Polymer Micro/Nanofiber Fabrication using Micro/Nanopipettes

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Abstract — One of the most significant barriers for enabling the breakthroughs promised by nanotechnology is mass production of nanoscale structures, devices, and systems. One of the main challenges of nanomanufacturing systems is three dimensional customized manufacturing of micro/nanofibers. In this article we present a specialized tool developed for reproducible and controlled fabrication of micro/nano polymer fibers using micro/nanopipettes. Development of this tool will facilitate controlled deposition and shaping of polymer materials at the sub-micron scale in precisely determined locations. We present experimental results obtained using concentrated solutions of high molecular weight poly(methyl methacrylate) dissolved in chlorobenzene. Results indicate that it is feasible fabricating high aspect ratio (length to diameter ratio) polymer fibers having diameters approaching less than 200 nanometers using this approach.

Index Terms — Nanotechnology, micro/nano polymer fibers

I. INTRODUCTION

Nanostructures are structures defined as having at least one dimension between one and hundred nanometers. Such one-dimensional (1D) structures have been a subject of intensive research due to their unique properties and intriguing applications in many areas. One of the most significant barriers for enabling the breakthroughs promised by nano-technology is mass production of nano-scale structures, devices, and systems. Therefore, novel manufacturing processes at the nano-scale are indispensable for the commercialization of future nano-scale devices, circuits, man-made materials, and sensors. These applications require customized three-dimensional (3D) framework of nanofibers, which, when taken individually, form the one-dimensional (1D) nanoscale building blocks in a bottom-up assembly manufacturing. This hierarchical approach first creates the individual components and then assembles them together into larger structures. The first step in such a manufacturing approach involves fabricating fibers.

Current fiber fabrication techniques such as template synthesis, channels in porous materials, self-assembly, and electrospinning [1-6] deposit or fabricate fibers essentially in one dimension whereby a fiber or series of fibers are deposited and aligned in one step. The procedure is repeated for stacking up different layers and this can have limited applications. The common feature among all these

techniques is that they can only form random or highly regular structures. Another common disadvantage is the overall quality of the fiber produced. These problems lead to a non-deterministic assembly of arrays of different types of wires into a particular aperiodic pattern. On the other hand, *drawing* is a process similar to dry spinning in fiber industry, which can make one-by-one very long single nanofibers. Drawing a fiber requires a material with a pronounced viscoelastic behavior to undergo strong deformations, while being cohesive enough to support the stresses developed during the pulling. The pulling process is always accompanied by a solidification of solvent that transforms the drawn fiber into a solid fiber. The fiber obtained is very dependent upon the drawing rate, the cooling or evaporation rate and the composition of the material. Using this approach, single metallic wires have been fabricated by retracting the tip of a scanning tunneling microscope (STM) after contact with a surface [7] and by using a glass micro-pipette [8] and AFM tips [9-12] polymeric micro/nano-fibers have been fabricated. This approach offers the following merits over other nano-manufacturing techniques:

- It enables pulling *precise* and *three-dimensional* customized polymer fibers, thus allowing fabrication of complex layouts such as criss crossed networks, parallel and three-dimensional fibers.
- It allows simultaneous manufacturing of conducting, non-conducting, and semi-conducting polymer fibers.
- It is possible to integrate *multi-length* scale fiber manufacturing in the same system by controlling the proximal probe shape and pulling strategy.
- Using the real-time force detection of the atomic force microscope (AFM) probe, closed-loop control automatic pulling schemes can be developed.
- Massively parallel fiber manufacturing is feasible by an array of probes.

A. Motivation:

Customized fabrication of individual polymer nanofibers has wide ranging applications and the potential of maturing and introducing new and existing novel technologies. This approach provides the ease of depositing a fiber between two contact points which do not lie on the same plane as shown in Fig. 1. This has profound implications: as now it makes it possible to build

novel architectures using a single interconnect (electrical applications) instead of a route of interconnects to perform the same objective [13,14]. In another example, these fibers can also be used as mechanical elements in micro-electro-mechanical systems (MEMS) or as biomimetic fibrillar adhesives [15]. In addition, this proposed approach can be employed as a sub-micron extensometer [16,17] to study the rheological behavior of polymer blends at reduced length scales.

Fig. 1. Polymer micro/nanofibers applications: (a) Interconnects in vertical IC chip packaging, (b) Interconnects on flexible substrates, (c) Biomimetic fibrillar adhesives

B. Fiber Pulling Approach:

In this approach, polymeric micro/nanofibers are formed by 3D pulling of a liquid polymer using a glass micropipette, through which polymer solution is pumped continuously as shown in Fig. 2. A liquid bridge between the polymer and probe tip is thus formed (Fig. 2(a)). As the probe tip is retracted and moved along a pre-determined 3D trajectory, the liquid polymer bridge reduces in cross section, solidifies due to solvent evaporation and increases in length until it finally detaches from the tip or the tip is brought back in contact with the substrate thus forming a suspended fiber (Figure 2(b)).

Fig. 2. (a) Schematic of polymer micro/nano fiber fabrication (b) Scanning Electron Microscopy (SEM) image of a fiber pulled

II. EXPERIMENTS

Fig. 3. Experimental setup (a) substrate, (b) solvent reservoir, (c) 2D stage, (d) vacuum outlets, (e) probe holder with one degree of freedom, (f) extensor arm, (g) 3D nanopositioner, (h) flexible tubing for delivering polymer solution to the probe from a pump, and (i) optical microscope

A. Experimental Setup:

Fig 3., illustrates our experimental setup. The substrate (silicon for this article) is vacuum mounted on a 2D manual stage which also has a solvent reservoir. The probe is attached to the extensor arm which in turn is mounted on a 3D nanopositioner. The probe mount has the ability to provide different tilt angles to the probe tip for optimizing the fiber pulling strategy. The polymer solution is pumped into the probe tip via a flexible hosing which is connected to a pump delivery system for pumping a calibrated amount of polymer solution. In our preliminary attempts all the experiments have been carried with the aid of top-view optical feedback as shown in Fig. 3. The extensor arm extends into a vacuum chamber which has been designed to minimize the content of moisture in the air as some polymer mixtures react adversely with the moisture in air thus segregating and losing the fiber forming ability. The probes are fabricated by pulling hollow glass cylinders in a needle pulling machine.

