INITIATION OF NANOPOROUS ENERGETIC SILICON BY OPTICALLY-TRIGGERED, RESIDUAL STRESS POWERED MICROACTUATORS

Christopher J. Morris[1], Kate E. Laflin[2], Wayne A. Churaman[1], Collin R. Becker[1], Luke J. Currano[1], and David H. Gracias[2]

[1]U.S. Army Research Laboratory, Sensors and Electron Devices Directorate, Adelphi, MD, USA
[2]Chemical and Biomolecular Engineering Department, Johns Hopkins University, Baltimore, MD, USA

ABSTRACT

The integration of energetic materials with chip-scale MEMS fabrication processes, and in particular the development of nanoporous energetic silicon (NES), is a promising path to provide significant quantities of energy for certain microscale applications. Here we demonstrate the low-power wireless initiation of an on-chip energetic reaction, by absorbing optical energy, transmitting mechanical energy, and releasing a large amount of chemical energy, without the use of any external wires or batteries. A novel actuator powered by residual thin film stress absorbed 25 W/cm^2 of optical power from a 532 nm visible laser, heated, and released up to 22 nJ of mechanical energy. The mechanical energy was sufficient to initiate 6.7 mg of NES and release up to 66 J of chemical energy.

INTRODUCTION

We are developing new technologies for fully self-powered sensing and actuating microsystems. Although the field of MEMS has produced several viable commercial applications, the ultimate miniaturization of sensors and actuators with their necessary power supplies has not quite reached the enthusiastic predictions of ubiquitous and distributed MEMS. For applications requiring only single or a small number of sense and/or actuation events, new energy sources such as integrated energetic materials can play a significant role.

Our group has been characterizing and developing applications for integrated nanoporous energetic silicon (NES) [1]. The nanoporous silicon network that remains following an electrochemical etch of bulk silicon acts as a fuel, and its combination with sodium perchlorate as an oxidizer leads to a material having an energy density of 9.9 kJ/g [2] and reaction front propagation rates ranging from 5 m/s to over 3 km/s [3]. We have demonstrated the utility of NES to launch jumping robotic platforms [4] and provide initiation energy for munitions fuzing, but this and other chip-integrated energetic materials may find additional uses as alternative microscale power sources. One requirement to use energetic materials is the supply of enough power for initiation. Although we have demonstrated direct laser initiation of NES with over 2 kW/cm^2 irradiance using a 532 nm laser [5], the conventional route for initiation is through an electrical hotwire supplied by a larger, more difficult-to-integrate power source.

Another approach to energy storage is the use of residual stress in commonly-deposited thin films. We have developed a circular arrangement of passive, battery-free microactuators which exploit this feature [6], and have used them to attach microtransponders to fibers, textiles, and insects [7]. Each actuator contains an initially rigid polymer which softens upon heating above 43°C, allowing pre-stressed structures to bend. We recently developed the ability to trigger these actuators with focused, coherent light from hand-held optical lasers, and we present here for the first time the application of these "microgripper" actuators to the wireless initiation of NES.

METHODS

Figure 1 shows the overall concept of dispersing microgripper actuators over the surface of a patterned, nanoporous silicon chip, dispensing an oxidizer, and using laser irradiation to trigger the release of residual stress in the actuators, which in turn initiates the nanoporous silicon reaction.

The fabrication of NES involved a silicon-nitride patterned, electrochemical etch in a 20:1 HF:ethanol solution with 2.5% H_2O_2 by volume, and with a Pt electrode on the back side of the wafer to drive the galvanic cell and provide the necessary internal current. After etching for 20 minutes, a nanoporous network extended 75 µm into the wafer, with pores 3-5 nm in diameter, a surface area approaching 1000 m^2/g [3], with a hydrogen-termination preventing any significant further oxidization of the pore surfaces. By drop casting a 3.2 M solution of sodium perchlorate in methanol onto the etched silicon material, the low surface tension of the solution carried the oxidizer salt into the pores, while the rapid evaporation rate of methanol allowed the oxidizer to precipitate and deposit on the hydrogen-terminated surfaces after drying for 15 minutes.

