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Microfabricated Chip for Calibration of Field Instruments

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Abstract- *Accurate, periodic calibration is required to operate IMS, GC, and portal security systems with maximum efficiency, surety, and operator confidence. To this end, we are presently developing a microfabricated device for on-demand calibration of fieldable contraband detection instruments. Using robotically-assisted picoliter dispensing methods, precise picogram or larger amounts of calibration compound(s) are placed on micron-sized bridge structures. Resistively heating these structures delivers precisely quantified low-levels of calibration compounds to the detector systems. This provides reliable calibration for identification and quantification of explosives, narcotics, and other contraband.*

1. INTRODUCTION

Accurate, periodic instrument calibration will improve field operation of ion mobility spectrometers (IMS), mass spectrometers (MS), gas chromatographs (GC), portal security systems, and unattended sensor networks for detection of explosives, narcotics, and chemical warfare agents. Calibration includes drift time for IMS, retention time for GC, collection efficiency, and detector mass response. Current low-level field calibration methods for explosives and drug detection have shortcomings that make it very desirable to create a highly transportable, robust calibration source to produce precision calibrations under all operating conditions. Common field calibration methods include bag standards, calibrated gas mixtures [1], diffusion vials, vapor generators, and permeation tubes. These sources can be cumbersome, and are susceptible to environmental changes. Many of these calibration methods also require peripheral equipment such as mass flow controllers, ovens, and power supplies. Excess equipment proves difficult to maintain in the field and increases the technical acumen necessary for system calibration. Furthermore, these methods are of limited use for low volatility compounds such as explosives, narcotics, and calibrant markers used in contraband detection. Additionally, a major problem for external calibration methods is adsorption of the desired picogram levels of analyte to the transfer lines between the source and the instrument inlet.

To create a fieldable calibration source, other research has produced high volatility vapors from thermal decomposition of thermally labile salts [2], though this effort does not feature the high density of calibrant charges as the work shown here, and it is based on a less physically robust design. Extensive work on vapor generation systems has also been performed, but these systems lack the small footprint and the ability to produce standardized samples desired by the user community.[3] Other technical work uses sorbent traps, which require the traps to be loaded onsite using laboratory equipment, or preloaded and stored at near freezing temperatures.[4] Newer work involving precision explosives deposition on swab sheets cannot be easily integrated with field systems nor automated, making it susceptible to error from human and environmental factors.

We have developed a microfabricated device consisting of a micro-bridge array with dozens of individual elements coated with precise nanogram (or larger) amounts of calibration analytes. The analytes can be thermally desorbed on demand from within, or by placement over, the heated inlet of an analytical instrument to provide calibration. Its use will be extremely cost effective compared to lab-based calibrations in terms of material, down time, transportation, and labor. In addition, the benefits of being able to recalibrate during changing field conditions are invaluable, and cannot be replicated by laboratory calibration.

2. DEVICE FABRICATION

To construct the micro-bridge devices, a simple, three mask, SOI wafer fabrication process was developed. The 100-mm diameter SOI wafers consisted of a highly doped, 10 micron thick N-type single crystal silicon device layer with a 1 µm thick buried oxide and a thin handle wafer. The first fabrication step consisted of a blanket aluminum deposition, and subsequent patterning via lift off, to form the bond pads and ground plane for the micro-bridges. The second mask step involved patterning a front side photoresist hard mask for Bosch etching. This etch stopped on the buried oxide layer, and defined the individual bridges, bond pads, and device ground plane in the highly doped silicon. The final mask step placed a thick photoresist mask on the back side of the SOI wafer. This mask defined trenches across the device that would serve to both release the micro-bridges and define the subsequent flow path through the device. This final Bosch etch progressed through the handle wafer and stopped on the buried oxide. After mask removal, a buffered oxide etch or dry plasma etch stripped the oxide to fully release the bridge elements. After dicing, each wafer yielded 124 devices of approximately 630 µm x 800 µm, each containing 20 bridge elements. Figure 1 shows a completed device with a detail of the suspended micro-bridges.

