Nanotechnology-Enabled Microthrusters: Nanoenergetic Materials and MEMS Paradigm

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ABSTRACT

We study microthrusters which can be used in various flight and underwater platforms. The MEMS-technology thrusters with Al/I_2O_5 and Al/Bi_2O_3 nanostructured energetic composites increase thrust-to-weight ratio and energy density, thereby ensuring enabling capabilities. The integrated micromachining ensures overall technology compatibility, scalability, simplicity, affordability, robustness, etc. These lead to advantages as compared to conventional solutions. The MEMS-technology microthrusters with solid-fuel are suitable in a wide range of applications, such as payload delivery, stabilization, guidance, navigation and other platforms.

Keywords**:** MEMS, microthrusters, nanoenergetics

1. INTRODUCTION

It is important to develop and apply new scalable and integrated technologies. We focus on applications of micro and nano technologies in design and developments of integrated microthrusters which use nanoenergetic materials [1-3]. The overall functionality may be ensured using integrated MEMS technology with high-energy-density nanostructured materials encapsulated in silicon-micromachined voids [4]. A scalable and *modular* system-level solution is achieved by integrating of microstructures, MEMS sensors and energetic materials. Our solution ensures enabling capabilities, such as safety, high stored energy capacity, high specific energy, high energy and gas release rates, optimal burning, etc. The MEMS design and integration of self-assembled nanoenergetic materials imply development of integrated MEMS and nano technologies.

Proof-of-concept MEMS-technology systems have been fabricate [5, 6]. Sensing, diagnostics, control and other attributes must be ensured guaranteeing safety, robustness, monitoring, data acquisition, uncontrolled ignition prevention, etc. Depending on vehicles, missions, requirements and specifications, various physical variables must be directly or indirectly measured. The fabricated devices include integrated ignition capabilities along with temperature and pressure sensors.

Our studies indicate that the synthesized Al/Bi_2O_3 and Al/I_2O_5 nanocomposites ensure energy release and generate transient pressure impulses which are three times higher than traditional nano-thermite reactive mixtures. The peak pressure is generated during the combustion of nanoenergetic mixtures. The bismuth trioxide nanoparticles, synthesized by combustion synthesis generates pressure, ensure pressure three times higher than pressure of commercial Bi_2O_3 nanoparticles [7].

We address and provide systems-level design solutions solving integration, packaging, diagnostics, control and other problems. The net thrust in a wide range (from ~μN to N) can be generated by a single or multi-array thruster cells. It is possible to ensure controlled impulse- and uniform near-continuous-thrust propulsion for micro-air, space and underwater vehicles. Depending on applications, high temperature, high pressure, specified combustion, desired flow rates, optimal energy conversion, effective energy release, and other desired features can be achieved.

2. NANOENERGETIC MATERIALS

The established and demonstrated nanoenergetic thermite composites include mixtures of Al and other metal oxides. Among numerous thermodynamically feasible nanoenergetic mixtures, the most widely studied are Al/Fe_2O_3, Al/MoO_3, Al/WO_3, Al/CuO, Al/Bi_2O_3 and others. The distinguishing features of these compounds are significant enthalpy release and adjustable rate of energy discharge. These features result in a wide range of combustion rates, energy release and ignition sensitivity.

Among common thermite composites, Al/Bi_2O_3 and Al/I_2O_5 mixtures ensure high energy density and generate the highest pressure impulses reaching ~11 MPa. The high pressure during the combustion of Al/Bi_2O_3 and Al/I_2O_5 results because the reaction product (bismuth or iodine) boils at temperature 1560°C and 184°C, respectively [1]. The aforementioned temperatures are lower than the maximum reaction temperature, which is ~2000°C. This causes bismuth or iodine evaporation, with the increase the released gas pressure. The energy release nanoenergetic reactions are

$$Bi_2O_3 + 2Al = Al_2O_3 + 2Bi + \Delta H\ (-15.2\ kJ/cm^3), \quad (1)$$

$$3I_2O_5 + 10Al = 5Al_2O_3 + 6I + \Delta H\ (-25.7\ kJ/cm^3). \quad (2)$$

Aluminium nanoparticles are highly pyrophoric in air, and, they are usually coated with a 4-8 nm thick coating oxide Al_2O_3 shell during their fabrication. The coating reduces the active Al content in a compound, thereby decreasing the ignition sensitivity. In most experiments, we use Al particles with an average size ~100 nm. This powder is not very active in air, and, can be safely mixed with metal oxides in the preparation of thermite reactions mixtures.