First the probe tip is cleaned in the solvent bath and attached to the polymer delivery pump. Then it is mounted on the extensor arm and the desired tilt angle is selected. At this point the probe tip is lowered and the top surface of the substrate is identified. This is done in three places thus establishing a plane of reference. We then proceed to calibrate the location of the solvent reservoir with respect to the substrate coordinates. At this point the tip is retracted by a known distance and the pumping of polymer solution is initiated. Due to the small orifice opening at the probe tip, the solvent evaporation rate is extremely high. This leads to the polymer solidification on the tip which hinders the ejection of the polymer solution from the tip. To overcome this, the probe tip is brought in proximity of the solvent reservoir where the solvent vapors react with the dried polymer on the tip thus

forming a solution. In situations where the solvent vapors do not have the desired effect, the tip is immersed in the solvent reservoir. Once the calibrated polymer solution starts flowing out of the probe tip, the tip is retracted and using a pre-defined trajectory fibers are pulled on the substrate.

B. Experiment Results:

In this section we present results of the proof of concept. We have chosen Poly(methyl methacrylate)

Fig. 4. A sample suspended polymer fiber with approximate diameter of 200 nanometers

(PMMA) for fiber pulling experiments as PMMA has superior fiber forming and optical properties and is readily available in different molecular weights with a narrow polydispersity ratio. Specifically we conducted our experiments with PMMA ($M_w=950K$ gms/mole and viscosity of 497 centistokes@25°C, Micro Chem Inc., USA) dissolved in Chlorobenzene by 9% weight.

Our initial interest was in forming horizontal suspended fibers as shown in Fig. 4., where high aspect ratio (ratio of length to diameter) have been fabricated with diameters approaching approximately less than 200 nanometers. Of key interest is the ability to fabricate polymeric nanowire networks (Fig. 5.), which should have the following characteristics:

Fig. 5. Classification of networks in one (a), two (b) and three (c) dimensions with different pitch separations and diameters.

- Compliant and free standing.
- Surface of wires free of defects.
- Wires should have consistent diameters.
- The process of making wires should be scalable.
- Diversity, i.e., the ability to include different types of wires (polymers, aspect ratios).

In Fig. 6., we present results of forming crossed networks in two dimensions.

Fig. 6. Crossed network of polymer fibers

Finally in Fig. 7., we present the results on the repeatability of this method. We were able to deposit

Fig. 7. *Stitching* operation exhibiting the repeatability of this process

multiple fibers analogous to a *stitching* operation as can be seen in the figure. This ability provides a continuous deposition and shaping of calibrated polymer material in pre-defined spatial coordinates.

III. FUTURE DIRECTIONS

A. Fiber Characterization

It is of paramount importance to characterize the mechanical properties of polymer fibers (beams). Of key interest are the Young's modulus and stiffness. We are currently conducting experiments in which the suspended fibers are sheared from one end, thus creating free standing cantilever structures. Force-Distance curves are being obtained using the Atomic Force Microscope (AFM) from which stiffness values can be determined. In addition due to the extreme small length scales involved, specialized equipment is being looked into to determine the resonant frequencies of these viscoelastic fibers which would help in determining the Young's modulus and the Q energy dissipation factor.

Due to the nature of extensional flow during fiber formation which is treated as a shear free flow, we are interested in determining the molecular chain orientations by performing Birefringence experiments under a polarizing microscope.

Specialized fibers such as conductive fibers need to be characterized for electrical properties. A general scheme for characterizing these properties is to deposit a single fiber on two electrodes and determine the electrical properties as a function of diameter, polymer concentrations and temperature dependence.

B. Experiments and Modeling:

The feasibility of this method needs to be extended over a range of polymers having different molecular weights and viscosities. In addition fiber pulling experiments need to be catered towards application specific polymers such as Kevlar (for integration in MEMS devices) and Polyaniline (conductive interconnect applications). We have successfully formed polystyrene fibers using this approach. Besides polymers, there is a need to create fibers on different substrates such as deformable plastics and conductive substrates.

A detailed study is underway to determine the fiber pulling parameters of interest. Speed of pulling, angle of probe tip, pumping rate of polymer solution are some of the parameters that are being currently investigated. This investigation is being aided by performing computer simulations using commercially available software such as POLYFLOW[®] and analytical models.

Controllability of this approach is also being addressed in which calibration of probe tip to the surface of the substrate is being investigated by electrical contact or computer vision based automated techniques. Furthermore, integration of MEMS based force sensors at the probe tip is under consideration for determining the forces experienced by the probe tip during fiber pulling.

IV. CONCLUSION

In this paper, a new approach for depositing continuous micro/nanoscale polymer fibers is presented. This approach allows for precise deposition of calibrated polymer solution in the form of fibers in precisely known locations. Preliminary results indicate the feasibility of this approach in forming PMMA fiber diameters in the range of 200 nanometers. Future directions are assessed to mature this approach to a nanomanufacturing technique and to scale this method of fiber formation to sub 100 nanometer domain.

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