In-situ measurements of nanoscale phenomena using diffraction phase microscopy

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ABSTRACT

In this work, we present recent results on several novel applications including optically monitoring the dissolution of biodegradable materials proposed for use in biological electronic implants, the self-assembly of microtubes during semiconductor etching, and the expansion and deformation of palladium structures for use in hydrogen sensing applications. The measurements are done using diffraction phase microscopy (DPM), a quantitative phase imaging (QPI) technique, which uses the phase of the imaging field to reconstruct a map of the sample's surface. It combines off-axis and common-path geometries allowing for single-shot, high-speed dynamics with sub-nanometer noise levels.

Keywords: diffraction phase microscopy, interferometric microscopy, quantitative phase imaging, optical inspection, biodegradable electronics, self-assembly, nanotubes, microtubes, material expansion, material deformation.

1. INTRODUCTION

Quantitative phase imaging (QPI) combines the principles of holography with high-end scientific-grade charge coupled device (CCD) cameras and imaging software [1]. Diffraction phase microscopy (DPM) is a particular QPI technique which combines both the common-path and off-axis geometries into a compact Mach-Zehnder interferometer [2-4]. Advantageously, this configuration possesses the low spatial and temporal noise of the common-path systems as well as the high acquisition speed and single-shot imaging capabilities of the off-axis approaches. A simplified schematic of a DPM imaging system is shown in Fig. 1, which can operate in either

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transmission or reflection mode to accommodate transparent and opaque samples, respectively. The system used in this work employs a 532 nm frequency-doubled Nd-YAG laser as the illumination into the microscope. The DPM module is placed at the output port of the microscope and contains a diffraction grating, 4f lens system, spatial filter, and a CCD. The periodic nature of the diffraction grating produces multiple copies of the image from different angles, some of which are captured by the first lens. Under a 4f configuration, the first lens then takes a Fourier transform. In the Fourier plane the spatial filtering is performed. The 0 order will remain unfiltered as it travels directly down the optical axis, through the center of all the optics, containing minimal aberrations. The +1 order is filtered down to DC using a small enough pinhole such that after the second lens takes another Fourier transform, a uniform reference field is produced at the CCD sensor. The two beams are then overlapped and interfere at the CCD to produce a spatially modulated signal which grants the user access to the phase information. The phase is obtained using a Hilbert transform and is subsequently converted to height with sub-nanometer accuracy.

