Thermal boundary conductance in heterostructures studied by ultrafast electron diffraction

B Krenzer, A Janzen, P Zhou, D von der Linde and M Horn-von Hoegen

Department of Physics, University of Duisburg-Essen, Lotharstr. 1, 47048 Duisburg, Germany
E-mail: boris.krenzer@uni-due.de

New Journal of Physics 8 (2006) 190
Received 13 June 2006
Published 14 September 2006
Online at http://www.njp.org/
doi:10.1088/1367-2630/8/9/190

Abstract. Ultrafast electron diffraction (UED) at surfaces is used to study the energy dissipation in ultrathin epitaxial Bi-films on Si(001) subsequent to fs laser pulse excitation. The temperature of the Bi-film is determined from the drop in diffraction intensity due to the Debye–Waller effect. A temperature rise from 80 to 200 K is followed by an exponential cooling with a time constant of 640 ps. The cooling rate of the Bi-film is determined by the reflection of phonons at the Bi/Si interface and is slower than expected from the acoustic and diffusive mismatch model.

With decreasing dimensions and increasing quality of heterostructures, heat transport is no longer governed by diffusion but ballistic transport processes of phonons become significant [1]–[3]. It is well known that the interface between two different materials acts as a barrier to heat transport [3]–[7]. The existence of such a thermal barrier results in a discontinuity of the temperature ΔT at the interface

\[ \dot{Q} = \sigma_K \Delta T. \]  

(1)

The thermal boundary conductance \( \sigma_K \) relates the net heat flow \( \dot{Q} \) across the interface to the temperature jump \( \Delta T \) and is mainly determined by the energy transmission probability \( \Gamma \) across the interface [6]–[8]. For the calculation of \( \Gamma \), the microscopic processes of thermal conductivity at the interface have to be known [6]. The two basic models to calculate
$\Gamma$ are the acoustic mismatch model (AMM) and the diffusive mismatch model (DMM) [6]–[8]. At temperatures far below the Debye temperature $\theta_D$ the dominant phonon wavelength is larger than the interface roughness and the AMM is the appropriate model to describe the interface conductance [6, 9]. With increasing temperatures the dominant phonon wavelength becomes comparable or smaller than the interface roughness resulting in diffusive scattering at the interface. This situation is described by the DMM [9]. However, the experimentally measured values of the thermal boundary conductance were up to two orders of magnitude larger than expected from the two models. This discrepancy was attributed to highly defective interfaces, and the models had to be modified in order to explain the enhanced interfacial thermal conductivity [6, 7, 9].

In this paper, we show that an abrupt, smooth hetero-interface exhibit—even at temperatures higher than the Debye temperature of the heated material—a thermal boundary conductance which is in good agreement but slightly lower than the values predicted by the most basic versions of the AMM and DMM theories. The remaining minor disagreement is explained by the non-equilibrium dynamics of the transient phonon distribution.

As a model system, we studied ultrathin epitaxial Bi films on Silicon with an abrupt interface and a low defect density. Due to the low Debye temperature $\theta_D = 120$ K of Bi, the dominant phonon wavelength at 80 K is already in the order of interatomic distances. The thermal boundary conductance $\sigma_K$ was determined via the transient thermal response of the Bi film upon laser excitation and measured by means of ultrafast electron diffraction (UED) [10, 11].

In a pump and probe experiment, the hetero structure is excited by a short pump laser pulse followed by a short probe electron pulse which is diffracted at the surface. The series of diffraction patterns taken at different time delays monitors the structural changes caused by the pump pulse [10–12]. Additionally, due to the Debye–Waller effect, the intensity of the diffraction spots is directly related to the surface temperature. This allows the determination of the temperature evolution in this time-resolved experiment [12].

The design of the UED experiment (figure 1) is described in detail elsewhere [13]. Briefly, a fs laser pulse is split into two beams. The more intense part is guided on to the sample. The second part is frequency tripled and directed on to the photocathode of the electron gun generating a short burst of photoelectrons. The electrons are subsequently accelerated to a kinetic energy of

**Figure 1.** Setup of the UED experiment.
several keV. The resulting diffraction patterns are recorded by a multi channel plate-detector and a cooled CCD camera. For electrons with high kinetic energy, surface sensitivity is only achieved at grazing incidence in a reflection high energy electron diffraction geometry (RHEED). In our experiment, the kinetic energy of the electrons was $E_e = 7$ keV, and the angle of incidence $5^\circ$—thus the perpendicular momentum transfer for specular reflection is $7.48 \text{ Å}^{-1}$.

