

Supplemental Material:

The influence of titanium adhesion layer oxygen stoichiometry on thermal boundary conductance at gold contacts

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I. CHOICE OF TI DEPOSITION RATE

We choose to deposit the Ti adhesion layers in HV at 0.1, 0.5, and 1.0 Å/s for a variety of reasons. The low deposition rates are chosen to reduce the surface roughness for experimental purposes, as a highly reflective surface (RMS roughness <10nm) is necessary for time-domain thermorefectance measurements. Various pieces in the literature have shown that increasing deposition rate has a profound effect on surface roughness across all films.^{1,2} Additionally, we keep the deposition rates to Å/s and below due to the restrictions of our electron beam evaporator. There is a finite rise time in the chamber to reach a desired deposition rate, and depositing 3 nm of Ti at a higher rate of deposition would have resulted in a non-constant deposition rate, another variable that could influence interfacial conductances. By restricting the deposition rates to 0.1, 0.5, and 1.0 Å/s, the deposition rate of the Ti in the chamber remained closest to their designated values.

II. CALCULATION OF TiO_x STOICHIOMETRY

The O:Ti ratio was calculated using intensities of the O 1s peak (I_{O1s}) and the Ti 2p_{3/2} ($I_{Ti2p_{3/2}}$) peak corresponding to Ti-O bonds normalized to their respective relative sensitivity factors (RSF). Intensities were determined from Voigt function fits generated using kolXPD software. The RSF for each core level was calculated using the transmission function for the Scienta Omicron R3000 detector and Hartree-Slater subshell photoionization cross-section energies at 1487 eV.³ Stoichiometry was determined by

$$\frac{O}{Ti} = \frac{\frac{I_{O1s}}{RSF_{O1s}}}{\frac{I_{Ti2p_{3/2}}}{RSF_{Ti2p_{3/2}}}}. \quad (S1)$$

III. CALCULATION OF TI THICKNESS

The thickness of the Ti film was calculated using the integrated intensity of the Ti 2p core level of the thin films measured by XPS (I_{TF}) and the integrated intensity of the Ti 2p core level of an infinitely thick Ti film (I_{∞}) measured by XPS separately. The equation for

the intensity of a thin film reported by Himpsel *et al.* is given as

$$I_{TF} = I_{\infty}(1 - e^{-\frac{d}{EAL\cos\theta}}) \quad (\text{S2})$$

where d is the thickness of the thin film, EAL is the effective attenuation length, and θ is the photoelectron take-off angle.⁴ The EAL is calculated using the NIST EAL database. In the ScientaOmicron system used in this work, the take-off angle is 45° . Solving for thickness, this yields

$$d = -EAL\cos\theta(\ln(-\frac{I_{TF} - I_{\infty}}{I_{\infty}})). \quad (\text{S3})$$

IV. TIME-DOMAIN THERMOREFLECTANCE

TDTR is an optical pump-probe metrology that monitors the thermoreflectance as a function of time at a specified pump modulation frequency to determine various thermal properties of thin film systems. We use a Ti:Sapphire oscillator at a 80 MHz repetition rate with laser pulses centered at 800 nm and 11 nm bandwidth (full width half maximum). The beam exiting the oscillator is energetically split into the pump and probe paths. The pump path is electro-optically modulated to create a frequency dependent heating event on the surface of the sample. For the purpose of this experiment, the modulation of the pump was fixed at 8.8 MHz to increase sensitivity to boundary conductances in quartz, MgO, and Al₂O₃. We also frequency double the pump path to allow for increased absorption in Au. The probe path is mechanically delayed in time up to 5.5 ns, and examines the change in reflectivity on the sample surface as induced by the frequency dependent heating event from the absorbed pump energy. The pump and probe $1/e^2$ radii are 18 and 9 μm , respectively. The reflection of the probe from the sample surface is monitored using a Si photodiode directed into a lock-in amplifier. We monitor the ratio of the in-phase to out-of-phase voltages recorded from the lock-in amplifiers. Using a radially symmetric, multilayer thermal model, we fit for the thermal boundary conductance between the Au and the respective substrate, leaving the adhesion layer as part of the interface.⁵ A more

robust description of TDTR and its analyses can be found in the literature.⁶⁻⁸

V. XPS SPECTRA OF TI DEPOSITED IN HV AND UHV

A comparison of the Ti $2p$ spectra for Ti deposited at 1.0 \AA/s in HV and Ti deposited at $<0.1 \text{ \AA/s}$ under UHV is shown in Fig. S1. Metallic Ti is indicated by a chemical state at 454.1 eV with a spin orbit splitting of 6.17 eV . TiO_2 has its $2p_{3/2}$ peak at 458.8 eV with a spin orbit splitting of 5.54 eV .⁹

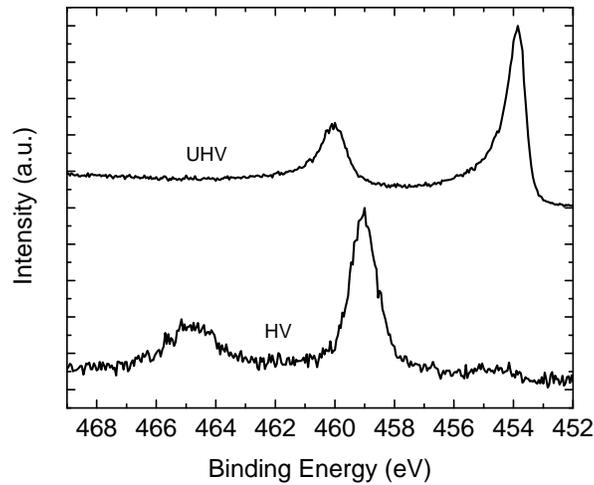


FIG. S1. XPS spectra of Ti $2p$ core level of Ti deposited in HV at 1.0 \AA/s and in UHV on Al_2O_3 .

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