CALIBRATION OF THIN-FILM THERMOCOUPLES ON SILICON WAFERS

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ABSTRACT

Thin-film thermocouples (TFTCs) can be fabricated from a much broader range of electrical conductors than wire thermocouples, but even with the same composition as the wire thermocouple, the TFTCs may have different thermoelectric coefficients. Also, the TFTCs are used to measure temperature differentials across short distances on the substrate and cannot be calibrated by standard procedures. Therefore, we at NIST have a continuing project to improve the calibration methods for TFTCs. We have developed a calibration test for TFTCs on 10 mm x 50 mm silicon wafer substrates using the comparison method up to 950 EC with NIST-calibrated, highly accurate, platinum/palladium wire thermocouples as the reference thermometers. The expanded uncertainty ($k = 2$) for our method for calibration of the thin-film thermocouples was less than 0.2 % of the emf at 800 °C .

1. INTRODUCTION

This paper describes a method for calibration of thin-film thermocouples (TFTCs). The thin-film thermocouples are to be used on a silicon calibration wafer for radiation temperature measurements in a rapid thermal processing (RTP) tool. Thin-film thermocouples are being used in a broad range of applications for measuring surface temperatures [1, 2]. The advantages of TFTCs include their small size (10^{-6} mm^3 junctions), fast response, low cost, and flexibility in design and materials. This fast response time was demonstrated with an excimer laser to be faster than 1 Φs [3]. Each application of TFTCs requires specific considerations of the materials of the thin films, their fabrication parameters, the substrate material, electrical insulation and connections, and the thermal and chemical environment of the measurement. The measurement of temperature using TFTCs also requires a calibration under the conditions present during service. Although standard reference tables [4] have been defined for the electrical response of wire thermocouples, it was determined from the earliest research [1] TFTCs would require a specific calibration reflecting the relationship between the substrate material and the thin film and its physical, chemical, and metallurgical condition.

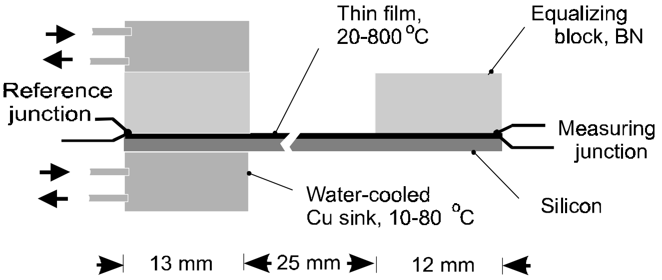
The problems of calibration of TFTCs have been recognized since their earliest use [1]. More recently, we at NIST have been developing a calibration method for applications on silicon wafers. We reported previously on this comparison test with calibrated wire thermocouples [5]. The calibration was limited in accuracy by the estimate of the thermal contact resistance between the hot junction thermocouple bead and the thin film at the electrical contact measuring the thermoelectric output. For the present study we have devised a strategy for measuring and reducing that uncertainty by comparing results of tests using welded and clamped junctions.

2. EXPERIMENTAL METHOD

Our calibration system for TFTCs on silicon wafers was designed to obtain the thermoelectric output of a TFTC on a silicon wafer compared to a pure platinum (Pt) wire. The design (Fig. 1) includes a water-cooled clamp at the cold junction with an electrical contact made by the platinum wire of the platinum-palladium (Pt/Pd) reference thermocouple. Because of the effectiveness of the water cooling, we could insert this water cooled block with insulation into a tube furnace maintained at temperatures up to 1000 EC. The calibration test coupons were 50 mm by 10 mm wide for ease of fabrication and their ability to simulate severe thermal gradients of various applications. The hot junction of the thin film was clamped to a Pt/Pd reference wire thermocouple that yielded the electrical contact and measuring junction. We used Pt/Pd reference thermocouples which were calibrated at NIST with an expanded uncertainty ($k = 2$) of 0.2 EC at 1000 EC. The clamp for the hot junction / electrical contact was a 0.5 mm Pt wire wrapped around the semi-cylindrical boron nitride heat sink and the silicon substrate (Fig. 1). This whole assembly was inserted into a tube furnace lined with a fused-quartz tube which permitted a N_2 purge. Typically we ran the test at mole fraction of 0.02 % O_2.

