Three-dimensional Nanoparticle Assembly by a Modulated Laser-induced Microbubble for Fabrication of a Micrometric Pattern

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Abstract

This project explores the use of laser-induced microbubbles for both two-dimensional and three-dimensional printing. At its most basic level, this novel printing concept begins with a laser heating up a nanoparticle substrate. The thermal energy input to the system forms a microbubble, and its corresponding convection currents pin nanoparticle deposits at the substrate/bubble interface. Extending this style of printing into three dimensions presents unique issues when exploring two different printing techniques. For the layer-by-layer technique (similar to a conventional 3D printer), wall height irregularities occur due to inconsistent deposition. To solve this problem, the velocity of the stage is programmed to decrease or increase in line with the areas which need more or less deposition. For the vector technique (similar to a printing pen), structures not parallel to gravity lose their stability and consistency. To correct this defect, a double-axis rotating stage was constructed in order to keep the build parallel to gravity to ensure a consistent print for any combination of shapes. So far, this project has successfully evened out layer-by-layer prints and has achieved the rotation required to construct slanted builds.

Introduction

As technology continues to rapidly evolve, the demand for manufacturing precision components has drastically increased. With recent technological developments, society has trended towards smaller devices, which initiated a need for more precise manufacturing techniques. People are accustomed to the concept of three-dimensional printing on the macro scale, but newer technology, including this project, allows for exploration of the micro-scale.

In order to reach this level of precision, the original materials used in printing must consist of nanoparticles or ions. These ultra-fine particles are harvested from the gas products of chemical reactions and are then spun into a dispersion with a different liquid, referred to as a substrate for the means of this project. The method utilizes a unique optical system consisting of a laser to heat the substrate and a microscope to observe the prints. The amplitude of this laser must be “modulated” by rapidly opening and closing the shutter. All of these components combine into one integrated system through which we print on the nanoscale.

Underlying Mechanism: 2D Printing

In the first step of this novel printing method, the nanoparticles/ions are mixed/dissolved into a solution. The underlying mechanism requires focusing a laser beam either into the liquid containing those particles or at the liquid/air interface. Through that laser medium, energy is transferred into the substrate and causes a microbubble to form. Due to this heating, convection currents surround the microbubble and pin deposits at the liquid/bubble interface.\(^1\,^2\)
Over the past nine years, a reliable method of two-dimensional, nanoparticle laser printing has been developed. The overall printing arrangement mainly relies on an optical system consisting of both a modulated continuous-wave laser and an inverted microscope (Figure 2). The laser reflects through the objective lens and onto the sample which is where the bubble forms.\textsuperscript{3,4} Without modulation, the microbubble forms, totally collapses, and moves on;\textsuperscript{5,6} however, the use of laser modulation doesn’t allow the bubble to totally collapse. Rather, the microbubble partially collapses and then advances and reforms, creating a much smoother line. Benefits of this printing format include achieving extremely narrow and precise lines (on the order of nanometers), the ability to print with a wide chemical variety of nanoparticles, and a seamless transition between many different nanoparticle chemistries.

**Extension to 3D Printing: Layer-by-Layer**

When extending the project into the third dimension, there are two main approaches: layer-by-layer and vector printing. The layer-by-layer style of printing has a design similar to a traditional three-dimensional printer but employs the laser technique described above. In this method, layers of material are stacked on one another to construct an object. However, when utilizing this printing style, an issue occurs during the layer deposition process: inconsistent material deposition. The origin of this phenomenon is a feedback-enhanced process starting at the very first printed layer. A minuscule
sinusoidal pattern of “hills and valleys” of material presents itself, and the areas with slightly higher deposition tend to absorb more light, thus leading to even more deposits at the same location with each additional layer. Essentially, in areas with hills, more deposition occurs than in valleys. As the number of layers increases, the difference between the high points and low points also increases which leads to very obvious irregular wall formations (Figure 3). In fact, in the camera following the laser, one can see the microbubble “jumping” in between peaks as it naturally attracts toward the higher areas.

Figure 3 - Stages of wall defect formation

The first step in developing a solution to this phenomenon involved identifying the optimal laser parameters for this style of printing, including the intensity of the laser, the frequency of the modulation, the translational velocity of the printing stage, and the duty cycle (percentage of modulation that the laser is on versus off). After extensive testing, two sets of optimized parameters were identified. The first set included a lower duty cycle and intensity combined with a slower-moving stage to allow for more time for the deposition. The second set used a higher duty cycle and intensity but moved at double the speed of the first set. Additionally, an improvement was discovered when the testing lines were printed at a frequency of 100 kHz instead of the previous 1 kHz. To visualize the pattern of deposition in the wall microstructure, a profilometer (optical probe) was used to simultaneously characterize the height and roughness of the lines.

