Chip-scale Magnetic Sensing and Control of Nanoparticles and Nanorods

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***Abstract*— We report on a system designed for the magnetic control of nanoparticles and nanorods. This is accomplished by arrays of current-carrying wires (electromagnets) and the associated control circuitry onto a single chip. The chip serves both as the source of localized programmable magnetic fields and the substrate on which the nanostructures rest. Sensing can be similarly performed through on-chip electromagnetic or optical measurements. As proof of concept, we utilize the catalysis of hydrogen-peroxide decomposition by platinum to propel hybrid nanorods through a fluid medium, and demonstrate basic control of nanoparticles in response to the applied currents (electromagnetic fields).**

I. Introduction

Much work has been done to develop nanorods with magnetizable segments for manipulation by external magnetic fields. However, current methods to manipulate these nanoscale rods are still fairly macroscopic. The platinum-gold (Pt-Au) nanorod propulsion system in [1] is a well-documented model system demonstrating one interesting functional capability of hybrid rods. When Ni segments are introduced in the structure [2] manipulating these rods in suspension by applying an external magnetic field becomes viable. Unlike traditional methods of magnetic manipulation [3] this system supplies its own propulsion mechanism, so the applied field merely needs to be strong enough to "steer" the rods, rather than move them directly. This suggests that lower fields may be sufficient for the manipulation of these nanostructures. Coupled with miniaturization, which can increase local field density, and integration of all functions onto a single CMOS chip becomes feasible.

In this paper we first report on fabrication of these hybrid multisegment nanorods using template electrochemical growth. We also describe design and testing of a prototype magnetic trapping chip. We discuss two issues encountered when operating a chip in an aqueous medium: imaging and isolation. Finally, we show our results on operating Pt-Au rods in hydrogen peroxide, and manipulating nanoparticles in aqueous media on the CMOS trapping chip.

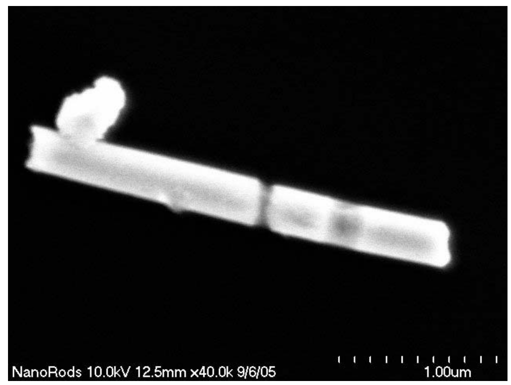

Fig. 1. A single nanorod under SEM

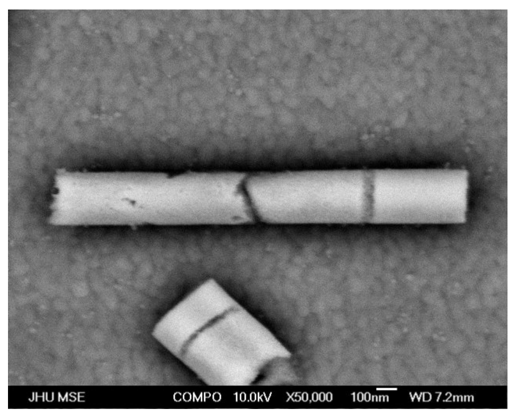

Fig. 2. Ni nonuniformity in nanorods

II. Fabrication of the Nanorods

A. Nanorods Fabrication

The nanorods were grown electrochemically in an alumina nanoporous membrane following the methods and experimental setup described in Martin [4] [5]. A layer of silver (Ag) was evaporated onto one side of the alumina filter, and then a layer of silver was electrodeposited inside the pores to fill the spaces and improve rod length uniformity. Then a layer of platinum (Pt), which act as the catalyst for peroxide decomposition, was electrodeposited within the alumina template, followed by a