Figure 2 shows the fabrication and release of microgripper actuators. First, we thermally evaporated a

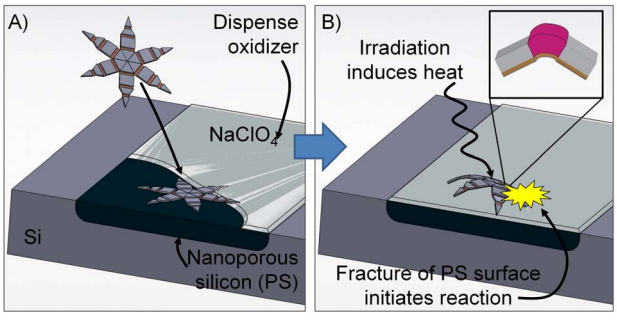

Fig. 1: Schematic showing residual stress powered microgrippers used to initiate nanoporous energetic silicon. In A), actuator devices are dispersed over the surface of a pre-etched nanoporous silicon region, the region is covered with an oxidizer solution, and the solution dries. In B) laser irradiation induces actuation which fractures or otherwise causes a localized heat buildup which initiates the nanoporous silicon reaction.

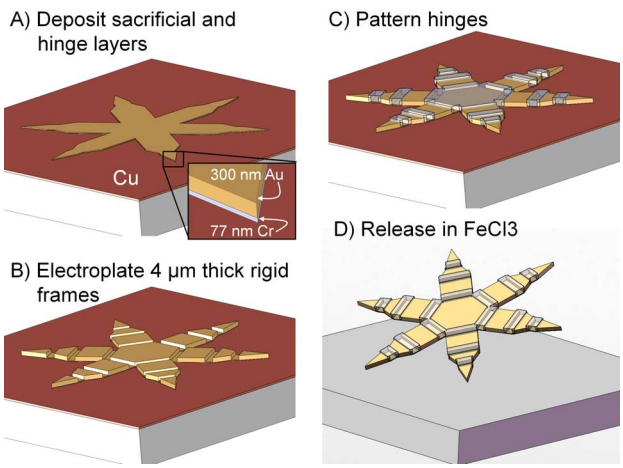

Fig. 2: Fabrication process for fully released microgripper actuators

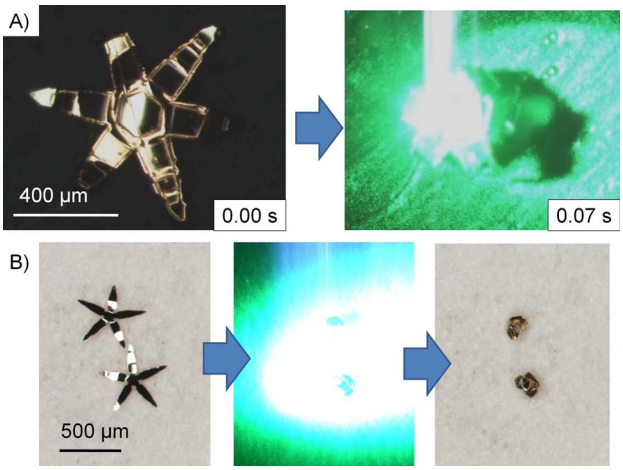

Fig. 3: Video frame sequences showing optically induced actuation of differently-sized microgrippers

250 nm Cu sacrificial layer, with a 20 nm Ti adhesion layer, and followed it with two evaporated thin film metallic hinge layers to provide the desired residual stress. These layers were 77 nm of Cr and 300 nm of Au, and they were patterned by liftoff in acetone as shown in Fig. 2A). Photolithography defined rigid, non-hinge "frame" areas, and electrodeposition filled these areas with a 4 µm thick layer of Au (Fig. 2B). Figure 2C) depicts the 3 µm thick Shipley 1827 photoresist (Microchem) patterned over the top of each hinge. This polymer prevented the hinges from bending until the appropriate thermal or chemical environment was supplied. Finally, Fig. 2D) shows the dissolution of the sacrificial layer in ferric chloride, after which we collected the microgripper devices and dried them.

