MICROENERGETIC PROCESSING AND TESTING TO DETERMINE ENERGETIC MATERIAL PROPERTIES AT THE MESOSCALE

Alexander S. Tappan, Anita M. Renlund, Gregory T. Long, Stanley H. Kravitz, Kenneth L. Erickson, Wayne M. Trott and Melvin R. Baer
Sandia National Laboratories*
Albuquerque, NM 87185

INTRODUCTION

The mesoscopic structure of energetic materials (EMs) greatly determines their response during ignition, growth and detonation.1-2 Mesoscopic properties such as particle size, porosity, heterogeneity and material interfaces determine rates of gas transfer, heat conduction, void collapse, and frictional heating, during ignition and growth.3-4 Once steady state detonation is reached, the mesoscopic heterogeneity determines the structure of the detonation wave. Discontinuities can be caused within the wave by the natural heterogeneity of the material. The word “microdetonics” has been coined to describe the study of mesoscopic effects that lead to a macroscopic response, such as curvature or discontinuities in a detonation wave.5 Miniature test devices provide a means of controlling the mesoscopic structure and studying its effect on EM performance and microdetonics.

At Sandia National Laboratories we have begun a program to study the mesoscopic structure of EMs and how that

A new technology for the creation of test devices for the study of the mesoscopic response of energetic materials is described. The premise of this study is that semiconductor manufacturing techniques can be applied to energetic material processing. PETN has been chosen as a material to investigate due to its small critical diameter, high vapor pressure at moderate temperatures, and our previous experience with its vapor deposition. Deposition of films of PETN and subsequent patterning resulted in high-quality films with well-defined features. A silicon-based test device, with integrated ignition, consisting of nine channels, 300-μm-wide, 100-μm-deep and 1.2-cm-long is described. The integrated ignition system consists of nine semiconductor bridges on a silicon or sapphire substrate. Preliminary testing of powder-loaded devices with lead styphnate and BTATz is described.

*Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy under contract DE-AC04-94AL85000.
mesoscopic structure affects combustion and detonation of EMs. The premise of this study is that semiconductor manufacturing techniques can be applied to EM processing to control precisely the mesoscopic structure in miniature devices. The nature of semiconductor manufacturing techniques is such that the experimental devices and EMs within them have controlled microscopic features. These materials are thus called “microenergetic materials.”

The application of semiconductor manufacturing techniques to EM processing is a relatively new field. Studies have been limited to: ignition systems, such as the semiconductor bridge (SCB),\textsuperscript{6} the tungsten bridge,\textsuperscript{7} and the reactive bridge;\textsuperscript{8} digital micropulsion;\textsuperscript{9,10} reactive multilayers;\textsuperscript{11-13} porous Si;\textsuperscript{14} and deposition of EMs.\textsuperscript{15-16}

The application of semiconductor manufacturing techniques to EM processing imparts on EM processing some of the benefits that the semiconductor industry has enjoyed. For the purpose of this study, the most important of these benefits is the precise, microscopic control over manufacturing. In addition, the fabrication of multiple test devices using batch processing and the associated quality control are also anticipated benefits. We foresee a new paradigm in the way processing of test devices of this scale is conducted, in which the substrate, EM and ignition system are all processed in an integrated sense, utilizing advanced manufacturing techniques adapted from the semiconductor industry. Furthermore, this would allow the rapid manufacturing of hundreds of similar test structures with controlled variations in one or more variables.

Semiconductor processing is typically a two-dimensional process. For this reason, the devices and features that one can create have little or no variation along the axis orthogonal to the substrate. A cylindrical void can be created, but a spherical one cannot. A columnar EM grain can be created, but a spherical one cannot. A typical processing scenario might involve depositing a film of EM, masking this film with a photosresist, developing this resist in the desired pattern, etching the EM film, and then removing the photosresist. With this line of processing, a thin EM film would be manufactured, with regular, engineered columnar EM grains and a patterned void component, corresponding to the grains and three-dimensional voids, respectively, in a traditional EM. This film would have structural variation only in the two dimensions of the substrate and little variation orthogonal to the substrate. Figure 1 shows the result of processing of this nature, with a pattern developed in a film using photosresist as a surrogate for an EM film. The fact that the test devices are two-dimensional has the implication that modeling of these devices may be reduced to two dimensions also.

