Cytochrome c thin film with high temperature of coefficient for infrared detection

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ABSTRACT

The cytochrome c (protein) thin film on the oxide surface has been reported high temperature coefficient of resistance (TCR). The protein thin film resistance acts as exponential grow under the constant voltage bias. The experimental results showed that the TCR exceeded 20% 1/K, which is 5times higher than popular vanadium oxide (VOx). We also found the protein thin film can be attached on to the SU8 photoresist surface by changing the SU8 surface more hydrophilic and simple spinning coat technique. The cytochrome c thin film on SU8 also showed the high TCR. With easy fabrication methods and lower thermal conductivity of SU8 and protein, we believe that it is possible to fabricate new generation microbolometer based on cytochrome c protein and SU-8 photoresist.

Keywords: Cytochrome c, TCR, SU8, microbolometer

1. INTRODUCTION

Infrared thermography devices were rapidly developed in last 20years. With easy manipulating, instant temperature information presentation, thermography device is a powerful tool in wide range of usage. At first, infrared thermography device was designed for military usage. In recent years, the commercial and academic usages are more popular. The common and potential applications are night vision, automobile, industrial monitoring, mine detecting, surveillance, medical imaging, and fire fighting.

The basic of infrared thermography is to detecting infrared radiations. There are two main categories of detecting principle, photon detector and thermal detector. Photon detector absorbs the incident infrared photon and produces the electron-hole pair. There are obvious advantages of photon detector. It has short response time and high responsivity compared with thermal detectors. However, there are some drawbacks that limit the application ranges of photon detectors. To suppress the noise from background, photon detectors need cryogenic devices outside to maintain the temperature far below the zero Celsius when operating. Cryogenic devices are bulky, heavy and expensive. Thus, infrared thermography devices based on photon detectors are very expensive and have low portability. On the contrary, thermal detectors can be operated at room temperature and hence do not need the cryogenic devices. Even though the response time is slower and responsivity is not so high compared with photon ones, thermal detectors still have the advantages of low cost, light weight. These are suitable for many commercial applications.

There are some thermal detectors been developed now: pyroelectirc detector [1], thermopile detector [2] and microbolometer [3]. Among three of them, microbolometer has been developed for longer time and could have better responsivity. Microbolometer's operating principle is that when sensing materials absorb the infrared radiation and turn the radiation into heat, the resistance of sensing materials would change due to the rising temperature. Hence, by measuring the resistance variance of sensing materials, the incoming radiation can be calculated and therefore presumes the temperature of observed objects. To have better response, the resistance variance of sensing materials should be as large as possible. Therefore, it is important to find sensing materials with high temperature coefficient of resistance.

Conventionally, the most used materials are vanadium oxide (VO_x) and amorphous silicon (α-Si). These two semiconducting materials present pretty good TCR, about -4%/K for VO_x [4] and about -3%/K for α-Si [5]. Titanium is a metal material that is used in microbolometer and has TCR about. 0.35%/K [6]. The other semiconducting material Yttrium Barium Copper Oxide (YBaCuO) is also studied. It could achieve TCR about -4%/K [7]. However, the

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semiconducting materials are toxic and need costly deposition techniques such as chemical vapor deposition or pulse laser deposition. Therefore, there is a trend to find out new materials in addition to materials mentioned above. Polymeric conducting materials and proteins are concerned. Poly (3,4-ethylenedioxythiophene):Poly (Styrenesulfonate) (PEDOT:PSS) thin film was reported to have TCR over -4%/K [8]. O. Yavuz and M. Aldissi examined the potential of using proteins as microbolometer sensing material [9]. K.K. Deb also reported cytochrome c thin film on the top of oxide could have TCR over 20%/K, which is the highest record [10]. These materials present high TCR and could be deposited by self-assembly monolayer (SAM), Langmuir-Blodgett (LB) or spin coating, which are quicker and cheaper than the deposition techniques of semiconductors.

