Supporting Information: Terahertz Spectroelectrochemistry (THz-SEC) Enables Bias Resolved THz Spectroscopy (BRTS) to Probe Trap State Occupancy and Energetics

Kendra Hamilton[1*], Mari Salinas[1] and Jens Neu[1,2*]

[1]Physics Department, University of North Texas, 210 Ave A, Denton, 76201, Texas, United States of America.
[2]Center for Microelectronics in Extreme Environments, University of North Texas, 3940 N. Elm Street, Denton, 76207, Texas, United States of America.

*Corresponding author(s). E-mail(s): KendraHamilton2@my.unt.edu; Jens.Neu@unt.edu;
Contributing authors: MariSalinas@my.unt.edu;

Contents

1 Electrolyte Dependence **2**

2 THz Cyclic Voltammetry Replica **2**

3 Complex Conductivity **2**

4 Replicate Conductivity Measurements **3**

5 Global Drude-Smith Fits **3**

1 Electrolyte Dependence

We measured TCV and BRTS of SnO_2 with 0.5M, 1.0M, and 2.0M KNO_3 electrolyte concentrations. We found that the electrolyte concentration has a minute impact on the TCV and BRTS traces. Overall, higher electrolyte concentration caused a decrease in THz transmission. The effect is minor, and bias of signal onset is consistent across all concentrations. The data are presented in Figure S1.

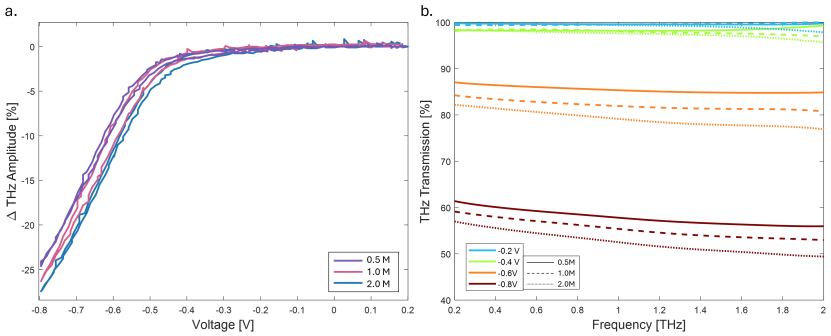

Fig. S1 a.) TCV measurements on SnO_2 with 0.5M, 1.0M, and 2.0M KNO_3 electrolyte. b.) BRTS measurements under the same conditions for representative applied biases.

2 THz Cyclic Voltammetry Replica

While the change in THz transmission is consistent across multiple samples of the same material, the magnitude of the current varies, as shown in Figure S2. This is attributed to differences in the surface area of the working electrode. Small differences in the width of the wires in the grid or the amount of the semiconductor doctor-bladed onto the electrode plate will affect the current magnitude. In particular, the amount of excess material outside the THz beam spot will still contribute to the CV results.

3 Complex Conductivity

The conductivity measured with THz techniques is complex, where the real part corresponds to the in-phase carrier response and the imaginary part corresponds to the out of phase, reactive carrier response. The real (solid lines) and imaginary (dotted lines) components are shown in Figure S3. We see that for small potential differences, there is a negative imaginary component of the complex conductivity consistent with Drude-Smith type behavior and indicative of carrier backscattering. The difference in THz transmission is minor at these biases, and as such the extracted conductivity values are less reliable. At stronger biases, the imaginary conductivity is positive and consistent with Drude-type behavior. In particular, the decrease in the ratio σ_1/σ_2, where $\sigma = \sigma_1 + i\sigma_2$, at higher frequencies is indicative of Drude behavior. At low frequencies, the carriers have sufficient time to respond to the field, and σ_1 dominates.

