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原子层沉积过程的多物理场耦合研究与工艺优化

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摘 要

作为一种纳米级薄膜制备方法，原子层沉积（atomic Layer Deposition, ALD）技术在太阳能电池、柔性显示、锂电能源等新兴领域具有广泛的应用前景。然而， ALD 是一个复杂的多尺度多物理场耦合过程，涉及宏观、特征、微观尺度和流场、浓度场、温度场的非线性耦合，且基底的运动和外场的引入会使薄膜沉积过程更加复杂。为了实现快速、低成本的薄膜制造，有必要充分理解 ALD 过程中的流体流动、传热传质、化学反应行为，并建立工艺结构参数与薄膜沉积速率、前驱体利用率的定量联系，为 ALD 的高效制备工艺提供理论指导。本文主要研究内容和创新之处在于：

（1）发展了耦合流动、传热、传质与表面反应的动网格 ALD 数值模型，研究了基底运动、超声振动对反应器流场、浓度场的影响，建立了基底速度、基底微结构高度、载气流量、前驱体分压、前驱体脉冲时间等参数与薄膜沉积速率、前驱体利用率的定量联系。通过与薄膜沉积速率的实验数据的对比验证了模型的有效性和准确性。

（2）揭示了空间隔离 ALD 中基底运动对前驱体的拖曳效应和微结构对前驱体传质的阻碍作用，发现前驱体供应不足和扩散速率慢是限制多孔极片内的前驱体渗透速率和薄膜沉积效率的主要原因。通过定量优化载气流量、基底速度与极片孔隙结构，可将极片内理论上的薄膜沉积深度提升一倍，且前驱体利用率提升两倍以上。

（3）阐明了超声振动通过增大颗粒间碰撞力和气固相间曳力实现颗粒解团聚的作用机理。通过定量调控超声振动频率、振幅和前驱体脉冲时间，可在保证颗粒包覆均匀性大于 99%的前提下，定量优化固定前驱体入口浓度条件下的前驱体利用率。

本文建立了耦合计算流体力学与化学反应的空间隔离 ALD 和流化床 ALD 数值模型，构建了宏观工艺结构参数与薄膜沉积速率、前驱体利用率的定量联系，通过定量结构与工艺优化提升了薄膜的沉积效率。最后面向米级幅宽的基底与百公斤级颗粒材料的沉积，对变微间隙带的空间隔离 ALD 与多点超声流化床 ALD 进行了建模与工艺优化，推动了 ALD 技术在太阳能电池、锂电能源领域的工程应用。

关键词：原子层沉积；多物理场耦合；计算流体力学；化学反应；工艺优化

Abstract

As a nanoscale thin film fabrication method, atomic layer deposition (ALD) has promising applications in emerging fields such as solar cells, flexible displays, and lithium-ion batteries. However, ALD is a complex multiscale and multi-physics coupling process which includes nonlinear coupling of macroscopic, feature, and microscopic scales, as well as fluid flow, heat and mass transfer, and chemical reactions. Besides, the movement of the substrate and the introduction of external fields will make the film deposition process even more complex. To achieve rapid and cost-effective manufacturing, it is essential to comprehensively understand the fluid dynamics, heat and mass transfer, and chemical reactions in the ALD process. Quantitative analyses between process parameters and deposition efficiency, including the thin film deposition rate and precursor utilization efficiency, should also be carried out to provide theoretical guidance for process optimization and equipment design. The main research focus and innovations of this paper are as follows:

(1) The dynamic mesh model of ALD coupling the fluid flow, heat and mass transfer, and surface reaction was established. The effects of the substrate movement and the ultrasonic vibration on the reactor flow and concentration fields were investigated. The quantitative correlation between the process parameters and the film deposition rate and precursor utilization rate were clarified, including the substrate velocity, substrate microgroove height, the carrier gas flow rate, and the precursor partial pressure. The validation and accuracy of the model are verified by the experimental data of the film deposition rate.

(2) The drag effect of moving substrate and the hindering effect of microstructures on the precursor concentration distribution in spatial ALD were revealed. It was also revealed that insufficient precursor supply and slow precursor diffusion rate within the electrode limit the precursor infiltration rate and the coating efficiency within the porous electrode. By quantitatively optimizing the carrier gas flow rate, substrate velocity, and electrode porosity, the theoretical film deposition depth can be doubled and the precursor utilization rate can be increased by more than twice.

(3) The mechanism of ultrasonic vibration to achieve particle deagglomeration by increasing the collision force between particles and the drag force between gas and solid phases was clarified. Under the condition of a fixed precursor concentration at the inlet, the frequency and amplitude of ultrasonic vibration, and the precursor pulse time were quantitatively optimized to optimize the precursor utilization with a coating uniformity greater than 99%.

By coupling the computational fluid dynamics and chemical reactions, the multi-physics modeling of spatial ALD and fluidized bed ALD was established. Effects of macroscopic process structural parameters on thin film deposition rate, and precursor utilization efficiency were quantitatively studied. Quantitative structural and process optimization were carried out to improve the film deposition efficiency. Finally, for the engineering application of thin film deposition on large-area solar glass panels and the coating of batch lithium battery particle materials, studies of modelling and process optimization of spatial ALD with variable micro-gap size and multi-point ultrasonic vibration-enhanced fluidized bed ALD were conducted, which promoted the application of ALD in solar cells, Engineering applications in the field of lithium battery energy.

Keywords: atomic layer deposition (ALD); multi-physics field coupling; computational fluid dynamics; chemical reaction; process optimization