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High-sensitivity chip calorimeter platform for sub-nano watt thermal measurement

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ABSTRACT

High sensitivity, on-chip calorimeter platform using V_2O_5 thin film thermistor was developed. Integration of a V_2O_5 thermistor with a high temperature sensitivity of −2.2%/K with a vacuum insulated, suspended SiN membrane structure enabled a low thermal conductance of 12 μW/K and a direct detection of 10 nW of heat with an estimated detection limit of 570 pW. We also investigated the feasibility of integrating the platform with a microfluidic system, and, suggest that, based on numerical simulations, a further 5-fold lowering of detection limit may be possible.

1. Introduction

Calorimetric measurement of the heat has several unique advantages over other methods of measurements for biological processes; it measures metabolic energy directly without labeling, and does not require sample preparation steps such as immobilization [1–3]. However, the sensitivity of calorimeters reported so far has been relatively low such that measuring the cellular metabolic rate required an ensemble average of $\sim 10^4$–10^6 cells, as reliable measurement of basal metabolism of a single mammalian cell requires a resolution of a few picowatts [4]. Furthermore, continuous measurement with living cells, not to mention a single cell, is quite difficult with present calorimeter technologies. Thus, there have been many attempts to develop an on-chip platform for such a calorimeter [5–7]. Chip calorimeters can provide high sensitivity and fast response due tiny thermal mass and conductance. They can be mass produced by leveraging the semiconductor processing infrastructure. Furthermore, such a platform can be integrated with a microfluidic system [8,9], providing the ability to control the environment of the reaction volume for a stable and reproducible operation.

The power resolution of chip calorimeter can be represented by product of their thermal conductance and temperature resolution ($\delta P = G\,\delta T$). Therefore the engineering of the chip calorimeter devices have been focused to achieve high sensitivity thermometry and low thermal conductance. Chip calorimeters achieve low thermal conductance by reducing the size of thermal conduction path: They typically have μm to mm scale calorimeter chambers and thin membrane structure such as suspended SiN that provides thermal insulation. Even though the membrane structure provides relatively decent thermal insulation, the substrate and microfluidic components represent too large of heat conduction paths to achieve high resolution. In this paper, we report on developing a chip calorimeter platform based on V_2O_5 thin film thermistors for high sensitivity thermometry and thermal engineering to achieve better resolution. A thin film thermistor was chosen as it can easily detect small changes of temperature with exponential changes of resistance. Furthermore, it can be fabricated on a microscale sensing area without sacrificing thermal insulation [10]. V_2O_5 was chosen as the thermistor material due to its large temperature coefficient of resistance (TCR, defined to be $(1/\rho)(d\rho/dT) = d(\ln\rho)/dT$) and relatively low electric noise property. In addition, V_2O_5 has a homogeneous TCR without metal-insulator-transition (MIT) within the temperature range of interest (<100 °C) [11]. Finally, a suspended SiN membrane structure was chosen to reduce both the thermal

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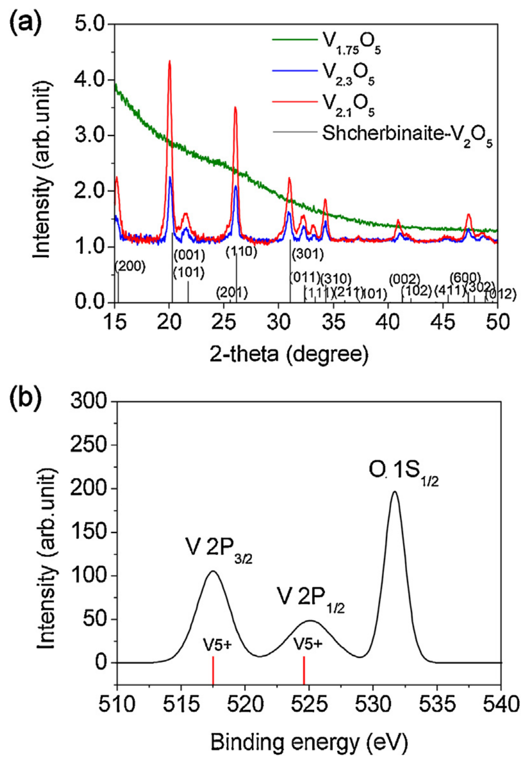

Fig. 1. Characterization of crystalline phase and oxidation state of the fabricated vanadium oxide thin film were performed by measurement of (a) X-ray diffractometry (XRD) (b) X-ray photoelectron spectroscopy (XPS). Red lines indicated expected positions for V5+ atoms in V_2O_5. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

conductance and the heat capacitance contribution from the underlying Si substrate, and to enable eventual vacuum insulation. We found that by controlling the oxygen content during RF sputter deposition, V_2O_5 thin film with a TCR of −2.2%/K could be formed after an anneal at 300 °C. This high TCR, when combined with a vacuum insulated, suspended SiN membrane structure with a low thermal conductance of 12 μW/K, enabled a direct detection of 10 nW of heat with an estimated detection limit of 570 pW. Finally, we demonstrated the feasibility of integrating the platform with a microfluidic system, and, suggested that, based on numerical simulations, a further 5-fold lowering of detection limit may be possible, which would enable direct calorimetric measurements of sub-nanowatt cellular metabolic rate.