3. SELF-ASSEMBLED NANOENERGETIC COMPOSITES

Controlled self-organization is an ability to synthesize robust, well-defined, atomically-self-*engineered* and self-aggregated structures, composites and mixtures from atoms, molecules and compounds in a pre-defined and controlled synthesis process with external control inputs such as heat, light, mechanical agitation, etc. Once initiated, the self-organized and self-aggregation processes utilize immense number of molecules, organized into integrated nanostructured mixtures, which possess specific performance, attributes and capabilities. In our synthesis, a polymer chain poly(4-vinyl pyridine) binds Bi_2O_3 or I_2O_5 with Al nanoparticles. The polymer is a structural link for the nanoparticles assembly process. The Al nanoparticles (~100 nm in diameter with 4 nm of passivation layer) with Bi_2O_3 and I_2O_5 were coated and bonded with the poly(4-vinyl pyridine) polymer in a sonic bath.

4. NANOENERGETIC COMPOSITES AND MEMS

The nanoenergetic materials can be used as explosives, solid-fuel propellants, pyrotechnics, additives for liquid propellants, etc. The spontaneous chemical reaction, as initiated, is driven by a large exothermic change (release of heat) as well as gas release. A very favorable rapid thermodynamic process is achieved by Al/Bi_2O_3 and Al/I_2O_5. The controlled uniform burning of the propellant produces a controlled thrust for continous and impulse propulsion of flight vehicles as well as to rocket-propelled supercavitation underwater vehicles.

The *net* thrust is

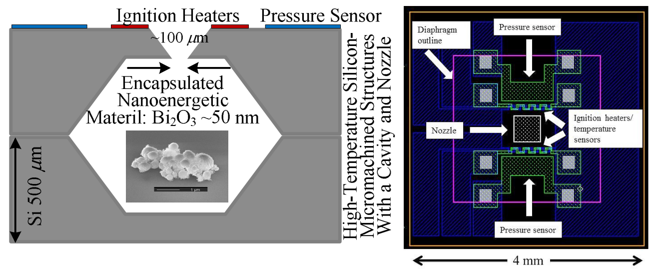
$$F=\dot{m}_e v_e=\dot{m} v_a + A_e(P_e - P_a), \quad (3)$$

where $\dot{m}_e$ is the propellant exhaust gas mass flow which depends on the propellant combustion rate $\dot{m}$; v_e is the effective exhaust velocity along the thrust axis; v_a is the actual exhaust velocity at nozzle exit plane; A_e is the flow area at the nozzle exit plane; P_e and P_a are the static pressure at the nozzle exit plane and ambient pressure.

The total impulse is defined as $\int F dt$, while the continuous thrust is Ft.

The combustion of self-assembled nanoenergetic clusters in micromachined micro-chambers ensures high and uniform exhaust velocity v_e and rate $\dot{m}$. The major thruster core and support structures are comprised from silicon-micromachined chamber and nozzle. There are no channels, pumps, valves, propellant tanks, fuel lines, etc. [8]. The designed microthruster is illustrated in Figure 1. The chamber, where the nanoenergetic materials are encapsulated, and nozzle are made from silicon and silicon-competitive materials. The MEMS sensors are used to measure temperature, temperature gradient, pressure and other physical quantities.