The development of methods to apply semiconductor manufacturing techniques to EM processing, in many

\begin{figure}[h]
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\includegraphics[width=\textwidth]{figure1.png}
\caption{Patterned Photosresist, Representing Desired Structure in PETN.}
\end{figure}
respects, involves reinventing each process. The results presented in this paper will be limited to progress that has been made in process development and less emphasis will be placed on the testing of complete devices that have been manufactured by semiconductor processing. Device design, deposition techniques, ignition systems, and integrated diagnostics will be discussed.

**ENERGETIC MATERIALS**

When choosing materials for manufacture of miniature test devices there are two main considerations. First, the material must have some possibility of functioning at small geometries. Second, the material must be compatible with semiconductor processing techniques. Only certain EMs exhibit these two characteristics. For both combustion and detonation, there is little literature on functioning of EMs at our desired geometries of hundreds of $\mu$m, principally because there are few traditional granular EMs that do function at these geometries, other than primary explosives, which are not compatible with semiconductor processing. For detonating devices, PETN (pentaerythritol tetranitrate) was chosen as a candidate material due to its small critical diameter (assumed from XTX-8003 (80% PETN, 20% Silicone Rubber), $D_c = 180$ $\mu$m, high vapor pressure at moderate temperatures, and our previous experience with its vapor deposition. For the combustion devices, candidate materials were determined through a series of tests.

This series of rapid screening tests was developed to select materials that might burn at small critical geometries. A small glass capillary tube, either a melting point capillary or similar, of nominal inner diameter from 300 to 1400 $\mu$m, was flame-drawn to achieve a taper to zero diameter on one end. The opposite end was left open. A NiCr hot wire loop, inserted into the EM through the open end, was used to ignite the material. If the material was difficult to ignite, an ignition mixture of 50% black powder/50% magnesium powder was used on top of the material to be tested. All tests were performed with the EM at bulk pouring density and at ambient temperature and pressure. The amount of material ranged from 1 to 5 mg, depending on the bulk density and inner diameter of the capillary used. Significant results of these tests are summarized in Table 1. Based on these tests, BTATz (3,6-bis(1H-1,2,3,4-tetrazol-5-ylamino)-1,2,4,5-tetrazine) was determined to be a likely candidate material and most likely to be compatible with our present deposition capabilities. Other potential materials include DAATO$_{3.5}$ (Diamino-azo-tetrazine, mixed N-oxides), TKP (Ti/KClO$_4$) and thermites, but for the purpose of this study we have not investigated deposition of these materials.

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<th>Internal Extinction Diameter ($\mu$m)</th>
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Table 1. Extinction Diameter for the Combustion of Several Materials at Ambient Pressure and Temperature.

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SILICON-BASED TEST DEVICES

A test device was developed as a universal substrate for integration of EMs and ignition devices. The basic device is deep-reactive-ion-etched into a 4-inch Si wafer. This wafer is diced into individual die, each 1.25 cm × 1.25 cm, yielding roughly 37 die per wafer at 100% die yield. The basic device (Figure 2) consists of nine channels, etched into each die, yielding a maximum of 333 test devices per wafer, at 100% yield. Other dies have been designed with integrated diagnostics, but initial studies will concentrate on the simplest design. The channels on the basic die are 300-µm wide, 100-µm deep and 1.2-cm long. At the proximal (ignition) end of the channel, the channel starts with a wider, 500-µm-diameter cylinder, also 100-µm-deep, which serves as the ignition site. At the distal end of the channel, the very end of the channel can be sawed off to allow for powder filling, or may remain closed if the EM is to be vapor-deposited. The channel may also be left open to allow release of pressure during device operation. The desired process is to vapor-deposit the EM into the channels and then attach a lid for confinement. For powder-filled devices, the lid can be epoxied onto the channel die and powder filling can be accomplished through the open distal end. The main channels on the die are each surrounded by a 30-µm-wide, 10-µm-deep channel, which is designed to prevent epoxy from flowing into the main channel and wetting the deposited EM.

