Violation of Boltzmann equipartition theorem in angular phonon phase space slows down nanoscale heat transfer in ultrathin heterofilms

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Supporting Information Available

Transient heating of Si substrate: finite element simulations

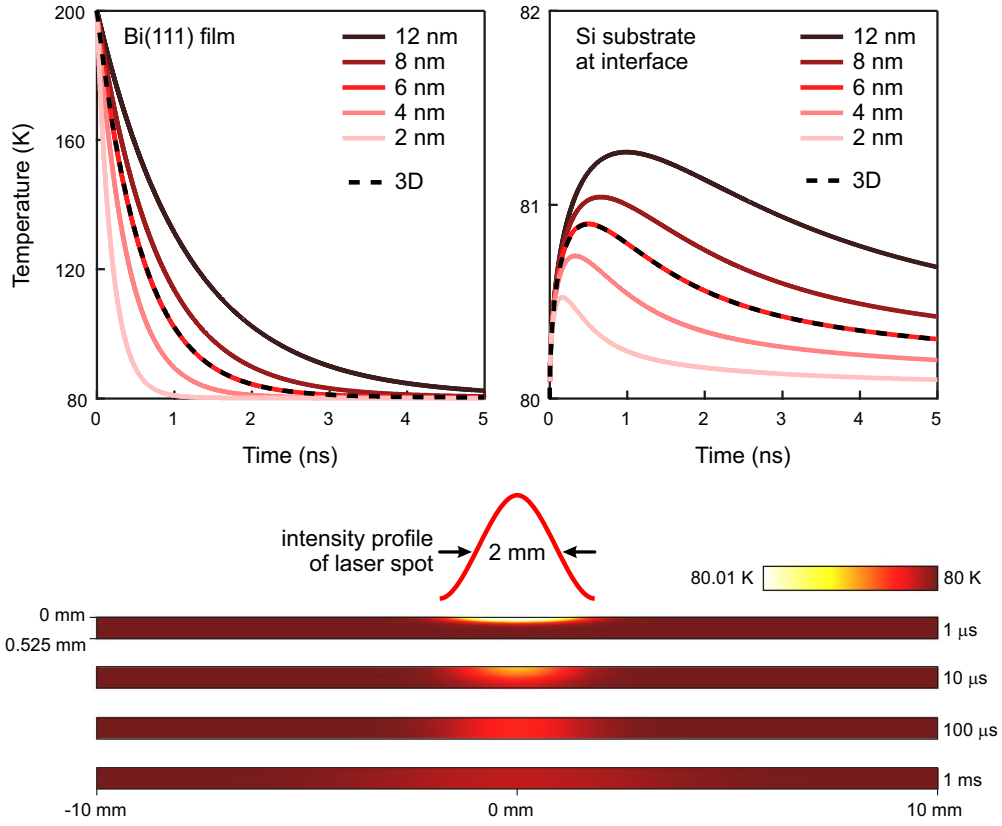

Figure S1: Finite element simulation of temperature evolution after excitation by fs-laser pulse. Upper panels exhibit temperature decay of Bi film T_{Bi} (left panel) and Si substrate T_{Si} just beneath the interface (right panel). The exponential cooling of Bi film T_{Bi} is determined by the thermal boundary conductance G and the film thickness d. The heating of the substrate T_{Si} is limited to less than 1.2 K, i.e., there is almost no rise of temperature. Lower panel: the 3D simulation exhibits a rise of temperature in the Si substrate on the μs to ms regime which is almost negligible. The left and right edge of the sample is held at 80 K. The laser spot intensity profile is indicated by the red Gaussian.

To justify the assumption of an almost constant temperature of the Si substrates in the case of fs-laser impulsive heating of the Bi film we performed finite-element simulation for the heat dissipation, we simulated heat transport from Bi films of $2-12$ nm thickness across the interface into the Si substrate for a realistic sample geometry of $0.525 \times 2.0 \times 20$ mm^3.

For short times ($0 - 5$ ns) we reduced the problem to one spatial dimension normal to the interface. For long times (5 ns to 1 ms) the simulation was carried out in quasi 3D to also account for lateral heat transport to the heat sinks of the cold head of the cryostat.

On short time scales after the impulsive excitation the temperature gradients lateral and vertical to the film are highly anisotropic. This allows reduction of the heat dissipation to a quasi-1D problem vertical to the film into the bulk Si substrate. Close to the Si-Bi interface the size of the discrete elements were chosen to be on the order of $\sim$ 1 nm, i.e., smaller than the mean free path of phonons, and gradually increasing to 10 μm in the bulk of the Si substrate at the opposite boundary of the simulated area, which is constrained to a constant temperature of 80 K. The interface between Si and Bi was modeled by a thermal boundary conductance of $G = 13$ MW/(m^2 K). The time steps of the simulation were chosen to be 1 ps which is slightly shorter than the relevant time constant of $2 - 3$ ps for electron-phonon coupling in Bi.