Figure 4 - Scanning Electron Microscope image of set 1

It was previously determined that the less the laser is on, the less deposition occurs due to a
shorter period of nanoparticle heating. To solve the problem of inconsistent deposition in layer-by-layer printing, a modulating laser was programmed to speed up and slow down depending on the height of the previous deposition at that point. Near the peaks, the stage is programmed to speed up so there is less time for deposition while it will slow down at the valleys. This dynamic control method evens out the height of the layers to ensure a smooth printing wall. Through analyzing multiple wall examples, the timing and frequencies of the pattern of deposition were determined and incorporated into the modulation calculation of the laser to correct (smooth) the deposition pattern, thus making the laser more accurate. By the conclusion of this portion of the project, the walls contained more pillars in the lower section and showed a smoother consistency in the upper section.

Extension to 3D Printing: Vector

The vector method of the three-dimensional printing process directs the laser onto a continuously growing “stack” of material—very similar to the concept of a 3D printing pen (Figure 5). When printing vertically, this method works beautifully; however, an issue arises when the laser deviates from a parallel-to-gravity, pillar-like structure. In these cases, the structure loses its stability and consistency leading to an undesirable product (Figure 6). This occurs due to a detail within the deposition mechanism of the microbubble. When printing on a slant, the newly forming bubble depositions, no longer sit directly on top of the location of the previous bubble. Deposits tend to accumulate unevenly at the bottom of the microbubble leading to the deformation of the microstructure.

In order to solve this issue, a double-axis rotating stage was developed to allow the immobilized nanoparticle liquid to be rotated to any orientation in all three dimensions (Figure 7). This system is composed of two cage motors and a clamp. A casing for these glass slides was designed using SolidWorks
and printed in-house in order to prevent the glass slide from falling off during rotations (extending to 180 degrees). A LabView program was then written to calculate the degree of rotation for both axes and to control the rotating stage to create more complex shapes. By rotating the stage, the “pillar” remains parallel to gravity and does not become unstable or irregular.

Figure 7 - Double-axis rotating cages

Conclusion

Understanding 3D technology and the tools to produce 3D structures on a nanoscale is critical for applications in many fields. Such implementation can allow for compact, stacked computer chips, precision micro-motors, and micro-probes. In addition, this technology can allow for stacking multiple electrical connections by alternating between conductors and insulators. The unique combination of micro/nano-size and high precision will likely also lead to unanticipated, novel applications.

Clearly, as the nano-printing process develops, several questions require attention. For example, what other parameters affect wall regularity? What advantage could modulation of the laser intensity have over changing the stage speed? Would other frequencies present better walls? The next immediate step in the project is to print longer walls to see if some periodicity presents itself as we print even longer wall lengths (refer to figure 3).

The subsequent step in the vector printing project is to combine the program of the cage motors with the program of the microscope stage. This system integration allows for both translation of the stage and rotation of the cage, resulting in an even wider range of motion. Another portion of this project is to finish the calculations for which rotation speeds correlate to which shape curves. Thinking even further ahead, problems such as the most efficient way of sending construction information to the printer arise, since as structural complexity increases, the programming instructions will also become more advanced. In some cases, it may remain efficient to transmit printing instructions in real-time. However, in other cases, it will likely be more efficient to program and compile the printing instructions separately in advance so they can be sent as a complete package for manufacturing. Other elements of the printing process will likewise also develop in response to the overall demand for optimization.

As the mechanical functioning of 3D nanotechnology develops to the point of applications, it lends itself to the biotechnology industry specifically and the medical industry in general. The
pharmaceutical industry can utilize this 3D printing to manufacture precision pill carriers that allow for a controlled release of multiple medication ingredients.\textsuperscript{10} Nano-printing can be utilized to produce medical and dental implants, and it can provide much more accurate surgical guides.\textsuperscript{31} Material fabrication on the nanoscale benefits burn victims or plastic surgery patients as it creates a bi-layer composite for tissue regeneration. A 3D-printed micro-swimmer can explore the body at a cellular level, either gathering data or delivering products such as drugs. The precision required in chemotherapy improves when able to work at the individual cell level. Another benefit within the oncology field is using the 3D nano-printing technique to form bone scaffolding as a base for rebuilding and regeneration following treatment for bone diseases such as osteosarcoma.\textsuperscript{3} This project, exploring layer-by-layer vs. vector printing techniques, has the potential to act as a launching pad for the exploration of critical steps in the process of three-dimensional nanoparticle printing.
References

12. Assistance from Eitan Edri on graphics