As in past reports [6], the photoresist layer provided sufficient stiffness to the hinges, preventing them from bending until the appropriate thermal stimulus was present, which for this study was in the form of laser irradiation. We characterized the actuation behavior of the hinges as a function of laser irradiation by placing different neutral density filters in the path of a 532 nm green laser, coupling that beam into a 400 µm core, 0.37 NA optical fiber, and focusing the light exiting the fiber with a 5 mm diameter, 0.243 NA lens. Holding this lens at an angle between the test sample and a long-working distance microscope objective resulted in a 1.09 mm^2 elliptical laser spot, focused on the sample. We measured total beam power exiting the fiber and lens using a Newport photodetector (818-UV) and power meter (1916-C). A high speed video camera enabled measurement of actuation time for each irradiance level.

We also modeled optical power absorption using a closed-form, analytical solution, as well as finite element analysis. In both cases, we considered conduction through the surrounding air to be the primary mode of heat loss. For a single, semi-infinite air domain with a heat flux boundary condition imposed on one side, the solution for the time to reach a particular ΔT at the surface is

$$t = \frac{\pi}{\alpha}\left(\frac{k\Delta T}{2}\right)^2\left(\frac{1}{I_0}\right)^2 \qquad (1)$$

where α is the thermal diffusivity of air, k is the thermal conduction coefficient, and I_0 is the heat flux magnitude given by the laser irradiance level. Assuming that the measured actuation time would correspond to the time taken to reach a particular ΔT, equation (1) should predict the relationship between actuation time and laser irradiance.

We also used ANSYS to model this scenario, and to include heat capacity effects of not only the surrounding air, but also the Au, Cr, and photoresist materials making up the hinge devices. The current model is only one-dimensional, in order to compare with the analytical solution in (1) and to more rapidly investigate different loading scenarios. The model contained 2100 nodes, with air domains extending away from both sides of the evaporated Cr, evaporated Au, electroplated Au, and photoresist stack making up a one-dimensional slice of the hinge device. The boundaries of the air domains were held at ambient temperature, and verified to be far enough away to model the case of two semi-infinite domains extending away from the hinge device. We have also started development of a two-dimensional axisymmetric model with 61,000 nodes, to account for the different hinge and frame segments along each microgripper arm.

Finally, for experimenting with the hinge devices and their ability to initiate a NES reaction, we fabricated patterned, 3 mm wide strips of NES, and tested different procedures to get 1.5 mm tip-to-tip microgripper hinge devices onto the NES surface. We manually manipulated the position of the focused laser spot to shine on different microgrippers, and captured the resulting reaction using a high speed video camera (Photron Fastcam SA5).

RESULTS AND DISCUSSION

We characterized laser-induced actuation of the microgrippers as shown by several representative video frames in Fig. 3. Figure 3 also shows the actuation of two different sizes of microgrippers, with the smaller being approximately 160 µm across when folded. Figure 4 shows that at higher irradiance levels, the measured actuation time varied according to a $1/I^{2.1}$ power law with laser irradiance I_0, which was close to the trend predicted by equation (1). At lower irradiance levels, additional heat loss due to convection was likely responsible for increasingly longer times required to actuate.

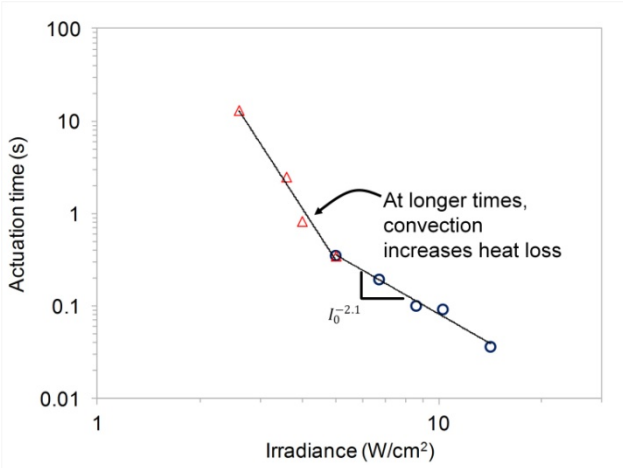

Fig. 4: Analytical and finite element model compared with experimental data for heat transfer imparted by laser irradiance