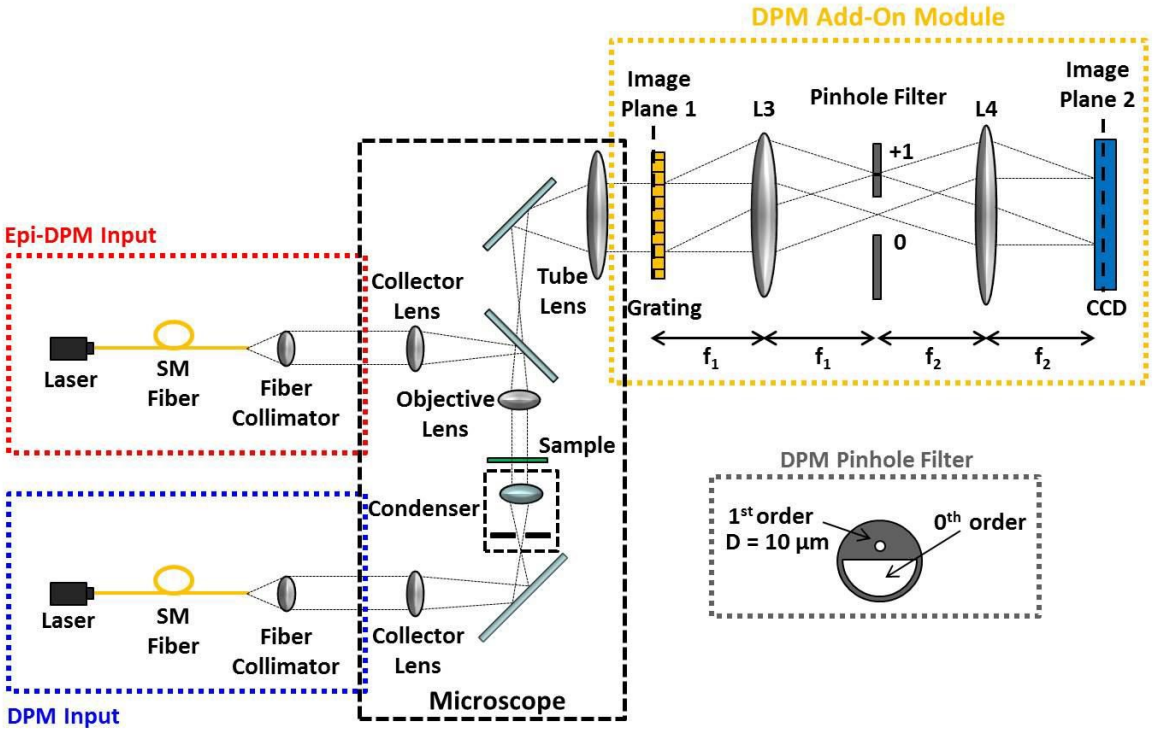

Figure 1: DPM Imaging System.

2. DISSOLUTION OF BIODEGRADABLE ELECTRONICS

Similar to dissolvable sutures which disintegrate over the course of several weeks without requiring surgical removal, implantable electronic devices have been fabricated using Si, Mg, MgO, and silk, which resorb into the human body after their task is complete without producing harmful by-products [5]. The samples were prepared using a silicon-on-insulator (SOI) wafer. First, a two-

dimensional (2D) array of holes was patterned onto the silicon and hydrofluoric acid (HF) was used to detach the top Si layer. The thin 100 nm Si layer was then transfer printed onto a glass substrate using spin-casted SU-8 as the glue layer. The University of Illinois at Urbana-Champaign (UIUC) logo was then created using standard photolithography. The samples were stored in various liquids at 37˚C to simulate conditions within the human body [6].

DPM was used to monitor the dissolution process in a spatially and temporally resolved manner. Using DPM, we were able to track small nanometer changes over the course of a day. The pH of the solution can be adjusted to control the dissolution rate. Figure 2(a-d) shows the logo throughout the dissolution process in phosphate-buffered saline (PBS). The recorded heights are displayed in the figure. Our groups are currently working on tracking the dissolution of other materials including Mg and MgO in order to characterize their performance as implantable electronic circuit components.