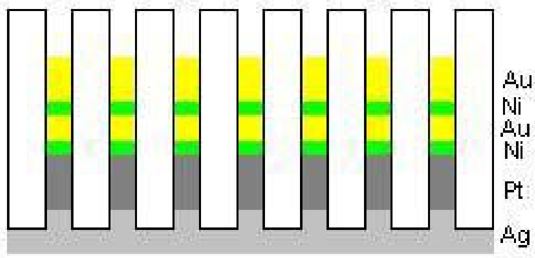

Fig. 3. Schematic diagram depicting nanorods electroplated in membrane prior to release

thin strip of nickel (Ni), then a spacer of gold (Au), another thin strip of Ni and then a longer tail segment of Au. The tail Au segment and the Pt segment serve to protect the Ni segments from corrosion during release, an issue we found to have a significant impact on our yield of usable rods. We included two fairly short segments of Ni to demonstrate steering; with short segments the magnetic domains are oriented transverse to the propulsion of the rod. This shows that the propulsion is entirely due to the catalysed reaction and not attraction of Ni.

The alumina membrane with embedded nanorods was coated on the front side with palmitic acid, which acts as a hydrophobic layer to protect the rods from the next step. The silver film on the backside was then dissolved in nitric acid. The membrane was dissolved in sodium hydroxide and the released rods were subject to several cleaning cycles, composed of alternating centrifugation, replacement of water or ethanol and sonication for mixing.

III. CMOS Magnetic Steering System

We have designed two different CMOS chips for the magnetic manipulation of the nanoparticles and nanorods.

A. Ring Trap Chip

The first system employs a magnetic steering scheme that was first reported by Lee and Westervelt [3]. In their paper they describe ring traps and a matrix of lines to demonstrate the principle of magnetic particle manipulation. The wires must be capable of supporting sufficient current to generate the magnetic fields required. Here we ran into the issue of metal migration. At high currents the wires must be sufficiently wide otherwise they will be damaged by the high currents. As most of our designs parallel trends in semiconductor fabrication (i.e. low power design) the expected currents of 100 mA seem ill-suited to any modern technology that we would use.

In the design of our CMOS system a compromise was reached by using large (100 micron wide) wires for connection to the pads and leaving the thinner wires (20 micron wide) exposed, so that we may do electro- or electroless plating onto the thin wires to increase their height if they were deemed insufficient to support the necessary current. The ground connection was connected to a submerged ring, such that every exposed ring would have a good grounding, and furthermore, we would be able to run the current through one ring, through ground and then sink it through any other ring, if so desired. Area constraints permitted the design of a system with only 12 pads (3 in each corner), of which 4 were ground, and so we could only fit 8 magnetic structures. Given the small number of coils (eight), the individual wires for the coils were brought to the pads.

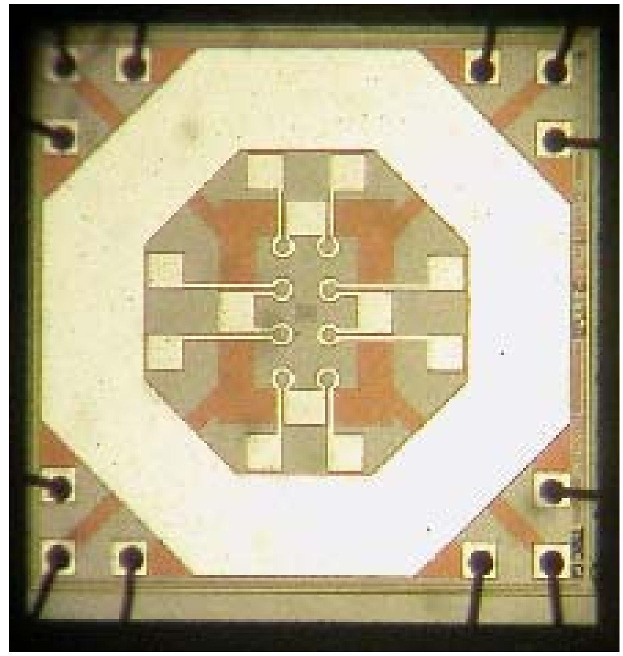

Fig. 4. Magnetic trap chip

The design layout was sent to the MOSIS foundry and received back with all bonding pads bonded. We coated the bonding wires and pads with clear nail polish to protect these delicate structures from washing steps when we re-used the packaged chips.