Given the large number of devices produced per wafer, a variety of different geometries and bridge lengths were produced. The bridge lengths varied from 200-600 µm in length, and 100-200 µm in width. Additionally, a unique diamond shaped bridge was fabricated, as well as a more typical straight-edged bridge. The diamond shaped bridge, shown in Figure 2, provides a larger central span for easier calibrant deposition and a more uniform axial temperature distribution. After fabrication, the bridge resistances ranged from 300 ohms to 500 ohms.

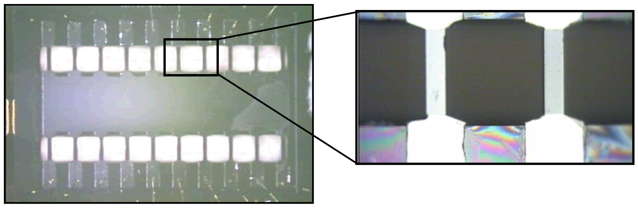

Figure 1- Image of micro-bridge chip with inset detail of bridge elements.

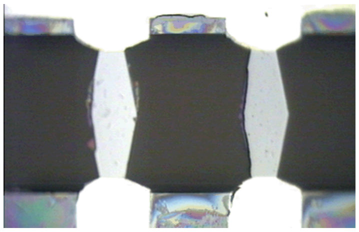

Figure 2- Detail of diamond shaped bridge.

3. EXPLOSIVES DEPOSITION

A number of different techniques potentially exist for the deposition of explosives on a microcalibration source. We have selected inkjet printing because it is additive, non-contact, and is suitable for the deposition of any material that can be dissolved in a solvent meeting the viscosity and surface tension requirements for inkjet printing.[5] Inkjet printing has been used for the deposition of a variety of materials as dispersions or solutions, including: carbon nanotubes,[6] ceramics,[7] polymers,[8] and explosives.[9]

Experimental

Commercially-available explosive standards are typically developed for chromatography calibration and typically are solutions in methyl alcohol, acetonitrile, or ethyl acetate at concentrations of 0.1 or 1 mg/mL.[10] These standards provide traceable inks that can be directly printed, without additional formulation. The majority of these standards employ acetonitrile as the solvent, so it was evaluated first to determine its printing characteristics. After finding satisfactory printing properties in acetonitrile, a 1 mg/mL 2,4,6-trinitrotoluene (TNT) standard in acetonitrile was chosen for evaluation in this work. All printing was conducted on as-received silicon wafers, with no additional cleaning.

The inkjet printing system consists of a motion control system (Robocaster),[11] which positions the printhead. Custom software allows for computer-aided design and fabrication of printing sequences. A 40-micron piezoelectric printhead (Microfab Technologies Inc., Plano, TX) is driven by a JetDrive™ III controller, which delivers a user-defined pulse sequence to define the jetting characteristics. This controller is triggered during printing sequences by a computer-controlled pulse generator to allow drop-on-demand printing.

Droplets exiting the printhead were photographed through a microscope mounted on the printer with a 10x Mitutoyo long-working distance objective, using a turning mirror on the stage. Sharp images of droplets were obtained using back-illumination with a pulsed light-emitting diode. Droplet diameter was measured using edge detection procedures in Image-Pro Plus software, calibrated against a 100-line-per-mm Ronchi rule.

Results and Discussion

Droplet size measurements were conducted on pure acetonitrile. The two critical jetting parameters: pulse shape and printhead backpressure, were adjusted to achieve a stable jet, with no satellites. A satellite is a secondary droplet that typically is smaller than, and off-trajectory from, the primary droplet. Images from two different cameras, with different magnifications, showing a droplet after exiting the printhead are shown in Figure 3. The droplet size at these printing conditions was determined to be 60-micron.