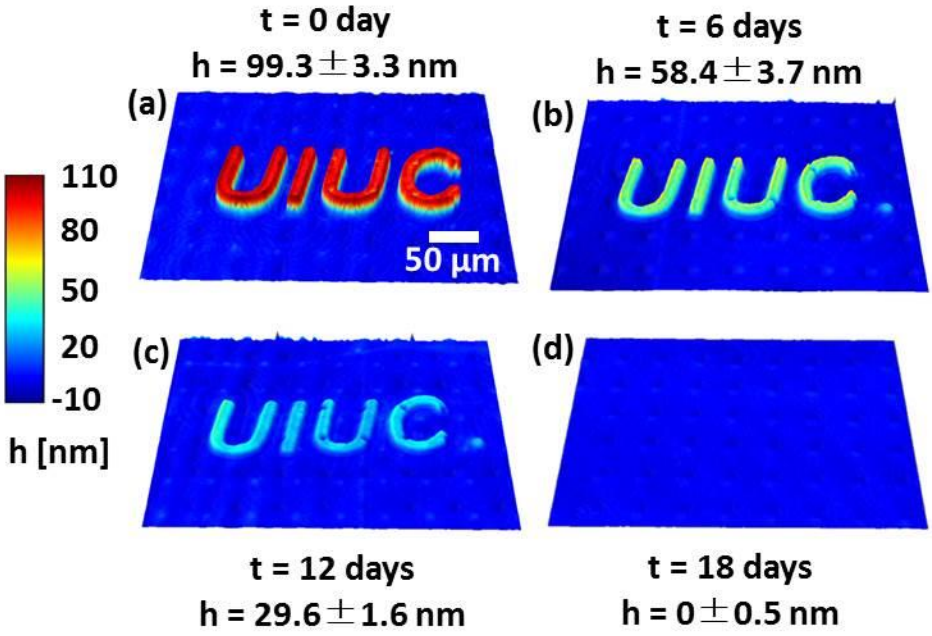

Figure 2: Si Dissolution in PBS at 37˚C.

3. SELF-ASSEMBLY OF NANOTUBES

DPM was also used to observe the self-assembly of microtubes from thin films. The samples were created on a Si <111> substrate which was first degreased and etched with HF to remove the native oxide. A 20 nm layer of low frequency SiN_x followed by a 20 nm layer of high frequency SiN_x was then deposited using plasma enhanced chemical vapor deposition (PECVD). The low frequency and high frequency deposition cause compressive and tensile strain respectively in the bilayer. An array of 19 µm x 50 µm rectangular pads were then patterned using standard photolithography. A solution of 45% KOH at 45˚C was then used to create an anisotropic etch in which the substrate is laterally etched a thousand times faster than the vertical etch rate. This releases the thin film and the strain in the bilayer causes it to roll up and self-assemble into a microtube [7].