It is interesting to investigate cytochrome c thin film performance onto the top of SU8. SU8 is negative photoresist which has low thermal conductivity approximate 0.2 W/mK. The value of thermal conductivity of SU8 is relative lower than other supporting materials such like silicon, polycrystalline silicon, silicon nitiride etc. Thermal conductivities of those materials are list as table 2. With good mechanical property and chemical resistance, SU8 are extensively used as microstructure [11, 12, 13]. Hence, SU8 could be a supporting layer or buffer layer to decrease the thermal conductance of microbolometer.

With high TCR of cytochrome c and low thermal conductance of SU-8, the combination of cytochrome c thin film and SU8 might be very promising for microbolometer application. In this paper, our experiment results demonstrated that cytochrome c thin film could be attached on to the top of SU8 by some modification and presented high TCR.

Table 1. Temperature coefficient of resistance comparison of different sensing materials.

Materials	Vanadium Oxide (VO_x)	Amorphous Silicon (α-Si)	Titanium	Yttrium Barium Copper Oxide (YbaCuO)	PEDOT:PSS	Cytochrome c
Type	Semiconductor	Semiconductor	Metal	Semiconductor	Polymetric Conductor	Bio-material
TCR	4%/K[4], 5.12%/K[14]	3%/K[5]	0.35%/K[6]	2.8~4%.K[7]	4%/K[8]	35%/K[9], 28%/K(in this paper)
Deposition Method	Evaporation, Pulse Laser Deposition	Evaporation	Evaporation	RF Sputtering	Spin coating	SAM, Spin coating

Table 2. Thermal conductivity of microbolometer structure materials.

Materials	Thermal Conductivity (W/mK)
Silicon	149
Polycrystalline Silicon	13.8 [15]
Amorphous Silicon	1.8 [16]
Silicon Nitride	29
Silicon Oxide	1.38
Epoxy SU8	0.3

2. INFRARED SENSING CHIPS AND EXPERIMENTAL SETUP

2.1 Chip preparation

To examine how resistance of protein varied with temperature on the top of negative photoresist SU8, we propose a simple method for verification. Silicon wafer with 6000Å silicon oxide was prepared and cut into 2cm square pieces by dicing saw device. The wafers were then cleaned in Piranha solution (H_2O_2:H_2SO_4 = 1:3) at 100 degrees Celsius for 20 minutes. Those wafers were stored and were cleaned by simple Acetone, IPA and water before usage. Negative photoresist SU8 3005 was prepared for making plate which protein thin film would be formed on the top. We spun SU8 at 2500rpm and patterned 1cm square area at the center of the chip. The height of SU8 was about 8um each. Copper was chosen to be the electrodes. The thermal expansion of copper is almost the same as SU8 and is harder to be oxidization in the air. To deposit the copper pattern, we use lift off process. The photoresist mask we used is AZ4620. We spun AZ4620 at 2500rpm and thus the thickness is enough for passivation. Then we deposited the copper layer by thermal evaporation and lifted off AZ4620 layer by immersing into acetone. The patterned electrodes were separated as about 1cm.

The protein solution was prepared by mixture of cytochrome c, phosphate buffer solution and DI water. We prepared phosphate solution by adding K_2HPO_3 and KH_2PO_3 in the water. The phosphate solution we made had concentration of 0.1M and at ph 6.8. They were mixed with the ratio 2mg cytochrome c: 1ml DI water: 1ml phosphate buffer solution. The concentration of protein is about 80μM.

Before dropping the protein solution onto the prepared chips, the chips were under the process of UV/Ozone with different time. We set four different time treatment, including 0 minute, 3minutes, 6minutes and 10minutes, to investigate the effect of UV/Ozone to the combination of SU8 and cytochrome c thin film. After that, we dropped protein solution onto the chips and maintained statistic 60 seconds then spin at 1000rpm 15seconds. Finally, we dried the chips for a day in ambient environment. The following pictures depict the flowing procedure and show the chip.