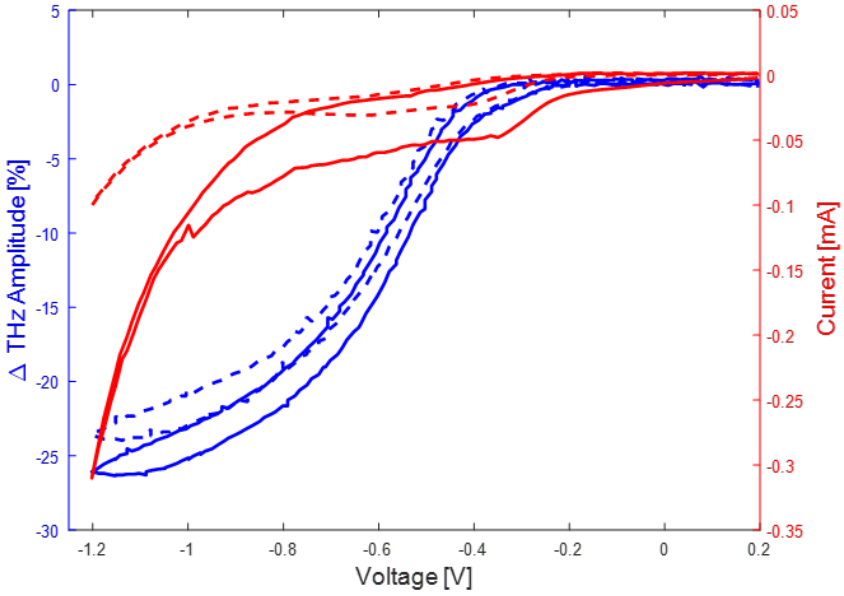

Fig. S2 Two cyclic voltammetry measurements of SnO_2. The current magnitude is inconsistent due to small differences in the surface area of the electrode.

At higher frequencies, carriers cannot fully respond to the rapidly oscillating field, and the reactive response becomes more significant.

4 Replicate Conductivity Measurements

The complex conductivity analysis was performed for three SnO_2 samples. Results outlined in the manuscript correspond to Sample 1, which exhibited the best agreement between the Drude-Smith model and the experimental data. The complex conductivity spectra for Samples 2 and 3 are shown in Figure S4, and the fit results listed in Table S1. Differences in the magnitude of the conductivity can be attributed to differences in the thickness of the SnO_2 layer.

5 Global Drude-Smith Fits

The complex conductivity spectra were globally fit with the Drude-Smith model for biases of -0.5 V to -1 V as described in the manuscript. The real (a) and imaginary (b) parts of the measured complex conductivity (solid lines) are plotted with their respective fit functions (dotted lines) in Figure S5. Table S1 gives the carrier density N from the fit for each applied bias.

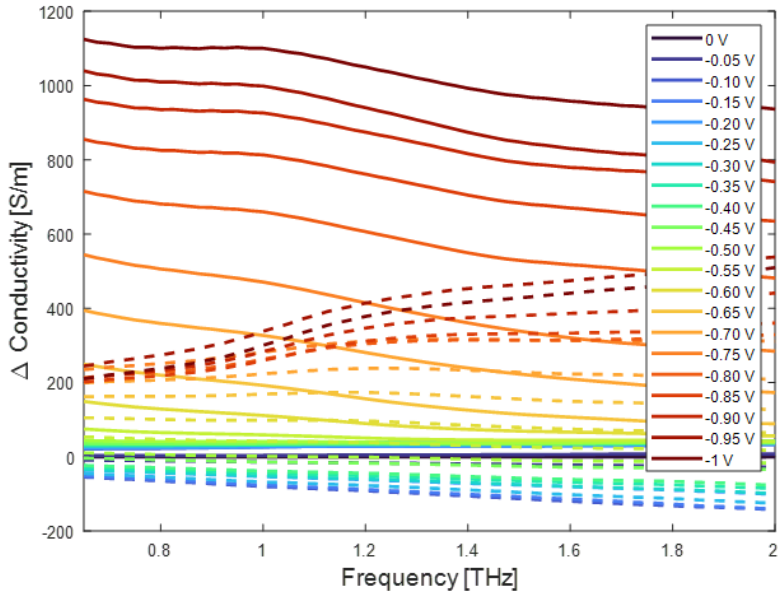

Fig. S3 Complex conductivity of SnO_2 with applied bias from 0 V to -1 V. Solid lines correspond to the real part, σ_1, and dotted lines correspond to the imaginary part, σ_2.

