Three-dimensional nanofabrication with a rubber sub-wavelength optical element

Advances in nanoscience and technology rely critically on techniques for fabricating structures with nanometer dimensions. Methods developed by the microelectronics industry—photolithography, electron-beam lithography, and others—are well-suited for patterning two-dimensional (2D) structures on ultraflat surfaces. Their limited depth of focus, however, makes it impossible to fabricate directly the types of three-dimensional (3D) nanostructures that are important for many areas of nanotechnology.

An indirect approach to 3D uses the repetitive application of steps for the 2D patterning of sacrificial resists: depositing functional materials, etching or polishing them, removing the sacrificial layers, and so forth. This method requires sophisticated facilities and is difficult to implement for structures that demand more than a few layers. A growing body of research involves developing unusual techniques for 3D nanofabrication, such as those based on colloidal sedimentation, polymer-phase separation, templated growth, fluidic self-assembly, multiple-beam interference lithography, two-photon lithography, and various approaches based on printing, molding, and writing. Each has important limitations, however, in the geometries and sizes of patterns that it can form and in the speed and simplicity of the processing steps.

High-resolution, conformable phase masks have very recently been shown to provide a means for fabricating, in an experimentally simple manner, classes of three-dimensional (3D) nanostructures that are technologically important but difficult to generate in other ways. In this approach, ultraviolet (UV) light passes through a transparent rubber optical element that has features of relief comparable in dimension to the wavelength. This generates a 3D distribution of intensity that exposes a photopolymer film throughout its thickness. Developing away the parts of the polymer that have not been crosslinked by the UV light yields a 3D nanostructure in the geometry of the intensity distribution, with feature sizes as small as 50nm. Figure 1 schematically illustrates the setup.

The rubber optical element forms a perfect, conformal contact with a photopolymer film. General surface forces (i.e. van der Waals type interactions) drive this contact; externally applied pressure is not required. This passive process yields optical alignment of the mask to the polymer with nanometer precision in the normal direction. Exposure of the polymer occurs in the proximity-field region of the mask: for this reason, we refer to the technique as proximity-field nano patterning (PnP). This geometry places requirements on the spatial and temporal coherence of the light source that can be easily met even with low cost setups (a handheld lamp with an interference filter is sufficient). Only the spot diameter of the light Continued on next page.
source and the size of the phase mask limit the dimensions of the patterned areas. Nanostructures with thicknesses up to 100\(\mu\)m can be achieved: the structural integrity and optical absorption of the polymer itself are the only features that limit this thickness.

Figure 2 shows a scanning electron micrograph (SEM) of a typical 3D structure formed using this technique. Rigorous coupled-wave analysis can model accurately the optics associated with this method. Simulations that quantitatively describe certain of the fabricated structures appear in Figures 1 and 2. The flexibility of the geometries of the structures that can be produced is considerable, since the design of the mask and the wavelength of the light used for exposure determine the intensity distributions.

There are many potential application areas for this technique, including photonics, sensors, catalysis, information storage, and micro/nanofluidics. Figure 3 shows a simple example in this last area. Here, PnP has formed a 3D polymer nanostructure integrated directly into a microfluidic channel for filtration, separation, and mixing purposes. The colorized SEM shows the separation of a suspension of 500nm from a flow that moves from left to right through the 3D structure. Our current work examines the use of similar structures for inducing mixing in systems where laminar flow dominates, for chromatographic separations, and for applications in other fields.

**John A. Rogers and Seokwoo Jeon**
Department of Materials Science and Engineering and Department of Chemistry Beckman Institute and Seitz Materials Research Laboratory University of Illinois at Urbana-Champaign E-mail: {jrogers, jeon}@uiuc.edu http://rogers.mse.uiuc.edu/

**References**
Silicon nanostructures for photonics

Using light to convey signals around electronic chips could solve several current problems in microelectronic evolution: these include power dissipation, interconnect bottleneck, input/output of the chip to optical communication channels, signal bandwidth, and so forth. Unfortunately silicon is not a good photonic material: it has very poor light-emission efficiency and a negligible electro-optic effect. Silicon photonics is a field with the objective of improving the physical properties of silicon, thus turning it into a photonic material and allowing full convergence between electronics and photonics. Two research directions based on the use of nano-sized silicon are briefly introduced here: the first is aimed at getting optical amplification in silicon, and the second at moulding the photon flow through the silicon.

