***Supplementary Material for*:**

Thermal resistance and heat capacity in hafnium zirconium oxide ($Hf_{1-x}Zr_xO_2$) dielectrics and ferroelectric thin films

Ethan A. Scott,[1] Sean W. Smith,[2] M. David Henry,[2] Christina M. Rost,[1] Ashutosh Giri,[1] John T. Gaskins,[1] Shelby S. Fields,[3] Samantha T. Jaszewski,[3] Jon F. Ihlefeld,[3,4] and Patrick E. Hopkins[1,3,5]

[1)] *Department of Mechanical and Aerospace Engineering, University of Virginia, Charlottesville, Virginia 22904, USA*

[2)] *Sandia National Laboratories, Albuquerque, New Mexico 87185, USA*

[3)] *Department of Material Science and Engineering, University of Virginia, Charlottesville, Virginia 22904, USA*

[4)] *Department of Electrical and Computer Engineering, University of Virginia, Charlottesville, Virginia 22904, USA*

[5)] *Department of Physics, University of Virginia, Charlottesville, Virginia 22904, USA*

CONTENTS

I. THERMAL RESISTANCE CALCULATIONS

Due to the thinness of the $Hf_{1-x}Zr_xO_2$ and TaN layers, we do not directly fit for the intrinsic thermal conductivity of the $Hf_{1-x}Zr_xO_2$ layer since we cannot explicitly separate the thermal conductivity of the layer from the interfaces using a single measurement on a single sample.[1,2] Rather, we treat the two layers as an effective resistive interface between the aluminum transducer and silicon substrate. As such, when modeling the TDTR data, we treat each sample as a two layer system and fit for the effective thermal boundary conductance (which we denote as h_1 for the samples with a layer of $Hf_{1-x}Zr_xO_2$, and h_2 for those without this $Hf_{1-x}Zr_xO_2$ layer, i.e. just Al and TaN layers). The other necessary parameters include transducer thickness, thermal conductivity, and heat capacity, as well as the substrate heat capacity. For the transducer, we verify the aluminum thickness through profilometry and picosecond ultrasonics[3] (80 ± 5 nm), calculate the thermal conductivity via the Wiedmann-Franz law from from four-point probe resistivity measurements (110 W m^{-1} K^{-1}), and assume a literature value of 2.43 MJ $m^{-3}K^{-1}$ for the volumetric heat capacity at room temperature.[4,5] For the substrate, we assume a literature value[6] of 1.65 MJ $m^{-3}K^{-1}$ for the volumetric heat capacity of intrinsic silicon at 300 K. The inverse of the measured conductance is the cumulative resistance of the $Hf_{1-x}Zr_xO_2$ and TaN layers and their respective interfacial resistances. For the samples with a layer of $Hf_{1-x}Zr_xO_2$, this resistance, which we denote as R_1, is as follows:

$$R_1 = \frac{1}{h_1} = \frac{1}{h_{\mathrm{Al/Hf_{1-x}Zr_xO_2}}} + R_{\mathrm{Hf_{1-x}Zr_xO_2}} + \frac{1}{h_{\mathrm{Hf_{1-x}Zr_xO_2/TaN}}} + R_{\mathrm{TaN}} + \frac{1}{h_{\mathrm{TaN/Si}}} \tag{S1}$$

For the sample without a layer of $Hf_{1-x}Zr_xO_2$, the cumulative resistance (R_2) is:

$$R_2 = \frac{1}{h_2} = \frac{1}{h_{\mathrm{Al/TaN}}} + R_{\mathrm{TaN}} + \frac{1}{h_{\mathrm{TaN/Si}}} \tag{S2}$$

With TDTR, we measure this thermal resistance as 19.87 ± 1.47 m^2 K GW^{-1}. Subtracting R_2 from R_1, it can be seen that the resulting resistance is:

$$R_1 - R_2 = \frac{1}{h_{\mathrm{Al/Hf_{1-x}Zr_xO_2}}} + R_{\mathrm{Hf_{1-x}Zr_xO_2}} + \frac{1}{h_{\mathrm{Hf_{1-x}Zr_xO_2/TaN}}} - \frac{1}{h_{\mathrm{Al/TaN}}} \tag{S3}$$

Bozorg-Grayeli *et al.*[7] have previously measured the thermal boundary resistance between aluminum and TaN, $R_{\mathrm{Al/TaN}} = \frac{1}{h_{\mathrm{Al/TaN}}}$, at room temperature to be 7.6 ± 0.4 m^2 K GW^{-1}. Adding this value to the previous subtraction leaves the effective thermal resistance, R_{Eff}, of the $Hf_{1-x}Zr_xO_2$ films. For an effective thermal conductivity for the film, κ_{Eff}, we take the product of the film thickness and the inverse of the thermal resistance.

Propagation of error is used to quantify uncertainty in the R_{Eff} measurements, which can be attributed to measurement repeatability, uncertainty in aluminum thickness ($\pm$ 5 nm), ΔR_2 ($\pm$ 1.47 m^2 K GW^{-1}), and also from the uncertainty in $R_{\mathrm{Al/TaN}} = \frac{1}{h_{\mathrm{Al/TaN}}}$ ($\pm$ 0.4 m^2 K GW^{-1}). An additional source of uncertainty is included for κ_{Eff} from uncertainty in the thickness of the $Hf_{1-x}Zr_xO_2$ layers ($\pm$ 0.068 - 1.72 nm, depending on composition).

II. TABULATED THERMAL MEASUREMENTS

TABLE S1. Effective thermal resistances (R_{Eff}) and conductivities (κ_{Eff}) for $Hf_{1-x}Zr_xO_2$ films. *Samples marked with an asterisk were subjected to a 600 °C anneal for 30 s.