The instrumentation for these tests included a Keithley 7001 scanner [6] , a Fluke 85056a voltmeter [6], and a PC for data acquisition. The calibrated thermocouples were terminated in a distilled ice-water mixture to establish the reference junctions. Meter uncertainties were minimized by reading the digital voltmeter to a resolution of 0.1 ΦV, averaging four readings, and using standard precautions in handling low voltage signals, such as shielding and correcting for the voltmeter zero offset. The sequence of emf measurements was designed to compensate for temperature drifts that were linear in time. Using the mean deviation data and checks of the voltmeter calibration, our estimate of the standard uncertainty of the emf is $u(E) = 0.4\text{x}10^{-4}\,E + 0.1\ \mu\text{V}$, which is equivalent to 0.03 EC at 800 EC for a Pt/Pd thermocouple.

Fig. 1 Calibration apparatus for thin-film thermocouples.



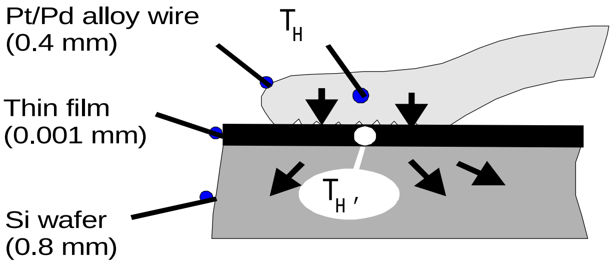
In our method, one Pt wire of the Pt/Pd reference thermocouple contacts the thin-film test sample at a point with a temperature near ambient and another Pt wire contacts the test sample at a point where the temperature is up to 900 EC (Fig. 2). The two Pt wires are routed to an ice bath, where connections are made to copper wires that are connected through a scanner to the digital voltmeter. For the ideal case of pure Pt wires in intimate contact with the film, the emf measured by the voltmeter can be expressed as:

$$E = E_{\mathrm{TF/Pt}}\,(t_{\mathrm{H}}) - \mathrm{E}_{\mathrm{TF/Pt}}(t_{\mathrm{C}}) \tag{1}$$

where E is the measured emf of the circuit, t_{H} and t_{C} are the temperatures of the hot and cold contact points between the Pt wires and the thin film, and $E_{\mathrm{TF/Pt}}(t)$ is the emf of the thin-film material versus platinum with a measuring junction at temperature t and reference junctions at 0 EC. The temperatures of the hot and cold ends of the thin-film test sample are measured with platinum-palladium thermocouples. The Pt thermoelements of the two wire thermocouples additionally serve as the Pt wires in the thin-film electrical circuit.

In practice, Eq. 1 is only an approximation of the relationship between the experimentally measured quantity E and the function $E_{\mathrm{TF/Pt}}\,(t)$. There are two effects of thermal gradients in the vicinity of the measuring junctions of the wire thermocouples. First, each thermocouple will measure an average temperature of the bead that forms the junction, and this temperature will differ from the temperature of the contact region between the thin film material and the bead. Second, because the beads are not pure Pt in composition, the electrical circuit for the thin-film emf measurement near the bead can be thought of as the sequence: thin film - platinum alloy - platinum. If there is a thermal gradient within the bead or in the vicinity of the contact region of the bead with the thin film, then there will be a contribution to the measured emf from the platinum alloy region of the circuit.