The samples were prepared under UHV-conditions ($p < 2 \times 10^{-10} \text{ mbar}$). Prior to the Bismuth deposition the $n$-doped Si(001) substrate was flashed at 1400 K resulting in a well-ordered surface showing a $(2 \times 1)$-reconstruction at room temperature. At a substrate temperature of $300 \text{ K}$ an equivalent of $6 \text{ nm}$ high purity Bismuth (99.9999\%) was evaporated from a Knudsen cell. The film quality was improved by short annealing to $\sim 400 \text{ K}$. Using scanning tunnelling microscopy (STM) and atomic force microscopy (AFM), we found that the above procedure resulted in the formation of a continuous film with a mean thickness of $(5.5 \pm 1) \text{ nm}$.

From the LEED pattern shown in figure 2(a), it is evident that Bi grows epitaxially as a continuous film in (0001)-orientation. The 12-fold symmetry of the diffraction pattern is attributed to the superposition of two hexagonal (0001) domains rotated by $90^\circ$ [14, 15]. The corresponding RHEED pattern of the Bi(0001) surface shown in figure 2(b) exhibits well-defined diffraction spots. In order to calibrate the time-resolved data, the (00)-spot intensity was first measured under stationary conditions with the sample in thermal equilibrium at various temperatures. The intensity of the (00)-spot in figure 2(c) is well described by the Debye–Waller effect (solid line) with a surface Debye temperature of $\theta_{\text{surf}} = (52 \pm 5) \text{ K}$ which matches the literature value for a single crystalline Bi(0001)-surface [16]. We therefore conclude that the thermal properties of the thin Bi film are similar to bulk Bismuth.

\[ \text{Figure 2.} \quad (a) \text{LEED pattern of a (}5.5 \pm 1\text{) nm thin Bi-film on Si(001) at } E_e = 100 \text{ eV.} \quad (b) \text{RHEED pattern of the same sample at } E_e = 7 \text{ keV and grazing incidence of } 5^\circ. \quad (c) \text{(00)-spot intensity from (b) as function of sample temperature.} \]
The time-resolved intensity of the (00)-spot after excitation with 45 fs laser pulses of 1.3 mJ cm$^{-2}$ energy (spotsize $\approx$ 4 mm) at 800 nm is shown in figure 3(a). At negative delay times, the intensity remains constant within the statistical error. At $t = 0$ ps, a sharp decrease of the (00)-spot intensity is observed. After reaching the minimum the intensity recovers asymptotically on a ns timescale.

The drop of the (00)-spot intensity is now converted into the temporal evolution of the surface temperature using figure 2(c) for calibration. The result of this conversion is shown in figure 3(b). For negative delays, the surface temperature stays constant at 80 K. At $t = 0$ ps, the temperature increases linearly within 90 ps to a maximum of 200 K. As the electron–phonon coupling occurs on a much faster timescale [17, 18] the observed rise time of the surface temperature is attributed to the finite temporal resolution of the experiment. The time resolution is limited to approximately 80 ps by the velocity mismatch between the 7 keV electrons at grazing incidence and the laser pulses at normal incidence [11, 19].

Figure 3. (a) Time-dependent intensity of the (00)-spot. (b) Surface temperature after conversion of (a) with the calibration curve of figure 2(c). The exponential fit (solid line) yields a time constant $\tau = (640 \pm 30)$ ps.
Table 1. Values for the thermal conductivities $\kappa_s$, heat capacities $C$, densities $\rho$, mean absorption depths $\alpha^{-1}$ for light of wavelength 800 nm, the sound velocities of the transversal $c_t$ and longitudinal polarized $c_l$ phonons, and the bulk Debye temperatures $\theta_D$ of Bismuth and Silicon [20].

|       | $\kappa_s$ (W/Km) | $C$ (J/Kkg) | $\rho$ (kg/m$^3$) | $\alpha^{-1}$ (nm) | $c_t$ (m/s) | $c_l$ (m/s) | $\theta_D$ (K) |
|-------|-------------------|-------------|-------------------|-------------------|-------------|-------------|----------------|
| Bi    | 7.9$^a$           | 122         | 9790              | 17                | 1074        | 1972        | 120            |
| Si    | 1000.0$^b$        | 702         | 2328              | 13000             | 5845        | 8433        | 650            |

$^a$ At 300 K.
$^b$ At 80 K.