B. Wire Array Chip

Following testing (see below) of the ring trap chip, we proceeded to design a successor to demonstrate digital control functionality with steering electromagnetic fields produced by an array of parallel wire lines. Unlike the ring trap chip, we chose instead to fabricate a series of lines running north-south, and another series of lines running east-west on the chip. Each line is individually addressed; furthermore, another bit is used in addressing to determine the direction of current flow. Finally, each set of current buffers is a set of current mirrors in parallel, and thus with the integrated two bits of on-chip memory per buffer we can control the amount of current flowing through the lines between four different levels: off (or at least to the level of leakage currents); approximately the level of the reference current; ten times the reference current and one hundred times the reference current. According to simulations we can obtain up to 90 mA current in a single line with an 800 microampere input reference current, with

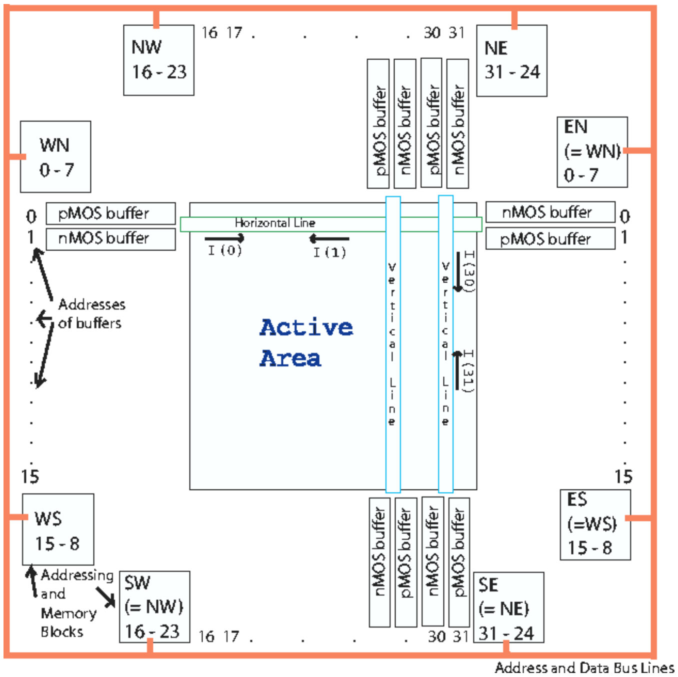

Fig. 5. Wire array chip

an "off" current of approximately 5 nA. As we have an array of 8 lines running north-south and another array of 8 lines running east-west, it is not expected that we can operate all 16 lines at full current (a total current requirement of 1.5 Amps) due to power constraints of the supply lines, hence the four gradations implemented. In addition, we have included temperature sensors on-chip to monitor the heat produced by the active circuits across the chip. This chip is currently queued for fabrication and we anticipate will be ready for testing in Summer 2006.

IV. The Rods In Operation

Imaging the rods in operation is no simple task. At the size scale of these structures, the rods appear as slightly elongated pin-pricks of light under magnification by a conventional light microscope (500X-1000X). Yet to observe the rods moving in suspension requires imaging in aqueous conditions, eliminating electron-microscopy as a possible solution. Furthermore, trying to view the nanorods operating in hydrogen peroxide poses its own difficulties, as the catalysis of hydrogen peroxide decomposition by the platinum segments of the nanorods, the primary property we are trying to exploit in this system, also has the unfortunate drawback of bubble accumulation obscuring the rods from view.

Despite these issues, we were able to ascertain that the rods in water do move in a Brownian fashion, and movement of the rods is intensified in the presence of peroxide. This movement is distinctly non-Brownian in nature. We cannot confirm the "two body lengths per second" claimed in [1] but we do observe some level of directionality consistent with their results (a video will be shown during the presentation of the paper). Further, placing a permanent magnet in close proximity

