Nanoscale interfacial heat transport of ultrathin epitaxial hetero films: Few monolayer Pb(111) on Si(111)

T. Witte,[a] T. Frigge, B. Hafke, B. Krenzer, and M. Horn-von Hoegen
Department of Physics and Center for Nanointegration (CENIDE), University of Duisburg-Essen, Lotharstr. 1, 47057 Duisburg, Germany

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We studied the phononic heat transport from ultrathin epitaxial Pb(111) films across the heterointerface into a Si(111) substrate by means of ultrafast electron diffraction. The thickness of the Pb films was varied from 15 to 4 monolayers. It was found that the thermal boundary conductance σ_{TBC} of the heterointerface is independent of the film thickness. We have no evidence for finite size effects: the continuum description of heat transport is still valid, even for the thinnest films of only 4 monolayer thickness. *Published by AIP Publishing.*
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With constantly shrinking dimensions of microelectronic devices in modern technology, the interfaces in materials become more and more important and might even dominate their properties. Interfaces connect grain boundaries, heterostructures, or nanocomposite materials and modify not only electronic but also thermal properties.[1–4] As a consequence of the discontinuous change in elastic properties across an interface, a sudden increase in temperature ΔT emerges, which results in a finite resistance for interfacial thermal transport. The ability of an interface to transfer heat is usually referred to as thermal boundary conductance σ_{TBC}. Following Fourier's law, it is connected to the temperature increase via $\Delta T = j_Q/\sigma_{TBC}$ upon a net heat flux density j_Q through the interface. If the heat flow is dominated by phonons, simplified models such as the acoustic mismatch model[5] (AMM) and diffuse mismatch model[6] (DMM) describe σ_{TBC} in a harmonic approximation by integrating over all acoustic phonon branches. At low temperatures, both models describe the heat transport across atomically clean interfaces of epitaxial grown films surprisingly good[7]—even in the framework of the Debye approximation. More sophisticated models include more realistic dispersion relationships,[8–11] optical phonon branches,[12] and non-linear coupling between phonon modes for a realistic description of σ_{TBC}.[13,14] For films of a few monolayer thickness, however, the continuum description of the phonon density of states must collapse at some thickness due to quantization of the vibrational modes. A similar process has recently been observed through the vibrational deexcitation in the 4/3 monolayer Si(111)-$\alpha(\sqrt{3}\times\sqrt{3})$R30°-Pb system.[4,15]

Here, we explore the regime of the validity of the continuum description through systematic lowering of the thickness d of a heterofilm to only a few atomic layers. The thermal boundary conductance σ_{TBC} is determined from the heterofilms thermal response upon impulsive heating in a pump-probe setup. Without electronic contributions, the thermal relaxation of the film is then governed by phonon transmission across the interface. This results in an exponential decay of temperature where the characteristic cooling time constant τ_{cool} reflects the energy flow across the interface and is thus proportional to the thickness d of the film via

$$\tau_{cool} = \frac{c_f\,\rho_f}{\sigma_{TBC}}\,d\,. \tag{1}$$

Here, c_f denotes the specific heat and ρ_f the mass density of the film. Deviations from the linear dependence $\tau_{cool} \propto d$ are therefore a clear indication for the onset of finite size effects.

Epitaxial Pb(111) films of uniform thickness from 4 to 15 ML (monolayers, 1 ML = 1.0×10^{15} Pb/cm^2) on Si(111) were used as a model system to study the heat transport across an abrupt heterointerface. Time-resolved ultrafast reflection high energy electron diffraction (RHEED) provides extreme surface sensitivity and was thus employed to determine the transient temperature change in the few monolayer thin Pb films upon fs-laser excitation [Fig. 1(a)].[4,16,17] The change in temperature was monitored through the Debye-Waller effect, which directly links an increase in incoherent atomic motion upon an increase in temperature to an exponential loss of diffraction spot intensity.[4,7,18]

