

## 直拉单晶硅氧浓度控制技术研究进展

刘文凯<sup>1</sup>, 刘 赞<sup>1</sup>, 薛忠营<sup>1,2</sup>, 魏 星<sup>1,2</sup>

(1. 集成电路材料国家重点实验室, 中国科学院上海微系统与信息技术研究所 上海 200050;

2. 上海市高端硅基材料重点实验室, 上海 200050)

**摘 要:** 直拉单晶硅是当前集成电路制造的主流衬底材料。在直拉单晶硅生长过程中, 石英坩埚的溶解会引入氧杂质, 而单晶硅中的氧浓度直接影响衬底的电阻率、机械强度、金属吸杂能力和载流子寿命, 因此, 深入研究掌握直拉单晶硅氧输运的物理机制并实现晶体氧浓度的精确控制至关重要。本文首先介绍了直拉单晶硅生长的氧输运物理机制, 并从坩埚溶解控制、熔体流动控制和自由液面挥发控制 3 个方面综述了氧浓度控制技术的最新研究进展, 最后展望了氧控制技术的未来研究方向。

**关键词:** 直拉单晶硅; 氧输运; 坩埚溶解; 熔体流动; 自由液面挥发

中图分类号: TM23 文献标志码: A 文章编号: 0454-5648(2025)12-3494-12

网络出版时间: 2025-10-16



单晶硅材料是集成电路产业最主要的衬底材料, 其质量直接影响器件性能和工艺良率。在主流制备工艺中, 直拉法(CZ)凭借其大尺寸单晶硅生长优势, 制成的硅片占据了全球硅片产量的 90% 以上。然而, 由于直拉法工艺中使用石英坩埚盛放硅熔体, 石英坩埚( $\text{SiO}_2$ )在持续高温下溶解, 不可避免地向硅熔体引入氧杂质, 最终氧杂质随硅熔体结晶进入晶体。

这种引入的氧杂质, 在单晶硅材料中表现出多种特性, 对衬底性能产生重要影响。氧在硅中通常以间隙氧原子、氧沉淀和热施主 3 种形式存在。间隙氧原子<sup>[1]</sup>和氧沉淀可以有效阻碍位错的滑移和增殖, 增强衬底的机械强度<sup>[2-3]</sup>, 此外, 氧沉淀周围还会形成应力场, 可以吸收金属杂质<sup>[4]</sup>, 热施主则会导致晶体电阻率发生变化<sup>[5-6]</sup>。这对不同的器件产生的影响不同, 对于太阳能电池, 较高密度的氧沉淀和热施主导致的少子寿命下降和电阻率失真会降低太阳能电池的光电转换效率, 因此, 通常需要控制在  $7 \times 10^{17} \text{ atoms} \cdot \text{cm}^{-3}$  以内<sup>[7]</sup>。对于半导体级单晶硅, 不同类型的衬底对氧的要求也不尽相同。如逻辑器

件使用的衬底通常为外延片, 其器件区域仅位于外延层中, 这要求衬底具有一定密度的氧沉淀, 用于吸收器件加工过程中的金属杂质, 同时还要避免氧沉淀过量而引起晶圆翘曲, 导致光刻误差。而功率器件如绝缘栅双极型晶体管(IGBT)是垂直型器件, 该器件使用整个衬底作为耐压区, 耐压区的氧沉淀会导致器件漏电流增加<sup>[8]</sup>, 而热施主导致的电阻率下降则会导致器件击穿电压降低, 因此这要求衬底具有极低的氧浓度以降低热施主和氧沉淀浓度, 通常要求氧浓度低于  $2.5 \times 10^{17} \text{ atoms} \cdot \text{cm}^{-3}$ <sup>[9]</sup>。存储器件如 3D-NAND 闪存采用数百层堆叠工艺, 要求衬底具有极佳的机械强度以平衡堆叠工艺产生的内应力<sup>[10]</sup>, 这也要求氧沉淀密度的精确控制。为保障器件性能和工艺良率, 直拉单晶硅生长过程中氧浓度的精确控制至关重要。

本文首先介绍了直拉单晶硅生长中的氧输运物理机制, 随后从坩埚溶解控制、熔体流动控制和自由液面挥发控制 3 个方面综述了直拉单晶硅中氧浓度控制技术的最新研究进展, 最后展望了未来氧浓度控制技术的发展方向。

收稿日期: 2025-07-08。 修订日期: 2025-07-29。

基金项目: 中国科学院基础与交叉前沿科研先导专项(B 类先导专项)(XDB0670102); 国家自然科学基金(62074152, 62304232, 62304233)。

第一作者: 刘文凯(1997), 男, 博士研究生。

通信作者: 魏 星(1981), 男, 博士, 研究员。

Received date: 2025-07-08. Revised date: 2025-07-29.

First author: LIU Wenkai (1997-), male, Doctoral candidate.

E-mail: liuwk@mail.sim.ac.cn

Correspondent author: WEI Xing (1981-), male, Ph.D., Professor.

E-mail: xwei@mail.sim.ac.cn

# 1 直拉单晶硅氧运输物理机制

目前, 关于直拉单晶硅氧运输物理机制已基本达成共识, 如图 1 所示。由图 1 可见, 直拉单晶硅中的氧来源于高温下溶解的石英坩埚, 在硅熔体中通过熔体流动和扩散运输。输运至熔体自由液面的氧原子会与硅原子结合形成 SiO 气体挥发后随氩气流排出炉体, 而输运至结晶界面的氧原子则会随硅熔体凝固进入晶体。

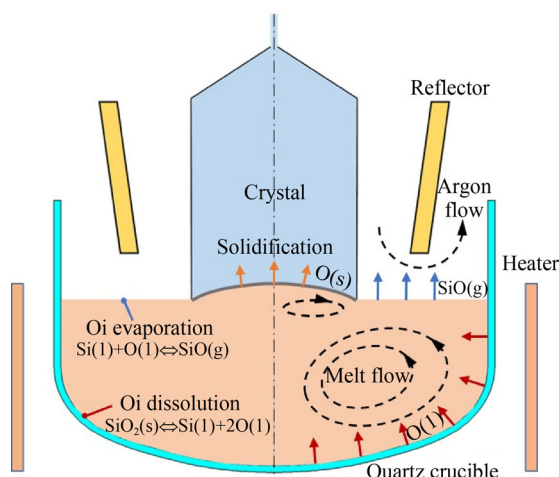
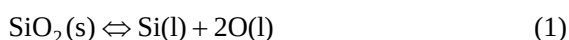


图 1 直拉单晶硅氧运输物理机制示意图

Fig. 1 Schematic diagram of oxygen transport in Czochralski silicon crystal growth

## 1.1 石英坩埚的溶解

石英坩埚由高纯石英砂(二氧化硅)烧结而成, 其在高温下与硅熔体接触时会缓慢溶解, 化学反应方程式如式(1)所示。Ekhult 等<sup>[11]</sup>、Hirata 等<sup>[12]</sup>和 Huang 等<sup>[13]</sup>通过实验分别测量了二氧化硅和硅熔体体系中氧在硅熔体中的溶解度, 对比结果如图 2 所示。其中, Hirata 等<sup>[12]</sup>的结果表明, 氧溶解度随硅熔体温度升高迅速增大。Ekhult 等和 Huang 等的结果则表明<sup>[11,13]</sup>, 氧溶解度随硅熔体温度变化不显著, 这是实验测量时, 系统冷却速度快慢导致系统偏离平衡态导致的。Huang 等<sup>[13]</sup>的实验冷却速率在  $20\text{ }^{\circ}\text{C}\cdot\text{s}^{-1}$ , 而 Hirata 等<sup>[12]</sup>的实验冷却速率在  $2\sim 7\text{ }^{\circ}\text{C}\cdot\text{s}^{-1}$ , 更高的冷却速率可以降低在冷却过程中氧原子的扩散距离, 使冷却后的系统中氧浓度更接近高温时的平衡状态。



在通过数值模拟方法研究氧运输过程中, 通常认为坩埚-熔体界面氧浓度和温度满足 Arrhenius 关系。目前, 较为常用的边界条件为方程(2)和方程(3), 分

别根据 Hirata 等<sup>[12]</sup>和 Huang 等<sup>[13]</sup>的实验结果分别拟合获得。

$$C_s(\text{atoms}\cdot\text{cm}^{-3}) = 4\times 10^{23} \exp[-2\times 10^4 / T(\text{K})] \quad (2)$$

$$C_s(\text{atoms}\cdot\text{cm}^{-3}) = 1.33\times \exp[-3.2\times 10^3 / T(\text{K})] \quad (3)$$

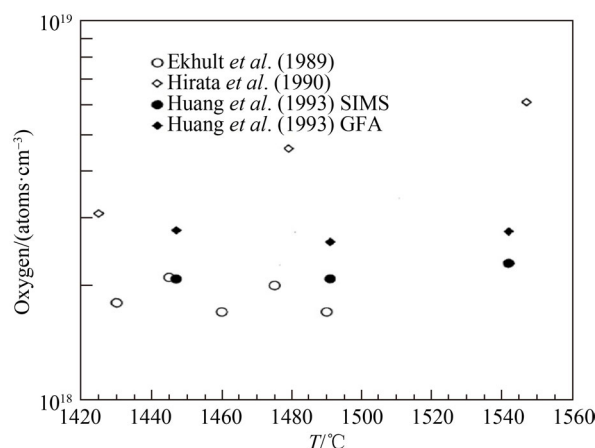


图 2 硅熔体中氧溶解度与温度的关系对比<sup>[13]</sup>

Fig. 2 A comparison of the dependence of oxygen solubility on temperature of silicon melt<sup>[13]</sup>