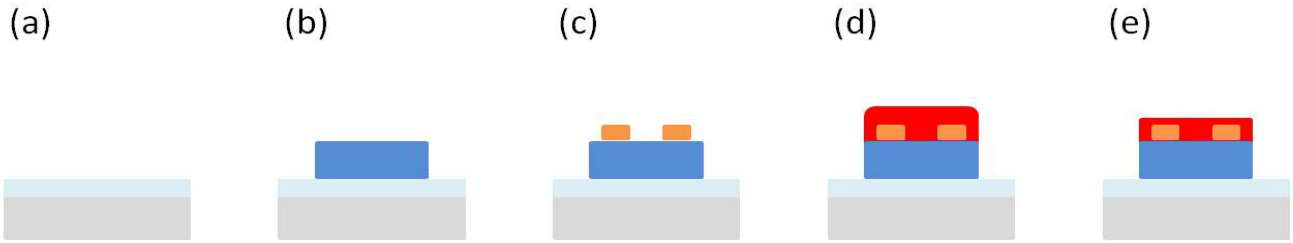

Figure 1. Sample preparation procedure. (a) Silicon substrate with oxide. (b) Patterned SU8. (c) Patterned electrodes. (d) Dropping protein solution and maintaining static 60 seconds. (e) Spin coating at 1000rpm 15 seconds.

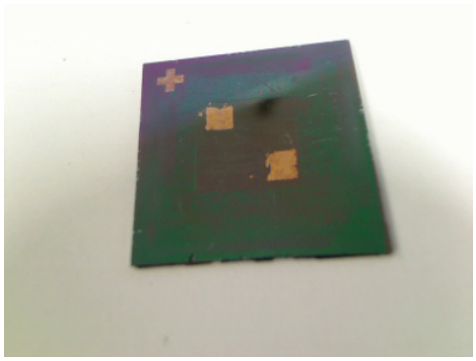

Figure 2. The photograph of prepared sample.

2.2 Measurement setup

The schematic of measurement setup is shown as figure 3. The chip was set on the top of hotplate which was connecting with temperature controlling unit. The chip surface temperature was measured by non-contact thermometer as we were more interested in surface temperature than hotplate temperature. The two probes were contacted with electrodes on the chip. Due to the self-heating phenomenon, the resistance of cytochrome c thin film was not measured by direct measurement building in Keithley 2400. To avoid continuous constant current heats the thin film, the pulse voltages were applied at different bias to measure the current flowing through the cytochrome c thin film. Each pulse voltages were given with stop periods of 100 ms, a period long enough to avoid self-heating. We measured the I-V curve at different temperature. I-V curves of cytochrome c thin film were linear, and we used the relationship to have resistance in specific temperature.

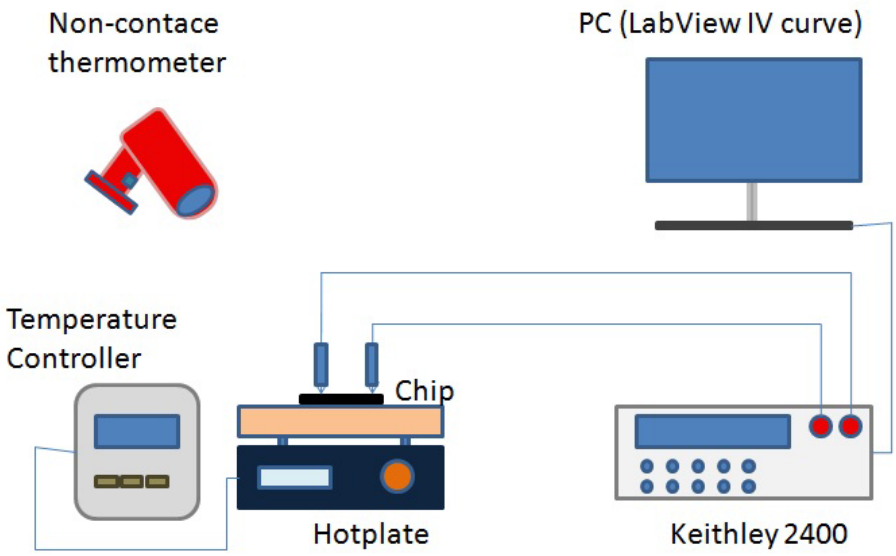

Figure 3. The schematic of measurement setup. Keithley 2400 was connecting to Labview for automatic measurement and data collection.