Silicon is an inefficient light emitter due to its indirect band gap, making radiative transitions very improbably with respect to non-radiative ones. By reducing the feature size to a few nanometers to obtain quantum confinement of excited carriers, strong visible luminescence at room temperatures is emitted from Si nanocrystals (Si-nc). This is the first necessary condition to get lasing in silicon. The second is to obtain stimulated emission, i.e. light amplification.

Positive optical gain has been demonstrated in Si-nc formed in a SiO$_2$ matrix. Evidence of light amplification was obtained by measuring the amplified spontaneous emission in a planar waveguide with a core layer rich in Si-nc: this grows exponentially when the optically-pumped volume is increased (see Figure 1, A and B). In addition, time-resolved measurements show that a critical balance exists between stimulated emission and non-radiative recombination processes, such as Auger recombination or confined carrier absorption (see Figure 1C). Population inversion in Si-nc is modeled by a four-level model based on the existence of silanone-like (Si=O) localized states that form at the interface between the Si-nc and the surrounding silica matrix (see Figure 1D). Such observations have been confirmed by other authors on different Si-nc systems. Thus, we now have hopes to produce a Si-nc laser.

Nanostructured silicon can also be used to produce complex photonic structures, such as 1D-optical superlattices. We exploited the analogy between electrons and photons and mimicked the action of an external bias, via a controlled change, in the optical path inside the optical superlattice. As a result, we recently observed the optical analogues of time-resolved electronic Bloch oscillations and resonant Zener tunneling. Optical superlattices have been grown by using electrochemical etching of silicon: i.e. porous silicon formation. Porous multilayers can be formed by varying the current during the etch (see Figure 2A).

If an optical path gradient is formed during growth, the photonic bands inside the structure tilt (see Figure 2B). Analogous to what happens in an electronic superlattice when a constant electric field is applied, we observed that the flat optical miniband transforms into an optical Wannier-Stark ladder of equidistant and localized photonic states. A photon pulse coupled into this experiences multiple reflections, yielding an oscillating transmission behavior (see Figure 2C). When two optical minibands are formed in the optical superlattice and an optical path gradient is applied, resonant photon tunneling between the two can be observed. This is the optical analogue of resonant Zener tunneling for electrons. High transmission intensity and the damping of the Bloch oscillations are also observed due to the presence of a resonant-tunneling channel in the middle of the photonic gap. The transition from low to high transmission is extremely sensitive to the variation of optical path gradient, making a Zener tunneling light valve a strong possibility (see Figure 2D). These fascinating parallels between electrons and photons not only show the potential of our complex photonic structures to study fundamental problems, but also add new functionalities to silicon.

Both these sets of results indicate that nanostructured silicon could eventually create a true convergence between photonics and electronics, thus promising new fundamental and applied breakthroughs in the near future.

Continued on next page.
Figure 2. All-silicon 1D-optical superlattices are built up of coupled microcavities with nanometer-thick layers grown electrochemically. Shown in A is a scanning electron microscope image of these structures. A controlled optical-path gradient allows us to tilt the photonic minibands (B) and hence to observe time-resolved photon Bloch oscillations (C, upper graph) and resonant Zener tunnelling of light waves (C, lower graph). The coupling between optical Wannier-Stark states turns to be extremely sensitive to slight changes in the optical-path gradient, which predicts an enhanced optical sensing mechanism (D) and the possibility of a new type of optical valve.