After the initial rise the surface temperature decreases exponentially to 80 K with a time-constant $\tau = (640 \pm 30)$ ps (solid line in figure 3(b)). This exponential decay is in clear contrast to the behaviour observed for bulk Bi crystals, where the temporal surface temperature evolution is determined by diffusive heat transport [16]. This reveals that the thermal properties of the Bi-film/Si-substrate interface play the dominant role in the cooling of the film.

From equation (1), the temporal evolution of the film temperature $T_f$ can be derived as follows:

$$C\rho d\frac{dT_f}{dt} = -\sigma_K(T_f - T_s),$$

where $C$ is the specific heat, $\rho$ the mass density, and $d$ the film thickness [7]. In equation (2), it was assumed that the substrate temperature $T_s$ at the interface is constant during the experiment. This is justified by the high thermal conductivity $\kappa_s$ of silicon and the large absorption depth of light $\alpha^{-1} = 13 \mu$m at a wavelength of 800 nm (see table 1). Thus the heating of the substrate is negligible and heat is efficiently carried away from the interface. Because the density of states above the valence band maximum is negligible [20] and due to the fact that a Schottky barrier is formed [21], we can rule out a substantial electronic heating of the substrate by hot carriers being transmitted through the interface. Thus, the silicon substrate acts as a thermostat held at $T_s = 80$ K.

Equation (2) results in an exponential decay of the film temperature with a time constant $\tau = C\rho d/\sigma_K$. Assuming that $C$ and $\rho$ of the thin Bi-film are similar to the literature values of bulk Bismuth, we obtain $\sigma_K = (1025 \pm 192)$ W cm$^{-2}$ K$^{-1}$ (cf table 1). The error originates from the uncertainties in the film thickness and the determination of the time-constant. Just recently similar values for the interface conductance of Bi and hydrogen terminated Silicon substrates have been reported [22].

The main effort in the theoretical evaluation of $\sigma_K$ is the calculation of the transmission coefficients $\Gamma$ for the energy transfer across the interface from medium one to medium two. The AMM treats both solids as continua in which the energy is carried by elastic waves [6]. Elastic waves from medium one are reflected and refracted at the interface [23, 24]. Depending on the acoustic impedances $Z = c\rho$ of the two solids, only a fraction of the energy is transferred through the interface into medium two. In addition, total reflection may occur for waves with incident angles larger than a critical angle $\phi_{max}$ because the speed of sound in Bi is less than in Silicon. The critical angle of total reflection is given by Snell’s law $\phi_{max} = \sin^{-1}(c_1/c_2)$ and gives rise to
Table 2. Critical angle $\varphi_{\text{max}}$ and angle integrated transmission coefficients $\Gamma_{\text{AMM}}$ for all combinations of longitudinal and transversal acoustic phonons both in Bi and Si including mode conversion.

| $L_{\text{Bi}}L_{\text{Si}}$ | $L_{\text{Bi}}T_{\parallel}^\perp L_{\text{Si}}$ | $T_{\parallel}^\perp L_{\text{Si}}$ | $T_{\parallel}^\perp L_{\text{Bi}}$ | $T_{\parallel}^\perp T_{\parallel}^\perp$ |
|-----------------------------|------------------------------------------|---------------------------------|---------------------------------|-----------------|
| $\varphi_{\text{max}}$     | 13.5°                                   | 19.7°                           | 7.3°                            | 10.6°           |
| $\Gamma_{\text{AMM}}$      | 0.0086                                  | 0.0137                          | 0.0014                          | 0.0036          | 0.0080°         |

* The mode polarized transverse to the interface $T_{\parallel}^\perp$ only couples to the $T_{\parallel}^\perp$ mode in Si.

A critical cone. Acoustic waves with incident angles larger than the critical cone do not contribute to the energy transfer. Because the speed of sound in Si is 4–5 times greater than in Bi the critical angle $\varphi_{\text{max}}$ is less than 20°. The critical angles $\varphi_{\text{max}}$ for all polarization combinations of acoustic waves are tabulated in table 2. Most of the phonons are trapped in the film!