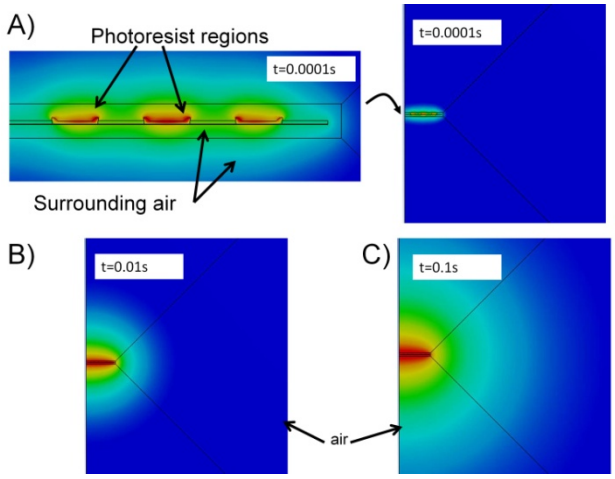

Fig. 5: Two dimensional finite element analysis showing temperature distribution at different times.

The $1/I^2$ power law was verified with the one dimensional finite element model for absorption in the Au frame layer. We also constructed a two-dimensional finite element model, with representative results shown in Fig. 5. Here we have modeled the optical absorption of the photoresist regions, which have an effect on the temperature distribution at early times, but at later times the local temperature distribution becomes much more uniform as the temperature gradient spreads out into the surrounding air domain. If a thin, 0.1 µm thick photoresist layer was used to model absorption of laser power, a $1/I^{1.8}$ power law was calculated, similar to the idealized one-dimensional analytical case. But for more realistic 3 µm thick photoresist layers, the additional heat capacity of the photoresist material led to a power law with an exponent approaching -1, instead of -2. These results are important to guide us in exploiting the absorption characteristics of photoresist and other polymers to minimize the amount of laser irradiance, and ultimately laser power, required for actuation of these devices.

To use these devices for initiation of NES, it is useful to consider the quantity of mechanical energy available from their actuation. Their design is guided by the calculation of hinge curvature resulting from the relaxation of the residually-stressed films [8]. From these calculations it is also possible to calculate a spring constant associated with each hinge, based on that of a fixed cantilever. These calculations result in a 1.81 N/m spring constant, for a 200 µm wide, 50 µm long hinge. We also made initial spring constant measurements of one hinge using an atomic force microscope (AFM) probe, resulting in a measured spring stiffness of 1.6 N/m. Although this measurement was performed on a hinge actuator with slightly different geometry, and although the application of force to a rigid frame segment rather than the precise end of a hinge complicated the interpretation of the measured hinge stiffness, the measured value supports the calculations. We are currently working on developing a better partial release process which will allow additional measurements and validation. In the meantime, a first order approximation of energy stored by each hinge actuator yields 1.2 nJ, assuming a travel distance of 36 µm consistent with observed 90 degree folding angles. Each microgripper contains 18 actuators, suggesting that as much as 22 nJ of stored mechanical energy is released upon laser irradiation. The energy quantity required for electrical hot-wire initiation of NES ranges from 25 to 800 µJ [1, 9]. Recent studies of NES initiation suggest that a local mechanical disturbance is more important than the application of heat to reach some initiation temperature [2]. Therefore, a mechanical form of initiation may be more efficient.

In order to combine microgripper hinge devices with NES for initiation, it is necessary to avoid damaging either the grippers or NES. It will be ideal to fully integrate specifically-designed hinge actuators with NES substrates, but for these initial experiments we chose to disperse them manually prior to dispensing the NES oxidizer solution. If the microgrippers were suspended in the methanol-based oxidizer solution prior to its introduction to NES, the photoresist layer eventually softened and caused the hinges to actuate prematurely. This possible risk was also present when dispersing oxidizer solution over a dry NES surface previously covered with hinge actuators, so we performed several tests to verify that the actuators would operate as intended. Figures 6a) and b) show close up images of a microgripper during the dispersion of methanol and following its evaporation. There was partial actuation of the hinges indicated by the curling segments in Fig. 6b), but irradiation with a laser verified that the segments could be actuated further. Figure 6c) shows a NES strip oxidized, dried, and ready for testing with several microgripper hinges dispersed over its surface.