2. Experimental

2.1. Vanadium pentoxide thin film thermistor fabrication

A 200 nm thick V_2O_5 film was deposited at room temperature on a Si wafer with 200 nm SiN layer via RF sputtering using V_2O_5 target (99.9% purity) with Ar and O_2 gas flow. The compositions of the deposited films were analyzed using Rutherford Backscattering Spectroscopy (data not shown). Post-deposition annealing at 300 °C for 30 min in flowing O_2 was performed to crystallize the as-deposited amorphous film. Fig. 1(a) shows the X-ray diffraction (XRD) spectra of the films after annealing. We found that for crystallization, controlling the stoichiometry of the vanadium oxide is critical. The strongest XRD peaks corresponding to the Shcherbinaite V_2O_5 phase were observed from the stoichiometric V_2O_5 film, while the vanadium-deficient film remained amorphous even after annealing. The formation of crystalline V_2O_5 film was further confirmed by its X-ray photoelectron spectrum. As shown in Fig. 1(b), the oxidation states of vanadium atoms were consistent with V_2O_5 phase.

2.2. On-chip calorimeter fabrication

In order to achieve the low thermal conductance required for high sensitivity calorimeters, it is important to carefully engineer the thermal insulation, including the design of the device and selection of the materials. For this purpose, we employed a SiN membrane structure formed by back-etching the entire wafer through a window in the backside SiN layer. First, windows were opened in the back side SiN layer by standard photolithography and dry etching. Afterward, the heater and electrode layer was formed by depositing a 50 nm thick gold thin film, with a 5 nm thick chromium layer acting as the glue layer, on the SiN layer. After the lift-off process to form the heaters and electrode, a 200 nm thick V_2O_5 thin film thermistor was created on top of the gold electrodes using deposition and lift-off. The thermistor was surrounded by the gold heater to enable power calibration. Finally, wet chemical etching of back side bulk silicon substrate using 30% KOH solution was performed to selectively remove the Si substrate under the sensing element, thus forming a suspended membrane structure. A schematic description of the fabricated thermistor platform is shown in Fig. 2(a).

Fig. 2(b) and (c) shows the optical microscope image of the fabricated platform and its circuit diagram, respectively. The thermistors were wired in a Wheatstone bridge configuration on the chip to provide accurate measurement [12]. Each thermistor is built on individual membrane structure to balance thermal transport, which allows rejection of base line temperature fluctuation. Two heaters are built next to the thermistors for calibration of thermal conductance. Their configuration is also identical in sensing area and reference area. For calibration electric power was applied to only one side of the heater, but the extra heater on the reference will help matching the thermal conductance.

3. Results and discussion

3.1. Temperature sensitivity of V_2O_5 thermal sensor

The temperature dependence of electrical resistance of fabricated V_2O_5 thin film thermistor was investigated using a temperature-controlled probe station (HP4156C, Agilent Technologies). As shown in Fig. 3, we measured the temperature dependence of the resistance of V_2O_5 thin film thermistor between 0 and 90 °C. The heating and cooling cycle display no MIT and small hysteresis of 2.08%. The hysteresis increases with temperature ramping speed, which we attribute to insufficient temperature stabilization on the probe station. The TCR was −2.2%/K, which is typically reported V_2O_5 TCR for image-quality bolometers [13].

3.2. Sensitivity enhancement using vacuum insulation

For a high sensitivity, however, heat loss must be minimized as well. For the fabricated thermistor, the heat conduction through the air is the most significant factor due to its high surface to volume ratio. To investigate the effect of heat conduction through the air, the sensing area was heated with a fixed power of 1 μW while placed inside a vacuum chamber. By measuring the steady state temperature difference between the sensing thermistor and the reference thermistor, the heat conduction can be readily extracted using the heat balance equation $P = G \times \Delta T$ where P, G, and ΔT are the power, thermal conductance, and the temperature difference in steady state, respectively. The results are shown in Fig. 4. We found that the heat conduction through air contributes as much as 90% of the total heat loss, indicating that vacuum insulation was