All experiments were performed under ultrahigh vacuum conditions with $p \leq 2\times10^{-10}$ mbar to ensure the preparation of flat and clean substrate surfaces and growth of continuous and flat Pb films. Si(111) substrates are flash-annealed to 1250 °C to remove the native oxide. Pb is evaporated from a quartz Knudsen cell. The Pb evaporator was calibrated through LEED intensity oscillations originating from the layer-by-layer growth mode as shown in Fig. 1(b).[19] The Pb film thickness η_{Pb} was additionally monitored *in-operandi* through RHEED intensity oscillations. In order to improve the film quality and orientation, a Si(111)-$\beta(\sqrt{3}\times\sqrt{3})$R30°-Pb was prepared as a template through desorption of excess Pb at 500 °C.[20] Subsequently, Pb films were grown at low substrate temperatures $T_{sub} = 80$ K (kinetic pathway to avoid islanding[21]) followed by an annealing step to 180 K to reduce the surface roughness. For substrate temperatures higher than 180 K, disintegration, de-wetting, and islanding of the Pb film were observed.[22] Pb films were always grown to a fully completed layer, i.e., a thickness in integer multiples of

[a]Author to whom correspondence should be addressed: tobias.witte@uni-due.de.

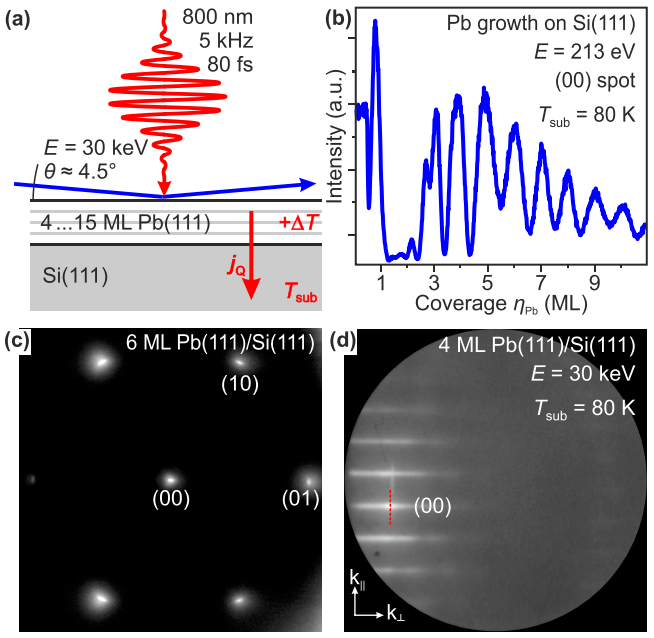

FIG. 1. (a) Sketch of an experimental setup and sample. (b) LEED intensity oscillations as a function of Pb coverage η_{Pb} during the layer-by-layer growth of epitaxial films for precise thickness calibration. (c) LEED pattern of a Pb(111) film of 6 ML thickness. The Pb film is well ordered, with a (1×1) surface unit cell. The surface exhibits a very small azimuthal disorder due to deposition on the $\beta(\sqrt{3} \times \sqrt{3})$ template layer. The pattern was recorded at 80 K and at an electron energy of 130 eV. (d) RHEED pattern of a 4 ML Pb(111) film at an electron energy of 30 keV recorded prior to optical excitation. The direction of the line profile for the transient analysis of (00) spot intensity is marked by a red dashed line.

the Pb(111) layer separation of $d_{Pb(111)} = 2.86$ Å. The desired thickness was prepared in a single deposition step on a freshly prepared Si(111)-$\beta(\sqrt{3} \times \sqrt{3})$R30°-Pb template. The LEED pattern shown in Fig. 1(c) proves the growth of continuous and smooth epitaxial Pb films.