SEMICONDUCTOR BRIDGE (SCB) LID

The lid for these channels is a transparent substance, either fused silica, quartz or sapphire. The lid is attached to the silicon die with low-viscosity, UV-curing epoxy (EPOTEK OG113). Ignition may be accomplished by direct laser ignition, laser heating of a vapor-deposited tungsten substrate in contact with the material, or by an SCB, depending on the ignition characteristics of the material and specifics of the experiment. The 500-µm ignition cylinder always serves as the point of ignition.

The desired ignition source for these test structures is an SCB, nine of which are integrated on the lid, with each SCB aligned over the center of its ignition site (Figure 3). Initial tungsten and palladium SCB ignition devices have been manufactured on silicon in order to refine the manufacturing process on an inexpensive substrate and to provide devices for preliminary testing. The final devices will be manufactured on sapphire, to allow visual alignment during assembly, and optical diagnostic access during testing. The

FIGURE 2. SILICON-BASED TEST DEVICE. THE NINE CHANNELS ON THE DIE ARE 300-µm-WIDE, 100-µm-DEEP AND 1.2-cm-LONG. THE 500-µm-DIAMETER IGNITION SITE IS AT THE BOTTOM OF THE FIGURE.
bridge of the tungsten and palladium SCBs consists of a two-material stack on an undoped polysilicon base, 1-µm thick, with a 0.66-µm-thick over-layer of either tungsten or palladium. The tungsten devices function similarly to a traditional, heavily doped polysilicon bridge and are more amenable to our current processing capabilities. The palladium devices function similarly to a hot wire. The lid is 1.7 cm × 1.7 cm, allowing greater than 2-mm overhang of the lid on each side of the test device. This overhang is especially important for electrical connection to each SCB via gold bond pads, which extend away from each SCB. Four sizes of SCBs have been manufactured on Si substrates, with bridge dimensions of 25 µm × 25 µm, 50 µm × 50 µm, 75 µm × 75 µm, and 100 µm × 100 µm. These devices are unique because both the SCB and gold bond pads have been manufactured on the substrate and therefore electrical connection to these devices is not made by the traditional wire bonds, which project up above the surface of the substrate. This allows flush mounting against the channel die, containing the EM. Electrical connection is accomplished with individual clips to each bond pad, or eventually by mounting this device into a multi-pin package. Another unique aspect of this device is that the nine SCBs are connected in series and thus each SCB shares bond pads with its nearest neighbor(s), allowing more devices to be built in a smaller area.

PETN DEPOSITION AND PATTERNING

Physical vapor deposition (PVD) of PETN films (Figure 4) was conducted in a vacuum chamber constructed of commercially-available vacuum components. The substrate was placed 3 mm above a heated crucible that holds the PETN powder. The system was pumped down to a pressure of 10⁻⁴ Torr and the crucible was heated to a temperature of 120 °C. Film deposition rates are on the order of 10 µm/hr. This process allows reasonably...
precise control of film properties. This method can be used with any material that exerts sufficient vapor pressure (~$10^{-5}$ – $10^{-3}$ Torr) at sufficiently low temperatures to ensure negligible decomposition of the EM. PETN films up to 40-µm thick were deposited on silicon substrates to investigate processing techniques to pattern the films. Additionally, the PVD of BTATz has been investigated, but thus far, has not produced films of sufficient quality to pursue further processing. This may have been due to a low vapor pressure or low sticking coefficient on silicon, not allowing sufficient nucleation for continuous film growth.