The evolution of temperature of the Bi film and 1 nm below the interface inside the Si are shown in the upper panels of Fig. S1, respectively. As expected, the temperature of the Bi films decays exponentially with a time constant ($\tau = 250$ ps to 120 ps) proportional to the film thickness d and dominated by the interfacial resistance. The simulations reproduce the cooling behavior measured experimentally. Simultaneously, the Si below the Bi film heats up on similar time scales to reach a maximum temperature between 80.5 K and 81.3 K about 0.5 ns to 1 ns after the impulsive excitation. These results confirm that the temperature of the Si substrate remains almost constant upon impulsive excitation of the Bi films. Considering the low thermal boundary conductance of the interface and the very high thermal conductivity of bulk Si this result, however, is not too surprising since the Kapitza length $\ell_{\mathrm{K}} = \kappa_{\mathrm{Si}}/G = 100$ μm in Si is of macroscopic scale!

To confirm the validity of our 1D approximation we carried out quasi-3D simulations with a geometry shown in the lower panel of Fig. S1 for a 6 nm thick Bi film. Here, the laser excitation is modeled by imprinting a Gaussian temperature profile with a full width at half

maxima of 4 mm along the surface. The discrete element size increases from 100 nm close to the interface to 30 μm on the backside of the Si substrate. To mimic the real experimental geometry the two lateral ends of the Si sample are held at a constant temperature of 80 K, where the Si is in intimate thermal contact to the cold head of the cryostat. On short time scales the results agree with the 1D simulations (see dashed curves in the upper panel of Fig. S1, yet these quasi-3D simulations also allow us to explore the heat dissipation at longer times. The lower panel of Fig. S1 includes color plots at 1 μs, 10 μs, 100 μs and 1 ms after the excitation.

Atomic Force Microscopy

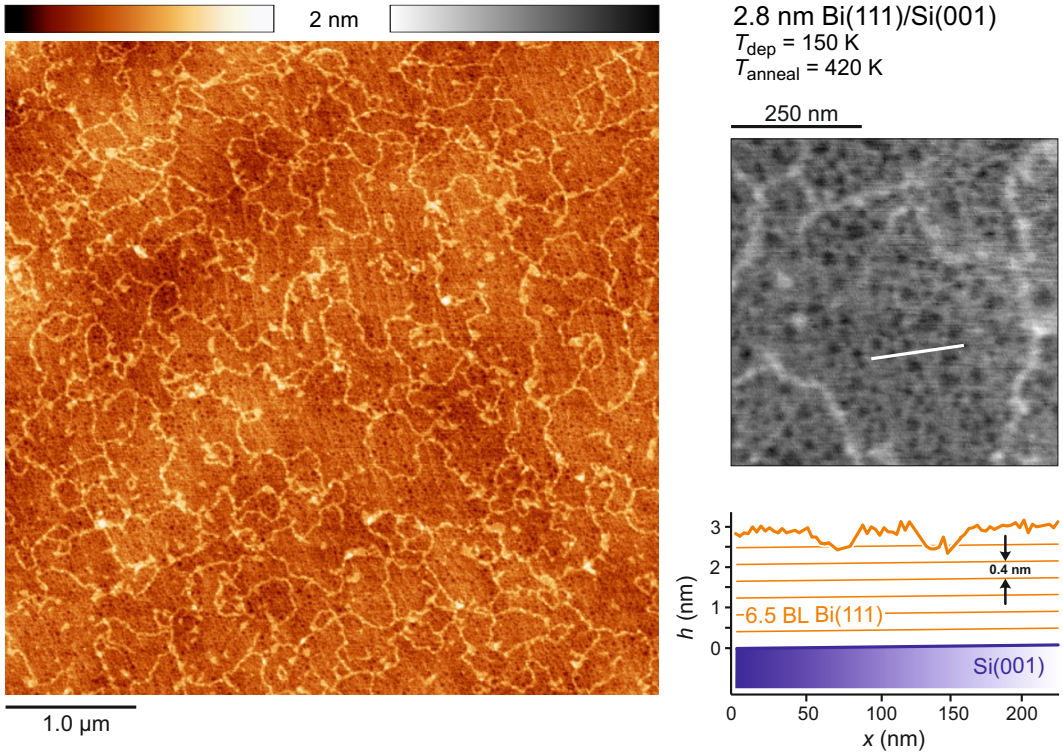

Figure S2: Non-contact atomic force micrograph (AFM) of a 2.8 nm thin Bi(111) film on Si(001) with a field of view of 5×5 μm^2. The film was grown at 150 K and annealed to 420 K. For additional 10 min the film was kept at 400 K. The grey micrograph shows an AFM image with a magnification factor of 4. The line profile exhibits a flat surface with single atomic steps with bilayer height (3.94 Å) of two adjacent terraces.