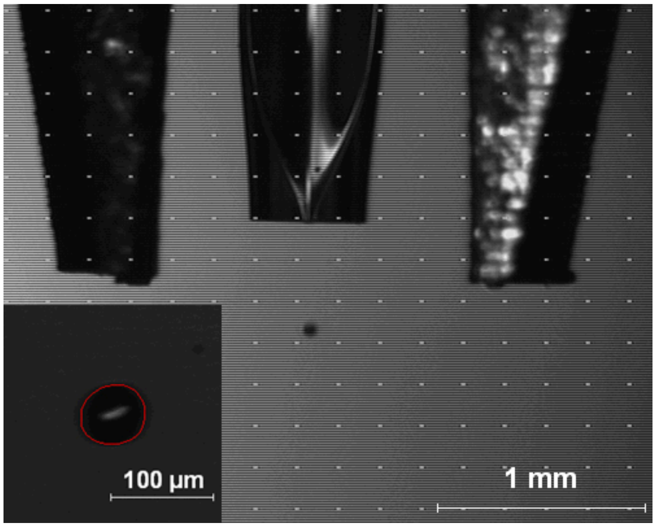

Figure 3 - Acetonitrile droplet after ejection from a 40-µm printhead. Inset shows the 60-µm software-determined diameter.

Based on the diameter of a droplet, the volume is given by:

$$V_{droplet} = (4/3\ \pi\ (d_{droplet}/2)^3)/1000, \qquad (1)$$

where $V_{droplet}$ is in pL and $d_{droplet}$ is in µm. Taking this value for the volume, the mass of solids deposited per droplet is given by:

$$m_{solids}/\text{droplet} = V_{droplet} \times [\text{solids}], \qquad (2)$$

where m_{solids} is in pg, and [solids] is in mg/mL. Commercially-available standards are typically available in 0.1 or 1 mg/mL, so typical droplets would contain solids of tens to hundreds of pg/drop. This is represented graphically in Figure 4. From this relationship, the mass of TNT contained in a 60-µm diameter droplet of 1-mg/mL solution would be 113 pg.

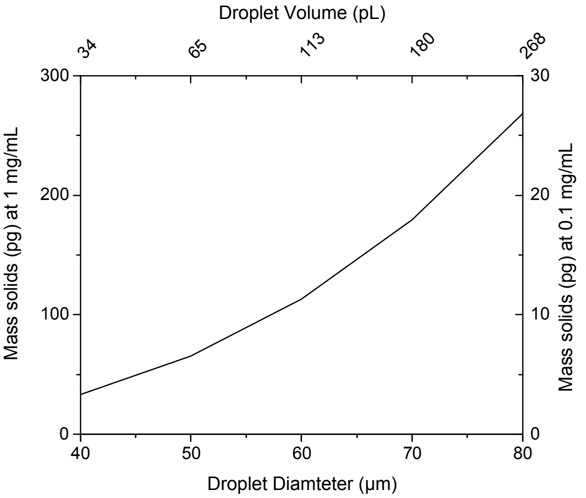

Figure 4 - Solids within a droplet of 1 mg/mL and 0.1 mg/mL concentrations versus droplet diameter and droplet volume.

Simple 2×10 arrays of TNT spots were deposited on silicon to qualitatively examine deposited material characteristics and to demonstrate feasibility of this technology for the deposition of explosives for a microcalibration source. The spacing was 1-mm between the two rows and 0.5-mm between spots within a row. An array of these spots is shown in Figure 5. The ringed appearance of these spots is due to TNT flux to the pinned perimeter during evaporation.[12] This figure shows spots that each consist of four droplets, thus each dried spot consists of about 400 pg of TNT.

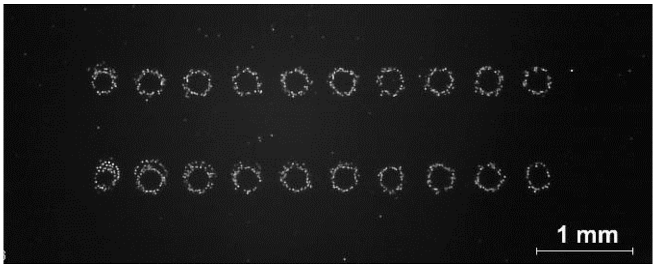

Figure 5 - 2×10 array of TNT spots on silicon. The spacing is 1-mm between the two rows and 0.5-mm between spots within a row. Each spot contains about 400 pg of TNT.

