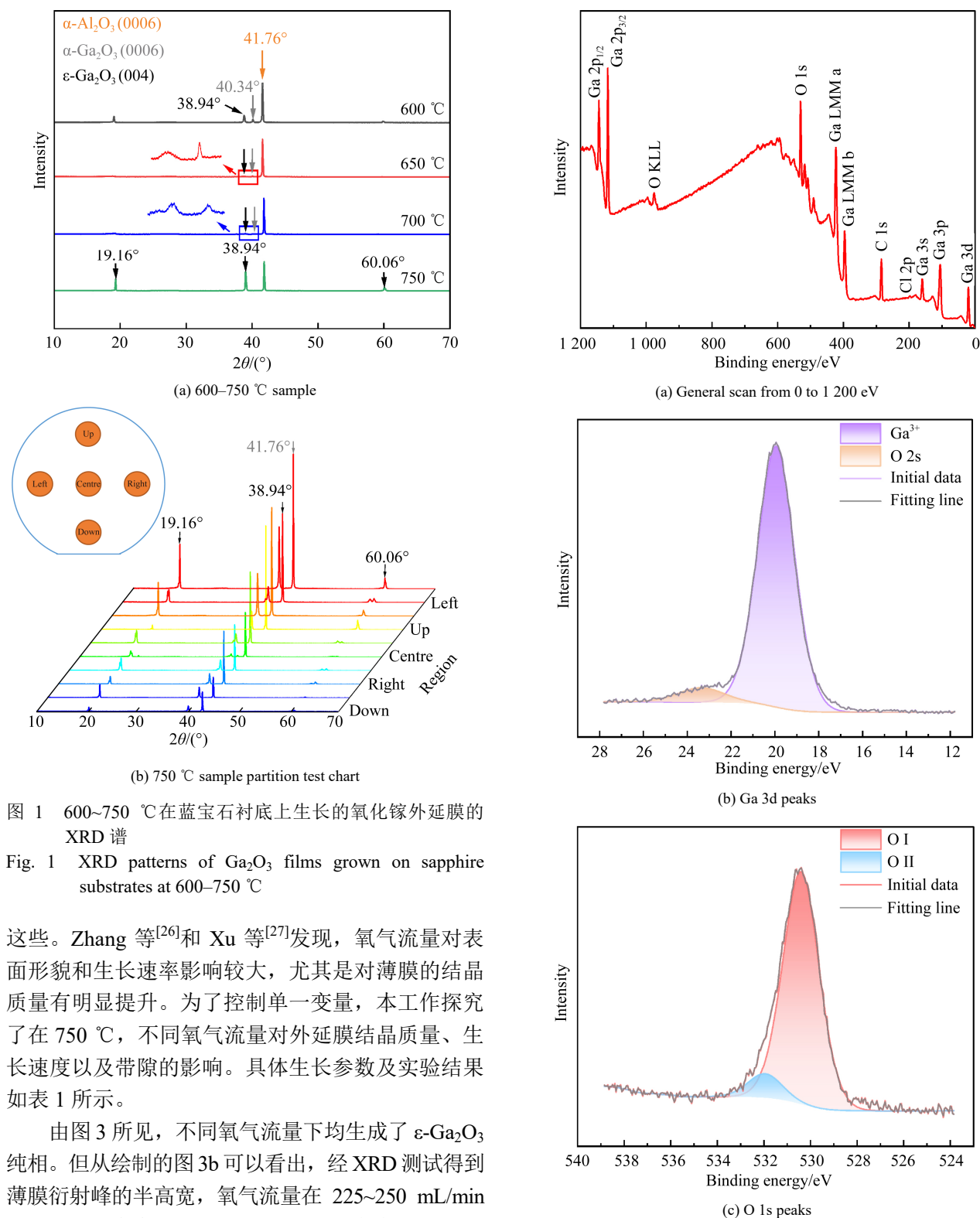


图 1 600~750 °C 在蓝宝石衬底上生长的氧化镓外延膜的 XRD 谱

Fig. 1 XRD patterns of Ga_2O_3 films grown on sapphire substrates at 600–750 °C

这些。Zhang 等^[26]和 Xu 等^[27]发现, 氧气流量对表面形貌和生长速率影响较大, 尤其是对薄膜的结晶质量有明显提升。为了控制单一变量, 本工作探究了在 750 °C, 不同氧气流量对外延膜结晶质量、生长速度以及带隙的影响。具体生长参数及实验结果如表 1 所示。