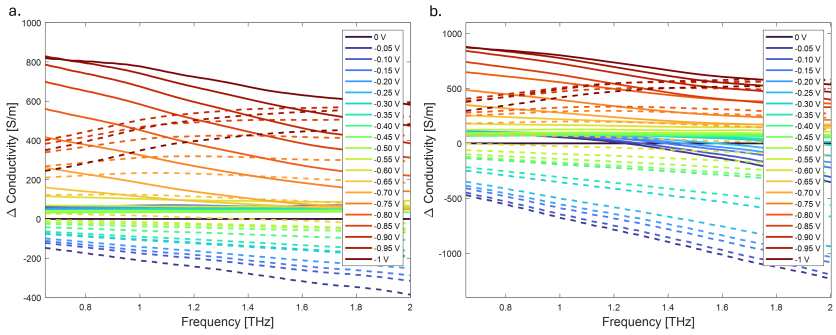

Fig. S4 Replicate complex conductivity of SnO_2 with applied bias from 0 V to -1 V. Solid lines correspond to the real part, σ_1, and dotted lines correspond to the imaginary part, σ_2. a.) Sample 2 and b.) Sample 3.

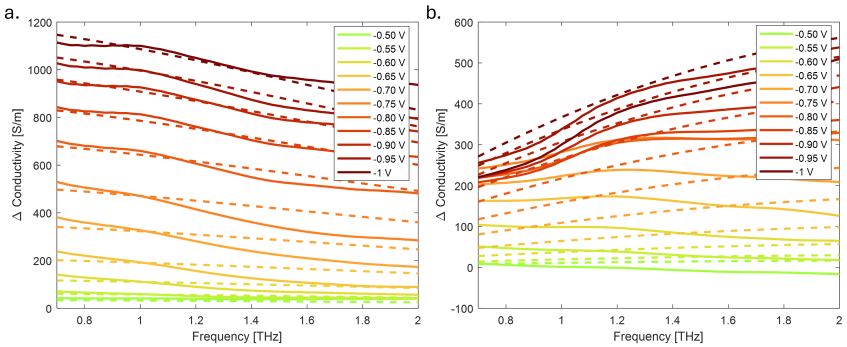

Fig. S5 a.) Real part of the complex conductivity of SnO_2 with applied bias from -0.5 V to -1 V. b.) Imaginary part of the complex conductivity of SnO_2 with applied bias from -0.5 V to -1 V. The solid lines correspond to measured data and the dotted lines correspond to the Drude-Smith fits. These correspond to Sample 1 measurements.

Table S1 Global Drude-Smith fit results

	Carrier Density [cm^{-3}]		
Bias [V]	Sample 1	Sample 2	Sample 3
-0.50	6.53×10^{15}	6.73×10^{14}	1.23×10^{4}
-0.55	1.66×10^{16}	3.46×10^{15}	3.10×10^{14}
-0.60	2.23×10^{16}	8.84×10^{15}	1.05×10^{16}
-0.65	3.86×10^{16}	1.66×10^{16}	2.26×10^{16}
-0.70	6.53×10^{16}	2.96×10^{16}	3.69×10^{16}
-0.75	9.53×10^{16}	4.84×10^{16}	5.47×10^{16}
-0.80	1.30×10^{17}	6.77×10^{16}	7.34×10^{16}
-0.85	1.59×10^{17}	8.52×10^{16}	9.14×10^{16}
-0.90	1.84×10^{17}	9.75×10^{16}	1.06×10^{17}
-0.95	2.01×10^{17}	1.03×10^{17}	1.12×10^{17}
-1.00	2.20×10^{17}	9.91×10^{16}	1.10×10^{17}
τ [fs]	53.9	105.6	96.7
c-parameter	-0.0013	-0.0094	-0.0006