Fig. 2 Highly magnified drawing of reference junction and thin-film electrical contact . (≥ = heat flow)



To obtain a simple quantitative expression that accounts for these effects, we assume that the thermocouple measuring junction can be treated as a homogeneous alloy A of the two thermoelements. We further assume that the wire thermocouples measure temperatures t_H and t_C at the hot and cold ends of the test sample, respectively, but the actual temperatures at the contact points, $t_{H=}$ and $t_{C=}$, are different from t_H and t_C. Denoting the Seebeck coefficient of the junction alloy with respect to Pt as $S_{A/Pt}(t)$ and the Seebeck coefficient of the thin film with respect to Pt as $S_{TF/Pt}(t)$, the relationship between the measured emf E and the function $E_{TF/Pt}(t)$ can be written as:

$$E \;.\; E_{TF/Pt}(t_H) + [S_{A/Pt}(t_H) - S_{TF/Pt}(t_H)](t_H - t_{H=}) - E_{TF/Pt}(t_C) - [S_{A/Pt}(t_C) - S_{TF/Pt}(t_C)](t_C - t_{C=}) \qquad (2)$$

under the conditions $|t_H - t_{H=}| * |t_H - t_C|$, $|t_C - t_{C=}| * |t_H - t_C|$.

In the limit that $t_H = t_{H=}$ and $t_C = t_{C=}$ or in the limit that $S_{A/Pt}(t) = S_{TF/Pt}(t)$, Eq. 2 reduces to Eq. 1, as expected. Because there is limited control over the composition of the alloy A at the thermocouple measuring junctions, the primary means of improving the accuracy of the measurement is to minimize differences between t_H and $t_{H=}$, and between t_C and $t_{C=}$.

To analyze the data of each test, the temperatures t_H and t_C are first determined using the emf-temperature relationship of the Pt/Pd thermocouples at the hot and cold ends of the test sample. Data for values of t_H close to t_C are used to determine the slope, S_0, of the function $E_{TF/Pt}(t)$ for temperatures near t_C. Approximating $E_{TF/Pt}(t_C)$ by $(t_C - 0\ \mathrm{EC})\, S_0$, the emf-temperature relationship for the thin film versus Pt can be expressed as

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$$E_{TF/Pt}(t_H) \;.\; E + (t_C - 0\ \mathrm{EC})S_0 \qquad (3)$$

In order to find the actual difference between the temperatures of the hot junction of the wire thermocouple and the temperature of the thin film at the contact point with the platinum wire of the wire thermocouple, the results of experiments using clamped and welded hot junctions were compared. Figure 2 illustrates this configuration. Because the hot junction of the film is being heated from the furnace and cooled through the silicon wafer, the temperature of the wire thermocouple junction (at t_H) is higher than the temperature of the thin-film/wire junction (at $t_{H=}$). Two thermal resistances lie between $t_{H=}$ and t_H: first, the alloy bead between the center and its surface at the film contact point; and second, any contact resistance between the bead and the thin film. The contact resistance and the dimensions of the alloy section can be made vanishingly small by welding the individual Pt and Pd thermoelements to the film. In fact, we made the comparisons with thin foils of Pt and Pd. This yielded strong welds which survived the assembly process of the comparison and enabled excellent matching of the thermoelectric potentials with the wires. The foils were backed with the same silicon wafer test coupons and replicated the performance of the thin films during the test since the primary heat transfer material in both cases is the silicon wafer.

To measure the effects of the alloy bead on the circuit with the clamped hot-junction thermocouple, we determine the emf of the Pt or Pd foil versus Pt wire as a function of temperature using Eqs. 1 and 3 and also emf readings from either the clamped or the welded hot-junction thermocouple. We label the emf of the foil or thin film versus Pt as $E_{TF/Pt(C)}$ and $E_{TF/Pt(W)}$ for clamped and welded hot junctions, respectively. For the welded junction, the quantity $t_H - t_{H'}$ is virtually zero. For the clamped junction, Eq. 1 neglects the terms describing the effects of the alloy bead that are included in Eq. 2. Therefore, the difference $E_{TF/Pt(C)} - E_{TF/Pt(W)}$, which we term $\Delta E_{C\text{-}W}$, is equal to the correction term $[S_{A/Pt}(t_H) - S_{TF/Pt}(t_H)](t_H - t_{H'})$ in Eq. 2.