Different concepts and designs are considered. The microthruster arrays can be made by using multi-layered silicon, glass and polymer layers, while the middle layer or cavities consist of encapsulated combustible nanoenergetic propellants in a solid form. The polysilicon heaters initiate combustion. Cells can be separately ignited, producing desired thrust and ensuring the thrust-vectoring capabilities. Microthrusters can be controlled and ignited within the desired sequence using ICs. Various sensors can be used in our highly-integrated MEMS platform. The microthruster array may be designed within different micro-chambers configurations and three-dimensional geometry.



(a) (b)

Figure 1. (a) Cross-sectional view of designed microthruster made using silicon technology. Nozzle, ignition heaters, and monitoring sensors are integrated. The chamber is created by bonding the top section to the *bulk*-micromachined bottom component with the bottom chamber cavity;
(b) Top view of micromachined microthrusters layout showing the ignition heaters, nozzle, and monitoring sensors.

Microthrusters are ignited by applying a dc voltage to a polysilicon resistor which is heated up to ~700°C due to the flow of current. The produced heat leads to ignition of encapsulated propellant. As a propellant is ignited, a high-pressure is formed during a high-temperature gas phase. Each micro-chamber can deliver a single impulse. The duration and thrust of an impulse can be controlled through a volumetric design, three-dimensional nozzle and chamber geometry designs, propellant used, etc.

The chamber, nozzle and propellant capsule volumetrics and three-dimensional geometry significantly affect the burning rate, thrust and other characteristics. A high degree of robustness, safety, reliability, controllability, integration and packaging can be achieved. The velocity of exhaust gasses can be controlled by nozzle and chamber geometries. The convergent, convergent-divergent and divergent nozzles are examined. Sustained and uniform combustion may be achieved.

5. MICROELECTRONICS AND MEMS SOLUTIONS

The MEMS technology allows one to fabricate structural silicon and silicon-compliant microstructures, semiconducting electronic and sensing devices, etc. The scalability, functionality and other features, pertained to a microelectronic compatibility, are guaranteed. We design structurally and functionally integrated MEMS. Sensing, diagnostics, control and other attributes are ensured. These guarantee safety, robustness, monitoring, data acquisition, uncontrolled ignition prevention, etc. Wireless communication and management systems can be designed. The aforementioned features significantly enable and enhance solutions reported in [8].

Processing, controlling, sensing and signal conditioning ICs comprise an *Integrated Electronic Management Module*. A proof-of-concept of the studied *NanoEnergetic MEMS MicroThruster Platform* is fabricated. The technology-, application- and platform-specific designs are performed. We design and tested MEMS system prototypes within different organizations and complexity which define the overall functionality. The solid-fuel high-energy-density propellant should burn in controllable and optimized manner, producing exhaust gases and thrust. The chamber and nozzle dimensions and three-dimensional geometries are designed to ensure the specified pressure and thrust produced from the exhaust gases. Depending on vehicles, missions, requirements and specifications, various three-dimensional chambers and nozzles are fabricated as illustrated in Figure 2. The physical variables must be directly or indirectly measured. In particular, temperature, pressure, velocity and other physical quantities are of interest. The ignition is accomplished by the p+ silicon or aluminum heater.