3. RESULTS AND DISCUSSIONS

3.1 SU8 surface modification

The epoxy-based SU8 negative photoresist shows hydrophobic surface initially after recommended procedure. To improve the adhesion of protein onto the SU8 surface, we would like to modify SU8 surface from hydrophobic into hydrophilic. SU8 is composed of the resin monomer and photo initiator. The resin monomer shows epoxy functional group. The hydrophobicity of SU8 could be changed by chemically treating the epoxy functional group. There are many reports stated how to change the epoxy functional group into others, such like amino function group [17], thiol function group [18] etc. Comparing the methods, we decided to use UV/Ozone process. UV/Ozone process turns epoxy functional group of SU8 surface into C=O and the phenol group (benzene-OH) [19]. The advantage of UV/Ozone process is simple and long lifetime. Due to the limitation of our device, we could not control the Ozone gas flow and UV wavelength. The only parameter we can control is the process time. We verify how hydrophobicity would be affected when increasing the UV/Ozone process time by measuring the contact angle. The contact angle between protein solution and SU8 with different time of SU8 is shown as figure 4. We could see the SU8 surface became more hydrophilicity under more process time in figure 5. The contact angle was measured by image processing. It shows after UV/Ozone process, the contact angle would decrease from 55 degrees to about 10 degrees.

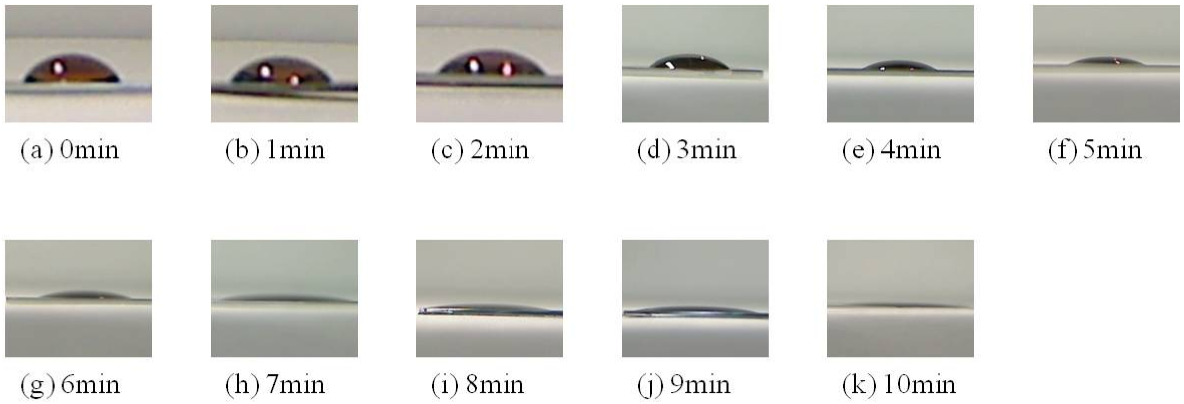

Figure 4. The contact angle between protein solution and SU8 surface after surface modification.

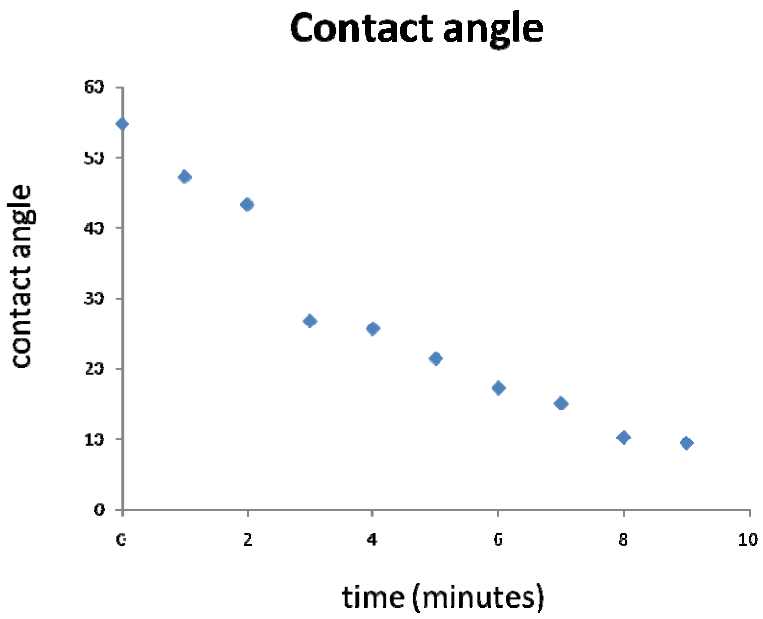

Figure 5. The contact angle variance versus time. After taking longer process time, the contact angle becomes small. The surface shows more hydrophilicity.