由图 3 所见, 不同氧气流量下均生成了 $\epsilon\text{-Ga}_2\text{O}_3$ 纯相。但从绘制的图 3b 可以看出, 经 XRD 测试得到薄膜衍射峰的半高宽, 氧气流量在 225~250 mL/min 之间时, 半高宽处于 0.141°、0.150°的较低水平; 当氧气流量超过 400 mL/min 后, 样品的半高宽变大, 分别为 0.178°、0.162°和 0.162°, 薄膜的结晶质量明显下降, 但 $\epsilon\text{-Ga}_2\text{O}_3$ 总体的结晶质量相较于其他研究来说较好。

经过 SEM 横截面测试薄膜厚度, 由图 4 可见, 随氧气流量的增加, 薄膜的生长速率先升高后降

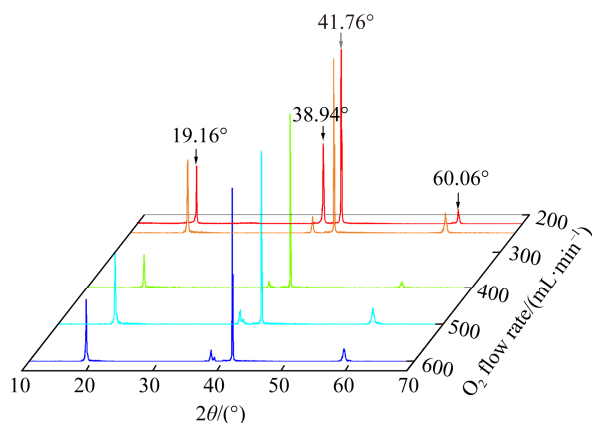
低, 在 250 mL/min 和 400 mL/min 下达到了 3 $\mu\text{m}/\text{h}$ 的生长速率, 预计在 250~400 mL/min 下会获得更高的生长速率。雾滴在设备内的状态同时受到初始直径、生长温度和流量的影响, 从而产生沉积行为^[28]。

图 2 $\epsilon\text{-Ga}_2\text{O}_3$ 的 XPS 谱

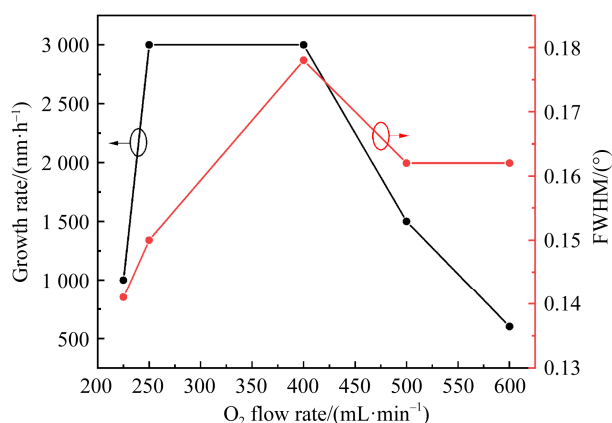
Fig. 2 XPS spectra of the $\epsilon\text{-Ga}_2\text{O}_3$ film

表 1 在 750 °C 不同氧气流量下 Ga_2O_3 薄膜样品的实验结果
Table 1 Experimental results of Ga_2O_3 thin film samples at different oxygen flow rates at 750 °C

Oxygen flow rate/($\text{mL} \cdot \text{min}^{-1}$)	FWHM/(°)	Growth rate/($\mu\text{m} \cdot \text{h}^{-1}$)	Band gap/eV
225	0.141	1.0	4.94
250	0.150	3.0	4.98
400	0.178	3.0	5.00
500	0.162	1.5	4.93
600	0.162	0.6	4.97