In order to prove that the 2.8 nm Bi film on Si(001) is not broken up into islands we performed *ex-situ* AFM measurements. One of the 5×5 μm^2 micro graphs is exemplarily shown in Fig. S2. The large micro graph shows a continuous film without any larger islands. Grain boundaries between 90° rotated Bi(111) grains appear as irregular brighter lines. Upon exposure to air the grain boundaries were decorated by adsorbates. Step edges of the underlying Si substrate can be identified running from upper left corner to lower right corner of the micro graph. The smaller grey micro graph depicts a close up with a 4 times higher magnification. The fine structure of small dark and bright features are atomically high 2D-islands: the topmost layer of the Bi film was not entirely completed during growth.

The atomic step height of 0.4 nm was proven through a calibrated line profile shown in the lower right corner of Fig. S2. The surface roughness of this 6.5 bilayer thick Bi film is δ_{rms} = 0.17 nm at a correlation length of $\xi = 35$ nm.

Transmission probability for ballistic phonon transport

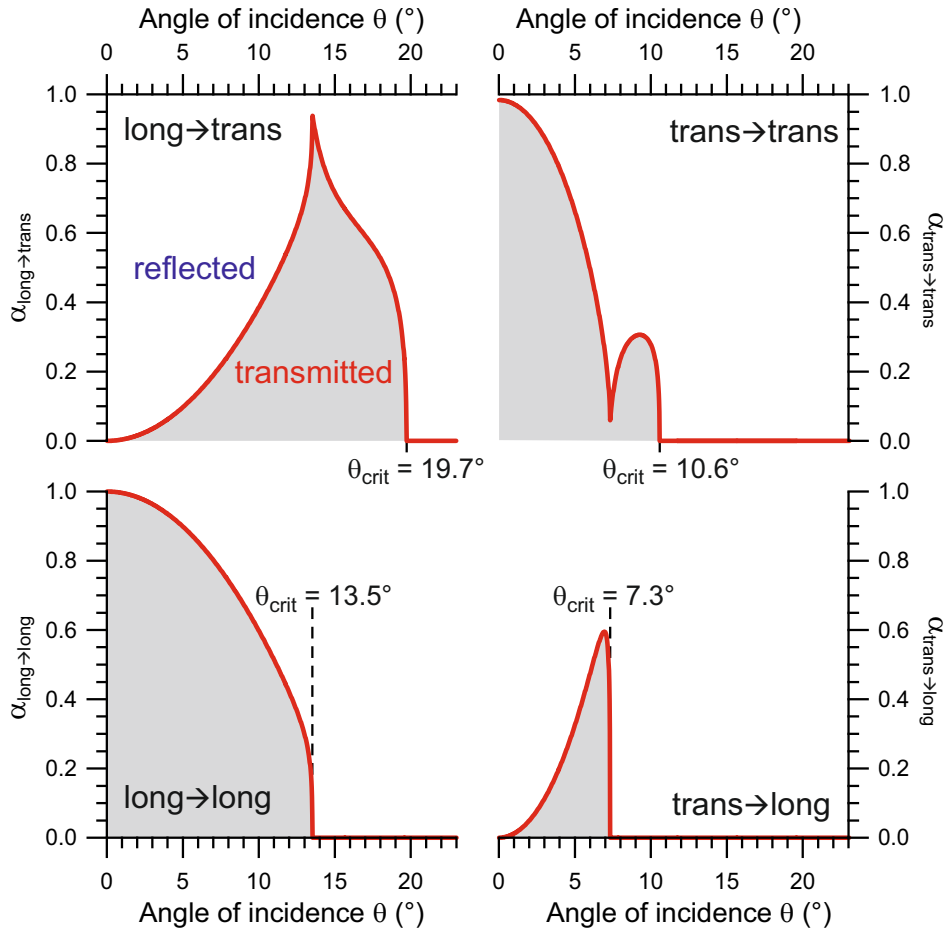

Figure S3: Transmission probability α in the framework of AMM for Bi(111) on Si(001) as function of incident angle for longitudinal and transversal waves. Mode conversion during transmission is considered. The critical angles for total internal reflection are indicated.

The transmission probability α for phonons in the framework of AMM has been calculated for Bi(111) on Si(001) using the analogy of Fresnel's equations for acoustic waves. The four panels of Fig. S3 show the probability as function of incident angle calculated for longitudinal and transversal waves. Mode conversion during transmission across the interface is considered. The grey shaded areas indicate the phonons transmitted from the Bi film to the Si substrate. The critical angle θ_{crit} for total internal reflection depends on phonon modes and varies from 7.3° up to 19.7°. The majority of heat is transferred across the interface through longitudinal phonons in Bi.