## 1.2 硅熔体中氧的输运

溶解在硅熔体中的氧原子在硅熔体中通过分子扩散和熔体对流输运, 可用对流扩散方程描述, 如方程(4)所示。根据斯托克斯-爱因斯坦关系, 氧的分子扩散系数取决于熔体温度和黏度, 通常在  $10^{-5}\sim 10^{-4}\text{ cm}^2\cdot\text{s}^{-1}$  量级<sup>[14]</sup>, 由方程(4)等式右边的扩散项描述。氧的对流输运则由等式左边第 2 项对流项描述, 等式左边第 1 项为瞬态项。随着晶体逐渐向大尺寸发展, 熔体体积随之增大, 熔体流动状态从层流逐渐转变为湍流, 具有强烈的瞬态特性, 使氧的输运进一步复杂化。工业上通常采用雷诺时间平均方法来求解湍流, 其中, 湍流效应通过向有效扩散系数  $D_{\text{eff}}$  中引入湍流扩散系数  $D_t$  来计算,  $D_{\text{eff}}$  的计算公式如式(5)所示, 其中,  $D_m$  为分子扩散系数。

$$\frac{\partial}{\partial t} \rho C_O + \nabla \cdot (\rho \mathbf{U} C_O) = \nabla \cdot (D_{\text{eff}} \nabla C_O) \quad (4)$$

$$D_{\text{eff}} = D_m + D_t \quad (5)$$

## 1.3 硅熔体自由液面氧的挥发

通过硅熔体输运至熔体自由液面的氧原子会以 SiO 的形式挥发, 其化学反应方程式如式(6)所示。Togawa 等<sup>[15]</sup>测量出硅熔体自由液面的氧浓度约为  $10^{15}\sim 10^{16}\text{ atoms}\cdot\text{cm}^{-3}$ 。进一步, Smirnov 等<sup>[16]</sup>通过化学反应平衡推导出了硅熔体自由液面氧浓度和一氧

化硅气体浓度关系, 该关系可以考虑氩气压强对 SiO 挥发速率的影响[见式(7)]。



$$C_{\text{O}} = a \cdot C_{\text{SiO}} \cdot P_{\text{Ar}} \exp(b/T + c) \quad (7)$$

式中:  $P_{\text{Ar}}$  为氩气压强;  $a$ 、 $b$  和  $c$  为常数。

#### 1.4 结晶界面氧的分凝

从熔体中输运至结晶界面的氧原子会随着硅熔体凝固进入晶体, 由于氧在硅熔体和硅晶体中的溶解度差异, 在结晶界面处会产生分凝现象。可以用式(8)来描述, 式中:  $C_s$  和  $C_l$  分别为氧在晶体和熔体中的溶解度。目前, 有大量关于氧分凝系数的实验测量报导, 但其结果存在较大偏差(0.25~1.48)<sup>[17–19]</sup>。这是因为硅熔体中的氧浓度是动态变化的, 与坩埚的溶解和氧在自由液面的挥发相关, 其分凝系数不能简单通过测量晶体在生长轴方向的氧浓度变化来确定。文献[18]通过将晶体直径增加到坩埚内径相当的尺寸, 消除了自由液面氧挥发的影响, 结果表明, 氧的分凝系数约为 1。近年来的一些研究, 也通常采用氧分凝系数为 1 的假设<sup>[20–22]</sup>。

$$k_0 = \frac{C_s}{C_l} \quad (8)$$

在直拉单晶硅生长过程中, 氧的输运主要涉及 3 个关键相界面(熔体–坩埚固液界面、熔体自由表面的气液界面、晶体和熔体的液固界面)以及熔体内复杂的流体动力学行为。其中: 熔体–坩埚界面主导着作为氧源项的坩埚溶解过程, 熔体自由表面主导着作为氧汇项的表面挥发过程, 而结晶界面则决定了氧进入晶体的分凝效应。与此同时, 熔体内复杂的流体动力学行为直接影响着氧的对流与扩散输运, 正是这种高度非线性的输运现象和熔体流动, 使得氧浓度的精确控制始终是直拉单晶硅生长过程中的核心科学难题。

## 2 直拉单晶硅氧浓度控制技术研究进展

直拉单晶硅中氧的输运受坩埚高温溶解、熔体流动输运、自由液面挥发和结晶界面分凝影响, 其中, 分凝效应主要取决于氧在硅熔体和晶体中的溶解度差异, 通常难以控制。因此, 直拉单晶硅氧浓度控制技术研究主要集中在坩埚溶解控制、熔体流动控制和自由液面挥发控制 3 个方面。

### 2.1 坩埚溶解控制

由于坩埚溶解速率和氧在硅熔体中的溶解度

受温度影响, 常规方法通常通过改进热场设计来降低坩埚温度, 从而降低坩埚溶解速率。热场设计优化通常可以通过优化加热器、隔热层和热屏结构来实现。

Zhou 等<sup>[23]</sup>、商润龙等<sup>[24]</sup>和 Liu 等<sup>[25]</sup>使用了一种双加热器结构(见图 3a), 通过合理分配加热功率可以有效避免坩埚局部高温。数值模拟研究表明, 该加热器系统相对于传统单加热器系统可将坩埚温度从 1730 K 降低至 1712 K (见图 3c 和图 3d), 使晶体氧浓度下降约  $3 \times 10^{17} \text{ atoms} \cdot \text{cm}^{-3}$ 。Sim 等<sup>[26]</sup>和 Teng 等<sup>[27]</sup>的研究表明, 加热器上沿与熔体自由液面距离越大, 坩埚温度越低, 晶体氧浓度越低。Zhao 等<sup>[28]</sup>和 Dezfoli<sup>[29]</sup>发现加热器开槽设计也会显著改变加热器功率, 进而影响坩埚温度。

李建铖 等<sup>[30–31]</sup>、王新强等<sup>[32]</sup>和 Xiao 等<sup>[33]</sup>通过在加热器底部添加隔热环, 从而减少加热器向坩埚底部的热辐射, 降低坩埚底部温度, 减少坩埚溶解。Nguyen 等<sup>[34]</sup>通过增加加热器上方侧保温层, 使得加热器温度降低, 进而降低了晶体氧浓度。坩埚温度分布还可以通过改变坩埚与加热器的相对位置来调整, 如图 4 所示。

Zhang 等<sup>[35]</sup>研究 3 种不同的热屏结构, 发现复合热屏结构可以有效阻碍熔体自由液面和加热器对晶体表面的辐射热输运, 提高晶体冷却速率。在相同晶体生长速率下, 可降低加热器功率约 40%, 从而减少坩埚的溶解。Nguyen 等<sup>[36]</sup>发现坩埚温度分布还会受到坩埚形状的显著影响, 由于石英坩埚受热会软化, 异形坩埚的可靠性和热场适配问题还需要进一步研究和解决。

由于单晶生长炉的高温封闭环境导致难以直接测量坩埚内壁温度, 上述研究均基于数值模拟开展, 缺乏实验测量的坩埚温度数据支撑。且根据图 2 的实验测量结果, 除 Hirata 等<sup>[12]</sup>的数据外, Huang 等<sup>[13]</sup>和 Ekhult 等<sup>[11]</sup>的数据均未体现出氧溶解度和坩埚温度的明显依赖关系。Liu 等<sup>[37]</sup>的研究表明, 晶体氧浓度与坩埚温度相关性弱, 而主要受熔体流速影响, 坩埚温度变化对晶体氧浓度的影响, 其背后机制是熔体对流形态的变化, 而非坩埚溶解速率的变化。因此, 通过改变坩埚温度分布来控制晶体氧浓度这一方法的物理机制还有待进一步探究。