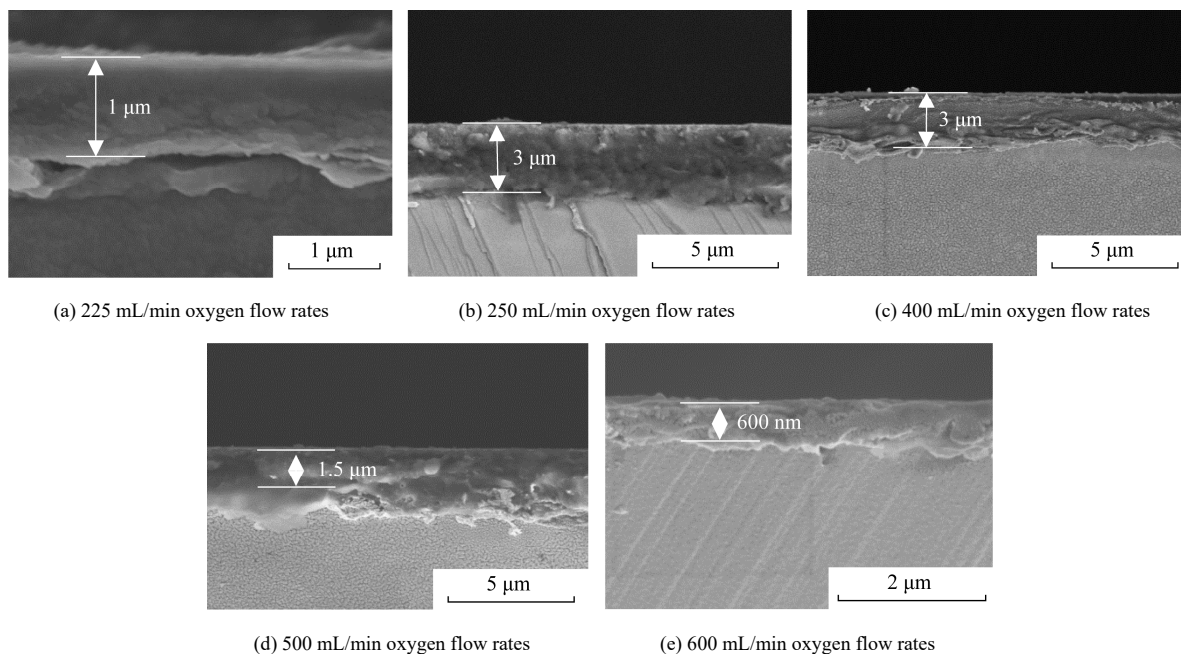
(a) XRD patterns



(b) Growth rate and FWHM variation graph

图 3 225~600 mL/min 氧气流量下生长的氧化镓外延膜 XRD 谱, 生长速率及半高宽变化图

Fig. 3 XRD patterns, growth rate and full width at half maximum (FWHM) diagram of Ga_2O_3 epitaxial films at 225–600 mL/min oxygen flow rates



(d) 500 mL/min oxygen flow rates

(e) 600 mL/min oxygen flow rates

图 4 225~600 mL/min 氧气流量下生长的氧化镓外延膜的 SEM 横截面照片

Fig. 4 SEM cross-sectional images of Ga_2O_3 epitaxial films grown at 225–600 mL/min oxygen flow rates

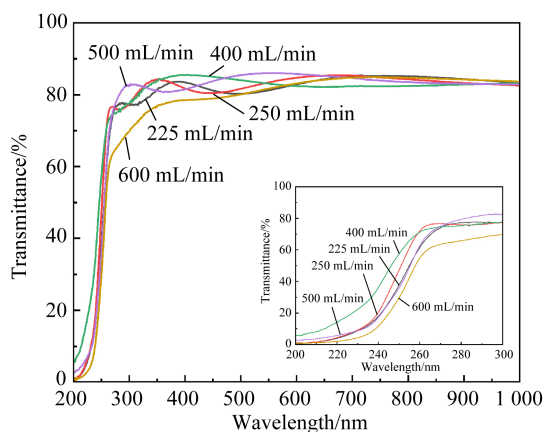
经过紫外透射光谱测试, 薄膜的透过率良好, 均在 80%左右, 紫外截止边在 240 nm, 通过 Tauc plot 法计算得到的带隙范围在 4.9~5.0 eV 之间, 符