Figure 7 depicts the successful initiation of 6.7 mg of NES. Approximately five of the microgrippers failed to initiate the desired reaction, but one did so approximately 0.03 s after the onset of laser irradiation at 25.2 W/cm^2. We are currently implementing an experimental setup which will allow better observation of the phenomena involved, such as whether the best folding direction is up or down, whether all actuators are operating as expected, whether the actuation event itself or the rate of actuation is more important for NES initiation, and what other initial characteristics of the microgripper might be necessary for the process to work. This experimental setup is challenging given the need to incorporate the

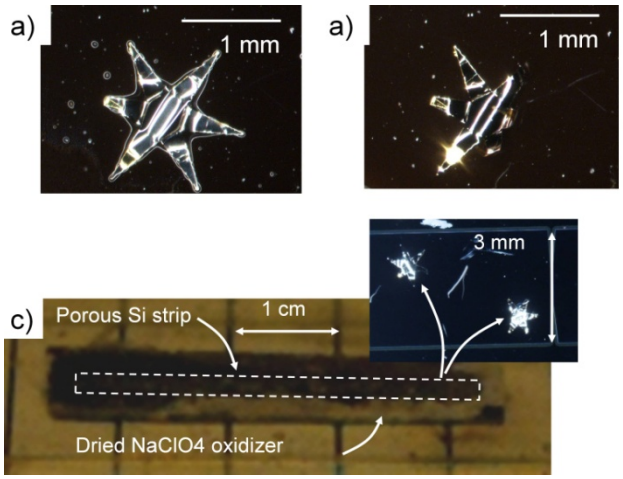

Fig. 6: Dispensing oxidizer and microgrippers on NES substrates. A) Image showing methanol meniscus around a microgripper as it dried. B) The same microgripper after complete evaporation of methanol, with partially-actuated hinges indicated by slightly curved segments. C) Nanoporous energetic silicon strip following evaporation and drying of methanol-oxidizer solution, with microgrippers dispersed over its surface.

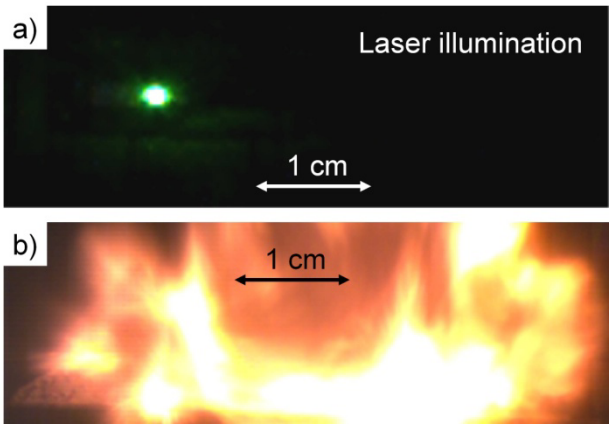

Fig. 7: Initiation of nanoporous energetic silicon with 25.2 W/cm^2 laser irradiance, resulting in approximately 80 J of thermal and mechanical energy released

positioning of a focused beam, a high speed camera, a vacuum or controlled-humidity environment for NES stability, and the necessary laser and energetic materials safety precautions, all within the confines of a limited working distance under a microscope objective.

Still, we were able to verify that NES did not initiate in the absence of microgrippers, under the same irradiance level. Compared to the previous irradiance level needed for optical initiation of NES at this wavelength [5], the use of microgrippers enabled an 80X reduction in required laser intensity. As much as 66 J was still liberated within 25 µs, based on the measured energy release of fully oxidized NES [2].

CONCLUSION

We have combined a novel actuator powered by residual thin film stress with an integrated energetic material, nanoporous energetic silicon. Irradiance from a 532 nm laser led to mechanical actuation of the actuators, with actuation time following a $1/I^2$ power law as predicted by a one dimensional analytical model, as well as by finite element analysis. We predicted that up to 22 nJ of mechanical energy was released upon actuation, using 25 W/cm^2 of optical irradiance. This level was sufficient to initiate 6.7 mg of NES and release 66 J of chemical energy, although this energy quantity could in principle be as high or as low as any particular application requires. The irradiance level was nearly 80X less than a previous study using NES optical absorption alone at this wavelength, indicating the benefit provided by the actuators. The actuators served to absorb optical energy, transmit mechanical energy, and enable the release of a large amount of chemical energy, all without the use of any external wires or batteries. We anticipate this work to enable new microscale power and energy sources for propulsion, optical or acoustic signaling, or thermal applications.

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CONTACT

Christopher Morris, christopher.j.morris58.civ@mail.mil