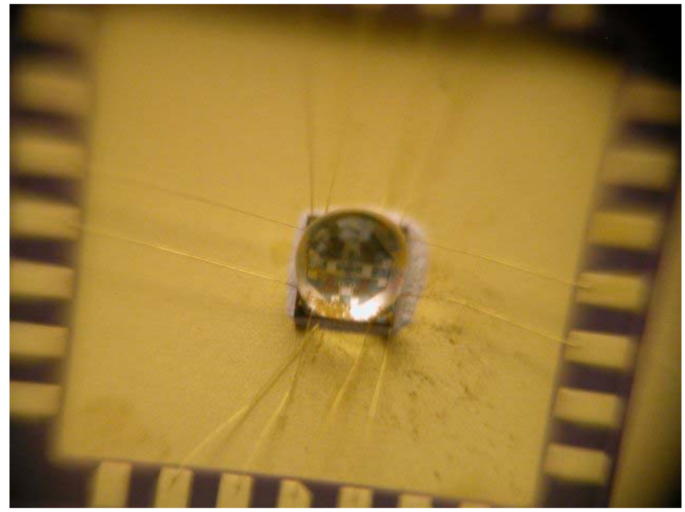

Fig. 6. Water droplet as lens

to the nanorods caused directional changes, and rotating the applied magnetic field correspondingly caused a rotation of the nanorods under observation. However, some rods lined up at angles other than 90 degrees, suggesting that for some rods, the domains may not be oriented exactly transverse to the rod length. This may be a result of yield issues, as we were able to find under SEM that some rods had non-uniform Ni segments. See Figure 2.

V. Magnetic Trapping on the Chip

Operating a CMOS chip under aqueous conditions is somewhat of a challenge, as the conductivity of water will short out any exposed contacts. Thus we originally intended to isolate all of the bonding wires and pads from the active area with a glass wall, in a similar manner to [6]. With a cylinder thus affixed, we proceeded to test our chip, and observed that the apparent magnification of the structures in the active area had been reduced. This was due to the meniscus of the fluid forming a concave lens. Once we realised this we removed the cylinder and instead utilised the hydrophobic/hydrophilic interaction to confine a droplet of liquid to the active area.

This acted as a convex lens and greatly improved resolution of small micrometer structures. In fact, Figure 6 was taken without microscope magnification, and the 20um lines can easily be seen by the naked eye.

One downside to imaging in this fashion is that as the droplet of fluid evaporated, the image will defocus. On this size scale the surface area to volume ratio is very large and consequently the structures on the surface of the chip become out of focus in a matter of minutes; the bubbles evaporate entirely in under an hour. This may not seem to be too restrictive, as the small size of these structures means that it only takes a couple of seconds to observe the trapping phenomena, but we must also take into account the motion of the surrounding fluid when it is first applied. This is a significant force on this scale as these particles in

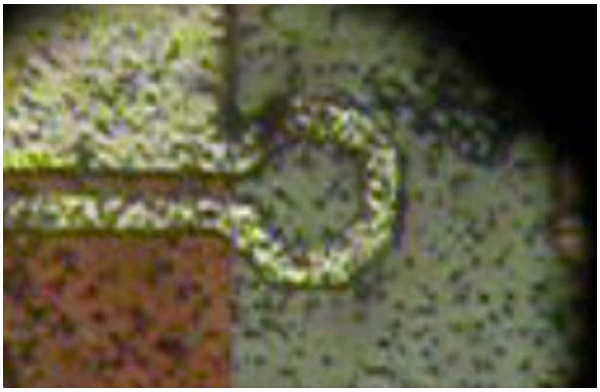

Fig. 7. Arrangement of magnetic beads in the vicinity of the coil before current is applied

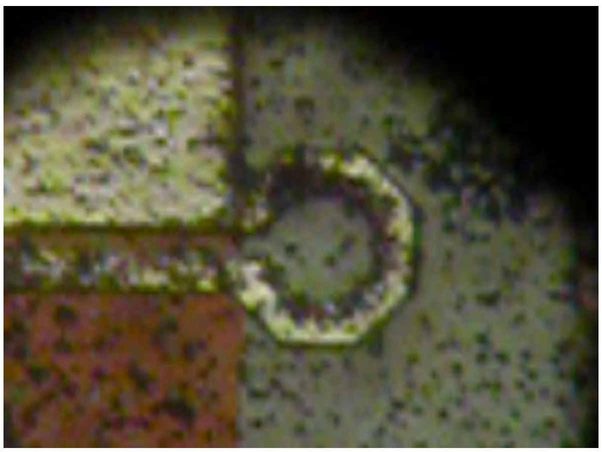

Fig. 8. Arrangement of magnetic beads in the vicinity of the coil after current is applied

suspension have especially small mass relative to their cross-sectional area, so microparticles are moved around for at least five minutes until the fluid settles. Electrowetting is another possibility to be used for manipulating the shape of the droplet and keeping it in focus [7].