The dependence of the transmission coefficients on the incident angle of acoustic waves are obtained by solving the wave equations and accounting for the boundary conditions at the interface [23, 24]. This results in a set of equations analogous to the Fresnel equations in optics. At the interface conversion from longitudinal to transverse polarized acoustic modes and vice versa can occur. The transmission coefficients $\Gamma_{\text{AMM}}$ integrated over the half sphere are given in table 2. It has to be noted that up to the critical angle $\varphi_{\text{max}}$, the transmission probability of all modes is almost one because the acoustic impedances of Bi and Si are nearly equal. The two materials are acoustically adapted. Within the Debye approximation the AMM yields in a thermal boundary conductance between $1350 \, \text{W cm}^{-2} \, \text{K}^{-1}$ for 80 K and $1450 \, \text{W cm}^{-2} \, \text{K}^{-1}$ for 300 K.

Optical phonons do not contribute to the heat transport across the interface. Due to their low frequency of 2.12 THz, the Bi optical phonon modes [17] do not couple to the Si optical phonon modes with a frequency of 10–15 THz [20], and the optical phonons can only couple to the acoustic phonons in Si. Due to their low group velocity, however, the critical cone for total reflection is extremely narrow. The optical phonons are therefore trapped in the Bi layer and can only decay into the acoustic phonons of Bismuth which occurs in a few picoseconds [25]. Thus, on the much longer time scale of the film cooling the optical and acoustic phonons are in equilibrium. The energy transport across the interface is solely determined by the transmission of acoustic phonons.

The DMM considers the diffuse scattering of phonons at the interface resulting in a transmission probability which is independent of the incident angle of the phonons and only depends on the density of states in the two media [6]. Using the Debye approximation for the density of states, the transmission probability is additionally independent on polarization and energy resulting in $\Gamma_{\text{DMM}} = 0.018$ for all phonon modes. With these transmission probabilities, the thermal boundary conductance lies between $1440 \, \text{W cm}^{-2} \, \text{K}^{-1}$ for 80 K and $1560 \, \text{W cm}^{-2} \, \text{K}^{-1}$ for 300 K. Note that the values for $\sigma_K$ calculated in the two models differ only slightly. This is characteristic for solid–solid interfaces [6].

A comparison shows that the experimentally determined value for $\sigma_K$ is in good agreement with the calculated thermal boundary conductances. This is in contrast to previous observations where the AMM and DMM predicted an up to two orders of magnitude lower thermal boundary conductance than found in the experiment [7, 9, 26].
We offer the following tentative explanation for the remaining small discrepancy. The theoretical models discussed here assume population equilibrium between all modes. The cooling rate of the thin film is solely determined by the phonon transmission probability through the interface. However, within the framework of the AMM, phonon modes with an angle of incidence smaller than the angle of the critical cone are rapidly depopulated. The transmission coefficient of these modes is nearly one and the transit time $t_{\text{tran}} = d_{\text{Bi}}/c_{\text{Bi}}$ through the Bi layer is less than 5 ps. Due to total reflection at the interface, phonons outside the critical cone are confined in the film. Further energy transport across the interface can only be achieved by the coupling of phonon states lying outside the critical cone to phonon states inside the critical cone. We propose that the overall cooling rate of the Bi film might be slowed down by the finite time for the energy transfer from the confined modes to the rapidly depleting modes of the critical cone.

In conclusion, we studied the heat transport from a thin epitaxial Bi-film to a Si(001)-substrate as a model system for ideal, abrupt hetero interfaces. From the time constant $\tau = 640$ ps of the exponential temperature decay, we obtain a thermal boundary conductance $\sigma_K = 1025$ W cm$^{-2}$ K$^{-1}$ which is smaller than predicted by the simplest models describing the heat conduction across a barrier, namely either the AMM or the DMM. The total internal reflection of the vast majority of the phonons leads to a trapping of the heat in the film: only phonons inside a small critical cone are transmitted from the thin film into the substrate. Repopulation of those depopulated states by the scattering of phonons creates a bottleneck which slows down the cooling of the hetero film.

Acknowledgments

We acknowledge fruitful discussions with M Aeschlimann and B Rethfeld. We thank Th Payer, Ch Wiethoff and T Roll for the help in determining the morphology of the films. This work is funded by the Deutsche Forschungsgemeinschaft through SFB 616 ‘Energy dissipation at surfaces’ which is gratefully acknowledged.

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