3.2 Cytochrome c thin film on SU8

Cytochrome c is a protein involving in electron transport chain in mitochondria. It transports the electrons by undergoing oxidation and reduction. Varies temperature would affect the conformation of heme groups, redox state and protein activity and hence make effects to electrons transportation. In durable temperature range, the higher temperature would cause the higher resistance of cytochrome c.

Cytochrome c is a water soluble protein. For this reason, we expect cytochrome c would be poorly attached to SU8 surface due to the hydrophobicity. The demonstration is shown as figure 6. There are two I-V curves in the graph, one is purely SU8 without spinning cytochrome c and another one is spinning the cytochrome c onto the top. It shows no significant different between these two. The curve indicates there is no current flowing through the chip. The result agrees the expectation that without further treatment, the hydrophobicity of SU8 surface makes it hard to coat the cytochrome c thin film.

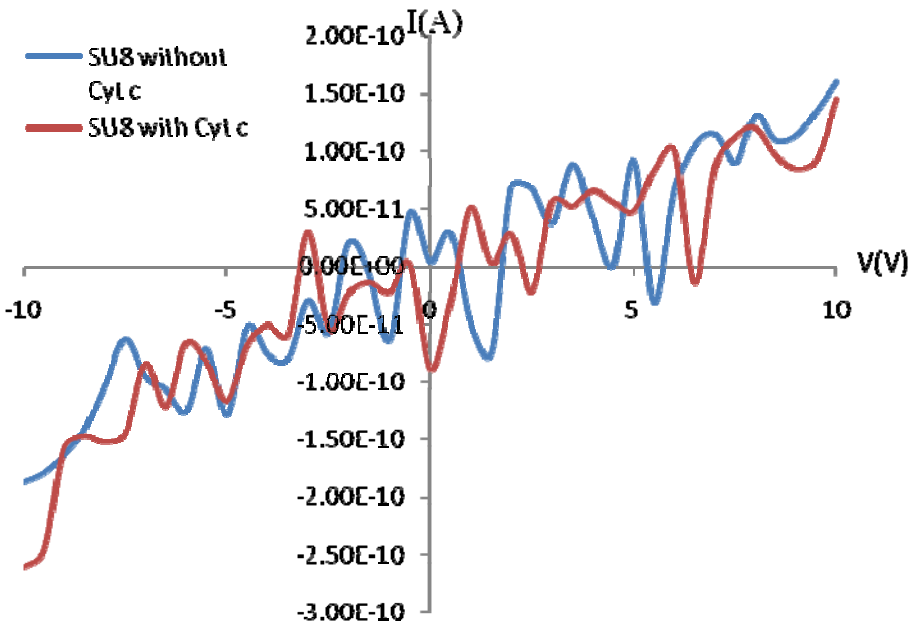

Figure 6. The IV curve of purely SU8 surface with cytochrome c spinning and without cytochrome c spinning. Without UV/Ozone treatment, cytochrome c thin film could not be attached on SU8.

After the UV/Ozone treatment, SU8 surface becomes more hydrophilicity and the attachment between SU8 and cytochrome c is improved. Hydrophilicity is the phenomenon after UV/Ozone process. The reason why protein could be better attached to SU8 might be the change of electricity affinity and functional group. The peptides of protein may have interactions between C=O and phenol group. These interactions provide attractive force of cytochrome c and SU8 then further causes the results.