Due to the unavailability of the nanorods at the time of testing, we bought commercially available microspheres (diameter approximately one micron) that comprise of embedded superparamagnetic nanoparticles from Bang's Laboratories[1] , as described in the Westervelt paper. The nanoparticle suspension was kept in the refrigerator until use, and diluted by eye to a slightly cloudy suspension before use in imaging.

Using a suspension of the beads on the chip, we applied current to the individual rings on the chip through a Keithley 236 SMU. The wires on-chip without additional post-processing could support 100 mA, and this current was sufficient to trap the microspheres with the protective oxide layer from the foundry unmodified (Figures 7 and 8). If the current was turned off the particles exhibited Brownian motion and eventually dispersed over a period of five to ten minutes.

[1]Bang's Laboratories, 9025 Technology Dr, Fishers, IN 46038-2886[8]

VI. Conclusion

We reported on the fabrication of multisegment nanorods, and have demonstrated functionality of the nanorods in solution with the presence of an externally applied magnetic field. A foundry CMOS chip consisting of wires capable of bearing enough current to induce sufficient magnetic fields to manipulate nanoparticles have all been detailed in the preceding sections. The true potential of this combined system, however, will only be realised when the nanorods and a chip designed to manipulate them will be used together. This requires a few major improvements to the work shown above. Firstly, the yield of the nanorods must be improved such that the ensemble movement of the mass of rods will be concerted and easily noticeable. This may require some amendments to our fabrication and purification protocols.

Secondly, the wire array chip must be used to manipulate these rods. For observing trapping of the paramagnetic microspheres, creating a magnetic field normal to the plane of the chip surface, as achieved with the ring trap chip, is ideal. The nanorods however have domains oriented perpendicular to the length of rod, thus the overall effect would be of orienting the rods such that the longitudinal axis is tangential to the plane of the surface. This result is indistinguishable from the normal mode of operation in the absence of a magnetic field. This issue has been addressed in the design of the wire array chip, and results from the new chip will be presented at the time of the conference.

Finally, a superior method of observing these nanorods must be utilised. This will enable such features as tracking or adaptive control which would benefit this system immensely.

VII. Acknowledgements

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References

[1] W. F. Paxton, K. C. Kistler, C. O. Olmeda, A. Sen, S. K. S. Angelo, Y. Cao, T. E. Mallouk, P. E. Lammert, and V. H. Crespi, "Catalytic nanomotors: Autonomous movement of striped nanorods," *J. Am. Chem. Soc.*, vol. 126, no. 41, pp. 13 424–13 431, 2004.

[2] T. R. Kline, W. F. Paxton, T. E. Mallouk, and A. Sen, "Catalytic nanomotors: Remote controlled autonomous movement of striped metallic nanorods," *Angew. Chem. Int. Ed.*, vol. 44, pp. 744–746, 2005.

[3] C. S. Lee, H. Lee, and R. M. Westervelt, "Microelectromagnets for the control of magnetic nanoparticles," *Applied Physics Letters*, vol. 79, no. 20, pp. 3308–3310, November 2001.

[4] C. R. Martin, "Membrane-based synthesis of nanomaterials," *Chem. Mater.*, vol. 8, pp. 1739–1746, 1996.

[5] D. J. Pena, B. Razavi, P. A. Smith, J. K. Mbindyo, M. J. Natan, T. S. Mayer, T. E. Mallouk, and C. D. Keating, "Electrochemical synthesis of multi-material nanowires as building blocks for functional nanostructures," *Mat. Res. Soc. Symp.*, vol. 636, pp. D.4.6.1–D4.6.6, 2001.

[6] T. Aytur, P. R. Beatty, B. Boser, M. Anwar, and T. Ishikawa, "An immunoassay platform based on cmos hall sensors," *Solid State Sensor, Actuator and Microsystems Workshop*, pp. 126–129, June 2002.

[7] F. Mugele and J. C. Baret, "Electrowetting: from basics to applications," *J. Phys. Condens. Matter*, vol. 17, pp. R705–R774, 2005.

[8] Bangs Laboratories, "http://www.bangslabs.com/," 2005.