It was discovered that the TNT spots were subliming within one hour of deposition, even at room temperature. Figure 6 shows time-lapsed photographs of this effect. For these photographs, the robotically-controlled microscope was moved to the TNT spot immediately after deposition and photographs were taken every 8 minutes.

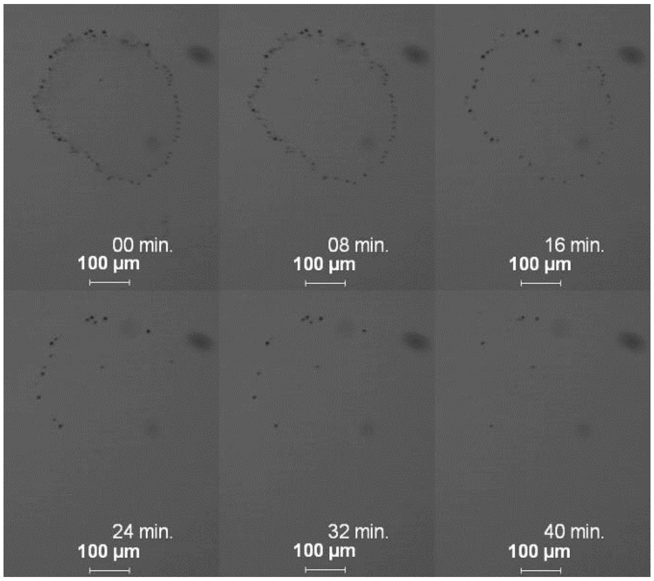

Figure 6 - Time-lapsed photographs taken every 8 minutes showing sublimation of a TNT deposit at room temperature.

For successful application of explosives via inkjet technology to a microcalibration source, this effect must be mitigated by decreasing the sublimation rate to an insignificant level until the prescribed volatilization at the time of use. This may be performed through trapping the solids in a matrix or with a capping layer that by design, doesn't affect the validity of the microcalibration source at the time of use.

4. TESTING

While stable application of TNT on the micro-bridge elements has not yet been fully realized, there is a wide range of alternative calibrant materials available. To test the device proof-of-concept, a nonvolatile salt, tetra-alkyl ammonium hydroxide, was deposited on the bridges. Simonson et al, had previously demonstrated these salts to be valid GC calibrants with stable and reproducible decomposition products and stable, long-shelf lives in an ambient environment. These salts were spray deposited over the micro-bridge structures in 5% weight solutions with water. Figure 7 shows an image of bridges coated with the salt solution. The poor salt coatings indicate surface modification of the bridge structure through oxygen plasma activation will be necessary for improved uniformity.

After bridge coating, the individual device dies were glued to a conventional printed circuit board and wire bonded to allow for easy electrical connection, as shown in Figure 8. A total of 21 wire bonds were made for each die; one bond for each bridge, and one to the large central ground plane at the device center. The circuit board below the die was removed, to allow a flow path perpendicular to the surface of the die. A perpendicular flow path will create a short path length for calibrant desorbtion directly into an analytical instrument inlet. Such a flow path also minimizes the distance a calibrant has to travel over relatively cooler features, such as other unheated bridges, and hence it minimizes calibrant losses to the surrounding environment.

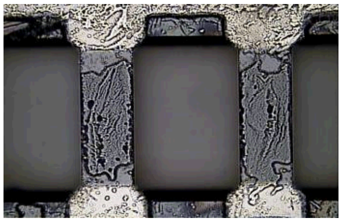

Figure 7- Image of coated bridge structures.