The cytochrome c thin film presents the exponential growing resistance when temperature rises. Compared with the chip under different process time, they all exhibit like it. We fit the curves and use the formula to calculate the TCR cytochrome c present. TCR is calculated as following:

$$TCR = \frac{1}{R}\frac{dR}{dT} \tag{1}$$

The figures below shows how resistance varies with temperature after different UV/Ozone process time. The curve fitting equations are shown in the figures. For curve fitting equations, we could calculate the TCR by applied the fitting equations into equation (1). The calculated TCR are 43%/K, 37%/K and 28%/K in each. It shows higher TCR in shorter process time of UV/Ozone, but the chip in shorter UV/Ozone process time was very unstable compared to the one which is under longer process time. The endurable temperature of the chip under 3 minutes UV/Ozone process is limited to about 34 Celsius degrees. And for 6 minutes one is about 39 Celsius degrees, 10 minutes one is about 42 Celsius degrees. The longer process time will make the thin film can endure higher temperature. It seems if SU8 surface was more hydrophilic, the combination force between SU8 and cytochrome c would be enforced, and it helps cytochrome c baring the temperature from degeneration. The TCR performances are pretty good even on SU8 surface. The most stable process of 10 minutes UV/Ozone shows TCR about 28%/K, much higher than conventional vanadium oxide and amorphous silicon. The TCR is also comparable to cytochrome c thin film on the oxide, which is reported to have TCR above 20%/K. This experiment results demonstrated cytochrome c thin film could be deposited by spin coating method on the top of SU8 under UV/Ozone treatment. Further, it shows high TCR even on the top of SU8.

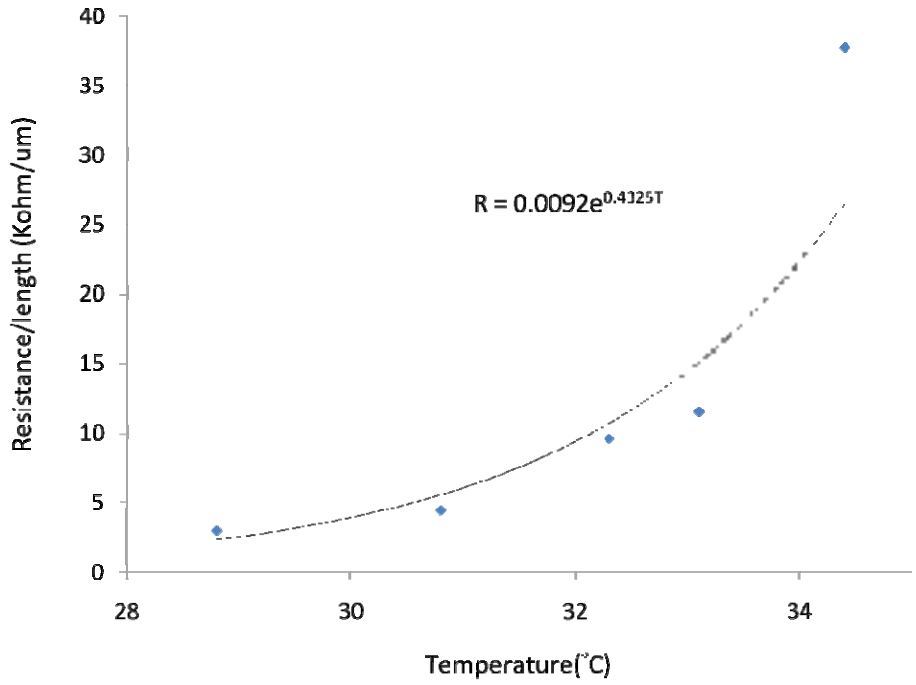

Figure 7. The cytochrome c thin film resistance versus temperature with 3 minutes UV/Ozone process time.

