Vanadium oxide thermal microprobes for nanocalorimetry

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Abstract — Highly sensitive thermal microprobes are presented, consisting of curved cantilevers with vanadium oxide thermistors located at their tips. The cantilevers are realized by stress-engineered metal thin films and the thermistors consist of reactively sputter-deposited vanadium pentoxide. The thermistors are electrically contacted through the stressed metal layer, and at the same time thermally insulated from the substrate due to the relatively small thickness and large length of the cantilevers. We propose to apply these novel thermal microprobes in a nanocalorimetry system, in order to lower the cost and increase the sensitivity of the measurements.

I. INTRODUCTION

Calorimetry is a powerful method for characterizing biochemical interactions [1,2,3]. It does not require labeling or immobilization of reagents, so concerns about the effects of such modifications on the behavior of the reagents can be avoided. At the same time, assay development time and cost can be minimized because neither labeling nor immobilization protocols need to be established. For binding reactions, calorimetry can be used to provide a complete thermodynamic characterization. However, the use of conventional calorimetry is limited by large sample requirements and low throughput.

Previously we have developed “enthalpy array” technology to enable calorimetry on a scale 200-times smaller than commercially available approaches (“nanocalorimetry”), substantially reducing reagent costs [4,5,6]. By enabling parallel measurements, this approach also reduces the measurement time by 100-fold. Both of these advantages are important in screening studies and other investigations requiring a large number of measurements. Enthalpy arrays achieve miniaturization and arrayed measurements by sacrificing some of the accuracy and capability of conventional calorimetry instruments, which is a winning trade-off for many applications. Examples of other recent nanocalorimetry efforts addressing similar applications and markets are [7,8,9,10].

In our approach, nanocalorimetry is being performed using reagents in the form of small droplets (each measuring approximately 250nl) deposited onto enthalpy arrays. These arrays consist of thermally insulating polyethylene naphthalate (PEN) membranes on which isothermal drop mergers and thin film thermometers are integrated. Upon drop merging and mixing, the integrated thermometers are used to detect small temperature changes between a sample and a reference site. The resolution of the detectors is on the order of 10’s of μK. The operation and microfabrication of these enthalpy arrays are described in more detail in [4] and [11].

The new configuration proposed and described in this paper consists of an array of thermal microprobes or cantilevers contacting the measurement sites from underneath the substrate holding the drops, and offers two main advantages: a potential for higher sensitivity, because of the lesser constraints in the sensor fabrication process, and perhaps more importantly, a lower overall cost per measurement. This is possible because in the new architecture, the temperature detectors are being reused and can be considered part of the instrument, as opposed to the previous configuration, in which the entire array is designed for single use and to be disposed of afterwards.

II. CONCEPT

Cantilever-based thermal microprobes have previously been reported, in particular for memory storage [12] and flow sensing [13] applications, but to our knowledge this is not the case for cantilever devices curved out of the plane of the substrate, which due to their geometry offer a very elegant and scalable solution to the presented application; novel also is the integration into the cantilevers of low-noise vanadium oxide (V2O5) material developed for the enthalpy arrays.

Fig. 1 compares the current design for enthalpy arrays containing thermistors (1a) and the proposed new design with thermistors on cantilever microprobes (1b). In Fig. 1a, heat conducts from the drop downwards through the PEN film, along an area of copper on the backside of the membrane, which defines an isothermal region, and back up through the PEN film to the thermistors. In Fig. 1b, the thermistor is on the tip of a ~3 μm thin cantilever that contacts the backplane copper. The cantilever is formed on a substrate that can be physically separated from the substrate on which the drops are manipulated.

During operation, the cantilever substrate is positioned such that the cantilever tip is in intimate contact with the backside copper of the drop merging substrate. The heat
conduction along the cantilever is small compared to the heat conduction through the air because the cantilever is kept thin, so the thermal time constant of the detector is not reduced, as desired. COMSOL® calculations presented below provide more detail. The cantilevers are realized by “StressedMetal” technology invented and developed at our research center [14,15,16]. It is based on microfabrication techniques that take advantage of the stress that occurs in a thin film sputter deposition process. To create StressedMetal microstructures, layers of metal films are sputter deposited with an engineered vertical stress gradient, on top of a sacrificial layer. After lithographic patterning, the sacrificial layer is etched away and the microstructures are released. The stress gradient in the metal stack causes it to lift or curl into a designed radius of curvature, creating 3D structures such as tiny coils, springs, or cantilevers. An example of an array of StressedMetal curved cantilevers is shown in the scanning electron micrograph of Fig. 2; it indicates the level of uniformity that can be obtained.

These fabrication techniques are combined with the low noise vanadium oxide thermistor material and process that was described in earlier work [11]: the reactively sputter-deposited vanadium pentoxide (V$_2$O$_5$) is characterized by very low 1/f noise and a temperature coefficient of resistance of about 3% / K, resulting in a noise equivalent temperature difference (NETD) of about 10 μK for best-of-class devices, and values ranging between of 10 μK and 30 μK for typical devices built on the PEN film [5]. These numbers are obtained for a sensor configuration consisting of a full Wheatstone bridge, with 2.5 μW of electrical power dissipated per thermistor and a nominal thermistor resistance of about 20 kΩ, measured over the bandwidth 0.1 Hz to 4.2 Hz (the Johnson noise limit amounts to about 6 μK for this configuration).