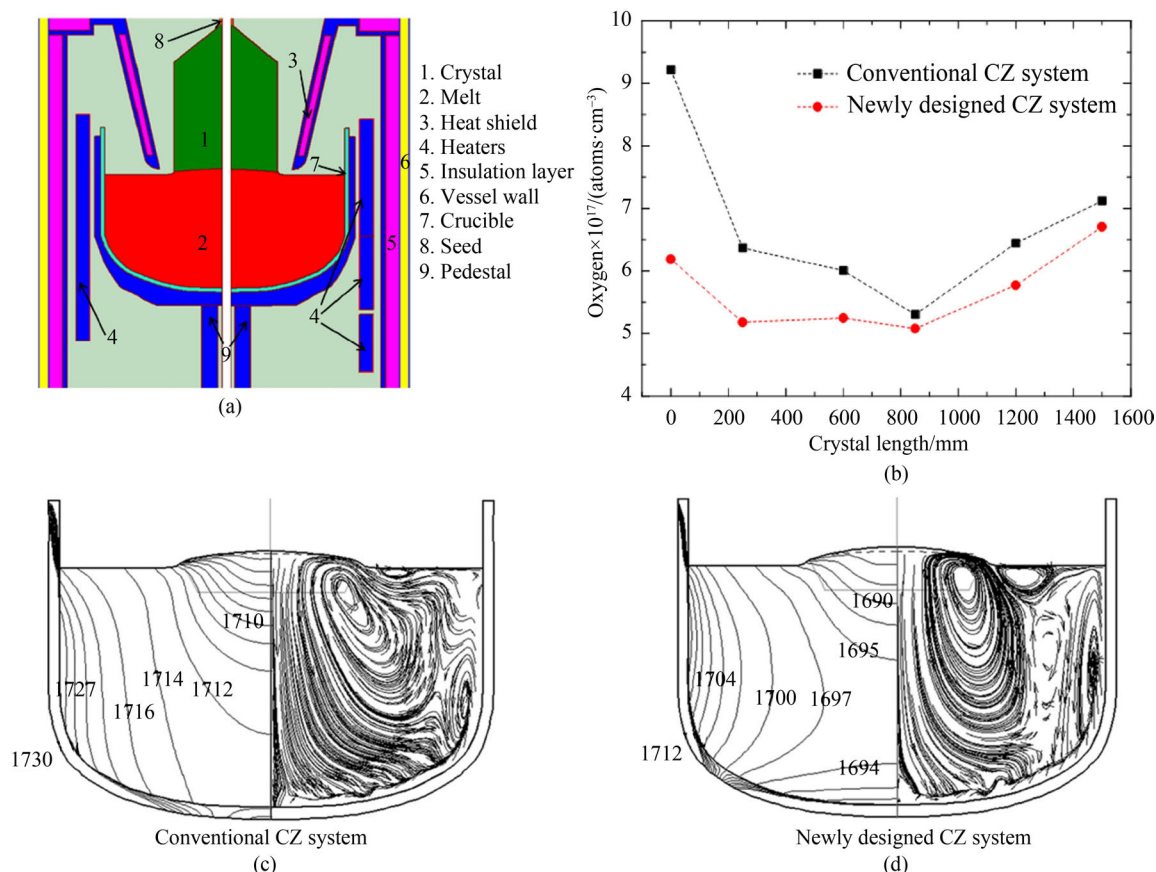


图 3 (a)双加热器系统结构示意图; (b)双加热器系统与传统单加热器系统晶体氧浓度对比; (c)传统单加热器系统熔体温度分布与流动形态; (d)双加热器系统熔体温度分布与流动形态<sup>[23]</sup>

Fig. 3 (a) Schematic diagram of dual heater system; (b) Comparison of crystal oxygen concentration between dual heater system and traditional single heater system; (c) Melt temperature distribution and flow structure of dual heat system; (d) Melt temperature distribution and flow structure of traditional single heat system<sup>[23]</sup>

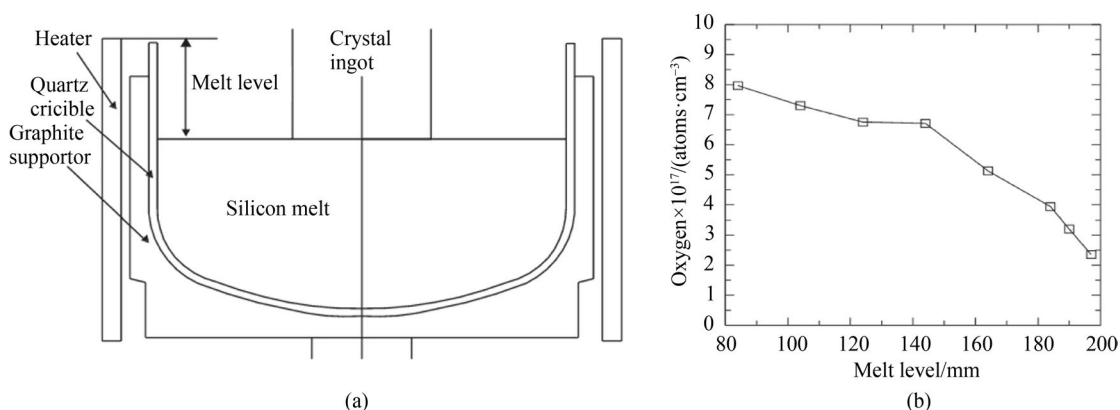


图 4 (a)加热器上沿与熔体自由液面距离(Melt level)示意图; (b)晶体氧浓度与 Melt level 的关系<sup>[33]</sup>

Fig. 4 (a) Schematic diagram of the distance between upper edge of the heater and free liquid surface of melt (Melt level); (b) Crystal oxygen concentration as a function of Melt level<sup>[26]</sup>

另一种减少氧溶解的方法是改变坩埚材质, 如在石英坩埚内壁增加涂层或将坩埚替换为不含氧的材质。光伏行业较早开始使用钡离子溶液在坩埚内表面形成致密的碳酸钡层, 减少坩埚气泡进入熔体, 提高成晶率<sup>[38]</sup>, 但对氧浓度的影响有限。Schwanke 等发现, 石英坩埚表面增加 150~350  $\mu\text{m}$  厚度的  $\text{Si}_3\text{N}_4$

涂层可以有效抑制坩埚溶解, 降低晶体氧浓度<sup>[39]</sup>。Sturm 等<sup>[40]</sup>则使用石墨坩埚替代石英坩埚并增加  $\text{Si}_3\text{N}_4$  涂层, 生长出的单晶硅氧浓度低于检测限  $10^{16} \text{ atoms} \cdot \text{cm}^{-3}$ 。但石墨坩埚的使用使晶体碳含量高达  $5 \times 10^{17} \text{ atoms} \cdot \text{cm}^{-3}$  (见图 5), 比常规值高了 3 个数量级, 过高的碳杂质会影响氧沉淀密度, 导致

载流子寿命降低<sup>[41–42]</sup>。此外,  $\text{Si}_3\text{N}_4$  涂层还引入了  $3 \times 10^{15} \text{ atoms} \cdot \text{cm}^{-3}$  的氮掺杂(见图 5), 这会显著影响单晶硅中的原生缺陷和外延缺陷<sup>[43–45]</sup>。目前, 在半导体级单晶硅生长过程中, 新坩埚和涂层技术仍未被广泛使用, 其带来的潜在影响和可能性还有待产业界进一步评估和验证。

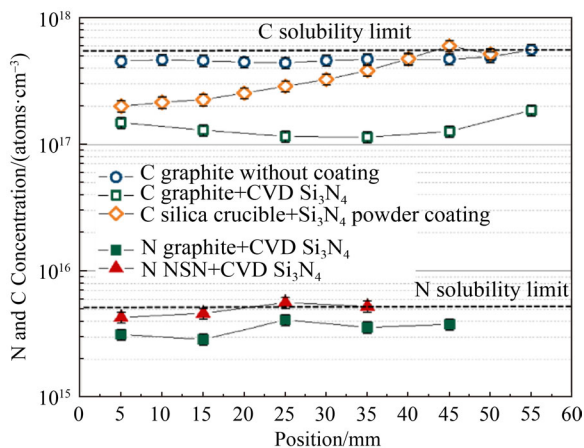


图 5 不同坩埚和涂层材料下单晶硅的碳和氮浓度<sup>[40]</sup>

Fig. 5 Nitrogen and carbon concentrations in silicon ingots in different crucible and coating materials<sup>[40]</sup>

## 2.2 熔体流动控制

直拉单晶硅中的熔体流动状态由多种驱动力共同作用决定(见图 6)。熔体的自然对流主要源于 2 种驱动力: 一是熔体内部温度分布不均产生的热浮力; 二是熔体自由液面表面张力差异引发的马兰戈尼应力。随着坩埚直径增大, 熔体自然对流通常表现出复杂的流动不稳定性, 为抑制这种不稳定性并提升晶体径向均匀性, 常采用晶体和坩埚旋转的技术手段, 这种旋转会在熔体内部产生周向剪切力, 既驱动强制对流稳定流场, 又显著影响氧等杂质的输运过程。

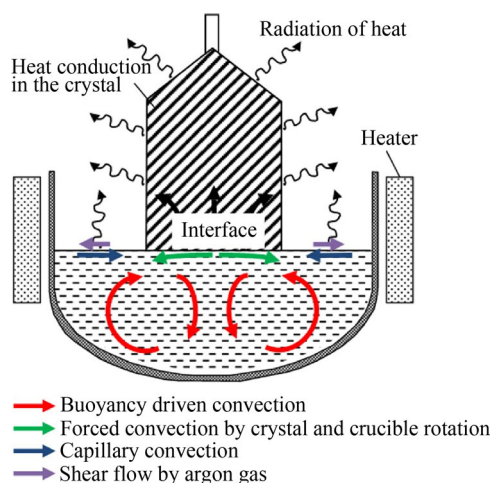


图 6 熔体流动驱动机制<sup>[46]</sup>

Fig. 6 Driven mechanism of melt flow<sup>[46]</sup>

然而, 为满足大尺寸晶体生长的需求, 坩埚尺寸和熔体体积不断增加, 熔体流动不稳定性也随之显著增强。此时, 仅依靠调整晶体和坩埚转速已难以有效抑制不稳定性。因此, 引入外加磁场成为必要手段。当导电的硅熔体在外加磁场中运动时, 将产生感应电流及与其耦合的洛伦兹力, 从而能有效抑制熔体的不稳定流动。