References
EPR: Progress towards spin-based quantum computing

Electron- and/or nuclear-spin-based quantum computing requires the control and measurement of a very small number of spins, ideally just one. Spin-dependent recombination (SDR) is an electron paramagnetic resonance (EPR) technique that is potentially useful in spin-based quantum computing. It is orders of magnitude more sensitive than conventional EPR and permits magnetic resonance measurements on the fundamental building blocks of modern microelectronics: metal oxide silicon field effect transistors (MOSFETs). SDR-detected magnetic resonance applied to an array of MOSFET-like devices may have particular promise in quantum computing because the response can be turned on and off at specific sites via application of voltage. In fact, a leading spin-based quantum computer proposal is based upon an exotic MOS system.

At 'modest' magnetic-field strength, the sensitivity of SDR is often, to zero-order, field independent. However, since SDR involves the polarization of charge carriers and deep-level spin systems, very-high-field SDR should provide additional high-sensitivity advantages. This could eventually allow for single-spin detection, because the high fields greatly increase polarization. However, at very-high fields and frequencies, the conventional microwave approaches (microwave waveguides, conventional cavities, etc.) become essentially impossible as the wavelengths of the electromagnetic irradiation—and consequently the dimensions of the microwave cavities and waveguides—extend from microwave dimensions (~cm) to far-infrared dimensions (~mm or less).

Recently, 'quasi-optical' approaches have been shown to have great promise for conventional EPR at extremely high fields. Here we report on high-sensitivity SDR measurements using a 'quasi-optical' spectrometer. These preliminary high-field measurements were made under circumstances very far from those that would yield optimal sensitivity. Several clearly possible modifications of our initial measurements should each yield improvements of one to several orders of magnitude: thus, our results strongly suggest that fairly-rapid single-spin detection will be possible with high-field SDR.

The experiment
At the National High Magnetic Fields Laboratory we made SDR-detected EPR measurements using SiC MOSFETs. These were configured as gate-controlled diodes with gate areas of 100µm x 100µm and measured using a high field 'quasi-optical' EPR spectrometer. The frequency we used was 110GHz: the resonance appeared at 4.26 Tesla. The 'quasi-optical' system is shown in Figure 1, and is described in detail elsewhere. A representative SDR trace (200s acquisition time) is illustrated in Figure 2. The signal-to-noise ratio is approximately 120, and the full width at half maximum of the (essentially Gaussian) line shape is 26 Gauss, yielding a sensitivity of about 4 x 10^4 spins/Gauss. This sensitivity was: achieved at room temperature, at quite low B1 (the resonance frequency field), without significant signal averaging, and at considerably less than the highest-possible fields that can be achieved.

Although a direct extrapolation of response is not possible, a comparison of SDR amplitude versus power at low and high field strengths is shown in Figure 3. This suggests that a large improvement in high-field sensitivity will be achieved by increasing B1. The low-field measurements were carried out using a 150mW microwave source and a TE102 microwave cavity with a loaded quality factor of about 5000. The polarization in our preliminary room-temperature measurements was less than 2%. Lower temperatures and even-higher fields will allow for a several orders of magnitude boost in the ratio of magnetic field to absolute temperature, permitting essentially-complete polarization of the charge carrier and the deep-level spin systems. The increased polarization will yield a large, if difficult to precisely quantify, increase in sensitivity. Although long-signal averaging is of questionable utility in quantum computing applications, it is worth noting that the practical limit for signal averaging is at least a day. Signal averaging for a day would increase sensitivity by about a factor of 20.