The Pb films were excited by 800 nm fs-laser pulses at a fluence of 6 mJ/cm^2 and a repetition rate of 5 kHz. The pump beam diameter had a width of up to 8 mm, which is much larger than the sample width of 2 mm. Moreover, the absorption lengths α^{-1} for 800 nm light in Pb and Si are 17 nm[23] and 12700 nm,[24] respectively. This ensures a homogenous excitation of the Pb films not only parallel but also vertical to the surface, while the Si substrate remains cold. RHEED patterns were taken under a grazing incidence of 4.5° at an electron energy of 30 keV. To maintain a constant time delay between the pump laser pulses and the probe electron pulses across the entire sample surface and thus to compensate the velocity mismatch,[25] a tilted pulse front scheme was employed.[26] However, the temporal resolution was limited to 2.5 ps due to a large number of electrons ($>10^4$) in the probing pulse.[27]

The thermal response of all Pb films upon fs-laser excitation has been derived from the corresponding transient intensity drop of the (00) diffraction spot using the Debye-Waller effect. From a stationary intensity versus temperature measurement, we obtained the surface Debye temperature $\theta_{Pb} = (96 \pm 8)$ K (see the inset in Fig. 2). Together with the momentum transfer in diffraction, we obtained the temperature evolution as a function of the time delay Δt. An example is shown in Fig. 2 for a film thickness of 1.1 nm (4 ML) and

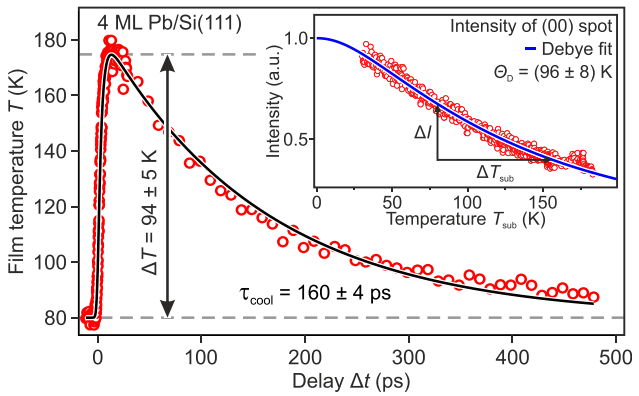

FIG. 2. Transient temperature of a 4 ML (1.1 nm) thin Pb film on Si(111), determined from the (00) spot intensity as a function of the delay time Δt. Photoexcitation through a fs-laser pulse at $\Delta t = 0$ causes a diffraction spot intensity drop. This drop of intensity was then carefully converted into a temperature increase of $\Delta T \approx 94 \pm 5$ K using the Debye-Waller effect. A calibration measurement on a sample of 5 ML Pb/Si(111) (inset), where the spot intensity is recorded as a function of the substrate temperature T_{sub}, yielded comparable results. The exponential recovery for $\Delta t > 5$ ps reflects the cooling of the film and is described by a time constant of $\tau_{cool} = 160$ ps.

a substrate temperature of $T_{sub} = 80$ K. For negative time delays $\Delta t < 0$, the initial state of the surface is probed before excitation. At temporal overlap $\Delta t = 0$, the film temperature rises from 80 K to 175 K, i.e., by $\Delta T = 95$ K, and slowly recovers on a timescale of a few hundred picoseconds. The latter one is described by an exponential function where a proper fit yields a cooling time constant of $\tau_{cool} = 160$ ps.

Thicker Pb films result in slower cooling and thus longer time constants τ_{cool}, plotted as green data points in Fig. 3 as a function of the film thickness d (lower axis) and coverage η_{Pb} (upper axis). The experimentally determined time constants clearly follow a linear behavior that is proportional to d, as expected from the continuum theory. From the slope of the linear fit (green straight line) and assuming bulk properties for the specific heat cf ($\theta_{Pb} = 90$ K[28]) and mass density ρ_f, a thermal boundary conductance of $\sigma_{TBC} = (10 \pm 1)$ MW m^{-2}K^{-1} was determined for a substrate temperature of 80 K.