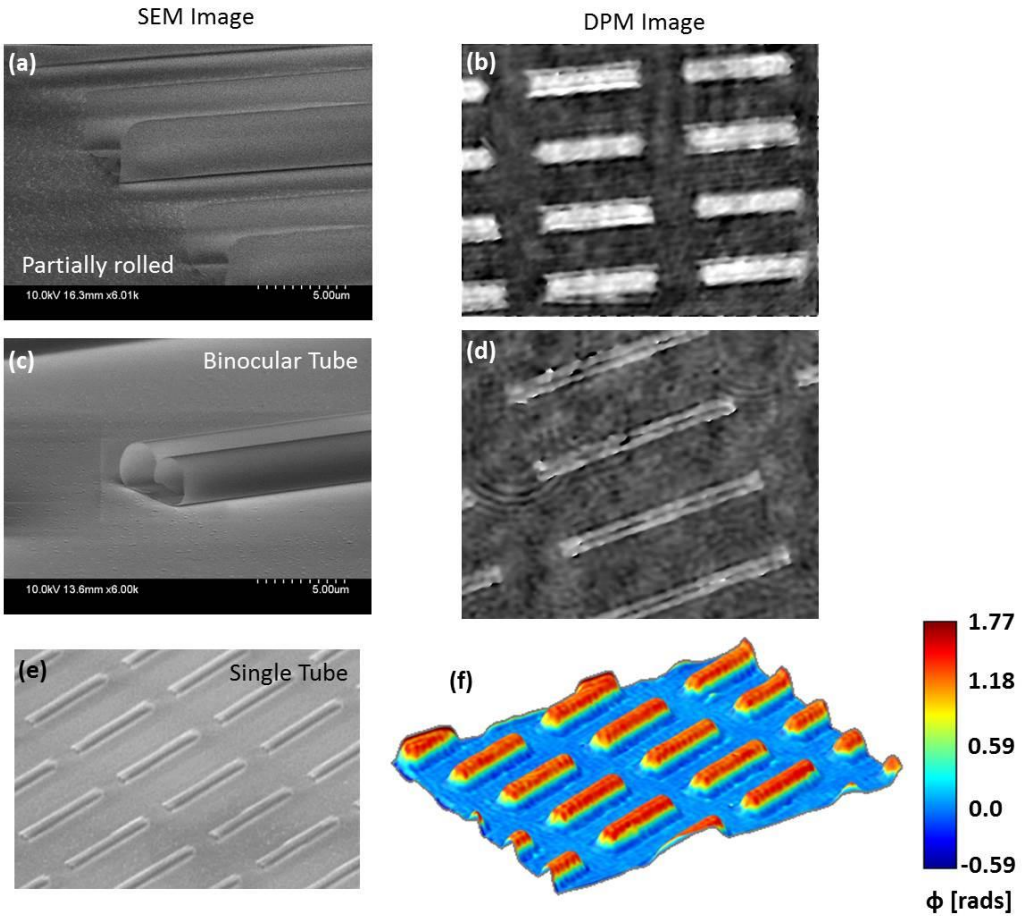

Figure 3: Comparison of SEM and DPM images of self-assembled nanotubes.

Figure 3 shows a comparison of the scanning electron microscopy (SEM) and DPM images for different stages throughout the rolling process. Figure 3(a) shows an SEM image of a partially rolled microtube. The corresponding DPM phase image is shown in Fig. 3(b) in grayscale. Figures 3(c-d) show the SEM and DPM images of a binocular shaped microtube [8]. The DPM images were left in grayscale and not converted to height. The recorded images during rolling were poor quality due to hydrogen bubbles formed during the etching of Si with KOH and the height measurements were not verified. Figure 3(e-f) shows the comparison of the SEM and DPM after the rolling process for a single roll microtube. The geometry of the self-assembly process depends on several factors including the initial size of the pads, the thickness of and strain within the bilayers, and speed of etching [7].

4. HYDROGEN-INDUCED LATTICE EXPANSION OF PALLADIUM

Palladium is known to reversibly dissociate and absorb large quantities of hydrogen, up to 900 times its volume, forming PdH [9]. Depending on the hydrogen content, PdH is either in the α or β phase, with the phase change depending on the grain structure of the film. In the β phase the lattice constant can increase by up to 3.5% through a process known as hydrogen induced lattice expansion (HILE) [10]. In order to help design and simulate PdH based sensors, this expansion was measured through DPM. Samples consisting of Pd microdisks were fabricated through a shadow masking technique on quartz substrates. The Pd film was deposited through e-beam evaporation and consisted of 295 nm thick disks, approximately 180 μm in diameter with a 350 μm pitch. Furthermore, an optically thick blanket coating of 40 nm was deposited because the reflection coefficient of the film also changes with hydrogen incorporation. Since metals have complex reflection coefficients, this information could be coupled to the phase, resulting in erroneous height information. A DPM image of one of the microdisks can be seen in Fig. 4(a).

To measure the effects of hydrogen exposure, a controlled baseline of nitrogen was measured first for 30 minutes. The sample was then exposed to 0.1% hydrogen from 90 minutes, and again purged in nitrogen for another 180 minutes. The height versus time for the microdisk can be seen in Fig. 4(b), with a measured height change of 1.2 nm, or 0.4%. In addition to temporal data, spatial information can be seen in Fig. 4(c), which shows calculated height change frames selected every 20 minutes during the pulse test and a histogram of height change image. The spatial results reveal possible hot spots, i.e. regions that expand more than others. In addition to visual inspection, the width of the histograms gives information about the heterogeneity of the expansion. At the 120 min mark the axial expansion can be seen to be fairly uniform throughout the sample. Finally, Fig. 4d shows instantaneous rates of expansion spaced every 30 min. These images show uniform expansion across the microdisk and also show how there is negligible expansion past the 60 min mark. The recovery, or contraction rate is also shown to slow significantly for the last 90 min. These results show that we can spatially resolve the height change and also the expansion rate at an H_2 concentration that is four times lower than in our previous report [11].