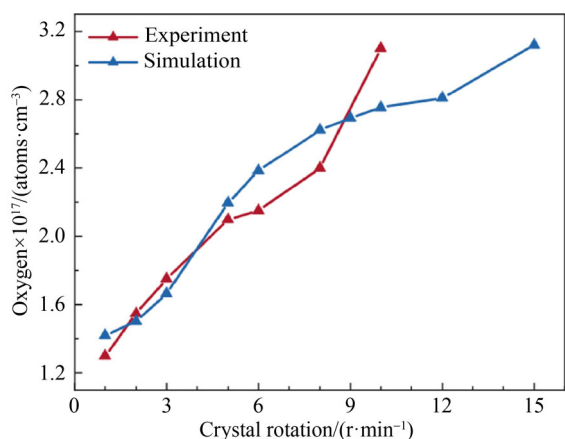
此外, 熔体的深宽比也是影响熔体流的重要参数<sup>[47–48]</sup>, 但深宽比通常由投料量决定, 并随晶体生长过程而变化, 难以人为精确控制。综合考虑以上因素, 在直拉单晶硅工艺中, 对熔体流动进行有效控制, 主要侧重于精准调控晶体与坩埚的旋转速度以及外加磁场的参数。

**2.2.1 晶体、坩埚转速控制** 针对晶体转速这一控制参数, 在无外加磁场时, Hoshi 等<sup>[49]</sup>和 Nguyen 等<sup>[50]</sup>发现, 随着晶体转速增大, 晶体下方泰勒涡增强, 晶体氧浓度上升。在横向磁场下, Hoshi 等<sup>[49]</sup>、Zhang 等<sup>[51]</sup>和 Liu 等<sup>[37]</sup>的结果表明, 晶体转速的增加会使晶体下方强迫对流增强, 从而抑制了熔体自由液面贫氧熔体向结晶界面的输运, 导致晶体氧浓度上升。而在勾型磁场下, 晶体氧浓度随晶体转速先降低后升高, 即存在使晶体氧浓度最低值的最佳转速<sup>[52]</sup>。

针对坩埚转速这一参数, 在无外加磁场时, Hoshi 等<sup>[49]</sup>研究表明, 晶体氧浓度随着坩埚转速上升而显著上升, 这是由于坩埚旋转使氧浓度边界层变薄, 增强了氧向熔体的输运。而在勾型磁场下, 随着坩埚转速的增加, 熔体中由于剪切应力产生的对流增强, 抑制了氧的径向传输, 晶体氧浓度逐渐下降。随着坩埚转速的进一步提升, 熔体中开始出现次级涡, 从而增强了氧的输运, 晶体氧浓度开始上升<sup>[53]</sup>。在横向磁场下, Hoshi 等<sup>[49]</sup>和 Chen 等<sup>[54–55]</sup>研究表明, 随着坩埚转速的增大, 熔体圆周方向流速显著增强, 但径向和轴向流速显著减弱, 自由液面贫氧熔体难以进入结晶界面导致晶体氧浓度显著上升。

此外, 晶体和坩埚同向和反向旋转对氧输运也有显著影响。无磁场时以及横向磁场下, 同向旋转生长的晶体氧浓度比反向旋转时更低<sup>[37,52,56]</sup>。而在勾型磁场下则相反, 反向旋转生长的晶体氧浓度更低<sup>[52]</sup>。

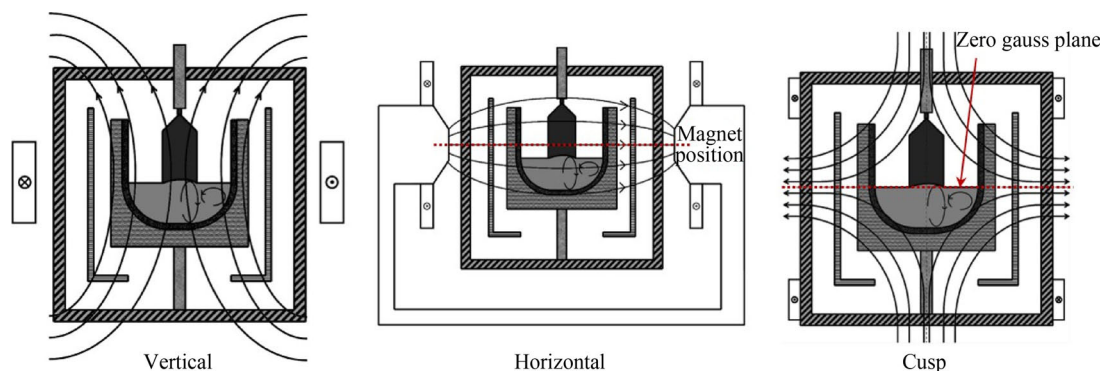
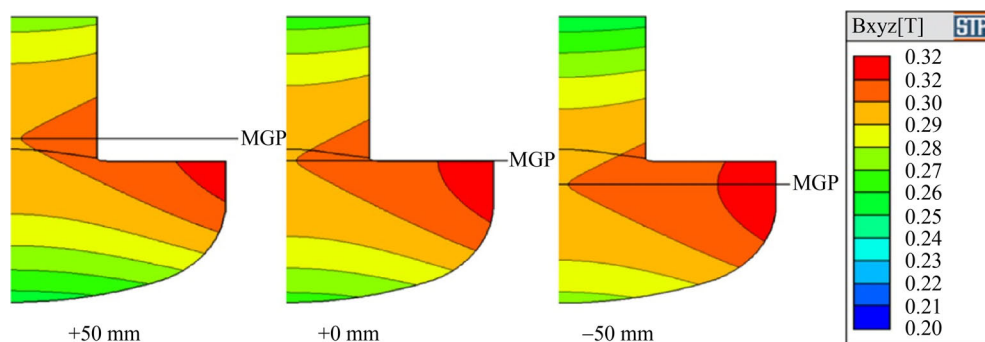
上述研究表明, 晶体和坩埚转速作为核心参数, 对晶体氧浓度具有决定性影响, 但这种影响大小依赖于熔体流动形态, 缺乏普适规律。

图 7 晶体氧浓度随晶体转速变化趋势<sup>[37]</sup>Fig. 7 Trend of crystal oxygen concentration changing with crystal rotation<sup>[37]</sup>

2.2.2 磁场参数控制 直拉单晶硅生长技术最初使用过轴向磁场、横向磁场和勾型磁场 3 种磁场(图 8), 其中轴向磁场由于抑制了径向方向的熔体流动, 导致晶体径向均匀性差和坩埚局部高温, 后被逐渐

弃用。目前, 工业上常用的磁场主要是横向磁场和勾型磁场。横向磁场可以提供高达 0.5 T 的磁场强度, 湍流抑制作用强, 熔体流动较为稳定, 且结晶界面处温度梯度较为平坦, 更容易控制晶体缺陷。勾型磁场能达到的磁场强度则较低, 通常在 0.1 T 左右, 熔体脉动效应较为明显, 但能提供更好的径向均匀性。

横向磁场通常由 2 个竖直放置的线圈通电产生, 其主要控制参数有磁场强度和磁场位置。研究表明, 随磁场强度升高, 晶体氧浓度降低<sup>[51,58]</sup>, 但由于横向磁场会导致熔体流动呈非轴对称, 因此, 晶体的氧径向均匀性通常较差<sup>[37]</sup>。近年来, 磁场空间分布不均匀性开始收到关注, 由于超导线圈无法产生绝对均匀的横向磁场, 磁场中心位置的变化会影响晶体和熔体中的磁场分布(见图 9)。Zou 等<sup>[59]</sup>和 Lou 等<sup>[60]</sup>通过数值模拟和实验发现, 当磁场中心位置位于熔体自由液面下面 75~100 mm 的位置区间时, 坩埚温度显著降低, 晶体的氧浓度下降至最低。

图 8 轴向、横向和勾型静态磁场示意图<sup>[57]</sup>Fig. 8 Schematic diagram of vertical, transverse and cusp magnetic field<sup>[57]</sup>图 9 不同磁场位置(MGP)时晶体和熔体中的磁场强度分布<sup>[60]</sup>Fig. 9 Distribution of magnetic field strength at various magnet positions (MGP)<sup>[60]</sup>

勾型磁场通常由 2 个水平放置嵌套在炉体外部的线圈产生, 在 2 个线圈中心处会产生零高斯面, 其控制参数包括磁场强度、零高斯面位置、线圈电流比等。勾型磁场的优势是在靠近坩埚壁面处可以

提供较高的磁场强度, 从而抑制高氧熔体向晶体输运; 而在晶体区域, 磁场强度几乎为零, 对熔体的抑制作用较弱, 因此, 晶体的径向均匀性较好。目前, 关于勾型磁场的研究较为充分。与横向磁场类

似, 勾型磁场强度越高, 对熔体流动抑制作用越强, 晶体氧浓度越低<sup>[61–62]</sup>。针对零高斯面位置的研究结论一致性较差, Cen 等<sup>[63]</sup>的结果表明, 零高斯面位置越低, 晶体氧浓度最低。Chen 等<sup>[53]</sup>和 Liu 等<sup>[62]</sup>的结果则没有体现出明显的趋势。Kakimoto 等<sup>[64]</sup>和 Vegad 等<sup>[65]</sup>的结果则在零高斯面位于熔体自由液面上方时, 获得氧浓度最低值, 这种结论的不一致性来自设备和工况不同导致的熔体对流状态差异。线圈电流比这一控制参数指的是勾型线圈上下线圈的电流比值, 这会影响勾型磁场的空间分布。如图11所示, 随着电流比增大, 勾型磁场的水平分量逐渐弱, 轴向分量逐渐增强, 且磁场强度整体有所增强, 从而有效抑制熔体流动, 降低晶体氧浓度<sup>[61,66]</sup>。