When the experiment is done with a Pt foil, the correction term is equal to $[S_{A/Pt}(t_H)](t_H - t_{H'})$. The sign of $S_{A/Pt}$ depends on the exact composition of the alloy bead, but the magnitude of $S_{A/Pt}$ will be no more than $S_{Pd/Pt}$, the Seebeck coefficient of pure Pd versus pure Pt. When the experiment is done with a Pd foil, the correction term is equal to $[S_{A/Pt}(t_H) - S_{Pd/Pt}(t_H)](t_H - t_{H'})$. Because $-S_{Pd/Pt}(t_H) = +S_{Pt/Pd}(t_H)$, which is positive, the correction term should be both positive in sign and more positive than the correction term determined for a Pt foil.

3. RESULTS

Platinum foil (99.99 %, 0.025 mm thick) was tested with both welded (w) and clamped (c) hot junctions as described above. The data were obtained from six runs with quasi steady-states near 700 °C and 900 °C. Fig. 3 shows the output of the welded Pt wire/Pt foil circuit, and the clamped Pt wire/Pt foil circuit on a typical thermal cycle with steady state conditions at 900 °C and 700 °C. From these tests the average value and standard deviation (SD) of ΔE_{C-W} was (-1.0 ∀ 2.1) µV and (2.5 ∀ 2.5) µV at 700 °C and 900 °C, respectively.

Similar comparison tests were run with palladium foil (99.95 %, 0.012 mm thick). As was mentioned before, the small numbers for ΔE_{C-W} can be obscured if the hot junction temperatures are changing too rapidly with time (> 5 °C/min). Therefore, we use the data from periods when the hot junctions are at nearly constant temperatures. The difference in temperature between the two hot junctions was between 3 °C and 4 °C for both the 700 °C and 900 °C quasi steady states. The corrected difference for ΔE_{C-W} averaged 10.9 µV (SD = 2.4 µV) for three runs at 900 °C and 2.4 µV (SD = 2.0 µV) for four runs at 700 °C. These tests indicate that clamped junctions can be used with less than a 1 °C temperature differential between the foil (or film) and the measuring junction of the TC.

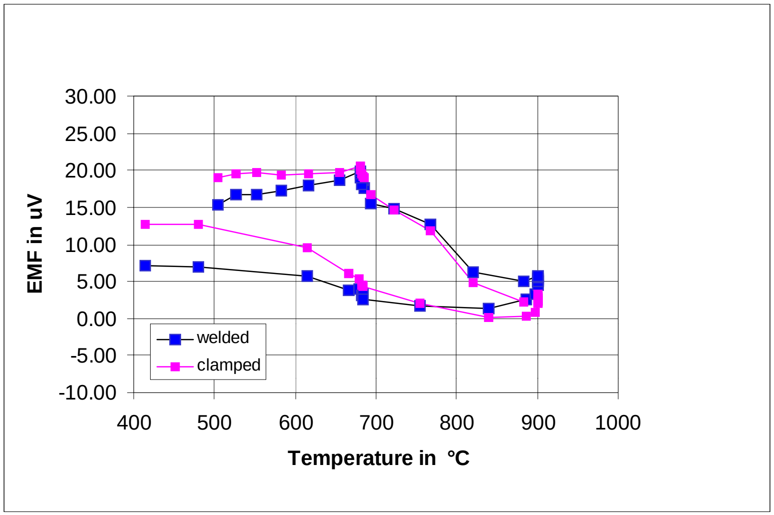


Fig. 3 EMF of Pt foil versus Pt wire.