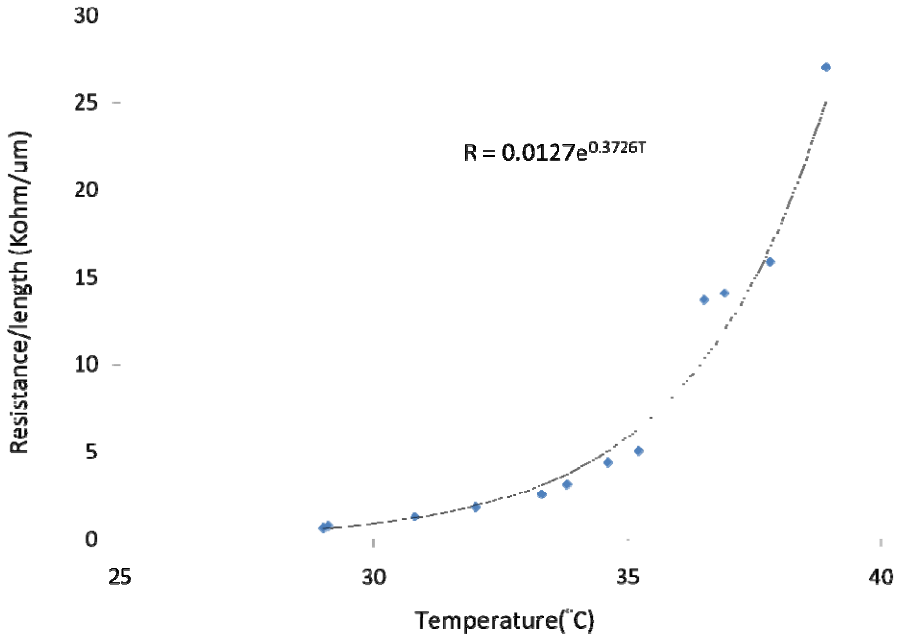

Figure 8. The cytochrome c thin film resistance versus temperature with 6 minutes UV/Ozone process time.

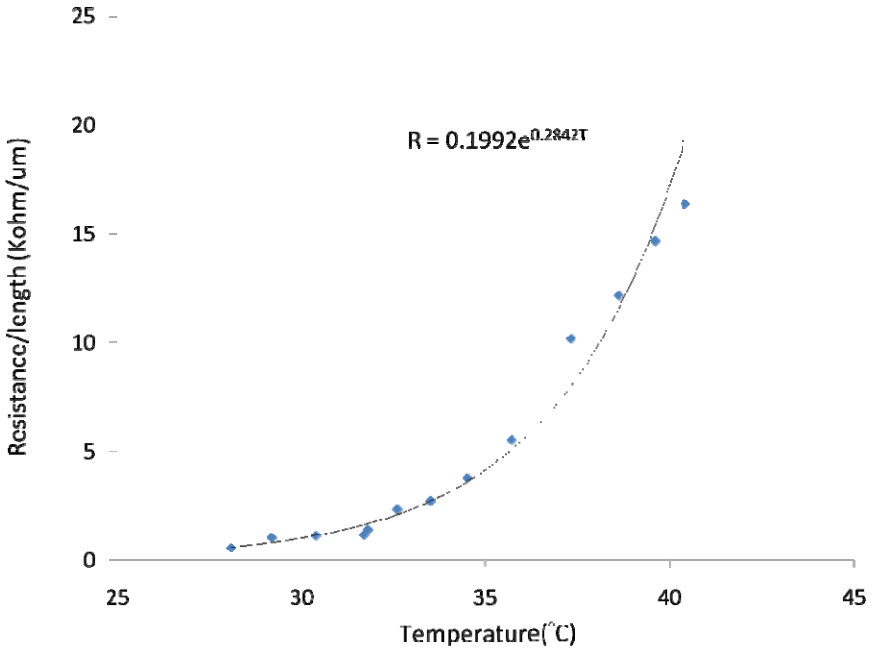

Figure 9. The cytochrome c thin film resistance versus temperature with 10 minutes UV/Ozone process time.

4. CONCLUSION

We demonstrated that cytochrome c thin film has relative high TCR on the top of SU8 surface. By UV/Ozone process, we changed SU8 surface form hydrophobic into hydrophilic. And cytochrome c thin film could be easy deposited by spin coating methods after SU8 surface modification. The combination of SU8 and cytochrome c thin film provides high TCR and lower the thermal conductance for infrared application. We also found that higher UV/Ozone treatment results in more stable protein on top of SU-8 surface. The highest temperature detected was about 40 degree. With highly self-absorption of protein in mid-infrared, we expect the work would help to inspire or create new type of microbolometer which could be fabricated as low cost, good performance and operational convenience.

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