在恒定的生长温度下, 薄膜的生长速率与到达衬底表面的前驱体雾滴的直径大小和数量直接相关, 只有合适尺寸的雾滴才能有效释放前驱体, 进行薄膜沉积。初期增加流量时, 更多有效雾滴到达衬底, 经过 Leyton-Frost 运动^[29]生成薄膜。继续增大流量, 过大直径的雾滴数量占据主体地位, 无法对外延做出有效贡献, 不仅会造成厚度降低, 还会使薄膜的结晶质量下降。

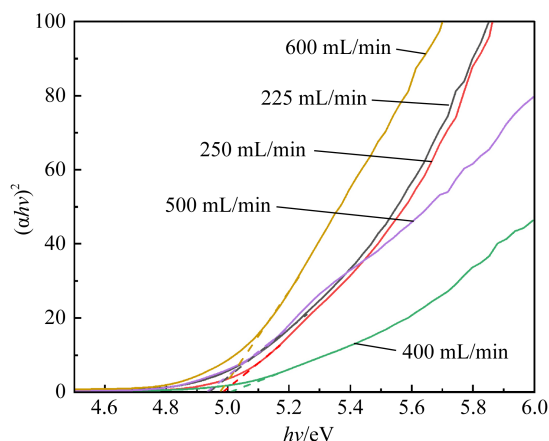
合 $\epsilon\text{-Ga}_2\text{O}_3$ 特性^[30]。

2.3 退火对 Ga_2O_3 晶相及表面形貌的影响

因 ϵ 相(001)晶面族与 β 相($\bar{2}01$)晶面族衍射峰



(a) Transmission spectrum from 200 nm to 1 000 nm

(b) Plot of $(\alpha h\nu)^2$ vs. $h\nu$

α is absorbance index. h is planck constant. ν is frequency.

图 5 225~600 mL/min 氧气流量下生长的氧化镓外延膜的紫外透射光谱

Fig. 5 Ultraviolet transmission spectrum of Ga_2O_3 epitaxial films grown at 225–600 mL/min oxygen flow rates

峰值的微小差异, 利用退火进一步验证区分了 ϵ 相与 β 相。在 750 °C 获得的 ϵ - Ga_2O_3 纯相外延膜基础上, 进行 900 °C、 N_2 气氛下退火 2 h 后, 如图 6 所示, 外延膜 XRD 峰位的整体向左偏移, 转变为 β - Ga_2O_3 。其中 18.95° 是 $(\bar{2}01)$ 面 β - Ga_2O_3 , 38.40° 是 $(\bar{4}02)$ 面 β - Ga_2O_3 , 59.19° 是 $(\bar{6}03)$ 面 β - Ga_2O_3 。