The magnitude of the correction term in Eq. 2 depends on the thermoelectric properties of the thin film or foil and the temperature difference t_H B $t_{H=}$. The temperature difference will vary from run to run, depending on the details of the contact of the bead with the specimen. Because thin foils may be more compliant than thin films on silicon, the thermal resistance at the contact point of the alloy bead may be substantially higher with a thin film than with the foils. In the absence of more information, we assume that the variations from run to run in ΔE_{C-W} arise from variations in this contact resistance. We further assume that the contact resistance of a relative compliant bead with a hard film will be twice that of a bead contacting a relatively compliant foil. The resulting uncertainty in E from this effect is then twice the pooled standard deviation of the ΔE_{C-W} measurements, or 4.5 µV.

As an estimate of the effects of variations in the specimen materials, we take the rms deviation from zero of the four averages for ΔE_{C-W} for Pt and Pd foils at 700 °C and at 900 °C, equal to 6.3 µV. Combining with the contact resistance uncertainty, we obtain a standard uncertainty, assuming Eq. 1 to be valid, of 7.7 µV for testing of unknown materials. In the special case of testing Pt or Pd specimens, it is possible to attain uncertainties as small as 4.5 µV by correcting the emf values obtained with a clamped junction by the amount ΔE_{C-W} determined for the foils. We have not measured the correction term in Eq. 2 for the cold junction. However, the magnitude of t_C- $t_{C=}$ is expected to be much less than that of t_H-$t_{H=}$, and the Seebeck coefficient below 100 °C of Pt/Pd thermocouples is three times smaller than at 800 °C. We conservatively estimate that the uncertainty of ΔE_{C-W} for the cold junction with its smaller thermal gradients is 1/3 of the uncertainty for the hot junction.

The combined uncertainty for $E_{TF/Pt}$ includes the following components: uncertainty of the emf measurement (0.4×10^{-4} E+0.1 μV), uncertainty of the ice-point temperature(<1 µV), calibration uncertainty of the Pt/Pd thermocouples at temperatures t_C and t_H (<2 µV), and the uncertainty of ΔE_{c-w} for both hot and cold junctions. The uncertainty of ΔE_{C-W} dominates, resulting in a combined expanded uncertainty (k = 2) for Pt or Pd films of 10 µV at 800 °C. If the films were combined into a thermocouple, the expanded uncertainty would be 14 µV, or the equivalent of 0.8 °C. For films where the correction for ΔE_{c-w} is unknown, the expanded uncertainty is 17 µV.
These calibrations were used to determine the Seebeck coefficient of the Pd foil versus the Pt wire on the silicon wafers. Using both the welded and clamped junctions, we used six comparison measurements to calculate the

average Seebeck coefficient between 700 °C and 900 °C for both methods. We found the average Seebeck coefficient to be 16.4 μV/K (u = 0.25 μV/K) for all twelve tests. There was better agreement between the welded and clamped junctions of a single run than among the separate runs.

Figure 4 is a plot of the results of testing a sputtered platinum thin film on an oxidized silicon wafer. The oxide is 310 nm thick and the Pt film is 700 nm thick. Both the heating (above) and cooling curves (connecting the points) are included from points taken at intervals of 360 s and demonstrate the stability of the film and test apparatus. In Fig. 4 and 5 the emf of the thin films vs the Pt wire [$E_{\mathrm{TF/Pt}}(t)$] are plotted. From these data we derived the emf and Seebeck coefficient of the film versus a Pt wire at temperatures up to 950 EC. Since we are primarily interested in the Seebeck coefficient for this application between 700 °C and 950 °C, we solve for the slope of this plot. The average Seebeck coefficient of this film relative to thermocouple grade Pt wire in this temperature range is 2.8 μV/K (u=0.25/K μV). This result may relate to impurities in the Pt film such as the Ti bond coat, surface effects of the thin film, or substrate generated stresses, but similar results have been found previously [1, 5, 7, 8].

Figure 5 is a plot of the emf of a sputtered Rh film on an oxidized Si wafer versus pure Pt wire. Both the heating and cooling curves are presented and it can be seen that Rh thin films have very little hysteresis. The Seebeck coefficient in the temperature range 700 °C to 950 °C can be represented by the equation S = 6.783 + 0.0130 T where T is expressed in K and S is in μV/K.