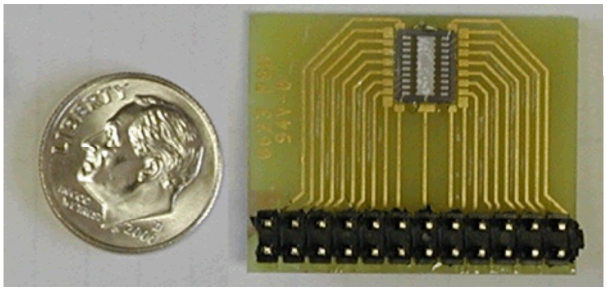

Figure 8- Microcalibrator die mounted and wirebonded to PCB for testing.

Results and Discussion

The coated micro-bridges were thermally desorbed with a 10 V DC pulse (unoptimized) into a GC/FID using a 3 psig helium carrier gas. Figure 9 shows an FID peak from one of the micro-bridges. Using previously derived calibrations and peak fitting software, the peak area represented approximately a 0.3 nanogram desorption. The peak shapes indicate a very fast thermal decomposition of the salts, followed by a probable overloading of the GC column, as indicated by the sharp peak trailing edge. As expected, the variability in desorbed mass was high across a device; calculated mass desorptions ranged from 0.3 -2.4 nanograms.

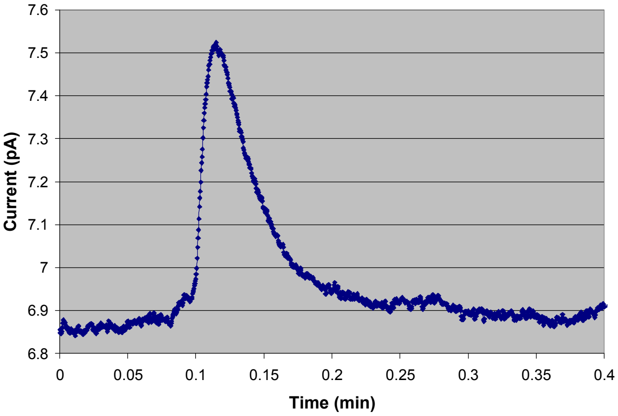

Figure 9- FID peak representing a calibrant mass of 0.3 ng.

5. CONCLUSION

We have fabricated and testing a 20-element micro-bridge device for field calibrantion of chemical detection systems. The device was fabricated using a simple, 3 mask SOI process which produced a large number of robust devices. The micro-bridge elements were produced in a number of varying sizes and shapes, including a diamond-shaped element to ease the challenge of calibrant deposition.

In parallel, we have shown that chromatography calibration standards can be used directly as calibrant inks and that acetonitrile is an acceptable solvent that meets the viscosity and surface tension requirements for inkjet printing. Many standards other than TNT can be purchased at 1 mg/mL concentration and thus this technique can likely be extended to many other materials. Ring-shaped TNT deposits of appropriate size and mass were deposited on silicon. The sublimation of deposits was shown to be an issue that must be mitigated for application of this technology to materials with significant vapor pressures at room temperature.

To allow proof-of-concept demonstration, a non-explosive calibrant, consisting of the nonvolatile salt tetra-alkyl ammonium hydroxide, was deposited on the bridges. FID system analysis of thermally-desorbed peaks found them to be in the low nanogram mass range. The peak shapes indicated a fast thermal decomposition of the calibrant and subsequent rapid desorbtion.

Future project work will concentrate on the development of encapsulants or coatings for direct TNT deposition on the micro-bridge elements. In parallel we will seek to demonstrate precision coating of other calibrants, such as the nonvolatile salts, with the inkjet printing technology. Finally, efforts at surface modification of the silicon bridges and the surrounding aluminum pads will be made to better confine the calibrant deposition.

Acknowledgements

J. Patrick Ball conducted the TNT printing experiments and James W. Colovos assisted with motion control programming. Devices were fabricated by Cody Washburn and John Anderson. Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy's National Nuclear Security Administration under Contract DE-AC04-94AL85000.

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