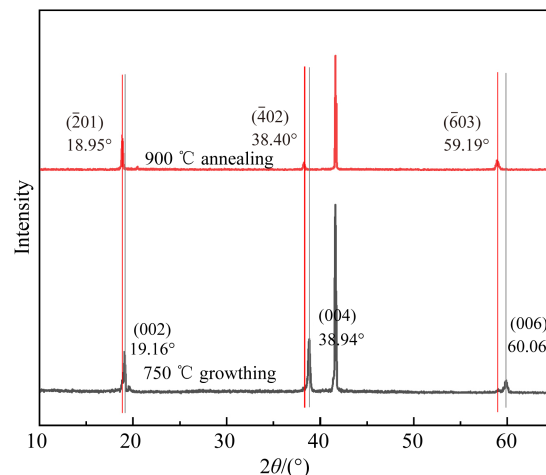
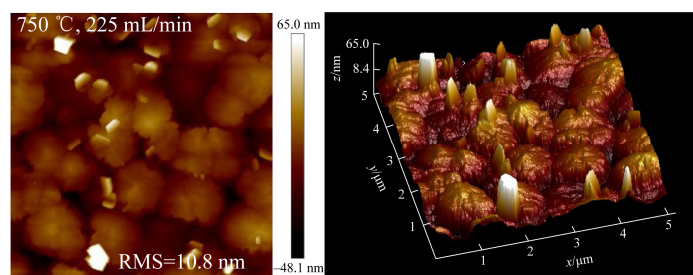
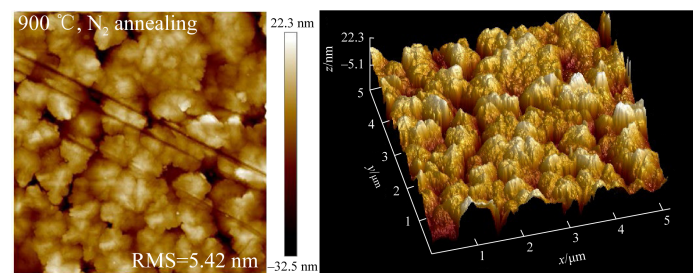


图 6 750 °C 生长的 ϵ - Ga_2O_3 外延膜退火前后的 XRD 对比
Fig. 6 XRD patterns comparison of ϵ - Ga_2O_3 epitaxial films grown at 750 °C before and after annealing

对于 750 °C 生长出的 ϵ - Ga_2O_3 样品, 进行 AFM 测试。由图 7a 所见, ϵ - Ga_2O_3 样品表面呈一簇簇云团状形貌特征的大颗粒, 其表面粗糙度为 10.8 nm。从 3D 立体图中可以看出表面形貌呈多个鼓包状或山丘状的凸起, 表面凸起高度在 50~100 nm 之间, 其整体高度大于薄膜的晶粒尺寸, 故可推测该外延膜

(a) ϵ - Ga_2O_3 epitaxial film grown at 750 °C(b) β - Ga_2O_3 epitaxial film annealed at 900 °C

RMS is root mean square roughness.

图 7 Ga_2O_3 外延膜 AFM 图像及 3D 图

Fig. 7 AFM images and 3D view of Ga_2O_3 epitaxial films

按照三维岛状生长模式生长。生长温度较低时, Ga_2O_3 薄膜制备过程中热能供应量少, 近衬底表面的原子无法获得足够的能量而迁移至与衬底晶格相匹配的位置, 而是在表面随机形成多个成核点, 成核点生长变大后形成一个一个的岛, 岛获得能量继续增大, 会与相邻的岛进行合并, 形成具有一定厚度的薄膜, 表面会继续有成核点的形成和岛的长大^[31–32]。将 900 °C 退火后的 $\beta\text{-Ga}_2\text{O}_3$ 样品同样进行了 AFM 表征。由图 7b 所见, $\beta\text{-Ga}_2\text{O}_3$ 样品薄膜表面粗糙度降低, $\text{RMS}=5.42\text{ nm}$, 晶粒尺寸变大, 在 50~80 nm 之间。表面粗糙度的优化源于表面凸起高度的大幅度降低, 因为退火时温度升高, 薄膜表面的原子获得了更多的能量进行横向迁移和岛的生长, 填补了晶粒间隙, 所以岛屿出现了高度降低, 凸起位点增多的现象。需要注意的是, 在高温下, 表面凸起高度 5~30 nm, 小于晶粒尺寸, 可以认为高温下薄膜致密度提高。此现象有望进一步优化 $\beta\text{-Ga}_2\text{O}_3/\alpha\text{-Al}_2\text{O}_3$ 的缺陷及表面形貌问题, 提高迁移率。