A *bulk* MEMS microfabrication process was used to fabricate microthrusters. For the proposed design, there is no need to use a deep reactive ion etch (DRIE) technique which results in the high aspect-ratio nozzle structure or the chamber cavity. We develop a hard-mask process to define the nozzle and chamber geometries using conventional RIE techniques. A wet KOH etch is used to form the chamber. Silicon is used as the structural material, SiO_2 forms insulating layers, doped p+ silicon is aimed for temperature and stress sensing, while aluminum forms interconnections and heater. The fabrication process starts with double-side-polished n-type silicon wafers. A silicon oxide is grown and used as a masking layer for the p+ spin-on-dopant process, which could be the heating element on the membrane, as well as the strain sensor to measure the membrane deflection and pressure. A pad silicon oxide is thermally grown. The silicon nitride is deposited using a low-pressure chemical vapor deposition (LPCVD). The silicon nitride and oxide are patterned on the backside of the wafer by dry SF6 and buffered oxide etch (BOE). Polysilicon is deposited by means of LPCVD to protect the patterned nitride on the backside of the wafer until the bulk silicon etch is performed. A 1 μm oxide layer is deposited, and, the contact openings to p+ silicon are etched in a BOE solution. After the contacts are etched, a 1 μm Al layer is deposited, and, then patterned to make the electrical connections, function as the ignition heater, and, function as the temperature sensor. 1 μm passivation oxide is deposited on the front of the diaphragm to provide a layer of separation needed for the hard-mask material used to etch the top hole. A 0.5 μm Al hard-mask is deposited and defined with the top-hole pattern. The front of the wafer is protected with Brewer Science's PROTEK™. The diaphragms are formed by etching from the back of the wafers. The patterned silicon nitride is used as a protection layer during the silicon KOH etching process. The depth of etching is measured until the desired diaphragm thickness is obtained. As desired depth is ensured, the PROTEK™ is removed. A bottom 0.5 μm Al layer is deposited to protect the back of the devices. The wafers are then diced in a conventional dicing saw. The top hole is etched using SF6 RIE. The aluminum hard mask on the front of the wafer, and, the Al on the back of the wafer, are etched away using a commercial wet aluminum etch solution. The final step consists on etching the oxide separation layer in SF6 to expose the aluminum contact pads to the devices. Temperature can be sensed by the Al resistor by measuring the change in resistance during ignition. In fact, the temperature-dependent resistance is given as

$$R=f(T)=R_0[1+\alpha(T-T_0)], \tag{4}$$

where R_0 and T_0 are the resistance and temperature at room temperature; α is the temperature coefficient, α_{Al}=3.6 %/K.

The pressure in the chamber is estimated by monitoring the change in resistance of the p+ resistor due the piezoresistive effect. The stress σ seen by the resistor at the edge of the diaphragm is

$$\sigma=0.3\rho L^2/h^2, \tag{5}$$

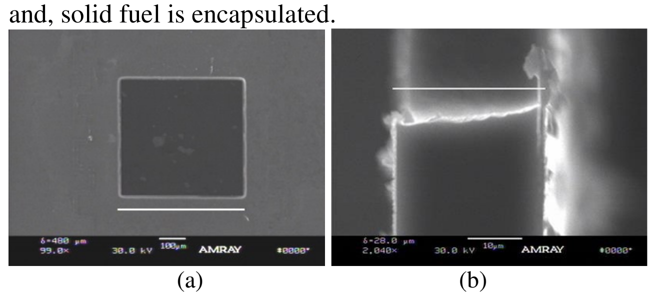
where L is the length of the diaphragm; h the thickness; ρ the pressure.

The change of resistance is a function of the strain. Using the piezoelectric coefficients of the p+ silicon,

$$R=R_0[1+\pi_L\sigma_{xx}+\pi_T(\sigma_{yy}+\sigma_{zz})], \tag{6}$$

where σ_{ii} is the stress in the specified direction; π_L and π_T are the longitudinal and transverse piezoelectric coefficient with respect to the direction of the charge carriers.

Two ignition heaters, which can be used as the temperature sensors, formed by deposited Al and p+ silicon, are on the opposite sides of the nozzle opening as shown in Figures 1 and 2. In the p+ silicon structure, the resistance changes due to both strain and temperature variations. The variations of R should be correlated taking into the account both factors. The SEM images, reported in Figure 2, show the desired near vertical nozzle sidewall with a slight retrograde shape as per optimal design. This 3D geometry optimizes the thruster performance. The thickness of the diaphragm may vary from ~30 to 150 μm. The refinements can be performed to further optimize microthrusters performance. The top and bottom structures are bonded, and, solid fuel is encapsulated.



(a) (b)

Figure 2. Nozzle structures: (a) Top view of nozzle opening; (b) Cross-sectional view of nozzle showing a nearly vertical opening.