### III. IMPLEMENTATION

#### A. Fabrication process

Fig. 3 shows a schematic outline of the device fabrication process. A layer of titanium is deposited onto a glass substrate coated with BCB (step 2). In step 3 an additional BCB layer is deposited by spin coating and patterned; this electrically insulating layer is used to provide structural support to the cantilever and its tip. The vanadium oxide thermistor material (V$_2$O$_5$) is sputter-deposited and patterned in step 4. The stressed metal material (step 5) is an alloy of 85% molybdenum and 15% chromium (MoCr) and can maintain large compressive and tensile stresses (in excess of 1 GPa in both cases). Two MoCr layers are sputter-deposited at different values of the argon plasma pressure, to provide the desired vertical stress gradient. In the same vacuum process, a gold layer (Au) is sputter-deposited on top of the MoCr. The MoCr/Au stack is patterned in such way that it contacts the V$_2$O$_5$ to form a coplanar electrical resistor.

The highly conductive MoCr/Au sections run along the length of the cantilevers and form the electrical leads to the resistive V$_2$O$_5$ material at the tip. In steps 6 and 7 the sacrificial titanium layer is selectively etched away through a photoresist mask, resulting in the release of the cantilever structures, as the stress in the MoCr layers is relieved.

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**Figure 1.** Current enthalpy array design and new design based on thermal microprobes.

**Figure 2.** SEM micrograph of array of StressedMetal cantilevers.
Figure 3. Schematic outline (cross-sectional and top views) of the thermal microprobe fabrication process.

This fabrication process is less constrained than the process used to integrate the thermistors on PEN films described in [11], in particular with regards to the maximum processing temperature, which here amounts to 350 °C (limited by the BCB), versus 180 °C (limited by the PEN). This enables alternative or additional processing steps, such as a modified V₂O₅ deposition process (at an elevated temperature) or higher temperature annealing which has the potential to further improve and optimize material properties such as 1/f noise and temperature coefficient of resistance.

B. Design

The cantilever dimensions are to be selected such that (a) sufficient thermal insulation is provided to the thermistor at the tip, and (b) such that the required lift height, dictated by the vertical distance to the PEN membrane holding the drops (about 700 μm), can be produced at reasonable MoCr stress levels and process conditions.

We performed finite element simulations using COMSOL® to verify initial design candidates. Fig. 4 shows simulation results for the temperature and evaporative flux fields for a detector with a cantilever-based temperature probe 1800 μm long, 150 μm wide and 3 μm thick, illustrating that the thermal isolation of the drop remains good. Fig. 5 shows the simulated temperature signal for a pulse of heat generated in the drop at time t=0 s, for both integrated and cantilever-based thermistors. As seen in Fig. 5, the signal for the cantilever design is slightly larger, so there is no loss in signal strength and in fact a predicted 9.4% increase, due to the increased proximity of the sensor element to the drop. At a cantilever thickness of 3 μm, very little heat conducts along it relative to heat conduction in the air, keeping it from being a “short circuit” of the heat generated in the drop.

Figure 4. COMSOL simulation with a cantilever-based thermal microprobe. A reaction in the drop is generating heat. The temperature and evaporative heat flux around the drop show that the thermal isolation is good.

Figure 5. Simulated temperature signal for a heat pulse at t=0s.
stress gradient of about 500 MPa in the MoCr bilayer, which is well within the boundaries of the fabrication process.

A number of design variations on this basic design have been implemented and prototyped. Fig. 6 depicts a few examples: (a) a dual thermistor, single beam device, (b) a single thermistor, dual beam device and (c) a triple beam device. With dual thermistor devices only two cantilevers are required to perform full Wheatstone bridge measurements (one for the sample site, one for the reference site). Multiple beam devices (such as shown in Fig. 6b and 6c) offer more thermal insulation but are more compliant and may deform more easily. Other design variations are based on varying cantilever length, width and tip design.

C. Measurements

The temperature coefficient of resistance (α) of a number of cantilever prototypes has been measured by inserting the devices in an environmental chamber together with a reference sensor (a NIST traceable thermometer/hygrometer by Cole-Parmer) and was determined to be -3.2% / K. Fig. 7 shows the device resistance measured by a Keithley 197A DMM as a function of temperature for two devices of different design and nominal resistance (a dual beam device of 24 kΩ with a lift height of 780 μm and a single beam device of 36 kΩ with 740 μm lift). Each datapoint was taken after allowing 6 or more hours for the environmental chamber to reach thermal equilibrium.

An exponential model was used to derive α, as the vanadium oxide material is an intrinsic semiconductor. The inset at the top right of the figure illustrates the exponential fit, which is within two significant digits identical for both devices.

IV. DISCUSSION

The first prototypes of the proposed vanadium oxide thermal microprobes demonstrate the feasibility of the concept and the microfabrication process. The initial measurement results indicate the thermistors located at the tip of the microprobe are functional and behave similarly to previously described thin film vanadium oxide thermistors on glass and PEN substrates.

Ongoing work focuses on a full characterization of the devices including a noise analysis, as well as performing nanocalorimetry experiments using the new architecture and comparing results to data acquired with the existing enthalpy arrays.

In addition, these devices are promising for other applications where a high sensitivity and large dynamic range are required, such as thermomicroscopy, anemometry and dynamic flow sensing.

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REFERENCES

Figure 7. Measurement of temperature coefficient of resistance of two cantilever prototypes.