Various methods for patterning films of PETN have been investigated. Oxygen plasma etching proved to be too harsh an environment and resulted in chemical reaction of the film, evidenced by solubility changes of the PETN and physical eruptions of the film, likely due to thermal stresses. A technique that has proved successful, within certain geometrical constraints, involves the use of a “lift-off” procedure in which, prior to EM film deposition, a silicon oxide layer is grown in regions of the surface where PETN will eventually be removed. After this patterned layer is grown, the PETN is deposited to achieve a continuous film across the substrate. Removal of the PETN from the masked surfaces involves dissolving the oxide layer in a HF bath, with slight agitation to facilitate removal of the overlying PETN. Reasonable patterning of larger features in PETN films has been achieved by this method, but finer features are disrupted, likely due to the lack of a continuous mass of sufficient material to support the remaining structures in the film. A representative patterned film is shown in Figure 5.

INITIAL TESTING

A test was conducted to evaluate the functionality of EMs at these small geometries. The primary explosive lead styphnate was chosen due to its sensitivity and likelihood of propagating at the device minimum geometry of 100 µm. A glass microscope cover slip was attached as a lid to a preliminary die with epoxy. The lid was attached in such a way that the 500-µm ignition hole was not covered to allow powder filling of the channel. Filling was achieved through a hand-made funnel made from a flame-drawn and blown glass capillary tube. The funnel was positioned above the die using optical positioning equipment. Small amounts of normal lead styphnate were added incrementally to the funnel and shaken into the bottom of the test assembly, using an engraving pen to vibrate the assembly. Due to the small amount of material in the device, it was not possible to measure accurately the mass of lead styphnate in the channel. The volume of this channel was calculated to be 170 nL and assuming that the bulk pouring density of lead styphnate lies between 40% and 60% of
Ignition of the lead styphnate was achieved by the 532-nm second harmonic of a Nd:YAG laser, delivering roughly 140 mW to the 500 µm circular ignition spot on the sample. The continuous-wave beam was shuttered open for 10 ms. High-speed images were taken with a DRS Hadland 200 framing camera. The timing on the camera was set for an exposure time of 20 µs and an interframe time of 40 µs, resulting in a frame-to-frame time of 60 µs. The high-speed images from times 360, 420, 480 and 540 µs are shown in Figure 6. Ignition of the material within the circular ignition site is first visible at 240 µs from the shutter opening (not shown in figure). Due to the low power of the laser, inconsistencies in ignition delay from setup tests, the large total ignition delay, and no evidence of detonation, ignition appears to have been thermally initiated rather than shock initiated. Propagation from the ignition hole into the channel is first visible at 420 µs. By 480 µs, roughly 2 mm of the material in the channel is consumed. By 540 µs, the cover slip can be seen fracturing away from the silicon substrate. The estimated reaction rate is less than 100 m/s and the material does not achieve detonation, but only deflagrates, at least up to the time of fracture of the cover slip. It is possible that the material underwent the deflagration-to-detonation transition at this time, but this is difficult to determine from the high-speed photographic record. There is no evidence that the glass cover slip breaks away from the silicon substrate until over half of the material is consumed. The silicon substrate was intact after this test but most of the cover slip had been blown off the channel and the adjacent area. The failure mode of the cover slip was fracture and epoxy joint failure. All of the lead styphnate was consumed.

A series of scoping experiments were conducted to test the usefulness of a planned combustion diagnostic involving an integrated micro-piston within a silicon substrate. These experiments were conducted using BTATz as a propellant to drive a small piston within a 930-µm-diameter cylindrical column in the center of a 6-mm-diameter glass tube. A continuous-wave, 1064-nm, Nd:YAG laser, transmitted through a 1-mm-diameter optical fiber, was used to heat a tungsten substrate, glued to one end of the glass tube. The fiber output was aligned to the axis of the 930-µm-diameter column. Typical power at the
output end of the fiber is approximately 50 W. A miniature thermocouple inserted through the column and placed in contact with the substrate was used to measure the heating rate of the tungsten. Using a shutter to switch out a 100-ms pulse at full power, a temperature rise to 1000 °C can be generated in a little over 100 ms. Various combinations of final temperature and heating rate can be achieved easily by altering the power and the time that the shutter is opened.