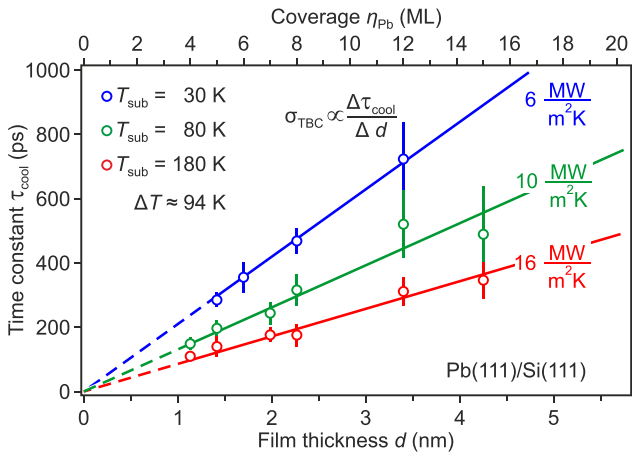

FIG. 3. Cooling time constants τ_{cool} in the dependence of the film thickness d for substrate temperatures of $T_{sub} = 30$ K, 80 K, and 180 K and a maximum temperature increase of 94 K. The data points clearly follow a $\tau_{cool} \propto d$ behavior. The corresponding thermal boundary conductance σ_{TBC} is derived from the slope of the linear regression following equation (1). This yields an error for σ_{TBC} of ± 1 MW/m^{2}K (s.d.).

To account for the temperature dependency of the specific heat, c_f was averaged over the corresponding temperature range mentioned above. Black body radiation at these low temperatures is several orders of magnitude smaller, and thus, radiative cooling effects can be neglected.

The variation in the substrate temperature caused changes in the cooling time constant as depicted in Fig. 3, with the blue and red data points for $T_{Sub} = 30\,K$ and $T_{Sub} = 180\,K$, respectively. Note that despite photo-exciting the sample at $T_{Sub} = 180\,K$ above the de-wetting temperature, there is no indication for a morphological change at the surface found in the diffraction patterns before and after the ultrafast laser excitation. Again, no evidence for the deviation from the linear correlation $\tau_{cool} \propto d$ is found, ruling out finite size effects. From the slope of the fit to the data, we obtained a thermal boundary conductance of $\sigma_{TBC} = (6 \pm 1)$ MW $m^{-2}K^{-1}$ and $\sigma_{TBC} = (16 \pm 1)$ MW $m^{-2}K^{-1}$ for 30 and 180 K, respectively. The low temperature value at 30 K is in reasonable accordance with the theoretically expected value of $\sigma_{TBC} = 7$ MW $m^{-2}K^{-1}$ in the framework of the DMM.[6] The significant increase in σ_{TBC} at higher temperatures indicates the onset of anharmonic phonon processes that start to dominate the interfacial thermal transport.[14,29] A similar effect was observed by Lyeo *et al.* for a much thicker, i.e., a 100 nm thick, Pb film on hydrogen-terminated Si.[29] It should be noted that the cooling of the film is governed solely by phonon transmission across the metal/semiconductor interface. Electronic contributions to σ_{TBC} can be neglected[29,30] because of a Schottky barrier of approximately 0.9 eV height.[30,31] After excitation, the electron system equilibrates with the lattice system on a timescale of a few picoseconds as reported by Rettig *et al.*[32,33]

In conclusion, we have found no evidence for finite size effects of the thermal boundary conductance even for films as thin as 4 monolayers, i.e., a thickness of only 1.1 nm. This surprising finding is independent of temperature. The absence of quantization effects originates from the absence of pronounced peaks in the phonon density of states for 2D-systems composed of a few atomic monolayers only. In a previous study, we have demonstrated that the vibrational density of states (VDOS) for a 2D metal system with a thickness of 1 or 2 ML exhibit clear peaks. The VDOS for a fcc metal film of 4 ML thickness, however, is almost identical to the bulk VDOS.[18] We thus have corroborated this prediction that heterofilms of a thickness of only 4 atomic layers still exhibit bulk properties when considering thermal transport properties across heterointerfaces.

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