3 结论

利用雾化学气相沉积法在蓝宝石衬底上生长了氧化镓薄膜, 探索了生长温度、氧气流量和后退火对外延膜晶相调控、结晶质量、生长速率和表面形貌的影响规律。在 750 °C 得到 $\varepsilon\text{-Ga}_2\text{O}_3$ 纯相薄膜, 呈三维岛状生长模式, 低温下薄膜表面粗糙度较高, 为 10.8 nm。 $\varepsilon\text{-Ga}_2\text{O}_3$ 在 225 mL/min 的氧气流量下薄膜的生长速率为 1 $\mu\text{m}/\text{h}$, 半高宽为 0.141°, 通过增大氧气流量, 薄膜的生长速率可增大至 3 $\mu\text{m}/\text{h}$, 且仍为 $\varepsilon\text{-Ga}_2\text{O}_3$ 纯相。但是 $\varepsilon\text{-Ga}_2\text{O}_3$ 结晶质量未有明显提升, 反而因氧气流量过大而恶化。900 °C 退火后得到 $\beta\text{-Ga}_2\text{O}_3$ 纯相薄膜, 表面形貌进一步优化, 粗糙度大幅度降低, 仅为 5.42 nm。利用自制的 Mist-CVD 设备和低成本的雾化学气相沉积方法探索出 Ga_2O_3 各晶相的生长区间, 实现对于亚稳相的混相抑制, 并能够稳定生长厚度可观的纯相。有望在将来进一步提高薄膜结晶质量、优化表面形貌的基础上, 生长出更好的 Ga_2O_3 纯相薄膜, 为后续氧化镓基光电探测器、2DEG、功率器件打下坚实基础。

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Growth Characterization of Heterogeneous Epitaxial Gallium Oxide Films by Mist Chemical Vapor Deposition

XIE Jiahui¹, MU Wenxiang¹, LI Zhucheng¹, LI Guangqing¹, LI Yang¹, JIA Zhitai^{1,2}, TAO Xutang¹

(1. State Key Laboratory of Crystal Materials, Institute of Novel Semiconductors, Institute of Crystal Materials, Shandong University, Jinan 250100, China; 2. Shandong Research Institute of Industrial Technology, Jinan 250100, China)

Extended Abstract

Introduction Gallium oxide crystal phase is widely used, and the metastable phase can be only obtained by means of epitaxy. Selecting suitable growth methods and improving the heteroepitaxy level are still the problems that the academic circles have been discussing. The mist chemical vapour deposition (Mist-CVD) method does not require a vacuum system, which is safe, economical, simple and controllable, demonstrating a potential application for metastable phase growth of gallium oxide. The level of heterogeneous epitaxy of various crystalline phases of gallium oxide still needs to be further improved. For instance, there is still a problem of mixing phases during the growth process, which leads to a difficulty of regulating the crystalline phases. In terms of the nucleation mechanism, there is a lack of process-specific research and explanatory notes. In this paper, the most suitable growth intervals of Ga_2O_3 crystalline phases on sapphire substrates were explored in a vertical mist chemical vapour deposition epitaxy furnace. The relationships among Ga_2O_3 crystal phase modulation, crystalline quality, growth rate and growth process parameters, as well as the optimisation of surface morphology by annealing were investigated respectively. The nucleation mechanism of the films and the precursor droplet motion law of Mist-CVD were analyzed, and the experimental results were discussed.

Methods Heterogeneous epitaxial Ga_2O_3 films were prepared by the Mist-CVD method in a vertical mist chemical vapour deposition epitaxy furnace with a 2-inch commercial sapphire substrate. Gallium acetylacetonate ($\text{Ga}(\text{acac})_3$) aqueous solution was used as a precursor for Ga and O at 0.05 mol/L, and 1.5% HCl was used as a co-solvent. High-purity Ar (99.999%) was used as a carrier gas with Ar flow rate of 2 250 mL/min and growth pressure of 101.325 kPa, respectively, and O_2 was used as a dilution gas. The growth parameters were adjusted in the growth temperature range from 600 °C to 750 °C and O_2 flow rate from 225 mL/min to 600 mL/min for 1 h.