Fig. 4 EMF of Pt film versus Pt wire.

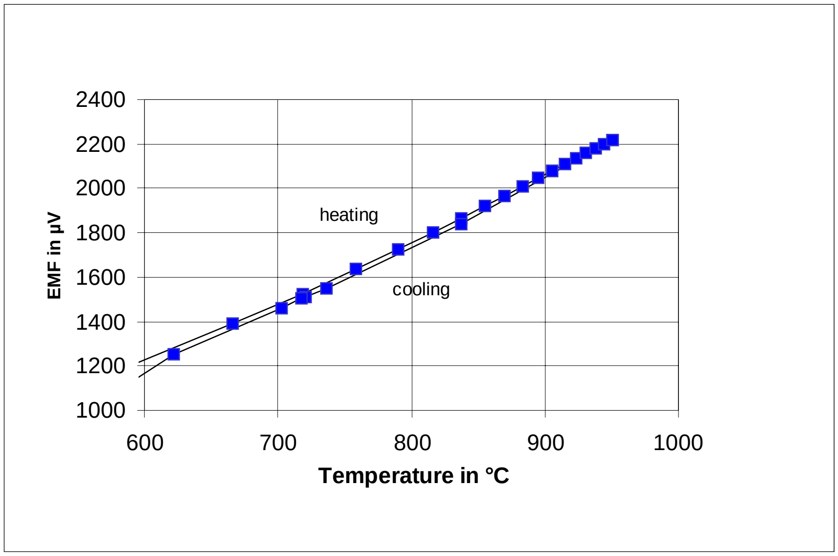
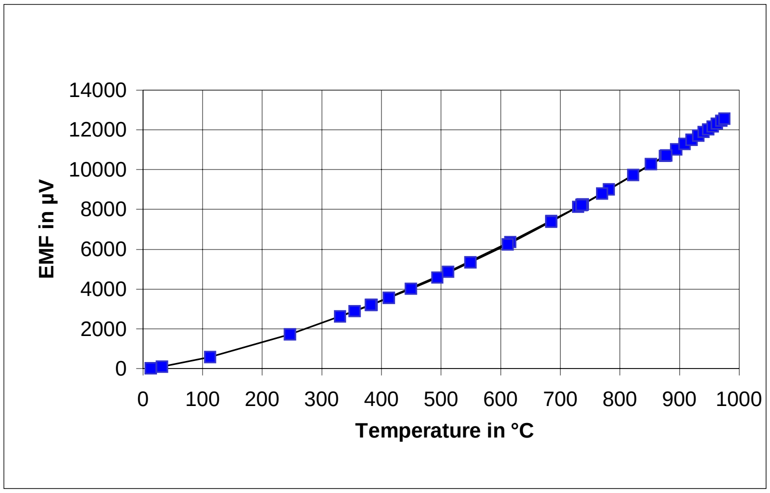


Fig. 5 EMF of Rh film versus Pt wire.



4. CONCLUSIONS

We have designed, modeled, and evaluated a calibration method for TFTCs. The calibration method is intended for thin-film thermoelectric materials on silicon wafer substrates. The sample size was 10 mm by 50 mm, and calibrations up to 950 EC were possible. The effects of heat flow on the measurement were modeled in order to evaluate the uncertainty of the calibration. The primary source of the uncertainty in the calibration apparatus was found to be temperature differences between the measuring junction of the calibrated thermocouple and the thin film itself. This uncertainty in the measurement of the thin film temperature leads to an expanded uncertainty of 0.9 °C at 950 °C which is intended as the highest temperature of the calibration. This thin-film thermocouple application has been coupled with Pt / Pd wire thermocouples for temperature measurement of calibration wafers in RTP tools and has enabled temperature measurements of the wafer with expanded uncertainties of less than 1EC at 900 EC.

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