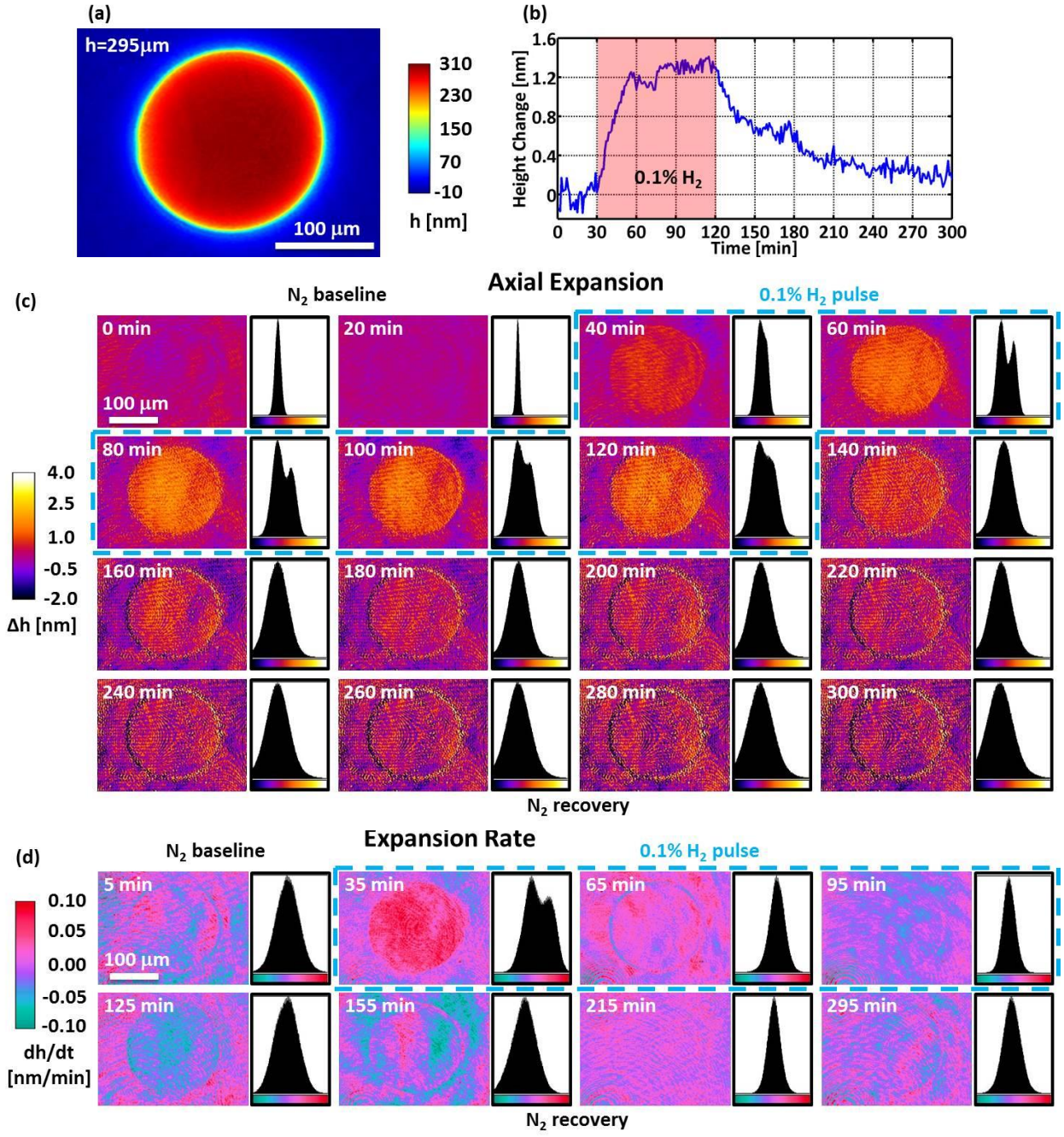

Figure 4: Hydrogen induced lattice expansion of palladium.