A model D8-ADVANCE X-ray diffractometer (XRD) was used to determine the crystal structure. The elemental composition and content of the epitaxial layer surfaces were determined using a model ESCALAB-250 X-ray photoelectron spectrometer (XPS). In addition, the cross-sectional image and thickness of the Ga_2O_3 epitaxial layer were characterized by a model S-4800 scanning electron microscope (SEM). The AFM images and root-mean-square (RMS) surface roughness of Ga_2O_3 epitaxial layers were analyzed by a model ICON-type atomic force microscope (AFM). A LAMBDA-950 UV-Vis spectrophotometer (UV-Vis) was used to characterize the transmittance of the samples and calculate the forbidden band width.

Results and discussion Based on the XRD analysis on the crystal structure of the epitaxial films of gallium oxide at 600–750 °C, there exist α and ϵ mixed phases at 600–700 °C, and the film diffraction peaks are weak with no obvious selective orientation. This is due to the higher lattice matching of the α phase to the c-plane sapphire substrate, which is more easily induced to grow on the sapphire substrate at low temperatures and stabilised under lattice mismatch strain. The ϵ -pure phase is grown at 750 °C with a selective orientation. The crystalline phase of gallium oxide at higher temperatures is not explored, and pure phase films of β -Ga₂O₃ are expected to be obtained at higher growth temperatures due to the limitations of the current epitaxial furnace equipment with a maximum set temperature of 750 °C.

ϵ -Ga₂O₃ pure phase is generated at different oxygen flow rates. However, the half-height width of the diffraction peaks of the films appears at a lower level of 0.141° and 0.150° for oxygen flow rates at 225–250 mL/min. When the oxygen flow rate exceeds 400 mL/min, the half-height widths of the samples become larger, *i.e.*, 0.178°, 0.162° and 0.162°, respectively, and the crystalline quality of the films decreases, but the overall crystalline quality of ϵ -Ga₂O₃ is better. Based on the analysis on the cross-section of the film thickness by SEM, the growth rate of the film firstly increases and then decreases with the increase of the oxygen flow rate, reaching a growth rate of 3 μ m/h at 250 mL/min and 400 mL/min. A higher growth rate can be obtained at 250–400 mL/min.

For the ϵ -Ga₂O₃ samples grown at 750 °C, the surface of the ϵ -Ga₂O₃ sample shows a cluster with coarser particles and a cloudy morphological features, and its surface roughness is 10.8 nm. From the 3D stereogram, the surface morphology shows multiple bulge-like or hill-like bumps, and the height of the surface bumps is between 50 nm and 100 nm, and its overall height is larger than the grain size of the film, indicating that the epitaxial film grows in accordance with the three-dimensional island-like growth mode. The β -Ga₂O₃ sample after annealing at 900 °C is similarly characterized by AFM. The surface roughness of the thin film of β -Ga₂O₃ samples decreases as RMS=5.42 nm, and the grain size becomes larger, ranging from 50 nm to 80 nm. At high temperatures, the height of the surface bumps is between 5 nm and 30 nm, which is smaller than the grain size, showing that the film densities increase at high temperatures.

Conclusions Pure phase films of ϵ -Ga₂O₃ were obtained at 750 °C in a three-dimensional island growth pattern with a high surface roughness of 10.8 nm at low temperatures. The growth rate of the film of ϵ -Ga₂O₃ at an oxygen flow rate of 225 mL/min was 1 μ m/h with a half-height width of 0.141°. The growth rate of the film increased to 3 μ m/h with increasing the oxygen flow rate, and the film was still in the pure phase of ϵ -Ga₂O₃. However, the crystalline quality of ϵ -Ga₂O₃ was not improved, while rather deteriorated due to the high oxygen flow rate. β -Ga₂O₃ pure-phase thin films were obtained after annealing at 900 °C, and the surface morphology was further optimized with a reduced roughness of only 5.42 nm. The pure crystalline phases of Ga₂O₃ with a considerable thickness could be prepared by a low-cost mist chemical vapor deposition method in a Mist-CVD equipment.

Keywords gallium oxide; heterogeneous epitaxy; mist chemical vapour deposition; sapphire substrate