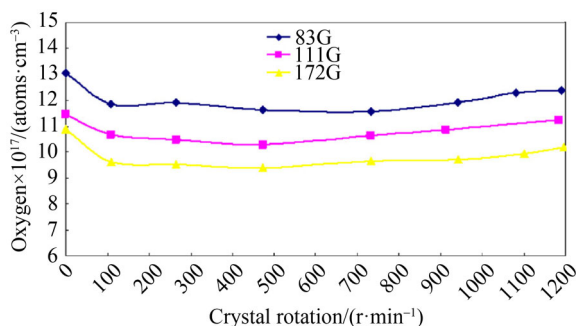


图10 不同勾型磁场强度下晶体氧浓度轴向分布<sup>[61]</sup>

Fig. 10 Axial distribution of crystal oxygen concentrations with various cusp magnetic field intensity<sup>[61]</sup>

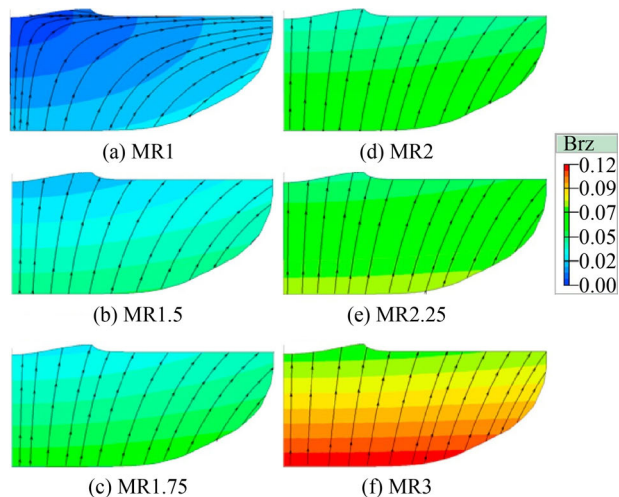


图11 线圈电流比对熔体磁场强度分布的影响<sup>[66]</sup>

Fig. 11 Effect of coil current ratio on distribution of cusp magnetic field in melt<sup>[66]</sup>

Ren 等<sup>[67]</sup>开发了一种新型四极磁场, 其磁场分布如图12所示。由图12可见, 主要磁场分量为横向, 且呈中心弱边缘强的特征, 有望在横向磁场基础上改善晶体氧的径向均匀度。

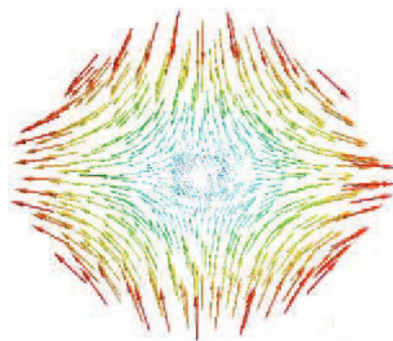


图12 四极磁场分布俯视图<sup>[67]</sup>

Fig. 12 Top view of quadrupole magnetic field distribution<sup>[67]</sup>

上述研究表明, 熔体流动受晶体和坩埚旋转速度、磁场分布和熔体深宽比等多种因素综合影响。在熔体不同流动状态下, 氧输运随控制参数变化规律也明显不同。传统控制变量法及正交实验极其耗时且成本高昂, 难以满足工业需求, 亟须开发高效率、低成本的熔体流动控制方法。

### 2.3 熔体自由液面挥发控制

在生长重掺杂磷、砷和锑单晶硅时, 重掺杂剂会与氧结合形成易挥发物, 从而增强氧在自由液面的挥发, 导致晶体氧浓度随掺杂剂浓度升高而下降<sup>[68]</sup>。在生长轻掺杂单晶硅时, 氧的挥发速率则主要受外部氩气气压和流速的影响。理论上讲, 氩气气压越低, 外部气体分子越稀薄, 更有利于 SiO 挥发反应的进行。而氩气流速越高, 挥发的 SiO 可以跟随氩气越快排出炉体, 从而提高 SiO 的挥发速率。如图13所示, Izunome 等、Teng 等和张文永等的结果表明, 氩气压强越低, 晶体氧浓度越低<sup>[69–71]</sup>。Sim 等<sup>[26]</sup>、Chen 等<sup>[53]</sup>和张文永 等<sup>[71]</sup>的结果表明, 氩气流速越大, 氧浓度越低, 这与理论相符。Teng 等<sup>[72]</sup>通过缩小热屏和坩埚之间的距离(相当于降低氩气流域面积)来增强氩气流速, 从而降低晶体氧浓度。Zhang 等<sup>[35]</sup>、芮阳等<sup>[73]</sup>和王新强等<sup>[74]</sup>则通过优化热屏结构, 抑制了自由液面上方氩气的回流, 从而减少 SiO 气体积累, 降低了晶体氧浓度。热屏结构优化技术通常应用于光伏级单晶硅生长以降低晶体氧浓度, 延长少子寿命。而在半导体级单晶硅生长过程中, 除少子寿命外, 对晶体微缺陷的控制通常具有更高的优先级, 这要求严格调控晶体生长速度( $v$ )与温度梯度( $G$ )的比值(即  $v/G$  值), 以生长出近完美单晶<sup>[75]</sup>。由于热屏结构的更改会显著影响晶体温度梯度<sup>[76–77]</sup>, 进而改变晶体缺陷, 因此, 在半导体级单晶硅生长中, 很少采用更改热屏结构的方法来降低氧浓度。

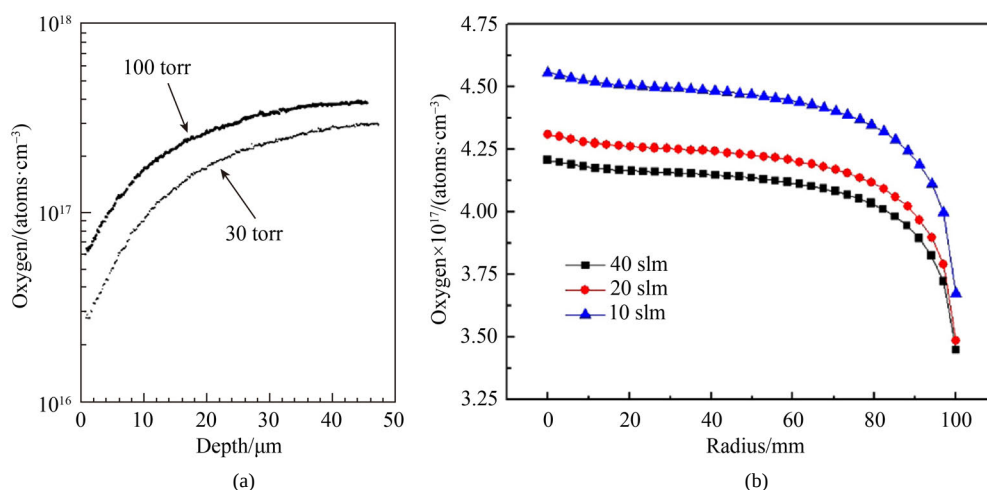


图 13 (a)不同氩气气压下凝固熔体中氧浓度分布<sup>[69]</sup>; (b)不同氩气流量下晶体氧浓度分布<sup>[53]</sup>

Fig. 13 (a) Oxygen concentration profiles for the solidified melts under different argon pressure<sup>[69]</sup>; (b) Distribution of crystal oxygen concentration under different argon flow rates<sup>[53]</sup>

Machida 等<sup>[78]</sup>实验发现, 在无磁场的情况下, 晶体氧浓度随氩气压强降低而升高, 随氩气流速升高而升高, 这与传统的分压理论不符。而在横向磁场下, 晶体氧浓度随氩气流速升高而降低<sup>[79]</sup>, 自由液面的氧挥发过程并非仅由气体压强和流速控制, 还受熔体流动的影响。而在熔体自由液面, 熔体流动主要由温差导致的表面张力差异和氩气流动剪切力驱动<sup>[80-81]</sup>, 其对氧运输的影响还有待进一步研究。

### 3 结论与展望

直拉单晶硅中的氧杂质是影响太阳能电池转化效率和半导体器件性能的关键因素, 其浓度的精确控制仍是该生长技术的核心科学问题。本文从坩埚-熔体界面、熔体自由液面、晶体-熔体界面和熔体流动运输 4 个方面系统阐述了直拉单晶硅生长系统中氧运输的物理机制, 并综述了氧浓度控制技术的研究进展:

1) 坩埚溶解控制: 通过热场优化降低坩埚温度, 或采用坩埚涂层技术改变材料特性以抑制坩埚溶解, 从而减少熔体中氧的来源, 降低晶体氧浓度。

2) 熔体流动运输控制: 通过调节晶体和坩埚转速、磁场参数等控制熔体流动状态, 进而优化氧在熔体中的对流运输过程, 实现对晶体氧浓度的控制。

3) 熔体自由液面挥发控制: 通过控制外部气氛的流量和压强, 影响氧在熔体自由液面的挥发速率, 进而控制晶体的氧浓度。

尽管上述技术在氧控制方面取得显著进展, 但若干关键科学问题尚未完全解决, 仍需进一步探索:

1) 氧溶解度与温度关系: 硅熔体中氧溶解度随温度变化的规律尚未完全明确, 降低坩埚温度减少氧溶解的内在物理机制仍需进一步研究。

2) 磁场分布与熔体流动的关联机制: 磁场线圈的几何形状决定了磁场的空间分布, 其对熔体流动模式及氧运输规律的显著影响有待更细致的研究。

3) 自由液面复杂作用机制: 熔体自由液面的马兰戈尼应力已受到了广泛关注, 但气体流动所产生的剪切应力对挥发过程的影响仍需深入探究。

直拉单晶硅生长系统具有多变量、强耦合的特征, 传统控制变量法和正交实验面临时间和经济成本高昂的挑战, 难以适应工业技术的快速迭代需求, 也难以实现多变量系统的最优调控。近年来, 人工智能与机器学习的兴起正在改变这一传统研究范式。已有研究开始探索基于数据驱动的方法来优化氧浓度控制技术<sup>[82-84]</sup>。未来, 工业级人工智能大模型在复杂系统建模与优化方面的强大能力, 有望为氧浓度的精准预测与智能控制提供新路径, 最终实现多变量系统的协同优化与高效调控。

#### 参考文献:

- [1] YONENAGA I, SUMINO K, HOSHI K. Mechanical strength of silicon crystals as a function of the oxygen concentration[J]. J Appl Phys, 1984, 56(8): 2346-2350.
- [2] HU S M, PATRICK W J. Effect of oxygen on dislocation movement in silicon[J]. J Appl Phys, 1975, 46(5): 1869-1874.
- [3] FUJISE J, KO B, ONO T, et al. Measurement and empirical equation of critical stresses for slip generation from oxide precipitates in silicon wafers[J]. Jpn J Appl Phys, 2018, 57(3): 035501.
- [4] DAWID K. Influence of vacancies introduced by RTA on the nucleation, size, morphology, and gettering efficiency of oxygen precipitates in silicon wafers[D]. Brandenburgischen Technischen

- Universität, Cottbus, 2013.
- [5] LI M H, LIU Y, WEI T, et al. Development of the conductivity type inversion caused by thermal double donors' formation in p-type high-resistivity silicon[J]. *Appl Phys Express*, 2023, 16(3): 031003.
- [6] HU Y, SCHØN H, ØVRELID E J, et al. Investigating thermal donors in n-type Cz silicon with carrier density imaging[J]. *AIP Adv*, 2012, 2(3): 032169.
- [7] 张梦宇, 李太, 杜汕霖, 等. 直拉法单晶硅制备过程控氧技术研究进展[J]. *硅酸盐通报*, 2022, 41(9): 3259–3271.
- ZHANG Mengyu, LI Tai, DU Shanlin, et al. *Bull Chin Ceram Soc*, 2022, 41(9): 3259–3271.
- [8] TSUYA H. Chapter 14 Oxygen Effect on Electronic Device Performance. WILLARDSON R K, BEER A C, WEBER E R. *Semiconductors and Semimetals: Vol. 42*. San Diego: Academic Press, 1994: 619–667.
- [9] IWAMURO N, LASKA T. IGBT history, state-of-the-art, and future prospects[J]. *IEEE Trans Electron Devices*, 2017, 64(3): 741–752.
- [10] JANG E K, KIM I J, LEE C A, et al. Analysis of residual stresses induced in the confined 3D NAND flash memory structure for process optimization[J]. *IEEE J Electron Devices Soc*, 2022, 10: 104–108.
- [11] EKHULT U, CARLBERG T. Oxygen solubility in liquid silicon in equilibrium with SiO and SiO<sub>2</sub>[J]. *J Electrochem Soc*, 136(2): 551–554.
- [12] HIRATA H, HOSHIKAWA K. Oxygen solubility and its temperature dependence in a silicon melt in equilibrium with solid silica[J]. *J Cryst Growth*, 1990, 106(4): 657–664.
- [13] HUANG X M, TERASHIMA K, SASAKI H, et al. Oxygen solubilities in Si melt: Influence of Sb addition[J]. *Jpn J Appl Phys*, 1993, 32(9R): 3671.
- [14] LUO J P, ZHOU C Y, LI Q H, et al. Diffusion coefficients of carbon, oxygen and nitrogen in silicon melt[J]. *J Cryst Growth*, 2022, 580: 126476.
- [15] TOGAWA S, HUANG X M, IZUNOME K, et al. Oxygen transport analysis in Czochralski silicon melt by considering the oxygen evaporation from the melt surface[J]. *J Cryst Growth*, 1995, 148(1/2): 70–78.
- [16] SMIRNOV A D, KALAEV V V. Development of oxygen transport model in Czochralski growth of silicon crystals[J]. *J Cryst Growth*, 2008, 310(12): 2970–2976.
- [17] TRUMBORE F A. Solid solubilities of impurity elements in germanium and silicon[J]. *Bell Syst Tech J*, 1960, 39(1): 205–233.
- [18] BORGHESI A, PIVAC B, SASSELLA A, et al. Oxygen precipitation in silicon[J]. *J Appl Phys*, 1995, 77(9): 4169–4244.
- [19] LIN W, HILL D W. Oxygen segregation in czochralski silicon growth[J]. *J Appl Phys*, 1983, 54(2): 1082–1085.
- [20] NGUYEN T H T, CHEN J C, LI C H. Controlling the heat, flow, and oxygen transport by double-partitions during continuous Czochralski (CCz) silicon crystal growth[J]. *Mater Sci Semicond Process*, 2023, 155: 107235.
- [21] NGUYEN T H T, CHEN J C, LO S C. Effects of different partition depths on heat and oxygen transport during continuous Czochralski (CCz) silicon crystal growth[J]. *J Cryst Growth*, 2022, 583: 126546.
- [22] POPESCU A, BELLMANN M P, VIZMAN D. Effect of crucible rotation on the temperature and oxygen distributions in Czochralski grown silicon for photovoltaic applications[J]. *CrystEngComm*, 2021, 23(2): 308–316.
- [23] ZHOU B, CHEN W L, LI Z H, et al. Reduction of oxygen concentration by heater design during Czochralski Si growth[J]. *J Cryst Growth*, 2018, 483: 164–168.
- [24] 商润龙, 陈亚, 芮阳, 等. 加热器结构对轻掺磷超低氧直拉单晶硅氧杂质分布的影响[J]. *人工晶体学报*, 2025, 54(5): 801–808.
- SHANG Runlong, CHEN Ya, RUI Yang, et al. *J Synth Cryst*, 2025, 54(5): 801–808.
- [25] LIU P D, HU Z C, YANG Y, et al. Reduction of oxygen concentration in 300 mm diameter n-type Czochralski silicon crystal growth using an optimized heating zone with dual side-heaters[J]. *CrystEngComm*, 2024, 26(29): 3920–3928.
- [26] SIM B C, LEE I K, KIM K H, et al. Oxygen concentration in the Czochralski-grown crystals with cusp-magnetic field[J]. *J Cryst Growth*, 2005, 275(3/4): 455–459.
- [27] TENG Y Y, CHEN J C, LU C W, et al. Numerical simulation of the effect of heater position on the oxygen concentration in the CZ silicon crystal growth process[J]. *Int J Photoenergy*, 2012, 2012(1): 395235.
- [28] ZHAO L, LI T, HUANG Z L, et al. Effect of heater structure on oxygen concentration in large diameter n-type Czochralski silicon study using numerical simulation[J]. *Appl Therm Eng*, 2024, 257: 124334.
- [29] DEZFOLI A R A. Engineering insights into heater design for oxygen reduction in CZ silicon growth[J]. *Case Stud Therm Eng*, 2025, 65: 105596.
- [30] 李建斌, 钟泽琪, 王军磊, 等. 直拉法单晶硅生长的氧含量控制研究[J/OL]. *人工晶体学报*, 2025.
- LI Jiancheng, ZHONG Zeqi, WANG Junlei, et al. *J Synth Cryst*, 2025.
- [31] LI J C, WANG J L, LIU L J, et al. A novel approach to reduce the oxygen content in monocrystalline silicon by Czochralski method[J]. *J Cryst Growth*, 2024, 630: 127608.
- [32] 王新强, 景华玉, 王小亮, 等. 隔热环的位置对直拉单晶硅氧含量的影响[Z]. *新技术新工艺*. 2024(1): 7376.
- WANG Xinqiang, JING Huayu, WANG Xiaoliang, et al. *New Technology & New Process*, 2024(1): 73–76.
- [33] XIAO Z C, WAN X H, MA W H, et al. Effects of heater and insulation ring designs on oxygen content of large-diameter silicon grown by czochralski method[J]. *Silicon*, 2025, 17(7): 1747–1756.
- [34] NGUYEN T H T, CHEN J C, CHEN C C. The effects on heat and oxygen transport of different heat shield and sidewall insulation designs during continuous Czochralski silicon crystal growth[J]. *J Cryst Growth*, 2024, 641: 127762.
- [35] ZHANG J, LIU D, ZHAO Y, et al. Impact of heat shield structure in the growth process of Czochralski silicon derived from numerical simulation[J]. *Chin J Mech Eng*, 2014, 27(3): 504–510.
- [36] NGUYEN T H T, CHEN J C, CHEN C C. Effects of different crucible shapes on heat and oxygen transport during continuous Czochralski silicon crystal growth[J]. *J Cryst Growth*, 2024, 626: 127474.
- [37] LIU W K, CHEN S S, JIANG F M, et al. Numerical and experimental investigation of oxygen transport in 300 mm Czochralski silicon crystal growth with transverse magnetic fields[J]. *Vacuum*, 2025, 233: 113994.
- [38] HUANG X M, KOH S, WU K H, et al. Reaction at the interface between Si melt and a Ba-doped silica crucible[J]. *J Cryst Growth*, 2005, 277(1/4): 154–161.
- [39] High Temperature Oxidation of Silicon Nitride Based Ceramics: A Review[M]. HIERRA E J, SALAZAR J A. *Silicon nitride: synthesis, properties and applications*. New York: Nova Science Publishers, 2012: 1–31.