5. CONCLUSIONS

We presented recent results on nanoscale studies performed using diffraction phase microscopy, an exciting new quantitative phase imaging technique. These applications include the dissolution of biodegradable materials, self-assembly of microtubes, and the hydrogen-induced lattice expansion of palladium. Various Si nanomembrane structures were stored in both Serum and PBS at 37˚C to simulate conditions within the human body. The dissolution rate of a few nanometers per day was recorded using DPM over the course of nearly 3 weeks. Also, strained bilayers formed from low and high frequency PECVD SiN_x films were deposited onto Si <111> that was subsequently anisotropically etched using KOH, which causes the strained bilayers to release fom the substate and roll up to self-assemble into microtubes. DPM was used to monitor the process and record images of the microtubes at various stages of the rolling process. Finally, the axial expansion of Pd microdisks was monitored during hydrogen exposure at levels more than an order of magnitude below the lower explosive limit (4% in air) and used to model the expansion and recovery process for sensor applications.

6. ACKNOWLEDGEMENTS

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7. REFERENCES

[1] G. Popescu, *Quantitative Phase Imaging of Cells and Tissues* (McGraw-Hill, New York, 2011).

[2] C. Edwards, A. Arbabi, G. Popescu, and L. L. Goddard, "Optically monitoring and controlling nanoscale topography during semiconductor etching," Light: Science and Applications **1**, e30 (2012).

[3] B. Bhaduri, C. Edwards, H. Pham, R. Zhou, T. Nguyen, L. Goddard, and G. Popescu, "Diffraction phase microscopy: principles and applications in materials and life sciences," Advances in Optics and Photonics **6**, 57-119 (2014).

[4] C. Edwards, R. Zhou, S.-W. Hwang, S. J. McKeown, K. Wang, B. Bhaduri, R. Ganti, P. J. Yunker, A. G. Yodh, J. A. Rogers, L. L. Goddard, and G. Popescu, "Diffraction phase microscopy: monitoring nanoscale dynamics in materials science [Invited]," Applied Optics **53**, G33-G43 (2014).

[5] S.-W. Hwang, H. Tao, D.-H. Kim, H. Cheng, J.-K. Song, E. Rill, M. A. Brenckle, B. Panilaitis, S. M. Won, Y.-S. Kim, Y. M. Song, K. J. Yu, A. Amee, R. Li, Y. Su, M. Yang, D. L. Kaplan, M. R. Zakin, M. J. Slepian, Y. Huang, F. G. Omenetto, and J. A. Rogers, "A physically transient form of silicon electronics," Science **337**, 1640-1644 (2012).

[6] S.-W. Hwang, G. Park, C. Edwards, E. A. Corbin, S. Kang, H. Cheng, J. Song, J. Kim, S. Yu, J. Ng, J. E. Lee, C. Yee, B. Bhaduri, Y. Su, F. G. Omenetto, Y. Huang, R. Bashir, L. L. Goddard, G. Popescu, K.-M. Lee, and J. A. Rogers, "Chemistry and biocompatibility of single crystalline silicon nanomembranes and associated materials for transient electronics," ACS Nano **8**, 5843-5851 (2014).

[7] P. Froeter, X. Yu, W. Huang, F. Du, M. Li, I. Chun, S.-H. Kim, K.-J. Hsia, J. A Rogers and X. Li, "3D hierarchical architectures based on self-rolled-up silicon nitride membranes," Nanotechnology **24**, 475301 (2013).
[8] P. Froeter, Y. Huang, O. V. Cangellaris, W. Huang, E. W. Dent, M. U. Gillette, J. C. Williams, and X. Li, "Toward Intelligent Synthetic Neural Circuits: Directing and Accelerating Neuron Cell Growth by Self-Rolled-Up Silicon Nitride Microtube Array," ACS Nano **8**, 11108 (2014).
[9] T. N. Veziroğlu and S. Şahin, "21st Century's energy: Hydrogen energy system," Energy Conversion and Management **49**, 1820-1831 (2008).
[10] T. Flanagan and W. A. Oates, "The pallaium-hydrogen system," Annual Review of Material Science **21**, 269-304 (1991).
[11] C. Edwards, S. J. McKeown, J. Zhou, G. Popescu, and L. L. Goddard, "In situ measurements of the axial expansion of palladium microdisks during hydrogen exposure using diffraction phase microscopy," Optical Materials Express **4**, 2559-2564 (2014).