$Hf_{1-x}Zr_xO_2$ (x)	R_{Eff} ($m^2K\ GW^{-1}$)	κ_{Eff} ($W\ m^{-1}\ K^{-1}$)
0	27.63 ± 3.01	0.72 ± 0.10
	28.25 ± 3.02	0.71 ± 0.10
0*	17.98 ± 2.58	1.11 ± 0.19
	16.80 ± 2.43	1.19 ± 0.20
0.5	26.41 ± 3.06	0.76 ± 0.09
	26.30 ± 2.95	0.76 ± 0.09
0.5*	20.47 ± 2.61	0.98 ± 0.12
0.7	28.79 ± 3.44	0.69 ± 0.08
	25.54 ± 2.93	0.78 ± 0.09
0.7*	19.06 ± 2.54	1.05 ± 0.14
1	24.72 ± 2.90	0.81 ± 0.10
	24.51 ± 2.91	0.82 ± 0.10
1*	16.12 ± 2.41	1.24 ± 0.19
	15.81 ± 2.38	1.27 ± 0.19

III. SENSITIVITY ANALYSIS

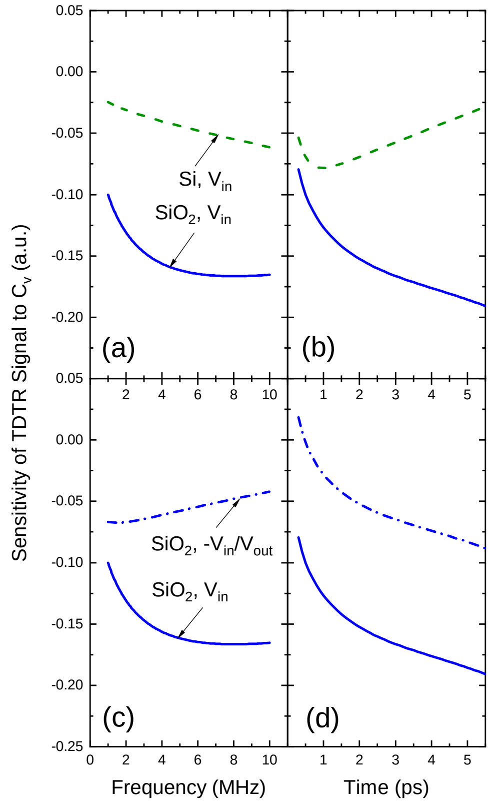

FIG. S1. In each panel, the solid blue curves display the sensitivity of the heat capacity of the $Hf_{1-x}Zr_xO_2$ films with SiO_2 substrates, for the in-phase signal, V_{in}. The blue dash-dotted line gives the sensitivity for the ratio of the in-phase to out-of-phase signal, $-V_{in}/V_{out}$. The dashed green line displays the sensitivity for the heat capacity of the $Hf_{1-x}Zr_xO_2$ layer with a silicon substrate. Panels (a) and (c) display the sensitivity as a function of frequency, whereas panels (b) and (d) provide the sensitivity as a function of probe delay time. For these calculations, we utilize the same material parameters for the Al, TaN, and SiO_2 layers discussed in the main manuscript; for the $Hf_{1-x}Zr_xO_2$, we assume a volumetric heat capacity of 2.7 $\mathrm{Jm^{-3}K^{-1}}$ and a thermal conductivity of 1 W $\mathrm{m^{-1}}$ $\mathrm{K^{-1}}$.

To determine the signal most sensitive to the parameter of interest, we calculate sensitivity in the same manner discussed in previous studies,[8,9] we find an increase in sensitivity to the heat capacity of the $Hf_{1-x}Zr_xO_2$ layer when there is an SiO_2 layer, as shown in Fig. S1(a), (b). Furthermore, we note that the in-phase signal, V_{in}, yields a higher sensitivity to heat capacity than the ratio of the in-phase to out-of-phase signal, $-V_{\mathrm{in}}/V_{\mathrm{out}}$. Therefore, we analyze the in-phase signal for samples of $Hf_{1-x}Zr_xO_2$ concentrations of $x = 0.5$ and $x = 0.7$, fitting only for the heat capacity of that layer. To enhance accuracy further, we analyze data at three different pump frequencies: 5.82, 8.4, and 12.2 MHz.

REFERENCES

[1] J. Liu, J. Zhu, M. Tian, X. Gu, A. Schmidt, and R. Yang, Review of Scientific Instruments **84**, 034902 (2013).

[2] E. A. Scott, J. T. Gaskins, S. W. King, and P. E. Hopkins, APL Materials **6**, 058302 (2018).

[3] O. Matsuda, M. C. Larciprete, R. Li Voti, and O. B. Wright, Ultrasonics **56**, 3 (2015).

[4] E. H. Buyco and F. E. Davis, Journal of Chemical and Engineering Data **15**, 518 (1970).

[5] A. Sood, R. Cheaito, T. Bai, H. Kwon, Y. Wang, C. Li, L. Yates, T. Bougher, S. Graham, M. Asheghi, M. Goorsky, and K. E. Goodson, Nano Letters **18**, 3466 (2018).

[6] P. Flubacher, A. Leadbetter, and J. Morrison, Philosophical Magazine **4**, 273 (1959).

[7] E. Bozorg-Grayeli, Z. Li, M. Asheghi, G. Delgado, A. Pokrovsky, M. Panzer, D. Wack, and K. E. Goodson, Applied Physics Letters **99**, 261906 (2011).

[8] B. C. Gundrum, D. G. Cahill, and R. S. Averback, Physical Review B - Condensed Matter and Materials Physics **72**, 245426 (2005).

[9] A. J. Schmidt, R. Cheaito, and M. Chiesa, Review of Scientific Instruments **80**, 094901 (2009).