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博 士 学 位 论 文

电纺直写射流的稳定性控制及应用研究

Control and Applications of Stable Jet in Electrohydrodynamic Direct-Writing Technology

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摘 要

电纺直写技术克服了传统喷印技术液滴体积大、墨水要求严格等缺点，已经在微纳制造领域显示出了巨大的应用潜力。如何提高射流稳定性和喷印结构的均匀性是目前研究的重点，也是促进电纺直写技术应用发展的前提。本文将针对电纺直写射流的喷射规律调控、喷射状态监测与控制等方面展开研究，并且探索电纺直写技术在微纳制造领域的应用。

首先，通过实验考察工艺参数对射流喷射过程的影响，分析了不同喷射模式及稳态射流的工艺调控规律；通过建立仿真模型分析了实验参数对射流直径的影响，电纺直写射流拉伸率较小，沉积于收集板时射流直径主要取决于初始直径。对于稳态喷射下的液态射流沉积，若收集板运动速度小于射流喷射速度，则其结构线宽 W 主要受供液速度 Q 和收集板运动速度 v 影响，有 $W^2 \sim Q/v$。

其次，考察了射流的两种不稳定现象：(1) 探索了射流悬挂珠链结构的形成机理，悬挂珠链结构源于收集板上已沉积溶液表面电荷的不断积累；当主液滴所携带的电荷达到“雷诺极限”时，就会抑制后续带电射流的继续融入；溶液表面电荷产生的库仑斥力促使后续射流在空中聚集成为悬空的珠粒，继而形成珠链结构；降低电压、提高溶液和收集板电导率都可以抑制这种不稳定现象的产生；(2) 研究了射流鞭动不稳定性的环境作用规律，真空度的减小可抑制射流的不稳定鞭动，但过小的真空度不利于射流的产生；当真空度从 101kPa 减小到 30kPa 时，PVP/甘油溶液的稳定射流长度由 31.4mm 增加到 100mm。环境湿度的增加也会增强射流稳定性，但增强幅度较小；而温度的增加则会增强射流的不稳定鞭动。通过调节真空度成功实现了远距离(100mm)条件下的有序纳米纤维电纺直写及图案化沉积控制，为传统静电纺丝技术提供了一种射流稳定性及沉积范围实时可控的新途径。

分析了不同喷射模式的电流特性，研究了稳定电纺直写过程中电流与实验参数的关系。电纺直写电流将随着电压和供液速度的增加而增加；电流与射流直径呈正相关性。根据电流规律搭建了电流闭环反馈控制系统，通过稳定喷射过程中

的电流值来提高射流的稳定性和电纺直写微纳结构的均匀性。加入电流闭环反馈控制后，电纺直写纳米纤维及微米薄膜的均匀性都有一定程度的提高，纳米纤维直径及微米薄膜线宽的变异系数均小于 0.1。

运用电纺直写技术制作了典型元件的原理样机。以银墨水为原料喷印导电功能性微纳结构，可获得直径 45~55 μm 的离散银液滴和 60 μm 线宽的直线结构；实现了电阻、电感、电容等无源元件及柔性电路的全喷印制造。利用电纺直写纳米纤维做牺牲层，实现了宽度 133nm~13.54μm 的微纳沟道的低成本、快速制作。利用电纺直写技术在图案化硅基底上制作 ZnO 半导体纳米纤维，构造了 n 型 ZnO 纳米纤维场效应器件及 ZnO/CuO 纳米纤维 pn 结等有源元件。

本文的研究结果有助于加深对电纺直写射流喷射规律的理解，实现射流喷射行为的有效监测与调控，进一步提高射流的均匀性和稳定性，对于推动电纺直写技术的产业化应用和精密电纺直写系统设备的开发具有推动作用。

关键词：电纺直写；射流喷印；稳定性控制；微纳结构；电流反馈

Abstract

Electrohydrodynamic Direct-Writing (EDW) is one of the inkjet printing technologies that untilizes electric field to generate droplets and lines. By overcoming the disadvantages of large pirnting droplet and poor material compatibility of traditional inkjet printing, EDW has displayed great potential micro/nano-manufacturing. Improving the stability of jet and uniformity of deposited patterns are the important issues which dominate the application and development of EDW technology. Thus, the control and applications of stable jet in EDW are discussed in this dissertation.

The influences of process parameters on EDW jetting are investigated, and the ejection modes as well as the control of stable jet are explored. A simulation of stable cone-jet is proceeded to investigate the effect of experimental parameters on the jet diameter. The results demonstrate that the the liquid jet has smaller stretching ration, and the diameter of liquid jet nearby the collector mainly depends on the initial stage. Both experimental results and model analysis indicate that the line width of deposited patterns W is mainly affected by the flow rate of liquid Q and the motion speed of collector v, scaled as $W^2 \sim Q/v$, when v is slower than the jet velocity.

Two types of jet instability are discussed. Firstly, the instability principle of suspended bead-on-a-string structure (SBS) in EDW jet is studied. It is found that the SBS results from the accumulation of free charges on the deposited pattern. The large Coulomb repulsive force blocks the coalescence of following liquid jet and the jet can only accumulates above the primary droplet to form a suspended secondary droplet. By reducing the applied voltage or increasing the conductivity of liquid/collector, this instability of SBS could be prevented. Secondly, the effect of environmental factors on instable whipping of EDW jet is investigated. Reducing the vacuum can inhibit the instable whipping but prevents the formation of jet. The stable segment of PVP/glycerol jet increases from 31.4mm to 100mm, when the vacuum is reduced from 101kPa to 30kPa. Increasing the ambient humidity will also enhance jet stability. In contrast, the increasing of temperature will enhance the instable whipping. Under low air pressure, orderly nanofibers and nanofibrous can be “direct-written” under a long nozzle-to-collector distance (100mm), which provides a new way to realize the realtime control of jet stability and nanofiber deposition area in electrospinning .

The electric current characteristics under various ejection modes are studied and the relationship between electric current and experimental parameters under stable cone-jet mode is investigated in detail. The current increases as the voltage or flow rate increases, and increases synchronously with the diameter of jet. A closed-loop feedback control system is established to stabilize the current during EDW process, which could improve the stability of jet and the uniformity of the deposited patterns. Experimental results show that the uniformities of both nanofibers and micro thin films can be also improved by the current feedback EDW contorl system.

Finally, three prototypes of typical components are produced by EDW. (1) Conductive silver patterns including discrete dots with diameter of 45~55μm and line with width of 60μm are obtained. Passive components, such as resistor, inductor, capacitor and flexible circuit are also fabricated. (2) By using EDW nanofibers as lift-off layers followed after metal deposition, micro/nano-channels with width ranges from 133nm to 13.54μm are generated. (3) The use of EDW for precise deposition of ZnO nanofibers as relevant device architectures is described. Active components including n-type ZnO nanofiber field-effect transistor and ZnO/CuO nanofibers pn-junction are constructed.

The results of this thesis would help to better understanding the control and applications of stable jet in EDW, which is important to achieve effective control of jet ejection and improve the uniformity of deposited patterns, and would promote the development of high precision EDW system.

Key Words: Electrohydrodynamic Direct-Writing; Jet Printing; Stability Control; Micro/nano-Structures; Current Feedback

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