- [40] STURM F, TREMPA M, SCHUSTER G, et al. Material evaluation for engineering a novel crucible setup for the growth of oxygen free Czochralski silicon crystals[J]. *J Cryst Growth*, 2022, 584: 126582.
- [41] LIU X, GAO B, NAKANO S, et al. Reduction of carbon contamination during the melting process of Czochralski silicon crystal growth[J]. *J Cryst Growth*, 2017, 474: 3–7.
- [42] GAO B, KAKIMOTO K. Carbon impurity in crystalline silicon[M]. *Handbook of Photovoltaic Silicon*. Berlin, Heidelberg: Springer Berlin Heidelberg, 2019: 437–462.
- [43] SUN Q, YAO K H, GATOS H C, et al. Effects of nitrogen on oxygen precipitation in silicon[J]. *J Appl Phys*, 1992, 71(8): 3760–3765.
- [44] TUO H, LIU Y, LI M H, et al. Secondary defects of as-grown oxygen precipitates in nitrogen doped Czochralski single crystal silicon[J]. *Mater Sci Semicond Process*, 2023, 163: 107583.
- [45] YU X G, YANG D R, MA X Y, et al. Grown-in defects in nitrogen-doped czochralski silicon[J]. *J Appl Phys*, 2002, 92(1): 188–194.
- [46] Friedrich J, Von Ammon W, Müller G. 2 - Czochralski Growth of Silicon Crystals. RUDOLPH P. *Handbook of Crystal Growth* (Second Edition). Amsterdam: Elsevier, 2015: 45–104.
- [47] LI J C, LI Z Y, LIU L J, et al. Effects of melt depth on oxygen transport in silicon crystal growth by continuous-feeding Czochralski method[J]. *J Cryst Growth*, 2023, 610: 127180.
- [48] LIU X, HARADA H, MIYAMURA Y, et al. Transient global modeling for the pulling process of Czochralski silicon crystal growth. II. Investigation on segregation of oxygen and carbon[J]. *J Cryst Growth*, 2020, 532: 125404.
- [49] HOSHI K, ISAWA N, SUZUKI T, et al. Czochralski silicon crystals grown in a transverse magnetic field[J]. *J Electrochem Soc*, 132(3): 693–700.
- [50] NGUYEN T H T, CHEN J C, HU C, et al. Numerical simulation of heat and mass transfer during Czochralski silicon crystal growth under the application of crystal-crucible counter- and iso-rotations[J]. *J Cryst Growth*, 2019, 507: 50–57.
- [51] ZHANG J, REN J C, LIU D. Effect of crucible rotation and crystal rotation on the oxygen distribution at the solid-liquid interface during the growth of Czochralski monocrystalline silicon under superconducting horizontal magnetic field[J]. *Results Phys*, 2019, 13: 102127.
- [52] NGUYEN T H T, CHEN J C, HU C, et al. Effects of crystal-crucible iso-rotation and a balanced/unbalanced cusp magnetic field on the heat, flow, and oxygen transport in a Czochralski silicon melt[J]. *J Cryst Growth*, 2020, 531: 125373.
- [53] CHEN J C, GUO P C, CHANG C H, et al. Numerical simulation of oxygen transport during the Czochralski silicon crystal growth with a cusp magnetic field[J]. *J Cryst Growth*, 2014, 401: 888–894.
- [54] CHEN J C, CHIANG P Y, CHANG C H, et al. Three-dimensional numerical simulation of flow, thermal and oxygen distributions for a Czochralski silicon growth with in a transverse magnetic field[J]. *J Cryst Growth*, 2014, 401: 813–819.
- [55] CHEN J C, CHIANG P Y, NGUYEN T H T, et al. Numerical simulation of the oxygen concentration distribution in silicon melt for different crystal lengths during Czochralski growth with a transverse magnetic field[J]. *J Cryst Growth*, 2016, 452: 6–11.
- [56] NGUYEN T P, CHEN J C. Effect of crucible and crystal rotations on the solute distribution in large size sapphire crystals during Czochralski growth[J]. *Int J Heat Mass Transf*, 2019, 130: 1307–1321.
- [57] VIZMAN D. Flow Control by Magnetic Fields during Crystal Growth from Melt[M/OL]. *Handbook of Crystal Growth*. Elsevier, 2015: 909–950.
- [58] RAVISHANKAR P S, BRAGGINS T T, THOMAS R N. Impurities in commercial-scale magnetic czochralski silicon: Axial versus transverse magnetic fields[J]. *J Cryst Growth*, 1990, 104(3): 617–628.
- [59] ZOU Q P, SHENG W, CHEN W N, et al. Effect of horizontal magnetic field position on oxygen distribution in CZ silicon crystal growth[J]. *Vacuum*, 2024, 225: 113271.
- [60] LOU Z S, XUE Z X, YUAN S, et al. Effects of horizontal magnetic field position on oxygen control in 12-inch Czochralski silicon[J]. *J Cryst Growth*, 2024, 646: 127861.
- [61] HONG Y H, SIM B C, SHIM K B. Effect of zero-Gauss plane and magnetic intensity on oxygen concentration in cusp-magnetic CZ crystals[J]. *J Cryst Growth*, 2006, 295(2): 141–147.
- [62] LIU X, LIU L J, LI Z Y, et al. Effects of cusp-shaped magnetic field on melt convection and oxygen transport in an industrial CZ-Si crystal growth[J]. *J Cryst Growth*, 2012, 354(1): 101–108.
- [63] CEN X R, GUO S X. Three-dimensional simulation of melt convection and oxygen transport in CZ-Si crystal growth with cusp magnetic fields[J]. *Crystals*, 2023, 13(10): 1436.
- [64] KAKIMOTO K, LIU X, NAKANO S. Analysis of the effect of cusp-shaped magnetic fields on heat, mass, and oxygen transfer using a coupled 2D/3D global model[J]. *Cryst Res Technol*, 2022, 57(1): 2100092.
- [65] VEGAD M, BHATT N M. Effect of location of zero Gauss plane on oxygen concentration at crystal melt interface during growth of magnetic silicon single crystal using czochralski technique[J]. *Procedia Technol*, 2016, 23: 480–487.
- [66] NGUYEN T H T, CHEN J C. Effects of different cusp magnetic ratios and crucible rotation conditions on oxygen transport and point defect formation during Cz silicon crystal growth[J]. *Mater Sci Semicond Process*, 2021, 128: 105758.
- [67] REN J C, LIU D, WAN Y. Effects of Control Parameters on Oxygen Distribution in Czochralski Crystal Growth Process[C/OL]. 2018 Chinese Automation Congress (CAC). 2018: 2353–2358.
- [68] SCALA R, PORRINI M, VORONKOV V. Impact of arsenic and phosphorus concentration on oxygen content in heavily doped silicon single crystal[J]. *J Cryst Growth*, 2020, 548: 125820.
- [69] IZUNOME K, HUANG X M, TOGAWA S, et al. Control of oxygen concentration in heavily antimony-doped Czochralski Si crystals by ambient argon pressure[J]. *J Cryst Growth*, 1995, 151(3/4): 291–294.
- [70] TENG Y Y, CHEN J C, LU C W, et al. Effects of the furnace pressure on oxygen and silicon oxide distributions during the growth of multicrystalline silicon ingots by the directional solidification process[J]. *J Cryst Growth*, 2011, 318(1): 224–229.
- [71] 张文永, 高德东, 王珊, 等. 磁控直拉法单晶硅熔料阶段氧碳杂质传输仿真研究[J]. *山东化工*, 2025, 54(4): 1–5.  
ZHANG Wenyong, GAO Dedong, WANG Shan, et al. *Shandong Chem Ind*, 2025, 54(4): 1–5.
- [72] TENG Y Y, CHEN J C, HUANG C C, et al. Numerical investigation of the effect of heat shield shape on the oxygen impurity distribution at the crystal–melt interface during the process of Czochralski silicon crystal growth[J]. *J Cryst Growth*, 2012, 352(1): 167–172.
- [73] 芮阳, 王忠保, 盛旺, 等. 热屏结构对 200 mm 半导体级提拉单晶硅中氧含量分布的影响[J]. *人工晶体学报*, 2023, 52(6): 1110–1119.  
RUI Yang, WANG Zhongbao, SHENG Wang, et al. *J Synth Cryst*, 2023, 52(6): 1110–1119.