A small amount of BTATz was packed in the capillary against the tungsten substrate using a small, weighted ram to achieve consistent packing. A 10-mg, 2 to 3-mm piece of steel rod was inserted on top of the packed BTATz. Ignition was very consistent, with rapid ignition occurring at 9 to 11 ms after the start of the laser pulse. Ignition under these conditions appears to produce a rapid convective deflagration and not a smooth laminar deflagration. Higher packing densities may achieve a more laminar deflagration. In one case, a very rapid acceleration of the 10 mg piston was observed. The piston left the column in one frame traveling at least 7 mm in 222 µs and possibly much more. This corresponds to a minimum velocity of 32 m/s. Two frames of a representative experiment are shown in Figure 7.

FUTURE WORK

Significant progress has been made in deposition and patterning of monomolecular EMs, such as PETN, but additional challenges lie ahead. Refinement of these processes will allow control over porosity parameters such as percentage, geometry, connectivity, and grain size. Once these techniques are in place, numerous experiments will be conducted to examine the mesoscale effects on the EM. Without a strict control over porosity, it may be necessary to use very sensitive materials to achieve a functional device. With refinement of deposition and patterning techniques, it will likely be possible to engineer materials that function at scales smaller than they would traditionally function by optimizing the geometry of void content.

The fact that these devices are manufactured using semiconductor processing techniques will allow integrated diagnostics to be manufactured directly onto the substrate. Several diagnostics of varying complexity have been designed. The simplest diagnostic involves a frangible silicon barrier across the channel. By varying the thickness of this barrier, the pressure and amount of EM consumed at the time of breakout can be measured for a deflagrating material. Additionally, this barrier may be able to be used as a reflector for an interferometry system to measure particle velocity behind a detonating EM. Another integrated diagnostic involves a
“bullet” within the channel, lightly held in place by a retaining strap until pressure from a deflagrating material breaks it free. The acceleration of this projectile will give information on the pressure exerted on it by the deflagrating EM. Still another diagnostic involves a break-wire array of several small wires which have been deposited across the channel and have bond pads for connection to each wire, allowing a high-speed resistance measurement to be recorded and for the velocity of a passing reactive wave to be measured as the break-wires open.

CONCLUSIONS

The application of semiconductor processing techniques to EM processing to create a new class of “microenergetic materials” has shown promise for the creation of test devices for the study of the mesoscale response of EMs. Advantages of semiconductor processing include precise control over material structure and the possibility of rapid throughput prototyping and manufacturing. Additionally, integrated diagnostics may be able to be co-manufactured with the test device, allowing minimal setup during testing and for many tests to be performed in a short period of time. With the successful creation of a technology base for the manufacture of these materials, a new paradigm in the manufacture of test devices may be realized. Beyond the creation of test devices for the study of monomolecular explosives, semiconductor manufacturing techniques may allow the creation and study of nano-structured materials, involving layers of reactive materials, or layered explosives with reactive materials.

ACKNOWLEDGEMENTS

The authors wish to thank Mike Hiskey of LANL for supplying the BTATz and DAATO_{3.5} used in the combustion studies. The authors wish to acknowledge Brian Wroblewski, John J. Nogan, and Sherry A. Zmuda, for their work designing and manufacturing test devices and in developing new processes for working with EMs. Additionally, we thank Jaime N. Castañeda, Jill C. Miller and Michael S. Oliver for fixturing and testing of devices. This work was supported by Sandia’s Laboratory Directed Research and Development program and the Nuclear Weapons Advanced Systems and Technologies Program.

REFERENCES