Since several fairly straightforward modifications of our measurements will each likely provide one to several orders of magnitude increase in sensitivity, our results strongly suggest that fairly-rapid single-spin detection will be possible via high-field quasi-optical SDR detected EPR. This sensitivity will be possible in MOS integrated circuits in which individual transistor spin sites may be rendered addressable via application of gate and source-drain bias. A very-recent study argues that somewhat similar high-field electrically-detected mag-
netic-resonance measurements (involving extensive periods of data acquisition) have produced single paramagnetic site sensitivity in a MOSFET.9

P. M. Lenahan, B. N. Bond*, J. van Tol†, and L. C. Brunel†
Pennsylvania State University
University Park, PA
*Present address: Dept. of Electrical Engineering
Massachusetts Institute of Technology
Cambridge, MA
†Center for Interdisciplinary Magnetic Resonance
National High Magnetic Fields Laboratory
Florida State University
Tallahassee, FL

References
Feasibility of laser-assisted remote release from nanoengineered capsules

Here we describe a laser-light-illumination-based method for the remote release of materials from nanoengineered polyelectrolyte capsules. Recently, a novel method based on layer-by-layer adsorption of oppositely-charged species on colloidal particles was introduced for the encapsulation of a variety of chemical and biological substances. This allows for the nanoscale engineering of the composition of the shells by depositing components in alternating layers. A large number of materials have been successfully encapsulated, ranging from enzymes and DNA to small dye molecules.

Microcapsules offer effective means for the delivery of the encapsulated compounds in biochemistry. Nano techniques are indispensable for controlling their properties. In addition, the field of nanotechnology would benefit by using such capsules as delivery vehicles for minute amounts of specified substances or nanomaterials to a specific site. However, once capsules containing nanomaterials, catalysts, enzymes or drugs are delivered to the location for reaction, it is essential to activate their contents: to release the encapsulated to such material. Indeed, the remote activation of encapsulated materials by deforming or cutting through the capsule is imperative for controlling biochemical reactions.

Here we present a novel technique for remote activation of encapsulated material using laser-light irradiation. To achieve this goal, capsules were nanoengineered in such a way that the polyelectrolyte shells contained a light-absorbing agent. The thickness of the walls of the capsules ranges from few nanometers to tens of nanometers. In designing the composition of layers at the nanometer scale, it must be ensured that the light-absorbing agents are incorporated into the walls and that their concentration and absorption properties are sufficient to induce a rupture in the capsules’ walls upon laser-light illumination.

Absorption of light by metal nanoparticles in the visible part of the spectrum is attributed to a collective oscillation of the electron gas in the nanometer-sized particles. However, with the increasing particle size and increasing concentration, the wavelength of plasmon absorption bands for metal nanoparticles shifts to the red side of the spectrum and, further, to the near IR-region. Various materials were introduced into the shells of the capsules to induce absorption of light: these were both organic, such as light-absorbing dyes, and inorganic, such as metals (including silver and gold nanoparticles). Under laser illumination, the capsules were cut enabling the release of the encapsulated materials into the surrounding environment. The experiments were conducted using a low-power near infra-red continuous-wave laser diode focused on a sample containing a water solution with the capsules.

We analyzed several types of capsules and the composition and design of the layers were verified by transmission electron-microscopy measurements. Figure 1 shows a section of the silver-doped microcapsule: the silver nanoparticles can be seen clearly. It was noted that the capsules containing no light-absorbing agent in the walls do not exhibit any effect due to laser-light illumination. Although our experiments were conducted with various metal- and dye-containing capsules, we present here only the results for those capsules containing silver nanoparticles. Figure 2(a) shows some of these before the interaction with laser light. The capsule at the top of the image was activated earlier and is shown open in this image. In Figure 2(b), the same capsules are shown during the laser illumination. It can be seen from Figure 2(c) that the capsule at the bottom of the image was cut and appears open after the exposure to laser light. The last capsule was moved away from the field of view. The process described above can be employed for the remote release of any encapsulated material.

We thank Prof. Dr. H. Möhwald for his comments and support during this work at MPI. We also acknowledge the support of the 6-th FP EU-project (STREP 001428 ‘Nanocapsules for targeted delivery of chemicals’) and Sofja Kovalevskaja Program of Alexander von Humboldt Foundation.

Andre G. Skirtach, Alexei A. Antipov, and Gleb B. Sukhorukov
Max-Planck Institute of Colloids and Interfaces
Potsdam/Golm, Germany
E-mail: ASkirtach@ieee.org

References