6. MICROTHRUSTER TESTING

For testing, the electrical connections are made by wire-bonding the top component to a PCB board as illustrated in Figure 3.

The thrust and force, produced by a single microthruster were measured experimentally. The microthrusters are attached to an analytical balance which is connected to a PC with the recording, data acquisition and processing capabilities. The microthrusters are ignited as illustrated in Figure 3. The measurements are made, thereby guarantying characterization and evaluation.

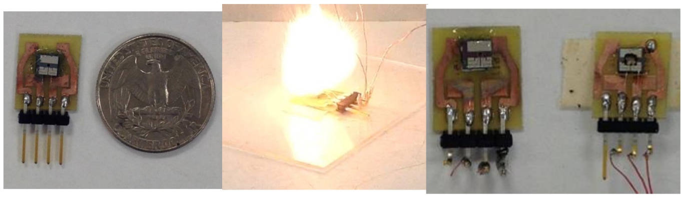


Figure 3. (a) Assembled microthruster with wire-bond connections to a PCB board; (b) Testing of a microthruster: Ignition by using a heater; (c) Microthruster before and after ignition test

Figure 4 illustrates the mass change of the microthruster during the combustion process using a sensitive balance. The exhaust gases are directed vertically upward, while a microthruster is exhibit the force on the balance during combustion. There is time delay due to inertia of the balance. However, the maximum force produced by microtruster is measured. The amount of Al/I_2O_5 nanoenergetic material was 4.82 mg. The inner volume of the chamber was 4.2 mm^3. Thus, the density of Al/I_2O_5 in the microthruster cavity is 1.15 g/cm^3. The packing density significantly affects the thrust and force. The produced force is 7.2 mN, ensuring the quantitative measure 1.5 N/g. The force produced by a single microthruster can be varied by using nanostructured materials with different stored energy, changing the solid-fuel density, varying amount of fuel in the chamber, etc. Changing the chamber size and volume, one refined the weight and density of the encapsulated nanoenergetic compound.

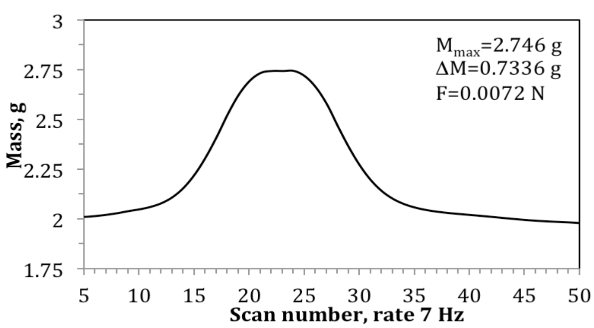


Figure 4. Evolution of mass change during the solid-fuel combustion

6. CONCLUSIONS

Departing from conventional solutions, new nanoenergetic materials were designed and synthesized. We reported fundamental, applied, experimental and technological studies for enabling high-energy-density nanostructured materials based on bismuth and iodine oxides. High-yield synthetic reaction and synthesis process were developed to precisely control molecular structure of nanoenergetic materials. These materials can be encapsulated in *integrated* MEMS which include controlling, sensing, diagnostics and processing capacities by means of microelectronics. We documented transformative developments towards *NanoEnergetic MEMS MiroThruster Platforms*. This solution guarantees sensing, diagnostics, control and functionality. The application-specific thrust impulses, thrust-vectoring and continues thrust can be ensured by microthrusters and their arrays. Various issues should be considered, such as:

- Optimization of three-dimensional chamber and nozzle volumetrics and geometries;
- Controlled combustion propagation and dynamics;
- Uniformity of reaction, burning, heat transfer, pressure, temperature, stress, combustion, flame, etc.;
- Data-intensive analysis, diagnostics, adaptation and optimization.

The system-level design was accomplished. The integration and functionalization of self-assembled nanoenergetic materials was archived by using an integrated MEMS technology. Novel technologies and transformative developments were initiated.

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