- [74] 王新强, 景华玉, 王小亮, 等. 导流筒的底部结构对直拉单晶硅氧含量的影响[Z]. 新技术新工艺, 2024(3): 63–66.  
WANG Xinqiang, JING Huayu, WANG Xiaoliang, et al. New Technology & New Process, 2024(3): 63–66.
- [75] 刘赞, 薛忠营, 魏星, 等. 直拉单晶硅晶体缺陷研究进展[J]. 微纳电子与智能制造, 2022, 4(1): 64–74.  
LIU Yun, XUE Zhongying, WEI Xing, et al. Micro/nano Electron Intell Manuf, 2022, 4(1): 64–74.
- [76] SU W J, ZUO R, MAZAEV K, et al. Optimization of crystal growth by changes of flow guide, radiation shield and sidewall insulation in Cz Si furnace[J]. J Cryst Growth, 2010, 312(4): 495–501.
- [77] SABANSKIS A, PLĀTE M, SATTTLER A, et al. Evaluation of the performance of published point defect parameter sets in cone and body phase of a 300 mm czochralski silicon crystal[J]. Crystals, 2021, 11(5): 460.
- [78] MACHIDA N, SUZUKI Y, ABE K, et al. The effects of argon gas flow rate and furnace pressure on oxygen concentration in Czochralski-grown silicon crystals[J]. J Cryst Growth, 1998, 186(3): 362–368.
- [79] MACHIDA N, HOSHIKAWA K, SHIMIZU Y. The effects of argon gas flow rate and furnace pressure on oxygen concentration in Czochralski silicon single crystals grown in a transverse magnetic field[J]. J Cryst Growth, 2000, 210(4): 532–540.
- [80] SUEWAKA R, NISHIZAWA S I. Impact of Marangoni effect of oxygen on solid–liquid interface shape during Czochralski silicon growth applied with transverse magnetic field[J]. J Cryst Growth, 2023, 607: 127123.
- [81] IIZUKA M, MUKAIYAMA Y, DEMINA S E, et al. Melt flow before crystal seeding in Cz Si growth with transversal MF[J]. J Cryst Growth, 2017, 468: 510–513.
- [82] KUTSUKAKE K, NAGAI Y T, HORIKAWA T, et al. Real-time prediction of interstitial oxygen concentration in Czochralski silicon using machine learning[J]. Appl Phys Express, 2020, 13(12): 125502.
- [83] KUTSUKAKE K, NAGAI Y, BANBA H. Virtual experiments of Czochralski growth of silicon using machine learning: Influence of processing parameters on interstitial oxygen concentration[J]. J Cryst Growth, 2022, 584: 126580.
- [84] QI X F, MA W C, DANG Y F, et al. Optimization of the melt/crystal interface shape and oxygen concentration during the Czochralski silicon crystal growth process using an artificial neural network and a genetic algorithm[J]. J Cryst Growth, 2020, 548: 125828.

## Research Progress on Oxygen Concentration Control Technology of Czochralski Monocrystalline Silicon

LIU Wenkai<sup>1</sup>, LIU Yun<sup>1</sup>, XUE Zhongying<sup>1,2</sup>, WEI Xing<sup>1,2</sup>

(1. State Key Laboratory of Materials for integrated Circuits, Shanghai institute of Microsystem and Information Technology, Shanghai 200050, China; 2. Shanghai Key Laboratory of Advanced Silicon-Based Materials, Shanghai 200050, China)

### Abstract

Czochralski (CZ) monocrystalline silicon is a dominant substrate material for integrated circuit manufacturing, accounting for over 90% of global silicon wafer production. During CZ silicon growth, oxygen impurities dissolve from quartz crucibles ( $\text{SiO}_2$ ) into silicon melt at sustained high temperatures, ultimately incorporating into the crystal lattice. Oxygen in silicon affects essential substrate properties, including resistivity, mechanical strength, metal gettering capability, and carrier lifetime. Different applications impose divergent oxygen specifications. For instance, solar cells require concentrations of  $<7 \times 10^{17} \text{ atoms} \cdot \text{cm}^{-3}$  to minimize minority carrier lifetime degradation. Insulate Gate Bipolar Transistor (IGBT) power devices demand ultra-low oxygen (*i.e.*,  $<2.5 \times 10^{17} \text{ atoms} \cdot \text{cm}^{-3}$ ) to suppress leakage current and breakdown voltage fluctuations. Furthermore, 3D-NAND flash memory necessitates a precise oxygen precipitate control to balance thermo-mechanical stress in multi-layer architectures. It is thus paramount for device performance and manufacturing yield to understand oxygen transport physics and achieve precise concentration control.

Oxygen transport in Cz silicon growth involves four primary mechanisms, *i.e.*, 1) Crucible Dissolution: Oxygen dissolves from the quartz crucible wall into the silicon melt *via* the reaction ( $\text{SiO}_2(\text{s}) \rightleftharpoons \text{Si}(\text{l}) + 2\text{O}(\text{l})$ ). The temperature dependence of oxygen solubility remains a subject of debate, 2) Melt Transport: Dissolved oxygen moves through the melt *via* convection and diffusion (governed by convection-diffusion equations), heavily influenced by melt flow dynamics, 3) Free Surface Volatilization: Oxygen evaporates at the melt surface as SiO gas ( $\text{Si}(\text{l}) + \text{O}(\text{l}) \rightleftharpoons \text{SiO}(\text{g})$ ), affected by argon ambient pressure and flow rate, and 4) Crystallization Segregation: The amount of oxygen that incorporates into crystal at the solid–liquid interface is affected by the solubility difference of oxygen between the silicon melt and the crystal. The complex, highly nonlinear interplay between these mechanisms presents a core scientific challenge. As segregation effects are dominated by the intrinsic characteristics of oxygen and silicon atoms and are difficult to control, the related research advancements involve.

1) Crucible Dissolution Control: Conventional approaches focus on thermal field optimization. Implementing dual-heater systems improves power distribution, compared to single heaters, effectively lowering localized crucible temperatures and subsequently reducing crystal oxygen content. Alternative strategies involve material modifications, such as applying  $\text{Si}_3\text{N}_4$  coatings to quartz crucibles or using graphite crucibles with similar coatings, which can significantly suppress oxygen dissolution. However, these material substitutions introduce substantial trade-offs, including elevated carbon contamination (*i.e.*,  $>5 \times 10^{17} \text{ atoms} \cdot \text{cm}^{-3}$ ) and nitrogen doping (*i.e.*,  $>3 \times 10^{15} \text{ atoms} \cdot \text{cm}^{-3}$ ), requiring a further evaluation.

2) Melt Flow Control: Melt convection plays a pivotal role in oxygen transport. Precise manipulation of crystal and crucible

rotation rates and directions impacts flow patterns and oxygen distribution, though identifying optimal settings becomes a challenge due to complex, field-dependent behavior. Magnetic fields are essential for stabilizing turbulent flow in large melts and reducing oxygen concentration consequently. Transverse Magnetic Fields (TMF) provide a strong turbulence suppression (*i.e.*, 0.5 T) but often induce radial oxygen non-uniformity. Conversely, Cusp Magnetic Fields (CMF) offer a better radial uniformity but with lower field strengths (*i.e.*, 0.1 T). The impact of Zero-Gauss plane (ZGP) position and coil current ratio varies considerably, indicating context-specific dependence. Innovations like quadrupole magnetic fields show a promise for unifying transverse-field stability with an enhanced radial homogeneity.

3) Free surface Volatilization Control: This strategy is to control oxygen concentration *via* SiO evaporation *via* manipulating the ambient argon environment. Lower argon pressure and higher argon flow rates generally promote SiO volatilization kinetics and reduce crystal oxygen incorporation, as reduced gas-phase partial pressure facilitates oxygen evaporation at the melt-gas interface. This relationship is consistently determined in both experimental measurements and theoretical models. Complementing gas parameter adjustments, heat shield design optimization offers a secondary control *via* altering the gas flow geometry above the melt. Specifically, tailored shield structures minimize argon recirculation zones that otherwise trap SiO vapor, thereby reducing local saturation and enhancing overall volatilization efficiency. However, shield modifications are less common in semiconductor-grade silicon production because they affect thermal gradients near the crystal, potentially disrupting the critical  $v/G$  ratio required for defect-free crystal growth. Furthermore, volatilization efficiency is not solely governed by gas dynamics. Complex interface phenomena on the melt surface (*i.e.*, Marangoni convection and argon shear stress effects) also significantly affect oxygen evaporation rates. The interaction between these melt-surface flows and gas-phase mass transfer remains inadequately quantified, representing an important area for future fundamental research to fully exploit volatilization-based oxygen control strategies.

**Summary and prospects** This review analyzes critical oxygen control strategies in CZ silicon growth, essential for achieving substrate specifications across diverse applications. The primary approaches focus on reducing oxygen dissolution through thermal field design and crucible modification, optimizing melt convection and oxygen transport *via* rotation and magnetic fields, and enhancing free surface volatilization by controlling argon atmosphere.

Some challenges persist, requiring a further research to clarify fundamental mechanisms. Key uncertainties include the temperature dependence of oxygen solubility and the precise mechanism relating crucible temperature reduction to lower crystal oxygen levels (primarily due to reduced dissolution or altered flow patterns). Understanding the complex coupling among detailed magnetic field distributions, resulting melt flow patterns and oxygen transport also requires a further investigation. Quantifying the influence of argon shear stress interacting with Marangoni forces on the melt surface is equally essential for refining volatilization models.

Furthermore, complicating these challenges is the multi-variable, strongly coupled nature of the CZ system, which makes conventional trial-and-error optimization approaches time-consuming and costly. A future research should therefore prioritize the developing intelligent control systems that leverage artificial intelligence (AI) and machine learning for data-driven modeling, prediction, and efficient multi-parameter optimization.

**Keywords** Czochralski monocrystalline silicon; oxygen transport; crucible dissolution; melt flow; melt free surface volatilization